Electronic Transport Properties of Some Liquid Metals and Alloys

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ABSTRACT

Measurements have been made of the resistivity of liquid nickel-cobalt and silver-palladium alloys as a function of composition and temperature together with some measurements on these systems in the solid state and a measurement of the thermoelectric power of a single liquid silver-palladium alloy as a function of temperature. Experiments have also been performed to determine the resistivity and thermoelectric power of liquid antimony as a function of temperature, and of liquid nickel-tellurium alloys as a function of temperature and composition. Apparatus has been developed to enable such experiments to be undertaken. In those cases where information is available, the results obtained here are generally in agreement with other experimental data.

Approximate expressions can be derived from a single site resonant scattering model which give the resistivity of suitable liquid transition metal alloys in terms of the resistivities of the pure components, and give the thermoelectric power of the alloy in terms of the resistivities and thermoelectric powers of the pure components and the resistivity of the alloy. Predictions derived using these expressions have been compared with the experimental data: this comparison indicates that the theory in its present form provides, at best, only a qualitative account of the observed transport properties of liquid transition metal alloys.

Calculations based on a percolation model of electronic transport in inhomogeneous liquids have been performed in an attempt to understand the experimentally observed variation of resistivity with concentration in the nickel-tellurium alloy system. Such a model appears to provide a reasonable qualitative description of the experimental data for the tellurium-rich alloys.
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CHAPTER 1

Introduction and Basic Theory

An early classical description of electronic conduction processes (Drude, 1900) was based on the application of Newton's laws of motion to the movement of free electrons. These were assumed to attain a drift velocity under the influence of an applied field and suffer randomizing collisions with the array of positive ions (spatially ordered in the solid state). This approach gave the following expression for the electrical conductivity (Mott and Jones, 1936):

$$\sigma = \frac{2n_e}{m}$$

where \(n\) is the number density of electrons, each having charge \((-e)\) and mass \(m\). The relaxation time, \(\tau\), may be defined in terms of a collision probability function. Attempts to allow for the variation in electron velocities using Maxwell-Boltzmann statistics were made (e.g. Ziman, 1960). This provided reasonable room temperature values for the electrical and thermal conductivity of metals but still over-estimated the electronic contribution to the specific heat. It was not until the classical formalism had been superseded by quantum mechanics, through the use of the Fermi-Dirac distribution function given below, that reasonable agreement was obtained here also.

The electrons in a metal or semiconductor which is free from externally applied fields will fill the available eigenstates according to Fermi-Dirac statistics, the probability of a level at energy \(E\) being:

$$f_{(E)}^{\circ} = \left\{ \exp \left( \frac{E - \mu}{k_B T} \right) + 1 \right\}^{-1}$$  \hspace{1cm} (E1)

where \(k_B\) is the Boltzmann constant, \(T\) the absolute temperature and \(\mu\) the electrochemical potential (which is constant throughout the material). It has been shown (e.g. Ziman, 1960) that \(\mu\) may be equated with the Fermi energy, \(E_F\), provided \(k_B T \ll E_F\) - a condition satisfied for metals at ordinary...
temperatures. The occupied states in momentum space (i.e. those whose associated energies do not exceed \( E_F \)) are enclosed within the spherical Fermi surface. Hence the net momentum will be zero since for every state at \( k \) there is a state at \(-k\), where \( k \) is the electron wave vector and the momentum is written as \( \hbar k \).

The Fermi surface will be displaced, however, by the action of external fields and temperature gradients on the electrons; the extra energy and momentum being dissipated through randomizing scattering processes of one form or another. When constant fields are applied then, we wish to consider the balance between such processes.

ii) The Boltzmann Equation

One approach to this is through the Boltzmann equation, which attempts to relate the equilibrium distribution function \( f^0(k) \), given in equation (I:1), to the steady state distribution in the presence of external forces, \( f(k) \). In a given volume \( f(k) \) will vary in time due to the effects of diffusion, external fields and scattering. For any value of \( k \) the Boltzmann equation says that the net rate of change of \( f(k) \) is zero:

\[
\frac{\partial f}{\partial t} = -\nu_k \cdot \nabla f - \frac{1}{h} \frac{\partial}{\partial t} \nabla \cdot \frac{f}{h} \nu_k - \frac{3f(k)}{\hbar t} \frac{\partial f}{\partial t} = 0 \tag{I:2}
\]

where the first term gives the rate of change due to electron diffusion, \( \nu \) being the electron velocity; the second gives the rate due to the external fields \( F \cdot \nu_k \) is the grad operator in momentum space. The final term describes the effect of randomizing collisions, here confined to elastic scattering (since we are considering collisions between an electron, say, and a relatively massive ion). We assume one dominant scattering mechanism which tends to return the distribution to its equilibrium value when the external forces are removed such
where $\tau(E_F)$ is now the relaxation time evaluated at the Fermi energy since, having assumed that only very small energy changes occur in any collision, only electrons having energies close to the maximum of the Fermi distribution are scattered. Associated with $\tau(E_F)$ is the mean free path $L$, given by:

$$L = \left( \tau(E_F) v_F \right)^{-1}$$

where $v_F$ is the velocity corresponding to the Fermi surface.

I: iii) Electrical Conductivity

Consider now an infinite medium under the influence solely of an electric field, $E$, which results in an electric current in the material corresponding to the displacement of the Fermi surface. The fundamental bulk property of a material known as the electrical conductivity, $\sigma$, relates the magnitude of the response to the applied field.

From equations (I 1, 2, 3) and using an expression for the current density of the form

$$J = \frac{2 e v_k f(k)}{\hbar^2} \frac{d\varepsilon}{dk} = \sigma E$$

it may be shown that (Mott and Jones, 1936; Ziman, 1960), for a current in the $x$ direction:

$$\sigma(E) = \frac{e^2}{4\pi^2 \hbar^2} \int \frac{d^2 f(k)}{dk x} \left( \frac{\partial E}{\partial k} \right)^2 \tau(k) \frac{d\varepsilon}{|\nabla_k E|}$$

the integral being over the surface, $\varepsilon$, in $k$-space with energy $E$. We continue to assume that $k_B T << E_F$ and note that $\frac{\partial f(k)}{\partial E}$ is negligible except in the range of energy of breadth $k_B T$ around the Fermi energy. $\sigma(E_F)$ is, then, the actual calculated conductivity of the material.

Equation (I 5) is much simplified for the case of a spherical Fermi
distribution – when $\tau$ loses its $k$ dependence and the free electrons have energy

$$E = \frac{\hbar^2 k^2}{2m}$$

- when we are left with the classical Drude formula (albeit modified by the application of Fermi–Dirac statistics),

$$\sigma = n e^2 \tau(E_F) \frac{\hbar^2}{m}$$  \hspace{1cm} (I.6)

we may attempt an estimate of $\tau(E_F)$ within the nearly free electron (NFE) approximation which introduces a perturbation in the electron gas of the metal due to an assumed small potential associated with the ions. Such a scattering potential implies a long mean free path and allows the continued use of $'k'$ as a well defined quantum variable.

The relaxation time may be related to a probability function, $P(k, k')$, describing the likelihood of the scattering of an electron in a state of wave vector $k$ into empty state defined by $k'$ having the same energy and magnitude of momentum (this follows from the assumption of elastic scattering).

If we neglect multiple scattering and adopt the Born approximation, then for scattering off the small potential $U$, $P(k, k')$ may be evaluated using time-dependent perturbation theory (Schiff, 1968) to give

$$P(k, k') \, d^2 \xi = \frac{V}{4\pi^2 \hbar} \frac{|<k|U|k'||^2}{|\langle k | U | k' \rangle|} \, d^2 \xi$$  \hspace{1cm} (I.7)

where $V$ is the volume of the material and $|<k|U|k'|>$ is the matrix element of $U$ between the states of wave vectors $k$ and $k'$ given by

$$<k|U|k'> \equiv \int \psi_k^* U \psi_{k'} \, d\tau$$

Now, if $P(k, k')$ depends only on the momentum transfer $|\xi| = |k-k'|$ (i.e. only on the angle, $\theta$, between the wave vectors and not on the initial state), and we again assume a spherical Fermi surface, then (Ziman, 1960):
\[ \frac{1}{\tau} = \int_0^\pi P(\theta) (1 - \cos \theta) \sin \phi d\phi d\omega \]  

(1.8)

where \( d\omega \) is an element of solid angle for \( \mathbf{k}' \) after scattering and the factor \( (1 - \cos \theta) \), weighting the integral heavily in favour of large angle scattering, arises because we are considering only the change, on scattering, of the projection of the wave vector along the axis of the electric field. If we now introduce the differential scattering cross section of a single ion \( Q(\theta) \), related to \( P(\theta) \) by:

\[ P(\theta) = \frac{N_C}{V} v_F Q(\theta) \]

where \( \frac{N_C}{V} \) is the density of random scattering centres, then the mean free path may be written as:

\[ \frac{1}{\tau} = \frac{N_C}{V} 8\pi \int_0^1 Q\left(\frac{q}{2k_F}\right) 3d\left(\frac{q}{2k_F}\right) \]

(1.9)

We have used the trigonometric relation for the momentum transfer on a spherical surface,

\[ q = 2k_F \sin \theta \]

(1.10)

\( k_F \) being the radius of the Fermi sphere (\( 2k_F \) therefore defines the upper limit of the integration).

\[ \text{iv) Thermo-Electric Effects} \]

When a material is subjected to an electric field we have seen that the resultant current is related to the field by the electrical conductivity of the material. Similarly, if a material is subjected to a temperature gradient the resulting heat flow is governed by the thermal conductivity (which may also be examined by the Boltzmann equation). There is another bulk property of a material which is related to the interaction effects between electric and thermal fields, and is known as the absolute thermoelectric power (thermopower). It
manifests itself in the Thomson, Peltier and Seebeck Effects (illustrated in the figures on p. 7).

If a current is caused to flow through a conductor in which a temperature gradient is already maintained the rate of heat production per unit volume is given by,

$$\rho J^2 - \mu J \cdot \nabla T$$

the first term, where $\rho$ is the resistivity of the conductor, $J$ is the Joule heat. The second is the reversible Thomson heat and $\mu$ is known as the Thomson coefficient (which is positive if heat is absorbed from the surroundings when $J$ and $\nabla T$ are parallel).

If an electric current flows across a junction between two dissimilar conductors heat will be reversibly liberated (or absorbed) at that junction. It is reversible in the sense that if heat is evolved with the current in one direction the same amount of heat will be absorbed if the current is reversed, thus it will be easily distinguished from the Joule heat which is independant of current direction. The Peltier heat is given by:

$$\Pi_{12} J$$

where the Peltier coefficient $\Pi_{12}$ is defined as the reversible heat generated per unit charge passed across the junction, the direction of current flow being from conductor 1 to conductor 2.

If junctions between two dissimilar conductors are joined (a) in the figure and are held at different temperatures as shown, the the resultant e.m.f. in the current is known as the Seebeck e.m.f. and may be used to relate the absolute thermopowers of the two materials:

$$\frac{\Delta V_{12}}{\Delta T} = s_1 - s_2$$  \hspace{1cm} (L11)

If $\Delta V_{12}$ is positive in the example then we take the thermopower of material 1 to be greater than that of material 2.
THERMOELECTRIC EFFECTS

a) The Seebeck Effect

\[ T + \Delta T \]

\[ \Delta V_{12} \]

b) The Peltier Effect

\[ \tau_{12} \text{ (heat evolved)} \]
\[ \tau_{21} \text{ (heat absorbed)} \]

\[ j_x \]

c) The Thomson Effect

\[ u \text{ positive (Heat absorbed)} \]

\[ \text{Low T} \]
\[ \text{High T} \]
\[ j_x \]
\[ \frac{dT}{dx} \]
The above coefficients may be related to the absolute thermopower through
the Thomson relations (Ziman, 1960; Barnard, 1972; Blatt et al, 1976) as follows:

\[ \mu_1 = \frac{dS_1}{dT} \quad ; \quad \Pi_1 = TS_1 \quad \text{and} \quad \Pi_{12} = T(S_1 - S_2) \]

The latter equation results from energy conservation whilst the former may be
derived using the Onsager equations (i.e. within the framework of irreversible
thermodynamics).

It is often most accurate and convenient, particularly with liquid samples
and at high temperatures, to determine the absolute thermopower for a given
sample in an indirect way using the Seebeck effect. This can only be accomplished
by completing an electrical circuit using a dissimilar conductor, hence the
absolute thermopower of our sample may be found only if the thermopower of the
reference electrodes is known. Values for such reference materials as a function
of temperature may of course be obtained by direct measurements of the Thomson
heat (e.g. Roberts, 1977), but a more convenient standard is provided by
materials in the superconducting state since they do not exhibit thermoelectric
effects and have an absolute thermopower of zero. Values for a number of
commonly employed reference electrode materials have been obtained by these
methods (see Cusack and Kendall, 1958; Bradley, 1962).

Using the Boltzmann formalism it has been shown (e.g. Mott and Jones, 1966)
that for a degenerate electron gas the absolute thermopower of a conductor is
given by:

\[ S = \frac{2}{3} \frac{K_B^2 T}{e} \left( \frac{1}{E} \frac{\ln \sigma(E)}{E} \right) \quad (1:12) \]

The derivation of this equation rests on those assumptions used for \( \sigma(E) \) and
also requires that both \( v_T^2 \) and \( \langle v^n \rangle^2 \) are negligible and that the characteristic
relaxation time is unaltered by the application of a temperature gradient.
So far we have considered the effects of a random distribution of scattering centres and associated potentials. However in a liquid sample the distribution is not purely random and the matrix elements containing the potential are not easily manageable in a direct way.

The situation is much simplified by the introduction of the pseudopotential (Ziman, 1961, 1967a; Bradley et al., 1962). The liquid is pictured as an assembly of ions carrying an attractive coulomb potential that is screened by the electron gas in which the ions are immersed. The conduction electrons interact with those filling the core states via the Pauli exclusion principle; the wave functions associated with the conduction electrons being orthogonal to those of the ionic core states. The cancellation theorem (Cohen and Heine, 1961) indicates that most of the effects of the strongly attractive bare-ion potential are counter-balanced by the interaction, leaving only a relatively weak pseudopotential which is then used to calculate the scattering of the electrons in the gas.

Since it is difficult to calculate a sufficiently accurate pseudopotential from first principles a convenient approach (Faber, 1972) is to develop a model of the bare (i.e. unscreened) potential $u_b(r)$ with Fourier components $u_b(q)$, having one or more parameters fixed by reference to various experimental data. The Fourier components of the screened ion model potential may then be written as:

$$u(q) = \frac{u_b(q)}{\varepsilon(q)}$$

where $\varepsilon(q)$ is a dielectric function introduced to allow for screening effects, this being a reasonable assumption in a metal where the electron gas has a high density and predominantly kinetic energy.

The potential at any point $r$ is supposed to be given by the sum of superposable pair potentials:
\[ U(r) = \sum_{i=1}^{N} u(r-R_i) \]

where \( R_i \) is the position of the \( i^{th} \) ion core.

If we also suppose that the conduction electrons exist in plane wave states when far from the ionic core, then we may write for the matrix element describing the transition of an electron from the state of wave vector \( k \) to the empty state of wave vector \( k' \):

\[ <k|u|k'> = \frac{1}{V} \int e^{-i\mathbf{k} \cdot \mathbf{r}} \sum_{i=1}^{N} u(r-R_i) e^{i\mathbf{k} \cdot \mathbf{R}_i} \, d\mathbf{r} \]

\[ = u(q) \frac{1}{N} \sum_{i=1}^{N} e^{i\mathbf{q} \cdot \mathbf{R}_i} \]

where

\[ u(q) = \frac{N}{V} \int e^{i\mathbf{q} \cdot \mathbf{r}} u(r) \, d\mathbf{r} \]

Hence,

\[ |<k|u|k'>|^2 = \frac{1}{N} |u(q)|^2 S(q) \]

where \( S(q) \), the static structure factor or interference function, is given by:

\[ S(q) = \frac{1}{N} \sum_{i=1}^{N} e^{i\mathbf{q} \cdot \mathbf{R}_i} \]

The structure factor (which gives the Fourier components of the pair distribution function \( g(r) \)) can be evaluated within certain approximations from x-ray or neutron diffraction experiments (Egelstaff, 1967; Howe, 1978).

By combining equations (L7, 8, 10, 15, 16) we have the expression first derived by Ziman (1961, but hinted at earlier in papers by Krishnan and Bhatia, 1945; Bhatia and Krishnan, 1948) for the resistivity of a liquid metal:

\[ \rho = \frac{1}{\sigma(E_F)} = \frac{6\pi m^2 e^2}{k_F^3 e^{3/2}} \int_0^1 |u(q)|^2 S(q) \left( \frac{q}{2k_F} \right)^3 \left( \frac{q}{2k_F} \right)^3 \, dq \]

which may be used in equation (L12) to give the thermopower of a pure liquid metal. These two expressions may be generalised to include liquid alloys (Faber and Ziman, 1965) when \( u(q) \) is no longer constant but depends on the different types of ion present and their relative spatial distribution. For a binary alloy
having an atomic concentration \( c \) of type A atoms with associated pseudopotentials \( u_A(q) \) and a concentration \((1-c)\) of type B atoms with pseudopotential \( u_B(q) \) the term \( \{ |u_A(q)|^2 S_A(q) \} \) in equation (I.17) becomes:

\[
|u_A(q)|^2 \{ c(1-c) + c^2 S_{AA} \} + |u_B(q)|^2 \{ (1-c) + (1-c)^2 S_{BB} \} + 2u_A(q)u_B(q)c(1-c)(S_{AB}-1)
\]

where \( S_{AA}, S_{BB}, S_{AB} (= S_{BA}^{-1}) \) are the partial structure factors. \( S_{\alpha\beta} \) \((\alpha \text{ and } \beta \text{ are dummy suffixes)}\) is related to the partial pair distribution function \( g_{\alpha\beta} \) which gives the probability of finding an ion of type \( \alpha \) at a radius between \( r \) and \( r + \Delta r \) from an ion of type \( \beta \):

\[
S_{\alpha\beta}(q) = \frac{1+4\pi}{V} \int_0^\infty g_{\alpha\beta}(r) (\frac{\sin qr}{q} \Delta r)
\]

These partial structure factors may, in suitable cases, be determined from three separate neutron diffraction experiments in which the scattering length of one of the constituents is varied by means of isotopic enrichment (e.g. Enderby et al, 1966). This is not always feasible, however it may be possible to simplify the expression if the ionic species are sufficiently similar by using a substitutional model, implying \( S_{AA} = S_{BB} = S_{AB} \).

I. vi) The Situation in Real Metals

On examination of the available experimental data (see for example the reviews by Cusack, 1963; Wilson, 1965; Busch and Guntherodt, 1974) it would seem possible to explain, at least qualitatively, many of the observed results using the NFE approximation described above. The theory, resting as it does on the assumption of a weak scattering potential (hence a long mean free path) and a spherical Fermi surface, is expected to have its most marked success in explaining the transport properties of liquid normal metals; those metals that are not transition, rare earth or actinide metals - and their mutual alloys.
The integral in equation (1.17), being heavily dependant on $S(2k_F)'$, accounts for two main trends in normal metal behaviour. The first of these is the increase in the value of the resistivity with increasing values of the Fermi energy (and hence $k_F$) resulting from the higher valence, $Z$, of some metals. Secondly, the positive linear variation of resistivity with temperature for metals having $Z = 1, 3, 4, 5$ and the negative temperature coefficient for divalent metals where $2k_F$ lies in the region of the first peak of $S(q)$. It has been suggested (Bradley et al., 1962) that this is due to the negative temperature derivative of $S(q)$ in this region.

Even, however, in the case of the alkali metals having very long mean free paths associated with them, calculations based on the NFE approach (e.g. Sundstrom, 1965; Ashcroft and Lekner, 1966; Paasch and Trepte, 1971; Feitsma et al., 1977; Srivastava, 1977) may give results in error by more than a factor of two. This does not necessarily invalidate the basic formulation since much of the discrepancy may have arisen from the uncertainties in $S(q)$ (especially in the low $-q$ region) and, more importantly, in $u(q)$ and its variation with temperature (Ziman, 1975, 1967a; Wang and So, 1977). Such a variation of the pseudopotential with thermal expansion is apparently also important for the divalent metals since the explanation of the negative temperature derivative of resistivity given above is called into doubt by neutron diffraction measurements (Wingfield and Enderby, 1968) showing that at least in the case of liquid zinc, the variation in $S(q)$ is not as large as would be needed.

Attempts at improving the performance of the NFE formulae by taking into account the non-locality (i.e. $k$ dependance) of the pseudopotential (Cubiotti et al., 1975) — especially important for the heavier polyvalent metals such as mercury, thallium and lead and the lower alkaline earths calcium, strontium and barium — have been made with some success (Evans et al., 1969; van Zytveld
et al, 1973). This energy dependence of the pseudopotential is taken to be due to the proximity of a narrow \(d\)-like band to the Fermi energy. The effects become more pronounced as the \(d\)-band moves closer to \(E_F\) (either from below or, as in the case of the alkaline earths, from above) as is evident if we consider a progression towards the noble metal and transition metals – the progression being reflected in a reduction of the mean free path.

