The resistivity and thermoelectric power of liquid Ag-Pd alloys

R J Newport, B C Dupree†, J E Enderby‡ and R A Howe

Department of Physics, University of Leicester, Leicester LE1 7RH, England, UK

Abstract. The resistivity (ρ) and thermoelectric power (S) have been measured as functions of concentration and temperature for the liquid alloy system Ag-Pd. Comparison is made between the experimental results and the theoretical predictions of a nearly free electron model adapted for liquid transition metals. It is concluded that such a theory is unable to reproduce the gross features of the concentration dependence of ρ and S even when concentration-dependent effective valencies are introduced. The close similarity between the concentration dependence of the resistivity and thermoelectric power of solid Ag-Pd alloys at high temperatures and that of the liquid alloys lends support to the alternative s-d scattering model proposed by Mott.

1. Introduction and theory

The electronic transport properties of transition metals and their alloys have been the subject of considerable discussion in recent years. The main point at issue throughout has been the extent to which the nearly free electron (NFE) model, which was used so successfully with simple metals, is applicable to liquid transition metals. Before the basic formulae for the resistivity ρ and thermoelectric power S of simple liquid metals (Ziman 1967) can be applied to liquid transition metals it is necessary to describe the scattering probability in terms of the single-site t matrix (Evans *et al* 1971, Dreirach *et al* 1972):

$$t_{(q)} = \frac{-2\pi\hbar^3}{m(2mE)^{1/2}V_0} \sum_l (2l + 1) \sin \eta_l(E) \exp i\eta_l(E) P_l(\cos \theta)$$

where V_0 is the atomic volume and $\eta_l(E)$ is the lth partial-wave phaseshift calculated at energy E; the remaining notation is standard. The resistivity and thermoelectric power are then given by:

$$\rho = \frac{12\pi m^2 V_0}{e^2\hbar^3 k_F^2} \int_0^1 \left(\frac{q}{2k_F}\right)^3 a_{(q)} \left|t\left(\frac{q}{2k_F}\right)\right|^2 d\left(\frac{q}{2k_F}\right) \tag{1a}$$

† Present address: Joint Speech Research Unit, Princess Elizabeth Way, Cheltenham GL52 5AJ, England, UK.

‡ Present address: H H Wills Physics Laboratory, Royal Fort, Tyndall Avenue, Bristol BS8 1TL, England, UK.

and

$$S = \frac{-\pi^2 K_B^2 T}{3e} \left(\frac{\mathrm{d}\rho}{\mathrm{d}E}\right)_{E=E_F}. \tag{1b}$$

If it is further assumed that the d wave ($l = 2$) phaseshift is much larger in magnitude and varies more rapidly with energy than the phaseshifts associated with other angular momenta and that the backscattering (i.e. momentum transfer $\hbar q = 2\hbar k_F$) contribution dominates, the expressions for the resistivity and thermoelectric power may be approximated by:

$$\rho = \frac{30\pi^3 \hbar^3}{mE_F V_0 k_F^2 e} \sin^2 \eta_2(E_F)\bar{a} \tag{2a}$$

$$S = \frac{\pi^2 K_B^2 T}{3|e|} \left(\frac{-2}{E_F} + \frac{1}{\bar{a}}\frac{\mathrm{d}\bar{a}}{\mathrm{d}E} + 2\cot\eta_2(E_F)\frac{\mathrm{d}\eta_2(E_F)}{\mathrm{d}E}\right) \tag{2b}$$

where $\bar{a}$ represents the structure factor evaluated by wavenumber $q = 2k_F$, which may be derived from x-ray or neutron diffraction experiments. These expressions may be extended to include binary alloys (Evans *et al* 1972, following the analysis of Faber and Ziman 1965) if the term $\bar{a}_{(q)}|t_{(q)}|^2$ in equation (1a) is replaced by:

$$|t_A|^2[c(1 - c) + c^2 a_{AA}] + |t_B|^2[c(1 - c) + (1 - c)^2 a_{BB}]$$

$$+ 2(t_A^* t_B + t_A t_B^*)c(1 - c)(a_{AB} - 1)$$

where c is the atomic concentration of type A atoms having t matrix $t_{A(q)}$ associated with them; a_{AA}, a_{BB} and a_{AB} are the partial structure factors. For simplification, we shall assume that t_A and t_B are concentration independent (except for a normalisation factor arising from the variation of the effective alloy atomic volume), an assumption consistent with the use of a single-site scattering model having E_F constant across the range of alloy compositions. For low concentrations of type A ions in a host of type B, however, the large separation of type A ions may cause their associated t matrix to deviate significantly from that for pure metal A (and vice versa). Accordingly, comparison of theory and experiment will ideally be restricted to a region $0.25 < c < 0.75$ where substantial overlap between like ions will minimise this effect (Mott 1972).

