A SENSITIVE METHOD TO STUDY THE ELECTRON-PHONON RESISTIVITY IN METALS (*)

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ABSTRACT — A detailed investigation of the thermal derivative of the electrical resistivity, $d\rho/dT$, as a function of temperature ($77\ K \leq T \leq 330\ K$), is presented here for a series of selected high purity metals: Cu, Al, Ta, V, Pt, Nb, In, Sn and Pb. The experimental results are compared with the theoretical predictions for $d\rho/dT$ based on the Bloch-Grüneisen theory. In contrast to the case of $\rho(T)$, considerable differences were found between theory and experiment for the case of $d\rho/dT$.

The role played by the transverse branches of the phonon spectrum is examined, and a simple model is presented leading to a better quantitative description of the results.

The anharmonicity in the vibrational lattice spectrum was found to be an important effect in the temperature range investigated for the case of the low melting point metals: In, Sn and Pb. In particular, it can explain the anomalous increase of $d\rho/dT$ at high temperatures ($T > \Theta$, Debye temperature), where, according to the Bloch-Grüneisen formula, $d\rho/dT$ should become constant.

The temperature dependence of the electrical resistivity due to electron-phonon scattering has been thoroughly investigated over the years [1], the results being generally analyzed in terms of the Bloch-Grüneisen expression based on the Debye model for the phonon spectrum:

$$\rho(T) = A(T/\Theta)^5 \int_0^{\Theta/T} x^5 [(e^x - 1)(1 - e^{-x})]^{-1} dx \qquad (1)$$

where Θ is the Debye temperature and A is a constant which involves the coupling constant for electron-phonon scattering.

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Good agreement of (1) with experiment is generally claimed, after a proper choice of Θ for each metal. This is not surprising since expression (1) gives the correct T-dependence both at high temperatures ($T >> \Theta$; $\rho \propto T$) and low temperatures ($T << \Theta$; $\rho \propto T^5$) and, as an intepolation formula, works reasonably well at intermediate temperatures. The reason for the correctness of the asymptotic temperature dependence predicted by (1) lies in the fact that at $T << \Theta$ the relevant part of the phonon spectrum corresponds to the long wavelength phonons (which closely follow the assumed Debye model), whereas at $T >> \Theta$ quantization effects become irrelevant and classical behaviour results ($\rho \propto T$). However, close examination of the experimental data reveals some discrepancies [1-3]: (i) The Θ-values derived from experimental fits to eq. (1) do not exactly agree with Θ-values derived from specific heat measurements; (ii) If we impose exact agreement at particular temperatures, slightly different Θ-values are required for each temperature. A better way to reveal these discrepancies is through the direct measurement of the temperature derivative $d\rho/dT$, which is a quantity far more sensitive to the peculiarities of the phonon spectrum than ρ. In fact, an important part of the resistivity change ($\Delta\rho$) produced by a small increase in the temperature (ΔT) in the vicinity of each T comes essentially from the number (and type) of extra phonons produced by the small increase of temperature. Furthermore, close agreement between experimental ρ-values and those given by (1) does not necessarily mean a good fit to the *derivative* $d\rho/dT$.

In this note we report the results of a fairly detailed investigation on the temperature dependence of the derivative $d\rho/dT$ over a wide range of temperature (80-330 K) for a series of selected high purity metals: (Cu, Al), (Ta, V, Pt, Nb) and (In, Sn, Pb). The first group was chosen to check whether agreement between experiment and theory exists in $d\rho/dT$ for these high conductivity metals. The second group (incomplete d-band transition metals) was chosen in order to investigate if $d\rho/dT$ could reveal discrepancies attributable to the more complex structure of the phonon spectra, and also to the existence of phonon-assisted interband electron transitions (between s and d-bands). The third group was chosen because the corresponding metals have fairly low melting points (156°C, 232°C, 327°C for In, Sn, and Pb, re-

spectively) and we wanted to see whether thermal expansion effects can be detected in $d\rho/dT$ measurements performed at moderate temperatures, i.e. from liquid nitrogen temperature up to room temperature.