I. vii) A Classification of Conductors

Mott has suggested a broad phenomenological classification of liquid conductors (Mott, 1971; Mott and Davis, 1971):

a) Typical metals having \(\sigma > 5000 \Omega^{-1} \text{cm}^{-1}\) and a long mean free path such that \(k_F l >> 1\). Electrons propagate freely between the weak scattering potentials and the NFE theory described in this chapter is thus applicable.

b) "Pseudometals" or liquids of an intermediate type whose conductivity is within the range 300-5000 \(\Omega^{-1} \text{cm}^{-1}\), the mean free path is of the order of the interatomic separation giving \(k_F l \sim 1\). Electrons are assumed to move through the medium in a diffusive way, their transport properties being governed by the density of states at the Fermi surface.

c) Semi-metals or narrow-gap semiconductors with \(\sigma\) in the range 1-100 \(\Omega^{-1} \text{cm}^{-1}\). Conduction in this case is via the parallel mechanisms of hopping (for electrons with energies within \(\frac{e k_B T}{\epsilon_F}\) of \(E_F\)) and band conduction (for electrons excited beyond the mobility shoulder, Mott and Davis, 1971).

d) Semiconductors in which the current is carried by those carriers excited above the band gap. In this case, for electrons, \(\sigma \approx \exp\left(\frac{(E_F - E_C)}{k_B T}\right)\) where \(E_C\) is the conduction band edge.

The regimes a) and b) above are considered in more detail in chapters II and III, being relevant to the results reported in this thesis.
The Nearly Free-Electron Regime and the Transition Metals

Although the formalism described in the previous chapter has provided considerable insight into electronic transport phenomena it has obvious limitations. These arise mainly from the constraint imposed by assuming a small scattering potential such that the Born approximation is valid. As a consequence of violating this condition we find only poor agreement between theory and experiment in the case of some noble metals and the transition metals (and also, of course, the heavy polyvalent metals, alkaline earth metals and actinide metals) where the presence of a d-(or f-) like band near the Fermi surface may give rise to a resonance energy (Ziman, 1965; Heine, 1967; Davis and Heine, 1978) and a strong scattering situation. This is especially important for the transition metals where the d-band overlaps the Fermi energy. That the proximity of the resulting resonance energy to the Fermi energy has an effect on the resistivity is demonstrated in the figures on p. 18. This figure also shows the form of the density of states assumed for a transition metal (Mott and Jones, 1936; Mott, 1964), consisting of a broad free-electron conduction band (s-band) and a narrow d-band which accommodates those electrons that, in an atom, would be in discrete d states (i.e. about ten per atom). The density of states in the region of $E_F$ is, then, very high.

II. ii) The t-matrix

The pseudopotential is clearly unable to deal elegantly with the problems associated with such d-bands. We may, however, generalise the treatment of electron scattering to take account of waves having non-zero angular momentum components by using the method of partial waves. For the case of a spherical scattering potential within the partial wave theory (Kittel, 1963; Schiff, 1968; Faber, 1972) the incoming plane wave associated with an electron is decomposed
into a set of partial waves which collapse inwards into the potential well and a similar set which radiate outwards from it. The difference between the asymptotic form of the actual outgoing waves (of angular momentum $l$) and that expected in the absence of a scattering potential is the phase shift, $\eta_l$. The potential may be fully described, then, in terms of the phase shifts of all the partial waves at all energies. The amplitude of a wave scattered elastically through $\theta$, relative to the incident amplitude, is proportional to:

$$\frac{\Sigma_{l}(2l+1)P_{l}(\cos \theta) \sin \eta_{l} \exp(i\eta_{l})}{\exp(i\eta_{l})}$$

where $P_{l}(\cos \theta)$ is the Legendre polynomial of order $l$. Hence, the scattered amplitude only oscillates as the atomic potential well is progressively deepened since all integral multiples of $\pi$ in each $\eta_l$ may be ignored; the function will have maxima whenever the phase shift approaches $\pi/2$.

The exact probability of scattering from a state of wave vector $k$ to a state of wave vector $k'$ may be written in terms of the elements of the total scattering matrix, or T-matrix. This may be expanded, however, in terms of the single site t-matrix, $t_{(q)}$ (Edwards and Beeby, 1963):

$$T = \Sigma_{l} t_{l} + \Sigma_{i\neq j} t_{i} G_{o} t_{j} + \Sigma_{i\neq j \neq k} t_{i} G_{o} t_{j} G_{o} t_{k} + \ldots$$

where $G_{o}$ is the free particle propagator and where the t-matrix gives the probability of an electron being scattered from a state $k$ to a state $k'$ by a single scattering event. Using the partial wave theory the t-matrix may be written as:

$$t_{(q)} = -\frac{2\pi n^3}{m(2\pi E)_0^2} \frac{1}{V_o} \Sigma_{l} \frac{(2l+1) \sin \eta_{l}(E) \exp in_{l}(E) P_{l}(\cos \theta)}$$

where $V_o$ is the atomic volume. If, following the discussion above, we can assume that $t_{(q)}$ is in some sense small then the expression for the total scattering matrix may be truncated after the first term. Having made this assumption it becomes possible to rewrite equation (I:17) in a more general form.
but still within the Born approximation - by allowing the t-matrix to replace the pseudopotential:

\[
\rho = \frac{12\pi v_0}{e^2 \hbar^2} \int_0^1 \left( \frac{q}{2k_F} \right)^3 d \left( \frac{q}{2k_F} \right)
\]

(II: 2)

iii) The Transition and Noble Metals

An explanation of the resistivity and thermopower values of liquid transition metals has been given (Evans, Greenwood and Lloyd, 1971; Evans, Gyorffy, Szabo and Ziman, 1972) using the t-matrix within a NFE framework. The model makes use of muffin tin potentials (Ziman, 1972b) - spherically symmetric within some radius about each site and constant in the interstitial regions. Mott's picture of the electronic band structure of a transition metal, described above, is employed. The current is assumed to be carried predominantly by electrons in plane wave states (in the nearly free \( s \)-band) which are scattered from ionic potentials whose character is dictated by the virtual bound \( d \)-states. The \( d \)-band is broadened and shifted by \( s-d \) hybridization where it crosses the \( s \)-band and gives rise to a wave function that, whilst having a large amplitude within the muffin tin well, is not completely localized there. The "centrifugal potential" term in the radial part of the Schroedinger equation for \( l \neq 0, l(l+1)/2 \) when combined with the attractive muffin tin well affords the electron a barrier (separating the virtual bound state from the conduction band) through which it may tunnel. The width of the resonance depends on the probability of such tunnelling.

In transition metals the \( d \)-wave (\( l=2 \)) phase shift is much larger in magnitude and usually varies more rapidly with energy than the phase shifts for partial waves of other angular momenta, thus the t-matrix may be approximated by:

\[
t_{(q)} = -\frac{2m\hbar^3}{m(2mE)^{5/2}} \frac{5}{V_0} \sin n_2, (E_p) \exp \ln n_2, (E_p, E_F, (cos \theta))
\]

(II: 3)
Since the integral in equation (II.2) is also dominated by the back-scattering (i.e. $\theta = \pi, q = 2k_F$) contribution we may reduce the expression for the resistivity to:

$$\rho = \frac{30\pi^3 h^3}{m e V k_F^2} \frac{\sin^2 \eta_2, (E_F) S(2k_F)}{2}$$  \hspace{1cm} (II.4)

For noble metals of course it is necessary to include the $s$- and $p$-wave phase shifts in $t_{(q)}$ and this simplification is not possible.

Equation (II.4) may be re-written using the relation:

$$\tan \eta_2, (E_F) = \frac{r}{(E_{\text{res}} - E_F)}$$ \hspace{1cm} \text{for } E \ll E_{\text{res}}$$

$$\rho = \frac{30\pi^3 h^3}{m e V k_F^2} \frac{S(2k_F)}{r^2 + (E_{\text{res}} - E_F)^2}$$  \hspace{1cm} (II.5)

where $r$ is the width and $E_{\text{res}}$ the position of the scattering resonance. With the expression in this form we see that there should be two main contributions to the resistivity: the structure factor and the position of the resonance with respect to the Fermi energy. The former will contribute only a small variation across the transition series, if the number of conduction electrons remains constant, since the structure factors are very similar (see for example the figures on p. 87).

Experiment shows the resistivity decreasing in the progression manganese to copper (i.e. with increasing $d$-band occupation), this is supposed to be largely due to the increase in $(E_{\text{res}} - E_F)$ and resulting decrease in the resonance scattering and is illustrated in the figures on p. 18.

Equation (II.12), although derived only to first order in $(k_B T / E_F)$, should remain sufficiently accurate in the light of those approximations already made for the present calculations and gives:

$$S = \frac{\pi^2 k_B T}{3e} \left[ -2 + \frac{1}{E_F} \frac{dS(2k_F)}{dE} + 2 \cot \eta_2, (E_F) \frac{d\eta_2, (E_F)}{dE} \right]$$  \hspace{1cm} (II.5a)

These expressions for the resistivity and thermopower may be extended to include binary alloys (Evans, Guntherodt, Kunzi, Zimmermann, 1972) -
A. Schematic representation of the position of the Fermi energy ($E_F$) and resonance energy ($E_{res}$) of some d-band metals, and their associated d-wave phase shifts ($\eta_2$)

B. The resistivity of some liquid transition metals at their melting points.
following again the analysis of Faber and Ziman (1965) presented in chapter I -
with \( s_{(q)} \left| t_{(q)} \right|^2 \) replaced by:

\[
|t_A|^2 \{ c(1-c) + c^2 S_{AA} \} + |t_B|^2 \{ c(1-c) + (1-c)^2 S_{BB} \} + 2(t_A^* t_B + t_A t_B^*) c(1-c) (S_{AB} - 1)
\]

where \( c \) is the atomic concentration of type A atoms having t-matrix \( t_A(q) \)
associated with them and \( (1-c) \) is the concentration of type B atoms having
t-matrix \( t_B(q) \). The partial structure factors are defined as in equation (1:19)
We are assuming \( t_A \) and \( t_B \) are concentration independent except for a
normalization factor arising from the variation of the effective alloy atomic
volume, given by:

\[
V_{\text{o(ally)}} = cV_{\text{o(A)}} + (1-c)V_{\text{o(B)}}
\]

This assumption is consistent with the use of a single site scattering model
when \( E_F \) is assumed not to vary with alloy composition. For low concentrations
of type A ions in a host of type B however the large mean separation of type A
ions may cause their associated t-matrix to deviate significantly from \( t_A \) (and
vice versa). Accordingly, any comparison of theory with experiment will ideally
be restricted to the region \( 0.25 < c < 0.75 \) where substantial overlap between like ions
will largely eliminate this effect (Mott, 1972a).

Values for the resistivity and thermopower of liquid noble and transition
metals, calculated using equations such as those above, have generally been found
to be well within a factor of two of the experimental results (Evans et al, 1971;
Dreirach, 1971; Brown, 1973; Guntherodt et al, 1975; Hirata et al, 1977; Lopez-
Escobar and Brown, 1977). Since, for the transition metals, the d-wave phase
shift varies rapidly with energy near the Fermi energy it is important to calculate
\( E_F \) with some precision. It may be estimated using the method of Dreirach
(1971) who wrote:

\[
E_F = E_B + \frac{\hbar^2}{2m^*} k_F^2
\]

(II: 7)
where \( m^* \) is a constant effective mass. \( E_b \) is the energy of the bottom of the band measured relative to the muffin tin zero and is calculated using the s-wave phase shifts (Ziman, 1967b) which do not vary rapidly near \( E_F \). Briefly, the solid s-wave phase shifts are used to give \( E_b \) in the solid then, using a Fermi level estimated from relevant solid state optical data, the width of the band is found and this is then approximated as a NFE band with effective mass \( m^* \). A similar approach is now employed to give \( E_F \) in the liquid: the solid state \( m^* \) is used to obtain the width of a NFE band at the appropriate liquid density, then \( E_b \) for the liquid is calculated using the liquid s-wave phase shifts.

The Fermi wave vector \( k_F \) is usually derived using the free-electron formula:

\[
k_F^3 = \frac{3\pi^2 Z_{\text{eff}}}{V_0}
\]

The number of nearly free electrons present in the metal per atom is represented by an effective valence, \( Z_{\text{eff}} \). Values for this quantity vary widely; for nickel for example estimates have been 1, 2, 0.46 (Evans et al., 1971; Dreirach et al., 1972 and Brown, 1973 respectively). Attempts have been made to evaluate \( Z_{\text{eff}} \) for palladium using a theoretically derived electronic bandstructure (Lopez-Escobar and Brown, 1977).

Calculations based on equation (II: 6) have been reported (Dreirach et al., 1972) for the resistivity of certain liquid noble/transition metal - non-transition metal alloys which reproduce the general form of the experimental results.

The t-matrix approach has also been applied with some success in the study of solid noble and transition metals (Dreirach, 1973; Khanna and Jain, 1974), alkaline earth metals (Ratti and Evans; 1973), rare earth metals (Guntherodt, Hauser and Kunzi, 1977; Waseda et al, 1978; Delley et al, 1979 a, b) and metallic glasses (Guntherodt, Kunzi et al, 1977). An attempt has been made (Dunleavy and Jones, 1978) to improve upon the single-site t-matrix approach by introducing the
effects of multiple scattering into calculations involving strong scatterers. The t-matrix is replaced by a Q-matrix, in which the final state now depends on a pair distribution function derived within the quasi-crystalline approximation.

This extension, whilst giving values of the resistivity of certain transition metals somewhat closer to experiment than is generally possible with the t-matrix, is still open to the limitations of the linearized Boltzmann equation within which it is formulated.

II: iv) An Alternative Approach

Mott (1972a) has suggested a theory fundamentally different to that based on the t-matrix for liquid transition metals. It represents a development of his solid state model (Mott and Jones, 1936; Mott, 1964) and carries the concept of two significant mean free paths for pure transition metals into the liquid state.

The d-band electrons have a large effective mass, when compared with the nearly free s-band electrons, due to the high and narrow nature of the d-band. As a consequence of this the current will be carried predominantly by the s-electrons. The probability of transition from one state to another is related to the density of final states by Fermi's "golden rule" (e.g. Schiff, 1968; c.f. equation L7), it is therefore considerably more probable that an s-electron near the Fermi surface will be scattered into a vacant d state than into a vacant s state, i.e.:

\[ \frac{1}{\tau_{s-d}} >> \frac{1}{\tau_{s-s}} \]

The resistivity is thus increased beyond the value it would have in the absence of the d-band. Mott's model, then, provides two mean free paths for consideration - a short one \( L_d \) associated with a d-like part of the Fermi surface and a longer (NFE like) one \( L_s \) associated with an s-like part of the Fermi surface - and implies that the conductivity of solid transition metals
may be written:
\[ \sigma = \sigma_s + \sigma_d \]
\[ \sigma_s \gg \sigma_d \]

In the liquid state Mott assumes that \( L_d \) has reached its minimum value of the interatomic separation (Ioffe and Regel, 1960) so that the \( d \)-electrons may be viewed within a tight binding framework (i.e. the electron wave functions may be written as linear combinations of atomic \( d \)-orbitals, the phases of the coefficients varying in a random way from atom to atom). Hybridization of \( s \)- and \( d \)-like orbitals is assumed small. A resonance of the sort described earlier can now only build up if:

\[ \frac{1}{\tau_{s-d}} > \frac{1}{\tau_{d-d}} \]

i.e. the likelihood of such a resonance developing depends on the relative strengths of the coupling between the \( s \)- and \( d \)-like orbitals integrated over one atom and the coupling between \( d \)-like orbitals on adjacent atoms. Clearly, since the \( d-d \) overlap integral is a strong inverse function of the inter-transition metal atom spacing, the resonance type approximation becomes feasible only for alloys containing a significant concentration (Mott suggests a minimum figure of 25%) of non-transition metal atoms.

According to this model the resistivity has no dependence on the structure factor, which implies a small temperature derivative of the resistivity of the liquid. Also, since the theory for the liquid is basically the same as for the solid at temperatures approaching the melting point, a small fractional change in resistivity upon melting is predicted. These implications are consistent with experimental observations on iron, cobalt, nickel and palladium (Guntherodt, Hauser, Kunzi and Muller, 1975); the relatively high change in resistivity for palladium may be due to \( L_d \) not having reached its minimum value by the melting point. Although no detailed calculations have been made for liquid transition
metals using this model, estimates of the resistivity are of the correct order of magnitude (but depends very strongly on the value of the s-d coupling integral).

Further support has been provided by the experimental thermopower measurements of Enderby and Dupree (1977; Enderby, 1978a) on the liquid transition metals iron, cobalt and nickel. They write the thermopower as the sum of two terms, $S_1$ and $S_2$, obtained by a substitution of equation 6 into equation 12

$$S_1 = -\frac{3}{2} \left(\frac{\pi^2 k_B T}{3 |e| E_F}\right)$$

and

$$S_2 = \left(\frac{E}{t \partial E} E_F \right) \left(\frac{\pi^2 k_B T}{3 |e| E_F}\right)$$

In Mott's scheme the relaxation time is inversely proportioned to the $d$-electron density of states at the Fermi energy so that, if the constant of proportionality is only slowly varying with energy, we may write:

$$S_2 = \frac{\pi^2 k_B T}{3 |e| E_F} \left(\frac{E}{N_d \partial E} E_F \right)$$

For liquid iron, cobalt and nickel at the melting point $S_1$, is approximately $-8 \mu VK^{-1}$ hence, using their experimental values for the total thermopower, they find $S_2$ equals +4, +4 and $-30 \mu VK^{-1}$ respectively. It is thus concluded that the $d$-band contribution to the density of states at $E_F$ is increasing with iron and cobalt and decreasing for nickel and that, once allowance is made for the energy dependance of the Fermi surface area, the results are consistent with Mott's s-d scattering theory.

II: v) The $d$-Electron Contribution to the Conductivity

The $d$-electrons, being partially localized on ionic sites, should be less sensitive to the onset of structural disorder on melting than the extended $s$-electrons. We therefore expect a smaller change in the $d$-electron part of the conductivity than in the $s$-electron part. In model calculations by ten Bosch and Bennemann (1975) it is suggested that the $d$-electron contribution may
become comparable to that of the s-electrons under certain conditions (c.f. the small correction assumed above). They found that the d-electron conductivity is proportional to the d-electron density of states and will be small for almost filled or almost empty d-bands with small values of $N_d(E_F)$. As the Fermi energy is swept through the d-band the s-electron contribution decreases and the d-electron part increases. The total conductivity is still dominated by the s-electrons except when $E_F$ lies near the maximum in the density of states where both contributions are of the same order of magnitude. As the d-band becomes more than half-full the total conductivity will fall due to a decrease in the d-electron contribution. Clearly for those cases in which the d-electrons play a major role, we expect a decreased fractional change of resistivity on melting. It would also seem likely that for transition metal – non-transition metal alloys the d-electron contribution will decrease rapidly with increasing non-transition metal concentration.

II: vi) Some Experiments Undertaken

Those experiments involving noble and transition metals and their alloys reported in this thesis were undertaken in order to provide further experimental data relevant to the discussion presented earlier. The materials investigated lie in the "lower levels" of the NFE regime as defined in Mott's classification (see I: vii) and so provide a rather useful tool in the examination of the limits of the NFE approach.

Two alloy systems were examined: an inter-transition metal binary alloy and a transition metal – non-transition metal one. For the former class nickel-cobalt was chosen on the grounds that it most closely fulfilled the conditions necessary for the use of the substitutional approximation. For the other binary alloy case silver-palladium was chosen because its well documented solid state properties facilitated a comparison between the solid and liquid alloys. These
choices are discussed in more detail in chapter VI.

The following measurements were undertaken:

**Resistivity:**

- Pure metals – Ni, Co
- Alloy systems – Ni-Co; Pd-Ag

**Thermopower:**

\[
Pd_{0.7}Ag_{0.3}
\]
CHAPTER III
The Diffusive Conduction Regime

In the first chapter the electron transport properties of simple liquid metal systems were discussed. Scattering potentials were assumed small, so that using the Born approximation within the Boltzmann equation framework was a tenable operation. For the materials described in chapter II, however, the situation was somewhat more complex in that whilst the current was still assumed to be carried mainly by nearly free-electrons, these carriers had a high probability of being scattered (into a vacant d-like state in the case of the transition metals). In an attempt to maintain the employment of the Born approximation the pseudopotential of the simple metals was replaced, in one approach, by the more general t-matrix. The situation is altered yet again if we now consider a material in which all the current carriers have their minimum mean free path (i.e. $L_k \sim 1$; Ioffe and Regel, 1960) since use of the Born approximation becomes highly suspect. Once the mean free path approaches this value we are no longer justified in using $k$ as a good wave vector associated with the electron wave functions since the uncertainty in $k$ is such that $\frac{\Delta k}{k} \sim 1$ and the Fermi surface becomes extremely blurred. The energy, hence also the density of states, remains a well defined quantity however. Whilst $N(E)$ may still be a continuous function of energy, there is now the possibility of deviations from the free-electron value - these having an effect on transport phenomena.