An alternative theory, fundamentally different to that outlined above, has been suggested by Mott (1972). It is based on a solid state model (Mott and Jones 1936, Mott 1964) in which the concept of two distinct mean free paths for pure transition metals (a short one associated with a d like part of the Fermi surface and a longer NFE like one associated with an s like part) is used. As a consequence of the relatively large effective mass associated with the d band electrons, the current will be carried predominantly by the s electrons. Since the density of possible final states is largely d like, there is a relatively high probability that a current carrying s electron will be scattered into a vacant d state.

In this way the resistivity is increased beyond the value expected in the absence of the d band. In the liquid state Mott assumes that the d electrons may be viewed within a tight-binding framework and that s–d hybridisation is small. In this case, the likelihood of a resonance developing, of the type postulated by Evans *et al* (1971), 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 approximation becomes feasible only for alloys containing a significant concentration (Mott suggests a minimum figure of 25%) of non-transition metal atoms. Although few detailed calculations have been made for liquid transition metals using this model, those reported (T Fujiwara, private communication) give some support to Mott's rather qualitative model. In general, however, it is anticipated that the electrical properties will be relatively insensitive to the structure factor and should not significantly change across the melting point.

For the transition metals, the d wave phaseshift varies rapidly with energy near the Fermi energy. Within the NFE picture, it is therefore important to calculate E_F with some precision (Dreirach 1971). The Fermi wavevector, k_F, is usually derived using the free electron formula. Any attempt to compare the predictions of equations (2a) and (2b) with the values of ρ and S obtained from experiment is made difficult by the uncertainty of the low q value of $a_{(q)}$, which can be as much as 25% in error. These problems can be avoided if the method developed by Howe and Enderby (1967) is employed. The thermoelectric power of the liquid alloy is predicted in terms of the resistivity of that alloy and the resistivities and thermoelectric powers of the pure liquid components, whilst the resistivities of the pure components alone are needed for the calculation of the alloy resistivity. The method requires that the Fermi energy, atomic volume and partial structure factors be independent of alloy composition. Two appropriate versions of equation (2a)—corresponding to ions of type A and type B respectively— are used to express the resistivity of the alloy. Equation (2b) may then be used to predict the thermoelectric power of the alloy:

$$\rho_{\text{alloy}} = \alpha c^2 + \beta c + \zeta \tag{3a}$$

$$S_{\text{alloy}} = \alpha' c^2 + \beta' c + \zeta' \tag{3b}$$

where c is the concentration of type A ions; the quantities $\alpha, \beta, \ldots, \zeta$ are defined fully elsewhere (Dupree 1976).

In an earlier paper (Dupree *et al* 1977), the values derived from equations (3a) and (3b) were compared to measured values of ρ and S for the Ni–Co alloy system. Agreement between theory and experiment could only be obtained by adopting an arbitrarily low effective valency. This series of experiments on the Ag–Pd alloy system was undertaken with the aim of investigating further the apparent weaknesses of the NFE model as applied to liquid noble and transition metal alloy systems.

The structure data available for liquid silver and palladium (Waseda and Ohtani 1974, 1975) and the alloy phase diagram (Hansen 1958) lend support to a substitutional model for $a_{(q)}$ and the atomic volume changes by only 10% across the composition range (Allen 1972). In pure silver the effect of the s wave phaseshift, however, is far from negligible when compared with that of the d wave phaseshift. Using the values of the phaseshifts 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 (2a) and (2b) must therefore be regarded as first approximations. Furthermore, the valence of silver is unity whilst a value of 0.36 has been suggested for the effective valence of pure palladium (Brown 1973). On the other hand a more recent value of the order unity has been obtained from a theoretically calculated electronic bandstructure (Lopez-Escobar and Brown 1977). Whilst being aware of the approximate nature of the comparison it remains a useful exercise to consider this alloy system within the framework of the NFE model (see §3 below).

