Temperature Dependence of the Thermal Resistivity of Noble Metals

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The temperature dependence of the thermal resistivity of copper, silver, and gold is calculated within the free electron approximation and using the anisotropic continuum dispersive model proposed by Sharma and Joshi for the lattice dynamics of cubic metals. The phonon spectrum has been calculated with the help of the modified Houtson's spherical six-term procedure as elaborated by Betts at al. Bardeen's matrix elements for the scattering of free electrons have been incorporated into the variational expression developed for the Boltzman transport equation. The theoretically calculated resistivity values of copper, silver, and gold are in reasonable agreement with the experimental data.

1. Introduction

Considerable progress has been made both in experimental and theoretical studies of the electrical resistivity of cubic metals [1-6]. However, very little work has been reported on the thermal resistivity of cubic metals [7-10]. These authors used the pseudo potential formulation with lattice dynamics to obtain the temperature variation of the thermal resistivity of simple metals. The knowledge of pseudo potential form factors, besides phonon frequencies and the polarization vectors is essential for such calculations. The electron ion scattering is considered through the pseudopotential form factor and the information about ion positions is obtained through the dynamical structure factor. The small changes in the pseudopotential by volume changes through thermal expansion, however, affect the resistivity. These effects are small but lead to relatively important changes in the resistivity which depends very sensitively on the details of both the structure factor and the pseudopotential form factor.

The purpose of the present paper is to study the temperature dependence of the thermal resistivity of copper, silver, and gold in the free electron approximation using the anisotropic continuum dispersive (ACD) model for the lattice dynamics of cubic metals proposed by Sharma and Joshi [11]. It has been found that this model represents fairly well the gross features of the frequency distribution and yields a satisfactory explanation for the lattice dynamical behaviour of lithium and copper. It has also been utilized, with success, to explain the Debye-Waller factors of cubic metals [12-14], the temperature variation of Grüneisen parameters of copper and germanium [15], and the electrical resistivity of alkali (Li, Na, K, Rb) [6, 16] and noble (Cu, Ag, Au) [5] metals. The choice of these metals for the study is motivated by the fact that the noble metals have the simplest fcc structure and appear to approximate well the free electron model of a metal. There is one electron per atom in a metallic state and the Fermi surface is believed to be very nearly spherical and not in contact with the Brillouin zone boundary as shown by the studies of the de Haas-van Alphen effects [17].

2. Theory

For a lattice of cubic symmetry the first order variational solution of the Boltzmann equation giving the thermal resistivity can be written as [18],

$$W_L = \frac{27\,\hbar}{2\,\pi\,m\,n\,k_B{}^3\,T^2\,k_F{}^2} \sum_j \left\langle\!\!\left\langle (K \cdot e_{q,j})^2\,C^2(K) \right.\right.$$
$$\left.\left. \frac{\left\{ \dfrac{K^2}{3} - \dfrac{K^2}{6\,\pi^2}\,(\beta\,\omega_{q,j})^2 + \dfrac{k_F{}^2}{\pi^2}\,(\beta\,\omega_{q,j})^2 \right\}}{v\,v'\,[1 - \exp\{-\beta\,\hbar\,\omega_{q,j}\}]\,[\exp\{\beta\,\hbar\,\omega_{q,j}\} - 1]} \right\rangle\!\!\right\rangle \quad (1)$$

where e is the electronic charge, k_B the Boltzmann constant, m the ionic mass, n the number of ions per unit volume, T the absolute temperature, k_F the Fermi radius, v and v' are the velocities of the electrons in the initial state k and the final state k', respectively, $C(k - k')$ is the matrix element corresponding to transition from k to k', β is $1/k_B T$, e_{qj}, ω_{qj} and q are the polarization vector, frequency and wave vector of the phonon, respectively, and the subscript j distinguishes three modes of vibration. The bracket $\langle\langle \dots \rangle\rangle$ represents the

double average over the Fermi surface and the summation is over the three polarization branches for each wave vector $\boldsymbol{q}$.

