

International School of Physics "Enrico Fermi," Course LI, edited by M. S. Green (Academic, New York, 1971); also see R. D. Williams and I. Rudnick, *Phys. Rev. Lett.* **25**, 276 (1970).

¹⁴P. C. Martin, O. Parodi, and P. S. Pershan, *Phys. Rev. A* **6**, 2401 (1972).

¹⁵F. Imura and K. Okano, *Chem. Phys. Lett.* **25**, 503 (1970).

Origin of Saturation Effects in Electron Transport

P. J. Cote and L. V. Meisel

U. S. Army Armament Research and Development Command, Benet Weapons Laboratory, Watervliet Arsenal, Watervliet, New York 12189

(Received 30 January 1978)

The diffraction model is generalized to incorporate a postulate on the electron-phonon interaction; viz., phonons with wavelength exceeding the electron mean free path are ineffective electron scatterers. This postulate leads to a limiting resistivity when the electron mean free path is of the order of the interatomic spacing. The generalized diffraction model is also shown to explain many anomalous features common to high-resistivity metals. Crystalline Nb, A15's, and glassy metals are discussed.

High-resistivity amorphous and disordered-crystalline metals exhibit many anomalous transport properties. The variety of explanations for these anomalies reflects the complexity of high-resistivity systems. Examples of mechanisms invoked to explain the behavior of these systems include virtual-bound-state formation,¹ breakdown of the Boltzmann equation,² electron localization,³ *s-d* scattering,⁴ vacancy formation,⁵ multiple-scattering effects,⁶ and thermal excitation of nearly degenerate core configurations.⁷

Many of these anomalies can be understood within the framework of the diffraction model, i.e., Ziman theory⁸ and its extensions.^{9,10} We have shown¹¹⁻¹³ that this model explains the $+T^2$ low-temperature dependence of the resistivity ρ , the variations of the temperature coefficient of resistivity (TCR), and the small resistivity maxima seen in alloys at concentrations for which the crossover from positive to negative TCR occurs.

However, a number of anomalies have not been explained by the diffraction model, including the following: (1) Breakdown of Matthiessen's rule in high-resistivity metals (the occurrence of small or negative TCR for all high-resistivity metals¹⁴). (2) Low-temperature anomaly (very-high-resistance amorphous alloys exhibit $\rho \propto 1$

$-AT^2$ at low temperatures rather than the predicted positive T^2 dependence and concomitant small maximum¹⁵). (3) Saturation¹⁶ (many intermetallic compounds, e.g., the A15 alloys,¹⁷ exhibit a loss of temperature dependence of ρ at high temperatures. Saturation has also been suggested to occur in pure Nb.^{2,18}). We shall show that these anomalies can be explained in the framework of the diffraction model if we invoke a plausible postulate concerning the electron-phonon interaction as follows:

Interaction postulate.—Phonons with wavelength exceeding the electron mean free path Λ are ineffective electron scatterers.¹⁹ The effect of the interaction postulate is to produce a low-wave-vector (or low-frequency) cutoff in the integrals over the phonon spectrum which occur in the diffraction model. In the following we shall consider a Debye spectrum so that the electron-phonon interaction will be turned off completely for $\Lambda = 2\pi/q_D$, where q_D is the Debye wave vector. The resistivity corresponding to $\Lambda = 2\pi/q_D$ is approximately $200 \mu\Omega \text{ cm}$ for a monovalent free-electron metal.

