TRANSPORT PROPERTIES OF NOBLE METALS

By Jai Prakash and P. K. Sharma

Physics Department, University of Allahabad*

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The temperature variations of the electrical and thermal resistivities of noble metals: copper, silver and gold have been investigated in the free electron approximation using Bhatia and Horton's model for the phonon spectrum. The normal and Umklapp contributions are considered separately from the geometry of the reciprocal space. From the computed resistivities, the Lorentz numbers of these metals are obtained. The calculated resistivities and Lorentz numbers are compared with available experimental data. The nature of the theoretical and experimental resistivity curves is found to be similar, though the agreement is not detailed.

1. Introduction

A knowledge of the vibrations of constituent atoms of metals is of considerable importance in the study of their thermal and transport properties. Early theoretical work [1] on lattice vibrations in metals using central interactions between ions turn out to be inadequate. It is now well known that electrons in metals influence considerably their lattice dynamical properties. Bhatia [2], and Bhatia and Horton [3] have proposed an elastic force model for the lattice dynamics of monovalent metals by considering the electronic effect *via* the screening of long-range Coulomb interaction between the ions and have applied it to sodium and silver to obtain their phonon spectra and lattice specific heats with satisfactory results. Joshi and Hemkar [4] have used this model to other alkali and noble metals and have obtained a fairly reasonable description of the gross features of their phonon spectra. Recently Sangal and Sharma [5–7] have utilised this model to explain many other solid state phenomena in alkali, noble and transition metals.

In this paper, we have studied the temperature dependence of the electrical and thermal resistivities of noble metals; copper, silver and gold in the free electron approximation using Bhatia and Horton's model [3] for the phonon spectrum. The normal and Umklapp contributions to the resistivities are considered separately from the conservation laws of wave vectors and the geometry of the reciprocal space. From the computed resistivities, the Lorentz numbers of these metals are obtained and compared with the values derived from experimental resistivity data.

* Address: Physics Department, University of Allahabad, Allahabad — 2, U. P., India.

2. Theory

The transport properties of metals depend in a complicated way on the nature of phonon spectrum and the electronic band structure. The crux of the problem lies in the determination of the scattering probability of conduction electrons. Ziman [8] has obtained expressions for the electrical and thermal resistivities of pure metals considering a first order trial function in the variational solution of the Boltzmann equation. For cubic metals, the ideal electrical and thermal resistivities due to phonon scattering can be written as

$$\varrho = \frac{3\pi\hbar}{2e^2mnk_BTk_F^2}\sum_j \left\langle\!\!\left\langle \frac{K^2(\boldsymbol{K}\cdot\boldsymbol{e}_{qj})^2C^2(K)}{(1-e^{-\beta\omega_{qj}})(e^{\beta\omega_{qj}}-1)} \right\rangle\!\!\right\rangle, \tag{1}$$

$$W = \frac{9\pi\hbar}{2e^2L_0mnk_BT^2k_F^2}\sum_j \left\langle\!\!\left\langle \frac{(\boldsymbol{K}\boldsymbol{e}_{q,j})^2C^2(K)\left\{\frac{K^2}{3}-\frac{K^2}{6\pi^2}(\beta\omega_{q,j})^2+\frac{k_F^2}{\pi^2}(\beta\omega_{q,j})\right\}}{(1-e^{-\beta\omega_{qj}})(e^{\beta\omega_{qj}}-1)} \right\rangle\!\!\right\rangle \tag{2}$$

Here, m, e, k_B and T are the ionic mass, electronic charge, Boltzmann constant and absolute temperature, respectively. v is the velocity of an electron in the state $\boldsymbol{k}$ on the Fermi surface, $\boldsymbol{K}=\boldsymbol{k}'-\boldsymbol{k}$ the momentum transfer vector, k_F the Fermi momentum, $C(K)$ the matrix element describing the transition of an electron from state $\boldsymbol{k}$ to $\boldsymbol{k}'$ and L_0 the free electron Lorentz number. $\omega_{q,j}$ is the angular frequency of phonon of wave vector $\boldsymbol{q}$ and polarization j, $\boldsymbol{e}_{q,j}$, the polarization vector, n the number of ions per unit volume and $\beta = \hbar/k_BT$. The angular brackets $\ll\!\cdots\!\gg$ represent the double average over the Fermi surface.