Denoting the scattering vector $\boldsymbol{k} - \boldsymbol{k}'$ by $\boldsymbol{K}$, the matrix element $C(K)$ for a spherical Fermi surface is given by [1]

$$C(K) = \frac{[V(r_s) - E_0] K^2 + W(K) q_s^2}{K^2 + q_s^2} G(K r_s) \qquad (2)$$

where $[E_0 - V(r_s)]$ is the kinetic energy of an electron in the lowest state at the boundary of the Wigner-Seitz sphere of radius r_s, q_s is the screening parameter defined by $q_s = 4 \pi n_e e^2 / W(K)$, n_e being the electron density, and $W(k)$ and $G(x)$ are given by

$$W(K) = \frac{2}{3} E_F \left[\frac{1}{2} + \frac{4 k_F^2 - K^2}{8 k_F K} \ln \left| \frac{2 k_F + K}{2 k_F - K} \right| \right]^{-1},$$

(E_F being the Fermi energy),

$$G(x) = 3 (\sin x - x \cos x) / x^3,$$

where E_F is the Fermi energy.

As the phonon frequencies ω_{qj} and the factor $(\boldsymbol{K} \cdot \boldsymbol{e}_{qj})^2$ vary with the direction of the scattering vector $\boldsymbol{K}$, the evaluation of the double average in Eq. (1) becomes difficult. Following Bailyn's method [3], to compute the average, one can write

$$\langle \langle A(K) \rangle \rangle = \frac{1}{S^2} \iint_{S \, S'} A(K) \, dS \, dS' \qquad (3)$$

where S is the area of the Fermi surface and each integral is carried out over the Fermi surface. In order to get rid of the above difficulty, we consider first all the vectors $\boldsymbol{k}$ and $\boldsymbol{k}'$ that have the same scattering vector $\boldsymbol{K} = \boldsymbol{k}' - \boldsymbol{k}$, and average over all such K vectors. For a spherical Fermi surface all such $\boldsymbol{K}$ can be imagined to be enumerated by allowing a rigid rod of length K oriented in the direction of $\boldsymbol{K}$ to roll inside a spherical shell of radius k_F. The ends of the rod will lie on a circle of circumference $l(K) = 4 \pi (4 k_F^2 - K^2)^{1/2}$, then we average over all $\boldsymbol{K}$ for a given magnitude K. This average is equal to the integral of $A(\boldsymbol{K})$ over all directions of K with the weighting factor equal to the ratio of $l(\boldsymbol{K})$ to the integral of $l(\boldsymbol{K})$ over the whole solid angle for a given K magnitude. Finally, we take average over all K magnitudes which are equal to one integral over all K with the weighting factor equal to $\int d\Omega \, l(K) / \int dK \int d\Omega \, l(K)$. This gives the required average over the Fermi surface as

$$\langle \langle A(K) \rangle \rangle = \frac{\int d\Omega \int dK \, l(K) A(K)}{\int d\Omega \int dK \, l(K)}. \qquad (4)$$

Now, for a spherical Fermi surface

$$\int d\Omega \int dK \, l(K) = 4 \pi^3 k_F^2.$$

Therefore, the above ecpression reduces to

$$\langle \langle A(\boldsymbol{K}) \rangle \rangle = \frac{1}{2 \pi^2 k_F} \int d\Omega \int dK \, A(K) \, (1 - u^2)^{1/2}, \qquad (5)$$

where $u = K / 2 k_F$.

Thus making use of relation (5) the expression (1) for the thermal resistivity due to phonon scattering becomes

$$W_L = \frac{27 \hbar}{4 \pi^3 m \, n \, k_B^3 \, T^2 \, k_F^2 \, v_F^2} \sum_j \int d\Omega \int dK$$
$$\times K^2 (1 - u^2)^{1/2} \, (\boldsymbol{K} \cdot \boldsymbol{e}_{q,j})^2 \qquad (6)$$
$$\times \frac{\left\{ C^2(K) \frac{K^2}{3} - \frac{K^2}{6 \pi} 2 (\beta \omega_{q,j})^2 + \frac{k_F^2}{\pi^2} (\beta \omega_{q,j})^2 \right\}}{[\exp \{ \beta \omega_{q,j} \} - 1] [1 - \exp \{ - \beta \omega_{q,j} \}]}.$$

3. Numerical Computation

The calculation of the temperature variation of the thermal resistivity of copper, silver, and gold has been made from Equation (6). The integration over K was performed numerically while the integration over Ω was carried out using the modified Houston's spherical six-term integration procedure as elaborated by Betts et al.[19], the applicability of which has been discussed by many authors: Horton and Schiff [20], Betts [21], Ganesan and Srinivasan [22]. The six directions for $\boldsymbol{K}$ used are: [100], [110], [111], [210], [211], and [221]. The phonon frequencies ω_{qj} and the polarization vectors $\boldsymbol{e}_{qj}$ were obtained from the solutions of the Christoffel equation for the propagation of elastic waves in a continuum for a face centered cubic lattice.

