

Electrical resistivity of an Einstein solid

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An upper bound to the resistivity of an Einstein solid is calculated using the variational method of Ziman with the usual trial function, and is shown to be proportional to the product of the local-mode specific heat and the temperature. This formula gives an improved fit to the results of recent measurements on the intermetallic compound Al_{10}V .

In an interesting letter (which is hereafter referred to as I) Caplin, Dunlop, and Grtner¹ showed that the intermetallic compound Al_{10}V has a local soft mode of characteristic temperature 22 K. This is associated with excess Al atoms which may occupy "holes" in the Al_{10}V unit cell, and apparently are very weakly coupled to the other atoms in the solid. The low-temperature specific heat and, to a lesser extent, the electrical resistivity could be described by an Einstein model with an Einstein temperature Θ of 22 K.

The formula used in I for ρ , the electrical resistivity of an Einstein solid, was

$$\rho \propto (e^{\Theta/T} - 1)^{-1} \quad (1)$$

That is, ρ proportional to the mean square oscillation amplitude, or the total energy of the oscillators (excluding the zero-point energy).

In this note we wish to point out that the above formula, which is based on the treatment of Mott and Jones,² should not be applied at low temperatures because it does not properly account for the fact that the electrons are always scattered inelastically from the oscillating Al atoms, with an energy change $k_B\Theta$, which may be much greater than $k_B T$. As far as we know, the Boltzmann equation has not been solved analytically for this problem in the region $T \leq \Theta$ or even in the limit $T \rightarrow 0$, and hence there is no exact expression for ρ in this region. However, as long ago as 1953, Howarth and Sondheimer³ considered this problem in connection with the electrical conductivity of polar semiconductors for an electron gas of arbitrary degeneracy. They solved the Boltzmann equation by a variational method. For a Fermi gas, their first approximation to ρ is an analytic expression which is not equivalent to Eq. (1) except as $\Theta/T \rightarrow 0$. They were also able to compute second- and third-order numerical corrections to their first approximation for particular values of T/Θ .

Their work was done before Ziman's formulation of the variational principle, and is quite complicated algebraically. Here we use Ziman's method to obtain an upper bound to ρ , which turns out

to be identical to the first-order approximation mentioned above. Instead of being proportional to the total energy of the oscillators this upper bound is proportional to the product of the local-mode specific heat (C_E) and the temperature (T). It gives a much better fit to the results for Al_{10}V , and, allowing for the normal phonon resistivity, this is good up to at least 40 K.

The expression for ρ is essentially a simple form of the one given in Ziman's book for calculating the electron-phonon resistivity.⁴ Using the standard trial function $\phi_{\vec{k}} = \vec{k} \cdot \vec{u}$, for a free-electron gas the resistivity is given in the usual notation by

$$\rho = \left(\frac{3\pi^2 \hbar^3}{e k_F^3} \right)^2 \frac{1}{2k_B T} \sum_n \int d\vec{k} \int d\vec{k}' \times (\vec{k} - \vec{k}')^2 \vec{u}^2 (P_{\vec{k},n}^{\vec{k}',n-1} + P_{\vec{k},n}^{\vec{k}',n+1}) \quad (2)$$

As usual, the integrals over $d\vec{k}$ and $d\vec{k}'$ represent sums over the initial and final electron states. The sum over harmonic-oscillator states n replaces the integral over the phonon momentum \vec{q} in Ziman's expression. The probability of scattering from the state $|\vec{k}, n\rangle$ known to be occupied, to the state $|\vec{k}', n-1\rangle$, known to be empty, is given to first order by

$$P_{\vec{k},n}^{\vec{k}',n-1} = Q(n) \frac{n\hbar}{2M\omega} \left| \langle \vec{k}' | \frac{\partial v}{\partial x} | \vec{k} \rangle \right|^2 f_{\vec{k}}^0 (1 - f_{\vec{k}'}^0) \times \delta(\epsilon_{\vec{k}'} - \epsilon_{\vec{k}} - \hbar\omega) \quad (3)$$

In this expression $Q(n)$ is the probability that the n th harmonic oscillator state is occupied. We have also used the elementary result that, for a linear oscillator of mass M and angular frequency ω , moving in the x direction:

$$|\langle n | x | n-1 \rangle|^2 = \frac{n\hbar}{2M\omega}$$

$v(r)$ is the interaction potential between the conduction electron and the Al atom at a separation r .

It is easy to show that energy-absorption processes such as those in Eq. (3) give the same con-

tribution to ρ as energy-emission processes.⁵ Therefore in calculating the temperature dependence of ρ we only consider absorption processes.

The sum over n in Eq. (2) can be evaluated immediately:

$$\sum_n Q(n)n = \langle n \rangle = (e^{\Theta/T} - 1)^{-1} \quad (4)$$

The number of states of one spin orientation, between \vec{k} and $\vec{k} + d\vec{k}$ is $(2\pi)^{-3} k^2 dk d\Omega$. As usual the Fermi factors limit the integrals to a small region around E_F , and in a free-electron model the integrals over \vec{k} and \vec{k}' can be separated into the product of angular integrals and energy integrals, i. e.,

$$\begin{aligned} \int d\vec{k} &= (2\pi)^{-3} \int k^2 dk d\Omega \\ &= (2\pi)^{-3} m k_F \hbar^{-2} \int d\epsilon_k d\Omega \end{aligned}$$