The polarization factor $(\boldsymbol{K}\cdot\boldsymbol{e}_{q,j})^2$ and the frequency $\omega_{q,j}$ vary with the direction of the momentum transfer vector. This situation complicates the evaluation of the double average in Eqs (1) and (2). Here we use Bailyn's [9] averaging procedure as elaborated by Sangal and Sharma [6] to simplify the double average. For a function $F(K)$ having cubic symmetry, this method leads to the following expression for the double average over a spherical Fermi surface:

$$\langle\langle F(\boldsymbol{K})\rangle\rangle = \frac{1}{2\pi^2k_F}\int d\Omega \int dK F(\boldsymbol{K})\,(1-u^2)^{1/2}, \tag{3}$$

where $u = K/2k_F$ and Ω is the solid angle in $\boldsymbol{K}$-space. Using Eq. (3) into Eqs (1) and (2), the expressions for the electrical and thermal resistivities may be written as

$$\varrho = \frac{3\hbar}{4\pi e^2mnk_BTv_F^2k_F^3}\sum_j \int d\Omega \int dK \frac{K^2(1-u^2)^{Y_2}(\boldsymbol{K}\cdot\boldsymbol{e}_{q,j})^2C^2(K)}{(1-e^{-\beta\omega_{qj}})(e^{\beta\omega_{qj}}-1)}, \tag{4}$$

$$W = \frac{9\hbar}{4\pi e^2L_0mnk_BT^2v_F^2k_F^3}\sum_j \int d\Omega \int dK \times$$

$$\times \frac{(1-u^2)^{1/2}(\boldsymbol{K}\cdot\boldsymbol{e}_{q,j})^2C^2(K)\left\{\frac{K^2}{3}-\frac{K^2}{6\pi^2}(\beta\omega_{q,j})^2+\frac{k_F^2}{\pi^2}(\beta\omega_{q,j})^2\right\}}{(1-e^{-\beta\omega_{qj}})(e^{\beta\omega_{qj}}-1)}. \tag{5}$$

3. Results and discussion

We have used the modified Houston's method to calculate the electrical and thermal resistivities of noble metals: copper, silver and gold from Eqs (4) and (5). The integration over K was performed numerically and the integration over Ω was carried out by a spherical six term integration procedure as elaborated by Betts *et al.* [10] The six directions for $\boldsymbol{K}$ used are: [100], [110], [111], [210], [211] and [221]. The phonon frequencies $\omega_{q,j}$ and the polarization vectors $\boldsymbol{e}_{q,j}$ were obtained from solutions of Bhatia and Horton's secular equation [3] for a face-centred cubic lattice. For $C(K)$ we used the free electron expression given by Ziman [8]. While integrating over K, we split the integrals in (4) and (5) into two parts corresponding to normal and Umklapp processes from the conservation laws of wave vectors. For the normal processes, $\boldsymbol{K} = \boldsymbol{q}$, where the phonon wave vector $\boldsymbol{q}$ is restricted to lie within the first Brillouin zone. The limiting values of K along the above six directions are given by the intersections of the corresponding $\boldsymbol{K}$ vectors with the planes of the first Brillouin zone. In the Umklapp processes, the wave vectors satisfy the conservation law

$$\boldsymbol{K} = \boldsymbol{q} + \boldsymbol{G},$$

where $\boldsymbol{G}$ is a vector of the reciprocal lattice. The minimum values of $\boldsymbol{K}$ at which Umklapp processes show up, can be obtained from the knowledge of reciprocal lattice vectors of a face-centred cubic lattice. To study the effect of temperature dependence of elastic constants on the resistivities, two sets of elastic data referring to 0°K and 300°K were used in calculation of the phonon spectrum. The numerical values of these elastic constants

TABLE I

Elastic constants and other parameters for noble metals used in the calculation

Metal	Elastic constants (10^{11} dynes/cm^2)			Temperature (°K)	$V(r_s)-E_0$ (eV)	Fermi energy (eV)
	C_{11}	C_{12}	C_{44}			
Copper	17.620	12.494	8.177	0	1.361	7.04
	16.839	12.142	7.539	300	1.361	7.04
Silver	13.149	9.733	5.109	0	1.10	5.51
	12.399	9.367	4.612	300	1.10	5.51
Gold	20.163	16.967	4.544	0	3.70	5.51
	19.234	16.314	4.195	300	3.70	5.51

and other relevant parameters of noble metals needed in the present study are given in Table I. The elastic constants for copper are taken from the work of Overton and Gaffney [11], while those for silver and gold are due to the measurements of Neighbours and Alers [12].