2. Experimental procedure

The electrical resistivity of liquid Ag–Pd was measured by a four-electrode, fast response, DC technique and thermoelectric and other spurious voltages were eliminated by the normal methods of current reversal and temperature profile analysis. The containment vessel was machined from high-purity high-density recrystallised alumina. The liquid sample was forced, under pressure, up four capillary tubes to produce electrical contact with four tungsten probes, the region of overlap being subsequently frozen to prevent continuous corrosion.

The thermoelectric power was measured in an open boat using a dipping tungsten electrode technique with differential temperatures of around 20°C. Contact between the sample and electrodes was made for periods of around 10 s and data were acquired and recorded using mini-computer interfacing. Values for the absolute thermoelectric power of tungsten were obtained from the collation of Cusack and Kendall (1958) and Bradley (1962).

The experiments were conducted at temperatures up to 1600°C on samples prepared from 99.998% silver and 99.99% palladium. Subsequent chemical analysis showed that the maximum tungsten contamination was below 0.4 at% and further measurements were made to establish that, at these levels of contamination, the effects on the measured values were within the errors quoted.

3. Results and discussion

The resistivity of various Ag–Pd alloys has been measured over a wide temperature range and the results of these measurements are presented in figure 1. The concentration dependence of the resistivity at a fixed temperature (the liquidus temperature (Hansen 1958)) for both solid and liquid alloys is shown in figure 2, together with data taken for solid Ag–Pd at 825°C. Present data for the concentration dependence of the thermoelectric power are compared, in figure 3, with the data of Rudnitskii (1956) on solid Ag–Pd at 1000°C. The data are summarised in tables 1 and 2.

Two schemes were adopted in attempts to describe the experimental results using equations (3a) and (3b).

Scheme I. Values for $\bar{a}$ and its derivative were taken from the x-ray diffraction data of Waseda and Ohtani (1974, 1975). The error associated with $\bar{a}$ was assumed to be ± 0.02 (subject to the condition that $\bar{a}$ must not be less than the long wavelength limit) whilst the error on $\mathrm{d}\bar{a}/\mathrm{d}q$ was taken as $\pm 10\%$. The Fermi energies for silver, palladium and their alloys were those of W Temmermann and B Gyorffy (1978, private communication). E_F was allowed to vary by ± 0.02 Ryd to allow for uncertainties in the muffin-tin zero. The effective valence for both silver and palladium was chosen as unity (Lopez-Escobar and Brown 1977) and the free electron formula used to calculate k_F. The results in figure 4 clearly show that, within this scheme, the predicted variation of resistivity and thermoelectric power with concentration is in gross disagreement with experiment. There is no improvement if the effective valencies of both Ag and Pd are reduced.

