Spectroscopic Studies
of Silver Atoms and Clusters.

by

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A thesis submitted for the degree of
Doctor of Philosophy
in the
Faculty of Science
of the
University of Leicester
April 1985
Dedicated To my Parents
STATEMENT.

The work reported in this thesis was carried out by the Author in the Physical Chemistry Research Laboratory at the Department of Chemistry, Leicester University, and at the Chemical Physics Laboratory at the Eastman Kodak Co. Rochester, N.Y.

All work recorded herein is original unless otherwise acknowledged in the text or by reference.

No part of this thesis is currently being submitted for another degree in this or any other educational establishment.

A.D.M. Stevens

A.D.M. Stevens

April 1985
ACKNOWLEDGEMENT.

I would like to thank Professor Martyn Symons for his constant support and encouragement throughout this project. I am also indebted to Dr. Ray Eachus for his considerable efforts on my behalf in making arrangements for two assignments to the Chemical Physics Laboratory at the Eastman Kodak Co., Rochester, N.Y., and for his unfailing help and enthusiasm (yes, Ray, I've finally written up!).

Thanks also go to everyone at Leicester University and Eastman Kodak who assisted with this work; in particular Dr. Graham Eaton, Dr. Ralph Jones, Joanne Brescia, Dr. Gordon McDugle and the work- and glass-shop personnel.

Lastly, I would like to thank the SERC, Kodak Ltd. and the Eastman Kodak Co. for financial support, Ann Crane for the figures and WORD-11 for all the typographical errors.
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An Introduction to Spectroscopic Studies of Silver Atoms and Clusters.
1.1 GENERAL INTRODUCTION.

This Chapter discusses previous spectroscopic studies of silver atoms and small silver clusters as an introduction to the ESR and optical studies reported in Chapters 2 and 3.

The spectroscopic detection and characterisation of these species is of great importance in the fields of (a) heterogeneous catalysis and (b) the silver halide imaging ("photographic") process. In (b) a tetrameric silver centre is often\(^1\) considered to play an especially important role [it is thought that such a centre forms the photographic "latent image", although no spectroscopic data has yet been obtained to support this assignment (see Chapter 4)].

Because of the difficulties involved in spectroscopic studies of photographic systems, (see Chapters 5 and 6) research has often necessitated the use of model systems. ESR and optical data have been obtained from silver species formed in a wide range of these. Centres detected by ESR have in general been well characterised. Difficulties have sometimes arisen, however, in the assignment of optical data to particular species. Although such difficulties remain for diamagnetic silver species, it should be possible to assign optical spectra from paramagnetic species on the basis of the results of conjoint ESR experiments.
The object of this work was to obtain collaborative ESR and optical data, in particular for the centre $\text{Ag}_4^{n+}$ ($n = 1$ or $3$), which, although well characterised by ESR$^{21}$, has not been optically detected. Chapter 2 reports the results of ESR and optical studies of silver atoms formed in aqueous and organic glasses. Chapter 3 reports the results of similar studies of silver clusters. [ESR studies of photographic systems are reported in Chapters 5 and 6.]

1.2. INTRODUCTION TO ESR AND OPTICAL STUDIES OF SILVER ATOMS

Silver atoms, $\text{Ag}^0$, have a $4d^{10}5s^1$ ground-state electronic configuration and are therefore paramagnetic. ESR spectra have been observed from these species (i) in the gas phase, (ii) isolated in rare gas matrices (iii) formed in $\text{Ag}^+$ doped KCl crystals, (iv) formed in aqueous and organic glasses and (v) prepared in $\text{Ag}^+$ ion-exchanged zeolites [see Table 1].

Spectra are characterised by two sets of lines of unequal intensity, corresponding to the two naturally occurring isotopes, $^{107}\text{Ag}$, ($I = 1/2$, 48.18% abundant) and $^{109}\text{Ag}$, ($I = 1/2$, 51.82% abundant. The large value of the hyperfine interaction, $A$, arises from the Fermi contact term, $|\psi(0)|^2$ of the $s$ orbital. The ratio of $^{109}A:^{107}A$ is equal to the ratio of the magnetic moments $^{109}\mu_N :^{107}\mu_N = 1.1543:1.0000$. 

- 2 -
It can be seen from Table 1 that marked reductions from the gas phase isotropic $A$ and $g$-values are observed depending upon the host matrix. Results from Ag$^0$ centres formed by the $\gamma$-irradiation of frozen Ag(II) solutions$^6,7,8,9$ are particularly noteworthy. In these systems a large number of different species or solvates have sometimes been observed, where reductions of the hyperfine interaction from the "free atom" value have been interpreted in terms of electron delocalisation onto ligands and reduced $g$-values rationalised in terms of p orbital population. Fig. 1a. shows the ESR spectrum obtained from $[\text{Ag(MeCN)}_4]^0$ centres, in which superhyperfine coupling to nitrogen atoms was observed. Fig. 1b shows the molecular orbital diagram proposed for this species.

Table 2 shows optical data obtained from Ag$^0$ in the conditions (i)-(v) outlined above. Absorption bands have been observed corresponding to the $5s^2 \rightarrow 5s^15p^1$ electronic transition and their position can be seen to be somewhat matrix dependent.

1.3. INTRODUCTION TO ESR AND OPTICAL STUDIES OF SILVER CLUSTERS.

Table 3 lists ESR data obtained from paramagnetic silver clusters formed in various matrices. Spectra exhibit a multiplicity of lines reflecting the delocalisation of the unpaired electron over the many metal atoms.
FIGURE 1

(a) The ESR spectrum of [Ag(MeCN)₄]° and (b) a proposed bonding scheme showing electron delocalisation onto the ligands (ignoring p and d orbitals) [Ref. 9].

\[ 3100 \text{G (9.100 GHz)} \]

\[ \text{\(10^9A_{iso} = -532 \text{G} \)} \]

\[ 5s \]

\[ \text{N(\(\sigma\))} \]

\[ [\text{Ag(MeCN)}_4]° \]
$\text{Ag}_2^+$ yields a triplet spectrum characteristic of two equivalent silver atoms. When naturally occurring silver is used, each component consists of three features with a 1:2:1 ratio of intensities, corresponding to the probabilities of the three possible isotopic combinations $^{109}\text{Ag}-^{109}\text{Ag}$, $^{107}\text{Ag}-^{109}\text{Ag}$ and $^{107}\text{Ag}-^{107}\text{Ag}$, respectively.

$\text{Ag}_3^{2+}$ and $\text{Ag}_4^{n+}$ ($n = 1$ or $3$) yield quartet and quintet spectra, respectively, characteristic of a triangular arrangement of equivalent silver atoms in the former and a tetrahedral arrangement of equivalent silver atoms in the latter. The isotopic lines become less resolved in $\text{Ag}_3^{2+}$ and disappear completely in the case of $\text{Ag}_4^{n+}$, resulting only in line broadening.

The assignment of a septet spectrum to $\text{Ag}_6^{m+}$ is at present only tentative, but might be representative of electron delocalisation over six equivalent silvers in an octahedral arrangement.

The ESR spectra of the neutral clusters $\text{Ag}_3^0$ and $\text{Ag}_5^0$ are more complex as a result of the inequivalence of the constituent silvers. $\text{Ag}_3^0$ yields a spectrum characteristic of a species with $C_v$ symmetry and spin density concentrated at the terminal nuclei. The spectrum of $\text{Ag}_5^0$, corresponding to three groups of inequivalent silver nuclei, has been interpreted in terms of a trigonal bipyramidal structure.
Tables 4a and 4b list optical data for neutral silver clusters $\text{Ag}_n^0$, which have mostly been formed by the low temperature cryo-clustering of silver atoms in rare gas matrices\textsuperscript{25}. It is claimed\textsuperscript{25} that trends in the energies of the HOMO→LUMO assignments of the lowest energy transitions for these species are in reasonable agreement with the theoretical predictions of Baetzold\textsuperscript{33} for linear aggregates using semi-empirical molecular orbital methods. However, it is important to realise that the assignments in Table 4 may be somewhat tentative as they do not have the support of corroborative magnetic data.

Table 4c lists optical data for charged silver clusters, $\text{Ag}_n^{m+}$. As shown in Table 3, many of these are paramagnetic. However, only the spectrum for $\text{Ag}_2^+$ has been conclusively assigned as a result of joint ESR and optical experiments\textsuperscript{14,29}.
<table>
<thead>
<tr>
<th>Matrix</th>
<th>$g_{av}$-value</th>
<th>$^{109}A_{iso}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. Gas phase</td>
<td>2.002(_3)</td>
<td>-706</td>
</tr>
<tr>
<td>ii. Ar @4K(^3)</td>
<td>1.999(_6)</td>
<td>-747</td>
</tr>
<tr>
<td>Xe @4K(^3)</td>
<td>1.992(_2)</td>
<td>-714</td>
</tr>
<tr>
<td>iii. KCl X-irr. 77K(^4)</td>
<td>2.000</td>
<td>-649 [(^{35})Cl SHF = 13.3]]</td>
</tr>
<tr>
<td>iv. (1) H(_2)O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Vap. Cond. 77K(^5)</td>
<td>2.002(_0)</td>
<td>-716</td>
</tr>
<tr>
<td>(b) Ag(^+) Soln. γ 4K(^6)</td>
<td>1.999(_3)</td>
<td>-628</td>
</tr>
<tr>
<td>(c) Ag(^+) Soln. γ 77K(^7)</td>
<td>A 1.997(_2)</td>
<td>-537</td>
</tr>
<tr>
<td></td>
<td>B 1.997(_6)</td>
<td>-585</td>
</tr>
<tr>
<td></td>
<td>C 1.997(_1)</td>
<td>-550</td>
</tr>
<tr>
<td></td>
<td>D 1.997(_7)</td>
<td>-493</td>
</tr>
<tr>
<td></td>
<td>E 1.998(_7)</td>
<td>-609</td>
</tr>
<tr>
<td></td>
<td>F 1.99(_5)</td>
<td>-433</td>
</tr>
<tr>
<td>Range of Solvates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2) EtOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Vap. Cond. 77K(^5)</td>
<td>2.000(_4)</td>
<td>-619</td>
</tr>
<tr>
<td>(b) Ag(^+) Soln. γ 4K(^6)</td>
<td>2.000(_4)</td>
<td>-641</td>
</tr>
<tr>
<td>(c) Ag(^+) Soln. γ 77K(^8)</td>
<td>A 2.000(_3)</td>
<td>-623</td>
</tr>
<tr>
<td></td>
<td>B 1.998(_9)</td>
<td>-568</td>
</tr>
<tr>
<td>(3) CD(_3)CN γ 77K(^9)</td>
<td>1.997</td>
<td>-532 [(^{14})N SHF = 6.0]]</td>
</tr>
<tr>
<td>v. Na-Y Zeo. γ 4K(^{10})</td>
<td>1.991</td>
<td>-529</td>
</tr>
<tr>
<td>&quot;     γ 77K(^{10})</td>
<td>2.001</td>
<td>-708</td>
</tr>
</tbody>
</table>
### Table 2

**Optical Data For Ag⁰ centres**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Absorption maxima</th>
<th>Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v (cm⁻¹)</td>
<td>λ (nm)</td>
</tr>
<tr>
<td>i. Gas phase¹¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30,473</td>
<td>328.7</td>
</tr>
<tr>
<td></td>
<td>29,552</td>
<td>338.9</td>
</tr>
<tr>
<td>ii. KCl 77K*¹</td>
<td>50,760</td>
<td>197</td>
</tr>
<tr>
<td></td>
<td>23,500</td>
<td>425</td>
</tr>
<tr>
<td>iii. Xe 20K¹²</td>
<td>29,710</td>
<td>336.6</td>
</tr>
<tr>
<td></td>
<td>30,423</td>
<td>328.7</td>
</tr>
<tr>
<td></td>
<td>30,595</td>
<td>326.9</td>
</tr>
<tr>
<td></td>
<td>30,925</td>
<td>323.4</td>
</tr>
<tr>
<td>iv.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1) H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) Vap. Cond. @12K¹³</td>
<td>31,645</td>
<td>316</td>
</tr>
<tr>
<td></td>
<td>29,761</td>
<td>336</td>
</tr>
<tr>
<td>(b) Ag⁺ Soln. γ 77K¹⁴*</td>
<td>27,030</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td>25,320</td>
<td>395</td>
</tr>
<tr>
<td></td>
<td>23,260</td>
<td>430</td>
</tr>
<tr>
<td>(c) Ag⁺ Soln. γ R.T.¹⁵</td>
<td>27,780</td>
<td>360</td>
</tr>
<tr>
<td>(2) 5.4M H₂SO₄⁴¹⁶</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag⁺ Soln. γ 77K</td>
<td>31,948</td>
<td>313</td>
</tr>
<tr>
<td>(3) EtOH</td>
<td>27,320</td>
<td>366</td>
</tr>
<tr>
<td>Ag⁺ Soln. γ 77K¹⁷*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>v. Na-Y zeolite</td>
<td>32,470</td>
<td>308</td>
</tr>
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</table>

*indicates assignment in conjunction with ESR data*
### Table 3.

**ESR Data For Silver Clusters.**

<table>
<thead>
<tr>
<th>Species</th>
<th>Matrix</th>
<th>Matrix</th>
<th>$g_{av}$-value</th>
<th>$^{109}$A$_{iso}$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^+\text{2}$</td>
<td>$\text{D}_2\text{O} \ 77K$</td>
<td>1.983</td>
<td>-284</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}^0\text{3}$</td>
<td>$\text{C}_6\text{D}_6 \ 77K$</td>
<td>1.962</td>
<td>-295</td>
<td>$^{107}$A(2) $^{107}$A(1)</td>
</tr>
<tr>
<td>$\text{Ag}^{2+}\text{3}$</td>
<td>Toluene $77K$</td>
<td>1.973</td>
<td>-203</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}^{n+}\text{4}$</td>
<td>Benzene $77K$</td>
<td>1.970</td>
<td>-147</td>
<td></td>
</tr>
<tr>
<td>(n = 1 or 3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}^0\text{5}$</td>
<td>$\text{C}<em>6\text{D}</em>{12} \ 77K$</td>
<td>2.057</td>
<td>-204.6</td>
<td>$^{107}$A(2) $^{107}$A(1)</td>
</tr>
<tr>
<td>(m = 1, 3 or 5)</td>
<td></td>
<td></td>
<td>-11.0</td>
<td>-5.0</td>
</tr>
<tr>
<td>$\text{Ag}^{m+}\text{6}$</td>
<td>A Zeolite</td>
<td>2.053</td>
<td>-72.3</td>
<td></td>
</tr>
</tbody>
</table>

[For data on larger, non-molecular, clusters, see Chapter 6, Table 6.]
### Optical Data for Neutral Silver Clusters

<table>
<thead>
<tr>
<th>Species</th>
<th>Matrix</th>
<th>Absorption maxima $\nu$ (cm$^{-1}$)</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>$\text{Ag}_2^0$</td>
<td>Gas Phase$^{24}$</td>
<td>40,159 249</td>
<td>$E \rightarrow X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>39,023 256</td>
<td>$D \rightarrow X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37,626 265</td>
<td>$C \rightarrow X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35,827 279</td>
<td>$B \rightarrow X$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22,996 434</td>
<td>$A \rightarrow X$</td>
</tr>
<tr>
<td>$\text{Ar} \text{ @12K}^{25}$</td>
<td></td>
<td>38,314 261</td>
<td>$1^+ \rightarrow 1^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37,879 264</td>
<td>$\Sigma \rightarrow \Sigma$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25,840 387</td>
<td>$\sigma_{5s} \rightarrow \sigma_{5s} \sigma_{5s}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24,272 412</td>
<td>(HOMO $\rightarrow$ LUMO)</td>
</tr>
<tr>
<td>$\text{CH}_4 \text{ @12K}^{13}$</td>
<td></td>
<td>25,642 390</td>
<td></td>
</tr>
<tr>
<td>$\text{Ag}_3^0$</td>
<td>$\text{Ar} \text{ 10-40K}^{25}$</td>
<td>40,816 245</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>22,727 440</td>
<td>(HOMO $\rightarrow$ LUMO)</td>
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<tr>
<td>$\text{Ag}_4^0$</td>
<td>&quot;</td>
<td>36,630 273</td>
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<td>35,375 283</td>
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<td>28,818 347</td>
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<td></td>
<td>27,548 363</td>
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<td>23,474 426</td>
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<td>20,408 490</td>
<td>(HOMO $\rightarrow$ LUMO)</td>
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<tr>
<td>$\text{Ag}_5^0$</td>
<td>&quot;</td>
<td>30,000 333</td>
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<tr>
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<td>27,027 370</td>
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<td>25,252 396</td>
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<td></td>
<td></td>
<td>19,801 505</td>
<td>(HOMO $\rightarrow$ LUMO)</td>
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<th>Species</th>
<th>Matrix</th>
<th>Absorption maxima</th>
<th>Assignment</th>
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</thead>
<tbody>
<tr>
<td>Ag^0_6</td>
<td>Ar 10-40K</td>
<td>29,411 340 19,230 520</td>
<td>HOMO→LUMO</td>
</tr>
<tr>
<td>Ag^0_7</td>
<td>&quot;</td>
<td>18,656 536</td>
<td>HOMO→LUMO</td>
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<tr>
<td>Ag^0_n</td>
<td>&quot;</td>
<td>28,818- 347-</td>
<td>Plasmon</td>
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<tr>
<td></td>
<td></td>
<td>27,027 370</td>
<td>Resonance</td>
</tr>
<tr>
<td>Ag^0</td>
<td>H_2O R.T.</td>
<td>26,660 376</td>
<td>Mie Resonance</td>
</tr>
<tr>
<td>n (≈56Å)</td>
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<tr>
<td>Ag^0</td>
<td>KCl</td>
<td>20,062 485</td>
<td>&quot; &quot;</td>
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<tr>
<td>n (600Å)</td>
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</tbody>
</table>

**Table 4b.**

Matrix Raman Data For Neutral Silver Clusters.

<table>
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</thead>
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<tr>
<td>Ag^0_2</td>
<td>Kr</td>
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<td>Vibrational excitation of linear molecule</td>
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<tr>
<td></td>
<td>&quot;</td>
<td>102.5</td>
<td>&quot; &quot;</td>
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</tbody>
</table>
Table 4c.

Optical Data For Charged Silver Clusters.

<table>
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<th>Absorption maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>v (cm⁻¹)</td>
<td>λ (nm)</td>
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<tr>
<td>Ag₂⁺</td>
<td>H₂O¹⁴⁺</td>
<td>29,400</td>
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<tr>
<td></td>
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<td>27,000</td>
</tr>
<tr>
<td></td>
<td>H₂O¹⁵</td>
<td>32,300</td>
</tr>
<tr>
<td></td>
<td>7.5M H₂SO₄²⁺</td>
<td>32,300</td>
</tr>
<tr>
<td></td>
<td>5.4M H₂SO₄¹⁶⁺</td>
<td>27,780</td>
</tr>
<tr>
<td></td>
<td>Na-Y Zeolite¹⁸</td>
<td>29,411</td>
</tr>
<tr>
<td>Ag₃²⁺</td>
<td>Na-Y Zeolite¹⁸</td>
<td>24,880</td>
</tr>
<tr>
<td>Ag₃²⁺</td>
<td>Na-A Zeolite³⁰</td>
<td>33,500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22,400</td>
</tr>
<tr>
<td>Ag₄²⁺</td>
<td>H₂O¹⁵</td>
<td>38,500</td>
</tr>
<tr>
<td>Ag₆⁺</td>
<td>Na-A Zeolite³⁰</td>
<td>27,500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>19,500</td>
</tr>
</tbody>
</table>

[* Indicates assignment in conjunction with ESR data.]*
REFERENCES

CHAPTER 2

E.S.R. and Optical Studies of Silver Atoms in Frozen Aqueous and Alcoholic Matrices.
2.1. INTRODUCTION.

There have been numerous ESR studies of AgO centres produced by the X- or γ- irradiation of frozen Ag⁺ solutions\(^1\)\(-\)\(^6\). The centres are formed as a result of the reaction of radiolytically produced electrons according to the reaction scheme shown in (1) and (2):

\[
\begin{align*}
\gamma \\
\text{Solvent} & \quad \rightarrow \quad h^+ + e^- \\
\text{Ag}^+ + e^- & \quad \rightarrow \quad \text{AgO}
\end{align*}
\]

(1)  
(2)

In aqueous solutions, a variety of centres are formed with different ESR parameters [see Chapter 1, Table 1]. Initially, the AgO centres are considered to be bound to the same solvent molecules that solvate the parent Ag⁺ ions [these solvates are considered to vary in their ability to trap electrons, accounting for the spread of yields of the various AgO centres formed from them]. They exhibit a reduced hyperfine interaction from the free atom value, almost entirely as a result of electron delocalisation onto the solvent ligands. On annealing these are thought to move away, forming a variety of partially desolvated centres. If this occurs one molecule at a time, the centre becomes asymmetric, with consequent admixture of 5p character into the predominantly 5s orbital. This has two effects on the observed ESR signals. First, a further reduction in \(A_{\text{iso}}\) is observed as a result of a reduction in the Fermi contact term and second, the signals become markedly anisotropic and there is a shift to lower g-values.
Ultimately, solvent molecules are completely lost and unsolvated atoms are formed. These sometimes remain trapped and can be detected but are often mobile and react with Ag⁺ to form clusters such as Ag₂⁺ and Ag₄ⁿ⁺ [see Chapter 3]. Fig. 1 shows how the experimental data for the predominant Ag⁰ centre observed in ice matrices has been rationalised in terms of the this model.

At 4.2K e⁻ is captured by Ag⁺(aq) to form centre (1)⁴. The ESR data indicates that the electron enters a symmetrical antibonding orbital comprised of ≈88% 5s(Ag) and 12% 3pₓ₋₃pₒ(0) character. Electron-spin echo modulation (ESEM) studies⁷ have established that this Ag⁰ centre is surrounded by four water molecules, tetrahedrally arranged, with the 8 protons in the first solvation shell equidistant at 0.31nm.

On annealing to 77K, conversion to centre (2) was observed⁴. This centre had ESR parameters very similar to one of the centres observed after irradiation at 77K³. ESEM studies⁷ have established that this Ag⁰ centre is surrounded by 7 protons at 0.335nm and 1 proton at 0.183nm. Symons⁸ considers that this centre is formed as a result of a distortion of centre (1) that results in the stabilisation of the antibonding electron. He proposes that the weakening of a single Ag-0 bond resulting in the electron acquiring 5pₓ character, where z is in the Ag-0 direction, would explain the reduction in Aᵯ₀, the observed anisotropy and reduction of the g-value. Further, the proposed breaking of a single O-H---O hydrogen bond and a pivotal motion about the remaining H bond, bringing the free O-H proton closer to
FIGURE 1
Models for electron trapping by Ag⁺(H₂O)₄ at 4.2 K and subsequent changes on annealing and photolysis. (A solvation number of three is used for illustrative purposes only) [Refs. 6 and 8].
silver, is in agreement with the ESEM data and successfully accounts for the 6G superhyperfine coupling observed from this centre.

$E_a$ for the conversion from centre (1) to centre (2) was found to be 0.09eV and it has been shown to be ~75% reversible on re-cooling to 4.2K and exposing to 25,000cm$^{-1}$ (400nm) light. This photochemical conversion is considered to involve a 5s→5p transition in centre (2) which is somewhat modified by electron delocalisation onto the solvent ligands. It is thought that this would form an excited state with considerable ionic character, enabling the solvent molecules to re-orientate to the positions they adopt for the solvation of Ag$^+$. [An alternative mechanism has proposed electron transfer, in the form of tunnelling, to neighbouring Ag$^+$ solvates.]

Studies of Ag$^0$ centres formed in ethanol matrices have shown that, although slight changes of the ESR parameters occur on annealing from 4K to 77K [see Chapter 1, Table 1], there is not such a marked change as in the case of aqueous solutions and no such re-arrangement of solvent structure has been proposed. ESEM data from Ag$^0$ centres in methanol concurs with this view.

Studies of Ag$^0$ centres formed in ethanol/water mixtures have provided interesting results. In 1971, Zhitnikov and Peregund studied this system at 77K. They observed a change in the ESR signals at M.F 0.13 ethanol
from those characteristic of a water-type Ag\(^0\) species [similar to centre (2) in Fig. 1] to signals with \(^{109}\text{A}_{\text{iso}} = 481\text{G}/^{107}\text{A}_{\text{iso}} = 417\text{G}\), which were not observed in pure ethanol and were ascribed to Ag\(^0\) centres with a mixed solvation shell. In 1980, Li and Kevan\(^6\) studied this system at 4K. They observed a sudden change from a water-type spectrum at M.F. 0.13 ethanol [centre (1) in Fig. 1] to an ethanol-type spectrum from M.F. 0.14 to 1.00 ethanol. This result was interpreted in terms of preferential solvation at M.F. 0.13 ethanol. On annealing to 77K, a sudden change was still observed at M.F. 0.13 ethanol, but in this case from a water type species [centre (2) in Fig. 1] to an atom-like species with \(^{109}\text{A}_{\text{iso}} = 706\text{G}\). No signals from the centre reported by Zhitnikov and Peregund\(^5\) were observed.

Because of the number of Ag\(^0\) centres formed in ethanol/water mixtures, this particular system was chosen for conjoint ESR and optical studies. It was hoped that these would also assist in the interpretation of solvent effects in the M.F. 0.13 to 0.14 ethanol region.
2.2. EXPERIMENTAL.

1. SAMPLES.

$D_2O$ (99.8% enrichment) and $d-6$ ethanol were supplied by Magnetic Resonance Ltd. De-ionised water and reagent grade ethanol were used. Silver perchlorate was Analar grade and was used as supplied by B.D.H Ltd. $^{107}Ag$ (98.2% enrichment) was supplied by Oak Ridge Laboratories, Tennessee. Sodium fluoride was reagent grade, (B.D.H.), and was used according to Bales and Kevan$^{12}$ to increase the yield of $Ag^0$ centres in aqueous solutions.

Samples were prepared by dissolving silver perchlorate in the required M.F. ratio of solvents. The latter were measured using a 0.00-1.00ml variable "Eppendorf" pipette. They were then placed into quartz ESR tubes and optical cells and frozen to 77K by slowly lowering them into liquid nitrogen. [When samples were used only for ESR experiments, ESR tubes were not used. In these cases, small frozen beads were prepared by dropping solutions from a teat-pipette into liquid nitrogen.]

Samples were irradiated using a "Vickrad" $^{60}Co$ source which had a dose rate of approximately $1.6x10^2$rd/s$^{-1}$ [doses within the range of 0.3-1.2Mrd were normally used].
2. INSTRUMENTATION.

ESR spectra were recorded using a Varian E109 X-band spectrometer equipped with a Bruker BH12E NMR gaussmeter and a Hewlett Packard 5253B frequency counter. Spectra were accumulated using a Hewlett Packard 9835B data acquisition system. g-values were measured using DPPH markers \( (g = 2.0036) \), and were corrected using the Breit-Rabi equation.\textsuperscript{13}

UV and visible spectra were recorded using a Pye-Unicam SP700 spectrophotometer. Conventional 1.0mm path-length cells (Specac) and demountable variable path-length (0.010-0.025mm) cells (Beckman) were used. These were inserted into specially fabricated quartz dewars, equipped with optical windows, which were filled with liquid nitrogen [see Fig 2a]. The interior of the spectrophotometer was purged with gaseous nitrogen and jets of nitrogen were also played across the optical windows to prevent condensation.

Samples for both ESR and optical studies were annealed by placing them into a specially constructed brass block at 77K [see Fig. 2b]. This was brought to a given temperature by raising or lowering the block in a surrounding bath of liquid nitrogen. Samples were placed in the block for a measured time, quickly cooled to 77K and then removed and replaced in liquid nitrogen. Temperatures were measured using a copper-constantan thermocouple and a Comark 5000 digital readout. The thermocouple was positioned very close to the centre of the optical and ESR samples.
FIGURE 2.a.
Apparatus used for Optical Studies at 77 K
FIGURE 2.b.
Apparatus used for Annealing Samples

- Cotton wool
- Brass Block
- Thermocouple
- Sample in optical cell or ESR tube
- Liquid nitrogen
- Polystyrene container on jack
Comparison of the ESR spectra of samples annealed using this apparatus to those obtained using a nitrogen flow-system with electronic temperature control (Varian) showed that results could be reproduced to within ±2.5K.

IR spectra were recorded using a Perkin Elmer 580 spectrophotometer equipped with a Specac 20000 vacuum jacketed cell holder and a proportional temperature controller. This enabled cooling to 103K ± 1K. Demountable cells (Beckman) were used with path lengths from 0.12 to 0.25μm.
2.3 RESULTS.

A number of discrete Ag\(^0\) centres produced by the \(\gamma\)-irradiation at 77K of frozen AgCl\(_4\) solutions in various ethanol/water mixtures were first observed and characterised by ESR. Fig. 3 shows a plot of \(A^{\text{iso}}\) for particular Ag\(^0\) species against the solvent composition(s) at which they were observed at 77K. The species were labelled in order of increasing hyperfine interaction, with species [i] having the smallest \(A\)-value and species [x] the largest. The ESR parameters for these centres are listed in the Appendix (Tables 1, 2 and 3) and are discussed in section 2.4. It can be seen from Fig. 3 that a dominant species was generally observed at a given solvent composition. A marked change in the dominant species was observed between M.F. 0.12 and M.F. 0.14 ethanol from species [iv], which was dominant centre in ice, to species [ii], which was only observed in mixtures. A gradual increase in the intensity of species [vii] was then observed until from M.F. 0.30 to 1.00 ethanol this became the dominant centre.

Optical spectra were also observed at various solvent compositions and absorptions were assigned to Ag\(^0\) on the basis of conjoint ESR data. It was possible to assign absorptions to particular Ag\(^0\) species when the magnetic data showed that they were present at high relative concentrations. Sections (1) to (4) report the experiments which enabled these individual optical assignments to be made, whilst section (5) reports detailed investigations of
FIGURE 3
Plot of $^{107}$A$_{iso}$ against mixture composition for the various Ag$^{0}$ centres observed by ESR in γ-irradiated AgClO$_4$ solutions in ethanol/water mixtures at 77 K. [Predominant species are shown in bold.]

4K results are shown by dotted lines.
the M.F. 0.12 to M.F. 0.15 ethanol region.

1. \( H_2O \).

(a). 77K.

Fig. 4a shows the ESR spectrum, Fig. 4b the optical spectrum, recorded at 77K, obtained from a 0.20M \( AgClO_4 \) + 0.20M NaF solution that had been \( \gamma \)-irradiated for \( 5.4 \times 10^3 \) s at 77K. The sample was bright yellow, polycrystalline and somewhat opaque. Table 1 lists the ESR parameters and optical data for the \( Ag^0 \) centres observed.

\[
\text{Table 1}
\]

<table>
<thead>
<tr>
<th>Species</th>
<th>( ^{107})Aiso (G)</th>
<th>( ^{109})Aiso (G)</th>
<th>gav</th>
<th>Absorption max. ( \nu ) (cm(^{-1})) ( \lambda )(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iii</td>
<td>-430</td>
<td>-498</td>
<td>1.998</td>
<td></td>
</tr>
<tr>
<td>iv*</td>
<td>-467</td>
<td>-540</td>
<td>1.998</td>
<td>24,600 406</td>
</tr>
<tr>
<td>v</td>
<td>-515</td>
<td>-596</td>
<td>2.000</td>
<td></td>
</tr>
</tbody>
</table>

* Estimated to ±5G, g to ±0.002, \( \nu \) to ±500 cm\(^{-1}\)

* Major Species [Apply to all Tables]

Species [iv] exhibited an additional 6G SHF to one proton.
FIGURE 4
(a) The ESR, (b) the optical spectrum of a γ-irradiated 0.20M AgClO₄ + 0.20M NaF in H₂O solution at 77 K.
The ESR spectrum was characteristic of a range of AgO centres. [The doublet with $A = 505$ G centred at free spin resulted from H trapped in the quartz sample tubes. Central features from OH have been deleted from the figures for the sake of clarity]. By using $^{107}$Ag in D$_2$O signal resolution was improved and small signals from other centres could be detected [see Appendix Table 1 for a complete listing of all the centres observed]. Species [iv] appeared very similar to centre (2) described in section 2.1. Although this was always the major species observed, the relative yields of the other centres were found to increase with irradiation time.

The broad optical absorption centred at 24,600cm$^{-1}$ (406nm) with a bandwidth of 6,500cm$^{-1}$ (470-360nm) was assigned to a modified $^2P\rightarrow^2S$ transition in AgO. This was considered to be mainly characteristic of centre [iv], as a result of the high relative concentration of this species indicated by the ESR spectrum, although there was probably a significant contribution from centres [iii] and [v]. Some very slight contribution from centres [vi] and [viii] was also likely. [A slight shift of the absorption peak from 24,200cm$^{-1}$ (413nm) after 0.25hrs irradiation to 25,000cm$^{-1}$ (400nm) after 4hrs irradiation, coupled with the observation of larger relative ESR signals from the latter suggested that these minority centres were responsible for the higher energy component of the absorption envelope.]
The assignment of the optical absorption to AgO was supported by the similar temperature profiles of the ESR and optical spectra [see section (b)] and was in reasonable agreement with the lowest energy absorption reported by Zhitnikov and Melnikov for AgO in \( \gamma \)-irradiated frozen AgNO\(_3\) solutions [see Chapter 1, Table 2]. Matrix broadening effects were considered responsible for the lack of resolution of the \( 2p_{3/2} \longleftrightarrow 2s_{1/2} \) and \( 2p_{1/2} \longleftrightarrow 2s_{1/2} \) transitions which have been clearly observed in the gas phase.\(^{17}\) The shift of the absorption maximum from the gas phase values will be discussed in section 2.4.

(b) ANNEALS TO HIGHER TEMPERATURES.

Fig. 5a shows the ESR spectrum, Fig. 5b the Optical spectrum obtained after the sample had been annealed to 127K for 300s and re-cooled to 77K. [The sample remained bright yellow.] Table 2 lists the ESR parameters and optical data of the AgO species observed.

\[\begin{align*}
\text{Species} & & 10^7A_{iso} \ (G) & & 10^9A_{iso} \ (G) & & g_{av} & & \text{Absorption max.} \\
\text{i} & & -375 & & -430 & & 1.995 & & \\
\text{iii}^* & & -430 & & -498 & & 1.998 & & 25,800 \ (387) \\
\end{align*}\]
FIGURE 5
(a) The ESR spectrum, (b) the optical spectrum of a 0.20M AgClO$_4$ + 0.20M NaF solution in H$_2$O $\gamma$-irradiated at 77 K, annealed to 127 K for 300 s, and re-cooled to 77 K.
The ESR spectrum showed that the Ag\textsuperscript{0} centres had converted during the anneal to species [iii] and to a new centre, [i], which was markedly anisotropic [see Appendix Table 1 for $g_\parallel$ and $g_\perp$ -values] and had a very reduced hyperfine coupling. A small signal characteristic of Ag\textsuperscript{+2} was also observed, indicating that some Ag\textsuperscript{0} centres had been lost as a result of reaction with Ag\textsuperscript{+} ions.

Before discussing the optical results, it must first be pointed out that the optical spectrum shown in Fig. 5b was obtained using a conventional 1.0mm path-length cell, whereas the spectrum shown in Fig. 4b was obtained using a demountable cell with a path-length of about 0.10mm. The use of the latter was found necessary to reduce light scattering from the samples and to bring the absorption within the dynamic range of the spectrometer. Unfortunately there was not time within the scope of this project to build a device in which this type of cell could be accurately annealed and a conventional 1.0mm cell had to be used. However, although there was some distortion of the absorption peak shown in Fig. 5b, as a consequence of working almost at the limits of the spectrometer, it provided some useful information.

The optical spectrum showed only slight changes from that observed before the anneal, taking into account the effects on lineshape described above. However, the following were considered significant:
A slight decrease of the broad absorption in the 25,000cm\(^{-1}\) region was observed.

There appeared to be a shift of this band to higher energy, although precise measurement was difficult for the reasons outlined above.

An increase in intensity of the shoulder in the 34,500-29,400cm\(^{-1}\) (290-340nm) region was observed.

It was considered that (1) correlated with the decrease in Ag\(^0\) concentration detected by ESR, that (2) may have been associated with the change in the predominant Ag\(^0\) species and that (3) was associated with the build up of Ag\(^+\)\(_2\).

When samples were annealed to 157K for 300s and re-cooled to 77K, ESR signals from Ag\(^0\) centres disappeared and the spectrum changed to that characteristic of Ag\(^+\)\(_2\) centres. The broad optical band centred at about 25,000cm\(^{-1}\) also disappeared, providing clear evidence for the assignment to Ag\(^0\), and a spectrum characteristic of Ag\(^+\)\(_2\) was observed [see Chapter 3]. Samples were colourless at this point.

**2.** M.F. H\(_2\)O **0.80**/ M.F. EtOH **0.20**

(a) 77K.

Fig. 6a shows the ESR spectrum, Fig. 6b the optical spectrum obtained from a 0.20M AgClO\(_4\) solution at this solvent composition after \(\gamma\)-irradiation for 3.2\times10\(^3\)s at 77K.
FIGURE 6
(a) The ESR spectrum, (b) the optical spectrum of a γ-irradiated 0.20M AgClO₄ in M.F. 0.20 EtOH/H₂O solution at 77 K.
The sample was pale yellow and was less opaque than the frozen aqueous solution reported in section (1). Table 3 lists the ESR and optical data.

**Table 3**

<table>
<thead>
<tr>
<th>Species</th>
<th>$^{107}<em>{\text{A}</em>{\text{iso}}}(G)$</th>
<th>$^{109}<em>{\text{A}</em>{\text{iso}}}(G)$</th>
<th>$g_{av}$</th>
<th>Absorption max. $\nu (\text{cm}^{-1})$</th>
<th>$\lambda (\text{nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii*</td>
<td>-415</td>
<td>-475</td>
<td>2.001</td>
<td>27,800</td>
<td>360</td>
</tr>
<tr>
<td>ix</td>
<td>-575</td>
<td>-665</td>
<td>1.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ESR spectrum showed that different AgO centres were formed in this system compared to the pure aqueous solution reported in section (1) [central features from ethanol radicals have been deleted for the sake of clarity]. In particular, species [ii] was observed as the major centre [this species was never observed in the pure solvents and had similar parameters to the centre reported by Zhitnikov and Peregund5]. The optical spectrum consisted of an asymmetric absorption with a linewidth of 10,300 cm$^{-1}$ (286-406nm). This was assigned mainly to AgO species [ii] according to the ESR data, although significant
contributions from centres [ix] and [x] would have been expected and may have contributed to the asymmetry.

(b) ANNEALS TO HIGHER TEMPERATURES.

Fig. 7a shows the ESR spectrum, Fig. 7b the optical spectrum of this sample after annealing to 123K for 300s and re-cooling to 77K. [The sample was still pale yellow.] Table 4 lists the magnetic and optical data.