Figures 1–3 give the calculated values of electrical resistivities of copper, silver and gold as a function of temperature, while the results of calculations for thermal resistivities are shown in Figs 4–6. In these figures, curve labelled A is obtained from 0°K elastic constant

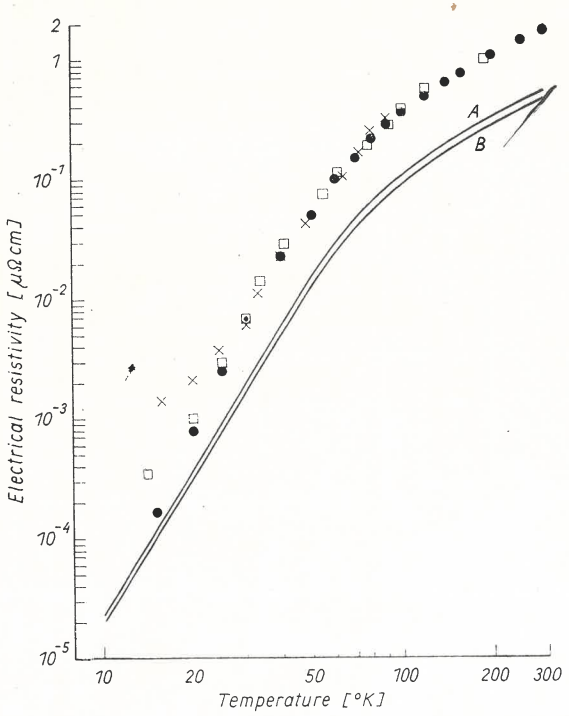

Fig. 1

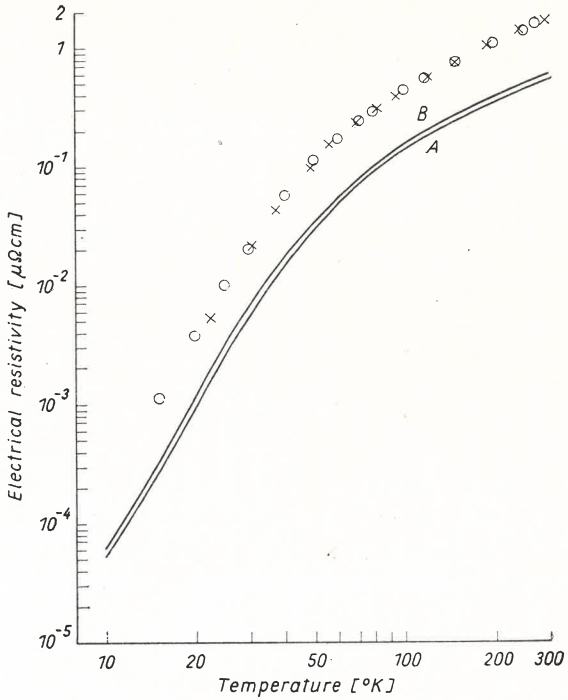

Fig. 2

Fig. 1. The electrical resistivity against temperature for copper. Solid lines show theoretical curves. Experimental points: × — Berman and MacDonald, □ — White, ● — White and Woods

Fig. 2. The electrical resistivity against temperature for silver. Solid lines show theoretical curves. Experimental points: × — Dugdale and Basinski, ○ — White and Woods