Within the second band of Mott's classification of conductors (see I: vii) such deviations are assumed small enough to allow the electrons to remain in extended states near the Fermi energy and to consider them as diffusing through the material when an external field is applied. The electron wave functions may be represented, within the random phase model (Mott, 1967; Hindley, 1970; Friedman, 1971), by a linear superposition of atomic wave functions (as were the d-electrons of the
transition metals in Mott's model):

\[ \psi = \sum_n a_n \phi_n(x) \quad (\text{III: 1}) \]

The coefficients \( a_n \) in this model have no phase correlation from one site to the next.

Because of the complexities involved in the study of this class of materials, being an intermediary between typical metals and typical semiconductors, such models as have been proposed are often heuristic schemes formulated in order to allow some treatment of experimental (or theoretical) information. An example of this type of material - and of special relevance to this thesis - is tellurium. The discussion within this chapter is presented in an effort to explain some of the properties of this element and its alloys.

III: ii) The Kubo-Greenwood Formula

In this context it will be useful to reformulate the conductivity in terms of the Kubo-Greenwood approach (Greenwood, 1958; Mott and Davis, 1971; Faber, 1972). The eigenfunctions for an electron of energy \( E \) are normalized to give one electron in a volume \( V_0 \). All electron-electron and electron-phonon interactions are neglected here - a more general derivation has been given by Luttinger (1964). We assume an applied electric field of the form \( E_0 \cos \omega t \) acting on the electron, giving a potential energy \( e x E_0 \cos \omega t \). The probability of a transition from a state with energy \( E_i \) to a state with energy \( E_f \) (separated by an energy \( \hbar \omega \) ) is, using the "golden rule" from first order time-dependant perturbation theory (Schiff, 1968):

\[ P(E_i, E_f) = \frac{\hbar}{2\pi} e^{2E_0^2} |\langle E_f | x | E_i \rangle|^2 \frac{\hbar}{2\pi} N(E_f) \quad (\text{III: 2}) \]

where \( N(E_f) \) represents the density of final states. The matrix element is averaged over all states having energies near \( E_i \). If this is re-written in terms of a diffusion operator \( D \), where:

\[ D = \frac{\hbar}{m\omega} \left( \frac{\partial}{\partial x} \right) \]
then equation (III:2) becomes (Messiah, 1970):

\[
P(E_i, E_f) = \frac{\pi e^2 h v_o}{2m^2 \omega^2} E_o^2 |D(E_f, E_i)|^2 N(E_f)
\]

(III:3)

This probability may now be used to obtain the rate of energy loss per unit volume: the expression is multiplied by the density of occupied initial states (i.e. \(\langle n_{E_i} \rangle \frac{dE_i}{dE} \)), by the probability that the final state is empty (i.e. \(\{1-n_{E_f}\} \)), by the energy absorbed in each transition (i.e. \(\tau \omega \)), and by a factor of two to take both spin directions into account. If, having performed this manipulation, we equate the result with the macroscopic mean rate of energy loss per unit volume given by \(\frac{1}{2} E_o^2 \sigma(\omega) \) - where we have introduced the conductivity for frequency \(\omega\) - we find:

\[
\sigma(\omega) = \frac{2 \pi e^2 h^2 v_o}{m^2 \omega} \left[ E_f \left\{ f(E_i) - f(E_f) \right\} |D(E_f, E_i)|^2 N(E_i) \right] \frac{dE}{E_F - h \omega} \]

(III:4)

For the d.c. conductivity, \(\sigma\), the limit as \(\omega\) tends to zero must be taken. Also, at absolute zero, the quantities in this equation are only significant at \(E = E_F\), hence:

\[
\sigma = \{ \sigma(E) \}_{E=E_F} = \frac{2 \pi e^2 h^2 v_o}{m^2} |D(E)|^2 \left\{ N(E) \right\}^2
\]

(III:5)

where,

\[
|D(E)| = |<E'|D|E>_{av}
\]

The average is over all states \(E\) and \(E'\) such that \(E = E'\). (The conductivity is not dependant on the volume as might appear from equation (III:5) since the matrix element will be reduced by a factor \(\frac{1}{\langle N(E) \rangle} \) on normalization). We may extend this to finite temperatures for a non-degenerate electron gas:

\[
\sigma = -\int \sigma(E) \frac{df(E)}{dE} dE
\]

(III:6)

This is the Kubo-Greenwood formula.

Using the random phase model described through equation (III:1):

\[
D(E) = N^E \tilde{J}
\]
where \( N \) is the number density of sites on which atoms are localized and,
\[
J = \int \psi_1 \left( \frac{\partial}{\partial \mathbf{x}} \right) \psi_2 \, d\mathbf{x}^3
\]
the integration being over a single atom (Mott and Davis, 1971; Mott, 1972b).

Assuming that \( J \) has the same value as for the periodic lattice:
\[
\left| D_{(E)} \right|^2 = \left( \frac{m^*}{m} \right)^2 \frac{\hbar^2 a}{\upsilon_0}
\]
where \( m^* \) is the effective mass (for the periodic lattice) and the wave number
has been replaced by \( \frac{\pi}{a} \), 'a' being the inter-atomic separation. On substituting
this into equation (III:5) we have:
\[
\sigma(E) = \frac{2\pi^3 e^2 \hbar^3 a}{m^*} \left\{ N(E) \right\}^2
\]

Returning to equation (III:6) and assuming that the motion of an electron at
energy \( E \) gives rise to a heat of transfer \( (E-E_F) \), then the thermopower will be
given by (Mott and Davis, 1971; Cutler, 1977):
\[
S = \frac{k}{\sigma} \left[ \sigma(E) \left( \frac{E-E_F}{K_B T} \right) \frac{3f(E)}{2E} \right] \, dE
\]

Recalling the form of the Fermi-Dirac distribution function given by equation (I:1),
it will be seen that the factor \( \left( \frac{E-E_F}{K_B T} \right) \frac{3f(E)}{2E} \) is similar in shape and
character to \( \left( \frac{3f(E)}{2E^2} \right) \). Hence, if the density of states and therefore \( \sigma(E) \)
changes only slowly near \( E_F \) on the energy scale \( K_B T \), we may approximate
equation (III:8) by the "metallic" form of equation (I:12). Moreover, if we assume
that the conductivity is proportional to the density of states as implied by equation
(III:7), it becomes apparent that the value of the thermopower will depend upon the
energy derivative of the density of states at \( E_F \), and that the sign of the thermo-
power will depend not only on the species of carrier but also on the sign of such
an energy derivative. This approach has already been mentioned (see section II:iv)
in connection with the transition metal thermopower measurements of Enderby and

It should be noted that equation (III:5) applies only to a single site model with
constant energy transfer; Hoshino and Watabe (1978) have suggested that for systems having bond-type disorder and random energy transfer, the conductivity is not related to the square of the density of states in such a direct way but also has some dependance on the transfer energies associated with the bonding and anti-bonding states.

III: iii) The Density of States and its Effect on Conductivity

As mentioned in the introduction to this chapter the electronic density of states forms a useful starting point in the discussion of those liquid conductors having a very short mean free path and various types of models have been put forward (e.g. the review by Cutler, 1977). Each approach begins by assuming an idealized case. The effects of deviating from this archetype are then considered. The models eventually lead to a density of states function which includes a dip in \( N(E) \) near the Fermi energy - assumed to correspond to the similar dip observed in solid semi-metals and semi-conductors. Of those models there are two of especial interest within the discussion presented in this chapter: the metallic model and the molecular band model.

The former begins with the free-electron model and introduces deviations through the electron-ion interaction. In a crystalline metal the (weak) interaction, combined with the effects of long range order, gives a discontinuity in the \( E - K \) curve and a corresponding small perturbation to the parabolic shape of the density of states curve. The deviation produced is structure sensitive and depends on the short range order. The absence of long range order in a liquid means that the Fourier components of the potential will no longer be selected using the reciprocal lattice vector, hence the perturbations in energy may now be written as an integral weighted by the structure factor. Although a simple perturbation approach fails for strong interactions, the qualitative results may be similar: a large dip developing in the density of states near the Fermi energy, the
depth of which will depend on the short range order (an increase in thermal
disorder will tend to result in a shallower dip). The dip may also be seen (e.g.
Mott, 1973a) as arising from the overlap of a full valence band and an empty
conduction band, both of which may have tails due to potential fluctuations. Such
a dip has been named a pseudogap by Mott (e.g. Mott, 1966; 1969; 1971; also
Cutler, 1972).

A second approach, much used in the study of the liquid semi-conductor
system tellurium-thallium by Cutler (1971, a, b; 1976), has its origin in the
discrete energy levels of widely separated molecules. Hence, in contrast to the
first model, we now begin with an existing gap but no bands. As the molecules
are brought closer together the energy levels are broadened into bands, described
within the tight binding approximation, that may then overlap to form a pseudogap
rather than a complete gap. The strength of this will once again depend on short
range order.

The application of such models in the determination of the density of states
for liquid tellurium is discussed later (see chapter VII).

We may now employ the concept of the pseudogap in an attempt to reconcile
the two types of formulae derived so far for the conductivity. Equation (I:6) may be
written in the form:

\[ \sigma = \frac{\varepsilon_F e^2 L}{12\pi^3 h} \]  

(I:9)

where we have expressed the relaxation time in terms of the mean free path and the
Fermi velocity - which may in turn be related to the Fermi surface area \( \varepsilon_F \).

This equation implies that, within the NFE approximation, the conductivity for a
given (long) mean free path is independent of the density of states. The conductivity
as derived using the more general Kubo-Greenwood approach (equation III:7) shows,
however, a direct dependence on \( \left(\frac{N_E}{n}\right)^2 \). Should a pseudogap exist, then, in the
region of the Fermi energy equation (III:9) clearly becomes inadequate, but may be
written in a revised form:

\[ \sigma = \frac{\pi e^2 L \omega^2}{12\pi^2 \hbar} \]  

(III: 10)

where the "mean free path", \( L \), is taken to be the distance in which phase memory is lost (i.e. a phase coherence length); and where \( \omega \) is introduced in order to express the depression of the actual density of states below its free-electron value (e.g. Mott, 1966; 1969; 1971):

\[ g = \left( \frac{N(E)}{N(E)_{\text{free}}} \right)_{E=E_F} \]  

(III: 11)

The factor \( \omega \) only affects the value of \( \sigma \) when \( L \) is of the order of the inter-atomic separation; for longer mean free paths it is found (Faber, 1972) that the value of \( L \) itself becomes inversely proportional to \( \omega^2 \).

States in the pseudogap will remain extended until \( g \) falls to about 0.3 when the gap states may then become localized (Mott and Davis, 1971).

**III: iv) An Alternative Approach**

The models described so far assume microscopic homogeneity (e.g. Friedman, 1971). Cohen and Jortner (1973 a, b, c; see also Hodgkinson, 1971; Cohen and Sak, 1972; Brenig, 1973) however, have argued the existence of a subdivision in the diffusive regime characterized by submacroscopic inhomogeneity. The microscopic inhomogeneities present in all disordered materials are associated with fluctuations in, for example, local density, composition or bonding configurations and give rise to fluctuations in the potential and consequently to inhomogeneities in the electronic structure. If, however, the inhomogeneities give rise to long range fluctuations the material may be pictured as consisting of a random submacroscopic mixture of metallic and semiconducting, electrolytic or insulating regions. If the phase coherence length is small compared with the correlation length of the potential fluctuations a semi-classical description is appropriate and leads to a classical percolation model for the transport phenomena.

Provided the density of states is independent of the geometry of the metallic
regions, it may be expressed, approximately, in terms of the metallic volume fraction \( c \) at the Fermi energy (Cohen and Jortner, 1973b):

\[
N(F) = N_0(F)c
\]

(III.12)

where \( N_0(F) \) is the mean density of states within a metallic region of macroscopic extent and we assume that the density of states at \( E_F \) is negligible in the non-metallic regions (otherwise a correction term \( N_1(F)c \{1-c \} \) must be added, where \( N_1(F) \) refers to the non-metallic regions).

The inhomogeneous regime is divided into two sections by the introduction of a critical allowed volume \( C^* \) corresponding to a percolation edge. For \( c \) greater than \( C^* \) there are assumed to be continuous metallic paths extending throughout the material and the electrons at the Fermi energy are in extended states. (The conductivity, however, will not be directly proportional to the percolation probability since many of the channels will contribute little by virtue of their constricted geometry). For \( c \) below \( C^* \) the electron states are localized at the Fermi energy. In their papers, Cohen and Jortner suggest that, for systems where \( N_1(F)/N_0(F) \) is about 0.2 - in contrast to the corresponding value of \( g \) of about 0.3 in the homogeneous regime. Within the pseudometallic region the conductivity, \( \sigma \), may be written:

\[
\sigma = \sigma_0 \left[ A + \left( \frac{3c}{A} - 1 \right) \left( 1 - \frac{\sigma_1}{\sigma_0} \right) - \frac{\sigma_1}{4\sigma_0} \right]
\]

(III.13)

where,

\[
A = \frac{1}{4} \left( 3c \right) - 1 \left( 1 - \frac{\sigma_1}{\sigma_0} \right) - \frac{\sigma_1}{4\sigma_0}
\]

An experimental determination of \( c \), as a function of temperature say, is possible using Knight shift data (e.g. Warren, 1972; 1977). We may write the Knight shift as (Cohen and Jortner, 1973c):

\[
\kappa = \kappa_0 c + \kappa_1 \{1-c \}
\]

(III.14)

where \( \kappa_0 \) and \( \kappa_1 \) are the resonance shifts in the metallic and non-metallic regions respectively. If data is available for the saturated condition (i.e. \( c = 1 \))
then $k_0$ may be fixed and the above expression used to determine $C_{EF}$ under other conditions.

Mott (1973b) has suggested that, except near a critical point where the potential fluctuations are slowly varying, this semi-classical description is invalid since tunnelling effects must be taken into consideration. If tunnelling is important the classical percolation channels will tend to be smoothed out. Cohen and Jortner (1973c) have, however, defended their assumptions using a model calculation for the mean tunnelling probability to show that the fluctuations' correlation length has only to reach about $\xi_R$ before tunnelling effects become negligible. It would appear that more experimental data is required: Knight shift data may be of use again in that, under certain conditions, it may suggest the relative suitability of either the homogeneous or the inhomogeneous picture for a given material. Since the Knight shift is proportional to the value of the density of states at the Fermi energy (Ziman, 1967a) we have that, for a homogeneous material, $k = \sigma^x$, whilst $k = \sigma$ for an inhomogeneous material. In the case of liquid tellurium, Warren (1977) has pointed out that it is impossible to distinguish between these two cases since the conductivity, with its associated experimental uncertainty, only varies by a factor of two over the region of interest.

III: v) Some Experiments Undertaken

Data is presented in this thesis for the temperature and composition dependance of the resistivity and thermopower of liquid nickel-tellurium. Such an alloy system can provide considerable insight into the conduction regimes discussed in this and the previous chapter since the transport properties show a migration - on increasing the temperature of pure tellurium or with the progressive addition of nickel from the diffusive regime to the metallic regime.

The following measurements of resistivity and thermopower in the liquid state were undertaken:
Pure metal  -  Te
Alloy system  -  Ni-Te
CHAPTER IV

Measurement of the Resistivity and Thermopower of Transition Metals

Although the two types of experimental method developed to measure resistivity and thermopower values differ in many respects, there are fundamental similarities between them due to the common difficulties presented. The materials investigated were highly corrosive in their liquid or vapour states and the provision of electrical contacts thus became a major problem. The development of computer-aided data acquisition techniques was of considerable use in this context. In the silver-palladium alloy system an additional problem arose from the high vapour pressure of silver relative to palladium at any given temperature (Weast, 1974; see the figure on p. 51). Since it proved impossible to reduce the differential vapourization of alloy constituents to negligible levels, estimates of the magnitude of such an effect had to be made. Also common to all experiments of this nature, of course, is the problem of reaching and maintaining a high, stable and accurately known temperature.

Part a) The Measurement of Resistivity

The resistivity was measured using a four point d.c. technique, electrical contact with the liquid sample being obtained by forcing the liquid up the four capillaries of a specially designed alumina probe to meet tungsten wires. The actual contact electrodes, then, were composed of the same material as the sample under investigation, thereby reducing any possible electrode contamination. The sample was contained in a cylindrical alumina crucible. Pure tungsten was used as the contact material since available data (Hansen, 1958) and past experience indicated that of the available refractory metals this would suffer the least corrosion from the liquid samples. Continuous corrosion was prevented by freezing the region of overlap between the sample and tungsten. Similar considerations dictated the use of pure (99.7%) high density recrystallized alumina
The sample was heated by an electrically powered furnace of large thermal capacity, the crucible being supported in an evacuable alumina furnace tube.

**IV: aii) The High Temperature Furnace**

The furnace used is a modification of one already in existence in the University of Leicester's Physics Department and its construction is shown in the figure on p. 38. There are two types of furnace bricks within the asbestos skin: high temperature refractory bricks (G-33 supplied by A. P. Green Fire Brick Co) and lower temperature bricks (G-28 also supplied by A. P. Green) having greater thermal insulating properties at lower temperatures. Any gaps between the high temperature bricks were filled with alumina cement (C.101 supplied by Thermal Syndicate Ltd).

Heating was supplied by four 'U'-shaped Kanthal Super-N elements (from Hall and Pickles Ltd) suspended from their relatively cool upper ends by asbestos clamps. The annular gap between the furnace tube and the high temperature bricks, in which the elements hung free, was plugged with ceramic fibre in an attempt to minimize convection currents within the furnace since these would have introduced temperature fluctuations and a loss of heat. This design enabled operational temperatures of up to $1650 \degree C$ to be achieved.

The elements were connected in series and supplied from a transformer capable of producing up to 7.2 kW at approximately 180 amps (see figure on p. 39). The input to the transformer was derived from the mains and adjusted by means of a variable transformer, the desired furnace temperature was achieved in this way. Such manual control gave adequate thermal stability, the temperature generally being constant to within $0.5 \degree C$ during the course of any one measurement. The sample temperature was determined using a platinum-platinum/10% rhodium thermocouple, the hot junction of which was positioned just above the liquid.
THE HIGH TEMPERATURE (1700°C) FURNACE

Power supply:
30 amps (max.) at 250 volts Input
180 amps (max.) at 38 volts Output
50 Hz
a) ELECTRICAL CONNECTIONS TO HIGH TEMPERATURE FURNACE

Primary
6:1 ratio
7.2 KVA transformer

38 V
180 A (max)

Secondary
variable voltage
0 - 290 V
30 A supply

flexible 200 A aluminised copper braid
heater elements (U-shaped)
aluminised contacts
aluminised copper strip connectors (12 mm x 3 mm)

b) SECTION THROUGH CAVITY OF HIGH TEMPERATURE FURNACE

mild steel supporting frame
G33 high temp. furnace bricks
G28 furnace bricks
aluminium reflector
6 mm "sindango" asbestos sheet
mild steel supporting frame

Four high temperature (1700°C)
"super N kanthal" elements
surface (as shown in figure 'B' on p. 41) and the reference junction kept in an ice/water bath. A closed end alumina sheath surrounded the thermocouple wires and their alumina insulators in order to protect the wires from contamination by sample vapour.

The temperature profile within the furnace tube could be altered quite rapidly by moving the furnace vertically with respect to it. To achieve this movement, which had particular usefulness during the filling of the probe, the furnace was mounted on an electrically operated screw jack.

IV; aiii) The Probe

The probe was made from a four bore alumina insulator of diameter 4mm and nominal bore 0.5 mm. Its lower end was fashioned as shown in figure 'A' on p. 41 using a diamond impregnated grinding wheel. The necessary four points of contact with the bulk sample were thus provided with the liquid forced up the four capillaries to overlap the tungsten wires (see figure 'B' on p. 41). The capillaries '1' and '4' were used to pass the primary current and the resulting potential difference measured using capillaries '2' and '3'. The probe design was chosen after many trials using liquid mercury (this development being mainly due to Professor J. van Zytveld) - the aim being to find a probe geometry that gave adequate output signal for reasonable primary currents and having a minimum sensitivity to small displacements of the probe tip within the crucible. In order to ensure reproducibility in the probe's position the crucible lid was made a close fit to both the crucible itself and the probe, and the peg (left at the probe tip after the grinding operation) was kept in contact with the crucible base. During trials of this arrangement no detectable variations were seen in measurements taken before and after the replacement of the probe.

Each probe, together with its associated crucible, was calibrated against doubly distilled mercury (having a resistivity of 95.78 μΩcm at 20°C) prior to a
The sections shown here illustrate:

**A** the arrangement of the probe tip after grinding,

**B** the filling configuration of the probe during an experiment.
high temperature experiment. Since the calibration experiments were performed at room temperature it was necessary to apply a correction to allow for thermal expansion. For this purpose the coefficient of linear expansion of alumina was taken as $8 \times 10^{-6} \text{K}^{-1}$ (from technical specifications supplied by Thermal Syndicate Ltd). Following calibration the crucible, thermocouple and probe were mounted in the apparatus, as shown in the figures on p. 43 (which also shows the vacuum and argon system used) with the probe tip just within the crucible lid but as far above the solid sample as possible. The probe was then filled as follows:

1) The whole vacuum jacket was evacuated to a pressure of about 0.03 torr and repeatedly filled with argon and re-evacuated to remove air and water vapour.

2) Whilst maintaining a vacuum the temperature of the furnace was raised by 400 - 500°C at a rate of approximately 250°C per hour. This ensured that all alumina in the region of the sample was thoroughly outgassed.