Table 4

ESR and Optical Data For AgO Centres Observed in a H2O/ETOH Mixture (0.80/0.20 M.F.) after Annealing to 123K

<table>
<thead>
<tr>
<th>Species</th>
<th>107A_{iso} (G)</th>
<th>109A_{iso} (G)</th>
<th>g_{av}</th>
<th>Absorption max. v (cm^{-1})</th>
<th>\lambda (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>-415</td>
<td>-475</td>
<td>2.001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ix</td>
<td>-575</td>
<td>-665</td>
<td>1.999</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x^*</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td>30,500</td>
<td>328</td>
</tr>
</tbody>
</table>

Fig. 7a shows that the result of the anneal was to cause the remarkable conversion of the AgO centres formed at 77K to species [x]. This centre gave rise to completely isotropic ESR signals with ESR parameters similar to the free atom values [in fact A was slightly larger] and was
FIGURE 7
(a) The ESR and (b) the optical spectrum of Ag$^\circ$ centres observed after annealing the system shown in Figure 5 to 123 K for 300 s and re-cooling to 77 K.
associated with a completely desolvated Ag$^0$ centre [see section 2.4 for discussion.]

Fig. 7b shows an absorption peak at 30,500 cm$^{-1}$ which was assigned to species [x] on account of the similar temperature profiles of the optical and ESR spectra for this centre. This can be seen to be very close to the value for the $^2p \rightarrow ^2s$ gas phase absorption, as would be expected for this species [in fact the absorption occurred at a slightly higher energy than the latter, see section 2.4 for discussion]. Neither of the small shoulders either side of this absorption was considered to be attributable to features resulting from the $^2p$ splitting which have been resolved in the gas phase [see Chapter 1, Table 2]. The shoulder at 27,800 cm$^{-1}$ (360 nm) was assigned to the residual amounts of species [ii] and [ix] detected by ESR. The small shoulder at 32,200 cm$^{-1}$ was associated with Ag$^+$ centres and will be discussed in Chapter 3.

On further annealing the sample to 150K for 300s, ESR signals from Ag$^0$ centres decayed completely and there was a concomitant fall in the 30,500 cm$^{-1}$ optical absorption, providing clear evidence for the assignment to Ag$^0$. The sample was extremely pale yellow at this point. Ag$_4^+$ centres were formed and their spectra are discussed in Chapter 3. Signals assigned to [Ag-CH$_2$CH$_2$OH]$^+$ centres with $A_{iso} = 130$ G were sometimes detected after annealing to 140-150K, however no additional optical absorption(s) attributable to these were observed.
3. M.F. H$_2$O 0.50/M.F. EtOH 0.50.

(a). 77K.

Fig. 8a shows the ESR spectrum, Fig. 8b the optical spectrum of a 0.20M AgClO$_4$ solution in the above solvent mixture which had been $\gamma$-irradiated for $3.6 \times 10^3$ s. The sample was purple/yellow and considerably more transparent than the 0.20 M.F. EtOH sample reported in section (2). Table 5 summarises the optical and magnetic data.

**Table 5**

ESR and Optical Data For Ag$^0$ Centres Observed in an H$_2$O/EtOH Mixture (0.50/0.50 M.F.) at 77K.

<table>
<thead>
<tr>
<th>Species</th>
<th>$10^7$ $A_{iso}$ (G)</th>
<th>$10^9$ $A_{iso}$ (G)</th>
<th>$g_{av}$</th>
<th>Absorption max. $\nu$ (cm$^{-1}$) $\lambda$(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>-415</td>
<td>-475</td>
<td>2.001</td>
<td></td>
</tr>
<tr>
<td>vii*</td>
<td>-540</td>
<td>-623</td>
<td>1.999</td>
<td>25,900</td>
</tr>
<tr>
<td>ix</td>
<td>-575</td>
<td>-665</td>
<td>1.999</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td></td>
</tr>
</tbody>
</table>

The ESR spectrum showed that the major Ag$^0$ centre observed at this solvent composition was species [vii], one of the two species observed in pure ethanol. Species [ii] was also present at a significant concentration. Large signals from Ag$^+$ centres were also observed. [Central
FIGURE 8
(a) The ESR spectrum, (b) the optical spectrum of a γ-irradiated 0.20M AgClO₄ in M.F. 0.50 EtOH/H₂O solution at 77 K.
features from ethanol radicals have been deleted from Figs. 7a and 8a for the sake of clarity]

The optical spectrum consisted of an absorption at 25,900 cm\(^{-1}\) (382 nm) with a linewidth of 4,600 cm\(^{-1}\) (353-422) and appeared very similar to that observed in pure ethanol and assigned to species [vii] [see section (4)]. The slight shift to lower energy compared to the latter was considered to arise from the presence of species [ii], which was shown in section (2) to absorb at approximately 27,800 cm\(^{-1}\) (360 nm).

(b). ANNEALS TO HIGHER TEMPERATURE.

Fig. 9a shows the ESR spectrum, Fig. 9b shows the optical spectrum observed from this sample after annealing to 123K. Table 6 lists the optical and magnetic data.

Table 6

<table>
<thead>
<tr>
<th>Species</th>
<th>(10^7 A_{iso} (G))</th>
<th>(10^9 A_{iso} (G))</th>
<th>(g_{av})</th>
<th>Absorption max. v (cm(^{-1}))</th>
<th>(\lambda (nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>vii</td>
<td>-540</td>
<td>-623</td>
<td>1.999</td>
<td>30,500</td>
<td>328</td>
</tr>
<tr>
<td>x(^*)</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- 41 -
FIGURE 9
(a) The ESR spectrum and (b) the optical spectrum observed after annealing the system shown in Figure 7 to 123 K and re-cooling to 77 K.
Both spectra can be seen to be very similar to those observed after the anneal of the 0.20 M.F. EtOH solution reported in section (3) and the optical absorption was similarly assigned to the "atom-like" species \([x]\). The ESR spectrum revealed the presence of some \(\text{Ag}^{n+}_4\) centres in this system, to which the small absorption at \(34,200\text{cm}^{-1}\) (292nm) was assigned [see Chapter 3].

On annealing the sample to 150K, ESR and optical signals from \(\text{Ag}^0\) disappeared and were replaced by signals from \(\text{Ag}^{n+}_4\) centres. These will be fully discussed in Chapter 3.

4. **EtOH**

(a). 77K.

Fig. 10a shows the ESR spectrum, Fig. 10b the optical spectrum of a 0.20M \(\text{AgClO}_4\) in EtOH solution which had been \(\gamma\)-irradiated for \(3.6\times10^3\)s at 77K. The sample was glassy and purple in colour. Table 7 lists the magnetic and optical data obtained.

The ESR spectrum showed that only two \(\text{Ag}^0\) species were formed in this system. Signals from \(\text{Ag}^{+}_2\) and \(\text{Ag}^{n+}_4\) centres were also observed, indicating that extensive agglomeration had occurred. [Central features from ethanol radicals have been deleted from Figs. 9-10a for the sake of clarity.]
FIGURE 10
(a) The ESR and (b) the optical spectrum of silver centres in a \( \gamma \)-irradiated 0.2M AgClO\(_4\) EtOH Solution at 77 K.
**Table 7**

ESR and Optical Data For Ag\(^0\) Centres Observed in EtOH at 77K.

<table>
<thead>
<tr>
<th>Species</th>
<th>107(<em>A</em>{iso}) (G)</th>
<th>109(<em>A</em>{iso}) (G)</th>
<th>(g_{av})</th>
<th>Absorption max. (\nu) (cm(^{-1})) (\lambda) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>vii(^x)</td>
<td>-540</td>
<td>-623</td>
<td>1.999</td>
<td>26,700 375</td>
</tr>
<tr>
<td>ix</td>
<td>-575</td>
<td>-665</td>
<td>1.999</td>
<td>26,700 375</td>
</tr>
</tbody>
</table>

The optical absorption with a maximum at 26,700cm\(^{-1}\) and a linewidth of 4500cm\(^{-1}\) (341-402nm) was assigned to Ag\(^0\) species [vii] on account of the ESR data. This value is in agreement with one of the absorptions observed by Zhitnikov and Melnikov for Ag\(^0\) in EtOH [see Chapter 1, Table 2].

The small, broad band at \(\approx\) 20,000cm\(^{-1}\) (500nm) was considered to be responsible for the purple colour and was assigned to solvated electrons. This band was observed in \(\gamma\)-irradiated pure EtOH and was in fact much larger in the absence of silver, indicating that Ag\(^+\) ions were acting as competitive electron traps. The other absorptions shown in Fig. 10b were assigned to Ag\(^+\)_2 and Ag\(^n+\)_4 centres and are further discussed in Chapter 3.

Experiments with \(\gamma\)-irradiated AgClO\(_4\) solutions of different concentrations supported these assignments. At low initial Ag\(^+\) concentration [0.05M], the ESR spectrum showed
that the yield of $\text{Ag}^+$ and $\text{Ag}_2^+$ centres was considerably reduced and the corresponding optical spectrum also reflected this. In contrast, at high initial $\text{Ag}^+$ concentration [0.50M], the relative yields of $\text{Ag}^+$ and $\text{Ag}_4^{2+}$ were considerably increased and larger optical absorptions from these centres were observed.

(b). ANNEALS TO HIGHER TEMPERATURES.

Fig. 11a shows the ESR spectrum, Fig. 11b the optical spectrum obtained after the sample had been annealed to 96K for 300s and re-cooled to 77K. It can be seen that the ESR signals from $\text{Ag}^0$ centres had completely decayed with the concomitant decrease of the optical band assigned to them. The ESR spectrum was characteristic of $\text{Ag}^+$ and $\text{Ag}_4^{2+}$ centres and the optical bands shown in Fig. 11b were assigned to these [see Chapter 3]. The sample became colourless after the anneal and the absorption band at 20,000cm$^{-1}$ assigned to solvated electrons disappeared, presumably as a result of their neutralisation at electron-loss centres.

5. Mixtures in the 0.12 to 0.15 M.F. EtOH Region.

(a) 77K.

Fig. 12a shows the ESR spectrum, Fig. 12b the optical spectrum of a 0.20M $\text{AgClO}_4$ + 0.20M NaF solution in an M.F. $\text{H}_2\text{O}$ 0.88/M.F. EtOD 0.12 mixture that had been $\gamma$-irradiated for $7.2\times10^{-3}$s at 77K. The sample was inhomogeneously yellow
FIGURE 11
(a) The ESR and (b) the optical spectrum of the system shown in Fig. 10 after annealing to 96 K for 300 s and re-cooling to 77 K.
and somewhat opaque. Figs. 13a and 13b show the respective spectra obtained from a solution of these salts at the same concentration in an M.F. H₂O 0.86/M.F. EtOH 0.14 mixture after the same irradiation. The sample was homogeneously very pale yellow and still somewhat opaque. The magnetic and optical data for these sample are listed in tables 9 and 10:

**Table 9**

<table>
<thead>
<tr>
<th>Species</th>
<th>107 A̅_iso (G)</th>
<th>109 A̅_iso (G)</th>
<th>g̅_av</th>
<th>Absorption max.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>v (cm⁻¹)</td>
</tr>
<tr>
<td>iii</td>
<td>-430</td>
<td>-498</td>
<td>1.998</td>
<td></td>
</tr>
<tr>
<td>iv*</td>
<td>-467</td>
<td>-540</td>
<td>1.999</td>
<td>25,300</td>
</tr>
<tr>
<td>v</td>
<td>-515</td>
<td>-596</td>
<td>2.000</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td></td>
</tr>
</tbody>
</table>

**Table 10**

<table>
<thead>
<tr>
<th>Species</th>
<th>107 A̅_iso (G)</th>
<th>109 A̅_iso (G)</th>
<th>g̅_av</th>
<th>Absorption max.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>v (cm⁻¹)</td>
</tr>
<tr>
<td>ii*</td>
<td>-415</td>
<td>-475</td>
<td>2.001</td>
<td>27,000</td>
</tr>
<tr>
<td>vii</td>
<td>-575</td>
<td>-665</td>
<td>1.999</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>-630</td>
<td>-730</td>
<td>2.002</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 12
(a) The ESR and (b) the optical spectrum of Ag\(^{\circ}\) centres in a \(\gamma\)-irradiated 0.20M AgClO\(_4\) + 0.20M NaF solution in M.F. 0.12 EtOH/M.F. 0.88 H\(_2\)O at 77 K.
FIGURE 13
(a) The ESR spectrum, (b) the optical spectrum of a
γ-irradiated 0.20M AgClO₄ + 0.20M NaF in M.F. 0.14
EtOH/H₂O solution at 77 K.
It can be seen that Fig. 12a is almost identical to the ESR spectrum of Ag$^0$ centres formed in H$_2$O at 77K [see Fig. 4a]. The optical spectrum was also very similar to that obtained from the latter [see Fig. 4b]. The small shift of the centre of the optical band from 24,600cm$^{-1}$ (406nm) for Ag$^0$ in H$_2$O was considered to arise from the presence of species [x] which was shown in section (2) to absorb at higher energy [Ag$^+$ centres were shown to be present by ESR and could also have contributed to this shift.]

Figs. 13a and 13b can be seen to be very similar the ESR and optical spectra observed from Ag$^0$ centres formed in the M.F. EtOH 0.20/M.F. H$_2$O 0.80 mixture [see Figs. 6a-b]. The small shift of the absorption peak from 27,800cm$^{-1}$ (360nm) in the latter was considered to be due to the lower concentration of species [x] in this system.

These results suggested that there was change from an Ag$^0$ species solvated by water at 0.12 M.F. EtOH (species [iv]) to an Ag$^0$ species with a mixed solvation shell at 0.14 M.F. EtOH (species [ii]). Fig. 14 shows plots of the peak to peak heights of these species in D$_2$O/EtOD mixtures over the 0.12 to 0.15 M.F. EtOD range after irradiation for various times, [these were considered to be approximately equivalent to the concentrations of these species as their linewidths were similar], from which it can be seen that the mixture composition at which species [ii] became the dominant species was also slightly dose dependent.
Yields of the predominant species observed in \( \gamma \)-irradiated EtOD/D\(_2\)O + 0.05M \( ^{107}\)AgClO\(_4\) mixtures in the M.F. 0.12 to 0.15 EtOD range after irradiation for various times at 77 K.

**a)**

- \( \triangle \) species [ii]
- \( \circ \) species [iv]

**b)**

\( \gamma \)-irradiated \( 1.20 \times 10^2 \) s

\( \gamma \)-irradiated \( 1.08 \times 10^3 \) s
FIGURE 14 (Continued)

\[ \text{ESR Signal Amplitude} \]

(c) \[ \Delta \text{Species [ii]} \]
\[ \circ \text{Species [iv]} \]

\( \gamma \)-irradiated \( 4.68 \times 10^3 \) s

(d) \[ \Delta \]

\( \gamma \)-irradiated \( 9.12 \times 10^3 \) s
The marked change in the visual appearance of samples from 0.12 to 0.15 M.F. ethanol suggested that a phase change occurred in this region. This was supported by data from IR studies. Fig. 15a-f shows IR spectra of EtOD/D₂O mixtures observed at 103K. These probed the symmetric O-H stretch, \( v_1 \), arising from residual protons. Table 11 lists the optical data.

**Table 11**

IR Data for \( v_1 \) Observed in EtOD/D₂O Mixtures at 103K.

<table>
<thead>
<tr>
<th>Solvent Composition</th>
<th>( v_{max} ) (cm(^{-1}))</th>
<th>( w_{1/2} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000 M.F. D₂O</td>
<td>3270</td>
<td>270</td>
</tr>
<tr>
<td>0.12 M.F. EtOD</td>
<td>3270</td>
<td>270</td>
</tr>
<tr>
<td>0.13 M.F. EtOD</td>
<td>3270</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>3250*</td>
<td>1600*</td>
</tr>
<tr>
<td></td>
<td>(Composite)</td>
<td>(Composite)</td>
</tr>
<tr>
<td>0.15 M.F. EtOD</td>
<td>3276</td>
<td>1200</td>
</tr>
<tr>
<td>0.50 M.F. EtOD</td>
<td>3244</td>
<td>1640</td>
</tr>
<tr>
<td>1.000 M.F. EtOD</td>
<td>3235</td>
<td>1700</td>
</tr>
</tbody>
</table>

\( v \) estimated to \( \approx 2 \text{cm}^{-1} \)

* Approximate values only.

Fig. 15a shows that at M.F. 1.000 D₂O a sharp band was observed. This contrasted with the extremely broad band observed in the liquid phase and was considered to be representative of polycrystalline ice. Fig. 15f shows
FIGURE 15
IR spectra of D₂O/EtOD mixtures at 103 K.
(a) M.F. 1.000 D₂O; (b) M.F. 0.120 EtOD;
(c) M.F. 0.134 EtOD; (d) M.F. 0.150 EtOD;
(e) M.F. 0.500 EtOD; (f) M.F. 1.000 EtOD.
that at M.F. 1.000 EtOD, which formed a good glass, a broad band was observed.

Fig. 15b shows that at 0.120 M.F. EtOD samples had an absorption similar to that observed in pure ice [the increase in absorption intensity compared with Fig. 15a was attributed to the lower level of deuteration of the EtOD used to make the solution than for the D$_2$O]. This was in agreement with the thermal analysis and X-ray diffraction results of Boultron and Kaufmann, which showed that up to this concentration of EtOH phase separation occurred into a hexagonal ice and an amorphous region, the latter having a higher ethanol concentration than the original solution.

Fig. 15c shows that at 0.13 M.F. EtOD a composite spectrum was observed. This appeared to consist of a sharp absorption very similar to that observed in pure ice, superimposed on a broad absorption similar to that observed in EtOD glasses. At 0.15 M.F. EtOD [Fig. 15d] the spectrum consisted only of a broad glassy absorption. This band occurred at a slightly higher energy and was slightly narrower than the band observed in pure EtOD. Boutron and Kaufmann reported that no hexagonal ice was formed at M.F. 0.14 ethanol and above and observed the formation of "clathrate I", which was determined to have a composition of 6-8 EtOH/46H$_2$O, on fast cooling to 77K.

Fig. 15e shows that at 0.50 M.F. EtOD the IR spectrum more closely resembled that observed from pure EtOD.
(b) ESR Studies at 4K.

ESR studies at 4K of Ag\textsuperscript{0} centres formed after the X-irradiation at 4K of \textsuperscript{107}AgClO\textsubscript{4} solutions in various EtOD/D\textsubscript{2}O + 0.20 M.F NaF solutions were generally in agreement with those reported by Li and Kevan\textsuperscript{6} for solutions in EtOH/H\textsubscript{2}O mixtures. A change from a water-type "A" spectrum to an ethanol-type "B" spectrum between 0.13 and 0.15 M.F. EtOD at 4K was similarly found. Table 12 lists the parameters of the species observed, which are also represented in Fig. 3:

Table 12

ESR Data for Ag\textsuperscript{0} Centres Observed at 4K After X-irrad at 4K.

<table>
<thead>
<tr>
<th>Solvent Composition</th>
<th>Spectrum</th>
<th>\textsuperscript{107}A_{iso} (G)</th>
<th>ΔH(G)</th>
<th>\textit{g_{av}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.00 M.F. D\textsubscript{2}O</td>
<td>A</td>
<td>-547</td>
<td>5</td>
<td>2.00\textsubscript{1}</td>
</tr>
<tr>
<td>0.13 M.F. EtOD</td>
<td>[v]</td>
<td>-508</td>
<td>5</td>
<td>2.00\textsubscript{0}</td>
</tr>
<tr>
<td></td>
<td>A</td>
<td>-547\textsuperscript{*}</td>
<td>5</td>
<td>2.00\textsubscript{1}</td>
</tr>
<tr>
<td>0.14 M.F. EtOD</td>
<td>B</td>
<td>-552</td>
<td>15</td>
<td>2.00\textsubscript{0}</td>
</tr>
<tr>
<td>1.00 M.F. EtOD</td>
<td>B</td>
<td>-552</td>
<td>15</td>
<td>2.00\textsubscript{0}</td>
</tr>
</tbody>
</table>

\textsuperscript{A} accurate to ± 5G, \textit{ΔH} to ± 2G, \textit{g} to ± 0.002

\textsuperscript{*} Major Species

When samples were annealed to 77K, spectra observed at
77K were identical to those observed at 77K after \( \gamma \)-irradiation at 77K [see sections 1, 4 and 5]. These results were in agreement with the observations of Li and Kevan after annealing to 77K apart from the 0.14 M.F. EtOD sample. In these studies species [ii] was the major centre observed at 77K whereas Li and Kevan reported that a centre with the same ESR parameters as species [x] was the only species observed at 4K. Their published spectra showed that species [ii] was in fact present, however, even though the accompanying text stated that it was not. Experiments at 4K showed that this signal was slightly distorted at 0.6mW microwave power [the level used by Li and Kevan] but was clearly visible.

Unfortunately, optical studies of the Ag\(^{0}\) centres formed at 4K were not possible within the scope of this project. It is suggested that future work includes such studies, since interesting optical shifts would be expected on annealing to 77K.
2.4 DISCUSSION.

(A) General Discussion of the Observed Ag$^0$ Centres and ESR Results in the M.F. 0.12 to 0.15 EtOH Region.

A number of the Ag$^0$ species observed by ESR in these systems have been previously reported and discussed$^1$-$^6$ [see Appendix and Chapter 1, Table 1]. However, there has been no satisfactory explanation of the ESR results obtained at 4K in the M.F. 0.12 to 0.15 EtOH region. The following model is proposed to account for the experimental observations:

It is considered that, in the pure solvents, electron capture at 4K by $[\text{Ag(H}_2\text{O})_4]^+$ and $[\text{Ag(EtOH)}_4]^+$ solvates produces Ag$^0$ centres which still retain the solvation of the parent ions, forming centres (1) and (5) [see below] and giving rise to spectra A and B respectively [see Fig. 3 and Table 12].

In ethanol/water mixtures a statistical distribution amongst the possible Ag$^0$ species (1)-(5) listed below would be expected to be formed at 4K:

\[
\begin{align*}
[\text{Ag(H}_2\text{O})_4]^0 & \quad (1) \\
[\text{Ag(H}_2\text{O})_2\text{(EtOH)}_2]^0 & \quad (2) \\
[\text{Ag(H}_2\text{O})_2\text{(EtOH)}_2]^0 & \quad (3) \\
[\text{Ag(H}_2\text{O})(\text{EtOH})_3]^0 & \quad (4) \\
[\text{Ag(EtOH)}_4]^0 & \quad (5)
\end{align*}
\]
Table 12 shows that the $A_{is}$ values for species (1) and (5) were identical within experimental error. This would be expected since the $Ag^0$ centres have been shown to be solvated by four oxygen atoms in both cases. The comparison of $A_{is}$ values was therefore shown to be of little use for distinguishing between species (1) and (5) and the observation of only two types of spectra over the complete mole fraction range of solvents showed that it was also impossible to distinguish between the centres (2)–(4) on the basis of only $A_{is}$ values.

The marked increase in the linewidth of centre (1) compared to centre (5) was considered to be associated with the less precise solvation associated with a glassy system. The observed change from a water [type A] to an ethanol [type B] ESR spectrum at $\approx$ M.F. 0.13 $^{5}$ EtOH at 4K was therefore not considered to reflect the preferential solvation of $Ag^+$ by EtOH, as suggested by Li and Kevan$^6$, but rather to be associated with the formation of a glass, as supported by the IR data at 103K [see Table 11].

On annealing to 77K or irradiating directly at 77K, the range of $Ag^0$ centres observed was considered to arise from the desolvation of species (1)–(5). For example, centre [iv] was considered to be formed as a result of the partial desolvation of one of the $H_2O$ ligands associated with species (1)$^8$ [see section 2.1]. Centre [ii] may have resulted from the desolvation of an EtOH ligand from an $Ag^0$ centre with a mixed solvation as shown for species (2)–(4).
Centre [x] was shown to be a completely desolvated silver atom. These centres were distinguishable by their different $A_{\text{iso}}$ and g-values, for the reasons outlined in the introduction. Signal linewidths were also found to vary. In many cases this was mainly as a result of anisotropy, however, it is considered significant that centre [ii], which was only observed in glassy systems, was broadened to the extent that the parallel and perpendicular components could not be resolved.

The observation of silver clusters formed directly after irradiation at 77K in ethanol-rich mixtures is considered to reflect the greater mobility of Ag$^0$ in these systems and to be indicative of extensive ion pairing before irradiation.
(B) ESR and Optical Correlations.

The optical absorptions which could be satisfactorily assigned to particular species are summarised in the Appendix (Table 4). Fig. 16 shows a plot of $\Delta A/A_F^{\max}$ against $v$ for these, where $\Delta A = \frac{107}{A_{iso}} A_{iso}$ for the particular $Ag^0$ centre $-A_F$ and $A_F = A_{iso}$ for the free atom in the gas phase.\textsuperscript{14}

It can be seen from Fig. 17 that $v$ decreased linearly with decreasing $\Delta A/A_F^{\max}$ from species [x] to species [vii]. This would be expected from the simple bonding scheme shown in Fig. 17. In this model, the decrease $A_{iso}$ from the free spin value is considered to arise only from electron delocalisation onto the solvent ligands. The resulting modified $5s \rightarrow 5p$ transition in the $Ag^0$ solvate can be seen to occur at a reduced energy to the free atom value, the extent of the reduction being to a first approximation linearly dependent on the extent of delocalisation. In the case of the desolvated species, [x], the increased energy of the absorption relative to the gas phase value is considered to arise from the destabilisation of the $5s$ orbital as a result of compression due to Pauli exclusion forces exerted by the matrix. [The observed increase in $A_{iso}$ for this species relative to the gas phase value has been previously rationalised in terms of these.]
FIGURE 16
Plot of $A/A_F$ against $\nu$ for optical absorptions assigned to various Ag$^0$ centres observed in ethanol/water mixtures.
FIGURE 17
M.O. diagram for a symmetric $[\text{AgL}_4]^\circ$ solvate showing the expected reduction in energy of the $5s \rightarrow 5p$ transition from the free atom value as a result of electron delocalisation.
It can be seen that this model does not apply to centres [ii], [iii] and [iv]. This is considered to be related to
the observed anisotropy of the ESR signals from these
centres. As outlined in the introduction, this anisotropy
has been attributed to the acquisition of 5p character as a
result of the the partial desolvation of one ligand. \( A_{iso} \)
would be significantly reduced for such centres, as a result
of the reduction of the Fermi contact term, not only through
electron delocalisation but by p-hybridisation. This would
be expected to contribute to the observed deviation from
linearity of the plot shown in Fig. 16, where only
delocalisation onto the ligands is considered. The
absorption assigned to species [ii], which is considered to
arise from \( \text{Ag}^0 \) centres surrounded by a mixed solvation
shell, can be seen to be particularly best described by this
partial desolvation model.
2.5 CONCLUSIONS.

Optical absorptions in the range of 24,600-30,500 cm⁻¹ (406-328 nm) were assigned to various Ag⁰ centres formed by the radiolysis of AgClO₄ solutions in ethanol/water mixtures.

The positions of the optical bands assigned to these species were shown to correlate with the ESR parameters, taking into account the effects of (a), delocalisation of the 5s electron onto the solvent ligands and, in some cases, (b), the acquisition of 5p character as a result of the partial desolvation of one ligand.

A sudden change observed both optically and by ESR between M.F. 0.12 and 0.14 ethanol at 77K was considered to arise from a phase transition. This was supported by IR data, which suggested that there was a change from a polycrystalline to a glassy matrix in this region. Ag⁰ centres observed at 77K changed largely from those associated with a solvent shell composed of water molecules at M.F. 0.12 ethanol to those associated with a mixed solvation shell at M.F. 0.14 ethanol. The optical and ESR data for these centres, especially the latter, were found to be best described by model (b).
REFERENCES.

APPENDIX

Table 1

ESR Data For Ag$^0$ Centres Observed in D$_2$O at 77K.

<table>
<thead>
<tr>
<th>Species</th>
<th>107</th>
<th>A (G)</th>
<th>g</th>
<th>A$_{\perp}$</th>
<th>A$_{\parallel}$</th>
<th>A$_{iso}$</th>
<th>g$_{\perp}$</th>
<th>g$_{\parallel}$</th>
<th>g$_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>-378</td>
<td>-385</td>
<td>-380</td>
<td>1.994</td>
<td>2.000</td>
<td>1.996</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iii</td>
<td>-435</td>
<td>-440</td>
<td>-437</td>
<td>1.995</td>
<td>2.003</td>
<td>1.998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>iv</td>
<td>-475</td>
<td>-480</td>
<td>-477</td>
<td>1.996</td>
<td>2.002</td>
<td>1.998</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>v</td>
<td></td>
<td>-510</td>
<td></td>
<td></td>
<td></td>
<td>2.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>vi</td>
<td></td>
<td>-534</td>
<td></td>
<td></td>
<td></td>
<td>2.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>viii</td>
<td>-554</td>
<td>-558</td>
<td>-555</td>
<td>1.996</td>
<td>2.002</td>
<td>1.998</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Observed only after annealing

Errors in g estimated to be ±0.001
Errors in A estimated to be ±2.5G

[For all Tables]

Table 2

ESR Data for Ag$^0$ Centres Observed in EtOD at 77K.

<table>
<thead>
<tr>
<th>Species</th>
<th>107</th>
<th>A (G)</th>
<th>g</th>
<th>A$_{\perp}$</th>
<th>A$_{\parallel}$</th>
<th>A$_{iso}$</th>
<th>g$_{\perp}$</th>
<th>g$_{\parallel}$</th>
<th>g$_{av}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>vii</td>
<td></td>
<td>-538</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.999</td>
</tr>
<tr>
<td>ix</td>
<td></td>
<td>-573</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.999</td>
</tr>
</tbody>
</table>

- 68. -
Table 3
ESR Data for Additional Ag\textsuperscript{0} Centres Observed in D\textsubscript{2}\textsuperscript{0}/EtOH Mixtures at 77K.

<table>
<thead>
<tr>
<th>Species</th>
<th>107\textsubscript{A} (G)</th>
<th>g</th>
<th>g\textsubscript{av}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>-415</td>
<td>2.001</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>-630</td>
<td>2.002</td>
<td></td>
</tr>
</tbody>
</table>

Species [i] $\equiv$ Centre G\textsuperscript{2}, Centre F\textsuperscript{3}
Species [ii] $\equiv$ Centre $\delta(\Delta \nu)/\Delta \nu = -0.32$\textsuperscript{5}
Species [iii] $\equiv$ Centre D\textsuperscript{2,3}
Species [iv] $\equiv$ Centre A\textsuperscript{2,3}
Species [v] $\equiv$ Centre E\textsuperscript{2}, Centre B\textsuperscript{3}
Species [vi] $\equiv$ Centre E\textsuperscript{3'}\textsuperscript{6}
Species [vii] $\equiv$ Centre EI\textsuperscript{3A}
Species [ix] $\equiv$ Centre EI\textsuperscript{3B}\textsuperscript{6}
Species [x] $\equiv$ Centre 2020\textsuperscript{6}

Table 4
Optical assignments to various Ag\textsuperscript{0} centres.

<table>
<thead>
<tr>
<th>Species</th>
<th>$\nu$ (cm\textsuperscript{-1})</th>
<th>$\lambda$\textsubscript{max} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii</td>
<td>27,800</td>
<td>360</td>
</tr>
<tr>
<td>iii</td>
<td>25,800</td>
<td>387</td>
</tr>
<tr>
<td>iv</td>
<td>24,600</td>
<td>406</td>
</tr>
<tr>
<td>vii</td>
<td>26,700</td>
<td>375</td>
</tr>
<tr>
<td>x</td>
<td>30,500</td>
<td>328</td>
</tr>
</tbody>
</table>

$\nu$ Estimated to $\pm$ 500cm\textsuperscript{-1}
CHAPTER 3

E.S.R. and Optical Studies of Silver Clusters in Frozen Aqueous and Alcoholic Matrices.
3.1. INTRODUCTION.

This Chapter reports the results of conjoint ESR and optical studies of silver clusters. The literature ESR and optical data for these species was presented in Chapter 1, where it was seen that only a few optical assignments have supportive ESR data and that the optical spectrum of the $\text{Ag}^{n+}_{4}$ centre, which has been previously observed and characterised by ESR in organic glasses, has not been reported.

The conjoint ESR and optical studies of $\text{Ag}^{0}$ centres formed by the $\gamma$-irradiation at 77K of $\text{AgClO}_4$ in $\text{EtOH/H}_2\text{O}$ solutions reported in Chapter 2 showed that $\text{Ag}^{+}$ and $\text{Ag}^{n+}_{2}$ centres were formed in good yield in these systems; directly after irradiation in the case of alcohol-rich mixtures and after annealing in the case of water-rich mixtures. These systems formed reasonably optically transparent glasses in the visible and UV regions and were therefore chosen for these studies.

The results reported in Chapter 2 showed that $\text{Ag}^{n+}_{4}$ centres were produced by the agglomeration of $\text{Ag}^{0}$ and probably $\text{Ag}^{+}_{2}$ centres with $\text{Ag}^{+}$ ions. It was hoped that careful relative spin concentration measurements during the course of this reaction would also enable the charge on the tetrameric centre to be conclusively determined.
3.2 EXPERIMENTAL.

Samples were prepared as described in Chapter 1. Similar instrumentation was also used. For relative spin concentration measurements, spectra were accumulated and doubly integrated using the Hewlett-Packard 9835B. Care was taken to minimise errors by positioning the sample in exactly the same position within the cavity for each measurement and using exactly the same instrument settings for microwave power, modulation amplitude, time constant and scan time.
3.3 RESULTS AND DISCUSSION.

1. Ag⁺

Fig. 1a shows the ESR spectrum, Fig. 1b the optical spectrum of a 0.20M AgClO₄ + 0.20M NaF in H₂O solution which had been γ-irradiated for 5400s at 77K and annealed to 160K for 300s. [The spectra obtained from this system directly after irradiation and after annealing to 127K were shown in Chapter 2, Figs. 4 and 5, respectively.] Table 1 lists the magnetic and optical data.

<table>
<thead>
<tr>
<th>Species</th>
<th>10⁷A(G)</th>
<th>g</th>
<th>Absorption max</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₀</td>
<td></td>
<td>A₀</td>
</tr>
<tr>
<td>A</td>
<td>-253</td>
<td>-263</td>
<td>-256</td>
</tr>
<tr>
<td>B</td>
<td>-253</td>
<td>*</td>
<td>-</td>
</tr>
</tbody>
</table>

* These values could not be determined.

[A estimated to ± 2G, g-values to ± 0.002, v to ± 300cm⁻¹]

Fig. 1a shows that Ag⁺ centres were formed as a result of the anneal. Comparison with Chapter 2. Fig. 5a shows that these were formed at the expense of Ag⁰, predominantly in the form of species [iii]. They were considered to have
FIGURE 1
(a) The ESR and (b) the optical spectrum of a $\gamma$-irradiated 0.20M AgClO$_4$ + 0.20M NaF H$_2$O solution annealed from 77 K to 160 K for 300 s and re-cooled to 77 K.
been formed by reaction with Ag\(^+\) ions according to (1).

\[
\text{Ag}^0 + \text{Ag}^+ \rightarrow \text{Ag}_2^+
\]  

The ESR spectrum suggested that two Ag\(^+_2\) species with slightly different parameters were produced. These were labelled (A) and (B) as shown. These may have been formed by the reaction of Ag\(^0\) with different Ag\(^+\) solvates, resulting in Ag\(^+_2\) centres with slightly different solvation structures.

Comparison of Fig. 1b with Chapter 2. Fig 5b showed that the broad optical band associated with Ag\(^0\) species [iii] became replaced by a narrower doublet assigned to Ag\(^+_2\). The assignment was based on the similar temperature profiles of the ESR and optical spectra and was in good agreement with literature values\(^1\) [see Chapter 1, Table 4c]. It was considered possible that each component of the doublet was associated with one of the two Ag\(^+_2\) species. According to the ESR spectrum, (A) was the major species. The largest component of the optical doublet was tentatively assigned to this centre.

The optical absorptions were considered to be associated with \(\sigma \rightarrow \sigma^*\) transitions between molecular orbitals largely constructed from the two atomic 5s orbitals, as depicted in Chapter 6.1, Scheme 1. The differences in the energies of the transitions for the two species may have arisen from small differences in the amount of p-character associated with these molecular orbitals, as shown by their different
g-values [the effect of the admixture of small amounts of p-character in the 5s orbitals of AgO solvates was shown in Chapter 2 to have a marked effect on 5s->5p transition in these centres].

The small shoulder at 33,700cm⁻¹ (297nm) may have arisen from Ag²⁺ centres, formed as a result of hole-trapping by Ag⁺ ions [it had a similar temperature profile to the ESR features from these.]

On annealing to 187K, ESR signals from both Ag⁺² species decayed considerably; species (B) slightly more than species (A). The optical absorbance associated with these centres decreased similarly. No larger silver clusters such as Ag⁴⁺ were observed. After annealing to 200K, both ESR and optical signals had decayed completely, providing conclusive evidence for the optical assignment.

Ag⁺² centres were also observed in annealed ethanol/water mixtures. Up to M.F. 0.13 ethanol, spectra were found to be similar to those shown in Fig. 1. and followed almost exactly the same temperature profile. Ag⁺² centres were also the only molecular silver clusters observed in these systems.

On annealing mixtures with the composition M.F. 0.14 ethanol and above, however, Ag⁴⁺ centres were the major cluster species observed. This sudden change in the properties of the matrix with respect to cluster formation...
was considered to be in accordance with the phase change observed in Chapter 2. [It is suggested that at M.F. 0.14 ethanol the predominantly glassy matrix is able to accommodate Ag⁴⁺ centres, whereas the predominantly icy matrix at M.F. 0.13 ethanol cannot]. Features from Ag⁺ centres were sometimes observed at the early stages of the anneals but they could never be isolated. Consequently optical spectra could not be unequivocally assigned to Ag⁺. [A shoulder at 32,200cm⁻¹ (310 nm) was tentatively assigned to this centre in a M.F. 0.20 ethanol mixture (see Chapter 2, Fig. 7b.)] In pure ethanol, however, a sharp optical band was observed directly after irradiation at 77K [see Chapter 2, Fig. 10b]. This was unequivocally shown to be associated with Ag⁺ by ESR data obtained after annealing to 96K [see Chapter 2, Fig 11]. According to the ESR spectrum, only one type of Ag⁺ species was present, and only one optical absorption was observed. The value of vₘₐₓ was in good agreement with the result of Eachus and Symons² for Ag⁺ centres formed in an H₂SO₄ glass [see Chapter 1, Table 4c]. Table 2 lists the magnetic and optical data for this centre.

A slight shift of the absorption maximum to 33,700cm⁻¹ was observed after annealing to 96K. On annealing to 117K, ESR signals from these centres decayed completely and the spectrum changed to that characteristic of Ag⁴⁺ centres. The optical band associated with Ag⁺ also decayed and a band assigned to Ag⁴⁺ appeared [see section 3].
Table 2.

ESR and Optical Data for Ag\textsuperscript{2+} observed in EtOH at 77K.