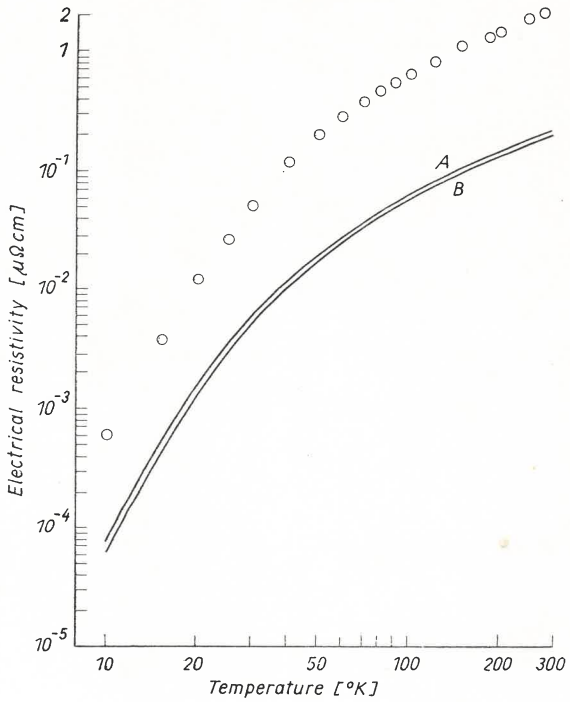

Fig. 3. The electrical resistivity against temperature for gold. Solid lines show theoretical curves. Experimental points: ○ — White and Woods

TABLE II

References for electrical and thermal resistivity data for noble metals

Metal	Electrical resistivity	Thermal resistivity
Copper	Berman and MacDonald[a] White[b] White and Woods[c]	Berman and MacDonald[a] White[b]
Silver	White and Woods[c] Dugdale and Basinski[d]	White[e]
Gold	White and Woods[c]	White[f]

[a] R. Berman, D. K. C. MacDonald, *Proc. Roy. Soc.*, **A211**, 122 (1952).
[b] G. K. White, *Austr. J. Phys.*, **6**, 397 (1953).
[c] G. K. White, S. B. Woods, *Phil. Trans. Roy. Soc.* (London), **A251**, 373 (1959).
[d] J. S. Dugdale, Z. S. Basinski, unpublished.
[e] G. K. White, *Proc. Phys. Soc.*, **A66**, 844 (1953).
[f] G. K. White, *Proc. Phys. Soc.*, **A66**, 559 (1953).

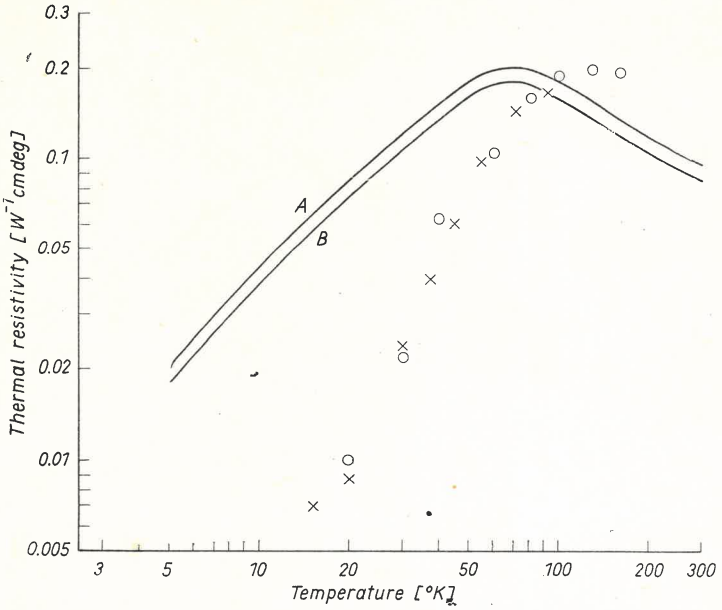

Fig. 4. The thermal resistivity *versus* temperature curve for copper. Solid lines show theoretical curves. Experimental points: × — Berman and MacDonald, ○ — White

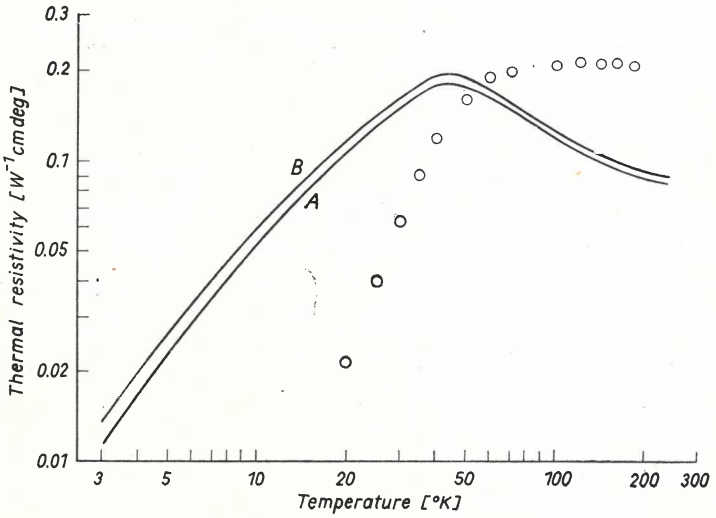

Fig. 5. The thermal resistivity *versus* temperature curve for silver. Solid lines show theoretical curves. Experimental points: ○ — White

data and curve labelled B is based on 300°K elastic constant data. For comparison, the available experimental data on resistivities have also been plotted in these figures. The sources of the experimental resistivity data are summarized in Table II. In Fig. 7, we have displayed the Lorentz number $L = \varrho/TW$ obtained from the calculated and observed tempe-