Fig. 1 shows a plot of $(d\rho/dT)/(d\rho/dT)_\infty$ as a function of T/Θ for Cu and Al, using Θ values derived from specific heat measurements quoted in the literature. Here $(d\rho/dT)_\infty$ is the

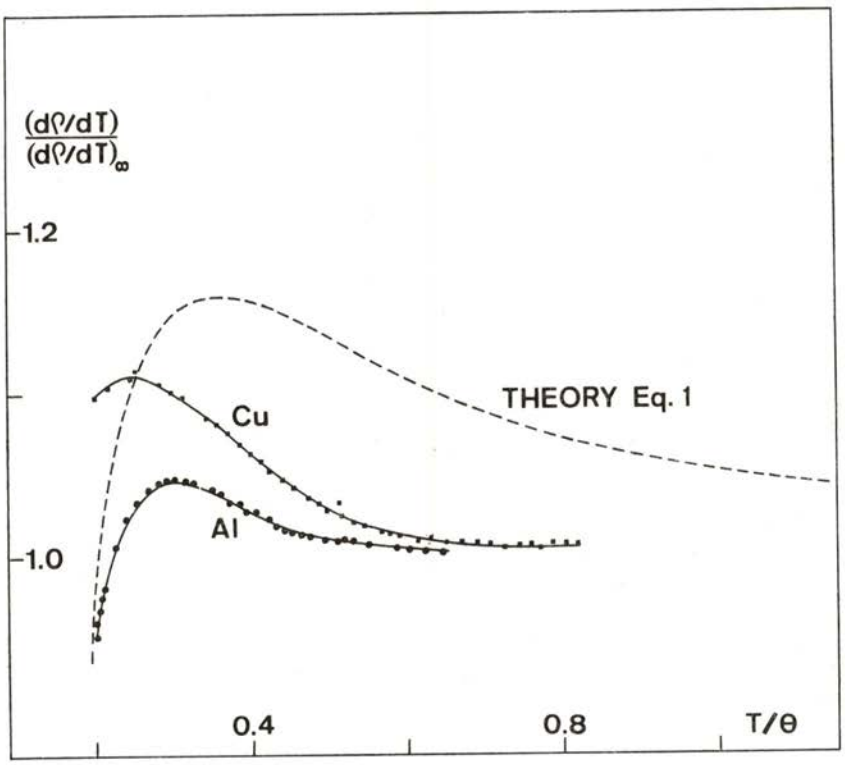

Fig. 1 — Normalised thermal derivative $(d\rho/dT)/(d\rho/dT)_\infty$ as a function of normalised temperature (T/Θ) for Cu and Al. The dashed curve represents $(d\rho/dT)/(d\rho/dT)_\infty$ obtained from differentiation of expression (1).

constant value attained by $d\rho/dT$ for T sufficiently above Θ. In the same figure we show the theoretical curve for $(d\rho/dT)/(d\rho/dT)_\infty$ obtained from differentiation of expression (1) and subsequent numerical computation.

We notice that for Cu and Al the derivative $d\rho/dT$ shows the general features predicted by the Bloch-Grüneisen expression: a sharp increase as T increases from zero, a broad maximum at $T/\Theta \simeq 0.3$, followed by a monotonic decrease towards a constant value at high temperatures.

Quantitatively, however, we observe that the normalized maxima are lower than the maximum predicted by the theory, and occur at slightly lower T/Θ values. We also notice that $d\rho/dT$ attains the high-T regime at much lower T/Θ values than predicted by the theory.

The fact that experimental and theoretical $d\rho/dT$ curves do not coincide is not surprising if we recall that the theory has some drastic oversimplifications, namely it always assumes a Debye model, taking no account of the particular phonon spectrum of each metal.

The phonon spectrum of copper, for example, exhibits two main peaks in the density of states [4], at frequencies close to $\nu_1 = 7 \times 10^{12}\,s^{-1}$ and around $\nu_2 = 3.5 \times 10^{12}\,s^{-1}$. The existence of two maxima in the density of states is essentially due to the existence of longitudinal and transverse phonons. It can be shown [1] that when the Fermi surface is spherical only longitudinal phonons are involved in the electron-phonon scattering process, but when the Fermi surface is anisotropic (as actually happens in Cu and Al) the role played by transverse phonons may become important: values of about 70 % of the total scattering processes have been quoted [1].

For Cu, a simple approach is to consider the total vibrational spectrum decomposed into three branches: one longitudinal branch with $\Theta_L = \Theta$, and two transverse branches with $\Theta_T = \Theta/2$, since $\nu_2 \simeq \nu_1/2$.