<table>
<thead>
<tr>
<th>10\textsuperscript{7}A(G)</th>
<th>g (g_{av})</th>
<th>Absorption max (\nu(cm^{-1}))</th>
<th>(\lambda(nm))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-266</td>
<td>-269</td>
<td>-267 1.96</td>
<td>1.97 \textsubscript{g}</td>
</tr>
</tbody>
</table>

2. Ag\textsuperscript{2+}.

This centre was occasionally observed by ESR in ethanol/water mixtures, but spectra were never well-defined as a result of the extremely low concentration. Consequently, it was not possible to obtain an unequivocal optical assignment. ESR studies of \(\gamma\)-irradiated AgClO\textsubscript{4} solutions in toluene\textsuperscript{3} have shown much higher yields of Ag\textsuperscript{2+}, however this matrix was found to absorb too strongly in the UV region to obtain any useful data. It is suggested that further studies should attempt to isolate this centre in alternative matrices or possibly in mixtures of toluene and non-absorbing diluents.

3. Ag\textsuperscript{n+}.

(A) The Determination of \(n\).

As outlined in Chapter 1, this centre has been well
documented by ESR studies. However, the value of n [which must be either 1 or 3 for paramagnetism] has not been conclusively established. As this species could only be formed either by the reaction of three AgO centres with one Ag+ ion according to reaction (1), or by the reaction of one AgO centre with three Ag+ ions according to reaction (2), [probably involving Ag+ as an intermediate] it was thought that relative spin concentration measurements should enable n to be determined, since reaction (1) would involve a 66.7% loss of spin, whereas reaction (2) would be expected to proceed with spin conservation, assuming that the AgO centres did not decay by other mechanisms.

\[
3\text{AgO} + \text{Ag}^+ \rightarrow \text{Ag}_4^{n+} \tag{1}
\]

\[
[\text{spin} = 3] \quad [\text{spin} = 1]
\]

\[
\text{AgO} + 3\text{Ag}^+ \rightarrow \text{Ag}_4^{n+} \tag{2}
\]

\[
[\text{spin} = 1] \quad [\text{spin} = 1]
\]

[Strictly, since some loss of spin is inevitable, an observed spin reduction to 33.3% or less of the original AgO spin would favour reaction according to (1) whereas an observed spin reduction to more than 33.3% would conclusively show that the reaction occurred according to (2).]

For these measurements a system had to be chosen in which no silver clusters were formed at 77K but in which Agn+ centres could be readily formed in high relative yield.
FIGURE 2

ESR Spectrum of a γ-irradiated 0.05M $^{177}$AgClO₄ in M.F. 0.20 EtOD/D₂O solution after annealing from 77 K to ≈123 K for the purpose of relative spin concentration measurements.
after annealing. The M.F. 0.20 ethanol/water system described in Chapter 2 fulfilled these requirements. Small frozen beads of 0.05M $^{107}\text{AgClO}_4$ in a M.F. 0.20 EtOD/D$_2$O solution were first $\gamma$-irradiated for 3600s at 77K. The ESR spectrum directly after irradiation showed that only Ag$^0$ centres had been formed, mainly species [ii] [the spectrum was very similar to the $^{107}\text{Ag}$ component of that shown in Chapter 2, Fig. 6a]. The relative spin concentration of these centres was obtained by accumulating and doubly integrating the first derivative ESR spectra of the $[M^I = -1/2]$ and $[M^I = +1/2]$ components of the Ag$^0$ signals. The value obtained, labelled $[\text{Espin}_1]$, is shown in scheme 1,(3).

The system was then carefully annealed. Signals from Ag$^0$ species [ii] were found to decay and a dramatic rise in the intensity of signals from Ag$^0$ species [x] was observed. Eventually, after annealing to $\approx$ 123K, signals from species [x] reached a maximum intensity and this was the only silver centre observed [see Fig. 2]. The relative spin concentration of this system, $[\text{Espin}_2]$, was measured as described above and is shown in scheme 1,(4). A considerable increase was observed compared to $[\text{Espin}_1]$. This was considered to have resulted from the formation of species [ii] by the capture at Ag$^+$ of electrons which had been thermally ejected from traps, in addition to the desolvation of species [ii] and [vii]. It was considered that at this stage all the electrons which had been initially trapped on irradiation at 77K had reacted. This was confirmed by the absence of the characteristic optical absorption of trapped
electrons at about 20,000cm\(^{-1}\) (500nm) in this sample.

On further annealing, signals from species \([x]\) decayed and signals from \([\text{Ag-CH}_2\text{CH}_2\text{OH}]^1\), \(\text{Ag}_2^+\) and \(\text{Ag}_4^{n+}\) centres appeared. Eventually, however, only signals from \(\text{Ag}^{n+}_4\) centres were observed. Fig. 3a shows the first derivative signals observed from these. Before discussing the results of the integrations of these signals, it must be mentioned that in order to eliminate solvent radicals from the centre of the spectrum for subsequent integration over the entire scan range of the \(\text{Ag}^{n+}_4\) signals, it was found necessary to anneal this system considerably, and some loss of \(\text{Ag}^{n+}_4\) signal intensity was also observed. Consequently, the measured relative spin concentration of this centre, \(\text{Is}_{\text{spin}}_3\), was subject to error, estimated to be at least -35% from double integrations of the \([M_1^I = +1]\) and \([M_1^I = +2]\) features at the stage at which \(\text{Ag}^{n+}_4\) signals were at a maximum. Fig.3b shows the first integral, Fig. 3c the second integral of Fig. 3a. The value of \(\text{Is}_{\text{spin}}_3\) is given in scheme 1,(5). The deduction of \(n\) from these measurements is also shown in scheme (1).

Taking into account the estimated error in \(\text{Is}_{\text{spin}}_3\) of at least -35%, this analysis was considered to provide conclusive evidence for the assignment to \(\text{Ag}^{3+}_4\), even allowing for experimental errors of ±10%. The reduction of term (6) from unity was considered to arise from \(\text{Ag}^0\) regression as a result of reaction with electron loss centres and/or the possible formation of diamagnetic silver
FIGURE 3
(a) ESR spectrum of Ag\textsuperscript{m+} centres observed after annealing the system shown in Fig. 2 to \( \approx 170\) K and re-cooling to 77 K.
(b) First integration of (a).
(c) Second integration of (a) showing relative spin concentration.

\[ \sum \text{spin}_3 = \int \int \text{Ag}_4\textsuperscript{m+} = 2.1 \times 10^3 \text{ (at unit gain)} \]

\[ \sum \text{spin}_3 = \int \int \text{Ag}_4\textsuperscript{m+} = 2.1 \times 10^3 \text{ (at unit gain)} \]
clusters such as Ag\(_2^0\), Ag\(_4^0\) and Ag\(_4^{2+}\), although the latter was considered unlikely since no optical absorptions associated with these centres were observed [see section (B) and Chapter 2, Tables 4a and 4c].

**Scheme 1.**

The Deduction of \(n\) for the Reaction (4-\(n\))Ag\(^0\) + \(n\)Ag\(^+\) \(\rightarrow\) Ag\(^{n+}\) from Relative Spin Concentration Measurements.

\[
\begin{align*}
\text{Ag}^0 \text{[ii]} + \text{[vii]} & : \text{I}_{\text{spin}_1} = 4.3 \times 10^2 \\
\text{Ag}^0 \text{[x]} & : \text{I}_{\text{spin}_2} = 4.5 \times 10^3 \\
\text{Ag}^{n+}_{\text{4}} & : \text{I}_{\text{spin}_3} = 2.1 \times 10^3 \\
\text{[I}_{\text{spin}_3}/\text{I}_{\text{spin}_2}\text{]} \times 100 & = 47\% \\
(6) > 33.3\% \quad \longrightarrow \quad n > 1 \\
(2) \quad \text{and} \quad (7) \quad \longrightarrow \quad n = 3
\end{align*}
\]

(B) Conjoint Optical and ESR Spectra.

Fig. 4a shows the ESR spectrum, Fig 4b the optical spectrum observed from a 0.20M AgClO\(_4\) solution in EtOH which had been \(\gamma\)-irradiated for 3.6x10\(^3\)s at 77K, annealed to 117K for 300s and re-cooled to 77K. The sample was very pale
FIGURE 4
(a) The ESR and (b) the optical spectrum of a γ-irradiated 0.20M AgClO₄ in EtOH solution after annealing from 77 K to 117 K for 300 s and re-cooling to 77 K.
pink. Table 3 lists the magnetic and optical data. [Spectra obtained from this sample directly after irradiation and after annealing to 96K were shown in Chapter 2, Figs 10 and 11, respectively.]

**Table 3.**

<table>
<thead>
<tr>
<th>$^{107}\text{A}_{\text{iso}}(G)$</th>
<th>$g_{\text{av}}$</th>
<th>Absorption max</th>
<th>$\nu(\text{cm}^{-1})$</th>
<th>$\lambda(\text{nm})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-137</td>
<td>1.95</td>
<td>37,000</td>
<td>270</td>
<td></td>
</tr>
</tbody>
</table>

On annealing this system above 117K the $^{3}\text{Ag}_{4}^{+}$ ESR signals and the optical absorption at 37,000 cm$^{-1}$ decayed simultaneously. After a 300s anneal to 137K they had disappeared completely, providing conclusive evidence for the optical assignment.

The absorption cannot be assigned to a particular transition as the bonding in this species is uncertain. The ESR parameters show that the unpaired electron occupies an orbital with largely s character. It is possible that a $\sigma\rightarrow\sigma^{*}$ transition between molecular orbitals constructed mainly from the four silver 5s orbitals was observed. [The large reduction in $g$ from the free spin value indicates that the unpaired electron in this centre has significant p character and this would be expected to modify this simple
model. It is also possible that the observed transition is from the ground state to a molecular orbital constructed from the silver 5p orbitals. Baetzold\textsuperscript{5} has calculated the energy levels in various silver aggregates of up to thirty silver atoms using extended Huckel and CNDO theories and has predicted energies for HOMO-LUMO transitions. Unfortunately, however, he has not considered the case of a tetrahedral Ag\textsuperscript{3+} \textsubscript{4} centre.

An optical absorption from Ag\textsuperscript{3+} \textsubscript{4} centres formed in various EtOH/H\textsubscript{2}O mixtures was also observed. In these matrices a shift to lower energy was observed as EtOH concentration decreased. At M.F. 0.13-0.14 EtOH, which the lowest ethanol concentration at which this centre could be formed, the absorption maximum was at 34,000cm\textsuperscript{-1} (291nm). An increase in linewidth was also observed, from 1,700cm\textsuperscript{-1} at M.F. 1.00 EtOH to 2,700cm\textsuperscript{-1} at M.F. 0.14 EtOH.

It is interesting to note that an optical absorption at 38,500cm\textsuperscript{-1} (260nm) previously assigned to the diamagnetic Ag\textsuperscript{2+} \textsubscript{4} cluster\textsuperscript{4} was not observed at any stage in these systems.

Interesting results were obtained using a more concentrated AgClO\textsubscript{4} [0.50M] solution in ethanol. Directly after the \textgreek{y}-irradiation of this system, Ag\textsuperscript{0}, Ag\textsuperscript{+}\textsubscript{2} and Ag\textsuperscript{3+} \textsubscript{4} centres were observed both optically and by ESR, as in the case of the 0.20M solution studied in Chapter 2 [see Chapter 2, Fig. 10]. However, the relative yields of the silver
clusters were larger and the yield of silver atoms reduced, as expected from the greater concentration of Ag$^+$ ions available for reaction with Ag$^0$. The sample was pale yellow in contrast to the purple $\gamma$-irradiated 0.20M AgClO$_4$ solution, indicating that the yield of solvated electrons in this sample was very low, presumably as a result of the overwhelming competition for electrons by the large number of Ag$^+$ ions.

On annealing this system to 96K, signals from Ag$^0$ centres decayed completely and similar spectra to those shown in Chapter 2, Fig. 11 were observed, although signals from Ag$^+_2$ centres were considerably larger. The solution was very pale yellow at this point. On annealing to 117K, however, the solution assumed an intense pink colouration and new optical absorptions were observed at 35,000cm$^{-1}$ (286nm) [very weak], 30,000cm$^{-1}$ (333nm) [strong] and 19,050cm$^{-1}$ (525nm) [weak] in addition to the absorption at 37,800cm$^{-1}$ (265nm), associated with Ag$^{3+}_4$, which had increased [see Fig. 5b]. Fig. 5a shows the ESR spectrum of this system. This showed that Ag$^+_2$ centres had decayed completely and that features which have previously been assigned to the asymmetric [Ag$_3$-Ag]$^{3+}$ unit$^6$ were present in addition to signals from the symmetric Ag$^{3+}_4$ centre.

At first it was considered that the optical absorption at 37,800cm$^{-1}$ was associated with Ag$_4^{3+}$ centres and that some of the additional features might be attributable to the asymmetric tetramer. However, on
FIGURE 5
(a) The ESR spectrum, (b) the optical spectrum of a γ-irradiated 0.50M AgClO₄ in EtOH solution after annealing from 77 K to 117 K for 300 s and re-cooling to 77 K.
annealing the system slightly further, the ESR spectrum showed that both tetrameric species persisted at a somewhat reduced overall but similar relative concentrations, whilst the optical features at 35,000cm⁻¹, 30,000cm⁻¹ and 19,050cm⁻¹ decayed completely, leaving only the 37,800cm⁻¹ absorption, which was somewhat reduced. [The sample was colourless at this point]. It therefore appeared that the [Ag₃-Ag]³⁺ unit had a similar optical spectrum to Ag⁴⁺ and that the additional features were associated with diamagnetic centres(s).

Reference to Chapter 1, Table 4c shows that optical absorptions at 27,500cm⁻¹ (370nm) and 19,500cm⁻¹ (513nm) have been assigned to the species Agm⁺ observed in Na-A zeolites⁷. The identity of this species, which was reported as being red in colour, was inferred from powder X-ray diffraction data. It was considered to have been formed from two Ag²⁺ units or to be associated with two interacting Ag⁺ units. This species would be paramagnetic and is therefore a possible candidate for these 30,000cm⁻¹ and 19,050cm⁻¹ absorptions. Such a species might have been formed in this system from two Ag⁺ units in close proximity agglomerating with two Ag⁺ ions according to scheme (1):

\[
\text{Ag⁺} + [\text{Ag---Ag}]^+ + [\text{Ag---Ag}]^+ \rightarrow \text{Ag}^4_6 \quad (1)
\]

Reaction (1) can be seen to be more more likely to occur
in systems in which Ag\(^+\)\(_2\) and Ag\(^+\) were present at high concentration, as was the case for the \(\gamma\)-irradiated 0.50M AgClO\(_4\) solution.

Texter et al.\(^8\) observed a salmon coloured species in studies of the activated dehydration of silver exchanged zeolite A which had absorptions at 22,000cm\(^{-1}\) (454nm) and 31,100cm\(^{-1}\) (321nm). This was assigned to a charged diamagnetic silver cluster, the precise nuclearity of which was uncertain but was considered to be greater than three and less than fourteen.

It can be seen from Chapter 1, Table 4a that features at 29,411cm\(^{-1}\) (340nm) and 19,230cm\(^{-1}\) (520nm) have been assigned\(^9\) to Ag\(_6^0\) centres formed in an Ar matrix by the clustering of Ag\(_2^0\), although the precise nuclearity of this centre has not been conclusively established. A hextuplet neutral species would be diamagnetic and is therefore a possible candidate for the 30,000cm\(^{-1}\) and 19,050cm\(^{-1}\) absorptions, although no simple mechanism can be proposed for its formation from Ag\(_2^0\) in this system since the ESR results showed that these centres had long since decayed.

The small shoulder at 35,000cm\(^{-1}\) may have been associated with Ag\(_3^{2+}\) centres. This assignment is very tentative, however, since no ESR signals characteristic of this paramagnetic centre were observed. However, signals could have been masked by those from the tetrameric species if Ag\(_3^{2+}\) were present at only a very low concentration, as
suggested by the very small absorption, and an optical absorption in this region might be expected from the observed progression to higher energy with increasing size for $\text{Ag}^{n+}_{n+1}$ clusters. If this assignment were correct, it would cast doubt on the assignment of Ozin et al.\textsuperscript{11} of an absorption at 24,900 cm$^{-1}$ (402 nm) to $\text{Ag}_3^{2+}$ centres formed in Faujasite-type Zeolites, for which there was also no supportive ESR data.

It was considered significant that the species associated with these additional absorptions decayed more rapidly than the $\text{Ag}_4^{3+}$ and $[\text{Ag}_3-\text{Ag}]^{3+}$ centres; an observation in accordance with the unusual stability associated with tetrameric species in some of the proposed theories for the photographic process (see Chapter 4). It is suggested that this system is probed further, perhaps in collaboration with relative spin concentration studies to assist in the identification of the diamagnetic species.

4. Ag$^0$

In some systems, broad optical absorptions were observed after extensive annealing. No ESR signals were observed at this stage. These absorptions were therefore assigned to diamagnetic silver agglomerates. In a M.F. 0.12 EtOH matrix an absorption was observed at 24,300 cm$^{-1}$ (411 nm) with a halfwidth of about 6,500 cm$^{-1}$. In a M.F. 0.20 EtOH matrix an absorption was observed at 23,800 cm$^{-1}$ (420 nm) with a halfwidth of about 7,500 cm$^{-1}$. These were assigned to Mie
resonances from metallic $\text{Ag}_n^0$ particles with colloidal dimensions by comparison with the literature values$^{11,12}$ (see Chapter 1, Table 4a). These absorptions decayed on further annealing and samples changed from yellow to black, presumably as a result of the formation of larger particles by agglomeration.

No ESR signals at $g \approx 2.003$ associated with pseudo-metallic $\text{Ag}_n^0$ particles such as those reported in Chapter 6 were observed at any stage, although it must be mentioned that these would have been difficult to detect, especially in the early stages of the anneals, as a result of the strong signals from solvent radicals in this region of the spectrum.
3.4. CONCLUSIONS.

Optical spectra of Ag$^+$ centres were observed in a variety of matrices and assigned on the basis of conjoint ESR data. Two Ag$^+$ species were identified by ESR in ice at 77K. These were associated with optical absorptions at 27,200 cm$^{-1}$ (337 nm) and 29,700 cm$^{-1}$ (367 nm). In an EtOH glass at 77K only one species was observed by ESR. This had a single optical absorption at 32,900 cm$^{-1}$ (304 nm).

There was never very clear evidence for the formation of the trimeric Ag$_3^{2+}$ species in these matrices. This was considered to be in accordance with theoretical predictions of alternating stabilities for silver particles with even and odd nuclearities. An absorption at 35,000 cm$^{-1}$ (286 nm) was (very) tentatively assigned to this species.

The charge on the tetrameric Ag$_4^{n+}$ species was determined to be $+3$ by spin concentration analysis. The optical spectrum of this symmetric Ag$_4^{3+}$ centre was unequivocally assigned on the basis of conjoint ESR data. It was found to absorb at 37,000 cm$^{-1}$ (270 nm) in an EtOH glass at 77K. A small matrix effect was observed, with $v_{\text{max}}$ shifting to 34,000 cm$^{-1}$ (291 nm) in a M.F. 0.14 EtOH/H$_2$O glass at 77K.

ESR features were observed from an asymmetric tetrameric centre, [Ag$_3$-Ag]$^{n+}$, formed in matrices with a high Ag$^+$ concentration. The optical spectrum of this centre appeared very similar to that of the symmetric tetramer.
Additional optical absorptions were observed at $30,000\text{cm}^{-1}$ (333nm) and $19,500\text{cm}^{-1}$ (525nm). These were assigned to a molecular diamagnetic centre(s) on account of their ESR silence. They were tentatively assigned to the hexameric species $\text{Ag}_6^{4+}$.

Broad optical absorptions in the region of $24,000\text{cm}^{-1}$ (411nm) from metallic silver clusters formed by the agglomeration of these molecular species were observed. No ESR or optical features attributable to pseudo-metallic species were detected during this agglomeration.
REFERENCES.


CHAPTER 4

An Introduction to the Silver Halide Imaging (Photographic) Process:
The Latent Image.
4.1. GENERAL INTRODUCTION.

The following section is concerned with spectroscopic studies of silver halide imaging (photographic) systems and attempts to identify the species involved in the primary photographic process, in particular latent images.

Photographic latent images are small silver particles which catalyse the chemical reduction of photolyzed silver halide to bulk metal. They have, until now, eluded direct detection by magnetic or optical spectroscopic techniques. Consequently, their compositions and structures have not been determined, although a great deal of information about their chemical properties has been obtained from empirical experiments.

This chapter briefly reviews the photographic process and models of latent image formation which have been proposed on the basis of existing data (see ref. 1. for an extensive review).

Following chapters will discuss original ESR studies, which we think have enabled us to identify surface defect centres that may act as sites for latent image formation, and in addition observe and characterise latent images, directly, in a wide range of model and actual photographic systems.
4.2. INTRODUCTION TO THE SILVER HALIDE PHOTOGRAPHIC PROCESS

i. THE COMPOSITION OF PHOTOGRAPHIC MATERIALS.

Conventional photographic systems contain silver halide microcrystals, usually silver bromide and chloride, dispersed in a gelatin matrix and coated, as an emulsion, onto a film or paper base.

The microcrystals, usually referred to as "grains", can be produced with well-defined morphologies and size distributions, depending upon the conditions chosen for their precipitation from solutions of silver nitrate and alkali metal halides and the photographic properties that are required. In commercial systems, grain sizes range from 0.1 to 1.0 μm and they may be either octahedral, cubic or tabular. Fig. 1. shows an electron micrograph of a cubic 0.13 μm silver chloride emulsion, similar to that used in the studies reported in chapters 5 and 6.

The gelatin has many functions; the following are some of the most important. It acts as a dispersion medium for the silver halide grains during and after precipitation, forming an emulsion which can be easily coated onto the base, and acts as a permeable support which allows the access of processing solutions. Additionally it acts as a sensitiser and a halogen acceptor, and is thought² to have a stabilising effect on latent image centres.
FIGURE 1

Electron micrograph of a cubic 0.13 μm AgCl emulsion.
ii. **PHOTO-DECOMPOSITION.**

Exposure of silver bromide and silver chloride grains to band-gap radiation decomposes them to molecular halogen and silver metal. Such molecular photochemistry would be inefficient at providing the basis for an image recording medium, were it not for the fact that an amplification step becomes possible, after only a few photons are absorbed, to form the silver speck that is labelled "latent image".

iii. **THE DEVELOPMENT OF LATENT IMAGE.**

The latent image acts as a catalytic centre for the grain to be chemically reduced during processing to filamentary, metallic silver. This constitutes the "photographic image". The "development" of the latent image speck into the photographic image is usually effected by the use of organic reagents with suitable reduction potentials, such as hydroquinone and metol. These are relatively very slow at reducing unexposed grains. The enormous amplification step that results from development, in effect the size ratio of the metallic photographic image to the latent image speck, is one of the key aspects to the success of silver halide imaging. It is estimated to be between $10^6$-$10^9$.

iv. **THE PHOTOGRAPHIC RESPONSE.**

The term sensitometry is usually applied to the study of
the response of photographic materials to light. Developed density is plotted against the logarithm of exposure to produce a "D-Log.E" curve. Fig. 2. shows a typical response.

It can be seen that there is a residual density, $D_{\text{min}}$. This is due to the presence of latent image specks in some grains prior to exposure. This is termed "fog". The fog density determines the darkest tone that can be represented by the material. Fog density increases if materials are stored at high temperatures, subjected to excess pressure, or if certain chemical impurities are present in the grains.

Above $D_{\text{min}}$ the "linear exposure region" is found. This is the region where intermediate tones are represented. Exposures in normal photographic situations should be centred here in order to obtain the maximum dynamic range from the system. Tone representation is thought possible because of a statistical relation between exposure and the probability of latent image formation, when summed over the entire ensemble of grains. This would be expected to arise from the distribution of grain sizes and imperfections, inevitable in any practical system, with consequent quantum efficiency variations. The gradient in this region, given the symbol $\gamma$, is a measure of the "contrast" of the material, a property that is also dependent upon the nature of the developer and the conditions of development.

For most materials there is a "reciprocity" effect, where density remains constant for reciprocally related
FIGURE 2
A typical D-log E curve showing sensitometric parameters.
[Ref.1]
combinations of exposure time and intensity, or total number of incident photons. However, inefficiencies usually occur at high and low intensities. This "reciprocity failure" has given clues to latent image composition and will be discussed later.

Eventually a maximum density, $D_{\text{max}}$, is reached. Beyond this, density falls on increasing exposure, a phenomenon called "solarisation". It is attributed to the build-up of excess halogen at the grain surfaces, which the surrounding gelatin is unable to absorb. This oxidises latent image specks on the grain surfaces back to their pre-cursors, reducing density. Latent image specks inside the grains are unaffected and continue to form at the expense of these centres.

4.3. INTRODUCTION TO THE LATENT IMAGE.

i. DEFINITION.

A functional definition of latent images is that they are silver aggregates of sufficient size to catalyse the reduction of host silver halide grains to silver metal by the action of a suitable reducing agent.

ii. COMPOSITION.

The compositions and structures of latent images in photographic materials have yet to be determined. It has
been shown that large silver particles formed by the continuous exposure of silver halides to light ("print-out silver") and silver particles vapour deposited onto silver halide matrices\textsuperscript{2,3} are capable of catalysing reduction to metallic silver in a similar way to the latent image. There is therefore thought to be a probabilistic developability over a wide silver particle size regime, the minimum of which has yet to be absolutely determined.

Optical and electron microscopy can be used to study latent images in photographic emulsions if they are partially developed ("arrested development"). Such studies have shown that they are formed at specific sites either on the surface (surface image) or inside the grains at a bulk physical defect or adjacent to a deep impurity centre (internal image). They have also revealed that, in the most efficient systems, only one centre is formed per grain. It appears, therefore, that the species involved in latent image formation become concentrated at one, or at most only a few sites. This is referred to as the "concentration mechanism".

Quantum efficiency observations\textsuperscript{4} and theoretical analyses\textsuperscript{5,7} have shown that, whilst the characteristic curve of a high-speed emulsion has an exposure range of from 3 to 100 photons/grain, the most sensitive grains in the most efficient systems are rendered developable by the absorption of only 3 or 4 photons. This has led to a general acceptance by the photographic community that the minimum size of the
latent image speck could be as few as 3 or 4 silver atoms. However, a more precise interpretation of the data is that only 3 or 4 atoms of the products of exposure need to be added to some possible pre-existing site in order to confer developability.

There is, perhaps, a range of latent images in photographic systems, with particle size distributions that are dependent on the composition, dimensions and morphologies of host grains as well as the duration and intensity of actinic radiation. One of the main reasons for seeking a direct method of latent image detection was to attempt to answer this fundamental question of latent image composition, which remains one of the greatest "unknowns" in photographic science, and must be resolved before any precise mechanism of formation can be proposed.

iii. PROPOSED MECHANISMS OF LATENT IMAGE FORMATION.

The mechanism(s) by which the latent image is formed is still a matter of conjecture. Most of the proposals are in agreement with the basic principles formulated by Gurney and Mott in 1938, who envisaged a two-step process.

The initial, electronic, step invoked the formation of a photoelectron. The second, ionic, step invoked the combination of the photoelectron with a pre-existing mobile silver ion to form a silver atom. It was further proposed that aggregation occurred by the continued concentration at
the same site of additional photoelectrons and silver ions. It is this latter stage which has recently been disputed.

Fig. 3. shows a graphic representation of 3 reaction pathways which have received attention. Two involve sequential electronic and ionic processes, in which transient silver aggregates are formed, whilst the third proposes the spontaneous aggregation of silver atoms. The following sections review the events involved in these proposals and the evidence for them.

4.4. MECHANISTIC PROPOSALS.

A. THE ELECTRONIC STEP.

i. OPTICAL ABSORPTION.

At room temperature, the intrinsic optical absorption of AgBr crystals begins at 2.5 eV and increases rapidly at higher energies. The absorption edge shifts to higher energies with decreasing temperature, reaching a maximum of 2.69 eV at 4.2 K. At 90 K two peaks appear at 4.2 and 4.7 eV which increase and shift to higher energies with decreasing temperature, reaching 4.25 and 4.82 eV respectively at 20 K. These absorptions are depicted in fig. 4.a. and can be rationalised in terms of band gap theory, using the energy level diagram shown in fig. 5.
FIGURE 3
Proposed mechanisms of latent image formation.

- Sequential electron trapping/ionic neutralization (Gurney-Mott)
- Atom diffusion/aggregation (Thermodynamic)
FIGURE 4
Temperature dependence of fundamental absorption spectra of (a) AgBr and (b) AgCl. [Refs. 11 and 12.]
FIGURE 5
Variation of electron energy with crystal momentum \( k \) along the \([111]\) and \([100]\) directions in momentum space resulting from the AgBr band structure. [Ref. 9(a)].
In AgCl the absorption edge begins at 2.81 eV at room temperature, shifting to 3.25 eV at 4.2 K. At 90 K there is a peak at 5.0 eV which shifts to 5.1 eV at 20 K with the appearance of a shoulder at 5.20 eV. (Fig. 4.b.)

In both materials the temperature dependent absorption near the absorption edge involves an indirect, phonon-assisted, transition from the higher occupied levels of the valence band to the conduction band, generating free electrons and holes:

$$\text{AgX} + h\nu \rightarrow e_{\text{cb}}^- + h_{\text{vb}}^+$$  \hspace{1cm} (1)

The phonon features become observable at low temperatures. The absorption peaks at higher energies arise from a direct transition which generates a direct exciton that quickly dissociates into a conduction electron and valence hole.

Pulsed illumination experiments on crystals in an electric field have provided evidence for the photolytic generation and fate of these carriers. Micro-second light pulses allowed for their field-induced displacement within a time regime that was too small for any ionic motion. Eventually, detectable amounts of elemental silver and halogen were formed at the positive and negative sides respectively of grains.
ESR spectroscopy has been used to observe and characterise the carriers directly. Free electrons in the conduction band of photolysed AgCl give rise to conduction electron spin resonance (CESR) at $g = 1.88^{15}$. Optically detected magnetic resonance (ODMR) studies$^{16}$ have also enabled trapped electron states to be observed, at $g_{av} = 1.977$ (Fig. 6.). ODMR studies of AgBr$^{17}$, interpreted in the light of previous ESR results, have revealed the presence of free electrons ($g = 1.49$) and free holes ($g = 2.08$). Two resonances were obtained at $g = 1.81$ and $g = 1.75$ that were attributed to carriers trapped at unidentified intrinsic sites (Fig. 7.)

ii. PHOTOELECTRON AND PHOTOHOLE TRAPPING.

The photocarriers become involved in a reversible cyclic scheme, as shown in Fig. 3. They are able to diffuse around the grains until they eventually become "trapped" at singularities below the conduction band (electrons) or above the valence band (holes) (equations 2 and 3). The precise structures of these intrinsic trapping centres, $t^-$ and $T^+$, are unknown.

\[
e^{-}_{cb} + t^0 \rightarrow t^- \quad (2)
\]

\[
h^+_{vb} + T^0 \rightarrow T^+ \quad (3)
\]

Photo-induced optical absorptions have been detected$^{11}$ in AgBr and AgCl using conductivity modulation techniques, and are shown in Figs. 8a. and 8b., respectively.
Figure 7
The ODMR spectrum of a single crystal of pure AgBr [Ref. 17].

ODMR
35.94 GHz
T = 4.2 K
AgBr

g = 2000
1.75
1.81
2.08
1.49

Free hole
Intrinsic sites
FIGURE

Excitation induced Absorption Spectra for (a) AgBr and (b) AgCl [Ref. 11].
A - Measured after exposure at 2 K ("Atomic" spectra);
C - Measured at 77 K after anneal to 300 K ("Aggregate" spectra).
The structured spectra, (A), obtained at 2K, have been assigned to centres in which unpaired electrons are shallowly trapped \( (E_a = 30-40\text{meV}) \) at intrinsic defects such as silver ion interstitials. These centres are considered to have very large orbit radii and to be unique examples of bound polarons. At higher temperatures these centres are unstable, until, above 77K, absorptions attributed to deep electron centres (C), are observed that Kanzaki proposes are silver clusters, although their broad, unstructured appearance precludes their assignment to a specific aggregate or small range of aggregates. Absorptions obtained at intermediate temperatures of 20-30K, (B), are thought to correspond to silver clusters containing two or three silver atoms.

Delayed field pulsed illumination\(^{18,19}\) and microwave photoconductivity techniques\(^{20}\) have also yielded data on trap depths and carrier lifetimes. Shallow electron traps, ineffective at room temperature, \( (E_a = 30-80\text{ meV}) \), have been detected in unexposed, unsensitised silver halide grains by these techniques. These intrinsic traps were considered to be provided by potential wells associated with \( \text{Ag}^+ \) ions at surface sites and internal imperfections\(^9\).

Electron lifetimes, \( \tau_e \), have been determined to be of the order of micro-seconds in silver halide microcrystals. For example, \( \tau_e = 1.7\mu\text{s} \) for unsensitised 0.5\( \mu\text{m} \) AgBr. They are thought to be determined by time taken for the first ionic event, as a result of their correlation with ionic
field decay times.

Saunders, Tyler and West\textsuperscript{21} reported photohole lifetimes, $\tau_h$, of from 1 to 4 $\mu$s in large AgBr crystals. Malinowski and Buroff\textsuperscript{22}, using mobility data, have estimated that the hole trap depth in pure silver bromide crystals is 0.41 eV. It has been proposed that these traps could be provided by impurity Cu\textsuperscript{+} and Fe\textsuperscript{2+} ions, known to be present in a few parts per 10\textsuperscript{7}. Kroger\textsuperscript{23} calculated a hole trap depth of 0.43 ± 0.1 eV for hole capture by substitutional Fe\textsuperscript{2+} in AgBr. Similarly, there is unambiguous evidence that hole trapping at the 0.40 eV level is provided by impurity iodide ions\textsuperscript{24}. An ionic event is thought to terminate the lifetime of the hole, as for the electron. It is postulated that the trapped hole interacts with a silver ion vacancy\textsuperscript{10}, to form the species $[h^+ v^-]_{Ag}$.

In contrast to their behaviour in AgBr, holes are able to become "self-trapped" at low temperatures in AgCl, forming the self-trapped hole (STH) centre, Ag\textsuperscript{2+}, identified by ESR\textsuperscript{25} and ODMR\textsuperscript{16} (Fig.7.).

\begin{equation}
{h^+}_{vb} + {Ag^+}_{(AgCl \text{ lattice)}} \rightarrow {Ag^{2+}}_{(STH)}
\end{equation}

The self-trapped exciton (STE), an electron weakly bound around the STH, has been characterised in this system using low temperature ODMR\textsuperscript{16}.

Electron and hole traps with particular depths, capture
cross-sections and positions can be generated, by various chemical treatments, in order to control latent image formation. This process of sensitisation will be discussed in detail in section 4.6.

iii. LOW TEMPERATURE SENSITOMETRY.

Low temperature studies on photographic emulsions, in which the electronic step was effectively isolated by the suppression of the ionic motion required for the successive step(s), have provided evidence for the reactions involved in the electronic preliminary to latent image formation.

It was found that considerable density could be developed (at room temperature) in emulsions which were exposed at low enough temperatures to suppress ionic motion to a considerable extent (see section 4.7. iii. for a further discussion of low-temperature effects). This was attributed to the storage of photoelectrons, in traps, at low temperatures (reaction 5), which could participate in a subsequent ionic reaction when warmed up prior to development (reaction 6). Measurements at 90 K indicated that some photoelectrons were deeply trapped ($E_a = 1-2$ eV) at possible "sensitivity centres" and that others were shallowly trapped at intrinsic sites. It was calculated that thermal excitation could be expected from traps with depth $E_a < 0.8$ eV on warming to room temperature.

$$e^-_{cb} + t^0 \rightarrow t^- (E_a 0-2.0 \text{ eV})$$  \hspace{1cm} (5)
Additionally, it was shown that low temperature band-gap exposure, followed immediately by low temperature red light exposure, caused a loss of expected developable density, whereas if the emulsions were warmed to room temperature, before cooling and exposure to red light at low temperature, there was no effect. This was been interpreted as resulting from long-wavelength absorption by trapped electrons (reaction 7), exciting them into the conduction band and facilitating recombination with trapped holes (reaction 8). Measurements of the spectral distribution of this effect showed that electron traps with depths $E_a = 0.4-0.6$ eV were involved.  

$$t^- (E_a < 0.8 \text{ eV}) \rightarrow t^0 + e^-_{cb} \quad (6)$$

$$t^- (E^a = 0.4 \text{ eV}) \rightarrow e^-_{cb} + t^0 \quad (7)$$

$$e^-_{cb} + T^+ \rightarrow T^0 \quad (8)$$

These, and some room temperature reactions, are schematically depicted in the energy level diagram shown in Fig. 9.

B. THE "IONIC" STEP

The formation of a developable latent image centre is generally thought to proceed in two successive stages, nucleation, in which one or more individual silver atoms are formed and growth, in which this centre(s) increases in size until it becomes developable. The major photographic
FIGURE 9
A Schematic Energy Level diagram showing electron and hole trapping effects at various temperatures in AgBr.
evidence for this has been provided by studies of reciprocity failure. Low intensity reciprocity failure, (LIRF), has been interpreted as arising from an inefficiency in the nucleation step, high intensity reciprocity failure, (HIRF), from an inefficiency in the growth step. These effects will be discussed in more detail later.

Whereas there are significant differences of opinion as to the mechanisms of nucleation and growth, there is a general consensus that the initial step is the formation of a silver atom.

i. THE FORMATION OF THE PRE-LATENT IMAGE SILVER ATOM

As a result of the intrinsic shallow trap depths, several sequences of electron trapping (reaction 2), thermal ejection from traps (9), and trapping at new sites may occur. A considerable quantum inefficiency can arise at this stage as a result of the recombination of free electrons with trapped photoholes (11), and trapped electrons with free holes (12). Direct recombination is extremely unlikely, requiring the additional participation of a phonon. However, the trapped electron can eventually become neutralised by a mobile interstitial silver ion (13). Such silver ions are known to be present in sufficient concentration as both AgBr and AgCl are cationic Frenkel defect lattices. The result is that a silver atom, \( \text{Ag}^0 \), is formed. These reactions are shown in the following scheme:
The neutralisation of the electron according to this scheme re-sets the electron trap. This would enable another photoelectron to be trapped in close proximity to the silver atom, possibly accounting for the concentration effect.