Scheme II. All parameters were as scheme I but the effective valence was allowed to be concentration dependent. A value of the effective valence of palladium was used up to a given alloy composition, after which it was taken to rise linearly to 1.0 at pure silver. $\bar{a}$ and $\mathrm{d}\bar{a}/\mathrm{d}q$ depend on the Fermi radius and therefore vary in a similar way.
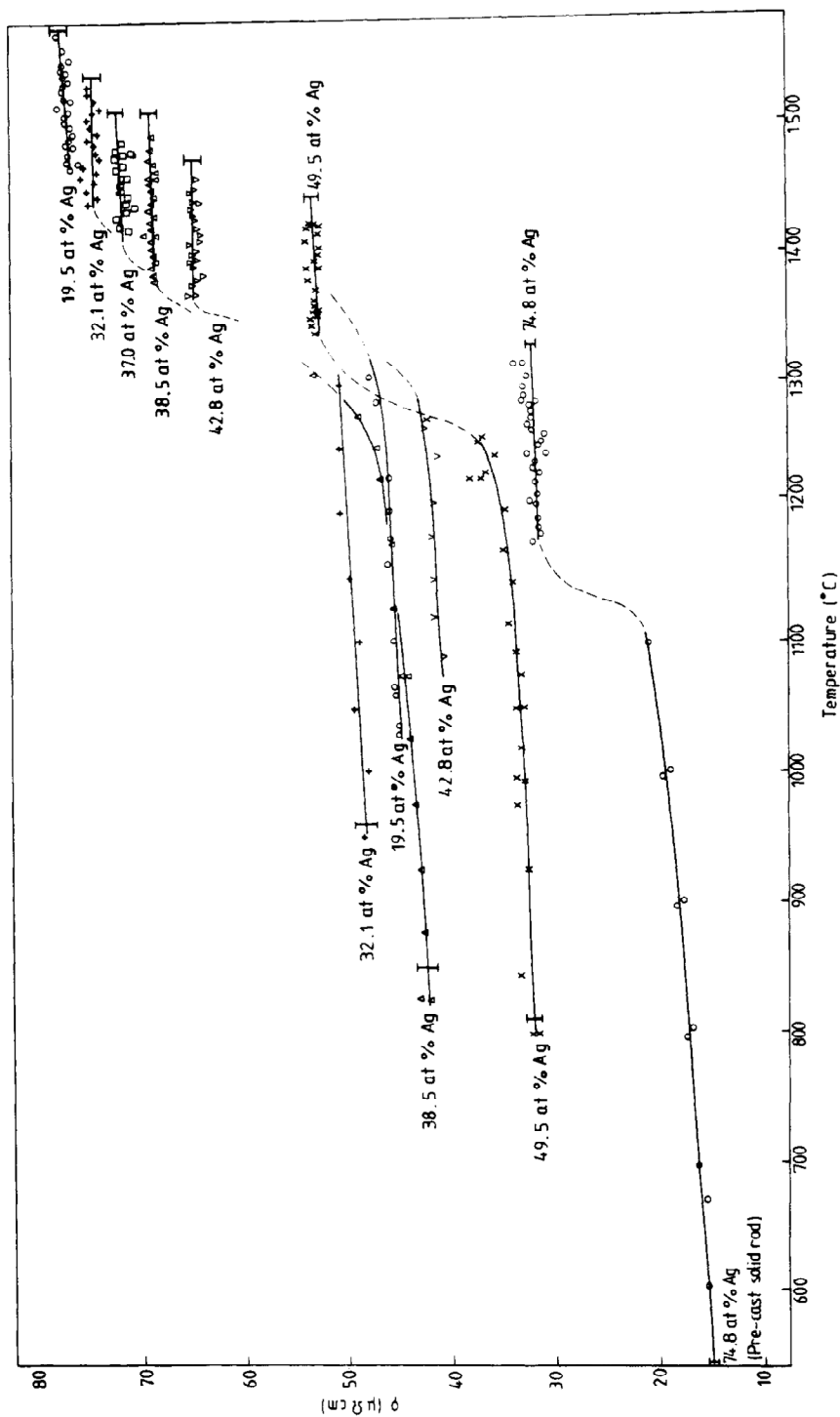
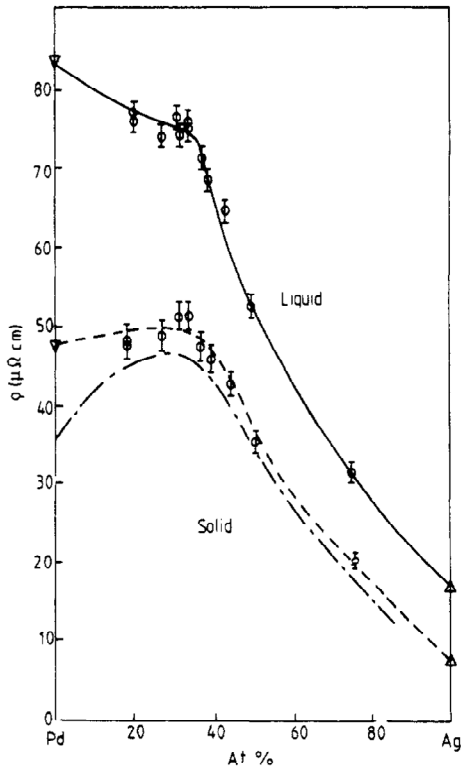**Figure 1.** Ag–Pd: resistivity at high temperatures.