The temperature dependence of ρ is essentially determined by that of the resistivity structure factor $S^\rho(K)$.^{20,21} Thus, consider the one-phonon resistivity structure factor neglecting the interaction postulate

$$S_1^\rho(K) \cong \frac{(\hbar K)^2 e^{-2W(K)}}{2Mk_B T} \sum_q [a(\vec{K} + \vec{q}) + a(\vec{K} - \vec{q})] n(q) [n(q) + 1], \quad (1)$$

where \hbar is Planck's constant, k_B is Boltzmann's constant, \vec{K} is the scattering vector, $e^{-2W(K)}$ is the

Debye-Waller factor, M is the ion mass;

$$\alpha(K) \equiv N^{-1} \sum_{\vec{m}, \vec{n}} \exp[i\vec{K} \cdot (\vec{m} - \vec{n})]$$

is the (geometrical) structure factor, $n(x) = (e^x - 1)^{-1}$, $x = \hbar\omega/k_B T$, ω is the phonon frequency, \vec{m} and \vec{n} are average ion positions, N is the number of ions, and the summation runs over the q values in the spectrum. Taking the interaction postulate into account we find the summation of \vec{q} is restricted such that only wave vectors whose magnitude lies between $2\pi/\Lambda$ and q_D are included. We thus define a generalized one-phonon resistivity structure factor $S_1^\rho(K, \Lambda)$ and, in analogy with the treatment of Refs. 11 and 20, a generalized average structure factor for resistivity $A^\rho(K, \Lambda)$ for amorphous metals as follows:

$$S_1^\rho(K, \Lambda) \equiv \alpha(K)(\Theta/T) \int_\gamma^1 (q/q_D)^2 d(q/q_D) n(x) [n(x) + 1] \int d\Omega a(\vec{K} + \vec{q})/4\pi, \quad (2)$$

$$\equiv \alpha(K)(\Theta/T) A^\rho(K, \Lambda) \int_0^1 (q/q_D)^2 d(q/q_D) n(x) [n(x) + 1], \quad (3)$$

where $\gamma \equiv 2\pi/\Lambda q_D$, $\alpha(K) = 3e^{-2W(K)}(\hbar K)^2/Mk_B\Theta$, and Θ is the Debye temperature. For $T \gtrsim \frac{1}{2}\Theta$ we obtain to a good approximation

$$S_1^\rho(K, \Lambda) = \alpha(K) \frac{T}{\Theta} \int_\gamma^1 d\left(\frac{q}{q_D}\right) \int \frac{d\Omega}{4\pi} a(\vec{K} + \vec{q}) \quad (2')$$

$$= \alpha(K)(T/\Theta) A^\rho(K, \Lambda). \quad (3')$$

The most important scattering vectors in the resistivity of glassy and liquid metals generally satisfy $K > k_F$.^{9, 10} For such scattering vectors and $T \gtrsim \frac{1}{2}\Theta$,

$$A^\rho(K, \Lambda) = \int_\gamma^1 d\left(\frac{q}{q_D}\right) \int \frac{d\Omega}{4\pi} a(\vec{K} + \vec{q}) \\ \approx (1 - \gamma) A^\rho(K), \quad (4)$$

where $A^\rho(K) \equiv A^\rho(K, \infty)$ is the averaged structure factor defined in Refs. 11 and 20.

In the crystalline case, where $a(K)$ is a δ -function sum, we apply the well-known idea (Baym's theorem²¹) that, for $T \gtrsim \frac{1}{2}\Theta$, $S^\rho(K) \approx S^x(K)$, where $S^x(K)$ is the x-ray structure factor. The x-ray expression²² for one-phonon thermal diffuse scattering is

$$S^x(K) \approx \frac{1}{3} \alpha(K) \frac{T}{\Theta} \sum_{\vec{G}} \left(\frac{q_D}{q}\right)^2, \quad T \gtrsim \frac{1}{2}\Theta, \quad (5)$$

where \vec{G} runs over the subset of reciprocal-lattice vectors satisfying $0 < q < q_D$ and $q = |\vec{K} - \vec{G}|$. The interaction postulate in this case restricts the sum to that subset of reciprocal-lattice vectors which satisfy $2\pi/\Lambda < q < q_D$. A fraction, $\gamma^3 = (2\pi/\Lambda q_D)^3$, of the phonon states whose contribution to S^ρ goes like q^{-2} is eliminated from the summation in Eq. (5). We are therefore led to the same conclusion as in the amorphous case; vis., the phonon part of ρ is approximately reduced by the factor $(1 - \gamma)$, and for both crystal-

line and amorphous metals,

$$\rho \approx (1 - \gamma)\rho_{ip} + \rho_0 e^{-2W^*}, \quad (6)$$

where ρ_{ip} is the ideal one-phonon resistivity ($\Lambda \rightarrow \infty$), and the elastic component is given by $\rho_0 e^{-2W^*}$ with $2W^*$ an averaged Debye-Waller exponent. We have neglected multiphonon terms, which should drop off faster than ρ_{ip} .