The formation of the silver atom is reversible. It is estimated that this species has a lifetime of one second at room temperature, with respect to decomposition into a silver ion and an electron \((E_a = 0.69\text{eV})\):

\[
\text{Ag}^0 \rightleftharpoons e^-_{\text{cb}} + \text{Ag}^+ (\text{int})
\]

In addition to this thermal regression, however, the silver atom is also liable to regress as a result of attack by holes:

\[
\text{Ag}^0 + h^+ \rightarrow \text{Ag}^+ (\text{int})
\]

The incidence of LIRF, which occurs in this time-regime, is thought to result from the regression of the silver atom and loss of the first photoelectron before a secondary photoelectron can cause growth of this centre to a more stable one (Hamilton talks in terms of the need for a
secondary "cyclic" electron)\(^7\).

ii. **THE REACTIONS OF PHOTOHOLES.**

The ultimate fate of photoholes which haven’t been involved in recombination (11, 12), or pre-latent image regression (15), is that they diffuse by the acceptance of electrons from neighbouring halide ions or by the mobility of hole-vacancy complexes, \([h^+\text{Ag}^-]^{10}\), until they reach the grain surface and cause the release of free halogen (16, 17). At this stage the reaction becomes irreversible.

\[
\begin{align*}
h^+ + \text{X}^- & \rightarrow \text{X} & (16) \\
2\text{X} \text{(surface)} & \rightarrow \text{X}_2 & (17)
\end{align*}
\]

iii. **NUCLEATION AND GROWTH: THE REACTION(S) OF THE PHOTO-PRODUCED SILVER ATOM**

Fig. 3. shows proposed reaction pathways for the silver atom. It can be seen that in order to contribute to latent image formation it reacts with more silver ions and photoelectrons either by;

(A) A sequential electron trapping/ionic neutralisation process, as favoured by Hamilton\(^7\) (scheme 1) and Trautweiler\(^8\) (scheme 2) and with slight modifications, Mitchell\(^9\);
or,

(B) Aggregation with other photoproduced silver atoms, a theory recently proposed by Malinowski$^{10}$ and others$^{28}$ in a thermodynamic approach (scheme 3.).

(A). SEQUENTIAL ELECTRON TRAPPING AND NEUTRALISATION.

i. THE QUANTITATIVE APPROACH: A MATHEMATICAL MODEL

Hamilton and Brady$^{7a}$ designed a mathematical model for latent image formation. This allowed the responses of hypothetical photographic emulsions to be computed and compared with sensitometric data.

The first stage to the model required the absorption of a photon to produce an electron-hole pair that was taken to be immediately equilibrated into the three-way reversible cycle shown in Fig. 3. Three equilibrium constants were specified, $\varphi$, $\beta$ and $\alpha$, which gave the average number of electrons to be found in free, bound or atom states respectively. Three analogous constants, $\psi$, $\gamma$, and $\Delta$, were defined for holes.

The silver atom was taken as being formed from an electron in a shallow trap and a mobile silver ion. The trap was not capable of accepting a second electron until it captured the silver ion, resetting the trap. The presence of the atom was considered to increase the trap depth. The atom
could decompose by releasing the silver ion, leaving the electron in the trap.

The nucleation process was defined as the capture of a free electron by a silver atom followed by the incorporation of a second silver ion, considered to be thermally stable for some time (there is some photographic evidence for the stability of such a possible Ag\textsuperscript{0} "sub-latent image" centre). A number of growth steps then followed, by the alternate capture of free electrons and mobile silver ions, to build up the latent image centre to some developable criterion.

The simplest model then gave the following expressions for reaction rates:

Absorption: \[ \lambda_A = \kappa I \]  
Recombination: \[ \lambda_R = (\psi e)(\gamma h)q_{R1} + (\psi h)(\beta e)q_{R2} \]  
Nucleation: \[ \lambda_N = (\psi e)(\alpha(e-1))q_N \]  
Growth: \[ \lambda_G = (\psi e)Aq_G \]

where \( \kappa \) is a constant, \( I \) is the light intensity, \( e \) = number of cycling electrons, \( h \) = number of cycling holes, \( A \) = number of stable silver aggregates and \( q_j \) = rate constant for event \( j \).

The rate constants were in the form \( q = v_0V^{-1} \),
where:

\( \nu = \) thermal velocity of the carriers,
\( \sigma = \) capture cross-section of the carriers,
\( V = \) grain volume.

It was assumed that \( \nu \) and \( \sigma \) were identical for electrons and holes, giving the simplified expression for recombination:

\[ \lambda R = (\psi e)(\omega h) \varphi \quad (5) \]

Where \( \omega = \gamma + \frac{\psi \beta}{\varphi} \quad (6) \)

These equations were used to give an expression for the number of photons, \( E_F \), required for the developability of an average grain:

\[ E_F = N + \omega/\alpha + \omega h \quad (7) \]

where \( N \) is the minimum number of silver atoms in a developable centre.

The four terms in expression (7) represent, respectively, the number of photons used in forming \( N \) silver atoms, recombative losses during nucleation and recombative losses during growth.

These equations were used in a computer simulation of the photographic process occurring in emulsions consisting of 100 grains. It was possible to select a set of parameters
that gave an excellent fit to the experimental characteristics of real emulsions. These were rationalised with known physical properties. Developable latent image centres of from 3 to 6 silver atoms were found to be appropriate.

Fig.10. shows reported simulated and sensitometric D-logE curves for an unsensitised 0.2 µm AgBr emulsion. The comparison of simulated and sensitometric curves was good, indicating that a random variation of efficiency among grains could account for the characteristic curve shape.

Reciprocity effects were also reproduced. LIRF was rationalised in terms of inefficiencies in accumulating two electrons in the nucleation step. The intensity for the onset of this effect, $I_L$, was found to be dependent on the time for the recombination of the electron/hole pair, which was much longer than the time for the single atom decay:

$$I_L = \varphi \omega = \lambda R$$

(8)

HIRF was taken to result from the competition of additional nucleus formation with the growth of the first nucleus, leading to the dispersion of latent images. An expression for the probability of second nucleus formation, $P_H$, was derived as:

$$P_H = \alpha E_F / 1 + \alpha E_F$$

(9)
FIGURE 10
Comparison of a simulated D-log E curve with an experimental curve for an unsensitized emulsion. Points represent the results of simulation; solid curve from experimental results of Spencer and Atwell [Ref. 7(a)].
This contrasts with the general consideration that HIRF results from the production of photoelectrons at such a fast rate that mobile silver ions are too sluggish to have a chance to neutralise the electron trapped at the atom site before another electron arrives, leading to trapping at other sites (dispersity) and increased recombination.

No HIRF was observed in unsensitised emulsions, giving a maximum value for $\alpha$ of about 0.02. However, $\varphi$ had to be small for the observed LIRF effect, giving, in turn, a large value of $\beta$ which indicated that the electron spent most of its time shallowly trapped.

An additional observation, important with respect to the mechanism of chemical sensitisation, was that sensitivity was determined by recombination during nucleation, being inversely proportional to the silver atom stability parameter, $\alpha$. The best fitting sulphur sensitisations were modelled using an increased value for this.

ii. A QUALITATIVE MOLECULAR ORBITAL MODEL

(i) AGGREGATION.

A qualitative model for the growth of pre-latent image centres by a sequential electron trapping/ionic neutralisation mechanism was proposed by Trautweiler. The model was based on quantum mechanical considerations, from
which it was claimed that reasonable values for the energies of intermediate states were deduced. The increasing stability of the growing aggregate and the approach to developability was explained in these terms. Fig. 11. shows the deduced energy diagram for these processes. The model was emphasised to be completely speculative, the only known data points being:

i. The instability of the one-atom centre at room temperature.

ii. The thermal stability of the two-atom centre, suggested by LIRF.

iii. The stability of the smallest developable centre; estimated to be 180 mV below that of bulk silver from redox potential measurements.

The proposed series of reactions were the following:

\[
\begin{align*}
\text{Ag}^0 + \text{Ag}^+_{\text{int}} & \rightarrow \text{Ag}^+_{\text{2}} \\
\text{Ag}_2^0 + \text{Ag}^+_{\text{cb}} & \rightarrow \text{Ag}_2^0 \\
\text{Ag}_2^0 + \text{Ag}^+_{\text{int}} & \rightarrow \text{Ag}_3^0 \\
\text{Ag}_3^0 + \text{Ag}^+_{\text{cb}} & \rightarrow \text{Ag}_3^0 \\
\text{Ag}_4^0 + \text{Ag}^+_{\text{cb/dev}} & \rightarrow \text{Ag}_4^0
\end{align*}
\]

It was assumed that \text{Ag}^0 was first formed according to the processes outlined previously. The stability of this centre was assumed to be 0.2 eV below the silver halide
FIGURE 11
Estimated ionization energy and electron affinity of small silver aggregates in AgBr [Ref. 8].
conduction band. It was thought unlikely that Ag$^0$ would be able to act as a competitive electron trap.

It was proposed, (1), that Ag$^0$ captured an interstitial Ag$^+$ ion, forming the dimeric cation Ag$^+_2$. A considerable stabilisation was expected from the binding energy resulting from the 5s silver atom electron moving into the Ag$^{+}_{2\sigma}$ molecular orbital. The stabilisation effect was estimated to be about 0.6 eV, putting this centre 0.8 eV below the conduction band.

Ag$^+_2$ was then expected to be able to capture a photoelectron, filling the \(\sigma\) molecular orbital, to form the neutral dimer Ag$^0_2$, (2). This was anticipated to lead to slight destabilisation, as a result of the Ag$^0_{2\sigma}$ orbital lying above that of the cation, by an estimated 0.3 eV. Ag$^0_2$ was therefore positioned 0.5 eV below the conduction band.

As an electron captured by Ag$^0_2$ would have to enter an antibonding orbital, with considerable destabilisation, the next step was thought to be Ag$^+_3$ formation by the bonding of another Ag$^+$ ion, (3). The stabilisation energy involved was estimated to be about the same as that involved in the formation of the dimeric cation, 0.6 eV, putting this centre 1.1 eV below the conduction band. This considerable stability was thought to be enough to possibly make this the stable "two electron centre" suggested by photographic experiments.1
Similar steps were proposed for the further aggregation process, forming the species $\text{Ag}_3^0$ and $\text{Ag}_4^+$ (4 and 5). It was deduced that $\text{Ag}_4^+$ would then have the necessary energetic requirements to act as the minimum development centre, (6).

There is experimental evidence for the existence of some of these proposed intermediates. $\text{Ag}^0$ and $\text{Ag}_2^+$ have been observed and characterised by ESR in other systems (see chapter 1) but have never been detected in silver halides. $\text{Ag}_2^0$ has been observed in the vapour phase and a value for its dissociation energy has been obtained, (1.74 eV). An ESR spectrum for $\text{Ag}_3^0$ in other systems has been reported, as has also for a paramagnetic tetrameric centre, which has been unequivocally characterised in this work as the triply charged $\text{Ag}_4^{3+}$ centre. This centre has also been shown to have an electronic absorption in the 265-290nm (4.67-4.25 eV) region (see results reported in chapter 3). This species has never been detected in photographic materials. $\text{Ag}_5^0$ has recently been prepared in an inert matrix and characterised by ESR, and an ESR spectrum has also been reported for $\text{Ag}_6^{n+}$ (see chapter 1).

(ii) DEVELOPMENT.

Fig.12. shows a model scheme for the AgBr/developer interface, in which the Fermi level of the developer is estimated, on the basis of redox potentials, to be 1.0 eV below the silver halide conduction band. The latent image is considered to be a surface state that has an empty state.
FIGURE 12
Diagram of the AgBr/developer interface [Ref. 8].
below the developer Fermi level prior to contact. On contact with the developer, this state is filled with an electron and another empty state is formed at or below the level of the state in which the first electron was trapped. Further electron acceptance then leads to a repetition of the process and a chain reduction to bulk silver.

Electron capture by $\text{Ag}_4^+$ from the Fermi level of the developer is seen to involve only a small activation energy. Further growth by ion and electron capture would then become more energetically favourable, at an exponential rate, resulting in development to bulk silver.

(iii) MOLECULAR ORBITAL CALCULATIONS.

Baetzold has also considered the possible sequence of growth in terms of molecular orbital theory, using model calculations. Results for aggregates formed at a modelled surface AgBr positive kink site gave the following to be the thermodynamically most favourable path:

$$\text{Ag}^0 \longrightarrow \text{Ag}^- \longrightarrow \text{Ag}_2^0 \longrightarrow \text{Ag}_3^+ \longrightarrow \text{Ag}_3^0$$

$$\text{Ag}_3^0 \longrightarrow \text{Ag}_3^- \longrightarrow \text{Ag}_4^0 \longrightarrow \text{Ag}_4^- \ldots \text{etc.}$$

(iv) MITCHELLS' GROWTH SEQUENCE.

Mitchell proposed a mechanism based upon classical calculations of the configurations and binding energies of
silver clusters. According to him, the initial photoelectron trapping process involves the diffusive approach of the conduction electron and an Ag⁺ ion, together, at a shallow intrinsic potential well provided by an Ag⁺ ion at surface sites or internal imperfections. The electron is thought to screen coulombic repulsion between the ions. The electrostatic energy of the system is thought to be lowered as the Ag⁺ ion approaches the well and combines with the electron to form the pre-latent image silver atom.

He maintains that the silver atom cannot trap electrons, nor capture an Ag⁺ ion and remain in thermodynamic equilibrium at room temperature. He therefore postulates a scheme of growth that depends upon a repetition of the silver atom formation process, stating that the trap depth is not significantly changed by the presence of the atom. However, once the triangular Ag³⁺ centre has been formed, it is suggested that Ag⁺ capture is possible to form the proposed tetrahedral latent image centre Ag⁴⁺, to which he ascribes a lifetime of 53 seconds at room temperature (Ea = 0.27 eV) with respect to decomposition back to Ag³⁺ and the ion. Ag⁴⁺ is then thought to act as a concentration centre, repelling holes and exerting a long range coulombic attraction on electrons. The centre is thought to provide a deep electron trap which is re-set by the absorption of a further silver ion.
i. AGGREGATION.

Whilst accepting the evidence for the formation of silver atoms by the electron/ion neutralisation process, Malinowski\textsuperscript{10} argues that it has not been unambiguously proved that all the constituent latent image silver atoms are formed by subsequent neutralisations at the same site.

Model investigations\textsuperscript{3} using evaporated layers of silver bromide led to the conclusions that coulombic attractive forces are not ultimately operative and suggested the formation of neutral species as the primary products of photolysis. Silver atoms and hole-silver ion vacancy complexes, \( [h^+_{V\text{Ag}}^-] \) were the proposed candidates. The low rate of intrinsic recombination and the observation of photographic sensitivity that was not critically dependent on the electric field gradient at grain surfaces (see section 4.5.) were explained in these terms. Instead, it was proposed that covalent forces operate and that the formation of the latent image is a special case of phase-change resulting from the spontaneous agglomeration of separate silver atoms which are brought to super-saturation concentration. It was further proposed that the formation of the new phase followed classical laws, determined by the thermodynamic condition of lowest free energy for the system.
Attention was drawn to metal vapour deposition studies\textsuperscript{10,32} which have shown that silver and gold atoms are mobile on a wide range of surfaces, forming widely spaced metal nuclei. Observations of such nucleation on glass and quartz substrates was seen as providing evidence for other mobility mechanisms to the generally accepted photographic theory; namely that in silver halides the silver atom valence electron is loosely bound ("shallowly trapped"), and is able to effect apparent mobility by entering the conduction band and becoming associated with another silver ion(s) elsewhere.

Nucleations on AgBr layers caused by illumination or silver vapour deposition were compared. Arrested development techniques revealed strikingly similar silver decorations in both systems. Grain boundaries and some grain surfaces possessed centers capable of catalysing, with equal efficiency, the nucleation of silver produced either by illumination or supplied from the vapour. It was concluded that these results indicated an identical primary nucleation mechanism. Further experiments with microscopically observable small silver particles, vacuum deposited from the vapour onto carbon and AgBr substrates\textsuperscript{3}, led to the formulation of a thermodynamic model for the developability and estimates of the size of latent image centres in real systems.
ii. DEVELOPMENT.

The process of development can be represented by an electrode reaction such as the following:

\[
\text{Ag}_{(\text{aggregate})}/\text{Ag}^+/\text{Red-Oxy}/\text{Pt} \quad E_{\text{cell}} = E_1
\]  

(1)

Development of a silver aggregate is therefore thought to be possible if the electrode potential of the developer redox system, represented by the Red-Oxy term in the right hand electrode, is more negative than the electrode potential of the silver aggregate/silver ion system on the left (\(E_1\) positive). Conversely, as a result of the reversibility of the system, bleaching of the aggregate will be expected in the case where the developer redox potential is more positive than that of the silver aggregate/ion system (\(E_1\) negative). When the potentials are equal, there will be no net effect and the system will be at equilibrium. Latent image centres are consequently thought to be slightly less negative than this equilibrium potential.

Difficulties have arisen in attempts\textsuperscript{33} to measure the electrode potentials of latent image centres, apparently due to the assignment of accurate values to the relative potentials of the redox systems operating on them. However, by observing particle size distributions of silver aggregates in model systems with sizes of between about 10 and 200 Å, Malinowski and Konstantinov\textsuperscript{2,3} were able to evaluate their equilibrium potentials and extrapolate back
Ferrous/ferric developing systems were used, the EMFs of which, $E_2$, could be varied by changing ionic concentrations. These EMFs were precisely measured, relative to a bulk silver electrode, and represented by the following equation:

$$\text{Ag}^{(\text{bulk})}/\text{Ag}^+ \parallel \text{Fe}^{2+}/\text{Fe}^{3+} /\text{Pt} \quad E_{\text{cell}} = E_2 \quad (2)$$

An expression was derived for the EMF of a small silver agglomerate electrode relative to bulk silver, $E_3$, according to the Gibbs-Thomson equation:

$$\text{Ag}^{(\text{bulk})}/\text{Ag}^+ \parallel \text{Ag}^+ /\text{Ag}^{(\text{aggregate})} \quad E_{\text{cell}} = E_3 \quad (3)$$

$$E_3 = \frac{2\sigma V_m}{rF} \quad (4)$$

where:

$\sigma$ = surface free energy of the silver aggregate/electrolyte interface,

$V_m$ = molar volume of silver metal,

$r$ = particle radius,

$F$ = the Faraday.

This enabled the following expression to be deduced for $E_1$:

$$E_1 = (2) - (3) = E_2 - \left[\frac{2\sigma V_m}{rF}\right] \quad (5)$$
Silver aggregates were vacuum deposited onto carbon or AgBr substrates. Some samples were also coated with a thin surface film of gelatin. Electron microscopy was used to determine particle sizes before and after samples were immersed for various times in the developers. Figs. 13a. and 13b. show particle size histograms of a control and a developed system. It was found that, for particular developer redox potentials, there was a critical size at which a minimum, \( r_0 \), appeared after partial "development". This was interpreted as a transient resulting from the development of centres in larger size classes and the bleaching of centres in size classes smaller than this critical quasi-equilibrium value. It was considered that the following relationships held at this point:

\[
\text{at } r_0, \quad E_1 = 0 \quad (6)
\]

\[
(6) \& (7) \quad \Rightarrow \quad E_2 = \frac{2\sigma V}{m} / r_0 F. \quad (7)
\]

It was found that a plot of \( E_2 \) against \( 1/r_0 \) produced a straight line, (Fig. 14.), as required by the Gibbs-Thompson derived equation (7). In addition it was shown that a gelatin coating had a stabilising influence on the silver aggregates, reducing the minimum size for developability. This was demonstrated by the smaller gradient in the resulting plot, compared to that obtained from uncoated surfaces. Values for \( \sigma \) were obtained from the gradients. A value of 920 erg/cm\(^2\) was obtained for uncoated particles on either substrate, which compared favourably with the literature value of silver against vacuum of 1100-1300
FIGURE 13

Particle size histograms of vacuum deposited silver aggregates, showing the effect of development [Ref. 3].
a) Control [sample treated only in deionised water].
b) Sample treated 2 minutes in a physical developer.
FIGURE 14
Plot of $E_2$ vs. $1/r_0$ for silver aggregates [Ref. 2].
- full line - uncoated samples;
- □ - substrate carbon film;
- ○ - substrate AgBr layer.
dashed line - gelatin coated samples;
- ■ - substrate carbon film;
- ● - substrate AgBr layer.
erg/cm^2. The gelatin coating reduced the value of \( \sigma \) to 400 erg/cm^2.

Although these experiments were with silver particles known to be very much larger than latent images, it was thought reasonable to extrapolate the \( E \) against \( 1/r_0^2 \) plots to the much more negative potentials thought to be necessary to develop them. The results of Berg and Frei\(^{33} \) showed some latent image bleaching at \(-170 \text{ mV}\), and it is assumed that an efficient conventional developer has a value of \( E_2 \) close to \(-200 \text{ mV}\). Extrapolations to these potentials gave \( r_0 \) values that corresponded to minimum developable centres composed of 100 silver atoms on uncoated surfaces and to 10 atom centres on gelatin coated ones (calculated for hemispheric particles). This latter value, deduced for centres in models resembling real photographic systems, is remarkably consistent with the evaluations of latent image size discussed previously.

Further support for these results was shown by the work of Platikanova and Starbova\(^{28} \), who found that gelatin enhanced the developability of real latent image centers formed by the photolysis of evaporated AgBr layers.

A thermodynamic mechanism for latent image formation has also been proposed by Galashin\(^{47} \). Using the model that silver atoms or small silver atom agglomerates were present before illumination and that the absorption of light eliminated the thermodynamic barrier to the formation of
secondary silver nuclei as latent image centres, Galashin\textsuperscript{47} argued that the critical number of actinic light quanta necessary for the formation of latent image centres, [which had been found to be as small as 3-4 for some grains, in the most efficient systems\textsuperscript{4,5}], was not directly equivalent to the number of atoms in latent image centres. Instead, the Gibbs-Thompson equation, (8), was applied to calculate the radii of latent image centres that would be expected to be formed after the absorption of various quanta:

\begin{equation}
  r^2 = \frac{3m\eta hv}{4\pi \sigma} \tag{8}
\end{equation}

Where:
\begin{align*}
  r &= \text{Radius of latent image centre} \\
  m &= \text{Critical number of light quanta with energy } hv \\
  \eta &= \text{Efficiency factor} \\
  \sigma &= \text{Specific free surface energy of silver on AgBr}
\end{align*}

Taking \( \sigma \) to be 525 ergs/cm\(^2\) in photographic systems (a value very close to the figure of 400 ergs/cm\(^2\) later deduced by Malinowski for gelatin coated silver particles\textsuperscript{2,3}), Galashin\textsuperscript{47b} calculated latent image radii as shown in Table 1.:
**Table 1.**

<table>
<thead>
<tr>
<th>m</th>
<th>r(Å)</th>
<th>η=1</th>
<th>η=1/2</th>
<th>η=1</th>
<th>η=1/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>13</td>
<td>9</td>
<td>68</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>11</td>
<td>120</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20</td>
<td>14</td>
<td>250</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>28</td>
<td>20</td>
<td>680</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>45</td>
<td>30</td>
<td>2700</td>
<td>960</td>
<td></td>
</tr>
</tbody>
</table>


It can be seen from Table 1. that calculated latent image sizes are much larger than those proposed by the Gurney-Mott type models, even for the most efficient grains. LIRF and HIRF were explained by the presence of competition between the process of photostimulated formation of latent image centres and other kinds of transformation of the electron excitation energy, such as conversion into thermal energy, photolysis of AgBr [particularly in unsensitised systems] and luminescence.

This theory has not received much support from the photographic community. However, the results reported in Chapter 6 suggest that latent images are larger than the molecular species proposed by the Gurney-Mott type
models and that they may fall within part of the size regime shown in Table 1.

4.5. THE ROLE OF STRUCTURAL DEFECTS.

Structural defects, either within or on the surfaces of silver halide crystals, may influence the mechanism and site of latent image formation. It is generally assumed that there are special surface defect sites on silver halide grains at which latent image formation is preferred. These sites are further assumed to be kink sites having a partial coulombic charge, although no direct evidence for their existence or involvement in latent image formation has been presented.

The types of defects found in silver halides include:

(i) Intrinsic defects.
(ii) Dislocations.
(iii) Plastic deformation.

(i) INTRINSIC DEFECTS.

A. FRENKEL DEFECTS.

Cationic Frenkel defects have long been recognised to be the dominant point defects in silver halides. Interstitial silver ions have been determined to be responsible for the ionic conductivity behaviour of these materials. They are
formed together with charge-compensating silver ion vacancies. The balance of these Frenkel defects can be controlled by the presence of other than monovalent impurities. For example, $S^{2-}$ ions have the effect of shifting the Frenkel equilibrium so as to increase silver ion interstitial concentration, whereas $Pb^{2+}$ ions have the reverse effect.

The conductivity of silver halide microcrystals is much greater than is found in bulk crystals, as a consequence of the existence of a space-charge layer of excess silver ion interstitials near the crystal surface. This has a dominant effect in the smaller crystals as the layer is of a comparable thickness. Hamilton and Brady$^{34}$ studied space-charge layers in emulsion grains and found the activation energy for conductivity to be $0.36 \text{ eV}$ in the space-charge layer compared to $E_a = 0.78 \text{ eV}$ for the bulk.

Saunders, Tyler and West$^{35}$ reported that the space-charge layer influenced the site of latent image formation in pure AgBr single crystals. They found that no latent image, as revealed by etching development, formed on the crystal surfaces, but that by applying an external field in opposition to the internal space-charge field, the spatial distribution of latent image was shifted towards the surface. Calculations$^{36}$, assuming that the latent image distribution reflected the spatial distribution of photoelectrons caused by the applied potential, showed the surface potential to be $-0.14 \text{ eV}$ relative to the bulk.
The effect of the space-charge layer in photographic systems has not been precisely determined, although it would account for the presence of a greater number of silver ion interstitials than expected and tend to reduce electron-hole recombination as a result of the tendency of the carriers to move according to the internal electric field. In addition, the negative surface charge would account for the observation that unsensitised emulsions preferentially form internal latent image if internal defects are present.

B. OTHER INTRINSIC DEFECTS.

In addition to Frenkel defects, other defect states may be present, either on the surfaces or interior of silver halide microcrystals.

Hamilton has invoked the presence of a small concentration of intrinsic or impurity surface states in an explanation of the de-sensitisation effect of environmental oxygen (see section 4.6.i).

The ESR results presented in chapter 5 provide evidence for the existence of paramagnetic surface defect centres in AgBr and AgCl microcrystals. They are shown to be photolytically active, possibly acting as electron and hole traps. They may, therefore, be the special surface states directly involved in latent image formation.
(ii) **DISLOCATIONS.**

The major types of dislocations found in silver halide crystals are edge and screw dislocations. Edge dislocations have been shown to act as sites for internal latent image formation. It has been proposed\(^3\) that electron trapping should occur within AgBr at jogs in dislocation planes, where there would be an effective charge of \(+ e/2\) if the last ion were to be a silver ion. These centres are thought to be possible sites for preferential latent image formation, although there is no direct evidence for their existence.

(iii) **PLASTIC DEFORMATION.**

Losses of surface sensitivity and gains in internal speed\(^1\) have been reported for deliberately deformed emulsion grains. Such stress could lead to a permanent deformation of the crystals and an increase in the concentration of dislocations. It is important to realise that the drying of silver halide emulsions can subject them to enormous strain, typically about 800 kg cm\(^{-2}\), and induce these effects in certain circumstances.

4.6. **SENSITISATION.**

The intrinsic light-sensitivity of nominally pure silver halide microcrystals is too low for most commercial applications and usually requires enhancement. The process
by which sensitivity is controlled is referred to as sensitisation and can be classified into two categories: (i) Chemical and (ii) Dye sensitisation. Chemical sensitisation involves treatments during or after precipitation which affect the quantum efficiencies with which latent images are produced, shifting the D-logE curve to the left along the exposure axis. Dye sensitisation, usually used in conjunction with (i), is used to extend the spectral response of the halides from the intrinsic blue band-gap absorption region to dye-dependent absorptions into the visible and possibly the infrared, depending on the intended application.

i CHEMICAL SENSITISATION.

Chemical sensitisation is classified according to the following regime:

A. Sulphur sensitisation.
B. Gold sensitisation.
C. Reduction sensitisation.
D. Sensitisation resulting from other addenda (usually transition metal ions)

A. SULPHUR SENSITISATION.

All photographic emulsions are sulphur sensitised to some extent, as a result of the inevitable contact of the halide microcrystals with gelatin, which has sulphur
containing constituents such as cysteine. However, deliberate sulphur sensitisation is achieved by treating emulsions with compounds that contain labile sulphur, such as thiosulphates and substituted thioureas. This results in sulphur adsorption and the formation of small mono-layer islands of Ag$_2$S sensitivity centres on faceted [001] crystal surfaces. Each adsorbed Ag$_2$S molecule is associated with one vacant surface anion lattice site which may have 3, 4 or 5 Ag$^+$ ion neighbours.

The formation of these centres has the effect of increasing sensitivity at low to moderate exposures. LIRF is reduced, but considerable HIRF is introduced. A topographic coincidence between Ag$_2$S centres and latent images, giving rise to surface sensitisation, has been proved by experiments on model emulsions.

The Gurney and Mott concentration theory attributed the sensitisation effect to deeper electron trapping at the sensitivity centres. Recent microwave photoconductivity measurements by Kellogg et al. have supported this idea. They found that sulphur sensitisation decreased free electron lifetimes and/or mobilities at 77 K, deducing that Ag$_2$S centres act as deep electron traps, each trapping one electron.

Further evidence has been provided by studies of surface/internal speed ratios, which are explained in terms of preferential electron trapping at these surface sites,
and the induced HIRF, attributable to electron trapping at many sensitisation centres, resulting in development inefficiency as a result of image dispersity.

Hamilton\textsuperscript{7b} found that the sensitimetric properties of sulphur sensitised emulsions could be duplicated in the mathematical model by increasing both the electron trap depth and the silver atom stability parameter, $\alpha$. The effect of increasing the trap depth was to decrease LIRF, at the expense of some sensitivity, whereas the effect of increasing the silver atom stability was to increase sensitivity and induce HIRF.

Mitchell\textsuperscript{9} argues that the sensitivity centres act as hole traps which, by subsequent electron trapping, can form stable $\text{Ag}_2^0$ pre-latent image specks. He also proposes that the free energies of $\text{Ag}_2^0$ and $\text{Ag}_2^{-}$ are reduced by the presence of neighbouring $\text{Ag}_2S$ centres, facilitating nucleation and growth.

B. GOLD SENSITISATION.

Gold sensitisation is accomplished by treating emulsions with tetrachloroaurate or dithiocyanatoaurate ions. The nature of the centre that is produced has not been agreed, proposals ranging from ionic to molecular, colloidal and metallic gold. The observations that internal speed is unaffected by gold sensitisation and that no new development centres are formed has led to the conclusions that gold does
not act as an electron trap. It is thought to enhance the developability of latent images by reducing the minimum size requirement. In fact a process termed latensification utilises treatment with gold solutions to make photolysed emulsions developable. Mitchell suggests that the smallest such centre then becomes AuAg or AuAg, as opposed to the Ag species thought to be required in unsensitised systems.

C. REDUCTION SENSITISATION.

Reduction sensitisation results from treating emulsions with mild reducing agents such as stannous chloride, hydrazine and ethanolamine. Small surface silver agglomerates are thought to be produced that are made developable by latensification and oxidised by mild oxidising agents. Ag centres are considered as likely candidates. Microwave photoconductivity measurements at 77 K have indicated that the reduction centres increase photoconductivity. The mechanism of reduction sensitisation is therefore thought to proceed by destructive hole trapping by the centres, leading to reduced recombination inefficiencies. It has been postulated that hole trapping by an Ag centre would generate a silver ion and a silver atom and that the latter would produce a conduction band electron after thermal decomposition. Consequently, the absorption of a single photon would produce two conduction band electrons, according to the following scheme:
HYDROGEN SENSITISATION.

It has recently been found\(^4\)\(^0\) that emulsions can be sensitised by treatment with hydrogen gas. The similarity of the effect to that obtained by reduction sensitisation has led to the conclusion that reduction centres are formed in this process. For example, \(\text{Ag}_2^0\) would be formed according to the reaction:

\[
2\text{Ag}^+_{(\text{int})} + \text{H}_2 \longrightarrow \text{Ag}_2^0 + 2\text{H}^+
\]

Both surface and internal sensitisation was found to result. It was found that extended hydrogen treatment led to a decrease in sensitivity, accompanied by a decrease in photoconductivity (measured at 77 K) and an increase in fog. This was interpreted as resulting from a change-over from hole to electron trapping as the reduction centres reached a critical size, beyond \(\text{Ag}_2^0\). Competition for electrons was then thought to explain the reduction in developed density, due to increased image dispersity.

MIXED SENSITISATION.

A, B and C are usually combined in pairs to give sensitisation with additive effects. Sulphur + gold is the
most common mixture and leads to some of the highest speeds attainable. Reduction + gold sensitisation is the most difficult to control because of the degree of fog produced.

D. SENSITISATION BY OTHER ADDENDA.

Dopant ions can have an important effect on silver halide photochemistry and transition metal ions are of particular interest from a photographic viewpoint. Examples include Rh\(^{3+}\), Ir\(^{3+}\) and Cu\(^+\). Photolysis usually causes a change in valence state of such incorporated ions which act as electron or hole traps. Whilst only having a very short lifetime at room temperature, these can be observed by spectroscopic techniques if the material is exposed at low temperature. Such studies have given valuable information on sensitisation mechanisms and latent image formation.

(i). IRIDIUM SENSITISATION.

The incorporation of Ir\(^{3+}\) into silver halide microcrystals internally sensitises them. From extensive EPR studies, in conjunction with microwave photoconductivity studies, optical absorption, luminescence and vibrational techniques, Eachus et al.\(^{41}\) have obtained a complete and unambiguous description of the sensitisation mechanism.

The ions are substitutionally incorporated into the interior of the halide crystals, forming molecular complexes of the form (IrX\(_6\))\(^{3-}\). As this centre replaces an (AgX\(_6\))\(^{5-}\)
unit, charge neutrality is maintained by the formation and association of two silver ion vacancies, shown by Raman studies to have $C_4$-symmetry, implying nearest neighbour locations (Fig. 15 ii. a).

Microwave photoconductivity results have shown that the $(\text{IrBr}_6)^{3-}$ centres in AgBr act as electron traps and become filled in $< 10^{-9}$ s at room temperature. Cooling reduces this rate, presumably as a result of competitive recombination. Electron capture produces the $\text{Ir}^{2+}$ state. Because this centre is such a deep electron trap, the electron is localised, occupying a molecular orbital characteristic of an $(\text{IrX}_6)^{4-}$ molecular ion.

Figs. 15 i. a. and 15 i. b. show EPR spectra obtained from an orientated AgBr crystal doped with $(\text{IrBr}_6)^{3-}$ ions, before and after exposure. The sample was exposed with 425 nm (2.91 eV) light at 200 K before cooling to 20 K to observe spectrum b. The spectrum is indicative of an $(\text{IrBr}_6)^{4-}$ molecular ion with a single cationic vacancy in an nnn position (Fig. 15. ii. b).

Kinetic studies, in which samples were warmed and re-cooled in "temperature jumps" enabled trap depths and lifetimes to be deduced. It was found that these were dependent on ligand environment and the host lattice. Data from $(\text{IrCl}_6)^{3-}$ doped AgCl samples showed that there were two first-order decay processes associated with the divalent Iridium centre, with lifetimes of 81 and 1400 seconds at 263
FIGURE 15(i)
ESR Spectra of an (IrBr₆)³⁻-doped AgBr crystal [Ref. 41(b)].

a) unexposed

b)

FIGURE 15(ii)
The mechanism of internal latent image formation at internal Ir³⁺ sites in Ir³⁺-doped AgBr and AgCl emulsions [Ref. 41(b)].
K. At 300 K the longer process had a lifetime of 10.8 seconds. Activation energies for the decays were determined. For the fastest decay, (1), and for the slower decay, (2), the values \( E_{a1} = 0.36 \pm 0.01 \text{ eV} \) and \( E_{a2} = 0.42 \pm 0.01 \text{ eV} \) were obtained.

An additional EPR signal was obtained that is attributed to a latent image centre on the evidence of the results presented in Chapter 6. Decay (1) was found to correspond to the build up of this feature, and an action spectrum was obtained for this process (Fig. 16.). Such a large activation energy in AgCl is usually associated with the spontaneous formation of Ag\(^{+}\) ions. It is thought that this process could occur at sites in close proximity to the Ir\(^{2+}\) centre, leading to the formation of the species [Ir\(^{3+}\).Ag\(^0\)]\(^-\) (Fig. 15. ii. c). This would re-set the electron trap and subsequent electron capture and ionic neutralisation at this site could lead to internal latent image formation, as depicted by the scheme in Fig. 17.

The lifetime of electrons involved in process 1 \([\tau_{e1}]\) was found to be 20 ms at 300 K for \((\text{IrCl}_6)^{3-}\) doped AgBr, which is shown to be about the optimum for such sensitisation to produce the high speed internal image that is obtained from this system. When \(\tau_e\) is of the order of tens of seconds, latent image formation would be expected to be inefficient, the long time of electron capture giving rise to a de-sensitising effect, whereas when \(\tau_e\) is of the order of a millisecond the trap cannot effectively compete
when $T \geq 190^\circ K$

$$- \frac{dA}{dt} = \frac{dB}{dt}$$

$E_a = 0.36 \text{ eV}$

$A = 1 \times 10^6$

for Both Processes

FIGURE 16

(IrCl$_6$)$_{3}^{3-}$-doped AgCl emulsion: action ESR Spectrum

[Ref. 41(b)].
FIGURE 17
Band-gap energy levels in (IrCl₆)³⁻-doped AgCl [Ref. 41(b)].
with the intrinsic shallow traps.]

Decay (2) was attributed to the thermal ejection of the electron from the Ir$^{2+}$ centre into the silver halide, as depicted in Fig. 17. The complete Ir$^{3+}$ internal image sensitisation mechanism is depicted in the scheme shown in Fig. 18.

(ii) RHODIUM SENSITISATION.

Rh$^{3+}$ has been shown by EPR studies$^{42}$ to act as an electron trap, forming the paramagnetic [(RhBr$_6$)$_4^-$ (Ag$^{+}$ vac$_{-}$)] species. It forms a very deep trap at room temperature, effectively preventing captured photoelectrons from participating in latent image forming reactions. It consequently acts as a de-sensitiser, and is used to increase contrast. The contrast increasing effect can be visualised in terms of a shift of the characteristic D-logE curve to the right, no latent images being able to form until all the Rh$^{3+}$ traps have been filled.

(iii) OTHER ADDENDA.

Other electron trapping addenda include Pd$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Ni$^{2+}$, Os$^{3+}$, Co$^{3+}$, Mn$^{2+}$ (deep traps), and Zn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$ and Mg$^{2+}$ (shallow traps).

Hole trapping addenda include Cu$^{+}$, Fe$^{2+}$, Ni$^{2+}$, Ru$^{2+}$, S$^{2-}$, Se$^{2-}$, Te$^{2-}$ (deep traps), and I$^{-}$ in AgBr, Br$^{-}$ in AgCl.
Figure 18

Ir\(^{3+}\) sensitization mechanism [Ref. 41(b)].
(shallow traps).

(ii) DYE SENSITISATION.

Cyanine and merocyanine dyes are most generally used to spectrally sensitise silver halides. Two mechanisms have been proposed for the process: (i) Electron transfer and (ii) Energy transfer.