Figure 2. Ag–Pd: resistivity as a function of silver concentration. $\oint$ present work at the liquidus temperature, ∇ Dupree *et al* (1975), $\triangle$ von Roll and Motz (1957), –·–·–· Ricker and Pfluger (1966).
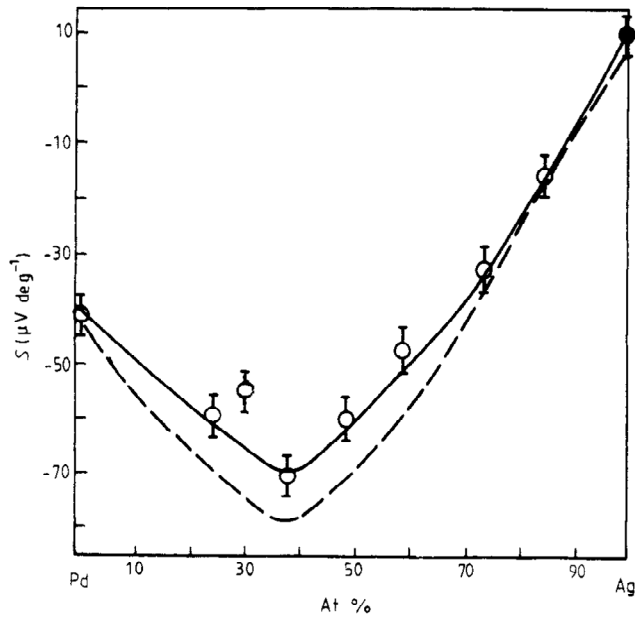

Figure 3. Ag–Pd: thermoelectric power, $\oint$ present work at 80°C above the liquidus temperature, $\oint$ Howe and Enderby (1967), ––– Rudnitskii (1956) at 1000 °C.

Table 1. Summary of resistivity data. (a) Dupree et al (1975), (b) Güntherodt et al (1975) and (c) von Roll and Motz (1957).

Sample composition (at%)	Liquidus temperature, T_L (°C)	Resistivity of liquid at T_L (μΩ cm)	Resistivity of solid at T_L (μΩ cm)	
Pure Pd	1552	83.0	48.0	(a)
		79.0		(b)
$Pd_{80}Ag_{20}$	1470	76.1	48.6	
		76.2	47.8	
$Pd_{73}Ag_{27}$	1435	73.7	49.2	
$Pd_{69}Ag_{31}$	1420	76.3	55.4	
$Pg_{68}Ag_{32}$	1420	74.0	51.3	
$Pd_{67}Ag_{33}$	1415	75.5	51.3	
		75.3		
$Pd_{63}Ag_{37}$	1410	71.2	47.8	
$Pd_{61}Ag_{39}$	1385	68.3	46.2	
$Pd_{57}Ag_{43}$	1370	64.3	42.7	
$Pd_{50}Ag_{50}$	1340	52.3	35.5	
$Pd_{25}Ag_{75}$	1180	31.3	20.3	
			20.2	
Pure Ag	960.5	17.2	8.2	(c)

For all sample compositions: $d\rho/dT|T_L = 0.01\ (\pm 0.02)\ \mu\Omega\,cm\,K^{-1}$.

Calculations were performed for palladium effective valencies between 0.36 (Brown 1973) and 0.75. These were held constant up to a silver concentration of 40 at% (an alternative value of 55 at% silver, suggested by the rigid band picture of Dugdale and Guenault (1966) was used but the theoretical results were in total disagreement with experiment). Calculated resistivity and thermoelectric power values for the effective valencies 0.6, 0.55 and 0.36 are shown in figure 4. Once again it is clear that a low effective valence for palladium cannot account for the observed trends when used within this theoretical model. The nature of the disagreement is such that we doubt whether it originates in the use of equations 2(a) and 2(b); rather we suspect that the basic model is not appropriate for the liquid Ag-Pd system.

Table 2. Summary of thermoelectric power data. (a) Howe and Enderby (1967).

