

Electrons in Transition Metals at High Temperatures*

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Abstract

At high temperatures kT may be large compared with the scale on which major changes in the electronic density of states occur near to the Fermi energy E_F , particularly for the transition elements. Mott first discussed the *qualitative* effects of this ‘smearing’ of the Fermi edge on the electrical resistance and thermopower of Pt, Pd, W, etc. Later Shimizu and colleagues examined the correlations in high-temperature behaviour of different transport properties, electronic heat capacity and susceptibility. Since then improved data have become available, largely through the use of sub-second measuring techniques. Is it now possible to provide a quantitative theoretical framework?

1. Introduction

Because of the need for high-temperature data in the design of nuclear reactors, turbines, space vehicles, etc., there are now better data on the electrical resistivity ρ , thermal conductivity λ , heat capacity at constant pressure C_P , and thermal expansivity β for a number of transition metals at high temperatures than there were in the 1950s or 1960s. This has been achieved partly as a result of sub-second measuring techniques developed at the National Bureau of Standards (NBS, now the National Institute of Standards and Technology or NIST) by Cezairliyan and colleagues [see for example the Proceedings of the NBS Workshop (Cezairliyan 1990)]. These measuring techniques involve pulse heating of a rod or tube and determination on a microsecond timescale of temperature profiles from which multiproperty data can be computed, that is values of λ , ρ , C_P , etc.

Some of the patterns of behaviour, that is, the magnitude and temperature dependence of the electron properties, were already evident to Mott and others in the mid-1930s (see e.g. Mott and Jones 1936). The question is whether the improved data can enable the theorist to interpret these patterns quantitatively or whether the problem of linking these data to the electronic bandstructure is intractable.

Mott and Jones first pointed out a probable correlation between the density of states at the Fermi edge E_F and the low-temperature electronic heat capacity $C_e = \gamma T$. Fig. 1 shows the electron density of states $N(E)$ calculated for Pd for

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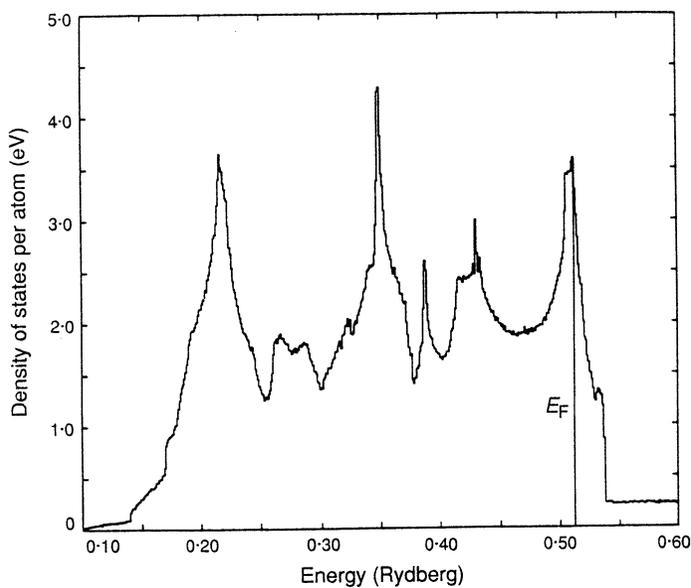


Fig. 1. Density of states of Pd from Mueller *et al.* (1970).