While integrating over $\boldsymbol{K}$ a distinction has been made between the Normal processes and Umklapp processes. Early workers neglected the contribution of Umklapp processes to the electrical resistivity. U-processes contribute a substantial part of the high temperature resistivity of monovalent metals [1]. Hasegawa [23] have assumed that the N-processes operate in the range of variable of integration u from 0 to 0.63 in the first Brillouin zone, while U-processes from 0.63 to 1. This separation between the range of N-processes and U-processes seems artificial when one goes beyond the Debye model. In the present calculations a more realistic procedure has been adopted.

	Elastic constants (10¹¹ Dynes/cm²)			Lattice constant (Å)	Fermi energy (eV)	$[V(r_\mathrm{s})-E]$ (eV)
	C_{11}	C_{12}	C_{44}			
Copper	16.51	11.99	7.56	3.616	7.48	1.36
Silver	12.22	9.07	4.54	4.080	5.51	1.10
Gold	19.29	16.38	4.15	4.070	5.51	3.70

Table 1. Physical constants for noble metals used in the calculation.

For the N-processes, $\boldsymbol{K}=\boldsymbol{k}'-\boldsymbol{k}=\boldsymbol{q}$, where the phonon wave vector $\boldsymbol{q}$ lies in the first Brillouin zone; the limiting values along the six directions pere determined from the interactions of the corresponding K vectors with the planes of the first Brillouin zone. For the U-processes the scattering vector is given by the selection rule $\boldsymbol{K}=\boldsymbol{k}'-\boldsymbol{k}=\boldsymbol{q}+\boldsymbol{g}$, where $\boldsymbol{g}$ is a reciprocal lattice vector. The minimum value of K, at which U-processes start up, have been easily obtained from the knowledge of the geometry of the reciprocal lattice vectors of a face centered cubic structure.

The values of the elastic constants and other relevant parameters of copper, silver and gold used in the present calculations are listed in Table 1. These values are taken from the measurements of Hiki and Granato [24] at 300 °K.

4. Results and Discussion

The calculated ideal thermal resistivities of the noble metals (Cu, Ag, Au) are plotted in Figs. 1 − 3 against the logarithm of the temperature, together with the experimental data. The sources of the experimental thermal resistivity data are summarized in Table II.

It may be seen that the theoretical and experimental resistivity curves appear to be of similar nature, but they show some disagreement at low temperatures. The discrepancy is greatest in the case of gold. The theoretical values of the thermal

Table 2. Experimental resistivity data for noble metals.

Metal	Source	Temperature range
Copper	Berman and MacDonald [2]	2 − 90 K
	White [7a]	2 − 160 K
Silver	White [7b]	2 − 160 K
Gold	White [7c]	10 − 150 K

resistivity at low temperatures are slightly lower than the observed ones, while the theoretical values exceed the experimental ones in the high temperature region. In general, the theoretical thermal resistivity curves qualitatively resemble the experimental results, yet the quantitative agreement at low as well as high temperatures is disturbingly poor.
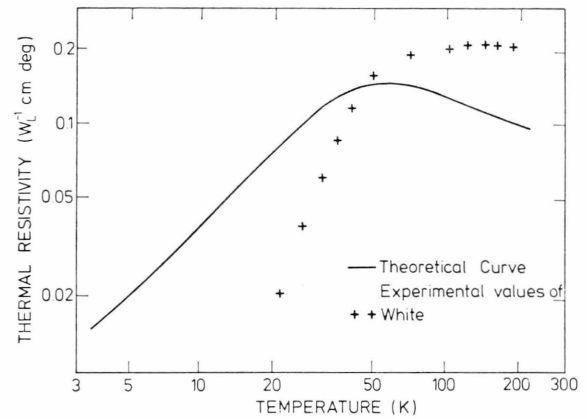