(i) ELECTRON TRANSFER.

According to this mechanism, electron transfer occurs between radiationally excited dye molecules and the silver halide electronic energy levels. Irradiation in the absorption region of the dye excites electrons into the dye LUMO. If this is on a par with the halide conduction band, the electron can be ejected into the band and participate in latent image formation. The resultant dye radical then becomes regenerated, as a result of electron tunnelling from a trapped state at the halide surface, at an energy level about equal to the dye HOMO. This results in the formation of a hole trapped at the grain surface, which may be thermally liberated if the HOMO level is only a few multiples of kT above the valence band.

As a result of thermalisation, sensitisation can occur if the dye LUMO is only a few kT below the conduction band. However, de-sensitisation results if the LUMO is sufficiently below the conduction band to act as a
competitive electron trap for tunnelling photoelectrons.

If the energy levels of the dye are such that the HOMO is on a par with the valence band, the radiationally excited dye molecules can spectrally sensitise the injection of free holes. Electron transfer from the dye LUMO to a vacant level within the halide band-gap can then result in the formation of trapped surface electrons.

By using a series of spectrally sensitising dyes, with varying oxidation and reduction potentials, and examining the thresholds for sensitisation, it has been estimated\(^4^3\) that the lowest conduction level of AgBr, at -3.3 eV, relative to vacuum, is matched by an excited LUMO level of reduction potential -1.1 V, relative to a silver/silver chloride electrode. The highest valence band, at -5.9 eV, is matched by a HOMO level with an oxidation potential of 1.2 V.

Tadaaki and Sano studied light-induced ESR signals in a wide range of dye-sensitised silver bromide emulsion systems\(^4^4\). Structureless signals at \(g = 2.005\) were observed and attributed to dye positive holes on the basis of their correlations with photographic behaviour. Signals were induced by illumination in either the band-gap or dye-absorption region and were thought to be formed according to the following reaction scheme:
\[
\text{AgBr} + h\nu(\text{band-gap}) \rightarrow e^-(\text{AgBr}) + h^+(\text{AgBr}) \quad (1)
\]
\[
\text{Dye} + h^+(\text{AgBr}) \rightarrow \text{Dye}^+ \quad (2)
\]
\[
\text{Dye} + h\nu(\text{dye abs.}) \rightarrow \text{Dye}^* \quad (3)
\]
\[
\text{Dye}^* \rightarrow e^-\quad (4)
\]

ESR signal intensities were found to increase with increasing dye HOMO level, consistent with their assignment to dye hole traps. The critical energy level for strong signals was found to correspond to \(E_{\text{ox}}\) values of between +1.27 V and +1.19 V for dyes on (111) AgBr crystal surfaces. Dyes with \(E_{\text{ox}}\) values less than these gave rise to the stronger signals. The signals were found to decay according to complicated kinetics, which are currently under investigation at Eastman-Kodak, Rochester.

The effects of sulphur sensitisation were investigated by monitoring signal intensities after the additions of various amounts of a thiosulphate sensitisier. In general, increasing additions reduced signal intensitiy, although a slight maximum appeared at an addition that corresponded to optimum sulphur sensitisation. The reduction in intensity was interpreted as being due to increasing competition for holes between dye molecules and sensitisation centres as the concentration of such centres was increased. The maximum was considered to be indicative of electron trapping at the sensitisation centres. These effects were more pronounced after band-gap than dye-absorption illumination. This was attributed to the formation of localised holes in the latter case, according to reactions (3) and (4), which would be
expected to reduce competition effects.

In addition, it was found that the addition of iodide ion hole traps, halogen acceptors such as acetone semicarbazone and the removal of oxygen from the environment (see section 4.7. (i) for discussion), decreased signal intensities.

Fig. 19. shows an EPR signal attributable to a dye hole produced by the photolysis of a sensitising dye with $E_{\text{ox}} = 0.976 V$.

(ii) ENERGY TRANSFER.

Although the electron transfer mechanism is thought to account for most dye sensitisations, an energy transfer mechanism is thought to apply in others. The principle involved is that the radiationally excited dye can transfer energy to the silver halide if its optical transition is in resonance with an equi-energy transition of an electron from a surface site to the conduction band. The result is the formation of a free electron and a trapped hole, the ground state of the dye being automatically regenerated.

4.7. ENVIRONMENTAL EFFECTS.

In addition to the sensitising effect of $H_2$, other environmental effects have been investigated and mechanisms proposed.
EPR obtained from single coated strip (10^5 spins grain)

\( g = 2.004 \)

**FIGURE 19**

EPR of hole trapped by sensitizing dye (425 nm exposure).
[Ref. 41(c)].

\[ E_{\text{OX}} = 0.976 \text{ V} \]

SENSITISING DYE
Lewis and James\textsuperscript{45} found that the removal of oxygen from the environment of emulsion grains led to a considerable sensitivity increase, with the virtual elimination of LIRF. The de-sensitising effect of oxygen was attributed to the formation of superoxide by reaction with photoelectrons shallowly trapped at the grain surfaces (reaction 1). The reaction was thought to be reversible and to be most effective if a further reaction(s) occurred to remove the superoxide. Reaction with holes, with oxygen therefore acting as the dominant recombination centre, was suggested (reaction 2).

\begin{align}
0_2^- + t^0_{(surface)} & \rightarrow 0_2^- + t^0 \\
0_2^- + h^+ & \rightarrow 0_2
\end{align}

The finding that reduction sensitisation, thought to produce centres that destructively react with holes, reduces the oxygen de-sensitising effect, is consistent with this theory.

Hamilton\textsuperscript{7c} included oxygen electron trapping levels at energies below the shallow intrinsic levels (as they would have to be to compete for electrons) in his mathematical model for latent image formation. He found that subsequent analysis gave inordinately high contrast and could not adjust parameters to give experimentally observed intensity.
dependences. He suggested that the phenomenon could be explained by a mechanism in part analogous to the role played by oxygen in ZnO and CdS photoconductors.

A series of electron levels were proposed, associated with the surfaces of the grains and deep within the band gap. They were considered to be either intrinsic or impurity surface states, filled to a level dependent upon the redox character of the crystal environment during precipitation and storage. The states were considered to be partially filled in the absence of oxygen, the unfilled level acting as ineffective electron traps and the filled levels acting as deep hole traps, preventing recombination (Fig. 20a). In the presence of oxygen, new empty or oxidising levels were invoked at a similar energy to these surface states (Fig. 20b), into which electrons could empty from them (Fig. 20c). By accepting such electrons the oxygen molecules were thought to become chemisorbed at the surface. This was considered to leave the surface states almost empty and unable to increase sensitivity by irreversible hole capture.

Such a mechanism would require the electrons to be returned to the surface states upon the removal of oxygen. Their population would then be dependent on oxygen partial pressure and, if an energy barrier were involved, finite times would be required for equilibration, as was the experimental observation by Lewis and James. The effect of oxygen on the dye hole ESR signals investigated by Tadaaki
FIGURE 20
Proposed schematic diagram of energy levels at a silver bromide crystal surface [Ref. 7(c)].
and Sano\textsuperscript{44} is more easily interpreted according to this proposal, since competitive hole trapping can be invoked.

Another, somewhat trivial, explanation of the oxygen effect is that latent images and/or their intermediates are oxidisable in this environment. Oxygen has been found to induce latent image "fading" in some emulsion studies\textsuperscript{1}.

\[ \text{(ii). } H_2O^- \]

The dependence of sensitivity on humidity has usually been studied in air and so results are complex, as a result of the additional effect of oxygen. In general, sensitivity increases as the relative humidity of the environment decreases\textsuperscript{1}. It is thought that moisture may increase the de-sensitisation effect of residual oxygen by facilitating diffusion through the gelatin, or by promoting $O_2^-$ destruction by secondary reactions. Alternatively, it may increase the halogen acceptance by gelatin.

Other possible mechanisms for the environmental effect of these gases will be discussed in the light of the spectroscopic studies reported in chapter 5.

\[ \text{(iii). TEMPERATURE.} \]

The photographic process becomes less efficient when materials are exposed at low temperatures, for a number of reasons.
The absorption edge of silver halides becomes shifted to higher energy, resulting in a decrease of absorption in the long-wavelength tail. In addition, electron-hole recombinations and electron trapping processes begin to dominate at low temperatures, as silver ion mobility decreases. The low-temperature luminescence that is observed from these materials is indicative of recombination processes, and photoconductivity measurements have shown that $\tau_e$ values are in a millisecond regime in AgBr emulsions at 77 K, compared to microseconds at room temperature.

It has still not been determined whether silver ions can react with temporarily trapped electrons to form silver atoms, and possibly latent images, during exposure at 100 K or less. The only method for detecting possible latent image formation at low temperatures, to date, has been to warm samples to a temperature suitable for development. Such studies have revealed that 77 K exposure results in the resultant formation of dispersed latent images, which develop more slowly than those formed by room temperature exposure. It was concluded that a unique feature of latent image formation resulting from low temperature exposure caused almost all of the latent image centres to be of a size corresponding to the threshold of developability.

Hamilton was able to duplicate low temperature sensitometry effects in his computer analysis by using a model which involved competition between a second order recombination of electrons and holes and first order
trapping of either or both carriers, followed by the random nucleation and growth of silver aggregates to form multiple centres of smaller size.

The threshold of the optically induced absorption band (C) reported by Kanzaki\textsuperscript{11}, assigned to silver clusters, was found to be slightly shifted to higher energy on increasing the irradiation temperature from 77K to room temperature. This energy shift was considered to be attributable to the formation of smaller sized clusters at 77K, on the basis of the estimated silver cluster electronic energy level scheme of Trautweiler\textsuperscript{8}.

(iv) PRESSURE.

The effect of pressure of the order of about 1000 kg cm\textsuperscript{-2} is to induce de-sensitisation. Pressures of this order can easily arise during emulsion drying. De-sensitisation increases with increasing pressure. The de-sensitisation has two or possibly more components. First, there is a decrease in the absorption of actinic light in silver halides under pressure. Second, deformation may occur and dislocation concentration may be increase, as discussed in section 4.5. Thirdly, excess pressure may cause a tribo-electric effect, in which carriers are "squeezed out" of traps. This effect will be discussed fully in chapter 5.
Latent images would be expected to be unstable at room temperature on thermodynamic grounds, as a result of the high free energy attributed to small silver particles\(^2,3\). It has been experimentally confirmed that they are somewhat unstable. A decrease in developable density usually occurs when exposed emulsions are stored prior to development, referred to as "latent image fading". The extent of the effect depends upon various factors.

It has been found that gelatin has a marked stabilising effect\(^1\). An interesting comparison can be drawn between this result and Malinowski's observation that the presence of gelatin reduced the surface free energy of microscopically observable silver particles\(^2\).

In addition, it has been found that latent image fading is accelerated by increasing humidity and retarded by decreasing temperature or increasing the pH or decreasing the pAg of the environment\(^1\).

Latent image fading can also be induced by extended long-wavelength exposure, referred to as the Herschel Effect\(^1\). This effect occurs over the range of 1.1-1.9 eV in AgBr and 1.7-2.3 eV in AgCl emulsions. It has been proposed that the mechanism of latent image destruction according to this process occurs initially by the absorption of a photon by the latent image to form a positively charged centre and
a conduction band electron. Diffusion of the silver ion away from the centre or the acceptance of a silver ion vacancy leads to the net loss of a silver atom. A repetition of the process then leads to silver atom loss to a sufficient extent to reduce the size of the centre beyond the threshold for developability.

The threshold for the onset of the Herschel effect is very nearly coincidental with the photo-induced optical absorption band (C), (see Fig. 8.), reported by Kanzaki\textsuperscript{11} and assigned to silver clusters.
REFERENCES.


-175-


(b) R.S. Eachus. Talk at the International Congress of Photographic Science, Cambridge University, September 6-10 1982.

(c) This work and private communications.


47. E.A. Galashin.

(a) Zhurnal Nauchnoi i Prikladnoi Fotografii i Kinematografii, 13, (4), 292, (1968).


(c) ibid. 14, (1), 12, (1969).
CHAPTER 5

E.S.R. Studies of Un-irradiated Silver Halides.
5.1. INTRODUCTION.

This chapter reports ESR studies of unirradiated silver halides. Three ESR signals were observed prior to exposure to light which may be associated with intrinsic surface states of photographic significance. As outlined in Chapter 4, latent images are thought to form at surface defect sites. It is generally assumed that these surface defects are kink sites having a partial coulombic charge. However, no direct experimental evidence has been presented for the existence of these diamagnetic sites or for their involvement in latent image formation. It is possible that the observed ESR signals are from paramagnetic centres which are the special surface sites that are directly involved in the formation of latent images.

Previous ESR studies have failed to detect any centres in either unirradiated or irradiated pure silver halides, although Chapter 6 reports the observation of novel silver latent image centres during the course of this work. There have, however, been a number of ESR studies of irradiated doped AgCl and AgBr crystals in which photo-produced electron and hole centres have been observed. In addition, ODMR has been extensively applied and has enabled a number of intrinsic electron and hole trapping centres to be identified in pure silver halides.

In 1962, Delbecq et al. observed ESR signals at $g = 2.165$ and $g = 2.041$ from the Ag$_{2+}^{\cdot}$"self-trapped hole" (STH)
centre in irradiated KCl:AgCl mixtures. The STH was later observed by Hohne and Stasiw\textsuperscript{2} in AgCl crystals doped with electron-trapping addenda such as Ag\textsubscript{2}S and Ag\textsubscript{2}Se. In 1977, Hayes \textit{et al.}\textsuperscript{3} identified the STH as a recombination centre contributing to the 2.52 eV emission from optically excited AgCl crystals using ODMR at 4 K. The self-trapped exciton (STE), thought to be an electron loosely bound at an STH, was also observed at $g = 2.0216$. The failure to detect these centres in AgBr using this technique was thought to be a result of electron-hole recombination occurring at some unidentified defect site. A broad resonance observed at $g = 1.8$ was assigned to electron-hole recombination at a silver speck consisting of two or more atoms.

By incorporating divalent impurities such as Cd\textsuperscript{2+} and Pb\textsuperscript{2+} and low levels of Br\textsuperscript{-} ions to extend the photo-electron lifetime, free electrons were observed in 1978 by Eachus \textit{et al.}\textsuperscript{4} in AgCl crystals at 30K using ESR. A symmetric signal was observed at $g = 1.8775$, assigned to conduction-electron spin resonance (CESR). Eachus and Graves\textsuperscript{5} used a similar technique to observe a CESR signal at $g = 1.4920$ in Pb\textsuperscript{2+} doped AgBr crystals at 4K. In 1981, Marchetti \textit{et al.}\textsuperscript{6,7} reported the observation of these centres in pure AgCl and AgBr using ODMR and were able to clarify some of the confusion amongst existing data.\textsuperscript{3,8,9,10} The ODMR spectra obtained from AgCl and AgBr are shown in Chapter 4, Figs. 6 and 7, respectively, and are discussed below.

In AgCl crystals, at least three species were observed
by ODMR at 4K in addition to the STH and STE. They were assigned to electron species on the basis of their disappearance on the incorporation of electron-trapping ions such as \( \text{Ir}^{3+} \) and \( \text{Rh}^{3+} \) [see chapter 4, section 4.6. (i)]. A signal at \( g = 1.881 \) was assigned to conduction band electrons by analogy to the ESR results of Eachus et al. The remaining resonances were assigned to electrons trapped at unknown intrinsic defect sites. Signals at \( g = 2.057 \) and 1.931 were assigned to the parallel and perpendicular resonances, respectively, of an electron trapped at a tetragonally distorted site. The remaining signal at \( g = 1.977 \) corresponded to the average (isotropic) position \( g_{av} = (g^x + 2g^y)/3 \) of these resonances and interconversion between the sites was observed.

In AgBr crystals, four ODMR signals were observed at 4K. A resonance at \( g = 1.49 \) was assigned to conduction band electrons by analogy to the ESR results of Eachus et al. A signal at \( g = 2.08 \) was assigned to resonance from free holes on the basis of doping experiments with electron trapping ions. The remaining signals at \( g = 1.81 \) and \( g = 1.75 \) were assigned to carriers shallowly trapped at bulk defect centres. It was suggested that they could be either (1) holes trapped at interstitial silver ions, (2), holes trapped at silver ion vacancies, or (3), electrons bound in large orbits to interstitial silver ions:

\[
\text{h}^+ + \text{Ag}^{+} \text{ (int)} \rightarrow \text{Ag}^{2+} \quad \text{(1)}
\]
\[ h^+ + [\text{Vac}] \rightarrow [\text{Vac}]^- \quad (2) \]

\[ e^- + \text{Ag}^+ \text{(int)} \rightarrow \text{Ag}^0 \text{(int)} \quad (3) \]

The signals reported here were observed in AgBr and AgCl emulsions at temperatures from 9 to 50 K and occurred at \( g = 2.003 \), \( g = 1.975 \) and \( g = 1.935 \) in AgBr. They did not resemble any previously reported signals. They exhibited an unusual environmental sensitivity (they were eliminated by evacuation at 12K) and were found to be photo-active. They were considered to arise from at least two different intrinsic electron or hole trap species.

5.2. EXPERIMENTAL.

1. SAMPLES.

A. SOLS.

High purity AgBr sols were prepared by dissolving Ag shot (m6N, Alfa Products) in doubly distilled HNO\(_3\) and reacting the resultant AgNO\(_3\) with doubly distilled HBr. They were washed with de-ionised water and dried by subsequent washing with acetone and ether.

B. SINGLE CRYSTALS.

Single AgBr crystals were grown in Br\(_2\) by the Bridgman technique from high purity AgBr sols.
C. EMULSIONS.

Table 1. lists the emulsions used in these studies. Emulsions with the RWJ prefix were prepared at Eastman Kodak by Dr. Ralph Jones, using re-crystalised AgNO₃ (Eastman Kodak) and ultrapure KBr (Alpha Products). Photographic gelatins 400F and DI (IV) were used. A Superselect instrument was used to control the pH and pAg during the precipitations. High purity emulsions were obtained composed of microcrystals with fairly well-defined morphologies, although emulsion no. RWJ 069 was found to be very polydisperse with many triangular grains and in emulsion no. RWJ 080 there was much clumping and many multiply twinned grains. Emulsion GWJ 103 was an experimental emulsion prepared by G. Janusonis. An electron-micrograph of a similar emulsion is shown in Chapter 4, Fig. 1.

Table 1.

<table>
<thead>
<tr>
<th>Emulsion #</th>
<th>Composition</th>
<th>Size (µm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>RWJ 080</td>
<td>Pure AgBr</td>
<td>0.9</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 102</td>
<td>Pure AgBr</td>
<td>0.9</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 069</td>
<td>Pure AgBr</td>
<td>0.2</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 117</td>
<td>Pure AgBr</td>
<td>0.1</td>
<td>Cubic</td>
</tr>
<tr>
<td>GAJ 103</td>
<td>Pure AgCl</td>
<td>0.1</td>
<td>Cubic</td>
</tr>
</tbody>
</table>
It was found necessary to de-gel liquid emulsions so that they could be inserted into ESR sample tubes in powder form. De-gelled samples were prepared by dispersing them in sodium bromide solution at 38°C and centrifuging down. This process removed excess gelatin, enabling a much greater quantity of silver halide to be placed in the microwave cavity, with a consequent increase in signal to noise ratio, but still left the microcrystals with a thin gelatin coating. This treatment has been shown not to have much effect on the photographic properties of such samples, although some speed loss has been observed when de-gelled emulsions have been re-dispersed and coated for sensitometric analysis.

All samples were prepared and handled in the absolute minimum of red "safe-lighting" conditions and stored at 278K.

2. INSTRUMENTATION

Spectra were recorded using a Varian E12 ESR spectrometer, equipped with a Hewlett-Packard 5343A frequency counter and a Varian NMR gaussmeter. An Air Products LTD-3-110 Heli-Tran™ helium-flow cryostat was used to obtain sample temperatures down to approximately 9K. The temperature controller was calibrated using a gold-iron/chromel thermocouple which was inserted into the sample position within an ESR tube.
Spectra were accumulated and analysed using a Varian V-72 computer and a Hewlett-Packard 9835B data acquisition system. g-values were measured relative to DPPH markers. These were inserted into ESR tubes on a sliding arrangement which enabled very dilute samples to be lowered into the sample region for calibration purposes and raised when not required. This enabled g-values to be measured to an estimated error of ± 0.0005. When experiments were conducted in vacuo, this arrangement could not be used and the magnetic field in the cavity had to be measured by using a separate DPPH sample. This resulted in an uncertainty in g of ± 0.001.

A vacuum assembly was constructed to enable samples to be evacuated and to allow various gases to be admitted to samples in situ [Fig. 1]. Pressures were measured using thermocouple and ion gauges. The latter had to be situated about 1m from the sample tube to prevent inadvertent irradiation. All experiments were conducted in either absolute darkness or in minimal red "safe-light" conditions, apart from the photo-activity investigations, for which an E.G.and G. model IV photographic sensitometer and optically flat quartz sample cells were used.
FIGURE 1
Diagram of Apparatus.

APPARATUS IN
DARKROOM
He from Cryostat
[T ≈ 4 → 323 K]
5.3. RESULTS

Fig. 2. shows the ESR spectrum obtained at 10K, in air, from the unexposed 0.9 µm octahedral AgBr emulsion RWJ 102. There were four strong signals with g-values of 2.069, 2.003, 1.975 and 1.935. These signals were always detected together in unexposed AgBr and AgCl emulsions. They were also seen in sols prepared from 6N silver shot and ultrapure acids.

The signal at \( g = 2.069 \) was the only signal which was also observed in the gelatins used in the preparation of the emulsions. It is assigned to \( g_{\perp} \) from impurity Cu\(^{2+}\) ions, mainly coordinated to the gelatin sheath remaining around the silver halide grains, which remained even after the "de-gelling" process. This assignment was confirmed by back-doping experiments with cupric nitrate. The signal did not show any environmental sensitivity and was observed over the temperature range of 9 to 250K.

The remaining three signals, hereafter referred to as signals 1, 2, and 3, in order of decreasing g-value, were only observed in silver halide systems. Signals 1 and 2 were super-imposed and could either have been associated with two different centres or to one centre with parallel and perpendicular components. Signal 3 displayed an asymmetry characteristic of an axially symmetric centre in which \( g > g \). The signals could not be identified from any existing ESR data. The following results report empirical experiments designed to probe the unusual properties of these signals.
FIGURE 2
ESR Spectrum of unexposed de-gelled AgBr emulsion RWJ 102 measured at 10 K in air.
A. THE EFFECT OF GRAIN COMPOSITION.

Signal lineshapes were independent of grain composition. The relative intensities of the signals were also fairly consistent. However, the g-values of all three signals were found to be dependent on grain composition. Table 2. lists g-values and linewidths of signals 1, 2 and 3 observed in pure silver bromide and silver chloride emulsions.

Table 2.

<table>
<thead>
<tr>
<th>Grain Composition</th>
<th>g-values</th>
<th>Linewidths (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>AgBr (RWJ 069)</td>
<td>2.0036</td>
<td>1.9754</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>21</td>
</tr>
<tr>
<td>AgCl (GAJ 103)</td>
<td>2.0010</td>
<td>1.9715</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>21</td>
</tr>
</tbody>
</table>

g-values and Linewidths of ESR signals Observed in Unexposed AgBr and AgCl Emulsion Grains [measured at 20K].

The variation in g-values for signals 1 and 2 was considered to be just outside experimental error and to suggest that signals 1 and 2 had some halide character.
Identical signals were observed in Ir$^{3+}$ doped emulsions, suggesting that the signals were not associated with electron traps within the silver halide crystals (see Chapter 4, section 4.6 (i) for a discussion of the electron-trapping mechanism associated with incorporated Ir$^{3+}$ ions).

**B. THE EFFECT OF GRAIN SIZE.**

Signals 1, 2, and 3 were not detected in single crystal samples of AgBr or AgCl, and were extremely small in the respective sols. The strongest signals were observed in the smallest-grained emulsions that were studied (0.2$\mu$m AgBr and 0.13$\mu$m AgCl). These observations of increasing signal intensity with increasing surface/volume ratio were thought to suggest that the signals were associated with surface states.

**C. TEMPERATURE DEPENDENCE.**

**(i). SIGNAL INTENSITY.**

Fig. 3. shows ESR spectra of an unexposed 0.13$\mu$m AgCl emulsion (GAJ 103) over the temperature range of 9 to 24K. Fig. 4. shows a plot of the peak-to-peak heights of signals 1, 2 and 3 against temperature over the range of 9 to 50K. The microwave power used for these measurements, (5 mw), did not cause any signal saturation over this temperature range.
FIGURE 3
ESR Spectra of unexposed de-gelled AgCl emulsion GAI 103, in air, recorded at various temperatures:

a) = 9 K
b) = 14 K
c) = 19 K
d) = 24 K.

Signal 1

3300G

25 G

Signal 2

Signal 3
Signals 1 and 2 decreased with increasing temperature. They were both fairly weak at 20K and could not be observed above 35K. Signal 3 increased as the temperature increased from 9 K, reached a maximum at 18-20 K and then decreased. It could not be observed above 55K.

The species associated with signals 1 and 2 may have been inter-converting to that associated with signal 3, however spin concentration estimates showed that this was unlikely.

(ii). g-VALUES.

It can be seen from Fig. 4. that signals 1 and 2 shifted with temperature. Signal 1 shifted up-field [towards decreasing g-values] with increasing temperature, while signal 2 exhibited a larger down-field shift [towards increasing g-values]. Fig. 5. shows a plot of g-value against temperature for the two signals in the AgCl emulsion GAJ 103. Extrapolation to higher temperatures showed that the signals would be expected to have coalesced at T ≈ 60K and g = 1.991. This would be exactly that expected for $g_{av} = (g_\parallel + 2g_\perp)/3$ if signals 1 and 2 were to correspond to $g_\parallel$ and $g_\perp$, respectively, of the same species, for which $g_{av}$ represented the motionally averaged isotropic g-value.
FIGURE 4
Plot of ESR signal amplitude against T for the 3 signals in unexposed, degelled AgCl emulsion on film [spectra recorded in air].
D. ENVIRONMENTAL EFFECTS.

(i). THE EFFECT OF GELATIN.

The intensities of the three signals did not depend upon the amount of gelatin associated with the grains. Similar signals were observed from samples which had only been through the de-gelling process once to those which had been de-gelled up to four times. This may indicate that the signals were associated with species on the grain surface or bound to gelatin molecules co-ordinated to the grain surface.

(ii). THE EFFECT OF pAg AND pH.

ESR spectra from samples of the 0.9 μm AgBr emulsion RWJ 102 which were washed with 10^{-3} M solutions of AgNO₃ or KBr are shown in Fig. 6a-b. Signal 1 increased with a decrease in the surface pAg [Fig. 6a.], while signal 2 showed the opposite effect [Fig. 6b.]. Signal 3 was unaffected by these treatments.

These results suggested that signals 1 and 2 were associated with different surface states, in apparent contrast to the results of section C(ii). It is difficult to rationalise the effects of these surface treatments. It could perhaps have been possible that signals 1 and 2 were associated with trapped hole and trapped electron states, respectively. The treatment with a solution of low pAg might
FIGURE 5
Plot of g-values for ESR signals against T for degelled, unexposed AgCl emulsion GAJ 103 [spectra recorded in air].

$g_{av} = 1.991 \pm 0.001$

Signal 1

Signal 2

$B = 2A$

T(K)
FIGURE 6
ESR spectra of an unexposed sample of de-gelled AgBr emulsion RWJ 102 measured at 12 K:
a) at low pAg
b) at high pAg.

Signal 1

Signal 2

Signal 3

Gain x 2

$g = 2.003$
$g = 2.069$
$g = 1.935$
$g = 1.975$
have removed electrons from the halide surface and increased the density of hole states giving rise to signal 1 [reaction (1)]. Similarly, treatment with a solution of high pAg might have transferred electrons to the halide surface and increased the density of electron states giving rise to signal 2 [reaction (2)]:

\[
e^-(\text{surface}) + \text{Ag}^+(\text{soln}) \rightarrow \text{Ag}_0 \quad (1)
\]

\[
h^+(\text{surface}) + \text{Br}^-\text{(soln)} \rightarrow \frac{1}{2}\text{Br}_2 \quad (2)
\]

However, (1) would have involved the formation of silver atoms, or possibly silver clusters, which would have been expected to give characteristic ESR signals. No signals with a hyperfine coupling of \(\approx 600 \text{ G}\) characteristic of Ag\(_0\) atoms or paramagnetic molecular silver cluster centres (see Chapter 1) were observed, neither were signals observed with the characteristics of the pseudo-metallic silver agglomerates reported in Chapter 6.

(iii). THE EFFECT OF EVACUATION.

Evacuation had a dramatic effect upon the three signals. Fig. 7a-d. shows the changes in the ESR spectrum of the 0.2\(\mu\text{m}\) octahedral AgBr emulsion RWJ 069 as the air pressure in the sample tube was varied between 1 atmosphere and \(10^{-4}\) Torr at 12K. Evacuation of the sample to \(10^{-2}\) Torr resulted in a loss of signals 1 and 2 with a diminution of signal 3 (Fig. 7b). Further evacuation to \(10^{-4}\) Torr eliminated the
FIGURE 7
The effect of air pressure on the ESR spectrum from the de-gelled unexposed AgBr emulsion RWJ 069 at 12 K.
a) 1 atmosphere;
b) evacuated to $10^{-2}$ Torr;
c) evacuated to $10^{-4}$ Torr;
d) air reintroduced at 12 K to a pressure of $10^{-1}$ Torr.
latter completely (Fig. 7c). The process was found to be completely reversible; the signals immediately re-appeared at their original intensity when air was reintroduced at 12K (Fig. 7d).

Fig. 8. shows an action spectrum, from the same sample, where the change in intensity of signal 1 with time after the start of evacuation of the sample tube at 12K was monitored. The spectrum was obtained by setting the magnetic field to exactly that required for the resonance maximum (3230 G) and scanning at constant field.

Similar results were obtained from the AgCl emulsion, GAJ 103, although it took longer for the signals to decay under the same conditions.

The behaviour of signal 3 at some stages of evacuation was different to that of the other signals. Whereas the latter steadily decreased in intensity during evacuation, the former showed an initial increase before reaching a maximum and then steadily decreasing (Fig. 9).

The g-value of signal 2 was found to vary during evacuation. Fig. 10. shows a plot of g-value against time after the start of evacuation for this signal, as observed in the 0.13 AgCl cubic emulsion GWJ 103.

Possible models for such signal behaviour will be discussed later.
**FIGURE 8**

Fixed field ($H_i = 3230.0$ G) scan of unexposed, degelled AgBr emulsion NWJ 069 at various air pressures ($T = 12$ K).

At point A, pressure = 1.0 Torr. Point B marks the start of evacuation. Pressure at point C = $10^{-6}$ Torr. At point D, air at 2.0 Torr was admitted.
Plot of the ESR signal amplitude of signal 3 against time after the start of evacuation at 12 K for degelled unexposed AgCl emulsion G0103.

$S_H$
FIGURE 10
Plot of $g$-value against time after the start of evacuation for ESR Signal 3, as measured in AgCl emulsion GAJ 103.
The possibility that oxygen containing radicals were responsible for the signals was investigated by an experiment. An ESR tube containing AgBr emulsion RWJ 069 was evacuated to $10^{-4}$ Torr to eliminate the three ESR signals and then re-filled with $^{17}\text{O}_2$ (80% enrichment, $I = 5/2$). The spectrum observed under an atmosphere of the enriched gas was identical to that in Fig. 2. No hyperfine structure was observed.

(iv). THE EFFECT OF DIFFERENT GASEOUS ENVIRONMENTS.

When samples were evacuated to $10^{-4}$ Torr to eliminate signals 1, 2 and 3 and then exposed to about 200 Torr of nitrogen, helium, hydrogen, oxygen, nitrous oxide, water vapour or chlorine, spectra identical to those obtained in air (Fig. 2.) were immediately obtained. In order to investigate possible differences in the rates of re-appearance of the signals in different environments, it was necessary to expose samples to small volumes of gases at very low pressures.

Fig. 11. shows the rate at which signal 1 re-appeared after a sample of the 0.1 AgCl emulsion GAJ 103 which had been evacuated to $10^{-4}$ Torr to eliminate all three signals was exposed to small volumes ($\approx 100$ mls) of different gases at various pressures from 2 to 200 mTorr. It can be seen that the signal re-appeared more rapidly when samples were exposed to the same gas at higher pressures and that exposure to different gases at the same pressure resulted in
FIGURE 11
Plot of ESR signal intensity against time after the addition of equal volumes of various gases at various pressures to unexposed, degelled AgCl emulsion GAI 103 at an indicated temperature of 12 K (previously at $10^{-4}$ Torr).

- $20 \text{mT } \text{H}_2\text{O}$
- $20 \text{mT } \text{He}$
- $2 \text{mT } \text{He}$
- $20 \text{mT } \text{O}_2$
- $40 \text{mT } \text{Cl}_2$

ESR Signal Amplitude ($S_H$)

$t(s) \times 10^{-2}$
different rates of re-appearance. These results will be discussed later in terms of various models that will be proposed for the origins of the signals.

**E. PHOTOACTIVITY.**

Fig. 12. shows the effect of exposure to 425nm band-gap radiation at 293K for 1.0s on the 0.1μm cubic AgBr emulsion RWJ 117. Signals 1, 2 and 3 decreased in intensity, indicating that they had reacted with the products of the photolysis of silver bromide; most probably with photo-electrons and/or photo-holes. The signal assigned to Cu$^{2+}$ underwent a concomitant increase in amplitude as a result of hole or bromine atom transfer from AgBr.

All three signals were also found to decrease in intensity as a result of sample storage for 3 months at 273 K (see chapter 6, Figs. 12a and 12b). This may have been as a result of the recombination of the trapped electrons or holes that could be associated with the signals with the thermally produced carriers which are known to be involved in the formation of photographic fog.
FIGURE 12
EPR spectra obtained from a 0.16 μm cubic AgBr emulsion measured
at 12 K and 20 mw microwave power level:
a) unexposed, and
b) [spectrum of the unexposed sample] - [spectrum of the sample
after 1 second exposure to 425 nm light at 300 K].

a)

T.C. = 0.01 sec

Cu^{2+}
g_\perp = 2.069

g = 2.0036

Signal 1

Signal 2

Signal 3

unexposed

b)

T.C. = 0.03 sec

increase (+)

(-)

(-)

(Unexposed) -

(1 sec. exposure R.T.)
5.4. DISCUSSION.

The results indicated that the three ESR signals were associated with at least two different species. The postprecipitation treatments at various pAg suggested that signals 1 and 2 were associated with different centres, however, the g-shifts and similar signal decays with increasing temperature provided strong evidence that they were attributable to a single centre with parallel and perpendicular components and \((g_\perp > g_\parallel)\). The following possible origins for the signals were considered:

i. They could have arisen from impurities in the silver halide grains.

ii. They could have arisen from impurities on the silver halide grain surfaces.

iii. They could have arisen from impurities in the gelatin peptiser.

iv. They could have been associated with intrinsic bulk states.

v. They could have been associated with intrinsic surface states.

The pAg experiments argued against (i) and (iv). Internal centres would be expected to be insensitive to
post-precipitation treatments. The signals were observed in sols produced from 6N silver and ultrex acids and were not detected in isolated gelatin. Signal intensity was also found to be independent of the extent of de-gelling. These results were considered to argue against (ii) and (iii). It was possible that impurities that were ESR silent in gelatin were transferred to the silver halide grain surfaces during precipitation. However, although the stability of the paramagnetic species and their peculiar temperature dependence suggested that they could be transition metal ions, they had ESR data, temperature characteristics and an environmental sensitivity quite unlike those expected for commonly occurring impurities such as Cu$^{2+}$, Fe$^{3+}$, Cr$^{3+}$ or Ni$^{2+}$. Signals in this region have been observed from silver centres, [see Chapter 1] where a reduction from the free spin value is rationalised in terms of silver 5p occupancy. Consequently, it was initially considered that the three signals might be associated with silver centres which could possibly have been formed during emulsion precipitation.

The central ($M_I=0$) features from Ag$_2^+$ occur in the same region as signals 1 and 2. The outer features normally associated with this centre might not have been observed because of extensive line-broadening. This could have arisen for a number of reasons, including possible molecular rotation, bond-length variation and matrix effects. These would all be expected to have a less pronounced effect on the central second-order splittings, although broader
signals than those reported in Chapter 1 should have been observed, as indeed was the case. Similarly, signal 3 could have been associated with a paramagnetic molecular silver centre with odd molecularity and corresponding central $M_1=0$ features. There is a general trend towards lower $g$-values with increasing size for cationic silver clusters. For example, the $Ag_4^{n+}$ species has a $g$-value of $\approx 1.97$. The considerable negative $g$-shift of signal 3 might therefore have been indicative of a larger molecular centre, perhaps near to the threshold for the CESR effects reported in Chapter 6.

However, it was difficult to rationalise the unusual properties of the ESR signals in terms of these assignments and it was considered that they were most likely associated with intrinsic surface states.

One explanation for the temperature dependence and environmental sensitivity of the signals was that they were associated with paramagnetic molecules that had been chemisorbed at the grain surface. For example, there are a number of compounds upon which molecular oxygen will chemisorb at ambient temperature with an effective electron transfer process resulting in the formation of $O_2^-$ or $O_2^+$ radicals. This process generally occurs at surface defects such as lattice anion vacancies; the zinc and titanium dioxides are typical examples of solids where these defects predominate$^{15,16}$. $O_2^-$ radicals are also formed by the adsorption of molecular oxygen onto supported silver particles$^{17}$. As outlined in chapter 4, Hamilton$^{18}$ has
proposed that $O_2$ adsorption occurs at the surfaces of silver halide grains as a result of electron transfer from intrinsic surface states.

The effectiveness of helium for causing the re-appearance of the signals argued against this chemisorption model, although trace amounts of common impurities such as $O_2$ and $H_2O$ could have been present. However, the ESR signals did not have $g$-values characteristic of rigid, surface supported $O_2^-$ or $O_2^+$ radicals and did not show any hyperfine structure when formed in an $^{17}O$ environment.

It was considered that the signals could alternatively have arisen from electrons or holes trapped on the surfaces or within the silver halide grains, and that they could be influenced by (i) band bending due to chemisorption at the grain surfaces and (ii) external pressure.

(i). **BAND-BENDING.**

ESR studies of doped amorphous silicon films$^{19}$ have shown that the absorption of gases causes changes in the occupation profile of electrons in localised gap states as a result of band bending at the surface. The adsorption of water vapour on $p$-type films and $O_2$ on $n$-type films was found to cause changes in ESR signals assigned to these states, which were interpreted as being due to changes in the density of the states as a result of Fermi level shifts,
caused by the formation of a surface space charge layer. A signal at \( g = 2.004 \), assigned to trapped electrons at the surface of n-type films, was found to decrease as a result of \( O_2 \) adsorption. A signal at \( g = 2.01 \), assigned to trapped holes at the surface of p-type films, was found to decrease as a result of \( H_2O \) adsorption. These effects were rationised in terms of electron acceptance by \( O_2 \), causing a downward shift of the Fermi level with a consequent reduction in the density of filled electron trap states, and electron donation by \( H_2O \), causing an upward Fermi level shift with a consequent reduction in the density of filled hole trap states.