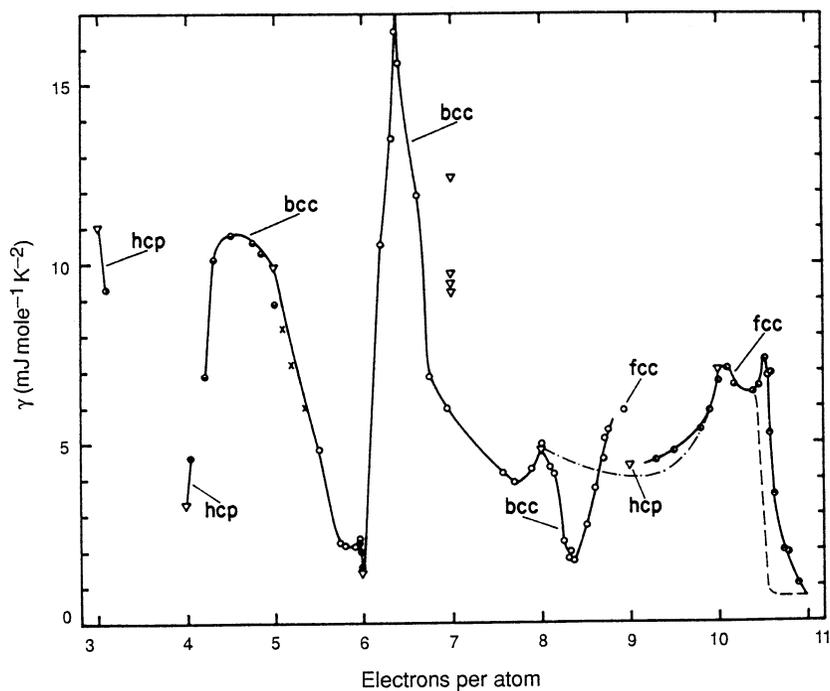


Fig. 2. Specific heat coefficient γ (from low-temperature heat capacity) versus number of valence electrons per atom for 3d elements and alloys (Heiniger *et al.* 1966).

$T = 0$ by Mueller *et al.* (1970) with the Fermi energy close to a peak in the $N(E)$ curve. Density of states curves and electron energy versus wavenumber curves for the transition and other metallic elements are compiled in a Landolt-Börnstein volume by Joss *et al.* (1983). Fig. 2 (from the review by Heiniger *et al.* 1966) shows the electronic heat capacity coefficient γ determined for the 3d transition metals at low temperatures. The value of 10 electrons per atom corresponds to Ni (and Pd and Pt) for which γ is relatively large.

Mott and Jones also noted that at high temperature $\rho(T)$ increases more rapidly than linearly with T for some transition metals (Mo, W), but much less rapidly for others such as Pt and Pd. They associated this result with the position of E_F vis-a-vis the slope and curvature of the density of states curve: for Mo and W, E_F is near the minimum of a rising $N(E)$ curve, while for Pd and Pt it is near the maximum of a sharply falling curve. Shimizu and his colleagues looked at these correlations more closely in the 1960s and 1970s, including the high-temperature behaviour of the apparent electronic heat capacity (see e.g. the review by Shimizu 1981). Since then data have improved so let us consider in turn the quantities $C_e = C_V - C_{\text{lattice}}$, ρ (or ρ/T), the thermopower $S(T)$ and the Wiedemann-Franz-Lorenz ratio L .

2. Heat Capacity

In order to obtain values for the electronic contribution to the heat capacity, we must first correct data from constant pressure to constant volume, that is from