3) The apparatus was then filled with argon to a pressure of one atmosphere and the same rate of temperature increase continued. During this phase of the procedure the furnace was positioned with respect to the sample such that the hottest zone lay somewhat above the crucible and therefore nearer the tungsten wires.

4) At a point just below the liquidus temperature of the sample, the apparatus was evacuated to a pressure of about 0.08 torr to minimize the possibility of including cavities within the liquid.

5) Having maintained an indicated temperature of at least 40°C above the sample's liquidus temperature for about twenty minutes to ensure that the sample was molten and well mixed, the probe was slowly lowered into the liquid until its tip was firmly grounded on the crucible base.

6) Then, with valves $V_1$ and $V_2$ closed (figure on p.43), argon was slowly admitted into the outer chamber through valve $V_A$. The differential pressure forced liquid metal up the probe capillaries to the region of the tungsten wires (about 18 cm
SECTI0N THROUGH VACUUM
HEAD AND DIAGRAMATIC
VIEW OF VACUUM SYSTEM
(High Temperature
Vertical Resistivity)

2 mm diameter tungsten
dipping rod

Wilson seal

Pirani
gauge head

Rotary Pump

cooling water
outlet and inlet
Diffusion Pump
(when used)

Bourdon gauge

Argon
Inlet

V_1

V_2

V_3

cooling water

Rotary Pump

Diffusion Pump

(when used)

Copper leads
to Probe
electrodes

Araldite
seal

Pt/Pt - 10% Rh
thermocouple
leads

'O'-ring
seal

Pt/Pt - 10% Rh
thermocouple,
sheathed in alumina

Alumina support
column

Four-bore alumina
Probe

Alumina crucible
and lid

Liquid metal

Recrystallised alumina
furnace tube

Speedi-valves
above the base of the crucible) where the ambient temperature was much lower. The furnace was immediately moved downward to bring the crucible into the centre of the hot zone, and thereby reduce the temperature in the region of the sample-tungsten overlap to well below the sample freezing point. Freezing this region not only prevented continuous corrosion of the tungsten but also stopped the migration of dissolved tungsten towards the sensitive probe tip. The length of overlap was usually about 1-2 cm.

To ensure the stability of the liquid sample during the course of measurements, a pressure of about one atmosphere was maintained in the outer chamber. A simple test on each sample for the presence of significant cavities in the liquid was performed by observing the output signal as a function of system pressure, any systematic variation indicating that such cavities were present and that the measurement was unreliable.

IV. aiv) Measurement Circuitry and Technique

The use of a method demanding the passage of a continuous current through the specimen was not practicable due to Peltier heating effects. The current crossing the tungsten-solid sample-liquid sample junctions in the current leads caused heating of one set of junctions and cooling of the other. Temperature variations thereby introduced into this region of the probe affected the junctions in those leads used for the measurement of the potential difference, giving rise to spurious thermoelectric e.m.f.s. Because of the reversible nature of this phenomenon, these e.m.f.s could not be cancelled out by the normal procedure of primary current reversal. The temperature of the junctions in the potential leads changes only gradually, however, due to their finite thermal capacity and to the (non-infinite) thermal conductivity of alumina. In order to take advantage of this a current step technique was evolved. Thus if a primary current of the form shown in figure 'A' on p. 45 is applied to the sample, the observed voltage across the
HIGH TEMPERATURE RESISTIVITY: THE CURRENT STEP TECHNIQUE

Wang 600

Interface

Delay Circuit
Current supply

D.V.M.

Sample

Primary current

0

-0.5 1.0 1.5 2.0

time (s)

A

Potential readings
(recorded by Wang 600)

0

-0.5 1.0 1.5 2.0

V

B

time (s)
potential leads will be of the form 'B'. The voltage change at this step is not affected by these spurious thermoelectric e.m.f.s.

The measurement circuitry employed is shown in the figure on p. 47. The primary current was supplied by a 0-4 amp constant current power supply unit (Coutant LA 400.2) which was chosen for its good response to sudden loading (the output current reached its steady state value within 0.2 seconds of the circuit having been completed). Successive completions of the primary current circuit revealed no detectable variation in output current. The digital voltmeter, or d.v.m. (Solartron A200), used to measure all output signals had an accuracy of ±1μV and was interfaced with a programmable desk calculator (Wang 600). Hence voltages received by the d.v.m., having been channeled through a selector switch, could be stored in the calculator's memory for later recall and use. Voltages displayed by the d.v.m. were updated every 0.1 second, thereby enabling the rapid acquisition of an adequate number of data points.

The 'Wang' was programmed such that an initiating command from the operator caused a trigger pulse to be sent to an interface unit and a delay circuit. From this time the calculator begins receiving information from the d.v.m. On reaching the delay unit the pulse activates a timing circuit which, after about 0.5 second, causes a reed switch to close thereby turning on the current supply to the sample. Readings continue to be stored for a further period of about 1.5 seconds, after which the reed switch is opened and the system re-set. The calculator has also been programmed to perform some analysis of its stored data. Initially it searches for a discontinuity in the data which corresponds to the time at which the current supply was turned on. The first three points after the reed switch closure are assumed to be unreliable due to the imperfect transient response of the d.v.m. and current supply unit and are therefore ignored. The program is then designed to fit straight lines to both pre- and post-step points by the method...
MEASUREMENT SYSTEM AND D.C. CIRCUITRY

(High Temperature Vertical Resistivity)

PRINTED PAPER OUTPUT

WANG INTERFACE UNIT

+5 V pulse

WANG 600 PROGRAMMABLE CALCULATOR

SIGNAL DELAY UNIT AND REED SWITCH

Reversing Switch

Standard Resistor (.005 Ω)

SWITCHING SYSTEM

"SAMPLE"

THERMOCOUPLE HOT JUNCTION

THERMOCOUPLE COLD JUNCTION

SOLARTRON A200 DIGITAL VOLTMETER

STABILISED D.C. POWER SUPPLY

#(LA L00.2)
of least squares, thus providing a way of calculating the voltage change at the instant that the current circuit was completed.

At any one temperature this procedure was repeated four times in the measurement of both the current and potential difference with the current flowing in each direction. This allowed a cancellation of spurious e.m.f.s other than those discussed above. Measurement of the primary current involved a straightforward use of a standard resistor as a shunt. Currents were typically in the region of one amp, giving an output voltage from the potential difference leads of the order of 100 μV.

The value of the temperature was obtained from the thermocouple in the usual way – measured voltages being interpreted in terms of temperature using British Standard tables (B.S. 1826: 1952). Before each measurement sequence the apparatus was allowed to stabilize for at least ten minutes, a drift of 2°C being the maximum tolerated in this period. The temperature was recorded immediately before and after each resistivity measurement and the mean of the two values taken as the experiment temperature and used to determine the necessary correction for the probe’s thermal expansion.

IV: av) Sample Details

The pure metals nickel, cobalt and silver were supplied by Koch Light Laboratories Ltd and had a nominal initial purity of 99.998%. The palladium was supplied by Johnson Matthey Chemicals Ltd who reported typical batch purities better than 99.99%.

The constituents of each alloy composition studied were weighed to an accuracy of ± 0.002 gm, then rinsed in acetone to remove all traces of grease before being transferred to an alumina crucible. The alloys were prepared in situ, the sample being heated to about 50°C above the highest melting point of those constituents included (see the figures on p. 49 and Hansen, 1958).
PHASE DIAGRAMS OF:

A) NICKEL-COBALT

B) SILVER-PALLADIUM

[Diagram of phase diagram for Nickel-Cobalt]

WEIGHT PERCENT NICKEL

0 10 20 30 40 50 60 70 80 90

0 10 20 30 40 50 60 70 80 90

ATOMIC PERCENT NICKEL

0 10 20 30 40 50 60 70 80 90

ATOMIC PERCENT PALLADIUM

0 10 20 30 40 50 60 70 80 90

WEIGHT PERCENT PALLADIUM

0 10 20 30 40 50 60 70 80 90

ATOMIC PERCENT PALLADIUM

0 10 20 30 40 50 60 70 80 90

TEMPERATURE °C

0 200 400 600 800 1000 1200 1400 1600

0 200 400 600 800 1000 1200 1400 1600

1115°

MAGN. TRANSF

420°

360°

1495°

1452°

1552°

(Ag, Pd)
Sophisticated stirring procedures were not required due to the high temperatures involved and the complete miscibility of the components (Hansen, 1958). No evidence of inhomogeneity was observed: a time-dependant variation on the results at any given temperature would be expected.

IV: avi) Errors

The error inherent in this method of resistivity measurement is difficult to quantify but is estimated at 2%. Contributions may arise from movement and distortion of the probe and crucible at high temperatures and the uncertainty in the determination of the voltage step (this being due not only to the scatter in the points but also to the uncertainty in estimating the time of the current step).

During the melting and probe filling procedure there was a considerable time in which the apparatus was evacuated. Some sample vapourization is unavoidable under such conditions but will not affect the composition of an alloy unless its constituents have significantly different vapour pressures. It is clear from the figure on p. 51 that nickel-cobalt alloys should be unaffected whilst silver losses from silver-palladium alloys may be severe at high temperatures. In an attempt to guage the effect of such a differential loss the sample remaining after an experiment was carefully weighed (allowance being made for the known overlap with the tungsten leads), any loss being ascribed to silver. Using this information it was possible to estimate the actual composition during the experiment itself. As a check on this, and on levels of impurity, samples from two alloys were commercially analysed (by the Butterworth Microanalytical Consultancy Ltd). The results confirmed the correction procedure adopted and also indicated that a tungsten impurity of less than 0.1 atomic % could be assumed (an estimate of 0.01 atomic % was obtained by direct examination of the sample-tungsten overlap). In view of these approximations it is possible to give silver concentrations to only ± 0.4 atomic %, whilst the concentrations of nickel and
VARIATION OF VAPOUR PRESSURE WITH TEMPERATURE FOR Te, Sb, Ag, Ni, Pd and Co. (↑ Indicates melting point.)
The possible error due to the increasing electrical conductivity of alumina with both increasing temperature and diffusion of metal ions into the alumina was neglected on the basis of the following test. At the conclusion of a series of measurements the probe was slowly raised until clear of the bulk sample, liquid in the capillaries, however, remained (this was confirmed by breaking open the probe when cool). In this configuration it was found impossible to generate a detectable voltage at the potential leads, even for primary power levels well in excess of those usually employed.

IV; avii) Solid Metals

Although primarily designed for liquid state experiments and so not particularly suited to determine the resistivity of solid metals, such experiments were attempted. The extra errors introduced into the results are again difficult to quantify accurately since they depend strongly on changes in sample geometry during and after freezing. A total error of 3% was used as a reasonable estimate following the examination of the variation between repeated cycles of freezing and melting. This assumption was supported by the comparison of resistivity values for pure solid nickel and cobalt with other published values (see chapter VI) and by undertaking some experiments, described below, more suited to the solid state.

These experiments employed a very simple design: a single bore alumina tube (outside diameter 3mm, nominal bore 1.5 mm) was dipped into the liquid sample, using the apparatus previously described, and a column of liquid forced up the tube under argon pressure. The temperature was rapidly lowered to approximately 200°C below the sample's freezing point and held there for at least 20 hours to anneal. After cooling to room temperature, four holes (nominal diameter 0.85 mm) were drilled through the solid rod extending over approximately 8 cm. These
provided firm points of attachment for tungsten wire electrodes. Once mounted in the apparatus with the hot junction of a platinum-platinum 10% rhodium thermocouple suspended midway between the two inner contact holes, the resistance of the sample was determined using a four point method and the measurement circuitry described above. The entire experiment was conducted at a pressure of about \(10^{-3}\) torr.

In order to evaluate the resistivity of the sample at high temperatures an allowance had to be made for the thermal expansion of the sample. This introduces a possible error since the expansion coefficients were only available at relatively low temperatures (Weast, 1975) and alloy values had to be estimated from pure metal data. No detectable irreversible change in sample dimensions was observed unless the sample temperature rose to within about 150\(^{\circ}\)C of the melting point. A correction was also necessary to compensate for the presence of small cavities in the solid rod. This was accomplished by determining the density of the sample at room temperature, comparing it with standard values and scaling the resistivity accordingly. Such a correction never exceeded 2.5%, and a total error of 3% for the resistivity values obtained seems a reasonable estimate. The high temperature solid resistivity values obtained in this way indicated that, within assumed experimental errors, the method of freezing the sample described above gave solid state information of adequate reliability.

Part b) The Measurement of Thermopower

Only one thermopower measurement was undertaken, on the liquid alloy palladium + 30 atomic % silver, since it was desired only to supplement the largely complete data reported by Dupree (Dupree et al, 1977; Dupree, 1978). The description of equipment and techniques will therefore be brief since a full account occurs elsewhere (Dupree, 1978). There are many features that are similar to the high temperature resistivity equipment; alumina being used for all sample
containment and electrical insulation, tungsten was used as the reference electrode material, a large electrically powered "muffle" furnace was employed for most of the heating (up to 1500°C) and temperatures were measured using platinum-platinum/13% rhodium thermocouples.

IV: bii) The Muffle Furnace and Vacuum System

The construction of the muffle furnace is shown in the figure on p. 55. It employs the same type of insulating bricks and alumina cement as did the resistivity furnace. The furnace is heated, however, by eight horizontal silicon carbide heating rods (5/8 inch diameter Crystolon Hot Rods supplied by Morganite Electroheat Ltd) supported at each end by pads of ceramic fibre. The heating rods were connected in series and supplied with power via a three phase, phase angle fired half controlled thyristor and rectifier bridge circuit (up to 440 volts and 30 amps d.c.). Power to the furnace was controlled by a servo circuit which adjusted the power input, via the thyristor bridge, so as to reach and then maintain the required temperature (temperature feedback being from a thermocouple situated within the muffle furnace itself). A second servo loop was used to set a maximum to the current level supplied to the furnace.

The furnace tube, which formed a vacuum jacket around the sample, was of high purity alumina (a "Purox" tube of nominal bore 89 mm supplied by Morgan Refractories Ltd). Since the manufacturers specified a maximum rate of temperature change of 100°C per hour, a programmer (type J.A. 06 supplied by Eurotherm Ltd) was connected to the main controller. This functioned by injecting a slowly decreasing ramp voltage in series with, and aiding, the feedback thermocouple.

The arrangement of the vacuum and argon system is shown in the figure on p. 56. Pressures of the order of $10^{-5}$ torr were attainable at 1500°C, but outgassing during the initial period of heating caused a deterioration in the vacuum
HIGH TEMPERATURE THERMOPOWER: MUFFLE FURNACE

0.97 m

Silicon carbide heating element

To Vacuum Pumps

Element support, ceramic fibre

12 mm asbestos outer case

High temperature furnace bricks

Low temperature furnace bricks

Alumina furnace tube

End assembly

Molybdenum heat shields
HIGH TEMPERATURE THERMOPOWER: VACUUM SYSTEM

Overpressure release device (Mercury)

Bourdon Gauge (0-2 atm)
Capsule Dial Gauge (0-20 torr)

Penning Gauge

Muffle Furnace

Furnace Tube

'O'-ring seal

Water cooled end assembly

Controls for dippers

Feedthroughs for signal and power leads

Argon inlet

Valve "A"

Magnetic Valve

Roughing Valve

Butterfly Valve

Back ing Valve

Pirani Gauge

Rotary Pump

Vent to atmosphere

Vent to atmosphere

2" oil diffusion pump
to a level nearer $10^{-4}$ torr. The penning gauge control unit was connected to the programmer via a pressure activated switch unit in such a way that should the pressure increase as far as $2 \times 10^{-4}$ torr, the programmer would change to a temperature run-down mode and only revert to a run-up mode if the vacuum improved to better than $5 \times 10^{-5}$ torr.

When required, the furnace tube was filled with argon to a pressure of a few centimetres of mercury above atmospheric pressure. To limit this overpressure and to allow for the expansion of the gas as the furnace temperature is raised, a mercury filled non-return overpressure release device was connected to the system.

**IV: biii) The Crucible and Carriage**

The alumina crucibles used to contain the samples were supplied in the form of "pipe-boats" (by Thermal Syndicate Ltd) as shown in the figure on p. 58. Also in this figure is a schematic representation of the essential features of the carriage which supported the crucible when in the furnace tube. The carriage was positioned in the furnace tube by molybdenum rods attached to the brass end plate which sealed off the end of the furnace tube. These rods also served to support the array of molybdenum disc heat shields necessary to prevent excessive heat loss down the long axis of the furnace tube. The thermocouples, within alumina insulators and a closed end sheath, pass through holes drilled in the two molybdenum heat sinks until they are in firm contact with the bowls of the crucible itself (this being a region of uniform temperature due to the presence of the surrounding heat sink). Heat losses from the thermocouple tip were kept to a minimum by using the thinnest practicable thermocouple wires and alumina of the smallest cross section.

When required, the tungsten contact electrodes (or "dippers") were dipped into the liquid surfaces by rotating the dipper rods. Two meshing gears affixed to the outer ends of the tungsten rods (i.e. outside the furnace tube assembly)
HIGH TEMPERATURE THERMOPOWER: SCHEMATIC DIAGRAM OF CARRIAGE OPERATION AND SAMPLE CONTAINER

Molybdenum clamp holding dipper in contact with dipper rods

Tungsten heater wound on threaded alumina former

Molybdenum heat sink

3 mm dia. tungsten dipper rod in alumina sheath

Tungsten dipper (1 mm dia.)

Pt/Pt-13% Rh thermocouple in alumina insulators in alumina sheath

Alumina sample container

26 mm

150 mm

0.0.19 mm

0.D. wall 8 mm 2 mm

wall 1.5 mm
ensured that the dippers moved down in synchronism, the ends touching the liquid surfaces simultaneously.

Small molybdenum wound difference heaters were used to establish the sample temperature (about $40^\circ C$ above the temperature of the muffle furnace) and required temperature gradients. These were powered, via a 5:1 power transformer to match impedances, from mains supplied single phase thyristor power units driven by temperature controllers (type 040 supplied by Eurotherm Ltd). Temperature feedback for these controllers being derived from the two thermocouples described above. Since the controllers not only sensed and allowed for the difference between the desired and actual temperatures but also the derivative and integral of this difference, it was possible to set and maintain the temperatures at either end of the crucible to within $0.2^\circ C$. Temperature differences were normally up to $\pm 25^\circ C$.

**IV: biv) Filling the Crucible**

Solid pieces of the sample were placed in both boats of the crucible before the carriage was inserted in the furnace tube. This was then evacuated and the furnace heated to above the melting point (or appropriate liquidus temperature). Argon was then admitted to force some of the liquid sample along the interconnecting crucible tube, the two parts meeting near the centre. For those samples having components of high vapour pressure (i.e. about $10^{-2}$ torr) at the experiment temperature, such as silver-palladium alloys, the furnace tube was only evacuated to a pressure of about 10 torr for ten minutes before and after melting, having been filled with argon during most of the heating process to avoid excessive sample loss.

**IV: bv) Measurement System and Procedure**

All leads leave the furnace tube via feedthroughs in the carriage end plate, the subsequent circuitry is shown schematically in the figure on p. 60. Wherever it was necessary to make junctions between different metals or provide a reference temperature for the thermocouples, ice baths were used to eliminate spurious
HIGH TEMPERATURE THERMOPOWER:
TEMPERATURE CONTROL AND SIGNAL MEASUREMENT SYSTEMS

Wang 600

Interface

Digital Voltmeter

Selector switch

copper leads

controller (1)

Power unit (1)

controller (2)

Power unit (2)

Power unit (1)

Furnace

Thyristor Power Unit

Main controller
(Select temp., max. current)

Programmer
(Select rise/fall rate of temp.)

Temperature Feedback

Ice bath

Heater (1)

Muffle

Ice baths

Heater (2)

Tungsten to dippers
thermoelectric e. m. f. s. The various signals for the d. v. m. could be reversed in polarity to allow for errors in its zero setting.

Measurement of the Seebeck e. m. f. for the sample circuit was difficult since the dipping period was of necessity short (it had been found in earlier experiments - Dupree, 1978 - that the reading could only be relied on for a total dipping period of 70 to 80 seconds. After this the magnitude of the observed e. m. f. decreased, this being attributed to reference electrode contamination). In order to overcome this problem the d. v. m. was again interfaced with a Wang 600 calculator, allowing the rapid acquisition of readings. Storage of data was initiated, upon the operator’s command, as soon as contact between the dippers and sample had been obtained. The calculator was also programmed to evaluate and print the mean and standard deviation of each series of readings. It was found that a contact period of about 5 seconds was adequate, further time giving no significant advantage. During the first few tenths of a second after dipping readings were unstable as the tip of dipper approached thermal equilibrium with the surrounding liquid, and were therefore disregarded. The slight contamination of the dipper tip during a normal short contact period does not significantly affect the Seebeck e. m. f. since the contamination occurs only in a small region of uniform temperature where the thermoelectric law of intermediate metals may be applied.

The experimental procedure was as follows:

1) Having filled the crucible as described above, the difference heaters were used to bring the bowl ends of the pipe to their required temperature. The apparatus was left for about one hour to ensure the complete thermal stability of the sample (initial tests had shown that reproducible results could be obtained after only one quarter of this period had elapsed).