Expression (1) will take the form

$$\rho/\rho_\infty = 2.25\,\Theta\,(T/\Theta)^5\,[\,1.28\,F\,(\Theta/2\,T) + F\,(\Theta/T)\,] \qquad (2)$$

where $$F(x) = \int_0^x x^5\,[\,(e^x - 1)\,(1 - e^{-x})\,]^{-1}\,dx$$

and ρ_∞ is the electrical resistivity at $T >> \Theta$; it is assumed the same electron-phonon coupling constant for the longitudinal and transverse branches.

Fig. 2 shows the temperature derivative $d\rho/dT/(d\rho/dT)_\infty$ obtained from (2). This curve is now closer to the experimental results than the curve derived from the standard formula (1). In particular the high temperature regime ($d\rho/dT = \text{const}$) is attained faster than predicted by (1), which is in agreement with the experimental results.

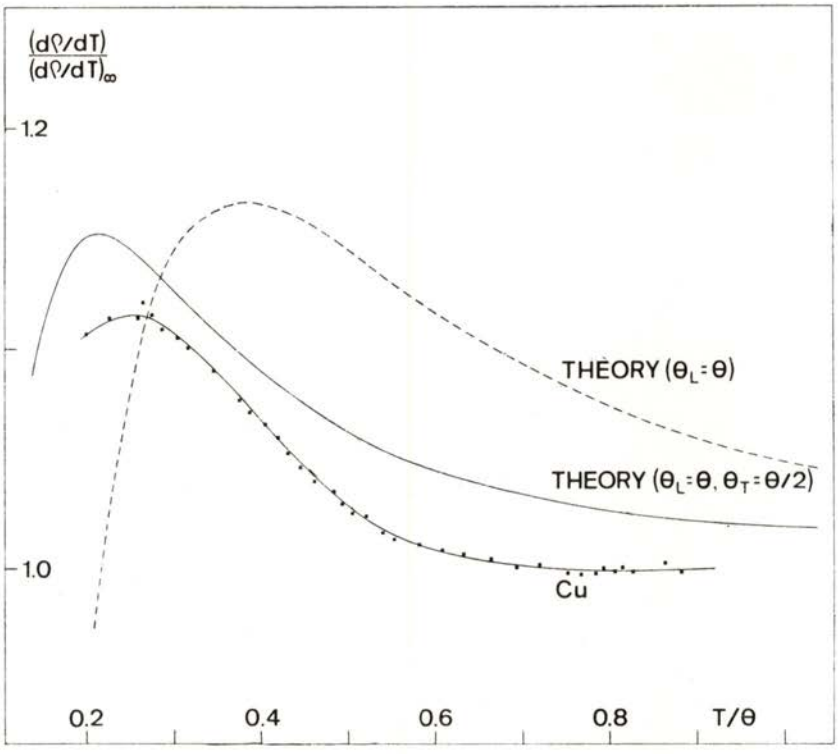

Fig. 2 — Normalised thermal derivative $(d\rho/dT)/(d\rho/dT)_\infty$ as a function of (T/Θ); the dashed curve was obtained from differentiation of expression (1), while the full curve was derived from expression (2), in which two maxima in the density of states of the phonon spectrum are considered. The third curve presents the experimental results obtained for Cu.

We believe that the remaining discrepancies can be removed through a realistic consideration of the different branches of the phonon spectrum, taking also into account the probable differences in the corresponding electron-phonon coupling constants.

In the case of the transition metals (Fig. 3) we notice that with decreasing temperature $d\rho/dT$ tends to increase much faster than predicted by the Bloch-Grüneisen expression. It is not surprising that transition metals exhibit a more complex behaviour than Cu or Al, because they have an extra resistivity contribu-