Since $\rho \propto 1/\Lambda$, ρ will be proportional to γ . We define the proportionality constant as the saturation resistivity ρ^* . Thus,

$$\rho = 3/N(E_F) e^2 \Lambda v_F \quad (7)$$

$$= \gamma 3q_D/2\pi N(E_F) e^2 v_F \equiv \gamma \rho^*, \quad (8)$$

where $N(E_F)$ is the density of states at the Fermi energy, e the electron charge, and v_F the Fermi velocity. For a monovalent free-electron metal $\rho^* \approx 200 \mu\Omega \text{ cm}$. However, Nagel and Tauc²³ suggest that in amorphous metals the peak in $a(K)$ produces a reduction in $N(E_F)$ below the free-electron value, so that in amorphous (and liquid) metals ρ^* may be significantly larger than $200 \mu\Omega \text{ cm}$. The appropriate density of states of conduction electrons in transition metals may be considerably smaller than the free-electron value which would also yield larger values for ρ^* .

Equations (6) and (8) yield

$$\rho/\rho^* = (\rho_{ip}/\rho^* + \rho_0 e^{-2W^*}/\rho_0)(\rho_{ip}^*/\rho^* + 1)^{-1} \\ = (T^* + \rho_0 e^{-2W^*}/\rho^*)(T^* + 1)^{-1}, \quad (9)$$

where the dimensionless normalized temperature T^* is defined in Eqs. (9) and (10). In particular, $\rho_{ip} \approx \beta T$ for $T \gtrsim \frac{1}{2}\Theta$ with β constant, so that

$$T^* \equiv \rho_{ip}/\rho^* = (\beta/\rho^*)T, \quad T \gtrsim \frac{1}{2}\Theta. \quad (10)$$

Figure 1 shows graphs of normalized resistivity

ρ/ρ^* vs T^* for a variety of conditions and is intended to indicate the general features of Eq. (9). The anomalies previously enumerated can be understood in the framework of Eqs. (9) and Fig. 1:

(1) Breakdown of Matthiessen's rule in high-resistivity metals (large ρ_0/ρ^*)¹⁴: The averaged Debye-Waller factor plays an important role in determining the temperature dependence of the resistivity when the elastic scattering is large. The dashed curve in Fig. 1 shows ρ^*/ρ vs T^* for $\rho_0 = \rho^*$ and the other parameters chosen to represent a typical transition metal. [W^* was set equal to $W(2k_F)$.] The negative TCR at all T^* is apparent. Since γ increases as ρ_0 increases, which implies that the positive-TCR inelastic term $(1 - \gamma)\rho_{ip}$ in Eq. (6) decreases, one will see small or negative TCR whenever ρ_0 is large enough. For a typical transition metal this occurs when ρ is of the order of $\frac{1}{2}\rho^*$.

(2) Low-temperature anomalous temperature dependence of resistivity in high-resistivity metals,¹⁵ i.e., $\rho \propto 1 - AT^2$: Essentially the argument given to explain the breakdown of Matthiessen's rule covers this anomaly also. At low temperatures ρ_{ip} and W^* are proportional to T^5 for perfect crystalline metals and T^2 for amorphous alloys. So for small- ρ_0 (small- γ) cases, saturation effects are negligible and the normal $+T^2$ and T^5 variations of ρ are given. However, if ρ_0 is large enough (γ large enough), then the elastic scattering term is dominant and $\rho \propto 1 - AT^2$. (In the extreme case, $\gamma = 1$, $\rho \propto e^{-2W^*} \approx 1 - 2W^*$.) For