2) The dippers were lowered until the tips just made contact with the liquid sample.
3) The calculator was instructed to begin storing the d.v.m. readings, and to calculate and print out their mean and standard deviation.

4) After about five seconds the dippers were removed.

5) The measurements were repeated with the signal polarity reversed.

This entire process was then repeated for a number of temperature differences, the average of the two end temperatures taken as the experiment temperature. The slope of the Seebeck e.m.f. versus temperature difference graph gave the difference between the absolute thermopowers of the sample and tungsten reference electrodes as in equation (I:11). Values for tungsten were obtained from the work of Cusack and Kendall (Cusack and Kendall, 1958; also Bradley, 1962) and are given in the table and figure on p. 63 and p. 64 respectively.

IV: Sample Details

The sample materials were obtained from the same suppliers and in the same grades as for the resistivity measurements. The alloy was prepared in the high temperature resistivity furnace, the constituents having been weighed to within \( \pm 0.002 \) gm and transferred to an alumina crucible. The sample was heated, under argon, to 1620°C and held at this temperature for one hour before cooling. To allow for any inhomogeneities, the ingot was cut into pieces and mixed before its transfer to the thermopower apparatus. No evidence of inhomogeneity was observed in the results (the phenomena to be expected are a large zero error in the e.m.f. versus temperature difference graph and irreproducibility in the e.m.f. at each experimental point).

IV: Errors

The absolute thermopower of tungsten has an estimated uncertainty of \( \pm 1 \muVK^{-1} \) associated with it and will give rise to a systematic error in all results. A source of error will also arise during the determination of the slope of the e.m.f. versus temperature difference plot. The statistical scatter of points is primarily due to
### The Absolute Thermopower of Copper, Platinum and Tungsten

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>Copper ((\mu V K^{-1}))</th>
<th>Platinum ((\mu V K^{-1}))</th>
<th>Tungsten ((\mu V K^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.83</td>
<td>-5.28</td>
<td>1.07</td>
</tr>
<tr>
<td>400</td>
<td>2.34</td>
<td>-7.83</td>
<td>4.44</td>
</tr>
<tr>
<td>500</td>
<td>2.83</td>
<td>-9.89</td>
<td>7.53</td>
</tr>
<tr>
<td>600</td>
<td>3.33</td>
<td>-11.66</td>
<td>10.29</td>
</tr>
<tr>
<td>700</td>
<td>3.83</td>
<td>-13.31</td>
<td>12.66</td>
</tr>
<tr>
<td>800</td>
<td>4.34</td>
<td>-14.88</td>
<td>14.65</td>
</tr>
<tr>
<td>900</td>
<td>4.85</td>
<td>-16.39</td>
<td>16.28</td>
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<tr>
<td>1000</td>
<td>5.36</td>
<td>-17.86</td>
<td>17.57</td>
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<tr>
<td>1100</td>
<td>5.88</td>
<td>-19.29</td>
<td>18.53</td>
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<td>1200</td>
<td>6.40</td>
<td>-20.69</td>
<td>19.18</td>
</tr>
<tr>
<td>1300</td>
<td>6.91</td>
<td>-22.06</td>
<td>19.53</td>
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<tr>
<td>1400</td>
<td>-23.41</td>
<td></td>
<td>19.60</td>
</tr>
<tr>
<td>1600</td>
<td>-26.06</td>
<td></td>
<td>18.97</td>
</tr>
<tr>
<td>1800</td>
<td>-28.66</td>
<td></td>
<td>17.41</td>
</tr>
<tr>
<td>2000</td>
<td>-31.23</td>
<td></td>
<td>15.05</td>
</tr>
</tbody>
</table>

(Cusack and Kendall, 1958)
THE ABSOLUTE THERMOPOWER OF TUNGSTEN

(cusack and kendall, 1958)
errors in the measured temperature difference - this being the difference of two large quantities and their associated errors. The contribution resulting from inaccuracies in the measurement of the Seebeck e.m.f. was small. A small systematic uncertainty due to the fact that the thermocouple junctions were not in perfect thermal contact with the ends of the sample was tolerated in preference to the unpredictable consequences of thermocouple contamination. The combined effects of all these potential errors mentioned above, for the measurement undertaken here, was estimated as $\pm 3 \, \mu V K^{-1}$.

After post-experiment analysis (by the Butterworth Microanalytical Consultancy Ltd) the sample was found to contain 0.25 atomic % tungsten; previous test experiments had shown that levels in excess of this produced no observable effects in the experimental results (a time-dependance of the slope of the e.m.f. versus temperature difference graph would be expected). The chemical analysis also obviated the need to estimate the silver loss during crucible filling by weighing sample plus electrodes both before and after the experiment.
CHAPTER V

Measurement of the Resistivity and Thermopower of Liquid Ni–Te

The experimental techniques described here are similar to those of the previous chapter in that the resistivity is measured using a four-point d.c. method and the thermopower using the Seebeck e.m.f. produced by small temperature differences. The equipment, however, has been designed to allow the measurement of the resistivity and thermopower of a common sample at a given common temperature. Principle differences between this technique and those described earlier arise from the problem of sample containment. It was possible to use vitreous silica (or fused quartz, being 99.9% SiO$_2$, supplied by Thermal Syndicate Ltd and Heraeus Silica and Metals Ltd) for the sample cell and furnace vacuum jacket because of the lower experiment temperatures ($1250^\circ$C maximum) thus enabling a more flexible approach to apparatus design. Electrical insulation within the vacuum jacket was still provided by alumina insulators.

After many preliminary investigations it was found that corrosion problems eliminated all those refractory conductors examined except spectroscopically pure graphite, which appeared inert with respect to this alloy system at these temperatures. It was therefore necessary to make all electrical contact through a graphite barrier.

V: ii) The Furnace and Vacuum System

The construction of the electrical resistance furnace and the arrangement of the vacuum and argon system are shown in the figures on p. 67 and p. 68 respectively. Two separate 18 cm elements composed of 20 swg Kanthal Al wire (supplied by Hall and Pickles Ltd) were wound onto the central aluminous porcelain tube (length 420 mm and bore 45 mm, supplied by Thermal Syndicate Ltd). The windings were encased in alumina cement (c101, from Thermal Syndicate Ltd) to prevent their possible movement during a heating cycle, and the assembly surrounded by a
THE THERMOPOWER FURNACE

Vacuum head

Silica vacuum jacket

Aluminous porcelain tube

Alumina C101 cement

Mullite bricks

6mm. Asbestos sheet

Top element supply

Eurotherm P.I.P. / S.C.P. temperature controllers or variable voltage A.C. supplies

Bottom element supply

Top heater element (Kanthal A1)

Bottom heater element (Kanthal A1)
SECTION THROUGH VACUUM HEAD AND
DIAGRAMMATIC VIEW OF VACUUM SYSTEM.
(Thermopower and Resistivity.)

Wilson seal
2mm. Tungsten wire
Leads to sample tube through 'araldite' seals
Cooling water
Silica plug
Silica filling tube
Liquid metal
Silica capillary sample tube
Silica vacuum jacket

Argon inlet
0-20 Torr gauge
Compound Gauge
Piranni gauge head
Speedivalve
To pump

Cooling water

To pump
layer of thermally insulating Mullite bricks (M128, supplied by Morgan Refractories Ltd) within a 6mm asbestos skin. The manufacturer's specifications show a maximum operating temperature of $1350^\circ C$ for Kanthal A1, this, it was found, enabled a maximum experiment temperature of $1250^\circ C$ to be reached within the furnace tube.

Power was supplied to the elements from the mains via two indicating temperature controllers (PID/SCR type with thyristor output stage, supplied by Eurotherm Ltd). Temperature feedback for these came from chromel-alumel thermocouples whose hot junctions were supported as near those electrodes used in the measurement of the Seebeck e.m.f. as possible. It was thereby possible to maintain a uniform temperature gradient across the central region of the furnace tube that was controllable to within $\pm 1^\circ C$ and constant over the period of one set of measurements to within $\pm 0.5^\circ C$. A further degree of freedom in the control of the temperature profile within the vacuum jacket was obtained by mounting the furnace on a manually operated screwjack, the principle being the same as that employed in the high temperature resistivity furnace.

During the long heating and cooling periods between room and experiment temperatures the temperature controllers were driven mechanically with the aid of a d.c. motor connected to each of the two controllers via a gearing mechanism. In the high temperature thermopower experiments, control was effected electronically through the temperature feedback circuits, in this case it is by the direct variation of the demand temperature. The rate of temperature rise or fall was governed by the magnitude and direction of the d.c. voltage applied to the motors.

In view of the vapour pressure and toxicity problems presented by tellurium, it was essential to keep the vacuum head as cool as possible to ensure rapid condensation and prevent tellurium vapour reaching the guages and rotary pump.
In addition to the cooling system associated with 'O'-rings, a further water collar was clamped around the vacuum jacket itself (just above the furnace) and a "baffle" plate covered that part of the silica tube mouth not already occupied by leads. No tellurium deposit was detected beyond the vacuum head at any time.

V: iii) The Sample Cell

The figure on p. 71 shows the cell and associated electrode assembly; its position within the furnace is shown in the figure on p.68. The cell was made from a length of thick walled silica capillary (outer diameter 5 mm and nominal bore 0.75 mm) and a length of normal walled silica tubing (outer diameter 8 mm and bore 6 mm). Four holes (with diameters of approximately 0.9 mm) were ultrasonically drilled through the wall of the capillary tube to meet the central column at distances of 3, 6, 9 and 12 cm from one end. The outer ends of these holes were countersunk to a depth of about 0.5 mm using a tapered fine carborundum stone. Rods of spectroscopically pure graphite were then accurately turned to make plugs having a shank diameter as close to the hole diameter as possible. Due to the nature of the ultrasonic drilling technique the holes were slightly tapered; this, together with the countersink, ensured a tight fit.

Having wedged a graphite plug into each of the four holes in the capillary wall, the capillary tube and normal walled filling tube were then fused together with a 10 mm insert of the capillary tube (at the graphite plug end) into the filling tube. Each cell so formed was calibrated against doubly distilled mercury by pumping the mercury up into the capillary. The calibration constant has to be corrected for the thermal expansion of the cell during an experiment; for this purpose the coefficient of linear expansion of silica was taken as $0.54 \times 10^{-6} \text{K}^{-1}$ (from technical specifications supplied by Thermal Syndicate Ltd).

Following calibration the lower end of the capillary was sealed off about 8 cm below the lowest drilled hole. An electrode assembly consisting of a sheet of
THE SILICA CELL & ELECTRODE ASSEMBLY

- Silica filling tube
- Silica plug
- Liquid metal
- Chromel
- Alumel
- Copper (or Molybdenum or Tungsten)
- Stainless steel clamping plates
- Molybdenum strip
- Molybdenum sheet
- Liquid metal
- Countersunk graphite plug
- Silica capillary
- Electrode 1
- Electrode 2
- Electrode 3
- Electrode 4

Silica capillary tube (I.D. 0.75 mm)
molybdenum (35 mm x 20 mm x 0.05 mm) was clamped, under tension between a pair of stainless steel plates bolted together with two 6BA stainless steel nuts and bolts, around each of the plugs. In addition to this, a thin strip of molybdenum sheet was clamped between the plates passing around the capillary tube at a position corresponding to the drilled hole. The chromel-alumel thermocouple wires were sandwiched between the molybdenum sheet and strip immediately over the plug, the junction being formed by twisting the ends of the two wires together and flattening by cold working (so enabling better thermal and electrical contact and reducing the overall size of the junction). A third wire, usually tungsten, was also clamped under the molybdenum strip; these acted as primary current leads and, should the more fragile thermocouple wires fail, the potential difference leads.

With the electrode assemblies in place and the prepared solid sample loaded into the filling tube, a silica plug was inserted into the filling tube. This was made from a length (15–20 cm) of closed end silica tubing whose outside diameter was slightly less than the internal diameter of the filling tube. The use of such a plug, whilst allowing the evacuation and pressurization of the cell, reduced the loss of tellurium vapour from the bulk sample.

The apparatus was then mounted into the vacuum chamber and furnace and the cell was filled as follows:

1) The apparatus was evacuated to a pressure of 0.02 torr and then repeatedly filled with argon and evacuated in order to clear the system of air and water vapour.

2) Whilst evacuated, the furnace temperature was raised at a rate of 300°C per hour to about 250°C to ensure the outgassing of the apparatus. Argon was then admitted to a pressure of 0.8 atmosphere (it had been found that such an initial value was sufficient to prevent the system pressure exceeding one atmosphere
at experiment temperatures).

3) The furnace temperature was then raised, at the same rate as above, to a level generally at least $150^\circ C$ above the estimated liquidus temperature (see V:vi). During the whole heating process the furnace is raised, relative to the vacuum jacket, to bring the solid sample in the filling tube nearer the central regions of the furnace tube. This was especially important for alloys having a high liquidus temperature due to a high nickel content.

4) The system was evacuated to at least 0.1 torr as rapidly as was possible without forcing any liquid sample past the silica plug. Argon was then introduced into the filling tube (i.e. valves $V_1$ and $V_2$ closed, $V_A$ open) until a pressure had been reached such that electrical contact was registered between electrodes '1' and '4' (usually less than 20 torr). Valve $V_2$ was then opened and the whole system brought up to one atmosphere of argon. By filling in the way described above it was possible to minimize the loss of sample by vaporization or leakage.

5) The furnace was lowered to bring the four electrodes into the centre of the furnace tube.

Significant cavities introduced within the liquid sample in the capillary by this filling method could be detected by observing the pressure dependance of the potential difference signal: a systematic variation indicating the presence of such cavities and the consequent unreliability of data.

V: iv) Measurement Circuitry and Technique

The primary current power supply and the digital voltmeter are employed in the same way as they were for high temperature resistivity measurements (IV: aiv) whilst the operational mode of the programmable calculator resembles that used for the high temperature measurement of thermopower (IV: bv). Resistivity measurements were much simplified in this system since rapid data acquisition was no longer vital due to the sample geometry and the low primary currents used.
Readings were therefore recorded from the d.v.m. and analysed using the program developed for thermopower measurements. A refinement to the program enabled voltages from the chromel-alumel thermocouples to be converted to their corresponding temperatures before the print-out stage. A cubic equation was derived for this purpose from standard calibration values (e.g. Weast, 1975):
\[0.00135 V^3 + 0.071 V^2 + 24.565 V + 11.1 = T (^\circ C)\]

where \( V \) is the recorded thermocouple voltage and \( T \) the corresponding temperature (accurate to \( \pm 0.15^\circ C \)).

The measurement circuitry, as shown in the figure on p. 75 was designed to allow the maximum practicable flexibility. The resistivity of the sample could be measured using either a thermocouple wire or a tungsten wire as potential difference leads. The Seebeck e.m.f. of the sample could be measured against any two of the chromel wires (see (V: v) below) or against copper reference leads (assuming the tungsten wires were replaced by copper wires and noting that the secondary lead feedthroughs were of copper). All junctions between dissimilar metals outside the vacuum system were immersed in ice/water baths. A switching system was used to select the relevant voltage for display on the d.v.m.

The experimental procedure was as follows:

1) Having filled the cell as described above, the two temperature controllers were adjusted to give the required junction temperatures. The apparatus was left for approximately 20 minutes to ensure the thermal stability of the sample (adequate stability was usually attained after about half of this period has elapsed).

2) The calculator was then instructed to perform its storage and analysis routine on the e.m.f.s from each of the electrode thermocouples in turn. Similar measurements were then taken of the sample Seebeck e.m.f. and the series completed by recording the temperatures again, which seldom varied from their
MEASUREMENT SYSTEM AND D.C. CIRCUITRY.
(Thermopower and resistivity)

Secondary leads for current input or auxiliary resistivity and thermopower measurements.
initial values by more than $0.4^\circ$C.

3) Since a differential method for the thermopower was to be used, the Seebeck e.m.f. in any one sequence was measured in each of five conditions: one junction, '4' say, was maintained at a constant temperature taken as the experiment temperature, whilst the other, '1' say, was held at five different temperatures in turn - two being above the experiment temperature, one approximately equal to it and two below. The slope of the Seebeck e.m.f. versus temperature difference graph plotted from these measurements gave the difference in the absolute thermopowers of the sample and chromel. When junctions '1' and '4', and therefore '2' and '3', were at the same temperature, an additional set of readings were taken prior to recording the Seebeck e.m.f. to give the primary current and resulting potential difference. These readings were of course repeated with the primary current reversed to eliminate spurious thermoelectric e.m.f.s, the average being used in calculations.

V: v) The Absolute Thermopower of Chromel

Having measured the e.m.f. generated by the sample-chromel couple it is necessary to know the absolute thermopower of chromel in order to evaluate the thermopower of the sample. Two batches of chromel wire were used during the series of experiments (both supplied by British Driver-Harris Co Ltd under the trade name T1 alloy, alumel being T2 alloy). In a series of experiments the first batch was calibrated against copper and platinum, and the second batch calibrated against platinum.

A junction was formed by twisting together the ends of chromel, alumel, copper, platinum and platinum/10%rhodium wires and this was clamped between two stainless steel plates, which were then bolted together. The wires were electrically insulated using alumina insulators, and the whole assembly mounted in a furnace and vacuum jacket similar to those described above. Using these
couples, and their associated reference junctions held in an ice/water bath, it was possible to measure the Seebeck e.m.f. of the chromel-copper and chromel-platinum couples as a function of temperature. The platinum-platinum/10% rhodium thermocouple was taken as a reference in determining the temperature: no significant difference between this and the corresponding value derived from the chromel-alumel thermocouple was detected (the difference was less than 1°C at 1100°C). The copper wire was removed for experiment temperatures above its melting point (1083°C). The Seebeck e.m.f. recorded in this way is plotted as a function of temperature in the graph on p. 78.

A least squares curve-fitting program was written in order to evaluate the temperature derivative of the curves produced. Rather than lose the inherent scatter of data points by fitting to a single polynomial, the program considered overlapping sets of five points each and used the method of least squares to fit a quadratic to each set. This quadratic was differentiated at the mean temperature of the set. The absolute thermopower of chromel then followed from a simple application of equation (I.11): the thermopower of copper taken by linear interpolation between those values given by Cusack and Kendall (1958; see the table on p. 63) and that of platinum by fitting the following cubic equation to their data:

\[ S_{pt} = - (8.333 \times 10^{-10}) T^3 + (3.693 \times 10^{-6}) T^2 - (1.854 \times 10^{-2}) T - 6.013 \]

where \( S_{pt} \) is the absolute thermopower of platinum at the temperature \( T \) (°C). Both reference values are assumed to an accuracy of ± 0.2 μVK⁻¹.

The results obtained in this manner for chromel are shown in the graph on p. 79, and were found to fit a straight line in the temperature range 450 - 1250°C:

\[ S_{ch} = 31.41 - 0.02233 \times T \]

where \( S_{ch} \) is the absolute thermopower of chromel and \( T \) the temperature (°C). Including the possible uncertainty in the reference metal values, it would appear
SEEBECK E.M.F. v. TEMPERATURE FOR THE COUPLES
CHROMEL-PLATINUM AND CHROMEL-COPPER

(refererence junctions at 0°C)

- o 1st batch chromel,
- x 2nd batch chromel,
- □ 2nd batch chromel, after use in experiment (data + 2mV)

emf. (mV)

Chromel-Platinum

Chromel - Copper

hot junction temperature (°C)
THE ABSOLUTE THERMOELECTRIC POWER OF CHROMEL

- Copper reference electrode (1st batch chromel)
- Platinum reference electrode (1st batch chromel)
- Platinum reference electrode (2nd batch chromel)
- Platinum reference electrode (2nd batch chromel, after use in experiment)
that this expression will generate the thermopower of chromel to an accuracy of
\[ \pm 0.5 \mu \text{VK}^{-1} \]. Much of this error, of course, will be of a systematic nature.

V: vi) Sample Details

The pure tellurium was supplied in ingot form by Johnson Matthey Chemicals
Ltd with a batch purity of better than 99.99%; nickel was supplied in sponge form
by Koch Light Laboratories Ltd, who claimed a purity of 99.99%.

The constituents of each alloy were weighed into a sealed end silica tube to
an accuracy of \( \pm 0.002 \) gm. The tube and contents were then connected to a
rotary pump, evacuated to a pressure of 0.02 torr, and the tube sealed off in situ.
For safety reasons a second silica tube was used as an envelope around the former,
the pressure between the two tubes at room temperature was about 250 torr. An
electrical resistance furnace (similar to the one shown in the figure on p. 67
but having only a single element) was used to heat the sample to the desired
temperature. In practice the maximum operational temperature of the furnace
(about 1200\(^{\circ}\)C) was used for most samples since the rate of solvation of nickel
in tellurium is accelerated with increased temperature, and the incomplete phase
diagram of the system introduced some uncertainty into the estimated liquidus
temperature (Elliot, 1965; some extension of this information was possible using
the observed discontinuities in resistivity and thermopower to estimate a liquidus
temperature and establish a trend with alloy composition). All samples were
held at this temperature for a period of at least 30 hours, which was extended to
50 hours for alloys having a high nickel content. A second period of baking
became necessary whenever the alloy did not solidify into a single rod. Any sample
inhomogeneity would be expected to produce a time-dependant variation in the
results at any given temperature and a large zero error in the e.m.f versus
temperature difference graph: no such effects were observed.
Errors

The uncertainty associated with the use of chromel as a reference material has already been discussed (V:v) and leads to a mainly systematic error of \( \pm 0.5 \ \mu V K^{-1} \). A further systematic error may be introduced into the measurements due to the fact that the thermocouple junctions were separated from the sample by a graphite plug and molybdenum sheet, this tending to give a small time-independant zero error in the e.m.f. versus temperature difference graph. As in the high temperature thermopower experiment, the scatter of points at any one experiment temperature is primarily due to errors in the determination of the temperature difference from two large quantities and their associated errors. All these effects may be combined in an estimated error of \( \pm 0.9 \ \mu V K^{-1} \).