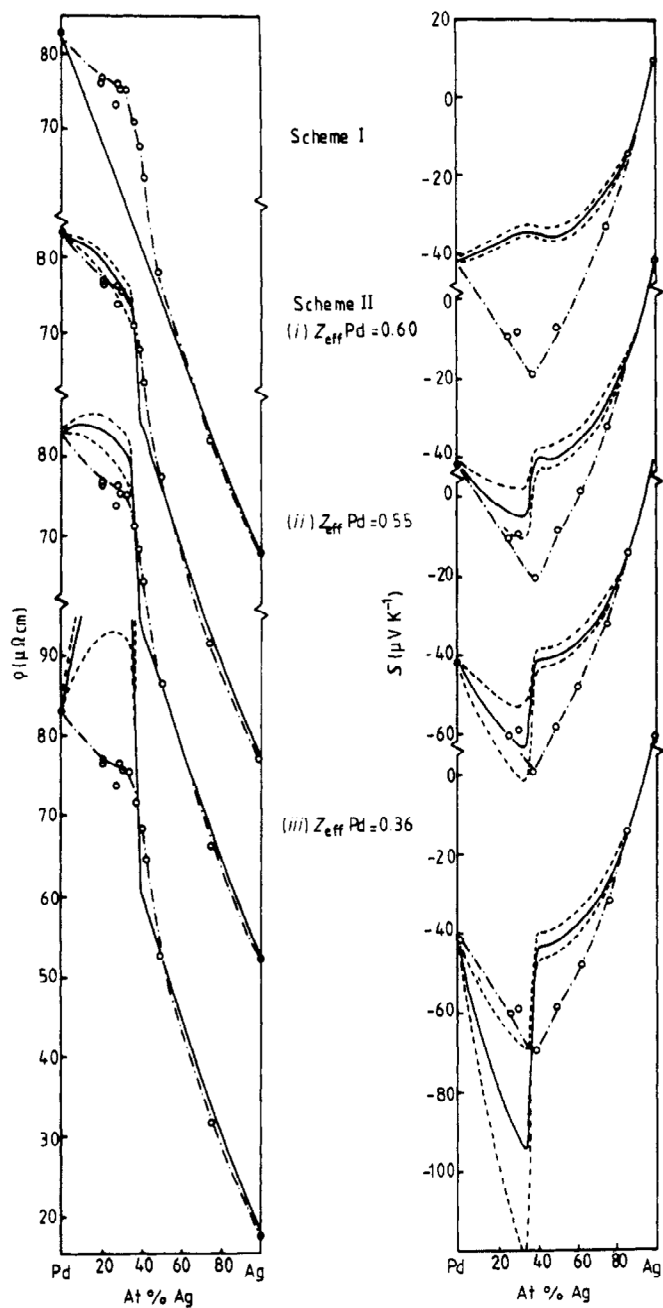| Sample composition (at%)	Liquidus temperature, T_L (°C)	Experiment temperature, T_E (°C)	Thermopower of sample, S (μV K^{-1})	
Pure Pd	1552	1581	−41	
$Pd_{76}Ag_{24}$	1450	1528	−60	
$Pd_{70}Ag_{30}$	1425	1507	−55	
			$dS/dT|T_E = 0.02$ $(\pm 0.02)\mu V\,K^{-2}$	
$Pd_{62}Ag_{38}$	1395	1478	−70	
$Pd_{51}Ag_{49}$	1345	1428	−59	
$Pd_{41}Ag_{59}$	1290	1378	−47	
$Pd_{26}Ag_{74}$	1190	1278	−32	
$Pd_{15}Ag_{85}$	1110	1110	−15	
Pure Ag	960.5	1040	+10.5	(a)

Figure 4. A comparison between the predictions of the NFE model and the present experimental results; chain curve with open circles, experiment; full curve with outer broken curves, theory.

On the other hand it should be noted that the experimental results shown in figures 2 and 3 demonstrate a strong similarity between the resistivity and thermoelectric power of liquid silver–palladium alloys and those of the high-temperature solid alloys. This suggests a common theoretical explanation of the behaviour. The s–d scattering model proposed by Mott has been used to predict the form of the observed resistivity and thermoelectric power of the solid alloy (Taylor and Coles 1956, Coles and Taylor 1962, Mott 1964) and the predictions of such a model should not be very sensitive to melting, since it does not depend significantly on the structure factors of the alloy at high temperatures (Mott 1972). However, the applicability of the s–d model for solid Ag–Pd has been questioned recently by Stocks and Butler (1981) and it is apparent from their work that further calculations should be made to determine the extent to which the d electrons can contribute to the transport effects in this system.

4. Conclusions

Whilst the calculations presented above must be viewed in the light of the rather severe approximations adopted, they do serve to demonstrate the inadequacy of a simple NFE model for liquid Ag–Pd alloys.

The results give support, albeit qualitative in nature, to the suggestion that Mott's s–d scattering model for transition metal based systems is a more appropriate starting point. These conclusions are strengthened by the experimental work of Dupree *et al* (1975) and Enderby and Dupree (1977) on the transport properties of liquid nickel–cobalt alloys and liquid iron and the theoretical studies of Fujiwara (1979 and private communication).

Acknowledgments

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