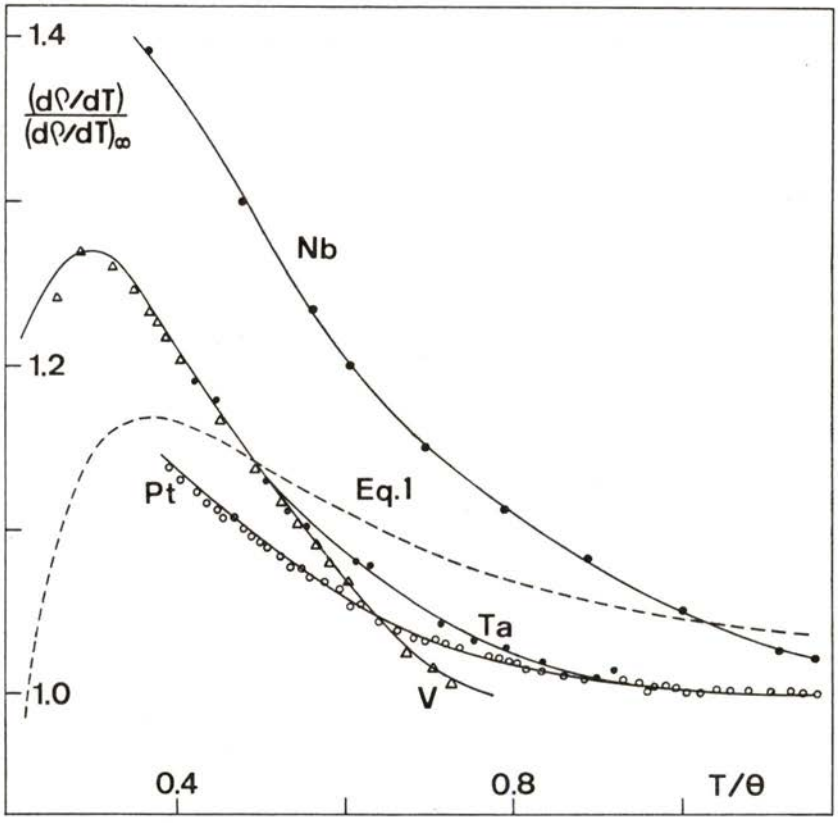

Fig. 3 — Normalised thermal derivative $(d\rho/dT)/(d\rho/dT)_\infty$ as a function of (T/θ) for Nb, V, Ta, Pt. The dashed curve was obtained from differentiation of expression (1).

tion, due to s-d electron scattering, which greatly increases the value of ρ; it is likely that such effect also affects the values of $d\rho/dT$.

In these transition metals there is also the systematic persistence of the high temperature behaviour ($d\rho/dT = \text{const}$)

down to temperatures considerably below the Debye temperature, as also found in Cu and Al. It is likely that such effect is also connected here with the contribution of the transverse branches of phonon spectrum to the electron scattering process.

We consider now the results of the investigation of $d\rho/dT$ in the low melting point metals In, Sn and Pb. These metals also have low Debye temperatures, $\Theta \simeq 108$ K, 199 K and 105 K, respectively. According to our previous findings, a classical regime should be expected for $T \gtrsim \Theta$, giving a $d\rho/dT$ term independent of temperature. As shown in Fig. 4, $d\rho/dT$ at T sufficiently