There is also an uncertainty in the alloy composition, arising from the relatively high vapour pressure of tellurium (see figure on p. 51) and the consequent danger of heavy losses during the cell filling procedure. The damping effect of the large reservoir of liquid remaining in the filling tube after filling and the absence of any systematic time-dependance in the observed e.m.f.s suggests that differential loss of materials during subsequent measurements, made under an argon atmosphere, was insignificant. Chemical analysis (by the Butterworth Microanalytical Consultancy Ltd) of a post-experiment sample indicated that, at a filling temperature of \( 1000^\circ C \), the tellurium loss did not exceed 0.7% of its initial atomic concentration. The sample submitted to this analysis suffered heavier than usual tellurium loss (as evidenced by the density of visible tellurium deposition in the vicinity of the cooling water jacket) and therefore provides an estimate of the maximum expected loss.

Tellurium loss could also have corroded the thermocouple wires and thereby affected both temperature measurement and the reliability of the sample-chromel Seebeck e.m.f. In order to examine this possibility, a junction was formed with a
"used" chromel-alumel thermocouple and a platinum-platinum/10% rhodium thermocouple, and a calibration procedure similar to that described above (V: v) was followed. Temperatures derived from the chromel-alumel thermocouple remained accurate when compared to the platinum-platinum/10% rhodium reference. The Seebeck e.m.f. of the chromel-platinum couple and the resultant absolute thermopower of chromel as a function of temperature are shown in the graphs on p. 78 and p. 79 respectively: no significant changes were observed.

As a final check on the apparatus and procedures, especially the reliability of the method of calibration and the correction for thermal expansion, an experiment was undertaken with pure antimony (having a purity of 99.999%, supplied by Koch Light Laboratories Ltd). The Seebeck e.m.f.s, measured using both copper and chromel reference electrodes, are plotted against temperature difference in the graph on p. 83. The resistivity and thermopower as a function of temperature are shown in the figure on p. 84, and are in satisfactory agreement with other published values.
SEEBECK E.M.F.

Liquid Antimony V. Chromel and Copper

- Chromel reference electrodes
- Copper reference electrodes

ΔT(°C) vs ΔV(µV)

- 758°C
- 650°C
ANTIMONY : RESISTIVITY AND THERMOPOWER

- Present work
- Roll and Motz (1957)
- Busch and Tieche (1963)
- Gasser and Kleim (1977)

- Present work, chromel electrodes
- Present work, copper electrodes
- Howe (1967)
CHAPTER VI

Experimental Results for the Transition and Noble Metal Systems

A description of the electronic structure of transition and noble metals was given in chapter II and used in an attempted explanation of the variation in their resistivity and thermopower values. This model may be applied to both the liquid and solid states and has been used to discuss the properties of alloys - particularly the concentration dependence of the resistivity and thermopower of solid silver-palladium alloys (Mott and Jones, 1936; Taylor and Coles, 1956; Coles and Taylor, 1962; Mott, 1964). A palladium d-band similar to that shown in the figure 'A' on p.18 was adopted, whilst the silver d-band was supposed well below the Fermi energy and near the bottom of the conduction band. A rigid band structure was assumed for the alloy with the s-band common and the holes in the palladium d-band pictured as being gradually filled with the addition of silver. Magnetic susceptibility and electronic specific heat measurements indicated that the d-band was just full at a concentration of 55 atomic per cent silver and, within the rigid band approximation, implied the existence of 0.55 holes per atom in the d-band of pure palladium. Hence, for silver concentrations in excess of 55 atomic per cent, s-d transitions can no longer take place since the d-band is full. Reasonable quantitative agreement between calculated and experimental values was obtained only after the contribution to the conductivity of d-band holes in palladium-rich alloys was included (Coles and Taylor, 1962) - which may be as high as 15-20% of the total in pure solid palladium (Coles, 1978).

The addition of silver to palladium effectively causes the Fermi energy to move away from the d-band to higher energies. This means that the energy derivative of the density of states becomes more negative and an increase in magnitude of the large negative thermopower with concentration is predicted until, at approximately 55 atomic per cent silver, the d-band is filled and the thermo-
power is expected to tend to a value comparable with that of pure silver. Experimental results obtained for the solid do, in fact, show this behaviour (Taylor and Coles, 1956; Rudinski, 1956; see the figure on p.102). Measurements of the de Haas-van Alphen effect in palladium at low temperatures (Vuillemin and Priestley, 1965), however, indicated that there were only 0.36 s-electrons per atom (and therefore only 0.36 holes per atom in the d-band) but the above model may be slightly modified to remain consistent with experiment. Using the trends observed in transition metal band structure calculations (Mattheis, 1964), it was suggested by Dugdale and Guénault (1966) that the common s-band shifts its position relative to the d-band - such that the energy shift is linear with atomic concentration of silver (until 55 atomic per cent silver, after which no further significant shift occurs) - thereby enabling the s-band to accommodate the extra electrons.

The situation is of course more complex than that of the simple model suggested above; the d-band holes, for example, play an appreciable role in conduction processes at high palladium concentrations as already stated. Also, photoemission experiments on solid silver-palladium alloys (Norris and Myers, 1971; McLachlan et al, 1975) and theoretical calculations within the coherent potential approximation (Stocks, Williams and Faulkner, 1973) indicate that the form of the band structure is not as simple as that described.

The alloys investigated in this work were made from elements adjacent to each other in the periodic table. They were known to have similar structure factors (see the figures on p. 87), and the phase diagrams indicate the formation of simple substitutional alloys. Thus the predominant influence in the concentration dependance of the electronic properties of these alloys should be their electronic structure rather than the direct effect of variation in their ionic distribution. Whilst the results of those theoretical calculations described in chapter II
STRUCTURE FACTORS OF LIQUID Ni, Co, Pd, and Ag

Ni (1600°C)  
Waseda and Ohtani, 1974  
(x-ray)  
Johnson et al., 1976  
(neutron)

Co (1600°C)  
Waseda and Ohtani, 1974  
(x-ray)

Pd (1580°C)  
Waseda and Ohtani, 1975  
(x-ray)

Ag (1300°C)  
Waseda and Ohtani, 1974  
(x-ray)
generally do not disagree strongly with experiment it is evident that the values so predicted depend heavily on the often poorly known input parameters, thus rendering a close comparison of theory and experiment dubious. The nickel-cobalt alloy system was investigated with this difficulty in mind since it fulfills those conditions necessary for the application of a substitutional approximation to the theory.

VI: ii) The Nickel-Cobalt System

The resistivity of nickel-cobalt alloys as a function of concentration and temperature is presented graphically in the figures on p. 90 and 91 and the results summarized in the table on p. 92. The temperature in column (2) is derived from the phase diagram of the alloy system (see the figure on p. 49); since the alloys melt over a temperature interval of only a few degrees (Hansen, 1958) the liquidus and solidus temperatures have been combined into one melting temperature, \( T_m \). A straight line was derived from the liquid resistivity data using the method of least squares, this being extrapolated to \( T_m \) to give the values in column (3). The errors associated with such resistivity values have already been discussed (chapter IV). A temperature derivative of resistivity was also obtained from the calculated straight line, all liquid alloys having a slope of 0.01 (± 0.01) associated with them. Such a small positive slope ensures that a resistivity isotherm would deviate only little from the curve at \( T_m \). Column (4) gives resistivity values of the solid alloys obtained by both those methods discussed in chapter IV: avii. The results of Guntherodt, Hauser, Kunzi and Muller (1975) are also listed for comparison and show a satisfactory measure of agreement with the present work. Earlier values reported by Russian workers (Vertman and Samarin, 1961) for this alloy system show no such agreement with data presented here. Although there is no clear explanation of this discrepancy it is interesting to note that an indirect eddy current technique - which involved measuring the torque on a specimen in a
rotating magnetic field - was used and may be subject to errors of a different nature from those occurring in the more direct four-point method.

The thermopower of nickel-cobalt alloys as a function of concentration is shown graphically in the figure on p. 102.

The method used here for the comparison of experimental results and theoretical calculations for nickel-cobalt alloys is similar to that developed by Howe and Enderby (1967) and avoids the difficulties inherent in a direct comparison of equations (II: 4) and (II: 6) with experiment (i.e. the problem of choosing values for $E_F$ and $K_F$, the sensitivity of the $d$-wave phase shift to the position and width of the resonance, and the uncertainty in the structure factor which may be as much as 50% in the low momentum transfer region). The thermopower of the liquid alloy is predicted in terms of the resistivity of that alloy and the resistivities and thermopowers of the pure components in their liquid state, whilst the resistivities of the pure components alone are required for the calculation of an alloy resistivity. Howe and Enderby considered only liquid "equal valency" alloys of normal metals in terms of the Faber-Ziman approach (Faber and Ziman, 1965; chapter I) and assumed the weak and local scattering potentials necessary for a theory based on the N.F.E. approximation. For transition-transition alloys within the resonance scattering approximation however, a partial wave analysis describes the scattering which is dominated by the back scattering contribution of the $d$-wave phase shift (chapter II: ii and iii). In this case the resistivity and thermopower of the liquid alloy may also be predicted within the Faber-Ziman framework (Evans, Guntherodt, Kunzi and Zimmermann, 1972) provided the Fermi energy, atomic volume and partial structure factors are substantially independent of alloy composition. These requirements are apparently satisfied for liquid nickel-cobalt: the atomic volumes of the constituents differ by less than 0.5% (derived from the density
NICKEL-COBALT SYSTEM:
High temperature resistivity

- Present work
- J. Van Zytveld (Private communication)
NICKEL-COBALT SYSTEM: RESISTIVITY AT THE MELTING POINT

![Graph showing resistivity of the nickel-cobalt system at the melting point.](image)

Present work

Present work (using pre-cast rod)

Van Zytveld (Private Communication)

Güntherodt, Hauser, Kunzi and Muller (1975)
<table>
<thead>
<tr>
<th>(1)</th>
<th>(2)</th>
<th>(3)</th>
<th>(4)</th>
</tr>
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<td>Melting</td>
<td>Resistivity of</td>
<td>Resistivity of</td>
</tr>
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<td>Liquid of $T_m$</td>
<td>Solid at $T_m$</td>
</tr>
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<td>($^\circ$C)</td>
<td>($\mu\Omega cm$)</td>
<td>($\mu\Omega cm$)</td>
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<td></td>
<td></td>
<td></td>
<td>60.8 (b)</td>
</tr>
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<td></td>
<td></td>
<td>83.0</td>
<td>60.0 (c)</td>
</tr>
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<tr>
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<td></td>
<td></td>
<td>73.4 (b)</td>
</tr>
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<td>89.3 (a)</td>
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<td>97.2 (a)</td>
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<td></td>
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<td>97.3 (a)</td>
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<tr>
<td></td>
<td></td>
<td>116.0</td>
<td>98.0 (c)</td>
</tr>
</tbody>
</table>

(a) Value obtained by direct freezing of the liquid sample
(b) Value obtained from a pre-cast solid rod
(c) Guntherodt, Hauser, Kunzi and Muller (1975)
values of Alfen, 1972) and their structure factors, as noted earlier, are similar
(Waseda and Ohtani, 1974; Johnson et al, 1976). Although the Fermi energies and
wave vectors are not well known for transition metals (chapter II: iii), the
available evidence implies a close similarity between nickel and cobalt – indicated
not only by their atomic weights, their atomic electron configurations (Phillips
and Williams, 1965) and the alloy phase diagram (Hansen, 1958), but also by
estimates of $\kappa_F$ for the solid metals (Heine, 1967) and the interpolated estimates
of $E_F$ provided by Dreirach et al (1972) which show a variation of less than 10%
across the composition range.

Using equations (II: 2, II: 4 and II: 6) we may write for the resistivity of a
transition metal alloy:

$$\rho_{\text{alloy}} = \frac{30n^3}{m^2e^2\kappa_F^2E_F} \left[ \text{csin}^2\eta_2(1-c+c\overline{s}) + (1-c)\text{sin}^2\eta_2(c+(1-c)\overline{s}) \right]$$

\hspace{1cm} + 2c(1-c)\text{sin}^2\eta_2\text{sin}^2\eta_2\text{cos}(\eta_2 - \eta_2) (\overline{s}-1) \right]$$

where the partial structure factors have been set equal and $\overline{s} = s(2k_F)$. The
resistivity of the alloy may now be expressed in terms of the experimentally known
resistivities of the two pure liquid components ($\rho_A$ and $\rho_B$) using two appropriate
versions of equation (II: 4). The thermopower of the alloy may also be predicted
using equation (I: 12) with $\rho_A$, $\rho_B$, $\rho_{\text{alloy}}$ and the measured thermopowers of the
pure liquid constituents ($S_A$ and $S_B$):

$$\rho_{\text{alloy}} = \alpha c^2 + \beta c + \zeta$$

$$S_{\text{alloy}} = \alpha' c^2 + \beta' c + \zeta'$$

where,

$$\alpha = \left\{ \frac{1-1}{S} \right\} (\rho_A + \rho_B - 2G)$$

$$\beta = \frac{1}{S} (\rho_A + \rho_B) - 2\rho_B + 2\left( \frac{1-1}{S} \right) G$$

$$\zeta = \rho_B$$
with
\[
G = \left( \frac{\alpha_A \rho_B}{D} \right) \left( 1 - \frac{\rho_B}{D} \right) \left( 1 - \frac{\rho_A}{D} \right) + \frac{\alpha_A \rho_B}{D}
\]
\[
D = \frac{30\pi^3}{m^2 k_F^4 v_o^2}
\]
and where,
\[
\alpha' = \frac{\pi L_B^2}{3|e| \rho_{\text{alloy}}} \quad \beta' = \frac{\pi L_B^2}{3|e| \rho_{\text{alloy}}} \quad \zeta' = \frac{\pi L_B^2}{3|e|} \left( \frac{W}{(\rho_{\text{alloy}} - 2)} \right)
\]
with
\[
U = \frac{2m}{Sh^2 k_F} \frac{dS(g)}{dq} 2k_F
\]
\[
V = \frac{4m}{Sh^2 k_F} \frac{dS(g)}{dq} \left( G - \rho_B \right) + \left( \rho_A X_A + \rho_B X_B \right) \quad 2 \left( \frac{F - 2 \rho_B X_B}{S} \right)
\]
\[
W = \frac{2m}{Sh^2 k_F} \frac{dS(g)}{dq} \rho_B + \rho_B X_B
\]
\[
F = \rho_A X_A \left( \frac{\rho_B}{DS} \right)^{\frac{1}{2}} \left( 1 - \frac{\rho_B}{DS} \right)^{\frac{1}{2}} + \frac{\rho_B}{DS}
\]
\[
+ \rho_B X_B \left( \frac{\rho_A}{DS} \right)^{\frac{1}{2}} \left( 1 - \frac{\rho_A}{DS} \right)^{\frac{1}{2}} \left( 1 - \frac{2 \rho_B}{DS} \right) + \frac{\rho_A}{DS}
\]
\[
X_A = \frac{3|e| S_A}{\pi L_B^2} + \frac{2}{E_F} \frac{dS(g)}{dq} \left( \frac{ds}{dq} \right) 2k_F
\]
\[
X_B = \frac{3|e| S_B}{\pi L_B^2} + \frac{2}{E_F} \frac{dS(g)}{dq} \left( \frac{ds}{dq} \right) 2k_F
\]
Before such calculations could be performed it was necessary to select suitable values for $E_F$ and $k_F$. In this method however, the magnitude of the d-wave phase shift at the Fermi energy for either type of ion was evaluated directly from the experimental resistivity of the relevant pure liquid and not from a theoretical expression for $\frac{\pi}{2}$ (which would be a rapidly varying function of energy near a d-wave resonance) using a calculated value of the Fermi energy. Thus the extreme sensitivity to the choice of $E_F$ inherent in a first principles calculation does not occur.

The structure factor used to determine $S$ and $\left(\frac{dS(q)}{dq}\right)_{2k_F}$ was an average of the structure factors for pure liquid nickel (at $1500^\circ$C) and pure liquid cobalt (at $1550^\circ$C) obtained from x-ray diffraction measurements (Waseda and Ohtani, 1974). Similarly, the density of the alloy was taken as the average of the pure component densities at the same temperature.

Calculations of the resistivity and thermopower of liquid nickel-cobalt alloys have been performed (Dupree, Enderby, Newport and van Zytveld, 1977) and results are presented in the figures on p. 96 together with experimental data for comparison. The parameters to be used in these calculations were chosen as follows:

**Scheme I**

The effective valence $Z_{\text{eff}}$ was chosen as unity following Dreirach et al (1972) and the Fermi wave vector, calculated using equation (II: 8), fixed at $1.33 \AA^{-1}$. To allow for uncertainties in the position of the band with respect to the muffin-tin zero, $E_F$ was allowed to depart from the free electron value appropriate to the above value of $k_F$ by $\pm 0.02$ Ryd. To allow for its experimental error, the value of $S$ was permitted to vary by $\pm 0.02$ subject to the condition that it must not be less than the long-wavelength limit. The error associated with $\left(\frac{dS(q)}{dq}\right)_{2k_F}$ was taken as $\pm 10\%$. When the input parameters are allowed to vary in this way the range of
NICKEL - COBALT SYSTEM: RESISTIVITY AND THERMOPOWER, COMPARISON WITH THEORY

- - o - o - Experiment

Theory (according to schemes I, II and III)

\[ \rho (\mu\Omega \text{cm}) \]
\[ s (\mu \text{VK}^{-1}) \]

at % Co
calculated values falls within the thickness of the theoretical lines; it is clear, therefore, that the predicted variations of thermopower and resistivity with concentration do not agree with experiment.

If the Fermi energy is fixed at 0.62 Ryd and an effective electronic mass of 0.81 m is assumed in accordance with the values obtained for nickel by Dreirach et al, (1972), the results are almost indistinguishable from those above.

Scheme II:

Scheme I was followed but with $Z_{\text{eff}}$ set at 0.46 (Brown, 1973) so that $k_F$ becomes 1.02 $\AA^{-1}$ and $\bar{s}$ is changed accordingly. The results are similar to those of Scheme I, showing only low sensitivity to errors in the input parameters.

Scheme III:

Scheme I was again followed but with $Z_{\text{eff}}$ arbitrarily taken as 0.2. The results are very sensitive to the input parameters in this case. It does appear, however, that if very low (and possibly unphysical) values of the effective valence are assumed, the theory may possibly be able to account qualitatively for the variation of the resistivity and thermopower with alloy composition. The comparison between theory and experiment should be restricted to the approximate concentration range $0.25 < c < 0.75$ where substantial overlap between like ions may be assumed to eliminate the possible difference between values of the $t$-matrix for an ion in a pure liquid metal and for a similar ion as an impurity in a dilute alloy (Mott, 1972; chapter II).

The above analysis of the experimental data suggest that the single-site resonance method does not account for the observed variation of resistivity and thermopower with alloy composition unless low values of $Z_{\text{eff}}$ are assumed. For effective valence values usually quoted, the predicted forms are essentially independant of the choice of $E_F$, $\bar{s}$ and $\left(\frac{dS}{dq}\right)_{2k_F}$ and do not agree with experiment.
SILVER-PALLADIUM SYSTEM
Resistivity at high temperature

O + O, A, V, X Present work

%8 at %Ag
(Pre-cast solid rod)
SILVER - PALLADIUM SYSTEM: RESISTIVITY AT THE LIQUIDUS TEMPERATURE.

Present work
Present work (using pre-cast rod)
Dupree, Van Zytveld and Enderby (1975)
Roll and Motz (1957)
Ricker and Pfluger (1966) at 825°C
<table>
<thead>
<tr>
<th>Sample</th>
<th>Liquidus Temperature, $T_1$ (°C)</th>
<th>Resistivity of Liquid at $T_1$ ($\mu\Omega$cm)</th>
<th>Resistivity of Solid at $T_1$ ($\mu\Omega$cm)</th>
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<tr>
<td>Pure Pd</td>
<td>1552</td>
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<td>79.0 (b)</td>
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<td>$\text{Pd}<em>{80}\text{Ag}</em>{20}$</td>
<td>1470</td>
<td>76.1</td>
<td>48.6 (c)</td>
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<td>76.2</td>
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<td></td>
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<td>47.8 (c)</td>
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<td>1435</td>
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<td>Pure Ag</td>
<td>960.5</td>
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<td>8.2 (d)</td>
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(a) Dupree et al (1975)

(b) Guntherodt, Hauser, Kunzi and Muller (1975)

(c) Present work

(d) Roll and Motz (1957)
SEEBECK EM.F.:

Liquid (Pd·30 at % Ag) vs. Tungsten

\( \Delta V \) (mV) vs. \( \Delta T \) (°C)

1507°C

1607°C
Nickel-Cobalt and Silver-Palladium Systems: Thermoelectric Power.