Within this approximation the angular integrals give a weighted average of the squared matrix element

$$\left| \langle \vec{k}' \left| \frac{\partial v}{\partial x} \right| \vec{k} \right|^2$$

and are independent of temperature. Integration over $d\epsilon_k$ eliminates the δ function in (3), so the only remaining temperature-dependent term is

$$\frac{1}{k_B T} \int_{-\infty}^{\infty} \frac{d\epsilon_k}{(e^{\beta\epsilon_k} + 1)(1 + e^{-\beta(\epsilon_k + \hbar\omega)})} \equiv \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}$$

The formula used in I does not include the above factor which arises because the arguments of Fermi factors $f_{\vec{k}}^0$ and $f_{\vec{k}'}^0$ differ by an energy $\hbar\omega$. The final expression for the resistivity is

$$\rho = \frac{KN}{MT(e^{\Theta/T} - 1)(1 - e^{-\Theta/T})} \quad (5)$$

where N is the number of oscillators per unit volume and K is a constant which is independent of the local-mode parameters but depends on the electron density of the metal and the electron-local-mode coupling strength. Since the specific heat for N linear oscillators is given by

$$C_E = Nk_B \frac{\Theta^2}{T^2(e^{\Theta/T} - 1)(1 - e^{-\Theta/T})} \quad (6)$$

we have:

$$\rho = \frac{KTC_E}{M\Theta^2 k_B} \quad (7)$$

As in the formula of Mott and Jones the high-temperature limit is

$$\rho = \frac{KNT}{M\Theta^2} \quad (8)$$

Equation (5) gives a good fit to the results of Caplin *et al.*, as shown in Fig. 1 (solid line), the

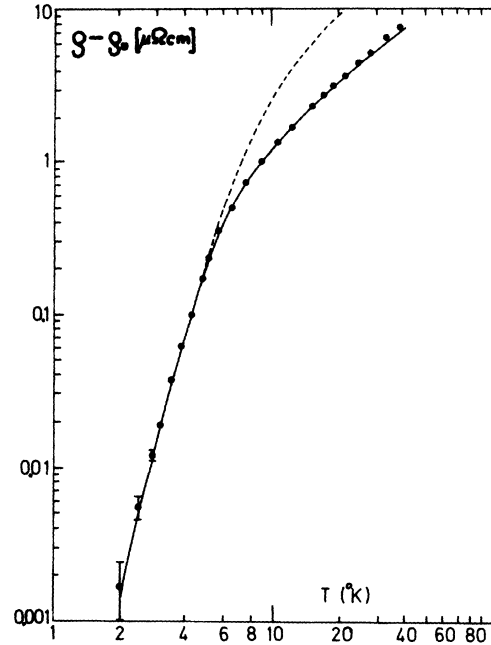


FIG. 1. The temperature-dependent resistivity of Al_{10}V . \bullet , experimental points from reference I. Solid line, ρ calculated from Eq. 5 in text. Dashed line, $\rho \propto (e^{\Theta/T} - 1)^{-1}$ as given in Ref. 1.

previous best fit¹ is shown as a dashed line. Θ has been taken as 22 K from the specific-heat results and K has been treated as an adjustable parameter. The small deviations that do occur between 20 and 40 K are consistent with the normal phonon resistivity which has been measured in other Al intermetallics (see, for example, the results for Al_3Co_2 in I). The large error bars in the low-temperature points correspond to an error of 1 in 10^4 in the total resistivity since the disorder scattering is large and gives rise to a residual resistivity of about $7 \mu\Omega \text{ cm}$.⁶ Compared with these errors the numerical corrections to Eq. (5) calculated by Howarth and Sondheimer and negligible. They are of the order of 20% of $\rho - \rho_0$ at 2 K and fall rapidly as T increases.

Because of the uncertainty in N for the resistivity specimens and in the electronic structure of Al_{10}V , reliable numerical estimates cannot be made, but the value of K needed to fit the data indicates that the electron-local-mode coupling in Al_{10}V is of a similar strength to the electron-ion coupling in pure Al.

For the more realistic case of three-dimensional harmonic oscillators, C_E and the inelastic part of the resistivity should be multiplied by a factor of 3. Although the n th localized level now has $\frac{1}{2}(n+1)(n+2)$ -fold degeneracy, elastic scattering between these levels involves higher order matrix

elements of the form $\langle \mathbf{k}' | \partial^2 v / \partial x \partial y | \mathbf{k} \rangle$, which are usually neglected in electron-phonon scattering in metals. Similar considerations apply to the scattering associated with the zero-point motion and

to processes involving the excitation of the local mode as an intermediate state.

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¹A. D. Caplin, J. B. Dunlop, and G. Grüner, *Phys. Rev. Lett.* **30**, 1138 (1973).

²N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover, New York, 1958), Chap. 7, Secs. 5 and 9.

³D. J. Howarth and E. H. Sondheimer, *Proc. Roy. Soc. Lond.* **213**, 53 (1953).

⁴J. M. Ziman, *Electrons and Phonons* (Oxford U. P., Oxford, 1960), Chap. 9, Sec. 5.

⁵For emission processes $n \rightarrow n+1$ and $\omega \rightarrow -\omega$ in Eq. (3),

because of the identity $\Theta(n)/T(1 - e^{-\omega/T}) \equiv -\Theta(n+1)/T(1 - e^{\omega/T})$, the contribution to ρ is unchanged.

⁶Since the major part of the residual resistivity is also caused by the excess Al atoms, ρ_0 should be proportional to $N|\langle v \rangle|^2$ for small N . Hence from the experimental ratio of ρ_0 to $d\rho/dT_{T \rightarrow \infty}$ ($0.21 \mu\Omega \text{ cm K}^{-1}$), we can estimate $\langle v \rangle / \langle \partial v / \partial x \rangle$, which roughly corresponds to the range of $v(r)$. This is apparently quite short, approximately 0.6 \AA .