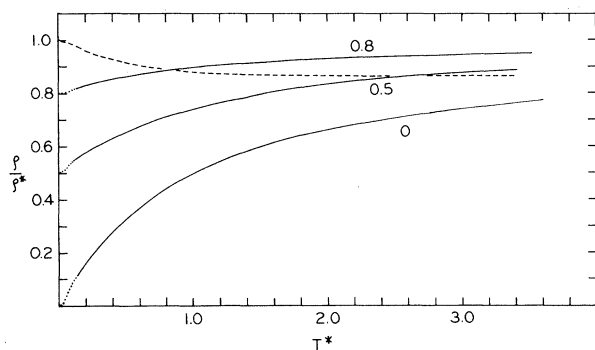


FIG. 1. Normalized resistivity ρ/ρ^* as a function of generalized temperature $T^* = \rho_{ip}/\rho^*$. The solid curves are plotted for a variety of values of normalized residual resistivity ρ_0/ρ^* (shown on each curve) with the Debye-Waller factor set equal to unity. The dashed curve is plotted for values chosen to represent a typical transition-metal system with large residual resistivity, i.e., $\rho_0/\rho^* = 1$, $\Theta = 300$ K, $\beta = 0.13 \mu\Omega \text{ cm/K}$, $2k_F = 3.0 \text{ \AA}^{-1}$, and $M = 90$ amu.

a typical transition metal the transition from positive to negative TCR's should occur for ρ_0 greater than about $\frac{1}{2}\rho^*$.

(3) Saturation¹⁶: Saturation appears to be a universal feature of high-resistivity metals whether phonon scattering or elastic (structure) scattering is dominant.¹⁴ That is, the resistivity of all metals becomes essentially temperature independent at high resistivities. The solid curves in Fig. 1 show ρ/ρ^* vs T^* for a variety of values of ρ_0 with W^* set equal to zero. The effect of the Debye-Waller factor is displayed in the dashed curve in Fig. 1. The increase of W^* effectively lowers ρ_0 as T^* increases.

(a) Resistivity of Nb_3Sb and Nb_3Sn ¹⁷: Good agreement with the measured temperature dependence of the resistivity of crystalline Nb_3Sb and Nb_3Sn may be obtained using $\beta = 0.33 \mu\Omega \text{ cm/K}$ and $\rho^* = 200 \mu\Omega \text{ cm}$.

(b) Resistivity of Nb ¹⁸: The temperature dependence of the resistivity of Nb has been the subject of controversy in the recent literature.^{2, 24, 25} The deviations from linearity in the high-temperature resistivity of Nb as shown in Fig. 2 are seen to be in excellent agreement with our theoretical result for $\beta = 0.047 \mu\Omega \text{ cm/K}$ and $\rho^* = 200 \mu\Omega \text{ cm}$. Thus, our results support Allen's conjecture that the deviations from linearity in Nb are saturation effects and that proposed alternative mechanisms, such as band-structure effects²⁴ and Debye-Waller damping of the phonon resistivity²⁵ yield small corrections at best.

Finally, consider the elastic-scattering term in high-resistivity metals which has been treated

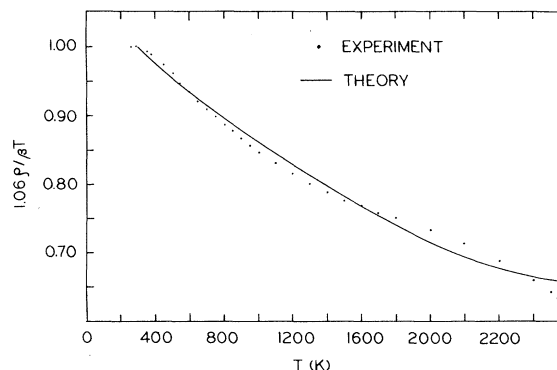


FIG. 2. Deviation from linearity in the resistivity of Nb as a function of temperature. The data are from Ref. 18. The factor 1.06 normalizes the theoretical result to unity at room temperature. (The ordinate for the experimental data is ρ/ρ_1 where ρ_1 is a linear extrapolation of the room-temperature resistivity.)