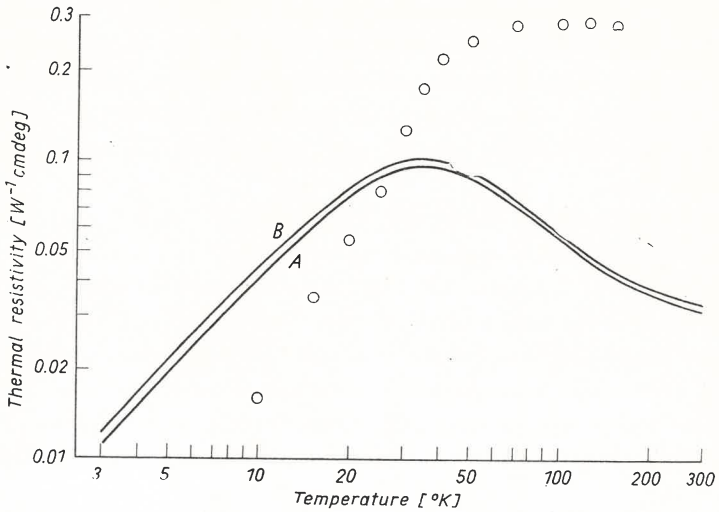

Fig. 6. The thermal resistivity *versus* temperature curve for gold. Solid lines show theoretical curves. Experimental points: ○ — White

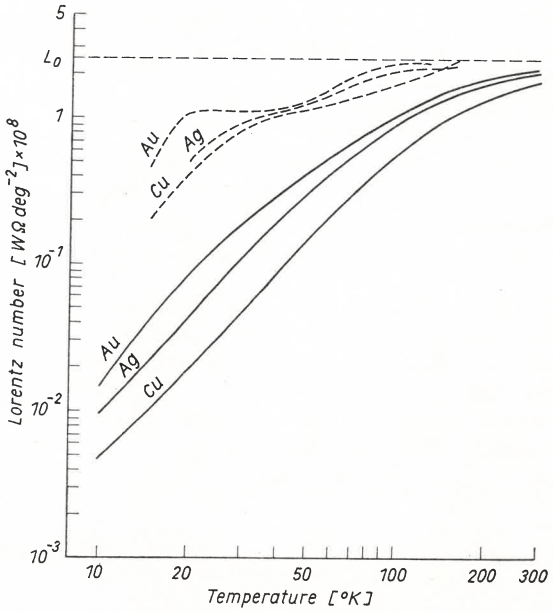

Fig. 7. Theoretical (full lines) and experimental (broken lines) Lorentz numbers of noble metals

rature dependence of electrical and thermal resistivities. It is seen from Figs 1–6 that the general shape of the theoretical and experimental resistivity curves is similar, though the agreement is not detailed. The experimental electrical resistivity values are throughout higher than the calculated values and the divergence between them increases with the

rise of temperature. In the case of thermal resistivity, the theoretical values are higher than the experimental values at low temperatures, but lie below the experimental curves in the high temperature region. The disagreement is more pronounced in gold. Further, the theoretical results do not seem to be very sensitive to the temperature dependence of elastic constants. The marked variation of Lorentz number with temperature shows in adequacy of the Wiedemann-Franz law.

The discrepancies between theory and experiment are attributable to the use of the free electron model for the electron-phonon matrix element $C(K)$, which ignores the exchange and correlation effects. It is known that transport coefficients of metals are very sensitive to the form of electron-ion matrix element used. The expressions (1) and (2) used in the present work are based on first-order trial function in the variational solution of the Boltzmann equation. This results in a certain overestimation of the resistivities. The poorer agreement obtained at higher temperatures may be partly due to the neglect of multiphonon processes and small change in $C(K)$ brought about by volume changes through the thermal expansions.

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