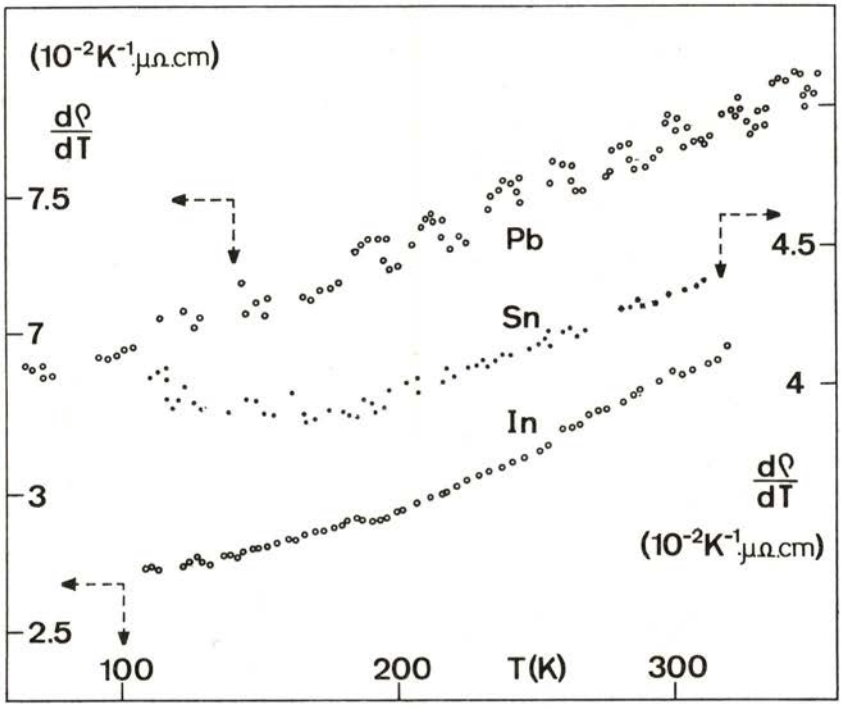

Fig. 4 — Thermal derivative, $d\rho/dT$, as a function of the temperature for the low melting point metals In, Sn and Pb.

above Θ still shows a steady *increase* with temperature in all cases. This cannot be attributed to insufficient temperature to attain the classical regime, since this regime is reached with $d\rho/dT$ *decreasing* steadily with T (see eq. 1). We believe that the

observed behaviour is at least partly due to a thermal expansion effect [1-3]. The increase of the lattice constants weakens the interatomic forces, reducing therefore the maximum vibration frequency, and thus Θ. This has a direct effect in ρ, and it can be shown [2-5] within the Debye model ($\rho/T \propto \Theta^{-2}$ at high temperatures) that the classical behaviour of ρ should have a correction:

$$\rho = A\,T\,(1 + 6\,\alpha\,\gamma\,T) \tag{3}$$

where α is the linear expansion coefficient, A is a constant and γ is the Grüneisen constant, $\gamma = -\,d(\ln\Theta)/d(\ln V)$, V being the volume of the sample. Since $\alpha \sim 10^{-5}\ K^{-1}$, the correction $6\,\alpha\,\gamma\,T$ is much smaller than unity for the temperature range under investigation. We can then obtain from (3) a useful expression to analyze our $d\rho/dT$ data (using $6\,\alpha\,\gamma\,T \ll 1$):

$$(1/\rho)\ d\rho/dT = (1/T) + 6\,\alpha\,\gamma \tag{4}$$

Our experimental data agree rather well with this expression, as illustrated in Fig. 5 for Pb. From such plots we obtain:

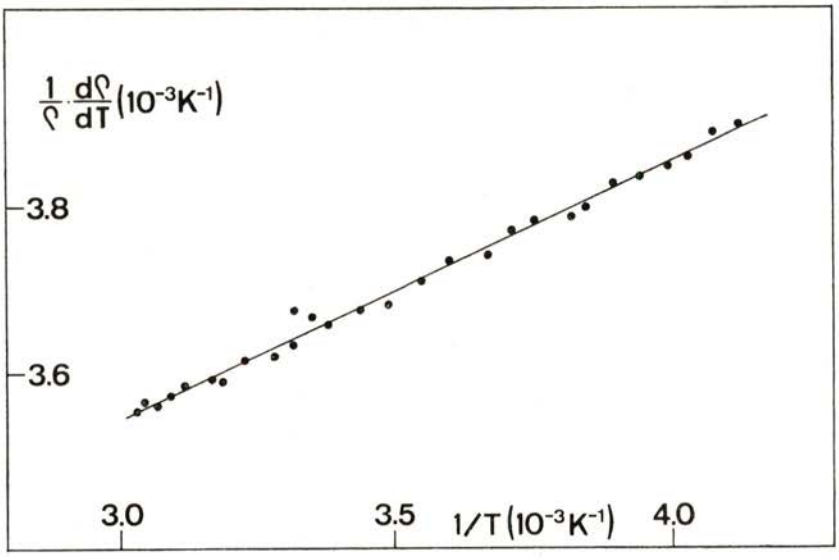

Fig. 5 — Fitting of the experimental results of Pb to expression (4).

$6\alpha\gamma = 6.7 \times 10^{-4}$ K^{-1} (In), 5.3×10^{-4} K^{-1} (Sn) and 6.8×10^{-4} K^{-1} (Pb). These figures are indeed of the right order of magnitude as expected from available α and γ-data; e.g. $6\alpha\gamma = 2.74 \times \times 10^{-4}$ K^{-1} (Sn), 4.72×10^{-4} K^{-1} (Pb). Our results appear, however, higher than the calculated values, and so further analysis seems necessary.

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