**Nickel-Cobalt**
- Solid alloys at 1094°C
  - Wang, Starr & Brown (1966)
- Liquid alloys at 1532°C
  - Dupree et al. (1977)

**Silver-Palladium**
- Solid alloys at 1000°C
  - Rudinski (1956)
- Liquid alloys at 80°C above the liquidus temperature
  - Dupree (1976)
- Present Work
The resistivity of silver-palladium alloys as a function of temperature and concentration is presented in the figures on p. 98 and p. 99, and summarized in the table on p. 100. The liquidus temperature in column (2) is derived from the phase diagram of the system (Hansen, 1958; see the figures on p. 49) and the resistivity values presented in columns (3) and (4) were extrapolated to \( T_L \) in a manner similar to that described above for the nickel-cobalt alloys. The temperature derivative of resistivity for these liquid alloys are again small and positive (0.01 ± 0.01), as were those measured for the Ni-Co system. Also shown in the figure on p. 99 are the values of resistivity for solid alloys at 825°C obtained by Ricker and Pfluger (1966). The measured values of Seebeck e.m.f. versus temperature difference for liquid Pd + 30 at % Ag are shown graphically on p. 101 and, within the context of those values already measured by Dupree (1976), in a figure on p. 102. The errors associated with these thermopower and resistivity measurements have already been discussed (chapter IV).

Resistivity values for liquid Ag-Pd alloys reported by Vatolin et al (1967) do not agree even qualitatively with those presented here. Some suspicion must be cast upon their results, however, since the reported value for pure liquid palladium (120 \( \mu \Omega \text{cm} \)) is far in excess of that value (83 \( \mu \Omega \text{cm} \)) measured by Dupree et al (1975) and later confirmed by Guntherodt et al (1975).

A direct comparison of theory and experiment using the substitutional model is not as easily justified for the silver-palladium alloys as it was for nickel-cobalt. In pure silver the effect of the s-wave phase shift is far from negligible when compared to that of the d-wave phase shift. Using values of the phase shifts at the Fermi energy calculated by Dreirach et al (1972) the terms \((\sin \eta_0)^2\) and \((5 \sin \eta_2)^2\) are of the order 0.04 and 0.25 respectively while \((3 \sin \eta_1)^2\) is about 0.001; equations (II: 3) and (II: 4) are therefore only poor approximations and the equation
for the resistivity should only be reduced to:

$$\rho = \frac{24\pi^3}{m^* n^3} \left\{ \frac{25\sin\theta_0}{\cos\theta_0} \right\}^2 \left( \frac{q}{2k_F} \right)^3 \left( \frac{\partial q}{2k_F} \right)$$

$$+ \sin^2\theta_0 \left( \frac{q}{2k_F} \right)^3 \left( \frac{\partial q}{2k_F} \right)$$

There are secondary problems associated with this system arising from the change in atomic volume of approximately 10% across the phase diagram (Allen, 1972) and from the possible variation of effective valence with alloy composition. The valence of silver is unity and a value of 0.36 has been suggested for pure palladium (Brown, 1973) on the basis of de Haas-van Alphen experiments (Vuillemin et al., 1965) - although more recent values of the order of unity have been obtained from a theoretically calculated electronic bandstructure (Lopez-Escobar and Brown, 1977). Whilst being aware of these difficulties it remains a useful exercise to consider this alloy system in a way similar to that discussed in the previous section. The following schemes were adopted for these calculations, the results of which are presented in the figures on p. 106:

Scheme I:

Values for $\delta_0$ and its derivative were taken from the x-ray diffraction data of Waseda and Ohtani (1974, 1975); the Fermi energies for silver, palladium and their alloys were those of Temmerman and Gyorffy (1978). The effective valence was chosen as unity (Lopez-Escobar and Brown, 1977) and equation (II: 8) used to calculate the Fermi wave vector. These input parameters were allowed to vary within the same margins as those defined for the nickel-cobalt calculations. It is clear from the figures that within this scheme the predicted variation of resistivity and thermopower with concentration do not agree with the distinctive experimental curves. Reducing the effective valence - and altering those other parameters dependant on $Z_{eff}$ accordingly - did not affect the basic shape of the predicted curves but merely increased the importance of the errors.
Scheme II:

All parameters were as scheme I but with some concentration dependence of the effective valence introduced: this obviously takes us yet farther from the spirit of the theoretical model and conclusions are necessarily more tentative. The effective valence of palladium was fixed and that of the alloy held at this value until some pre-set alloy composition, after which it was allowed to rise linearly to 1.0 at pure silver. $\bar{s}$ and $\frac{d\sigma}{dq}$ remain dependent on the Fermi radius and therefore vary in the same way. Calculations were performed for palladium $Z_{eff}$ values of 0.36 (Brown, 1973), 0.55, 0.60, 0.65, 0.70 and 0.75. These were held until an experimentally suggested silver concentration of 40 atomic % had been reached; an alternative value of 55 atomic % silver (Dugdale and Guènault, 1966) was also used but, as expected, the results derived using this concentration did not reflect the experimental situation. Calculated resistivity and thermopower values for the effective valences 0.60, 0.55 and 0.36 are shown in the figures on p.106. It is clear from these figures that a very low palladium effective valence cannot account for the observed trends when used within this theoretical model. Some qualitative agreement between theory and experiment would seem possible however (if only for the resistivity values) for a palladium $Z_{eff}$ in the region 0.55 and 0.60 — values similar to those suggested in early work on solid palladium and palladium-silver alloys (Mott and Jones, 1936; Taylor and Coles, 1962; Mott, 1964).

It is interesting to note that the experimental results shown in the figures on p.99 and p.102 clearly indicate a strong similarity between the resistivity and thermopower of liquid silver-palladium alloys and those of the high temperature solid alloys, which suggests a common theoretical explanation of the behaviour. The s–d scattering model proposed by Mott has been seen to predict correctly the form of the observed resistivity and thermopower of the solid alloy (chapters II: iv and VI: i) and the predictions of such a model should not be very sensitive to
SILVER-PALLADIUM SYSTEM: RESISTIVITY AND THERMOPOWER.

COMPARISON WITH EXPERIMENT

- - - Experiment
- - Theory (according to schemes I and II)

\(s(\mu\text{V}k^{-1})\)

Scheme I

- i) \(Z_{\text{eff. Pd}} = 0.60\)
- ii) \(Z_{\text{eff. Pd}} = 0.55\)
- iii) \(Z_{\text{eff. Pd}} = 0.36\)

\(\rho(\mu\text{Î¿cm})\)

Pd Atomic •/• Ag

Atomic % Ag
melting, having no significant dependence on the structure factors of the alloy at high temperatures (Mott, 1972). It must be remembered, however, that the thermopower measurements for the liquid alloys were not obtained at constant temperature and that no reliable temperature derivatives were measured; although the results shown on p. 101 give some justification to the assumption of a small temperature dependence (of the order of 0.02 $\mu$V K$^{-2}$).
CHAPTER VII

Experimental Results for the Nickel–Tellurium System

The difficulties encountered in formulating a theoretical description of conduction processes in those materials, like liquid tellurium, having mean free paths approaching their minimum value were seen within the discussion presented in chapter III. By virtue of the variation of its physical characteristics with temperature, pressure or impurities, liquid tellurium may exhibit properties typical of a diffusive conductor whilst, under other conditions, may best be described within a 'metallic' framework similar to that used for the transition and noble metals. The results presented in this thesis for the variation of both the resistivity and thermopower with temperature and concentration of liquid nickel–tellurium are intended to add to the existing body of experimental information and provide further insight into such transport phenomena.

VII: ii) The Structure of Pure Tellurium

Solid tellurium has a strongly covalent character, the tellurium atoms forming helical chains with well defined bond lengths and angles and is similar to those elements above it in the periodic table (selenium and sulphur). The inter-chain cohesion become relatively stronger as one progresses from sulphur to polonium (-a good metal, having a cubic structure) and are only 2 – 3 times less strong than the intra-chain bonds in tellurium itself (Blakemore et al, 1962 and references therein).

The choice of a model for the structure of liquid tellurium, however, remains in some doubt despite extensive investigations (Tourand and Breuil, 1971; Cabane and Friedel, 1971; Tourand, Cabane and Breuil, 1972; Waseda and Suzuki, 1972; Hawker, 1974; Enderby, 1974; Hoyer et al, 1975; Tourand, 1975; Waseda and Tamaki, 1975, 1977) but that suggested by Cabane and Friedel (1971) on the basis of the elastic neutron scattering data of Tourand and Breuil (1971) has
received especial attention. Earlier workers (Epstein et al, 1957; Ioffe and Regel, 1960; Cutler and Mallon, 1962; Tièche and Zareba, 1963; Glazov et al, 1969) had suggested that the electronic properties of liquid tellurium were due to the retention of a chain structure. The relatively large density of conduction electron states at the Fermi energy (about 2.5 per atom) as indicated by the Knight shift (Cabane and Froidevaux, 1969; Warren, 1972) tends, however, to argue in favour of a metallic model. Long range oscillations in the high temperature pair potential, as derived from Tourand and Breuil's work (Waseda and Suzuki, 1972), favours a similar approach. There are also difficulties for a chain model arising from the observed low viscosity and high self diffusion coefficient (Ioffe and Regel, 1960). Cabane and Friedel therefore concluded that although the interatomic forces are not of a simple pair-wise type, well defined chains do not exist in liquid tellurium. They propose an alternative model in which the local order derived from neutron diffraction data at various temperatures may be explained in terms of a random network of covalent bonds. In such a network local order persists only up to second neighbours, and the life-time of the bonds is comparable to typical liquid metal relaxation times.

Some of the data reported by Tourand and Breuil is shown in the lower figures on p.110. They claim to resolve three peaks at 3.01, 3.82 and 4.52 Å in their derived radial distribution function which are quite sharp, implying strong correlations. The second and third peaks vary little with temperature whilst the first moves steadily to larger values of r as the temperature increases. The area under the first peak gives the coordination number of the first shell - it is found to increase from its solid state value of 2 to approximately 3 at 900°C, rising to a projected metal-like value of 6 at very high temperatures. The value of this coordination number is used to describe the type of covalent bond present at any one temperature (i.e. binary or ternary bonds at intermediate temperatures). The
STRUCTURE FACTOR AND RADIAL DISTRIBUTION FUNCTION OF LIQUID TELLURIUM

S(q) vs q (Å⁻¹)

- 500°C
- 800°C
- 675°C
- 900°C
- 1100°C

Hawker (1974)

Tourand and Breuil (1971)

g(r) vs r (Å)

0 2 4 6 8 10
relative concentration of binary and ternary bonds within the liquid will depend, then, on the temperature and there will be a corresponding variation in the effective concentration of current carrying electrons due to the progressive erosion of the pseudo-gap (which would be consistent with the observed variation in resistivity) a decrease as the number of carriers per atom increases until the effects of the decreasing liquid density becomes dominant (Hensel, 1976; Ohkawa, 1978). An increase in pressure would be expected to produce a similar decrease in resistivity, which the work published by Tamara et al (1977) and Endo et al (1977) confirms, as the graph on p.112 shows).

An objection has been raised to Tourand and Breuil's radial distribution function, however, by Hawker, 1974; Enderby, 1974) who emphasizes that significant truncation errors may occur in the 4 Å region of g(r) due to the rather slow damping of S(q). It is found that the experimentally obtained structure factor - in broad agreement with the other published results (Tourand and Breuil, 1971; Hoyer, Thomas and Wobst, 1975; Waseda and Tamaki, 1975, 1977) - can be regenerated from a g(r) in which the only peaks resolved are at 3.01 and 4.52 Å (see the figures on p.110). The network description remains a plausible model: the absence of the 3.82 Å peak may be due to vacancies in the structure.

VII: iii) The Electronic Structure of Liquid Tellurium

On the basis of their model Cabane and Friedel then considered the bonding mechanisms and resulting band structure. The energy bands at high temperature are assumed to be filled as follows: two electrons in a non-bonding band about 4 eV below the bonding levels and having about 45% p-character; three electrons in bonding states, each having about 15% s-character; the one remaining outer electron in a conduction band having the traits of a NFE description associated with it. The binary sites, found predominantly at temperatures near the liquidus point or within the region of supercooling, may be assumed to contribute little to the
LIQUID TELLURIUM: EFFECT OF PRESSURE ON CONDUCTIVITY

Present work, 1 bar
Baker and Webb (1974), 25 bar
Endo et al. (1977), 500 bar
Endo et al. (1977), 750 bar
Endo et al. (1977), 1000 bar
density of states at the Fermi energy. Hence, tellurium is an example of a metal-like electron gas coexisting with a system of covalent bonds. After considering the effects of thermal vibration, a band structure of the form shown on p. 114 was proposed. Note that the Fermi energy lies on the conduction band side of the pseudogap minimum. Whilst accepting the above structural model, Mott (1971) suggests that the antibonding conduction band is very much more broadened than the valence band thus giving a density of states as shown on p. 114, where $E_F$ lies on the low energy side of the pseudogap.

An alternative route towards a band structure, very similar to that suggested by Mott but originating in atomic p–orbitals, has been proposed (Cutler, 1971 a, b, 1977; ten Bosch, Morán-López and Bennemann, 1976). A linear combination of atomic p–orbitals along the bond directions is assumed to form a Te–Te molecular bond orbital, with two bonding states (including spin) having an energy below the atomic level and two antibonding states at a raised energy level. Two non-bonding p–electrons are left at approximately their original energy once the tellurium atom has formed bonds with the neighbouring atoms. Each broken bond then adds two electron states and one electron to this band, giving rise to one hole. Near-neighbour interactions will broaden these discrete states, and a band structure of the form shown on p. 114 will be seen. Further broadening may arise from hybridization with the lower energy s– or d– states and from the effects of thermal vibration on the potential energy. X–ray photoemission spectra are also shown on p. 114 for comparison.

**VII: iv) The Structure of Nickel–Tellurium**

Solid nickel–tellurium alloys have a structure varying between a NiAs type at NiTe and a CdI$_2$ type at NiTe$_2$ (Hansen, 1958; Elliot, 1965), more recent neutron diffraction results (Coffin et al, 1974) have shown that there is a continuous variation of stoichiometry between these two classes achieved by the preferential
THE DENSITY OF STATES FOR TELLURIUM

Cabane and Friedel (1971) (schematic)

Cutler (1976) (schematic)

Mott (1971) (schematic)

Joannopoulos, Schluter and Cohen (1975)

- Trigonal (theory)
- - - - Trigonal (XPS)
- - - - - - Amorphous (XPS)
introduction or removal of nickel atoms in alternate layers normal to the c direction. X-ray diffraction studies on the system Ni$_{3+x}$Te$_2$ (x = 0.15) indicate a tetragonal structure at temperatures of about 700°C where nickel atoms are situated in octahedral-like sites (Colaitis et al., 1977). Little information is available on the structure of liquid nickel-tellurium although some neutron diffraction data is reported by Soper (1977) for the alloys NiTe and NiTe$_3$; he attempts, with reasonable success, to simulate the total structure factors by a thermally broadened NiAs type structure. For NiTe$_3$ the abundance of tellurium over nickel is represented by decreasing the lattice site occupation probabilities of the nickel to one third of those of the tellurium. If this model is correct it would appear that nickel continues to occupy octahedral-like sites in the liquid.

VIIv) The Nickel-Tellurium Results

Values of Seebeck e.m.f. versus temperature difference, at various experimental temperatures, for each of the compositions studied are shown graphically on p. 116 to 124; these figures indicate the magnitude of the quantities involved and the relatively small size of any zero error. The derived values of absolute thermopower are shown in the graphs on p. 125 and p. 126. The resistivity of nickel-tellurium alloys as a function of temperature and composition is shown in the graphs on p. 127 and p. 128. The temperature derivative of the resistivity and thermopower at the liquidus temperature as function of composition is shown in the graphs on p. 129. All the above values are summarized in the table on p. 131; other published data for liquid tellurium are included for comparison.

The temperature listed in column (2) is an estimate based partly on the limited existing phase diagram (Westrum and Machol, 1958; Elliot, 1965; Spunk, 1969) but mainly on the resistivity curves shown on p. 125. The final stage of each experiment involved allowing the sample to cool, whilst continuing the measurement of resistivity and thermopower, until either a discontinuity in the
SEEBECK E.M.F.:
Liquid Te V. Chromel

\[ \Delta V (\mu V) \]

\[ \Delta T (^\circ C) \]
SEEBECK E.M.F.:
Liquid (Ni + 96 at% Te) V. Chromel
SEEBECK E.M.F:
Liquid (Ni+80 at % Te) V Chromel
SEEBECK EMF

Liquid (Ni - 66 at % Te) V. Chromel

ΔV (μV)

ΔT (°C)

998°C

3.9°C

200

150

100

50

0

-50

-100

-10

-20

-30
SEEBECK EMF:
Liquid (Ni + 50 at% Te) V Chromel

\[ \Delta V (\mu V) \]

\[ \Delta T (°C) \]

1164°C
1060°C
SEEBECK E.M.F.
Liquid (Ni + 40 at \% Te) v. Chromel
SEEBECK E.M.F.
Liquid (Ni + 33 at % Te) v. Chromel

$\Delta V (\mu V)$ vs $\Delta T (^{\circ}C)$

- $1077^\circ C$
- $1183^\circ C$
SEEBECK E.M.F.
Liquid (Ni + 22 at % Te) v. Chromel

\[ \Delta V (\mu V) \]

\[ \Delta T (^\circ C) \]

1084\(^\circ C\)
1200\(^\circ C\)
NICKEL-TELLURIUM SYSTEM: ABSOLUTE THERMOPOWER
AT THE LIQUIDUS TEMPERATURE AND AT 1150°C

![Graph showing absolute thermopower](image)

- **O** Present work (Liquidus Temperature)
- **X** Present work (1150°C)
- **Δ** Enderby and Dupree (1977)
- **■** Perron (1967)
NICKEL-TELLURIUM SYSTEM: RESISTIVITY AT THE LIQUIDUS TEMPERATURE AND AT 1150°C

\[ \rho (\mu \Omega \text{ cm}) \]

- Present work (Liquidus Temperature)
- Present work (1150°C)
- Perron (1967)
NICKEL-TELLURIUM SYSTEM: TEMPERATURE GRADIENT OF RESISTIVITY AND THERMOPOWER AT THE MELTING POINT.
PARTIAL MELTING POINT CURVE AND PHASE DIAGRAM OF THE NICKEL-TELLURIUM SYSTEM

Elliot (1965)

Present work, Liquidus temperature

Present work, Estimated solidus temperature

T(°C)

Ni$_2$Te

NiTe

Ni$_2$Te$_2$

448.5

(99.7)

Ni

Te

20

40

60

80

Te

at % Te
<table>
<thead>
<tr>
<th>Sample Composition (atomic %)</th>
<th>Liquidus Temperature, ( T_L ) (°C)</th>
<th>Resistivity at ( T_L ) (μOcm)</th>
<th>Resistivity at 1150°C (μOcm)</th>
<th>Thermopower at ( T_L ) (μV/°C)</th>
<th>Thermopower at 1150°C (μV/°C)</th>
<th>( \frac{dS}{dT} ) (μV/°K) at ( T_L )</th>
<th>( \frac{dS}{dT} ) (μV/°K) at 1150°C</th>
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<tr>
<td>Pure Ni</td>
<td>1452</td>
<td>85.8</td>
<td>159.9</td>
<td>-3.8</td>
<td>-3.8</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Ni₆₇Te₂₂</td>
<td>1025</td>
<td>154.4</td>
<td>162.7</td>
<td>2.3</td>
<td>6.1</td>
<td>0.04</td>
<td>0.04</td>
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<tr>
<td>Ni₆₀Te₄₀</td>
<td>1040</td>
<td>165.9</td>
<td>172.1</td>
<td>4.2</td>
<td>5.7</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Ni₆₀Te₄₀</td>
<td>1040</td>
<td>165.9</td>
<td>172.1</td>
<td>4.2</td>
<td>5.7</td>
<td>0.03</td>
<td>0.03</td>
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<tr>
<td>Ni₅₀Te₅₀</td>
<td>865</td>
<td>185.5</td>
<td>217.2</td>
<td>2.3</td>
<td>3.6</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Ni₅₀Te₅₀</td>
<td>875</td>
<td>185.5</td>
<td>217.2</td>
<td>2.3</td>
<td>3.6</td>
<td>0.01</td>
<td>0.01</td>
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<td>Ni₅₀Te₆₆</td>
<td>780</td>
<td>201.3</td>
<td>263.6</td>
<td>-1.7</td>
<td>1.5</td>
<td>0.01</td>
<td>0.01</td>
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<tr>
<td>Ni₅₀Te₆₆</td>
<td>780</td>
<td>201.3</td>
<td>263.6</td>
<td>-1.7</td>
<td>1.5</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Ni₃₄Te₉₀</td>
<td>690</td>
<td>277.4</td>
<td>300.4</td>
<td>0.5</td>
<td>5.3</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Ni₃₄Te₉₀</td>
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<td>277.4</td>
<td>300.4</td>
<td>0.5</td>
<td>5.3</td>
<td>0.02</td>
<td>0.02</td>
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<tr>
<td>Ni₂₀Te₉₀</td>
<td>690</td>
<td>334.0</td>
<td>367.0</td>
<td>0.06</td>
<td>8.4</td>
<td>0.00</td>
<td>0.00</td>
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<tr>
<td>Ni₂₀Te₉₀</td>
<td>690</td>
<td>334.0</td>
<td>367.0</td>
<td>0.06</td>
<td>8.4</td>
<td>0.00</td>
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<td>367.0</td>
<td>413.0</td>
<td>0.13</td>
<td>13.5</td>
<td>-0.06</td>
<td>0.00</td>
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<tr>
<td>Ni₁₀Te₉₀</td>
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<td>367.0</td>
<td>413.0</td>
<td>0.13</td>
<td>13.5</td>
<td>-0.06</td>
<td>0.00</td>
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<td>449.5</td>
<td>570.0</td>
<td>530.0</td>
<td>22.7</td>
<td>26.0</td>
<td>23.0</td>
<td>23.0</td>
</tr>
<tr>
<td>Pure Te</td>
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<td>570.0</td>
<td>530.0</td>
<td>22.7</td>
<td>26.0</td>
<td>23.0</td>
<td>23.0</td>
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<tr>
<td>(c)</td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>(d)</td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>(e)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

gradient was observed or until electrical contact was lost through sample contraction (this was only observed for those alloys have large concentrations of nickel; tellurium, it should be noted, has an anomalous coefficient of expansion on melting. The effect was reversible). Since the series of experiments began with alloys having relatively small concentrations of nickel, and therefore low melting points, it was possible to allow a large temperature margin above the likely value and subsequently establishing a more definite value as described above. It was therefore possible to build up a picture of the variation of liquidus temperature with composition, as shown on p.130. The values in this graph should be taken as tentative - especially the solidus temperature estimates, these having been based on a much less pronounced change of gradient than the liquidus temperatures. It is encouraging, however, to note the correspondence with the partial phase diagram in Elliot (1965) and the qualitative similarity with the Co–Te phase diagram of Moffat (1978). The resistivity, thermopower and temperature derivative values presented in columns (3) to (8) were derived in the way already described in chapter (VI: ii); in the case of pure Te and Ni$_4$Te$_9$, the least squares program introduced in chapter (V: v) was used to put a quadratic to the results, and allow the evaluation of the figures shown. The errors associated with these resistivity and thermopower values have already been discussed (chapter V: vii).