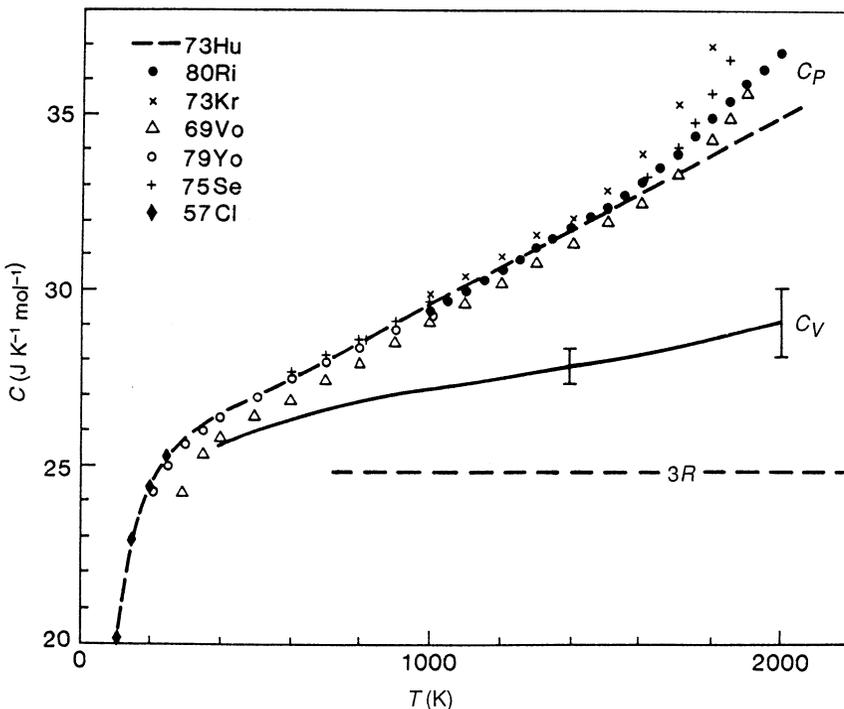


Fig. 3. Experimental values of C_P for Pt and curve of C_V evaluated by White (1988). At high temperatures, $C_D \approx 3R$ and the difference $C_V - C_D$ is attributed to electrons.

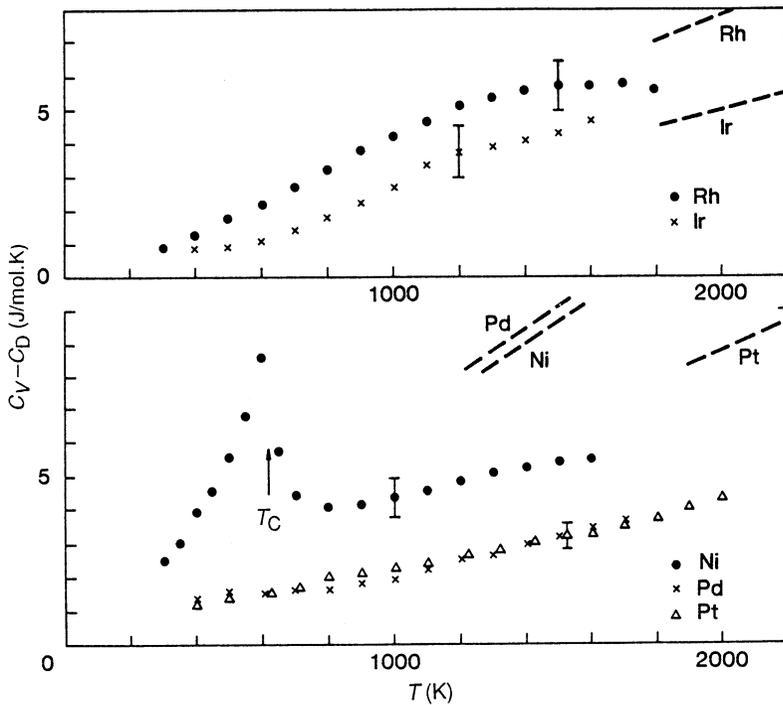


Fig. 4. Values of $C_V - C_D$ for Rh and Ir (*top*) and for Ni (Curie temperature = 629 K), Pd and Pt (*bottom*). Dashed lines are extrapolations of $C_e = \gamma T / (1 + \lambda)$.

C_P to C_V . We use the relation $C_V = C_P / (1 + \beta \gamma_G T)$, where β is the volume coefficient of thermal expansion and γ_G is the thermal Grüneisen parameter. The latter is calculated from $\gamma_G = \beta V / C_P \chi_T$ (χ_T is the isothermal compressibility and V is the molar volume) and is fairly constant at high temperatures, with values between 1.5 and 2.0 for most transition elements. From C_V we subtract the Debye lattice contribution C_D , which approaches $3R = 25 \text{ J K}^{-1} \text{ mol}^{-1}$ at high temperatures, and compare the resulting quantity $C_V - C_D \approx C_e$ with the value $\gamma T / (1 + \lambda)$ extrapolated from low-temperature heat capacity measurements (e.g. Fig. 2). The factor $(1 + \lambda)$ corrects the extrapolated values for the disappearance of the phonon enhancement factor λ at high temperature (Grimvall 1981). Fig. 3 illustrates the process for Pt.