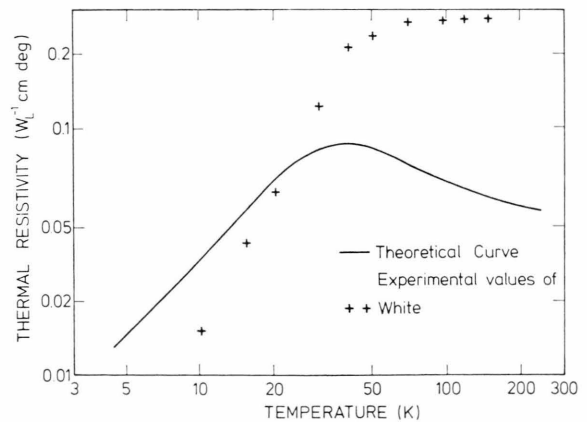Fig. 1. Thermal resistivity of copper as a function of temperature.

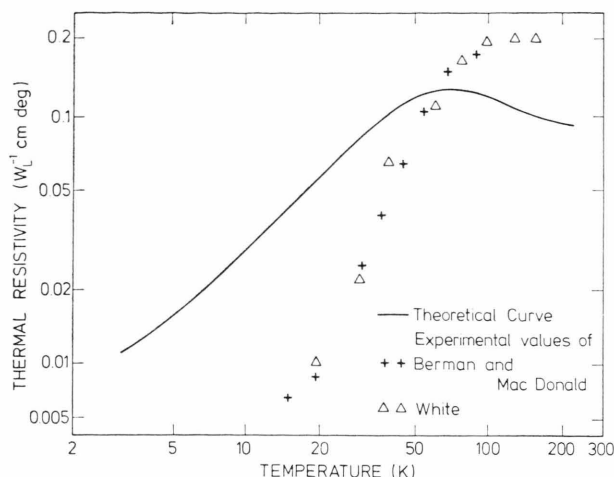Fig. 2. Thermal resistivity of silver as a function of temperature.

Fig. 3. Thermal resistivity of gold as a function of temperature.

In the present study the distinction between the N-processes and the U-processes affects considerably the numerical values of the resistivities, thus the contribution due to U-processes can not at all be neglected. A systematic increase with temperature in the U-process contributions to the total resistivity is observed. This gradual increase in the Umklapp contribution can be ascribed to the fact that the temperature dependence of the resistivity is unexpectedly sensitive to the details of the anisotropic phonon spectrum which becomes more and more important a the temperature increases, because of the strange geometry of the Umklapp interactions in the wave vector space.

The discrepancies between theory and experiment are attributable to the use of the Bardeen model for the electron phonon matrix element $C(K)$, which ignores the exchange and correlation effects. No account has been taken of the complete temperature dependence of the elastic constants. The use of the first order trial function in the variational solution of Boltzmann's equation results in the over estimation of the resistance [25, 26]. In addition to the influence of lattice vibrations on the resistivity, the effect of the shape of the Fermi surface on the resistivity is dominant due to systematic contributions of the Umklapp processes to the total resistivity. Experimental studies of Shoenberg [27], Joseph and Thorsen [28], Joseph et al. [29], and Jan and Templeton [30], have shown that the Fermi surfaces of all these metals deviate from sphericity despite the topologies of the Fermi surfaces in the noble metals are very similar. Compared to silver and gold, the asphericity of the Fermi surface of copper is smallest. The anisotropy of the Fermi surface of noble metals enhances the probability of the Umklapp scattering of electrons, leading thereby to an increase in the numerical value of the resistivity. Thus the effect is significant in gold where the Fermi surface bulges towards the zone faces. It, therefore, appears that there is a need of more detailed studies to account for these effects in order to provide a satisfactory description of the thermal resistivity of the noble metals. The whole problem is of great complexity and involves almost all the basic properties of metals. However, the present study shows that the anisotropic continuum dispersive model coupled with free electron interaction gives a reasonable description of the thermal resistivity of copper, silver, and gold.

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