It was thought that if the species responsible for the three ESR signals in silver halides grains were associated with electron or hole traps at the grain surfaces, the following model might account for their behaviour in these undoped systems:

As the signals were found to disappear on evacuation, the traps would have to be considered to be virtually empty in vacuo. This would demand that they were very deep traps situated almost at the Fermi level, as shown in Fig. 13a. The adsorption of an electron donor such as \( H_2O \) at the surface might cause an upward shift of the Fermi level, as shown in Fig. 13b, which would increase the density of filled electron traps, possibly giving rise to an ESR signal. The adsorption of an electron acceptor such as \( O_2 \) at the surface might cause the downward shift of the Fermi
Density of states diagrams showing the possible effect of evacuation on ESR signals from electrons and holes trapped at intrinsic centres in AgBr.

(a) In vacuo

Filled electron traps $\Rightarrow$ ESR Signals

(b) After absorption of an electron donor

(c) After absorption of an electron acceptor
level as shown in Fig. 13c, which would increase the density of filled hole trap states, giving rise to a hole-type ESR signal.

It is difficult to rationalise the results reported in section D(iv) in terms of this model. First, He would not be expected to chemisorb on the grain surfaces and yet it was seen to be particularly effective in causing the reappearance of the signals. Second, the possibility that the signals were generated by the adsorption of trace amounts of common impurities such as O$_2$ and H$_2$O was ruled out by the observation of almost identical effects from O$_2$, water vapour and He that contained no more than 10 parts per million of these. Third, Cl$_2$ was seen to be the least effective at causing the re-appearance of the signals. Cl$_2$ would be expected to be a particularly good electron acceptor from AgCl, so this result suggested that the signals were associated with hole states. However, if the signals were associated with these, their appearance should not merely have been slowed by a Cl$_2$ environment, it should have been completely prevented. The only remaining, and somewhat remote possibility was that the gases were all contaminated with some other impurity. Further experiments with ultra-pure gases may be able to prove this point conclusively. Optical experiments might also provide useful information, as it would be expected that irradiation of systems such as those shown in Figs. 13a. and 13b. with red light of approximately 1/2 band-gap energy [≈ 1.25 eV] would empty the traps and reduce the ESR signal intensities.

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(ii). PRESSURE.

It is known that the application of mechanical pressure to silver halides can influence their properties. Unexposed emulsion grains which have been mechanically deformed can be developed to silver similarly to grains which have been exposed to actinic light. Conduction electrons and valence holes are thought to be generated by the deformation which can follow identical reaction pathways to optically produced carriers. Evidence has been provided by emission studies. The U.V. excitation of AgBr at 77K gives rise to a luminescence at 2.14 eV which is attributed to electron-hole recombination. AgBr powders that have been mechanically abraded at 77K have also been found to luminesce. The effect is termed Triboluminescence and occurs at an almost identical energy (2.03 eV) to the optically generated luminescence.

It was considered that the evacuation experiments may have been causing deformations of the silver halide microcrystals as a result of changes in the external pressure. The ESR signals grains might therefore have been associated with electron or hole traps, empty in vacuo at 12 K but becoming filled with carriers generated by the influence of the external pressure when exposed to various gases. However, according to this model, signal intensity would be expected to be dependent upon the external pressure but independent of the nature of the environment. The results showed that this was not the case.
The failure of any of these models to explain the evacuation effects led to the consideration that these could just be temperature related phenomena arising from the extreme temperature sensitivity of the intrinsic signals and imperfect sample cooling. Two pieces of evidence pointed to this. First, the g-shift of signal 2 during evacuation [Fig. 10.] was compared with the temperature-induced g-shift [Fig. 5]. It was apparent that the g-shift observed in the former could have resulted from a linear increase of sample temperature from 10K at the start of evacuation (t = 0) to 22K at t = 1000s. Second, the intensities of signals 1 and 2 were extremely small at 22K [Fig. 4.], and the intensity of signal 3 followed the same peculiar profile during evacuation [Fig. 9.] as during warming from 10K to 22K [Fig. 4]. The following model was proposed to explain these results.

Samples consisted of de-gelled emulsion particles that ranged in size from about 0.05mm to 0.5mm. They were placed in ESR tubes which were positioned in a helium-flow cryostat (Fig. 1). A thermal gradient was known to exist along the length of the tubes, since the connection to the vacuum system was almost at room temperature. There was also no barrier to the transfer of radiant heat to the sample. It was postulated that contact between the particles in the sample tubes occurred at very few points when they were in vacuo. This would be expected to result in poor heat conduction and may have resulted in them being at a higher temperature than would be measured by a thermocouple at the
same position. The admittance of, for example, water vapour to this system at about 50K would result in the vapour freezing on the inside of the sample tube and around the particles. The frozen vapour might fill the gaps between the particles, resulting in improved thermal contact and a lower sample temperature. Evacuation would be expected to cause a complete reversal of the effect.

According to this model, the rapid re-appearance of the signals on exposure to various gases at high pressures can be explained in terms of their rapid liquefaction or solidification around the silver halide particles; the variation in the rates of signal increase with different gases at reduced pressures to their different rates of freezing and thermal conductivities. The effectiveness of He can be seen as arising from the particularly high thermal conductivity of this gas. However, this model fails to explain the complete suppression of signal 3 by evacuation (Fig. 7a-d) as this signal could be observed at temperatures as high as 50K and it is difficult to see how samples could have reached such high temperatures.

Future experiments should concentrate on trying to measure sample temperatures directly by incorporating a suitable thermocouple within samples. Unfortunately, this proposed a number of problems which could not be solved within the scope of this project. First, there was the difficulty associated with the incorporation of a thermocouple probe within a vacuum system, second, there
were problems associated with heat leakage from the thermocouple and third, there was the problem of Q-spoiling due to the presence of the probe within the cavity.

3.5. CONCLUSIONS.

Three ESR signals were observed in unirradiated AgBr and AgCl sols and photographic emulsions. Signals at $g \approx 2.003$ and $g \approx 1.975$ could only be observed below 35 K and were thought to be associated with perpendicular and parallel resonances, respectively, from the same centre. The g-values were slightly matrix dependent. The signals appeared to become motionally averaged and it was estimated that they would have reached the isotropic g-value, $g_{av} = (g_\parallel + 2g_\perp)/3 \approx 1.991$, at $T \approx 60$ K in AgCl. A signal at $g = 1.975$ was observed below 50 K that was thought to be associated with an axially symmetric centre for which $g_\perp > g_\parallel$.

It appeared unlikely that the signals were associated with impurity centres, although this possibility could not be ruled out. They were assigned to unidentified intrinsic surface defect states which had different characteristics to the intrinsic centres previously observed using ODMR techniques.3,6,7,8,9,10

As a result of their photoactivity, the centres were considered to be likely candidates for the surface sites at which latent images are formed.
REFERENCES.


CHAPTER 6

E.S.R. Studies of Irradiated Silver Halides.
6.1. INTRODUCTION.

This chapter reports ESR studies of irradiated silver halide systems. Photo-produced resonances were observed which are attributed to small silver particles with similar properties to photographic latent images.

As outlined in Chapter 4, there are no non-destructive techniques for studying latent images. Studies of these species have generally been indirect and have involved chemical processing. Even the assignment to a silver particle is intuitive. This project was aimed at establishing the identity of latent images, to find a spectroscopic technique which might be used to characterise them in practical systems and to see if there was a range of species which behaved in similar ways during photographic processing.

In view of the problems associated with the detection and spectral assignment of latent images by optical absorption studies, ESR spectroscopy has been applied, since the proposed models for their formation have invoked silver atoms and clusters, some of which would be expected to be paramagnetic and have been detected and observed by ESR in other systems. Magnetic susceptibility measurements would be expected to have sufficient sensitivity to detect such species, but such techniques integrate over all of the sample and would not be able to take into account either the photoactive intrinsic sites detected by ESR in this work.
As latent images have, until now, eluded spectroscopic identification, there is a dearth of publications in this field. In 1962, Smith and Ingram\textsuperscript{1}, using commercially available AgBr powders, observed a single-line isotropic ESR signal produced by x-ray, ultra-violet and optical irradiation at room temperature. The signal had a $g$-value of about 2 (an accurate value was not reported) and a linewidth of 7 G. It was assigned to conduction electron spin resonance (CESR) from colloidal silver particles with diameters $<100$ Å. No evidence was presented that associated the species responsible for the signal with latent images. Greenslade\textsuperscript{2} was later unable to reproduce these results using ultra-pure materials and considered that the signal was associated with impurity states.

For a number of years, Dr. Eachus' group in the Chemical Physics Laboratory at Eastman-Kodak, Rochester, have been trying to detect and characterise latent images in practical emulsion systems using ESR\textsuperscript{3a,b} and have reported the observation of a possible Ag\textsubscript{n}\textsuperscript{0} signal at $g \approx 2$. This work is an extension of their research. Before designing further experiments, first the electronic properties of the small aggregates of silver atoms and/or ions which are thought to constitute the latent image and second the experimental problems encountered when attempting to detect them in photographic systems had to be considered.
1. THE ELECTRONIC STRUCTURE OF THE LATENT IMAGE.

Attempts have been made to predict the electronic structure of isolated silver aggregates as a function of their size and geometry. ESR and optical experiments have been performed to test these predictions. In this section, we will examine the results of a variety of experiments on such species trapped by matrix isolation techniques in inert hosts such as frozen rare gases or condensed organic media. The effect of the matrix will also be considered in order to predict the spectroscopic properties of these species trapped in the covalent silver halides.

A. SILVER ATOMS.

Silver atoms, $^{\text{Ag}}^0$, have a $4d^{10}5s^1$ ground-state electronic configuration and are, therefore, paramagnetic. They give well-typified ESR spectra in rare gas matrices, covalent glasses and the gas phase (see chapter 1). In weakly interacting hosts, spectra are characterised by two sets of lines separated by about 600 gauss and centred very close to the free spin g-value [Fig. 1a.]. The two sets are composed of two lines of unequal intensity, corresponding to the two naturally occurring isotopes $^{107}\text{Ag}$ ($I = 1/2$, 48.18% abundant) and $^{109}\text{Ag}$ ($I = 1/2$, 51.82% abundant).

In strongly interacting hosts, where the unpaired electron is delocalised over adjacent anions, the spectra usually contain superhyperfine structure characteristic of
A) Weakly Interacting Matrix.

B) Strongly Interacting Matrix

FIGURE 1
ESR spectra for silver atoms in various hosts.
the host lattice. In Fig. 1b, chlorine superhyperfine structure complicates the Ag⁰ spectrum in KCl. One would predict that qualitatively similar spectra would characterise silver atom centres in AgBr and AgCl, if they occupy cationic sites in the cubic salts and the electron is strongly localised on the silver atom. If significant delocalisation occurs, superhyperfine structure resulting from interaction with the abundant magnetic nuclei of the host may broaden the ESR signal; perhaps beyond detection. The failure to detect these centres previously as intermediates in latent image formation may be entirely a result of this effect.

B. SILVER CLUSTERS.

When silver clusters form, their electronic properties will depend on the size of the aggregate, and their spectroscopic properties will depend on the average electronic energy level spacing, Δ:

i. THE CASE WHERE Δ>>kT: THE MOLECULAR REGIME.

In the molecular regime the particle will be very small, its electronic energy levels will be discrete (Δ>>kT), and it will be described by simple molecular orbital theory. For example, Scheme 1 shows Δ corresponding to the σ→σ* transition in Ag₂⁺:
Neutrally charged aggregates consisting of an even number of atoms will have singlet ground states and will therefore be diamagnetic. These species have been studied optically (see chapter 1). Well-resolved optical spectra have been assigned to molecular $\text{Ag}_2^0$ and $\text{Ag}_4^0$ centres, prepared by vacuum deposition in rare gas matrices. They do not yield the broad plasmon resonance absorptions characteristic of metallic aggregates. Certain cations of these species are paramagnetic and have been characterised by ESR. Spectra from $\text{Ag}_2^+$ and $\text{Ag}_4^{3+}$ prepared by the $\gamma$-irradiation of glassy solutions at low temperatures are well documented (see chapter 1). The spectra exhibit a
multiplicity of lines [Fig. 2.], reflecting the delocalisation of the unpaired electron over the many metal atoms and have been interpreted on the basis of electronic structures calculated from molecular orbital theory. g-values have been found to exhibit a general decrease with increasing cluster size, although they are also slightly matrix dependent. For example, in a CD OD matrix at 77 K, $\text{Ag}_2^+$ has a g-value of 1.997, whereas for $\text{Ag}_4^{3+}$, $g = 1.971$. (in benzene, the values are 1.988 and 1.970, respectively). However, an ESR spectrum assigned to $\text{Ag}_6^{n+}$ (where $n = 5, 3$, or 1) has been recently been observed in a hydrogen-reduced silver exchanged zeolite matrix, with a g-value of 2.053$^4$.

The optical spectra of $\text{Ag}_2^+$ and $\text{Ag}_4^{3+}$ have recently been unequivocably assigned as a result of the simultaneous optical absorption / ESR experiments reported in chapter 3. The cationic cluster $\text{Ag}_3^{2+}$ has been identified by ESR [Fig. 2.]. The neutral aggregates $\text{Ag}_3^0$ and $\text{Ag}_5^0$, consisting of an odd number of silver atoms, have been prepared in covalent hosts by vacuum deposition and have yielded well-resolved molecular ESR spectra compatible with molecular descriptions (see chapter 1). The optical spectrum of $\text{Ag}_3^0$, prepared by vapour deposition in an inert gas matrix has also been reported (see chapter 1).

ii. THE CASE WHERE $\Delta \ll kT$: THE METALLIC REGIME.

When the silver atom aggregate is very large, $\Delta \ll kT$, the electronic energy levels form a quasi-continuum (Scheme 2.)
**FIGURE 2**

ESR spectra for cationic silver aggregates.
and the magnetic properties of the particle are adequately predicted from band theory.

![Scheme 2. Schematic Conduction Band Electronic Energy Level Spacing in Metallic Particles.](image)

The particle is metallic and the magnetic resonance spectrum will consist of a single CESR signal. The shape and g-value of this line is informative. The lineshape is a function of the particle diameter, $a$, the classical skin depth, $\delta$, the electron diffusion time, $T_d$, the spin relaxation time, $T_2$, and the mean free path of the electron, $\Lambda$. When the sample thickness is much less than the skin depth, the line shape will be Lorentzian. When $a \gg \delta$, the lineshape can be interpreted according to the theory of Dyson$^5$ and will depend on the ratio $T_d/T_2$. Fig. 3. shows a typical such signal observed in a 0.63 µm sample$^6$ (thick samples do not give CESR signals in a normal reflection spectrometer because of line-broadening from spin-orbit effects). The CESR g-value, as measured by transmission electron spectroscopy$^7$, is 1.9827.
FIGURE 3
CESR Signal from an Ag film on a quartz substrate [Ref. 6].

FIGURE 4
ESR Spectra from silver atom aggregates in a CO$_2$ matrix [Ref. 16].
iii. The Case Where $A>kT$ and $a<<\delta$: The Intermediate Regime

In the intermediate size region, where $A>kT$ and $a<<\delta$, the magnetic and optical properties of a silver metal cluster cannot be adequately predicted by band or molecular orbital theories. The properties which arise from $A$ values near the Fermi level are known as quantum size effects. The electronic theory of these particles has been developed principally by Kubo$^8$ and Kawabata$^9$. Using a model based on a free-particle-in-a-box approach, Kubo$^8$ predicted that the quantum size effect associated with these small aggregates should lead to an enhanced magnetic susceptibility compared to the bulk, at low temperatures, as a result of electrons in the highest occupied orbital requiring more than the available thermal energy to change their spin states. Only neutral particles were considered. They were predicted to behave differently depending on whether they were composed of an even or odd number of atoms/conduction electrons, as shown in scheme 3.

Considering a Poisson distribution of energy levels, Kubo showed that the high temperature susceptibilities of both even and odd particles should be equal and constant (Pauli), whereas at low temperatures the odd particles should exhibit Curie-law paramagnetism of the unpaired spin while the even particles become diamagnetic. This treatment has since been developed by Denton et al.$^{10}$ for all applicable energy level distributions and extended by Shiba$^{11}$ and Sone$^{12}$ to take into account spin-orbit
interactions (see discussion). There is some experimental support for these predictions from susceptibility measurements of platinum particles with an average diameter 21 Å.13

\[ 
\begin{array}{c|c|c}
\text{EVEN} & \text{ODD} \\
\hline
\text{----------} & \text{-----} & \epsilon_{+1} \\
\text{------} & \uparrow & \Delta \\
\text{-------} & \downarrow & \epsilon_{0} \\
\text{-------} & \epsilon_{-1} \\
\text{-------} & \epsilon_{-2} \\
\end{array}
\]

\textbf{Scheme 3.}

SCHEMATIC ENERGY LEVEL DIAGRAM (AT T = 0) FOR SMALL, NEUTRAL, PARTICLES HAVING EVEN AND ODD NUMBERS OF ELECTRONS [AFTER KUBO].

Kawabata\(^9\) extended the theory developed by Kubo\(^6\) to show that the quantum size effect would be give rise to differences in the CESR spectra from the bulk metal, as a result of the expected lengthening of relaxation times. It was proposed that, in microcrystals smaller than about 100 Å, where \(h\nu<\Delta\), the g-value and square of the linewidth (\(\Delta H^2\)) of the CESR signal would be dependent on \(a\) [see Appendix (iii)]. Unfortunately, there has been a paucity of
experimental data with which to compare these predictions. The best results have been provided by the ESR experiments of Monot et al.\textsuperscript{14,15} which were in conjunction with particle size evaluations by electron microscopy.

Monot\textsuperscript{14,15} prepared small silver particles with diameters of the order of 10 Å by (a) the reduction of an aqueous Ag\textsubscript{2}O solution with hydrogen, from which silver particles were deposited on various substrates and (b) by deposition in CO\textsubscript{2} and organic glass matrices at 77 K using an atomic beam technique.

After treatment (a), single-line ESR signals were observed at room temperature with $g$ values which ranged from 1.89 to 2.01 and $\Delta H$ values that ranged from 0.7 to 12.7 G depending upon the particular sample and substrate. The signals were assigned to silver particle CESR. The variations in $g$ and $\Delta H$ values were attributed to variations in particle size that were also observed microscopically. No precise correlation of CESR parameters with particle size was possible, as a result of the particle size distributions which were always observed, although it was concluded that the size regime in which CESR could be observed was narrow (between 10 and 60 Å).

After treatment (b), more complex signals were observed. At 77 K signals corresponding to silver atoms were detected, although it was estimated that only about 1% of the deposited silver was in this form. In addition to these
signals a resonance was observed in the \( g = 2 \) region (see Fig. 4a.) whose intensity and complicated structure depended on the concentration of silver that was deposited. It was considered that this resonance was the sum of two contributions:

i. Narrow signals which were rather vaguely assigned to various agglomerates having molecular rather than metallic properties. These were found to disappear at about 120 K. They could possibly have been the central \( (M_I = 0) \) features from \( \text{Ag}_2^+ \) centres (see Fig. 2. and chapters 1-3), although there is no mention of the \( M_I = -1 \) and \( M_I = +1 \) outer features which should also have been present. Some of the features observed in the \( \text{CO}_2 \) matrix may have been attributable to \( \text{Ag}^0 \) centres with very reduced hyperfine coupling compared to the free atom value as a result of electron donation to \( \text{CO}_2 \) according to the following reaction:

\[
\text{Ag}^0 + \text{CO}_2 \rightarrow \text{Ag}^+ + \text{CO}_2^-
\]

The possible hyperfine coupling of \( \approx 70 \) G would be indicative of approximately 10\% spin density on silver.

ii. A wider asymmetric signal attributed to CESR from small particles, on which the narrow lines were superimposed. This line increased in intensity on annealing at the expense of the narrower lines (Fig. 4b). There was a low-field tail to the spectrum that became reduced in
intensity as the main signal increased. Monot concluded from this behaviour that the low field (high g-value) tail was associated with the smallest particles and that the main signal was associated with particles reaching the size limit at which the transition from quantum size regime to metallic behaviour occurred. The g-value of the main signal varied from 2.000 to 2.017. ΔH ranged from 15 to 21 G at 77 K, according to the sample, and was 26 G at 194 K.

Monot interpreted the results described in (ii) using Kubo-Kawabata theories. The correspondence between a-values determined microscopically and calculated from the ESR data was quite good (see discussion). However, the theory predicts that g-values should approach the bulk-metal value as particle size decreases, which is opposite to the experimental observations.

Chatelain et al. proposed a mathematical model to explain the asymmetry of these signals based on Kubo-Kawabata theories. CESR lineshapes, as envelopes of contributions from various Gaussian particle size distributions, were calculated and compared with experimental results. The best fit was obtained at a calculated mean a-value of about 20 Å (Fig. 5).

The prediction that ΔH should be proportional to the measurement frequency was experimentally confirmed. The samples were found to exhibit Curie-law paramagnetism over the temperature range of 8-190 K. This was also considered
FIGURE 5
(a) Calculated $A_g^0$ CESR lineshapes for various mean particle sizes [Ref. 16].
(b) Experimentally observed CESR signals from $A_g^0$ particles in a $C_6H_6$ matrix at 77 K [Ref. 16].
to correlate with Kubo's predictions. The predicted change-over from Curie to Pauli paramagnetism was not detected, however, within this temperature range.

Knight\(^1\) pointed out that the correspondence of Monot's results with Kubo-Kawabata theory was probably fortuitous because the latter did not take into account the finite probability of conduction-electron density extending beyond the surface of a small metal particle. This delocalisation could result in exchange interactions with paramagnetic impurities in the surrounding medium with a consequent line-broadening effect. Electron-nuclear hyperfine coupling may compound this broadening and further affect particle size calculations. However, Monot's experiments were on silver particles trapped in matrices where such contributions to CESR line-width would be expected to be minimal.

Myles, Buttet and Car\(^1\) have recently re-examined the problem of predicting the spin resonance characteristics of small metal particles from their size. Using a model that employed a single orthogonalised standing wave (OSW) approach for the conduction-electron wave functions, that accounted for electron density at the particle surfaces, they found that they could successfully account for the magnetic behaviour of small sodium particles. Millet and Borel\(^2\) have also proved the value of this model with small magnesium clusters.
The OSW model predicts that the g-value of a metal particle will approach the bulk-metal value as its size increases, as observed experimentally for Na and Mg, for which there was complimentary microscopic size data. It has not yet been determined if this also holds true for silver particles because of the paucity of correlated microscopic and ESR data.

In summary, there are three possible size regimes by which to classify the silver metal aggregates known as latent image centres:

(a). If the aggregates are small, [<5-7 atoms], ESR measurements should produce multiline spectra for the paramagnetic species. This spectral multiplicity should easily translate into structural assignments for these molecular species if they are produced photochemically in silver halide emulsions, provided that the signals are not obliterated as a result of spin-lattice effects. Fingerprint ESR spectra for the species Ag\(^0\), Ag\(^2^+\), Ag\(^2^+\), Ag\(^3^+\), Ag\(^3^+\), Ag\(^4^+\), Ag\(^5^+\) and possibly Ag\(^\text{m}^+\) are available. Optical data are available to characterise the diamagnetic clusters in this size regime, if it should become possible to solve the serious experimental problems associated with a study of small scattering particles dispersed in a gelatin matrix.

(b). If the latent image aggregates are intermediate in size between the metallic and molecular regimes, the g-value and linewidth of the CESR signal could possibly be used to
deduce their average size if a suitable electronic theory can be developed.

(b). If the particles are large, [>45 Å ± 25 Å, according to Chatelain et al.16], they will be metallic. Their reflection ESR spectra will be broadened by spin-orbit effects and their presence will be difficult to observe by this technique.

2. EXPERIMENTAL CONSIDERATIONS.

Early ESR experiments were thwarted because emulsion samples exhibited strong signals before exposure and photo-induced signals were unconvincingly weak. Studies of these systems present problems which can be categorised as follows:

i. One is trying to observe latent images in silver halide micro-crystals composed of about 1010 ions, each containing only a few latent images, possibly only one such centre, which are known to be sub-microscopic and possibly composed of only a few silver atoms. Calculations [see appendix (i)] show that this extremely small expected spin concentration can result in an instrument sensitivity limit to detection if photographic materials are sampled in their usual format.

ii. This extremely low latent image concentration can result in the expected number of latent image spins being a
very small fraction of the spins from possible paramagnetic impurity ions such as Cu\(^{2+}\) and Fe\(^{2+}\), even when such are present in silver halide crystals in concentrations of less than one part per million. It would be fairly simple to subtract out the contributions of these impurities to the ESR data if they were to be chemically inactive. However, transition metal ions incorporated into silver halide grains during precipitation may act as deep photo-electron or photo-hole acceptors (see chapter 4), with their magnetic properties changing appropriately as the material is irradiated.

iii. In practical photographic systems the silver halide microcrystals are dispersed in a medium composed of gelatin or a synthetic peptising agent and water and coated onto a polymeric support. The system also usually contains a variety of chemical addenda added to control crystal growth and induce chemical and spectral sensitisation. Each addendum to the system introduces impurities, many of which are found to be paramagnetic. The film support itself has been found to have about \(10^{12} - 10^{13}\) spins /g (probably as a result of incomplete polymer cross-linking), and gelatin, being a natural product with a propensity to complex transition metal ions, has been found to introduce impurity species such as Fe\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\) and Ni\(^{2+}\), all of which contribute to ESR spectra. Even ions complexed by gelatin and apparently not in contact with a grain surface have been found to act as donors or acceptors during exposure or they may react with photochemically produced halogen atoms.
Problems associated with (i) were reduced by the choice of a suitable sample format. Calculations showed that it was extremely optimistic to expect to detect latent images in film slices stacked into ESR sample tubes. Instead, it was found necessary to study model systems in which the silver halide grains had been extracted from liquid emulsions by centrifugation, leaving them with only a thin covering of gelatin. These "de-gelled" grains could be packed into sample tubes with much greater efficiency and enabled sensitivity requirements to be met [see Appendix. (i)]. These grains could be re-constituted by the addition of aqueous gelatin and coated for photographic evaluation. It was found that their photographic properties were essentially unaffected by the de-gelling procedure.

By using high purity samples, problems arising from (ii) were minimised. Residual signals were assigned to transition metal impurities on the basis of results obtained at Rochester from extensive research into the effects of deliberate doping with these ions. The use of de-gelled samples led to a reduction in the signals mentioned in (iii). By using uncoated samples, background signals from backing materials were eliminated. The experiments on unexposed de-gelled emulsions, reported in chapter 5, enabled background signals from possible intrinsic defect centres, which had confused previous results to be positively identified. As these signals were found to be extremely temperature dependent, experimental conditions could be chosen to minimise spectral complications from
these centres.

In the studies reported here, high-purity and iridium (III) doped (internally sensitised) AgBr and AgCl single crystals, sols and emulsions were exposed to band-gap irradiation at various temperatures and in various environments. Single-line resonances were observed in sensitised sols, and pure and sensitised emulsions. $\Delta H$ varied from 7.1-21.0 G and $g$-values varied from 2.002$g$-2.033$g$ depending on the matrix and exposure conditions. These signals are attributed to CESR from small quantum size regime silver particles, $\text{Ag}_n^0$, as a result of the reasonably good correlation of the ESR parameters with literature values for such centres, their unusual temperature dependences and the consideration of all possible alternative spectral assignments. Further support for the assignment of some of these signals was obtained from the results of a series of ESR/photographic crossover experiments which demonstrated that the centres giving rise to signals with a $g = 2.002_g$-2.005$g$ and $\Delta H = 9.2-21.0$ G are likely candidates for latent images.

The ESR parameters and temperature dependences of the signals are analysed according to the theoretical proposals of Kubo$^8$, Kawabata$^9$ and Myles et al.$^{18,19}$ in an attempt to deduce the dimensions of the silver particles. The results are discussed in relation to the current proposals for the composition of latent images and the mechanisms of formation that were presented in chapter 4.
6.2. EXPERIMENTAL.

1. SAMPLES.

A. SOLS.

High purity AgBr sols were prepared by dissolving Ag shot (m6N, Alfa Products) in doubly distilled HNO₃ and reacting the resultant AgNO₃ with doubly distilled HBr. They were washed with de-ionised water and dried by subsequent washing with acetone and ether. Iridium (III) doped AgBr sols with a nominal 100 parts per million (molar) iridium concentration were prepared by the addition of solutions of K₃Ir(Cl)₆ during the precipitations.

B. SINGLE CRYSTALS.

Single AgBr crystals were grown in Br₂ by the Bridgman technique from high purity AgBr sols prepared by the method described above.

C. EMULSIONS.

Initially, emulsions were prepared from acidified solutions of re-crystallised AgNO₃ (Eastman Kodak) and ultrapure KBr (Alpha Products) using the double-jet precipitation technique. Photographic gelatins 400F and DI (IV) were used. However, most of the results reported here were obtained from emulsions which were specially prepared
at Eastman-Kodak by Dr. Ralph Jones, using these materials and a Superselect instrument to control the pH and pAg during the precipitations. High purity emulsions were obtained composed of microcrystals with fairly well-defined morphologies, although emulsion no. RWJ 069 was found to be very polydisperse with many triangular grains and in emulsion no. RWJ 080 there was much clumping and many multiply-twinned grains. Table 1 lists the emulsions used:

Table 1.

**EMULSION SAMPLES USED FOR THESE STUDIES.**

<table>
<thead>
<tr>
<th>Emulsion #</th>
<th>Composition</th>
<th>Size (μm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>RWJ 080</td>
<td>Pure AgBr</td>
<td>0.9</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 079</td>
<td>AgBr/Ir$^{3+}$</td>
<td>0.9</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 069</td>
<td>Pure AgBr</td>
<td>0.2</td>
<td>Octahedral</td>
</tr>
<tr>
<td>RWJ 069-1</td>
<td>AgBr/Ir$^{3+}$</td>
<td>0.2</td>
<td>Octahedral</td>
</tr>
<tr>
<td>GAJ 103</td>
<td>Pure AgCl</td>
<td>0.13</td>
<td>Cubic</td>
</tr>
</tbody>
</table>

Extremely weak signals were obtained from irradiated emulsion coatings, in the form of film strips on an "Estar" base. However, it was usually found necessary to de-gel liquid emulsions so that they could be inserted into ESR sample tubes in powder form. De-gelled samples were prepared by dispersing them in sodium bromide solution at 38°C and centrifuging down. This process removed excess gelatin,
enabling a much greater quantity of silver halide to be placed in the microwave cavity, with a consequent increase in signal to noise ratio [see appendix (i) for sensitivity calculations].

D. COATINGS.

Emulsions were coated onto an "Estar" base by Dr. Ralph Jones. In addition, coated samples of emulsion no. GAJ 103 were kindly supplied by G. Janusonis at Eastman Kodak. Samples were prepared for ESR by carefully cutting them into strips of dimensions 0.40 cms x 1.5 cms. with the minimum of mechanical abrasion. These were then individually inserted into ESR tubes.

All samples were prepared and handled in the absolute minimum of red "safe-lighting" conditions and stored at 278 K.

2. INSTRUMENTATION.

Spectra were recorded using a Varian E-12 ESR spectrometer, equipped with a Hewlett-Packard 5343A frequency counter and a Varian NMR gaussmeter. Oxford Instruments ESR-10 and Air Products LTD-3-110 Heli-Tran™ helium-flow cryostats were used to obtain sample temperatures down to approximately liquid helium temperatures. Temperature controllers were calibrated using a gold-iron/chromel thermocouple. Temperatures above 160 K
were found to be more accurately maintained by using a Varian nitrogen-flow cryostat.

To avoid unnecessary spectral complication, spectra were usually recorded at temperatures which were sufficiently high to eliminate the signals from intrinsic centres (see chapter 5), unless these had been reduced by evacuation techniques. Spectra were accumulated and analysed using a Varian V-72 computer and a Hewlett-Packard 9835B data acquisition system. It was found that in some instances signals were so weak as to require a considerable number of spectral accumulations and the subtraction of background impurity signals. This was complicated by the photoactivity of some of these signals.

\[ g \text{-values were measured relative to DPPH markers. These were inserted into ESR tubes on a sliding arrangement which enabled very dilute samples to be lowered into the sample region for calibration purposes and raised when not required. This enabled } g \text{-values to be measured to an estimated error of } \pm 0.0005. \text{ When experiments were conducted } \textit{in vacuo}, \text{ this arrangement could not be used and the magnetic field in the cavity had to be measured by using a separate DPPH sample. This resulted in an uncertainty in } g \text{ of } \pm 0.001. \]

Samples were irradiated \textit{in-situ} using a Bausch and Lomb model 200 super pressure mercury lamp and monochromator equipped with a lens, iris and electronic shutter. The assembly was positioned 30 cms from the ESR cavity and
focussed on the cavity window to give as even a field of illumination as possible. Further selective filtration was accomplished by inserting other filters as required. 420 nm band-pass (AgBr) or 360 nm band-pass (AgCl) filters were always used when attempting to generate latent images. This additional filtration ensured that the irradiation was just at the absorption edge of the silver halides, and allowed actinic light into the samples with high penetration. Infrared filtration was additionally used to prevent long wavelength (Herschel effect\textsuperscript{22}) latent image destruction.

Samples were also irradiated outside the cavity using an E.G.and G. model IV photographic sensitometer and neutral density filters. Powdered samples were irradiated in optically flat quartz cells to give uniform exposure. The cells were laid directly across the top of the sensitometer.

The vacuum assembly described in chapter 5 was used to give in-situ gaseous environmental control. It was found necessary to evacuate samples when working at low temperatures in order to eliminate the signals assigned to intrinsic centres. The system was also used to compare the effects of exposure in vacuum and in air, and to investigate the effects of hydrogen sensitisation.

Sensitometric data were obtained by developing emulsions in Kodak rapid X-ray ("KRX") developer for 6 minutes at 293 K and fixing in a standard sodium thiosulphate fixer.
6.3. RESULTS.

1. SINGLE CRYSTALS.

A. PURE AgBr CRYSTALS.

Samples of pure AgBr single crystals were exposed, in air, to 425 nm (2.91 eV) radiation at temperatures from 4 K to 293 K for various times from $10^{-3}$ s to 10 s. Resultant ESR spectra were recorded at various temperatures from 4 K to 293 K.

A signal at $g = 2.069$ was observed before exposure. Signal intensity only became significant below about 250 K. Computer subtractions from spectra obtained after exposure showed that the signal was photo-active, usually increasing slightly in intensity after exposure, although decreases were noted under some conditions. This signal is assigned to $g_\perp$ from impurity Cu$^{2+}$ ions, at a concentration of a few molar parts per million, on the basis of correlations with literature ESR data for Cu$^{2+}$ ions deliberately incorporated in AgCl$^{21}$ and the Cu$^{2+}$ back-doping experiments with AgBr sols described in section 2. The photo-induced increase in signal intensity is attributed to Cu$^{2+}$ formation as a result of photo-hole trapping by diamagnetic Cu$^+$ impurity ions, the photo-induced reduction in intensity to photo-electron trapping by impurity Cu$^{2+}$ ions [Cu$^+$ is known to act as a deep hole trap in silver halides and a photo-induced optical
absorption band assigned to colloidal-size aggregates of silver and Cu\(^{2+}\) ions in AgCl has been reported \(^{22}\). Extensive spectral accumulation (128 x 2 minute scans) and computer subtractions did not reveal any other photo-induced signals. The failure to detect any of the Ag\(^0\) latent image centres observed in the systems described in later sections is attributed to a combination of factors:

(1). Only a few grain boundaries would be present in these samples, restricting the number of sites at which latent images would be expected to form. The failure to detect this low latent image concentration might then just have been a result of insufficient instrument sensitivity [see appendix (i)].

(2). The photolysis of these samples could have resulted in the formation of differently sized Ag\(^0\)\(_n\) particles to those detected in sols and photographic emulsions [see sections 2, 3, and 4], which might be undetectable by reflection ESR [we shall see later that the ESR signals assigned to Ag\(^0\)\(_n\) centres in the latter are considered to be small quantum size regime particles which are only considered to be observable by ESR over a small range of sizes].
B. IRIDIUM DOPED AgBr CRYSTALS.

Samples of iridium (III) doped AgBr single crystals were exposed under the same conditions reported in (A).

The signal at $g = 2.069$, assigned to Cu$^{2+}$ impurity ions, was also observed in these samples and found to be photo-active. However, significant decreases in signal intensity were not observed, in contrast to the control crystals. This is attributed to competitive photo-electron trapping at incorporated (IrCl$_6^-$) centres.

When crystals were irradiated at 160 K and cooled to about 30 K, signals from (IrCl$_6^-$)$_4^-$ centres were observed, similar to those shown in chapter 4, Fig. 15 i. (b). This confirmed that extensive photo-electron trapping was occurring at incorporated (IrCl$_6^-$)$_3^-$ centres. The formation, ESR characterisation and reaction pathways of these centres has been fully discussed in chapter 4.

No other photo-induced signals were observed.

It was hoped that by carefully annealing samples in which (IrCl$_6^-$)$_4^-$ centres had been formed by exposure at 160 K, internal Ag$_n^0$ centres would be produced that would give rise to additional ESR signals. However, no signals attributable to silver centres were observed in these samples after annealing and re-cooling to 160 K, even after a series of careful anneals up to room temperature, when it
was found that the signals from the \((\text{IrCl}_6)^{4-}\) centres had decayed completely. One of the following arguments could account for the failure to detect any such signals:

1. Internal \(\text{Ag}^0_n\) centres may have been formed during the anneals that could be ESR invisible for the reasons discussed in the introduction and (ii) above.

2. An insufficient number of electrons might have been trapped at 160 K to produce a suitable concentration of observable \(\text{Ag}^0_n\) centres during the anneals.

3. The decay of the \((\text{IrCl}_6)^{4-}\) centres could have proceeded exclusively via electron ejection into the AgBr conduction band. The electrons would then have been subsequently lost by recombination processes, [see chapter 4], instead of forming \(\text{Ag}^0_n\) centres.

2. SOLS.

A. PURE AgBr SOLS.

The \(g = 2.069\) signal was detected in these samples and found to be photo-active. Back-doping experiments with \(\text{Cu}^{2+}\) ions increased the intensity of this signal and provided further evidence for its identification.

No convincing photo-induced signals were detected in pure AgBr sols using the exposure and temperature conditions
reported in section 1. Similar factors to those described in section 1. are considered to have prevented the formation of detectable silver species.

B. IRIDIUM DOPED AgBr SOLS.

i. THE EFFECT OF IRRADIATION at 140 K.

Fig. 6a. shows the ESR spectrum obtained at 140 K, in vacuo (10⁻⁴ Torr), from an un-irradiated AgBr sol that had been doped with K₃Ir(Cl)₆ at a nominal level of 100 molar parts per million. This level is known to give optimum internal chemical sensitisation for the room temperature irradiation of photographic materials.