The main conclusions are that the high-temperature values deduced for C_e are comparable with the extrapolation from low temperatures for Nb, V and Ta (Group V B) and for Rh and Ir; they are much larger for Cr, Mo and W (Group VI B), and smaller than the extrapolated values for Pd and Pt (Group VIII B) (see e.g. Fig. 4 here reproduced from White 1988). In equating C_e with $C_V - C_D$ we are neglecting contributions from the higher-order anharmonic terms and from vacancies as we believe these are small compared with experimental uncertainties. We note that a rather different conclusion concerning anharmonic

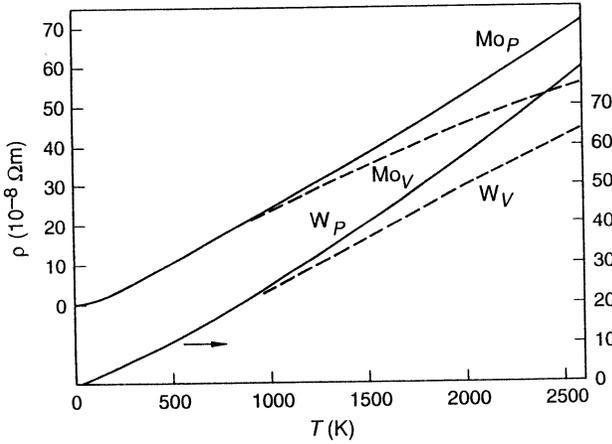


Fig. 5. Electrical resistivity of Mo and W as measured at constant pressure (subscript P) and converted to constant volume (subscript V).

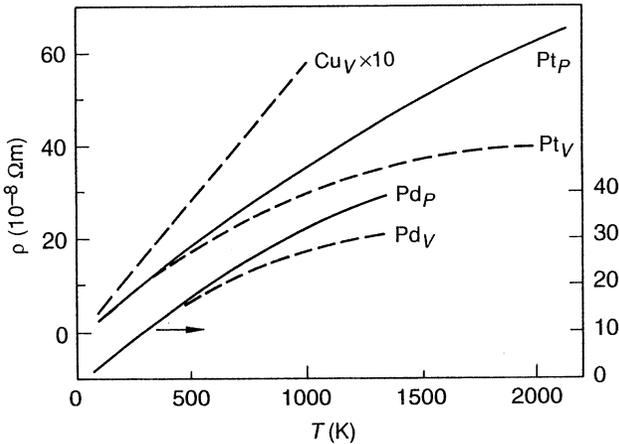


Fig. 6. Electrical resistivity for Pd and Pt at constant P and constant V .

contributions has been reached by Guillermet and Grimvall (1991) for Mo and W in their analysis of thermodynamic data at high temperatures: they have used an alternative approach of estimating the electronic contribution to the entropy, S_e , at high temperature from band calculations and attributing the difference $C_V - C_{e(\text{band})}$ to anharmonicity. They do not give details of their calculation of S_e and whether the volume dependence is taken into account. However, a more recent calculation by Eriksson *et al.* (1992) of the entropies of the transition metals at high temperatures concludes that the anharmonic terms are small for V, Nb, Ta, Pd and Pt but large for Cr, Mo and W. Eriksson *et al.* (1992) integrated over the density of states $N(E)$ to find S_e as a function of temperature and volume (see also Wallace 1992).

3. Electrical Resistivity

Again for comparison with theory we must first convert values of ρ measured at constant P (obtained from compilation by Bass 1982) to constant volume, using values for $d \ln \rho / d \ln V$ from Dugdale and Myers (1985). Resulting values of ρ_V show a roughly linear variation with temperature for Mo and W (see Fig. 5), that is ρ_V/T is roughly constant. For the V–Nb–Ta and Pd–Pt groups there is a marked decrease in ρ_V/T at high temperatures, that is $\rho(T)$ increases less rapidly than linearly as seen in Fig. 6. This also applies to Rh and Ir. It is interesting to compare the behaviour of the monovalent metals—Cu, Ag and Au (and potassium)—for which ρ varies roughly linearly with T after correction to constant volume.