as independent of Λ up to this point. We expect that a maximum elastic resistivity also occurs corresponding to Λ of the order of interatomic distances.¹⁶ This effect could be considered in an analogous manner to the inelastic scattering by assuming that periodicities in the radial distribution functions of characteristic spacings which are greater than Λ in amorphous metals are ineffective in scattering electrons, leading to a cutoff in the low-momentum-transfer contributions to ρ . In transition metals, backscattering is dominant⁹ so that the diffraction model is expected to remain reliable beyond the point where strong saturation effects appear in the inelastic component.

The uncertainty-principle blurring of the Fermi surface is an additional effect which can contribute to saturation.²⁶ In most of the systems under consideration, it is not expected to play an important role for phonon scattering.¹⁹

¹W. J. Nellis, M. B. Brodsky, H. Montgomery, and G. P. Pells, Phys. Rev. B 2, 4590 (1970).

²P. B. Allen, Phys. Rev. Lett. 37, 1638 (1976).

³K. L. Chopra, A. P. Thakoor, S. K. Barthwal, and P. Nath, Phys. Status Solidi 40, 247 (1977).

⁴F. Brouers and M. Brauwers, J. Phys. (Paris), Lett. 36, L17 (1975).

⁵L. W. Shacklette and W. S. Williams, Phys. Rev. B 7, 5041 (1973).

⁶R. Harris, M. Shalmon, and M. Zuckermann, J. Phys. F 7, L259 (1977).

⁷L. V. Meisel and P. J. Cote, J. Phys. F 7, L321 (1977).

⁸J. M. Ziman, Philos. Mag. 6, 1013 (1961); A. H.

Wilson, *Theory of Metals* (Cambridge Univ. Press, Cambridge, England, 1958).

⁹R. Evans, D. A. Greenwood, and P. Lloyd, Phys. Lett. 35A, 57 (1971).

¹⁰O. Dreirach, R. Evans, H.-J. Guntherodt, and H.-V. Kunzi, J. Phys. F 2, 709 (1972).

¹¹P. J. Cote and L. V. Meisel, Phys. Rev. Lett. 39, 102 (1977).

¹²P. J. Cote and L. V. Meisel, in *Proceedings of the International Conference on the Physics of Transition Metals, Toronto, Canada, 1977*, Institute of Physics Conference Series No. 39 (Institute of Physics, London, 1978).

¹³L. V. Meisel and P. J. Cote, Phys. Rev. B (to be published).

¹⁴J. H. Mooij, Phys. Status Solidi (a) 17, 521 (1972).

¹⁵R. Hasegawa, Phys. Lett. 36A, 425 (1971).

¹⁶See, for example, N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974); and A. F. Ioffe and A. R. Regel, Prog. Semicond. 4, 237 (1960).

¹⁷Z. Fisk and G. W. Webb, Phys. Rev. Lett. 36, 1084 (1976).

¹⁸J. M. Abraham and M. Deviot, J. Less-Common Met. 39, 311 (1972).

¹⁹For a discussion of this postulate, see J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, 1960), Chap. V. See also A. B. Pippard, Philos. Mag. 46, 1104 (1955).

²⁰L. V. Meisel and P. J. Cote, Phys. Rev. B 16, 2978 (1977).

²¹G. Baym, Phys. Rev. 135, A1691 (1964).

²²B. E. Warren, *X-Ray Diffraction* (Addison-Wesley, Reading, Mass., 1969).

²³S. R. Nagel and J. Tauc, Phys. Rev. Lett. 35, 380 (1975).

²⁴M. J. Laubitz, C. R. Leavens, and Roger Taylor, Phys. Rev. Lett. 39, 225 (1977).

²⁵L. V. Meisel and P. J. Cote, unpublished.

²⁶N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1971).