The g = 2.069 signal was detected in these samples and was again found to be photo-active.

Fig. 6b. shows the resulting spectrum after a 1500s exposure to 425 nm light, in vacuo, at 140 K. It can be seen that the exposure has caused the formation of a species giving rise to a single-line resonance at g = 2.0035. The lineshape, g-value and linewidth of this signal are in reasonable agreement to literature values for CESR from quantum size regime silver particles (Agₙ)⁰. Fig. 7 shows this signal in more detail. It had a linewidth of 19.3 G and was slightly anisotropic.

No signals characteristic of silver atoms or the
FIGURE 6
ESR Spectra from an AgBr sol doped with Ir$^{3+}$:
(a) unexposed, in vacuo,
(b) exposed for 1500 s at 140 K with 425 nm hv in vacuo.
Spectra recorded at 140 K.
FIGURE 7
ESR Spectrum recorded at 27 K from an Ir$^{3+}$ doped AgBr Sol exposed for 1800 s at 140 K with 425 nm hv in vacuo.

FIGURE 8
ESR Spectrum recorded at 27 K from an Ir$^{3+}$ doped AgBr Sol exposed for 1500 s at 140 K with 425 nm hv in vacuo.
molecular silver clusters \[ n<7 \] that have been characterised by ESR in other systems were observed.

Fig. 8. shows the spectrum obtained at 27 K from this sample, \textit{in vacuo}, after the 1500s exposure at 140 K. The \( g = 2.003_g \) photo-signal was not found to have increased in intensity relative to the 140 K spectrum; in fact a small decrease was observed. Microwave power variation experiments showed that this was not a saturation effect. As outlined in the introduction, such deviations from Curie-type susceptibility have been predicted for small metal particles. Similar results were obtained from the Ag\(^0\) signals photo-produced in model emulsion systems [see section 3. (xi)] and are discussed fully in section 6.4.

Features assigned to \([\text{IrCl}_6]^4^-\) centres, at \( g_\perp = 2.81 \), could be observed at 27 K. Their presence showed that iridium (III) had been incorporated into the silver bromide lattice as \([\text{IrCl}_6]^3^-\) centres, which were acting as photo-electron traps according to the mechanism detailed in chapter 4. The observation of Ag\(^0\) centres in this sol was attributed to iridium sensitisation at 160 K. These centres are therefore likely candidates for assignment to internal latent images.

Figs. 9a-e. show spectra obtained in the region of the \( g = 2.003_g \) photo-signal as a result of 425 nm irradiation, in air at 150 K, for various times. The spectra were recorded at 40 K. Signal intensity, linewidth and \( g \) values varied
FIGURE 9
ESR Spectra, recorded at 40 K, from an Ir$^{3+}$ doped AgBr sol exposed for various times with 425 nm hv at 150 K in air.

a) 60 s exposure

b) 300 s exposure

c) 600 s exposure

d) 900 s exposure

e) 2420 s exposure
according to exposure time. The ESR parameters for these signals are presented in Table 2:

Table 2.

**ESR PARAMETERS FOR Ag\(_n^0\) CENTRES IN AgBr/Ir\(^{3+}\) SOLS.**

<table>
<thead>
<tr>
<th>Exposure (s)</th>
<th>g-value</th>
<th>(\Delta H) (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>2.005(_g)</td>
<td>11.3</td>
</tr>
<tr>
<td>300</td>
<td>2.005(_g)</td>
<td>14.8</td>
</tr>
<tr>
<td>600</td>
<td>2.004(_g)</td>
<td>15.4</td>
</tr>
<tr>
<td>900</td>
<td>2.003(_g)</td>
<td>13.5</td>
</tr>
<tr>
<td>2400</td>
<td>---</td>
<td>(\geq)50(composite)</td>
</tr>
</tbody>
</table>

[g-values are estimated to be accurate to \(\pm\) 0.0005, \(\Delta H\) values to \(\pm\) 0.5 G.]

This variation in the ESR parameters may be directly comparable to the size distribution effect that was observed and discussed by Chatelain et al.\(^{14}\) with quantum size regime Ag\(_n^0\) particles produced in other matrices. In particular, the unusual signal with a broadenened low-field wing observed after extended exposure (Fig. 9e) may be attributable Ag\(_n^0\) centres with a significantly different size distribution to those produced at lower exposure levels.

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ii. ANNEALS TO ROOM TEMPERATURE.

Signals from the (IrCl$_6$)$_4^-$ centres were found to have decayed completely after warming to room temperature for a few seconds and re-cooling to 160 K. Small concomitant increases in the intensity of signals in the $g = 2.0035$ region were also observed, providing further evidence for their assignment to internal Ag$^0$ centres.

It was found that when the sample was irradiated for 60s at 150 K in air, producing the photo-signal shown in Fig. 9a, annealed to room temperature for 1 day and then re-cooled to 40 K, the original $g = 2.0058$ photo-signal had decayed almost completely. In addition, a new anisotropic signal was observed, shown in Fig. 10a. This appeared to be a possible combination of two signals with $g$-values of 2.033 and 2.025. Re-exposure of this sample at 150 K with 425 nm light for 300s regenerated the original photo-signal to its former intensity, although there was a $g$-shift to $g = 2.0051$. [Fig. 10b.] The doublet in the $g = 2.03$ region was almost completely eliminated by this exposure. An additional small signal was observed at $g = 2.013$.

These signals may all be attributable to Ag$^0$ centres with different sizes or different composition. The centres formed by the initial exposure may have converted to other differently sized and more stable species on anneal to room temperature. Two such species appear to have been formed, although the ESR signal could well reflect a particle size
FIGURE 10
ESR Spectra recorded at 40 K from an Ir$^{3+}$ doped AgBr Sol exposed for 60 s at 150K with 425 nm hv in air.
a) Annealed to R.T. for 24 hrs at 150 K.
b) Given a further 300 s exposure at 150 K.

FIGURE 11
ESR Spectrum recorded at 4 K from an Ir$^{3+}$ doped AgBr Sol exposed for 10$^{-4}$ s at R.T. in air. [EG&G +2.5 ND].
distribution with maxima corresponding to the absorption where the g-values were measured. Re-exposure may then have caused these centres to have grown, by the addition of photo-produced silver atoms, until they became too large to observe using reflection ESR [Jain et al. have demonstrated that silver particles >300 Å in diameter cannot be detected by conventional reflection ESR]. These reactions would consume photo-electrons, accounting for the relative inefficiency of the secondary exposure.

Recent experiments by Brescia using sulphur sensitised emulsions [see Chapter 4, section 6(i)A for a discussion of the proposed mechanisms of sulphur sensitisation] have indicated that a signal at \( g = 2.030 \pm 0.001 \) is associated with \( \text{Ag}_n \)-sulphur centres at grain surfaces. The signal observed here could have been associated with similar centres. \( \text{Ag}_2\text{S} \) specks may have been present in this sample at low concentration as a result of unintentional sulphur sensitisation [a common problem in emulsion preparation]. Electrons produced by the decay of internal \( \text{Ag}_n^0 \) centres (1) could have migrated to the grain surfaces and led to the formation of \( \text{Ag}_n^0 \)-sulphur centres by successive reactions such as (2) and (3):

\[
\text{Ag}_n^0 \quad \text{(internal)} \quad \longrightarrow \quad n\text{Ag}^+ + ne^- \quad (1)
\]

\[
\text{Ag}_2\text{S} \quad \text{(surface)} + e^- \quad \longrightarrow \quad \text{Ag}_2\text{S}^- \quad (2)
\]

\[
\text{Ag}_2\text{S}^- \quad \text{(surface)} + \text{Ag}^+ \quad \longrightarrow \quad \text{Ag}_3\text{S} \quad \text{(surface)} \quad \text{etc.} \quad (3)
\]
These results might correspond to a combination of the Villard and Clayden effects\textsuperscript{22} that are observed with latent images. The Villard effect involves the destruction of latent images formed by high-irradiance light at room temperature or various levels of irradiance at low temperature by a second, longer imagewise exposure to moderate irradiance light. The Clayden effect involves the de-sensitisation of an emulsion towards subsequent exposure as a result of a very brief exposure to high-irradiance light. It has been suggested that these effects arise from the preferential formation of internal image and the attack on potential surface image sites by photo-holes generated during the initial exposure. Furthermore, the halogenation of the surface environment by holes from the initial exposure is thought to increase the probability of competitive electron trapping and surface recombination.

iii. \textbf{THE EFFECT OF ROOM TEMPERATURE IRRADIATION.}

Extensive experimentation with these samples was not conducted at room temperature. However, Fig. 11. shows an interesting spectrum obtained at 4 K after a room temperature $10^{-4}$s exposure, in air, on an E.G. and G. sensitometer. There is a photo-produced signal with $\Delta H = 15.0$ G. This signal may be best interpreted as a composite of two signals with $g$ values of 2.0013 and 2.0063 and $\Delta H = 7.5$ G. These might be representative of two different Ag$_n^0$ centres with different sizes or size distributions. It may be significant that the mean $g$-value of the two signals is
2.003 g. This value very closely corresponds to the g-values of signals observed after the low temperature irradiation of this and other samples, and the combined ΔH value is also similar.

iv. **SAMPLE AGEING.**

The experiments described above were run within two weeks of sample preparation. In experiments conducted 3 months later, additional signals were detected in unexposed samples.

Fig. 12a. shows the spectrum obtained from the unexposed sample, two weeks after preparation, recorded at 10 K in air. Fig. 12b. shows the spectrum obtained from the same sample under identical conditions after 3 months storage in the dark at about 278 K. A small single-line feature can be seen to have been produced at \( g = 2.0029 \) with \( \Delta H = 10.7 \) G. There are also possible additional signals at \( g = 2.016 \) and \( g = 2.033 \), although these are very near to the noise level, and may not be real. Fig. 13a. shows the signals in more detail.

The \( g = 2.0029 \) signal is assigned to an \( \text{Ag}_n^0 \) centre formed from electrons thermally ejected from traps. These electrons are thought to be responsible for the "thermal fog" that results when photographic materials are stored for long periods, even under refrigeration. Such fog centres would quite possibly be of different size to latent images.
FIGURE 12

ESR Spectra of an unexposed AgBr/Ir$^{3+}$ sol:
a) 2 weeks after preparation,
b) 3 months after preparation,
c) 3 months after preparation, peptised with DI(IV) gelatin.
Spectra recorded at 10-15 K.

a) $g = 2.069$

b) $g = 2.016$

g = 2.033  g = 2.003

$c) g \approx 2.003$

$\Delta H = 9.2G$
This may be reflected by the different $g$ and $\Delta H$ values compared to the photo-produced centres observed in these materials.

It was found that certain levels of room temperature exposure of this sample led to a reduction in intensity of the $g = 2.0029$ signal [Fig. 13b.]. This could have involved a similar mechanism to that proposed in section 2. B. (ii).

This sample was peptised with D (IV) gelatin, principally to investigate the effect of gelatin on the intrinsic centres reported in chapter 5, however, it was found that this process led to an increase in intensity of the signal in the $g = 2.0029$ region by a factor of about 5, as shown in Fig. 12c. The signal was not detected in the pure gelatin [Fig. 14a.]. Unfortunately, the spectrum was not accurately calibrated, so any possible $g$-shift could not be determined, although $\Delta H$ was accurately determined to be 9.2 G. The signal was observed up to 293 K, although there was a reduction in intensity of about 75% compared to the 10 K spectrum.

Malinowski (see chapter 4) determined electrochemically that gelatin reduces the surface free energy of small silver particles$^{14}$. In this experiment the effect of the additional gelatin could therefore have been to enhance the stability of $\text{Ag}_n^0$ size regime responsible for the $g = 2.0029$ signal and caused the conversion of smaller, ESR invisible and
FIGURE 13
ESR Spectra of an Ir$^{3+}$ doped AgBr sol three months after preparation;
a) unexposed
b) exposed $10^{-2}$ s [EG & G 2.5 ND]
Spectra recorded at 12 K.

FIGURE 14
ESR Spectra of photographic gelatins
a) DI (IV)
b) 400 f
Spectra recorded at 20 K.
therefore perhaps even-sized, thermally produced Ag\textsuperscript{n} centres to these. The slightly different temperature dependence of the signals from these thermally produced centres may be also be indicative of different particle size(s) compared to the optically produced centres.

3. DE-GELLED EMULSIONS.

A. PURE EMULSIONS.

i. THE EFFECT OF IRRADIATION AT 160 K.

Fig. 15a. shows the ESR spectrum obtained at 160 K from an un-irradiated, nominally pure, de-gelled 0.9 μm edge-length octahedral AgBr emulsion (RWJ 080) in vacuo. The signal at \( g = 2.069 \) was more intense in this sample compared to that observed in AgBr sols. This is attributed to the presence of additional, gelatin-complexed Cu\textsuperscript{2+} ions. Figs. 14a,b. show spectra, recorded at 20 K, of the two photographic quality gelatins used in these studies, in which similar signals can be seen. Recent NMR studies by Hewitt et. al.\textsuperscript{24} have indicated that gelatin complexation of Cu\textsuperscript{2+} occurs primarily by the glutamic and aspartic acid moieties.

ESR spectra of unexposed samples recorded at 15 K revealed a signal at \( g = 4.2 \) [Fig. 16.] This signal was observed in every emulsion sample studied. Extensive spectral accumulations and subtractions showed that this
FIGURE 15
ESR Spectra of AgBr emulsion
RWJ 080 (de-gelled)
a) unexposed
b) exposed at 164 K for 1560 s with 425 nm hv in vacuo.

FIGURE 16
ESR Spectrum of AgBr emulsion
RWJ 080 (de-gelled) unexposed, at 15 K in vacuo.
signal was not photo-active. It is tentatively assigned to Fe\(^{3+}\)\(^{24}\), possibly complexed with gelatin.

Fig. 15b. shows the spectrum obtained at 160 K after the sample was exposed at 164 K in vacuo (10\(^{-4}\) Torr) with 425 nm irradiation for 1560s. A symmetric single-line resonance at \(g = 2.0035\) is seen to result, assigned to Ag\(^{0}_n\) centres; possibly latent images. Such latent images are likely to have been formed both internally and on the grain surfaces in this system. Figs. 17a-h show the effect of intermediate exposures. Fig. 18a. shows a plot of signal intensity against \(\log_{10}[\text{Exposure}]\). ESR signal intensity can be seen to increase with exposure in a similar manner to the optical density from developed latent images [the expected proportionality between ESR signal intensity and optical density is discussed in Appendix (ii)].

Fig. 19. shows the signal after 480s exposure in more detail. It has a linewidth of 21.0 G. Linewidth and \(g\)-value were found to be independent of exposure, within the limits of experimental error. According to Kubo-Kawabata theories,\(^{8,9}\) this would indicate that the Ag\(^{0}_n\)/latent image centres formed in this system were highly uniform in size.

ii. THE EFFECT OF IRRADIATION AT LOWER TEMPERATURES.

Ag\(^{0}_n\) signals were observed at irradiation temperatures as low as 90 K. Extensive irradiation (several hours) was required to give a measurable signal intensity at this
FIGURE 17
RWJ 080 AgBr emulsion (degelled) exposed for various times in vacuo with 425 nm hv at 160 K. [Spectra recorded at 160 K unless otherwise indicated.]

- 3230G -

\[ 50G \]

\[ \text{a) unexposed} \]

\[ \text{b) 15s exposure} \]

\[ \text{c) 30s exposure} \]

\[ \text{d) 60s exposure} \]

\[ \text{e) 120s exposure} \]

\[ \text{f) 240s exposure} \]

\[ \text{g) 480s exposure} \]

\[ \text{g=2.003} \]

\[ \text{h) 1560s exposure} \]

\[ \text{i) 1560s exposure at 160K, Annealed to R.T. Spectrum recorded at 270K.} \]
FIGURE 18
Plot of ESR Signal Amplitude measured at 160 K, against $\log_{10}$ [Exposure]

- $a = 0.9$ $\mu$m degelled AgBr emulsion RNJ 080 exposed in vacuo 160 K;
- $b = 0.2$ $\mu$m degelled AgBr emulsion RNJ 069-1 exposed in vacuo 160 K;
- $c = 0.2$ $\mu$m degelled AgBr emulsion RNJ 069-1 exposed in air 160 K.

$\text{gain} = 2 \times 10^4$

$g = 2.003_s$

$E_{\text{SR Signal Amplitude}} = (S_0)$ (cns)
FIGURE 19
ESR spectrum of degelled AgBr emulsion
BM 080 exposed for 480 s with 425-nm hv
at 160 K (spectrum recorded at 170 K).

$g = 2.0035$

$\Delta H = 21.0 G$

3230 G
temperature. Line-shape and ESR parameters were identical to signals observed after 160 K irradiation.

As discussed in chapter 4, it has not been absolutely established by sensitometry whether latent images are formed at these low temperatures, as a result of the need to anneal systems to at least 230 K for development purposes. If the assignment of the ESR signal to latent image centres is correct, this result shows that such centres are indeed formed under such conditions. The reduced yield at lower temperatures can be explained in terms of the increased recombination and decreased ionic mobility effects discussed in chapter 4.

It was found that low temperature irradiation followed by dark anneals to higher temperatures resulted in the formation of Ag\textsuperscript{0}\textsubscript{n} centres. For example, irradiation at 60 K followed by a dark anneal to 160 K resulted in the formation of an observable $g = 2.0035$ signal. These results correlate with the low temperature photographic studies of Berg [see chapter 4, 2, (iii)] in which the formation of latent images as a result of low temperature exposures was attributed to the thermal ejection of photo-electrons from traps as a result of annealing prior to development.

It was hoped that low temperature exposure followed by careful annealing might have enabled the growth of the silver agglomerates to be slowed sufficiently to allow for the isolation and identification of either:
(i). The molecular intermediates predicted by the Gurney and Mott type mechanisms of latent image formation [see chapter 4], some of which would be expected to be paramagnetic; in particular \( \text{Ag}_2^+ \) and Mitchell's concentration centre, \( \text{Ag}_4^+ \). Or:

(ii). Smaller \( \text{Ag}_n^0 \) aggregates, perhaps formed according to the thermodynamic mechanism proposed by Malinowski and Chibisov [see chapter 4], which might have been expected to exhibit different \( \Delta H \) values and g-shifts from the centres formed at higher temperatures.

However, no signals from any of the molecular species expected from (i) were observed and there were no observable changes in the ESR parameters.

iii. ANNEALS TO ROOM TEMPERATURE.

The \( \text{Ag}_n^0 \) signal was found to persist after annealing to room temperature without any loss in intensity or change in the ESR parameters [Fig. 17.(i)]. However, it was found to decay after a few days at room temperature in vacuo. The broad signal shown in Fig. 20. was found to result. This signal was observed at 293 K and 160 K [Figs. 20a,b] but not at 15 K [Fig. 20c].

This \( \text{Ag}_n^0 \) decay may be comparable to latent image fading. Unsensitised silver halide emulsions are known to be very susceptible to this. Experiments at room temperature on
FIGURE 20

ESR Spectra of AgBr emulsion RWJ 080 (de-gelled) exposed for 1560 s with 425 nm hv in vacuo and annealed to R.T. for 2 days.
(a) Recorded at R.T.
(b) " 160 K.
(c) " 15 K.

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3230G

\[ g \approx 2.003 \]

\[ g_{1} = 2.069 \]

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commercial emulsions have shown that there can be as much as a two-thirds loss of developed density two days after exposure. The results reported in section 3.(vii). show that the $\text{Ag}_n^0$ centres formed after exposure at room temperature decayed more slowly than those formed at 160 K. This would be expected if larger, more stable centres were formed at higher temperatures, as sensitometric studies have indicated.

The broad feature seen after the decay of the $g = 2.0035$ signal was similar to that observed after the extended exposure of AgBr sols and might be expected to have resulted from particle agglomeration. However, this line-broadening and apparent shift of the CESR signal in the direction of increasing $g$-value for larger particles is opposite to the expected trend towards more metal-like narrow lines at lower $g$-values (towards $g = 1.9827$).

iv. THE EFFECT OF GRAIN SIZE.

Fig. 21. shows the effect of 425 nm irradiation at 160 K on a de-gelled 0.2 µm edge-length nominally pure octahedral AgBr emulsion (RWJ 069-1) in vacuo (10-4 Torr). Spectra were recorded at 160 K. A photo-produced signal was observed at $g = 2.0035$ with $\Delta H = 20.0$ G. The signal was similar to that observed in the exposed 0.9 µm emulsion, although it had quite a pronounced asymmetry, in contrast to the almost completely symmetric signal observed in the larger-grained system. The ESR parameters were again found to be invariant.
FIGURE 21
ESR spectra of AgBr emulsion RWJ 069-1 (de-gelled) after various exposures at 160 K with 425 nm hv in vacuo. Spectra recorded at 160 K unless otherwise indicated.

- a) unexposed
- b) exposed 180 s
- c) exposed 360 s
- d) exposed 540 s
- e) exposed 1080 s
- f) exposed 2160 s, $g = 2.003_s$
- g) as f) but at 90K
- h) as f) but at 15K
with exposure times. For example, lineshape did not appear to change significantly with increasing exposure time.

Fig. 18b. shows a plot of signal intensity against $\log_{10}[\text{Exposure}]$. It can be seen that the smaller-grained emulsion required considerably more exposure to produce a given signal intensity and that the limiting maximum signal intensity obtained after extended exposure was much smaller than observed in the 0.9$\mu$m emulsion.

These results provide further evidence for the assignment of the $g = 2.0035$ signal to $\text{Ag}_n^0$ latent image centres. It is well known that the sensitometric behaviour of photographic emulsions is highly dependent on grain size. The asymmetry of the signal observed in the small-grained emulsion may be indicative of less uniform latent image sizes compared to the 0.9$\mu$m emulsion. Alternatively, the asymmetry could result from a different distribution of surface and internal latent images in the two emulsions. Each type of image might consist of silver centres with a slightly different size distribution, giving rise to ESR signals at about the same $g$-values but with slightly different line-shapes (see section 3. B. for results from internally sensitised emulsions).

[The differences in behaviour between these emulsions might be also attributable to the sensitometric effects caused by the higher proportion of triangular grains in emulsion RWJ 069 or the multiple twinning in RWJ 080.]
V. THE EFFECT OF AIR.

(a). DURING EXPOSURE.

ESR signals attributed to $\text{Ag}_n^0$ centres formed after exposures in air at 160 K were identical to those formed in vacuo. However, signal intensities for corresponding exposures were found to be significantly reduced under air. Fig. 18c. shows a plot of ESR signal intensity against $\log_{10}[\text{Exposure}]$ for the 0.2 μm emulsion RWJ 069-1 exposed in air at 160 K. Comparison with Fig. 18b. shows a considerable reduction in sensitivity.

The correspondence of these results to the oxygen de-sensitisation effect on latent image formation [see chapter 4], is highly supportive of the assignment of the $\text{Ag}_n^0$ signal to latent images.

No signals from the paramagnetic $\text{O}_2^-$ centres, thought by Lewis and James$^{22}$ to be responsible for the oxygen de-sensitisation effect, were observed after irradiations in air. The failure to detect such signals might be indicative of the rapid hole attack on $\text{O}_2^-$, postulated by the above. Alternatively the de-sensitisation could have involved the formation of the electron-accepting surface states proposed by Hamilton$^{22}$. 

-277-
(b). AFTER EXPOSURE.

The admission of air to RWJ 080 emulsion samples exposed in vacuo was found to have no effect on the $\text{Ag}_n^0$ signal at 160 K. However, the signal was found to have decayed completely after a 12 hour room temperature anneal in air. The faster decay at room temperature in air compared to vacuum may be attributable to aerial oxidation [oxygen has been shown to accelerate latent image fading, see chapter 4]. The broad signal observed after the anneal in vacuo was not detected.

vi. THE EFFECT OF $\text{H}_2$.

Emulsion RWJ 069-1 was kept at room temperature in an $\text{H}_2$ environment at a pressure of 20 mm Hg for 20 hrs. These conditions would have been expected to give a reduction sensitisation effect, as discussed in chapter 4. ESR spectra were recorded, before and after the sensitisation treatment, at temperatures between 160 K and 15 K. No new centres were detected. A signal at $g = 2.0035$, identical to that observed in the untreated emulsion was observed after irradiation in vacuo at 160 K. A small sensitisation effect on signal formation compared to the control was observed.

These results showed that no $\text{Ag}_n^0$ "reduction centres" attributable to this hydrogen treatment were observable by ESR. The $\text{Ag}_2^0$ centres thought to be produced by low levels of hydrogen treatment would not have been detected, since
they are not paramagnetic. However, extended hydrogen treatment is thought to produce larger $\text{Ag}_n^0$ centres and it was hoped that these might have been formed and detected. Larger, even-electron molecular $\text{Ag}_n^0$ centres such as $\text{Ag}_4^0$ and $\text{Ag}_6^0$ would not be expected to give ESR signals, since they would also be non-paramagnetic. Signals would only be expected from neutral molecular species consisting of an odd number of silver atoms, for example $\text{Ag}_3^0$ and $\text{Ag}_5^0$, or if $\text{Ag}_n^0$ particles large enough to exhibit quantum size regime CESR were formed. The failure to detect any such signals in this experiment may have been indicative of insufficient reduction. Future experiments with more extensive hydrogen treatment may produce such centres and provide a means of generating progressively larger $\text{Ag}_n^0$ particles that would enable the threshold for the quantum size effect to be determined. Such results might also provide valuable data on possible $g$-value and $\Delta H$ correlations with particle size.

vii. **THE EFFECT OF ROOM TEMPERATURE IRRADIATION.**

Fig. 22. shows spectra recorded at room temperature, resulting from the exposure of the 0.9$\mu$m emulsion RWJ 080 to 425 nm irradiation, at room temperature, in air. A somewhat asymmetric signal assigned to $\text{Ag}_n^0$ centres was observed at $g = 2.0035$ with $\Delta H = 21$ G. This was the only signal observed at this temperature. $g$ and $\Delta H$ values were found to be independent of exposure time, within the limits of experimental error. Fig. 23. shows a plot of signal intensity against $\log_{10}[\text{Exposure}]$. It can be seen to have
FIGURE 22
ESR Spectra, recorded at R.T., from emulsion RWJ 080 (degelled) after various exposures with 425 nm hv in air.
FIGURE 23
Plot of ESR Signal Amplitude against 
log_{10} Exposure for 0.9 μm Aigr
emulsion fog 080 exposed at room temperature 
with 425 mW. (spectra recorded at room 
temperature)

gain = 2 \times 10^4

ESR Signal Amplitude (S') cm

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the three important characteristic regions, A, B and C, exhibited by D-logE curves. The possible reasons for this correspondence are discussed below:

REGION A.

This may correspond to the fog region of the D-logE curve. ESR signals from possible pre-existing Ag\textsuperscript{n}O centres associated with photographic fog may be present but buried below the noise floor.

REGION B.

This may correspond to the "linear exposure region". It may represent a linear increase with \( \log_{10}[\text{exposure}] \) of the number of observable Ag\textsuperscript{n}O centres until a maximum, \( S_{\text{max}} \), is reached. The consistent ESR parameters are taken to be indicative of the formation of uniformly sized centres, or a consistent size distribution of centres, over this exposure range.

REGION C.

This may correspond to latent image solarisation and reflect halogen or hole attack on the Ag\textsuperscript{n}O centres. Alternatively, the fall in ESR intensity beyond \( S_{\text{max}} \) may be attributable to the agglomeration of the Ag\textsuperscript{n}O particles responsible for the signal with the formation of centres outside the quantum size regime, and, therefore, undetected.
by ESR.

The asymmetry of the signal observed after room temperature exposure compared to the almost completely symmetric signal observed after 160 K exposure might reflect increased internal image formation at higher temperatures. Alternatively, or possibly in addition, it may be indicative of a broader size distribution for latent images formed at room temperature. Sensitometric studies on emulsions exposed at different temperatures have also been interpreted in terms of changes in the sizes of the latent images which are formed. Emulsions exposed at low temperature have revealed marked differences in developed density compared to room temperature exposures (see chapter 4). This has been attributed to the formation of extremely small latent images. Low temperature sensitometry studies have revealed that latent image formation is much less efficient at 160 K than at room temperature, a result also reflected by these ESR results.

viii. THE EFFECT OF RED LIGHT.

A sample of the 0.20 \( \mu \text{m} \) AgBr emulsion RWJ 069-1 was exposed, at room temperature, to a 425 nm light for the time required to give half the maximum \( g = 2.0035 \) signal intensity. The sample was then exposed, in situ, to a second broadband irradiation between 700 and 900 nm at room temperature. There was a loss of signal intensity as a result of the red-light exposure, as shown in Fig. 24. The.
FIGURE 24
The effects of red-light bleaching on the ESR signal from latent image (left ordinate) and $D_{\text{max}}$ (right ordinate) for an AgBr emulsion [Ref. 3(b)].
experiment was repeated for coated samples of the same emulsion, in which the 425 nm exposure was at a level necessary to give a density corresponding to $D_{max}$ if it were to be developed. Developable density was found to decay at the same rate as the ESR signal intensity [Fig. 24].

These results showed that the $g = 2.0035$ centre exhibited the well-known Herschel effect. The correlation of the behaviour of the species responsible for this signal with latent images provides further evidence for its assignment.

ix. THE EFFECT OF GRAIN COMPOSITION.

Fig. 25. shows the the effect of room temperature 365 nm irradiation, in air, on a 0.13 μm edge-length unsensitised AgCl emulsion (GAJ 103).

An almost completely symmetric signal was observed at $g = 2.0048$ with $\Delta H = 18.5$ G, considered to arise from latent image $Ag^0_n$ centres. The Line-shape was different to that observed from $Ag^0_n$ centres produced by the room temperature exposure of AgBr emulsions, though similar to that observed after exposure at 160 K. $g$ and $\Delta H$ values are both different to those observed after 160 K and room temperature exposures of AgBr emulsions, although they fall within the wide range of values of the signals observed after the low temperature exposure of the internally sensitised AgBr sols, reported in section 2.
FIGURE 25
ESR Spectra of degelled AgCl emulsion GAJ 103:
(a) unexposed,
(b) after 240 s exposure with 365 nm hv at R.T. in air.
Spectra recorded at R.T.
Although these observations might just be a result of a matrix effect on the ESR signals, it is considered that they could indicate that latent images formed in AgCl emulsions are of slightly different composition to those formed in AgBr emulsions (though perhaps similar to some of those formed in AgBr sols), having a slightly different Ag\textsuperscript{0} particle size distribution. The different sensitometry shown by these materials may, in part, result from these differences.

x. SIGNAL DECAY AND COMPARISON WITH LATENT IMAGE FADEING.

The ESR signals observed after room temperature exposure of these emulsions were found to decay at a significant rate at room temperature. Fig. 26. shows plots of signal amplitude (a), g-value (b), and ΔH (c), against time after a 240s exposure (corresponding to approximately S\textsubscript{max} of the 0.13 μm AgCl emulsion, GAJ 103, to 365 nm light in air. Fig. 27. shows a reported,\textsuperscript{25} sensitometrically obtained curve of developed density against time after various exposures for a commercial 0.055 μm cubic AgBr emulsion (SO 343) for comparison purposes. The fall in developed density with time in this emulsion was attributed to latent image fading. The reasonably good comparison of the shapes and time-scales of the ESR signal and latent image decay curves, in particular with the latent image curves corresponding to high initial densities, provides further evidence for the assignment of the signal to latent images.
FIGURE 26
Plots of ESR signal amplitude, g-value and ΔH against time after exposure measured at room temperature. [GAI 103 de-gelled emulsion exposed 240 s with 365 nm hv at room temperature.]
Latent image fading of cubic 0.055 μm AgBr emulsion SO 343 in ambient conditions, as determined sensitometrically [Ref. 25].
Both curves show an initially slow decay (the ESR signal amplitude was found to be constant for the first 300s within experimental error), followed by a faster decay. However, the greatest rate of ESR signal decay is seen to occur after about $5 \times 10^3$ s, whereas in the latent image curves it occurs after about $5 \times 10^5$ s. In addition it was found that after $5 \times 10^5$ s ESR signal intensity had been reduced to the noise floor, whereas there were still some developable latent images present in the developed emulsion after this interval. This difference in behaviour may be due to result of a combination of factors. The ESR signals were detected in de-gelled samples in which there was a much smaller amount of gelatin associated with the silver halide microcrystals than in the coated SO 343 emulsion. As reported in chapter 4, gelatin has been shown to increase latent image stability. In addition, the samples have different compositions and morphologies. The AgBr emulsion used for the latent image studies was also slightly sulphur sensitised. It is therefore possible that the stabilities of different sizes of latent images are being compared. Also, it is possible that only a fraction of the developable $\text{Ag}_n^0$ particle size distribution is detectable by ESR (see section 4.) and that these may decay at a slightly different rate to the others.

Fig. 26. shows that in the region of maximum signal decay there is also a marked change in g-values and $\Delta H$. This might reflect a change in the $\text{Ag}_n^0$ particle size distribution.
It was found\textsuperscript{25} that latent image fading was completely eliminated in emulsion SO 343 in \textit{vacuo}, and that the effect was much more pronounced in pure \textit{O}_2. Further ESR experiments with this particular emulsion in these environments should therefore provide useful additional information. [As reported in section \textit{v. (b)}, ESR signal decay after 160 K exposure was found to be faster in air than \textit{in vacuo}].

Signal amplitude was also found to decay significantly at 77 K. A 26\% reduction was observed after an exposed sample had been stored for \(6 \times 10^3\) s at 77 K [compared to a 32\% reduction at room temperature].

\textbf{xi. THE TEMPERATURE DEPENDENCE OF THE SILVER SIGNALS.}

Fig. 28. shows a plot of Ag\textsubscript{n}\textsuperscript{0} signal amplitude against 1/T for the 0.13\(\mu\)m AgCl emulsion GAJ 103. The sample had been exposed to 365 nm radiation for 240 s to produce the signal, which corresponded to approximately \(S_{\text{max}}\). A microwave power level that avoided signal saturation at low temperatures was chosen (5 mW). Temperatures lower than 23 K were not used due to the excessive signal interference that resulted from intrinsic centres in the same region of the spectrum. Points are corrected for any loss of signal amplitude expected from signal decay as a result of time differences between exposure and measurement, although these were kept as short as possible. Table 3 shows \(g\) and \(\Delta H\) values recorded at these temperatures. They can be seen to be invariant, within experimental error.
Plot of ESR signal amplitude against measurement temperature for degelled emulsion GAJ 103 exposed for 240 s with 365 nm hν at room temperature.
Table 3.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>g-value</th>
<th>ΔH (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.0048</td>
<td>18.5</td>
</tr>
<tr>
<td>215</td>
<td>2.0047</td>
<td>17.0</td>
</tr>
<tr>
<td>188</td>
<td>2.0050</td>
<td>18.0</td>
</tr>
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<td>106</td>
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<td>67</td>
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<td>17.0</td>
</tr>
<tr>
<td>35</td>
<td>2.0047</td>
<td>17.0</td>
</tr>
</tbody>
</table>

[Temperatures are estimated to be accurate to ± 2 K, g-values to ± 0.0005 and ΔH to ± 1 G.]

The results demonstrate that the integrated signal intensity for this species does not increase with 1/T according to the normal Curie law. Similar results were observed from the photo-produced Ag\(^0\) centres produced in other emulsions and sols assigned to latent images. The temperature behaviour of these centres is considered to be indicative of Pauli paramagnetism and is discussed fully in section 6.4.
B. IRIDIUM DOPED EMULSIONS.

i. THE EFFECT OF IRRADIATION AT 160 K.

Fig. 29. shows ESR spectra recorded at 160-175 K (a-c) and 15 K (d) after the irradiation with 425 nm light at 160 K, in air, of an iridium (III) doped (100 molar parts per million) 0.9µm edge-length octahedral AgBr emulsion (RWJ 079). This emulsion was the doped analogue of the pure control emulsion RWJ 080.

An extremely small signal at about \( g = 2.013 \) was observed prior to exposure. This may have originated from pre-existing \( \text{Ag}_{n}^{0} \) centres, possibly associated with photographic fog.

An assymetric \( \text{Ag}_{n}^{0} \) signal was observed after exposure at \( g = 2.004 \), with \( \Delta H = 21.0 \) G. Line-shape, \( g \)-value and \( \Delta H \) appeared invariant with increasing exposure time. \( g_{\perp} \) features from \([\text{IrCl}_{6}]^{4-}\) centres were observed on cooling to 20 K. When samples were annealed, the \([\text{IrCl}_{6}]^{4-}\) signal intensity was found to decrease with a concomitant increase in the intensity of the \( \text{Ag}_{n}^{0} \) signal.

Fig. 29d. shows the \( \text{Ag}_{n}^{0} \) signal observed at 15 K. It can be seen that the broad feature contributing to signal asymmetry at 175 K, [Fig. 29 c], became resolved into a separate symmetric feature at \( g = 2.029 \), with \( \Delta H = 7.1 \) G. This signal may have been from the internal images that
FIGURE 29
ESR Spectra of FWJ 079 (de-gelled) emulsion exposed for various times at 160 K in air with 425 nm hv:
(a)-(b) recorded at 160 K; (c) recorded at 175 K;
(d) recorded at 15 K.

a) unexposed

3250G

50 G

b) 1s exposure

c) 1800 s exposure

g = 2.004, \Delta H = 21 G

d) 1800 s exposure

g = 2.029, \Delta H = 7.5 G

-295-
would be expected to be formed in this emulsion. The different ESR parameters and temperature behaviour compared to the $g = 2.004_0$ signal, which appeared very similar to that observed in the control, may reflect different $Ag_n^0$ sizes between internal and surface latent images.

As already mentioned in section B(ii), Brescia\textsuperscript{26} has recently observed signals at $g = 2.030 \pm 0.001$ in exposed sulphur-sensitised emulsions which are thought to be associated with $Ag_n$-sulphide centres. The signals had a different line-width to that reported here ($\sim 40$ G) and were not observable below 20 K. However, if the signals are related, it would imply that emulsion RWJ 079 was inadvertently slightly sulphur sensitised during preparation.

\textbf{ii. THE EFFECT OF ROOM TEMPERATURE EXPOSURE.}

Samples were exposed at room temperature with 425 nm irradiation, in air, and ESR spectra recorded at room temperature. Somewhat asymmetric signals were observed at $g = 2.004_5$ with $\Delta H = 20.0$ G. Line-shape, $g$-value and $\Delta H$ appeared invariant with increasing exposure times.

The slight difference in the $g$-value of the signal compared to that observed in the control may be real (it is just outside the estimated experimental error), however, the signals were otherwise very similar. As the exposed control would be expected to contain a significant concentration of
surface latent images, as demonstrated by the solarisation effect [see section 3. A. (v).], this result may indicate that the $\text{Ag}_n^0$ particle size distributions associated with surface and internal latent images formed at room temperature are very similar, a point also demonstrated by the results of section 3. A. (v). Further experiments with surface sensitised samples should prove this point conclusively.