A particular feature of the V–Nb–Ta group is that curvature of $\rho(T)$ begins at a relatively low temperature ($T \sim 500$ K) and may be linked to the unusual curvature of the elastic shear modulus $c_{44}(T)$ which occurs in the same temperature region. The curvature is sufficient to produce a minimum in c_{44} for Nb (near 400 K) and for V (near 600 K), which indicates a ‘hardening’ of the lattice above this temperature, and appears to arise from electron redistribution between four ellipsoids in the third zone of the Fermi surface (Mattheiss 1970; Collins 1985, personal communication).

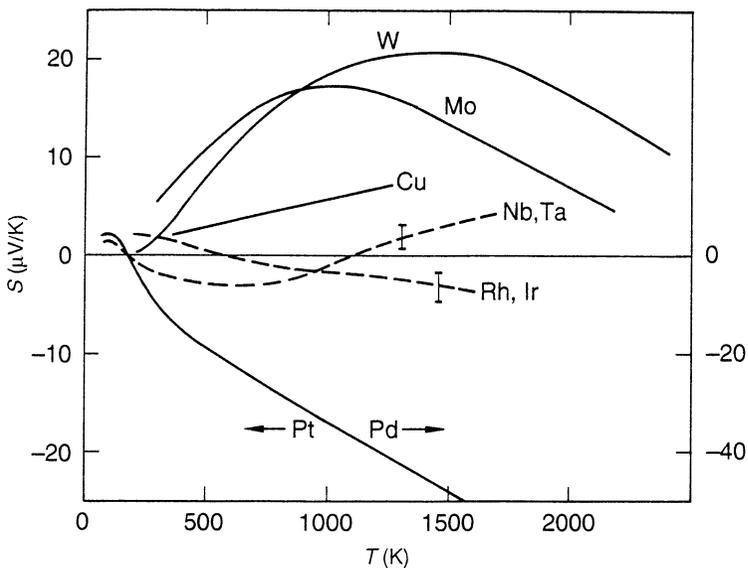


Fig. 7. Absolute thermopower $S(T)$ of some transition elements.

4. Thermopower

The absolute thermopower S is proportional to the energy derivative of the conductivity:

$$S = (\pi^2 k^2 T / 3e) (d \ln \sigma / dE)_{E=E_F}.$$

Therefore we might expect a connection between the sign of S and the curvature of $\rho(T)$. Fig. 7 shows $S(T)$ from data compiled by Vedernikov (1969), Blatt

et al. (1976) and Roberts (1985). For Pd and Pt there is a strong correlation between the large negative values of S and convex curvature of ρ_V (see also Mott and Jones, p. 311). For Rh and Ir, curvature of ρ_V is much less, at least below 1500 K, and S is also negative and much smaller than for Pd and Pt. For Mo and W there is very little curvature in $\rho(T)$ below 1000 K, where S is increasingly positive, while above 1000 K, S decreases. For Nb and Ta, the picture is more confused.

The fact that the thermopower is a *derivative* of the electron scattering and therefore of the complicated $N(E)$ function adds an extra degree of difficulty in reaching quantitative conclusions for any of these elements.

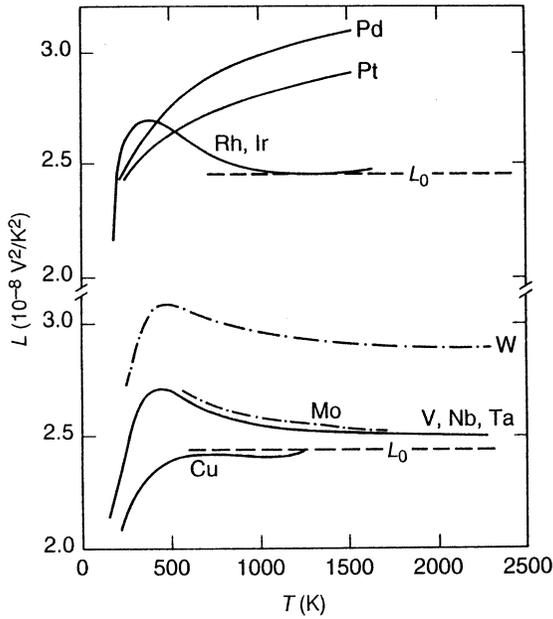


Fig. 8. Lorenz ratio $L = \rho\lambda/T$, where L_0 denotes the Sommerfeld value of $2.445 \times 10^{-8} \text{ V}^2/\text{K}^2$. Values of λ include the lattice conductivity.