Good agreement between the present work on pure tellurium and other workers is apparent. There is some indication of a more rapid increase in resistivity with temperature beyond 900°C than that observed by Baker and Webb (1974; figure on p.125). This may be due to deterioration of the electrical contacts as the vapour pressure of tellurium approaches the ambient argon pressure of one atmosphere (see figure on p. 51). The problems associated with high vapour pressure are rapidly reduced with the addition of nickel (Westrum and Machol, 1958). The resistivity measurements of Ioffe and Regel (1960) on NiTe$_2$ show no such agreement
with the present work, though their estimate of the liquidus temperature is quite close. It is difficult to offer an explanation of this large discrepancy, especially in view of their corresponding data on CoTe₂ which shows a strong similarity to the present results for NiTe₂. In a study of transition metal 3d-states Takeda et al (1976) measured the temperature variation of resistivity for some dilute alloys of nickel in tellurium (2 atomic % Ni); their results show a rapid decrease in resistivity with the addition of nickel and, although there is only a small region of overlap, are quite consistent with the present work.

A graph has been plotted of log ρ (and of S) against inverse absolute temperature; neither of the plots shown (p.134) are straight lines in any temperature region and it is therefore reasonable to conclude that the picture of tellurium as an intrinsic semi-conductor is incorrect (Perron, 1967, 1972) since that would imply that the following equations hold true (Mott and Davis, 1971):

\[ \rho = c_1 \exp \left( \frac{E_g}{2KB} \right) \]  (VII:1)

and

\[ S = c_2 \left( \frac{E_g}{2KB} \right) + c_3 \]  (VII:2)

where \( c_1, c_2 \) and \( c_3 \) are quantities assumed to vary only slowly with temperature \( T \), \( KB \) is the Boltzmann constant and \( E_g \) is the band gap. If, however, the gradient of the \( \log \rho \) v. \( 1/T \) curve is taken, an effective band gap may be calculated using equation (VII:1) - giving a value of 0.4 (±0.05) eV at the melting point which agrees well with an estimate of 0.54 eV suggested by Perron (1972). This effective \( E_g \) clearly decays to zero rapidly as the temperature rises to 1100K. The addition of nickel has a similarly dramatic effect: an effective value of \( E_g \) for an alloy containing only 4 atomic % nickel is vanishingly small.

Phase shifts, the Fermi energy and the back-scattering factor, \( f(\pi) \), of tellurium have been calculated by Gurman (1978) and are shown as a function of energy on p.135. The back scattering factor is defined as:

\[ f(\pi) = \frac{1}{k} \sum_{l=0}^{\infty} (2l+1) \sin \eta_l \exp(i\eta_l) P_l(\pi) \]
LIQUID (Te) AND (Ni+96 at % Te): RESISTIVITY AND THERMOPOWER

\[ \ln \rho (\mu \Omega \text{cm}) \]

\[ S(\mu \text{V/k}^{-1}) \]

Pure Te

Ni+96 at % Te

\( T_m \)
TELLURIUM PHASE SHIFTS AND BACK-SCATTERING FACTOR

\[ \delta \]

\[ \frac{\mu}{f(\pi)} \]

\[ l = 0 \]

\[ l = 2 \]

\[ l = 1 \]

\[ l = 3 \]

Energy (Ev)
and is therefore very similar to the t-matrix of equation (II: 1). At the calculated Fermi energy the s and p-wave phase shifts are seen to be the only ones of significance, the p-wave phase shifts dominating when weighted by the factor \((2l + 1)\). It is also of interest to note that, in this energy region, \(f(\pi)\) is almost energy independant. Using the above values a resistivity has been calculated in the spirit of chapter II, using the equation:

\[
\rho = \frac{24\pi^3 n^3}{v_o e^2 m k_F E_F} S(2k_F) f^2(2k_F)
\]

(VII: 3)

The Fermi radius was taken from Waseda and Tamaki (1976), the structure factor from Waseda and Tamaki (1975), Hoyer et al (1975), and Enderby and Hawker (1974); the atomic volume was calculated from values of the density of liquid tellurium (Weast, 1974). This choice of parameters gives a theoretical resistivity value of 965 \(\mu\Omega cm\) at 480°C. If the equation (III: 10), due to Mott, is valid for liquid tellurium then a value for 'g' of 0.6 is implied – which is close to that of 0.5 \(\pm\) 0.15 suggested by Warren (1972). Similar calculations also indicate a positive temperature coefficient of resistivity unlike the observed strongly negative temperature derivative.

In the light of those models of liquid tellurium discussed in the previous sections (also Valiant and Faber, 1974) one would naively expect that the addition of tellurium to nickel would reduce the density of current carrying electrons and move the Fermi energy further back into the nickel d-band, thereby increasing the resistivity and making the thermopower less negative. Adding nickel to tellurium would increase the number of current carriers and move the Fermi energy to the conduction band side of the pseudogap hence decreasing the resistivity and making the thermopower less positive. The experimental data presented here are in broad qualitative agreement with such a picture.
Some consideration of possible structural changes is called for however, since the magnitudes of the observed variations - especially at the tellurium rich end - are possibly larger than would be expected from purely electronic causes. On the basis of the neutron diffraction results presented by Soper (1977) and those of Nguyen (unpublished), Enderby (1978b) has suggested that each nickel atom added to tellurium will tend to group six tellurium atoms around itself as nearest neighbours and that the Te-Te distance within the group is less than that within pure tellurium itself. Such a change could rapidly destroy the random covalent network of pure tellurium and, since the tellurium atomic overlap integrals would be expected to increase, the pseudogap will become progressively weaker. It is postulated that the observed rapid decrease in resistivity with increased nickel concentration may be due to the formation of such clusters, having a much higher contribution to the conductivity than that from an equivalent volume of "unmodified" tellurium atoms.

This model lends itself to investigation using the percolation theory for inhomogeneous conductors introduced in chapter (III: iv); the results of first order calculations that have been performed using equation (III: 13) are reported. Parameters within this equation were estimated as follows: the conductivity $\sigma_1$ was taken as 1750 $\Omega^{-1} \text{m}^{-1}$ (i.e. 570 $\mu \Omega \text{cm}$, the experimentally measured resistivity of pure tellurium near its melting point); the atomic volumes of nickel and unmodified tellurium were calculated using the liquid density values of their respective melting points (Weast, 1974) and by assuming that nickel will lose its 4s electron and therefore suffer a volume decrease similar in magnitude to that observed on ionizing solid nickel; this one electron is assumed to be shared amongst amongst the six tellurium atoms of the local cluster thereby increasing their volume slightly - again in line with observed solid state trends. The conductivity
\( \sigma_0 \) associated with the cluster was chosen as 5000 \( \Omega^{-1} m^{-1} \) (i.e. 200 \( \mu \Omega \text{cm} \)) which seems a reasonable empirical estimate based on the position of the change of slope of the experimental resistivity curve. Using this value of \( \sigma_0 \) in conjunction with the measurements of the pressure dependance of liquid tellurium's resistivity reported by Tamuro et al (1977) it is possible to determine the effective decrease of tellurium atomic volume within the cluster from the relation:

\[
\left( \frac{\Delta V}{V} \right) = \frac{P}{\chi_I}
\]

where \( P \) is the pressure applied and \( \chi_I \) the isothermal compressibility. The adiabatic compressibility of liquid tellurium is experimentally available from velocity of sound measurements (Gitis and Mikhailov, 1966) and may be related to \( \chi_I \) through a standard thermodynamic equation (Zemansky, 1968):

\[
\chi_I = \frac{c^2 \rho_o + \Delta}{\rho_o}
\]

where \( c^2 \rho_o \) is the adiabatic compressibility - \( c \) is the velocity of sound and \( \rho_o \) the density, and \( \Delta \) is a function of temperature, molar volume, volume expansion coefficient and specific heat at constant pressure. Estimates indicate that \( \Delta \) is small compared to \( c^2 \rho_o \) and it was therefore ignored. Liquid tellurium, near its melting point, reaches a resistivity of 200 \( \mu \Omega \text{cm} \) under a pressure of about 1.4 K bar which, using equation (VII 4), implies a volume reduction of about 3%.

The figure on p. 139 shows the results of these calculations. Curves corresponding to modified (i.e. cluster) tellurium volumes reduced from the unmodified volume by 2% and 5% are indistinguishable from that derived using a cluster volume unchanged with respect to the pure tellurium value; experimental values are included for comparison. Some general trends were investigated: reducing the cluster volume causes the initial drop in predicted resistivity to be less severe and eventually leads to a convex curve rather than the concave shape shown, an increase in cluster volume will give a sharper initial fall as expected; decreasing the number of tellurium atoms per cluster moves the end point of the
THE NICKEL-TELLURIUM SYSTEM: A COMPARISON OF THEORY WITH EXPERIMENT (RESISTIVITY).

--- Experiment

Theory:
(a) six tellurium atoms per cluster, modified volume =0.95, 0.98 and 1.0 of unmodified volume.
(b) as (a) but modified volume =1.2 x unmodified.
(c) as (b) but with four tellurium atoms per cluster.
predicted curve (i.e. that point at which the alloy is saturated with clusters) to higher nickel concentrations and therefore reduces the gradient. Bearing in mind the extent of the approximations made during these calculations, the theory does seem to be able to reflect the dominant features exhibited by the experimental results: that of a very rapid decrease of resistivity from the pure tellurium value as nickel is added.
CHAPTER VIII

In Summary and Conclusion

Experimental Technique

The development of the apparatus described in chapters IV and V has enabled measurements to be performed of the resistivity and thermopower of some corrosive materials at high temperatures. The designs - especially those relating to the transition metal experiments - have some disadvantages, however, in that the large size of ceramic components and the difficulty in machining both these and other refractory materials requires the use of large samples and therefore a large furnace. This in turn causes long heating and cooling periods, though their effects may be reduced by using automatic temperature controllers. With increased experience in the use of ceramic and other refractory materials, more sophisticated furnace control devices and fuller use of computer assisted data acquisition techniques, it is likely that smaller and more convenient apparatus could be developed. Apparatus allowing the use of Argon pressures up to 5-10 atmosphere, say, would be particularly useful since the effects of vapour loss from volatile materials - and, more seriously, from alloys having a relatively volatile component - could be drastically reduced.

In order to complete the present study of the concentration dependence of the resistivity and thermopower of liquid nickel-tellurium alloys (i.e. the nickel rich alloys) several experimental problems would have to be overcome. One of the most serious of these is that of containment: silica could not withstand the temperatures involved and all the refractory metals tested suffered severe chemical attack even at lower temperatures; alumina or single synthetic sapphire crystals may be suitable as containers but would only allow electrical contact with difficulty. Changing from a four point method for the measurement of resistivity to a parallel conductor method with the alloy contained in narrow walled
graphite tube would seem to be the most promising possibility. It would be especially interesting to investigate the behaviour of the thermopower in nickel rich alloys since the present work indicates a rapid increase in magnitude as the composition approaches pure nickel.

**Experimental Results**

It was noted in chapter II that the predictions of liquid metal resistivity and thermopower values based on theories founded within the N.F.E. approximation (Ziman's theory for simple metals, (Ziman, 1961, 1967a) and its modification in single site resonant scattering model (Evans, Greenwood and Lloyd, 1971)) could give a qualitative description of many observed results - the agreement being better for simple metals and their alloys. For pure transition metals and for those alloys having more than about 25 atomic % transition metal, Mott (1972) has suggested a quite difference model in which the s-electrons are regarded as being the main current carriers but where their transport properties are dominated by scattering into available d-band sites. The conductivity is therefore regarded as being dependant on the density of states at the Fermi energy (predominantly d-band states) and as having no significant dependance on the structure factor - in contrast with the resonance approximation.

If the substitutional approximation is valid for those transition metal alloys studied here, the calculations of chapter VI show that the predictions of the resonant scattering model do not agree with experiment for liquid nickel-cobalt alloys (i.e. transition metal-transition metal) unless an arbitrary assumption of a very low effective valence is made. The results of the liquid silver-palladium (i.e. noble metal-transition metal) work are less conclusive in that the application of computational methods similar to those used for nickel-cobalt alloys rely on the adoption of much more drastic assumptions. If use is again made of an effective valence, however, which in this case is allowed some concentration dependance,
the theory is able to remain consistent with experimental resistivity values—though not with the observed thermopower results. Deviations from the predictions of the resonance approximation are expected to be more severe for palladium rich alloys than for silver rich alloys—a situation clearly reflected in the calculations of chapter VI, and in the results of similar calculations on other transition-nontransition alloys reported by Dreirach et al (1972). The failure of the resonant scattering model under those conditions described above, together with the marked similarity between the concentration dependence of resistivity and thermopower values of liquid and solid silver-palladium alloys, and the qualitative success of Enderby and Dupree (1977; Enderby, 1978a) in interpreting the thermopower values of liquid iron, cobalt and nickel in terms of an s-d scattering model, gives support to the ideas advanced by Mott.

To facilitate a closer examination of the application of the resonant scattering model to liquid nickel-cobalt alloys it would be necessary to have available the three partial structure factors as a function of concentration. These could be obtained from neutron diffraction experiments by isotopic enrichment and substitution of the nickel (nickel is a particularly useful element in this context since one of its stable isotopes has a negative scattering length, thereby enabling the production of a nickel sample exhibiting zero coherent scattering). There would be some experimental difficulty however due to the high neutron absorption coefficient of cobalt. Similar experiments could be performed on liquid silver-palladium alloys using isotopic enrichment of the silver, but the high absorption coefficient of silver would again cause some difficulty.

The development of quantitative predictions based on the model suggested by Mott, being dependant on the density of states and the extent of atomic overlap, some knowledge of the electronic band structures of liquid transition metal alloys such as nickel-cobalt is essential. Photoemission experiments using ultra-
violet, x-ray or synchroton radiation could provide this data. The partial structure factors would be of use here also since the pair distribution functions available from them would give information on the variation of atomic separation and overlap.

Any conclusions derived from the nickel-tellurium results are necessarily more tentative due to the dearth of available information. Some of the relevant work that has been reported is discussed in chapter VII, notably the random network model for tellurium, based primarily on the work of Cabane and Friedel (1971). The atomic and electronic structure of tellurium within this model varies strongly with changes in temperature, pressure or on alloying. The limited neutron diffraction data for two liquid nickel-tellurium alloys reported by Soper (1977, and Nguyen, private communication) suggest that nickel occupies octahedral-like sites similar to those in the solid state alloys: it is suggested that a possible structural model for tellurium rich nickel-tellurium alloys may be one of clusters, each containing one nickel atom which tends to attract six tellurium near-neighbors around itself. In the light of this suggested model, and using the percolation-type theory advanced by Cohen and others (chapter III; Cohen and Sak, 1972; Cohen and Jortner, 1973 (a, b, c), 1974) which readily lends itself to the semi-quantitative examination of such a system, calculations were presented in chapter VII for the resistivity of tellurium rich alloys. Although the errors associated with those parameters required by the theory may be undesirably large due to the first order approximations made, the results demonstrate that the model and theory are able to reflect qualitatively the dramatic effect of alloying tellurium with nickel.

For a fuller understanding of this alloy system it is clearly desirable to have a more complete structural picture, which would be made possible by performing neutron diffraction experiments on samples containing isotopically enriched nickel
"zero" nickel, as mentioned above, would enable the relatively rapid acquisition of the Te–Te partial structure factor and its dependence on nickel concentration; such results would be particularly significant when considering tellurium rich alloys. It would also be interesting to see the effect of pressure on the structure of pure liquid tellurium since this would provide an indication of the effects of increased atomic overlap.

Neutron diffraction experiments on liquid tellurium and a dilute alloy of nickel in tellurium have recently been undertaken using the facilities available at A. E. R. E. Harwell. Although the analysis of these results is in an early stage it does suggest that changes in the tellurium–tellurium structure are not as large as those postulated above. Further work is in progress.

Another avenue of approach lies in the use of the parameter 'g' introduced by Mott (this being the ratio of the actual to the free-electron density of states at the Fermi energy, see chapter III), but without the prior knowledge of its value for the nickel–tellurium alloys (from Knight shift measurements for example) this would not be very fruitful. Compounding the difficulties of taking this route is the fact that Mott's model evolves from a N. F. E.-like base, this process may not be suitable for tellurium. An experimental examination of the density of states for the liquid alloys using photoemission techniques would give information on the variation in electronic structure with alloy composition, and help explain the behaviour of the thermopower. It would also provide values for 'g' and therefore give a clearer view of the validity of Mott's model for such a system – especially if used in conjunction with resistivity and thermopower values calculated with a N. F. E. framework (using theoretically derived alloy phase shifts).
In the closing section of chapter I Mott's classification of conducting materials was presented, in which each region is semi-empirically centred around an archetype whose behaviour may be seen to be described well by certain theories. Implicit in the nature of such a division is that the regional limits are artificial and should be far from rigid; it is no surprise then to find systems, such as those with which this thesis is primarily concerned, having the defining characteristics of a region yet not being satisfactorily described by its theories. One question that the present results raise concerns the relationship between the density of states and the electronic transport properties of materials. Although the transition metals are commonly pictured within N. F. E. models (i.e. having resistivities and thermopowers that are density of states independent), the results of the experiments and calculations presented here indicate that a theory more closely allied to the tight binding approximation and explicitly containing the density of states may be more suitable. It is also uncertain whether, on moving towards tellurium and the diffusive conduction regime, a similar density of states factor remains entirely sufficient. It is possible, however, that some functional dependence of electronic transport properties on the density of states may prove to be the link between at least the first two of our artificial regions.

It is hoped that the work presented here will provide some of the information needed for a closer examination of current electronic transport theories.
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Measurements have been made of the resistivity of liquid nickel–cobalt and silver–palladium alloys as a function of composition and temperature together with some measurements on these systems in the solid state and a measurement of the thermoelectric power of a single liquid silver–palladium alloy as a function of temperature. Experiments have also been performed to determine the resistivity and thermoelectric power of liquid antimony as a function of temperature, and of liquid nickel–tellurium alloys as a function of temperature and composition. Apparatus has been developed to enable such experiments to be undertaken. In those cases where information is available, the results obtained here are generally in agreement with other experimental data.

Approximate expressions can be derived from a single site resonant scattering model which give the resistivity of suitable liquid transition metal alloys in terms of the resistivities of the pure components, and give the thermoelectric power of the alloy in terms of the resistivities and thermoelectric powers of the pure components and the resistivity of the alloy. Predictions derived using these expressions have been compared with the experimental data: this comparison indicates that the theory in its present form provides, at best, only a qualitative account of the observed transport properties of liquid transition metal alloys.

Calculations based on a percolation model of electronic transport in inhomogeneous liquids have been performed in an attempt to understand the experimentally observed variation of resistivity with concentration in the nickel–tellurium alloy system. Such a model appears to provide a reasonable qualitative description of the experimental data for the tellurium–rich alloys.