4. EMULSION COATINGS.

Early experiments with emulsion coatings proved unsuccessful, for the reasons outlined in the introduction. Fig. 30. shows an example spectrum obtained from a coated strip of the pure AgBr emulsion, RWJ 080. Although extensive data accumulation had been used, it can be seen that the spectrum was very noisy and dominated by signals assigned to free radicals and paramagnetic impurities in the Estar base. Computer subtractions were complicated by the photo-activity of these centres. Subtractions from spectra obtained after room temperature exposures, at levels found to produce the $\text{Ag}_n^0$ centres observed in the de-gelled material reported in section 3, did not reveal possible similar $\text{Ag}_n^0$ signals amongst this photo-active background.

However, on the basis of the expertise obtained in the identification of $\text{Ag}_n^0$ centres in the systems reported in sections 1, 2, and 3, and by using a pure AgCl emulsion coating, which had proved to give a good yield of such
FIGURE 30
Typical ESR spectrum from a coated emulsion sample.
centres in the de-gelled state and had been coated onto a remarkably signal-free base, ESR signals from \( \text{Ag}_n^0 \) centres were finally detected in exposed coating strips. These ESR results were correlated directly with sensitometric data obtained by developing the exposed emulsion strips for which ESR data had been obtained.

Fig. 31a-f. shows spectra obtained after the room temperature exposure of coated strips of the pure 0.1 \( \mu \text{m} \) cubic \( \text{AgCl} \) emulsion, GAJ 103, with 365 nm light. Spectra were recorded at room temperature and are the result of data accumulated from 64 scans [The spectra shown in Fig. 31b-f. are the results of the individual subtraction of the spectra obtained from the unirradiated samples, which were all similar to the spectrum shown in Fig. 31a, from spectra obtained after exposure].

It can be seen that the effect of short-duration exposures was to produce a signal at \( g = 2.005 \) with \( \Delta H = 19 \) G, \( \pm 4 \) G. This signal appeared identical to that observed after room temperature exposures of the de-gelled form of this emulsion [see section 3. (ix)] and is therefore assigned to similar \( \text{Ag}_n^0 \) centres. It can be seen that the duration of exposure necessary to form this signal is very much smaller in the case of the coated emulsion. This result correlates with the general observation of loss of photographic sensitivity for the sample in the de-gelled state, thought to arise from a reduction in exposure effectiveness as a result of grain clumping. Fig. 32a. shows
FIGURE 31

ESR Spectra (recorded at R.T.) of film strips coated with AgCl emulsion GAJ 103 exposed for various times at R.T. with 365 nm hv in air.

a) unexposed

b) exposed 0.09s

c) exposed 0.49s

d) exposed 0.99s

e) exposed 1.9s

f) exposed 4.9s

g) exposed 9.9s

h) exposed 99s
a plot of signal intensity against $\log_{10}[\text{Exposure}]$. Extended exposures were found to cause a considerable decrease in signal intensity. The signal was found to have disappeared to the noise floor after a 9.9 s exposure [Fig. 31f].

The emulsion strips corresponding to the ESR spectra shown in Fig. 31 were subsequently developed and fixed. Fig. 33 shows a print made from the developed samples [unfortunately the contrast of the emulsion was too large to enable a very satisfactory reproduction in this way]. Fig. 32b shows the D-logE curve obtained from these strips. Before discussing the curve, a few points concerning its derivation should be mentioned:

The data points for Fig. 32b were obtained by micro-densitometer analysis of the developed emulsion strips. The conditions imposed by the ESR experiments required that these samples were irradiated whilst they were within the microwave cavity. This in situ irradiation through the slatted cavity window unavoidably led to the exposure of the emulsion samples in a pattern corresponding to the window design. This resulted in the formation of the light and dark strips evident in Fig. 33. This would not have mattered, per se, were it not for the fact that some lower levels of developed density were apparent between the light and dark strips, presumably as a result of light diffraction and reflection within the cavity. This uneven exposure resulted in micro-densitometer results such as those shown in Fig. 34. Fig. 32b was plotted from points
FIGURE 33
Print of AgCl film strips giving ESR results shown in Figure 31.

a = unexposed
b = exposed 0.09 s
c = exposed 0.49 s
d = exposed 0.99 s
e = exposed 1.9 s
f = exposed 4.9 s
g = exposed 9.9 s
h = exposed 99 s

[Exposures at R.T. with 365 nm hv].
FIGURE 34
Optical Densitometer results from an exposed G4103 AgCl film strip [sample (d) Figure 31].

Distance along film strip x 10 (mms.)

Optical Density
corresponding to the average maximum density, but allowances must be made for the exposure spread.

One of the immediate points apparent from Fig. 32 is that the exposures necessary for the generation of the ESR signal are of the same order as those required for latent image formation. The fact that there was not an exact correlation between increasing ESR signal intensity and optical density after equivalent exposures may be due to a number of factors, as discussed below:

In region A of Fig. 32 it can be seen that a detectable ESR signal was produced at an exposure level which was insufficient to produce optical density above the fog level. The ESR signal was not associated with pre-existing $Ag_n^0$ centres, since it was not observed in the unexposed material. This result is considered to indicate that $Ag_n^0$ centres associated with very small latent image centres are responsible for the ESR signal. By using a different developing agent and extending development, some optical density from these centres might have been revealed.

In region B, ESR signal intensity is seen to follow a similar characteristic to optical density. The slight shift of the ESR curve to the left along the $\log_{10}[\text{Exposure}]$ axis may be a result of the exposure spread mentioned above.

In region C, ESR signal intensity starts to fall at an exposure level corresponding to about $0.5[D_{\text{max}}]$. Signal
intensity is significantly reduced at the point corresponding to $D_{\text{max}}$ and is at the noise level at the exposure level corresponding to latent image solarisation. These results are thought to indicate that the ESR signal is associated with the smaller $\text{Ag}_n^0$ centres contained within the latent image particle size distribution. The fall in signal intensity is attributed to two possible effects:

(1). The small $\text{Ag}_n^0$ centres responsible for the ESR signal may have reached a concentration at which they began to agglomerate to form larger silver centres. Since no new signals were detected, these centres would have to be considered to be outside the CESR size-regime. However, these larger centres would still be expected to contribute to the optical density, accounting for the continued increase of the latter (in fact they would be expected to be more easily developable).

(2). The $\text{Ag}_n^0$ centres responsible for the ESR signal may have decreased in concentration as a result of photo-hole attack: an effect that would have to be considered to be insignificant at the larger centres contributing to the continued increase in optical density until higher exposure levels had been reached.

Additional joint ESR/sensitometric experiments with a variety of emulsion systems and developers may be able to clarify these points. It is imperative that such experiments are designed so that samples can be evenly exposed in-situ,
so as to prevent the density variation problems encountered here. Experiments at high and low exposure levels may prove interesting, particularly if emulsions which are known to be highly susceptible to low and high intensity reciprocity failure are used. For example, it would be expected that the proposed 1:1 correspondence between ESR signal intensity and optical density would be especially liable to break down in the HIRF region [see Appendix (ii)] and that, in addition the signal g-value and line-width might reflect the expected smaller latent image sizes. Arrested development techniques might also be used to give some idea of the numbers of latent images that are being formed in the grains and perhaps some idea of their size using calculations similar to those given in section 6.4.B(iii).
6.4. DISCUSSION.

A. ASSIGNMENT.

The absence of fine, hyperfine, or superhyperfine structure on the photo-signals at \( g = 2.003^\pm 2.004 \) rules out their assignment to atomic silver or to small neutral or ionic molecular silver aggregates [see chapters 1, 2 and 3], or, in the case of signals observed in AgBr, to \( Br^- \) or \( Br^0 \) [as deduced from ref. 28]. Also, the spectrum cannot be interpreted on the basis of photo-electron or photo-hole donation from emulsion grains to \( NO_3^- \), \( Br^- \), or \( K^+ \) in the surrounding gelatin matrix [the observation of the signals in high purity sols also mitigates against this assignment]. The \( O_2^- \) radical is thought to be produced when silver halides are exposed to light\(^{22}\), and has been found to have \( g \)-values in this region when formed on a silver substrate\(^{29}\). However, \( O_2^- \) would give axial or orthorhombic ESR spectra (2 or 3 \( g \)-values) which were not observed here. In addition, \( O^- \) would not be expected to be formed by exposure in \( vacuo \).

The photo-signal was found to be invariant between emulsions prepared from ultra-pure salts and from commercial grade silver halides, so it is not considered to arise from impurity centres. Furthermore, transition-metal ions provide the only paramagnetic impurity states known to be stable at room temperature in silver bromide and at best these give broad (\( \Delta H = 40-90 \) G) ESR signals because of unresolved ligand or metal isotope couplings\(^{3C}\). Another possibility is
to associate the signal with intrinsic paramagnetic defects structurally analogous to the V-, F-, H-, or U centres in the alkali halides. Single inhomogeneously broadened lines without resolved hyperfine structure have been reported for one such defect centre in a number of materials (the F-centre in LiCl, NaCl, NaBr, KF, KCl: $\Delta H = 40-100 \text{ G}^3$), but rich, multilines spectra are normally observed and it is generally accepted that colour centres other than the STH in AgCl (see Chapter 5; Introduction) are not stable in the silver halides. Therefore, considering all possible alternative assignments, the only known photo-products that could be expected to produce the signals at $g = 2.0029-2.0050$ are quantum size regime silver atom clusters. This assignment is supported by the unusual temperature dependence of the signals and the reasonable agreement of the ESR parameters with literature values for CESR from small silver particles, in particular with those reported by Monot et al.\textsuperscript{14,15,16.} [It is suggested that future experiments might probe at Q-band for a possible microwave frequency dependence of $\Delta H$ for these centres as predicted by Kawabata\textsuperscript{9} and observed by Monot\textsuperscript{14}.]

Table 4. lists the data obtained from these experiments for Ag\textsubscript{n}O centres in various silver halide systems. Table 5. summarises g-value, line-shape and size data that have been reported for silver aggregates isolated in a variety of host matrices, from which it can be seen that the g-values reported in Table 4. are in the broad range previously obtained for Ag\textsubscript{n}O particles:
### Table 4

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$g$-value</th>
<th>$\Delta H$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr/Ir$^{3+}$ sol</td>
<td>$2.002_9$-$2.005_8$</td>
<td>$9.2$-$19.3$</td>
</tr>
<tr>
<td>&quot;</td>
<td>$2.001_3$, $2.006_3$</td>
<td>$15$</td>
</tr>
<tr>
<td>&quot;</td>
<td>(Composite)</td>
<td></td>
</tr>
<tr>
<td>&quot;</td>
<td>$2.025_5$, $2.033_3$</td>
<td>$22.6$</td>
</tr>
<tr>
<td>&quot;</td>
<td>(Composite)</td>
<td></td>
</tr>
<tr>
<td>Pure AgBr emulsion</td>
<td>$2.003_5$</td>
<td>$19.0$-$21.0$</td>
</tr>
<tr>
<td>AgBr/Ir$^{3+}$ emulsion</td>
<td>$2.003_5$-$2.004_5$</td>
<td>$20.0$-$21.0$</td>
</tr>
<tr>
<td>&quot;</td>
<td>$2.029_1$</td>
<td>$7.1$</td>
</tr>
<tr>
<td>Pure AgCl emulsion</td>
<td>$2.004_2$-$2.005_0$</td>
<td>$12.0$-$18.5$</td>
</tr>
</tbody>
</table>

All these signals had Lorentzian line-shapes that exhibited various degrees of asymmetry depending upon the sample matrix, irradiation temperature, exposure time and time elapsed between exposure and observation.

*These particular signals are thought to arise from centres composed of small silver clusters and sulphur.*
### Table 5

<table>
<thead>
<tr>
<th>Particle size</th>
<th>g-value</th>
<th>Line-shape</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;5 Å</td>
<td>1.988</td>
<td>Lorentzian</td>
<td>Reduced AgA Zeolite</td>
</tr>
<tr>
<td>≈10 Å</td>
<td>2.007</td>
<td>Composite</td>
<td>Vapour-deposited Ag^0</td>
</tr>
<tr>
<td>&lt;20 Å</td>
<td>2.008-2.010</td>
<td>Composite</td>
<td>Vapour-deposited Ag^0</td>
</tr>
<tr>
<td>Unknown^1</td>
<td>2.013-2.028</td>
<td>Composite</td>
<td>Vapour-deposited Ag^0</td>
</tr>
<tr>
<td>50-300 Å^2</td>
<td>2.034</td>
<td>Lorentzian</td>
<td>Ag^0 in KCl</td>
</tr>
<tr>
<td>Bulk metal^3</td>
<td>1.982</td>
<td>Dysonian</td>
<td>Silver metal</td>
</tr>
<tr>
<td>Bulk metal^4</td>
<td>1.983</td>
<td>---</td>
<td>Silver metal</td>
</tr>
</tbody>
</table>

The centres giving rise to g-values in the range of 2.002_9^-2.005_8 are assigned to latent images as a result of the correlations of ESR and photographic data, the most important of which are summarised below:

i. Correlations of the effects of increasing exposure time on the ESR signal with the photographic responses of emulsions (the optical density corresponding to developed latent images).

ii. Comparison of the effect of exposure in air and in vacuo and correlation with the desensitising effect of
iii. Studies of the effect of red light bleaching of the signal and correlation with the Herschel effect on latent images.

iv. Studies of signal decay and comparison with latent image fading.

Before discussing these results in terms of current photographic theory it is useful to attempt some deductions of the size of these $\text{Ag}_n^0$ centres.

**B. SIZE CONSIDERATIONS.**

The following methods are used to deduce the size of the silver particles observed in these experiments:

i. Calculations from $g$ and $\Delta H$ values of the CESR signals, according to the small metal particle electronic theories proposed by (a) Kubo$^8$ and Kawabata$^9$ and (b) Myles et al.$^{18,19}$.

ii. Deductions from the comparison of the temperature dependence of the CESR signal intensities with the predictions of Kubo-Kawabata theory and the additional theoretical treatments of Denton$^{10}$ and Sone$^{12}$.

iii. Deductions from sensitivity calculations in conjunction
with photographic data.

i. SIZE CALCULATIONS FROM g AND $\Delta H$ VALUES

Table 6. shows particle sizes calculated from Kubo-Kawabata [K.K.] and Myles et al [M] theories for a selection of the $\text{Ag}_n^{0}$ CESR data presented in Table 4, according to the equations shown in Appendix (iii).

<table>
<thead>
<tr>
<th>g-value</th>
<th>$\Delta H$</th>
<th>$a(\AA)$</th>
<th>$L(\AA)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0029</td>
<td>9.2</td>
<td>25.8</td>
<td>7.5</td>
</tr>
<tr>
<td>2.0035</td>
<td>20.0</td>
<td>55.7</td>
<td>11.2</td>
</tr>
<tr>
<td>2.0042</td>
<td>12.0</td>
<td>33.4</td>
<td>8.7</td>
</tr>
<tr>
<td>2.0048</td>
<td>18.5</td>
<td>51.6</td>
<td>10.7</td>
</tr>
<tr>
<td>2.0058</td>
<td>11.3</td>
<td>31.6</td>
<td>8.3</td>
</tr>
<tr>
<td>2.0255</td>
<td>11.3</td>
<td>31.6</td>
<td>8.3</td>
</tr>
<tr>
<td>2.0333</td>
<td>11.3</td>
<td>31.6</td>
<td>8.3</td>
</tr>
<tr>
<td>2.029</td>
<td>7.1</td>
<td>19.8</td>
<td>6.6</td>
</tr>
</tbody>
</table>
(a) CALCULATIONS FROM KUBO-KAWABATA THEORY.

Calculated particle diameters, (a), (Table 6.) are seen to fall within the range of 6.6 to 11.2 Å. [Figures are subject to an additional error of ± 20% as a result of the uncertainty in $\Delta g_{so}$]. Fig. 35. shows the theoretical plot of $a^2$ against $\Delta H$ on which results from a number of signals are superimposed. Monots results are also shown.

Two important points emerge from this analysis. First, the calculated particle sizes are all larger than are expected by most for primary latent image centres, although they are close to the 68-680 atom regime favoured by Galashin (see chapter 4) [a 12 Å spherical silver particle might consist of as many as 100 atoms in a metallic f.c.c. arrangement, whereas a 10 Å particle may consist of as few as 13 Ag atoms in a cubo-octahedral structure$^{31}$]. One explanation for this could be that there are contributions to $\Delta H$ as a result of matrix broadening effects not accounted for by this theory because the particles' wavefunctions extend beyond the surface, as suggested by Knight$^{17}$. Second, the relationship between $g$ and $a$ does not follow the prediction that $g$ should approach the bulk-metal value as particle size decreases [calculations from Monots' results also show an opposite relation between $g$ and $a$].
FIGURE 35

A plot of $a^2$ versus ESR linewidth for latent image centres in silver halides, calculated according to Kubo-Kawabata theories [Refs. 8, 9].
CALCULATIONS FROM MYLES et al. THEORY.

(b) Calculated particle edge lengths, \( L \), are seen to fall within the range of 4.1-4.9 Å. These are closer to the values expected by most for primary latent image centres. However, they appear too small for pseudo-metallic species when it is considered that the \( \text{Ag}_5^0 \) centre, for which a molecular ESR spectrum has recently been reported\(^{33}\), would be expected to have a diameter of about 4.5 Å. The validity of these calculations for small silver particles is also suspect for the following reasons:

The theoretical model of Myles et al. uses the following equation relating the g-shift of small metal particles relative to the free-spin g-value, \( \Delta g \), to the g-shift of the bulk-metal relative to the free-spin g-value, \( \Delta g = \) :

\[
\Delta g \approx \Delta g = [1 - \alpha (a/L)] \quad (1)
\]

Where: \( \alpha \approx 1.0 \)

\( a = \) Lattice constant (4.0)

\( L = \) Edge length of cubic aggregate.

Equation (1) has been applied to CESR data obtained from small sodium\(^{18,19}\) and magnesium\(^{20}\) particles. Good correlations with microscopic data have been obtained. However, for both these metals both \( \Delta g \) and \( \Delta g = \) have been found to be positive quantities\(^*\). For example, for
magnesium, where $\Delta g^-$ = +0.059 for the bulk metal, $\Delta g$ for particles with a size of about 25 Å was determined to be +0.030.

In the case of silver, $\Delta g^-$ is negative ($\Delta g^- = -0.0196$). The silver centres detected in silver halides, together with the majority of literature data for small silver particle CESR give $\Delta g$ values which are positive. For example, the signal observed by Monot et al.\textsuperscript{14,15} assigned to particles with a size of about 20 Å gives $\Delta g = +0.004_7$, and the signal observed here in AgBr at $g = 2.003_5$ gives $\Delta g = +0.002_2$. The $a$ values shown in Table 6. were calculated using $|\Delta g^-|$. However, difficulties subsequently arose when attempting to calculate $a$ for the centres giving rise to the signals with marked $g$-shifts, where $|\Delta g| > |\Delta g^-|$. In addition, such calculations gave values for $a$ that increased with increasing $g$-shift, in contrast to the prediction of Myles et al.

It is concluded from these calculations that neither of these theories can be applied to latent image CESR signals to give unequivocal particle size evaluations.

*It may be significant here to point out that $\Delta g$ was found to be zero for the smallest Mg particles that were prepared ($a = 10.2$ Å). A change in the sign of $\Delta g$ might be found from smaller particles.
ii. SIZE DEDUCTIONS FROM SIGNAL TEMPERATURE DEPENDENCE.

The intensity of the \( g = 2.004 \) signal in the irradiated silver chloride emulsion did not follow the Curie law (see Fig. 28). This observation is considered to provide strong evidence against the assignment of this signal to impurity centres and in favour of small silver particles. As outlined in the introduction, small metal particles in the quantum size regime were predicted by Kubo\(^8\) to exhibit anomalous magnetic behaviour to either metals (Pauli-type paramagnetism) or molecules (Curie-law paramagnetism). It was predicted that the magnetic behaviour of the particles would depend upon \( \Delta \) (which would in turn be dependent on the particle size), temperature, and whether there were an even or odd number of electrons in the particles.

The mathematical treatment of the expected spin susceptibilities of quantum size regime particles was further developed by Denton et al.\(^{10}\) for a variety of energy level distributions. Fig. 36a. shows a plot of calculated susceptibilities against \( kt/\Delta \) (where \( \Delta \) is equal to the average energy level spacing) for even and odd-electron particles. For a collection of particles in which there are equal numbers of odd and even electrons, the net paramagnetism, \( \chi_{\text{spin}} \), is considered to be the sum of the individual contributions of the even and odd-electron species. \( \chi_{\text{spin}} \) can therefore be calculated from Fig. 36a. according to (2).

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FIGURE 36(a)

Temperature dependence of the electronic spin susceptibility for small particles with even or odd numbers of electrons. $X_p$ is the high-temperature Pauli susceptibility. The orthogonal and symplectic energy level distributions are appropriate to the cases of weak and strong spin-orbit coupling, respectively [Ref. 13].
\[ x_{\text{spin}} = 0.5(x_{\text{odd}} + x_{\text{even}}) \]  

It can be seen that all particles are expected to exhibit Pauli-type paramagnetism \((x=x_P)\) at high temperatures. In all but the Poisson energy level distribution, however, a transition temperature is reached at which the odd particles begin to exhibit Curie-type paramagnetism, whereas the even particles become diamagnetic. The rate of increase of diamagnetism is less than the rate of increase of Curie-type paramagnetism so that from (2) the overall paramagnetism would be expected to increase below the transition temperature.

According to Sone\(^{12}\), however, spin-orbit coupling will modify the temperature dependence, as shown in Fig. 36b. When the parameter \(q \rightarrow 1\) (strong coupling), size effects disappear and both even and odd particles are expected to have \(x=x_P\). Marzke\(^{13}\) has interpreted spin susceptibility results from small platinum particles using this approach.

From Fig. 28. it can be seen that the amplitude of the \(g = 2.0048\) Ag\(_n^0\) CESR signal was almost constant, within experimental error, over the temperature range of 298-23 K. As \(\Delta H\) was also constant over this temperature range, within experimental error, Fig. 28. can be considered to represent a plot of \(x_{\text{spin}}\) against \(1/T\). The observed temperature behaviour of \(x_{\text{spin}}\) for the particles may be interpreted according to the following arguments:
FIGURE 36(b)

Effect of spin orbit coupling upon the spin susceptibility according to Sone [12]. \( \rho \) is a parameter which is proportional to the spin-orbit coupling strength when this is smaller than the energy level spacing \( \Delta \), but which cannot increase beyond the value of 1 in the limit of very strong coupling.

\[ \frac{X}{X_p} \]

Spin susceptibility for:
- Even particle
- Odd particle

\( \rho = 0 \)
\( \rho = 1 \)

\( \Delta \)

-321-
i. The $\text{Ag}_n^0$ particles could be exhibiting Pauli paramagnetism over the temperature range studied. They would therefore be expected to have a $\Delta$ value corresponding to a transition temperature below 23 K.

ii. The majority of the particles could contain an even number of conduction electrons. In the case of orthogonal and sympletic energy level distributions this might lead to a balancing of the increased paramagnetism from the odd particles by the increased diamagnetism of the even particles.

iii. Extensive spin-orbit coupling might be reducing the size effect.

If (i) applies, a maximum value for the mean energy level spacing, $\Delta$, can be deduced. From Fig. 36a. and using equation (2), the Curie-law increase would be expected to become observable at about $kT/\Delta = 0.4$. Substituting $T = 23$ K gives (3):

$$\Delta < 0.0035 \text{ eV}$$

The number of constituent atoms in the particles, $N$, which will be equal to the number of conduction electrons, assuming neutrality, can then be estimated according to the following:

$$\Delta = \frac{E}{N}$$

-322-
Where $E_F = \text{the Fermi energy} = 5.51 \text{ eV}$

(3) & (4) ---\(\Rightarrow\) \(N > 1.6 \times 10^3\) \hspace{1cm} (5)

This value for \(N\) corresponds to a particle diameter, \(a\), of about 25 \(\AA\). This falls well within the quantum size regime postulated by Kubo et al. As reported in section 6.3, the \(Ag^0\) centres detected in silver halides probably form a size distribution. The effect of this distribution upon the overall susceptibility has not been taken into consideration in these calculations. However, this value of \(a\) is still seen to be much larger than that expected by most for primary latent image centres.

iii. SIZE DEDUCTIONS FROM SENSITIVITY CALCULATIONS.

As reported in section 6.3.4. ESR signals were observed from \(Ag^0\) centres photo-produced in an AgCl emulsion coating containing 0.1\(\mu\)m edge-length micro-crystals. Although the calculations in Appendix (i) showed that it was optimistic to expect to be able to detect latent image centres in typical emulsion coatings, the eventual observation of such signals in this relatively small grained emulsion can possibly be rationalised in terms of particle size according to the following:

The number of micro-crystals, \(N_s\), in a coated strip of dimensions suitable for ESR study (as used in the experiments reported in section 6.4), of 0.1\(\mu\)m crystals can
be estimated (6) according to equations (1) & (2) [Appendix (i)]

\[ N_s \approx 1.5 \times 10^9 \] (6)

The minimum number of spins, \( s_{\text{min}} \), necessary to produce the largest ESR signal \( S_{\text{max}} \) that was observed after the photolysis of these samples [see equation (3), Appendix (i)] can be estimated according to (7):

\[ s_{\text{min}} \approx 4 \times 10^{11} \] (7)

From (6) and (7) the minimum number of spins/crystal, \( s_{\text{crystal}} \), can then be deduced (8):

\[ s_{\text{crystal}} \approx 300 \] (8)

As reported in chapter 4, it is considered that in the most efficient silver halide micro-crystals only one latent image centre is produced. However, arrested development techniques have revealed that it is not uncommon for more than one latent image centre to be formed, particularly in unsensitised emulsions. In fact the number of latent image centres formed per grain can be as large as \( 10^3 \). Using these data, an evaluation of the likely size range of the centres responsible for the ESR signal reported in section 6.4 becomes possible, according to the following:
i. At one extreme, if only one ESR visible latent image centre were formed per crystal, the number of spins attributable to this centre will be about 300. This could imply that the agglomerate was composed of this number of silver atoms (or that this figure corresponds to the mean of the particle size distribution summed over all crystals). This would still be considered to be a rather large number for a primary latent image centre.

ii. Taking an intermediate case, if about 30 latent image centres were formed in each crystal, which is quite probable, the number of spins attributable to the observable centres would be about 10. A size distribution around $\text{Ag}_{10}^0$ would be quite a reasonable figure for primary latent image centres.

iii. At the other extreme, if more than 300 latent image centres contributing to the signal were formed per grain, this would imply that each centre was contributing fewer spins than predicted from this simple calculation, [see section (ii)].

Further ESR experiments using an instrument with an accurately calibrated spin sensitivity, in conjunction with arrested development studies might be able to distinguish between (i) (ii) and (iii) and possibly provide the best answer yet to the question of latent image size, in addition to providing valuable data on the magnetic properties of small silver agglomerates.
C. CORRELATION WITH PHOTOGRAPHIC THEORY.

It is apparent from the results reported in section 6.3. that there was a good correlation between latent image ESR and sensitometric results in a range of empirical experiments similar to those from which current photographic theory has evolved. The generation of the latent image signal from photo-electrons trapped at low temperatures and the observation of the oxygen de-sensitisation effect are in agreement with the proposed two-step process. The species involved in the steps can not be absolutely identified from these results, although the following points emerge from the analysis:

i. NUCLEATION.

No ESR signals attributable to Ag\(^0\) centres [see Chapter 4: 4.B(i)] were observed, although these would be expected to have a reasonable lifetime at 160 K with respect to thermal decomposition, using Mitchells' figure of \(E_a = 0.69\) eV. The failure to detect these centres was probably a result of the broadening effects discussed in section 6.1.

ii. GROWTH.

No ESR signals from the intermediates and latent image centres postulated by Trautweiler, Hamilton and Mitchell according to the Gurney-Mott model [Chapter 4: 4.B(iii)] were observed. In particular the paramagnetic centres Ag\(_2^+\)
and Ag\textsuperscript{+}, [the latter forms the central part of Mitchell's concentration theory] were not detected. The failure to detect these centres could have been either a result of the signal broadening effects outlined in section 6.1 or that these centres are not in fact formed during the photographic process and that latent images are formed by the spontaneous aggregation of silver atoms, as proposed by Malinowski and Galashin (see chapter 4).

The observed CESR signals suggest that somewhat larger agglomerates are associated with latent images than have been proposed by the ionic theories. However, as demonstrated in the preceeding part of this section, there is at present no method for deducing the exact size of these centres from the ESR data, although it can be said that they are definately larger than Ag\textsubscript{5}\textsuperscript{0} and are pseudo-metallic rather than molecular. Approximate size deductions range from about 4 to 25 Å. They would appear to form a size distribution, if the slight asymmetry of the signals can be equated with the rather more pronounced size distribution effects observed by Chatelain et al\textsuperscript{16}. It is highly probable that only a fraction of the distribution of silver agglomerates that might describe "the latent image" are observable by ESR techniques. The joint ESR/sensitometric results reported in section 6.4. would seem to indicate that it is the smaller particles which are detectable.
6.5. CONCLUSIONS.

1. The photographic latent image can be detected by ESR.

2. The ESR data suggest that latent image centres have magnetic properties characteristic of pseudo-metallic species.

3. Latent image centres appear to form an ensemble of aggregates having a range of particle sizes, although this range is probably fairly small since no ESR signals with the marked asymmetry of the silver particle distribution formed and observed in organic glasses, condensed inert gases or alkali halides were observed.

4. The polarizability of the silver halide host lattice and the abundance of magnetic nuclei in its immediate environment do not significantly broaden the ESR signal from the latent image centres. This may suggest that the electronic wavefunction does not extend much beyond the surface boundaries of these silver aggregates.

5. There is no adequate theory to allow calculation of exact particle sizes from ESR data for silver aggregates. There is also no way to account for the effects of magnetic host lattices on the line-widths or g-values of trapped small metal particles. A quantitative analysis of the (C)ESR data must await the development of a better theory to explain the particle size dependence of CESR g-shifts and
line-widths and susceptibility with more supportive experimental data. Alternatively, joint ESR/arrested development experiments may provide data on latent image sizes.

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REFERENCES.


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APPENDIX (i).

SAMPLE/SENSITIVITY CONSIDERATIONS.

A. EMULSION COATINGS

Calculations, such as those detailed below, showed that it was optimistic to expect to detect latent images by simply placing emulsion coating samples in the microwave cavity in the form of film strips.

The number of silver halide microcrystals, \( N_s \), present in the largest film strips that could be practically sampled, can be calculated in the following way:

For 0.2 \( \mu \text{m} \) edge-length cubic crystals, the number of crystals/m\(^2\), \( N_0 \), in a practical coating can be approximated to:

\[
N_0 = \frac{0.5}{(2 \times 10^{-7})^2} = 1.25 \times 10^{13}. \tag{1}
\]

Film strips could be used with maximum dimensions of 2.5 \( \times \) \( 10^{-3} \) m \( \times \) 2.0 \( \times \) \( 10^{-3} \) m. The number of crystals per sample, \( N_s \), can then be calculated (2):

\[
N_s = 6.25 \times 10^8 \tag{2}
\]

The minimum spin concentration, \( s_{\text{min}} \), for detectable ESR signals can be calculated from the ESR instrument
manufacturers' sensitivity specifications, as follows:

For a sample giving a signal with a line-width of 20 G, detected by the E 12 under the following conditions,[which were those corresponding to the observed Ag$_n^{0}$ centres reported in section 6.3]:

\[ \mu \text{wave power} = 5 \text{ mW.} \]
\[ \text{Mod amp.} = 5 \text{ G.} \]
\[ S/N = 4:1 \ (64 \text{ scan CAT)} \]

\[
\text{-----} \ s_{\text{min}} \approx 4 \times 10^{11} \text{ spins/sample.} \quad (3)
\]

Only one latent image centre might be expected to be formed in each crystal. If each centre were to have only one effective spin, the number of samples needed to be inserted in the cavity to give a minimum detectable signal can be calculated (4):

\[
s_{\text{min}} / N_s = 6.4 \times 10^2 \text{ samples.} \quad (4)
\]

As a maximum of only 4 film strips could be inserted together into ESR sample tubes, some means had to be found of improving sensitivity [see section (B)].

B. DE-GELLED EMULSIONS.

The following calculations apply to de-gelled samples:
ESR sample volume, \( V = (2 \times 10^{-3})^2 \cdot \pi \cdot 1.25 \times 10^{-2} \)
\[= 1.5 \times 10^{-7} \text{ m}^3. \quad (5)\]

Volume of an 0.2 \( \mu \text{m} \) crystal, \( v = (2.0 \times 10^{-7})^3 \)
\[= 8.0 \times 10^{-21} \text{ m}^3. \quad (6)\]

\( \Rightarrow \) Number of crystals in sample, \( N_D = \frac{V}{v} \cdot 2 \times 10^{13} \quad (7) \)
(Assuming complete de-gelling).

\[\Rightarrow N_D / s_{\text{min}} \approx 50. \quad (8)\]

The sensitivity threshold for latent image detection could therefore be expected to be met by the use of de-gelled samples, within the limits of these approximations.

**APPENDIX (ii).**

**THE RELATIONSHIP BETWEEN LATENT IMAGE ESR SIGNAL AMPLITUDE AND DEVELOPED OPTICAL DENSITY.**

The optical density, \( D \), resulting from the development of latent images, is related to the size of the bulk silver grains by the Nutting equation (see chapter 4, ref. 1):

\[D = (\log_{10} e)na/A \quad (1)\]

Where: \( n = \text{Number of grains in an area } A \)
\( a = \text{Mean projected grain area} \)
A = Sampling aperture of the densitometer

The integrated ESR signal intensity, $\int S$, from latent image centres might be expected, at constant temperature, to be related to the number of silver halide host grains/unit area (n) by the following equation:

$$\int S = o n A \quad (2)$$

Where $o$ = Number of latent image centres per grain

($\approx 1$ in the most efficient systems)

(1) & (2) ---> $\int S = o D A^2 / (\log_{10} e) a \quad (3)$

If it is assumed that $a$ is constant for a given emulsion under consistent development conditions, the following relation will apply:

$$\int S = o a D \quad (4)$$

Where $a$ = a constant for a given sample area

If the ESR line-shape is constant, $\int S$ will be equivalent to the peak-to-peak signal amplitude, S. If $o$ is constant at all exposure conditions (i.e. if there is no HIRF), equation (5) will apply:

$$S = k D \quad (5)$$

Where $k$ is another constant
Under these conditions it is seen that ESR signal amplitude will be expected to be directly proportional to optical density. However the following points apply:

1. If HIRF does occur, the ESR signal intensity would be expected to be more than that predicted by equation (5).

2. The derivation of equation (5) assumes that JS is constant for all latent image centres, whereas in fact this might vary considerably depending upon the size of the latent image centre giving rise to the signal (see discussion). This might lead to a deviation from equation (5) for different emulsions and within the exposure range of any one emulsion if, in addition, latent image size or size distribution varies with exposure.

APPENDIX (iii.)

A. THE PREDICTED RELATIONSHIP BETWEEN PARTICLE SIZE AND CESR PARAMETERS FOR METAL PARTICLES IN THE QUANTUM SIZE REGIME, ACCORDING TO KUBO AND KAWABATA.

At resonance, equation (1) applies to the CESR signal:

\[ v = g\mu_B H/h \]  

If the observed ground-state is shifted from the free-electron value by \( \Delta g = g - g_f \), the principle relaxation process arises from the spin-orbit coupling and can be
estimated from the theory of Elliot\textsuperscript{34} (2):

\[ \frac{1}{\tau} = V_F \Delta g^2 / a \]  \hspace{1cm} (2)

Where: \( \tau \) = Spin relaxation time
\( V_F \) = Fermi velocity
\( a \) = particle diameter

\( \tau \) provides a major contribution to the line-width until the particle size is less than that for which equation (3) applies:

\[ \phi \approx \hbar / \tau \Delta = 1 \]  \hspace{1cm} (3)

Where: \( \Delta \) = Average energy level spacing = \( 4E_F / 3N \)
\( E_F \) = Fermi Energy (5.51 eV)
\( N \) = Number of conduction electrons.

(2) & (3) \[ \Rightarrow \phi \approx 3N^2 / 3 \Delta g^2 / 4r_s k_F \]  \hspace{1cm} (4)

Where: \( r_s \) = Metallic cell radius
\( k_F \) = Fermi wave vector

Using a particle-in-a-box model, Kawabata\textsuperscript{9} calculated the residual CESR linewidth, \( \delta \nu \), and shift of resonance, \( \Delta \nu \), for such small particles at low temperatures and found that in the quantum size regime, where \( \hbar \nu < \Delta \), equations (5) and (6) should apply:

\[ \delta \nu \approx \hbar / \tau \Delta \]  \hspace{1cm} (5)
From (4), (5) and (6), the equation (7) can be derived.

\[ a = \left[ \frac{8\pi E_F \Delta H}{3h\nu V_F K(\Delta g_{SO})^2} \right]^{1/2} \]  

(7)

Where: 
- \( a \) = Metal particle diameter
- \( \nu = \) Observation frequency (\( \approx 9.3 \) GHz)
- \( K = \) Number of atoms/cm\(^3\) (\( = 6.25 \times 10^{22} \) for Ag)
- \( \Delta g_{SO} = \) Contribution of spin-orbit coupling to \( \Delta g_{bulk} \) (\( \approx (2.5 \pm 0.5) \times 10^{-2} \) for Ag\(^{14} \))

B. PREDICTIONS OF THE RELATION BETWEEN CESR SIGNALS AND THE SIZES OF METAL PARTICLES ACCORDING TO MYLES et al.\(^{18,19} \)

Using an orthogonalised standing wave approach, Myles et al. calculated the size dependence of the CESR g-shift, \( \Delta g(L) \), in a small sodium particle and derived equation (8):

\[ \Delta g(L) = [1-a(a/L)]\Delta g(\infty) \]  

(8)

Where:
- \( \Delta g(\infty) = \) bulk metal g-shift
- \( a = \) lattice constant [\( a = 4.0 \) for Ag]
- \( L = \) edge-length of cubic metal aggregate
- \( a \approx 1.0 \)
SPECTROSCOPIC STUDIES OF SILVER ATOMS AND CLUSTERS

ABSTRACT

Conjoint ESR and optical studies of silver atoms (Ag⁰) and silver clusters formed in aqueous and alcoholic matrices resulted in the unequivocal assignments of optical absorptions to a range of Ag⁰ solvates and to the molecular clusters Ag^+^ and Ag^3+^.

ESR studies of un-irradiated silver halides revealed the presence of at least two intrinsic centres which might act as the special sites at which latent images are formed during the primary photographic process. On irradiation, these materials exhibited additional signals which were thought to be CESR resonances associated with pseudo-molecular silver particles, Ag^0^_n_. The size of these centres is uncertain. The data suggests that they consist of more than 5-6 atoms and are smaller than 45Å. They were shown to be likely candidates for photographic latent images as a result of a series of photographic/ESR crossover experiments.

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