5. Lorenz Ratio

The Lorenz ratio of electrical to thermal resistivity (W), $L = \rho/WT = \rho\lambda/T$, reflects the relative efficiency of the electron scattering processes in restoring electrical and thermal ‘equilibrium’. For example, if elastic scattering by static defects predominates, then it should be equally efficient in limiting the transport of charge or heat, that is the relaxation time should be the same for each and L would have its theoretical Sommerfeld value, $L_0 = 2.445 \times 10^{-8} \text{ V}^2/\text{K}^2$. This is generally the case at very low temperatures because static (impurity) scattering is dominant. At high temperatures for the monovalent metals Cu, Ag and Au, L does approach this value within one or two per cent (see the compilation by White 1991). For the transition metals at high temperatures, data are less reliable except for Pt where L clearly exceeds L_0 significantly and for Pd (see Fig. 8). For most of the others, L seems to be approaching L_0 .

Note that the maxima at lower temperatures evident in Fig. 8 occur because of the lattice contribution to λ for which we have made no correction: the lattice term $\lambda(\text{lattice})$ varies approximately as $1/T$ at normal and high temperatures and therefore should be small above 1000 K compared with the usual experimental errors of a few per cent.

Obvious questions which arise are the reason for the departures of L for Pt and Pd (and also for W). Do they arise from degeneracy effects or electron–electron interactions, and if so, why are the deviations positive?

6. Conclusion and Discussion

I have not included group IV elements (Ti, Zr, Hf) in the preceding analysis as anisotropy and phase transformations affect the accuracy and interpretation of the data for them. Available measurements do indicate that C_e for Ti and Zr at high temperature is larger than the low-temperature extrapolation and also that ρ_V/T decreases at high T . Regrettably, available data on Re, Tc, Os and Ru are quite inadequate for the present analysis.

If we examine the qualitative behaviour pattern of these properties for each group of transition metals we observe:

Group V B elements V, Nb and Ta. C_e/T increases with T from being less than the low-temperature extrapolation to approach equality, while ρ_V/T decreases with curvature beginning at 500 K or less; S is small and negative, becoming positive above 1000 K, and $L \approx L_0$ at high T . The patterns are complex like the Fermi surfaces.

Group VI B elements Cr (?), Mo and W. C_e/T is much larger than the low-temperature extrapolation and increases, while ρ_V/T is fairly constant; S is large and positive with a maximum near 1000 K; L is large for W but not for Mo, which is puzzling in view of the similarities of their Fermi surfaces. The only notable difference between them is in the strain dependence of the Fermi surface and of the density of states (Joss *et al.* 1983).

Group VIII B elements Rh and Ir. Data are poorer but indicate C_e/T to be fairly constant and consistent with low-temperature values, ρ_V/T decreases; S is small and negative, and $L \approx L_0$. The patterns are consistent.

Group VIII B elements Pd and Pt. C_e/T is smaller than the low-temperature extrapolation, ρ_V/T falls markedly; S is large and negative—all consistent but why is L so much larger than L_0 ?

It appears that this jigsaw puzzle is difficult even in its qualitative aspects so is there any possibility that energy band calculations can explain the quantitative details? It seems likely that the methods used by Wallace (1992) and by Grimvall (1981) and their respective colleagues may give answers for the thermodynamic properties of those elements for which there are adequate data on the phonon spectrum and volume corrections, but the transport properties are more difficult as they involve scattering cross sections as well as phonon energies and electron energies.

Acknowledgments

I thank Dr G. C. Fletcher for illuminating discussions many years ago about the shape of the density of states curve of chromium and its possible influence on electron contributions to thermal expansion (see his more recent paper on the electronic Grüneisen parameter of the transition metals, Fletcher and Yahaya 1979); thanks also to Professor P. G. Klemens and Dr Duane C. Wallace for their interest and advice.

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