PHYSICAL REVIEW B VOLUME 15, NUMBER 8 15 APRIL 1977

# Calculation of electrical resistivity of highly resistive metallic alloys

D. Markowitz

*Physics Department and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268*

(Received 17 November 1976)

The new feature in an otherwise standard calculation is the inclusion of the temperature-dependent Debye-Waller factor. At low temperature a resistance minimum is predicted which is not of the logarithmic form, such as occurs in the Kondo system, but is instead a polynomial in $T$. Its magnitude scales with the residual resistivity $\rho(0)$ and is unobservably small unless $\rho(0)$ is very large. At higher temperature a contribution linear in $T$ is predicted with coefficient small in magnitude and possibly of either sign, becoming more negative as $\rho(0)$ increases. Behavior almost in line with these predictions has been observed for many metallic glass alloy systems containing transition-metal atoms. But two drawbacks are the uncertain validity of the model for these systems and the prominence of competing effects due to the $d$ electrons.

## I. INTRODUCTION

It is well known that in phenomena in which particles scatter off of lattice ions, a large set of scattering terms add coherently and should all be considered simultaneously. Each successive term represents a higher-order process, i.e., higher in the number of phonons involved, which fact normally makes it negligible with respect to the primary low-order scattering process. However, coherent summation makes their resultant significant. They produce a measurable effect on scattering of x-rays and of particles in an externally introduced beam,[1] as well as on the recoil of nuclei which are $\gamma$ emitters, in particular on the recoilless emission known as the Mössbauer effect.[2] Mathematically these effects yield a multiplicative factor, known as the Debye-Waller factor, which acts to decrease a scattering rate. Since it is sensitive to the state of excitation of the lattice, this factor is temperature dependent.

It is a natural extension to consider the effect of these same terms on the scattering of nearly free band electrons off of the lattice. The electron-lattice mutual scatterings are primarily responsible for acoustic attenuation and electrical and thermal resistivity in many materials in a wide temperature range. This paper considers electrical resistivity $\rho(T)$ in metals.

At low $T$ the main contribution to $\rho$ is the residual resistivity due to defects, which is substantially temperature independent. At higher $T$ the main contribution comes from single-phonon emission and absorption processes. Called the ideal resistivity, since for most metallic systems it is relatively unchanged by the introduction of defects, it has a well-known temperature dependence, whose leading terms are proportional to $T^5$ below the Debye temperature and to $T$ near or above the Debye temperature of the sample.[1] By combining the calculation of the Debye-Waller factor with these accepted results on resistivity, one can quickly conclude that the corrections to the leading terms are negligibly small in the usual cases. However, if the residual resistivity is unusually large compared to the ideal resistivity, then the corrections to the one become significant compared to the other. This outcome requires a heavily alloyed and distorted structure; i.e., one with an unusually high density of defects, and this is the situation to be considered here.

One last point deserves mention before the calculation is outlined. It would be incorrect to introduce the zero-point motion into the primary processes of defect scattering and real single-phonon excitation by electrons. Ziman[1] points this out and it is not in question. However, it is demonstrably correct to include the zero-point motion as part of the higher-order scattering terms whose coherent sum yields the Debye-Waller correction to the primary terms, the reason being that these terms involve virtual phonon excitations.

## II. CALCULATION

The processes considered in this calculation are multiple scattering of an electron by a collection of randomly situated nonmagnetic defects, electron-induced real single-phonon emission and absorption, plus the infinite series of virtual phonon or polarization corrections to these primary processes. Vertex corrections are neglected.

The equations for resistivity which emerge from summing all of these terms are written as[1]

$$\rho(T)=\rho_{\text{bare}}(T)e^{-2W(T)}, \tag{1}$$

where

$$\rho_{bare}(T)=\rho_0+\rho_i(T) \tag{2}$$

and[1(a)]

$$W(T)=\frac{3\hbar^2K^2T^2}{2Mk_B\Theta^3}\int_0^{\Theta/T}\left(\frac{1}{e^z-1}+\frac{1}{2}\right)z\,dz. \tag{3}$$

$\rho_0$ is independent of $T$ and is the "bare" residual resistivity. $\rho_i(T)$ is the bare ideal resistivity. The bare resistivities obey Matthiessen's additivity rule. The exponential is the Debye-Waller factor.

In the usual way,[1(a)] a sum over virtual phonon wave vector $\vec{q}$ has been replaced by an integral over a reduced variable $z$, where $z=\hbar\omega_q/k_BT$ and the Debye model has been used. $\vec{K}$ is the electronic wave-vector transfer; that is, it is the difference between final and initial wave vectors for the real scatterings. Important values of $K$ are expected to be slightly different in $\rho_0$ and $\rho_1$. In $\rho_0$, electron-defect scattering gives typical values of $K$ roughly $K_F$, the Fermi wave vector. In $\rho_1$, electron-phonon scattering gives typical values of $K$ roughly $K_D$, since probably only normal scatterings occur, with umklapp scatterings being suppressed due to structural disorder.

Below we use the conventional forms for the leading terms in $\rho_0$ and $\rho_i(T)$ at low and at high $T$, which have been validated by experiment. We evaluate the leading terms in an expansion for the Debye-Waller factor in those temperature ranges, a rather simple calculation. The results follow:

Low $T$:

$$\rho(T)\cong\rho_0[1-2\overline{W}_0-3.290\overline{W}_1(T/\Theta)^2]+124.4\rho_1(T/\Theta)^5. \tag{4}$$

High $T$:

$$\rho(T)\cong\rho_0\left(1-2\overline{W}_1\frac{T}{\Theta}\right)+\rho_1\frac{T}{\Theta}=\rho_0+(\rho_1-2\overline{W}_1\rho_0)\frac{T}{\Theta}. \tag{5}$$

In these equations $W_1(K)=3\hbar^2K^2/2Mk_B\Theta$, $W_0(K)=\frac{1}{4}W_1(K)$; that is, the factors are originally functions of of momentum transfer $\hbar\vec{K}$. The bars over $W_0$ and $W_1$ in Eqs. (4) and (5) indicate that averages over $\vec{K}$ have been taken. In retaining just leading terms, it turns out that only the corrections to $\rho_0$ are of low enough power in $T$ to be significant. Therefore, as discussed above, we will take the average value of $K^2$ to be $K_F^2$ in those correction terms. Judging from representative values of $M$, $\Theta$ and $K_F$ (taking $M\approx10^5$ times the mass of a free electron, $\Theta\approx300$ °K and $K_F\approx10^8$ cm$^{-1}$), we estimate the value of $\overline{W}_1$ to be roughly 0.01. Equivalently, we find $2\overline{W}_0\approx0.005$ and therefore Eq. (4) may be rewritten for low $T$:

$$\rho(T)\cong0.995\rho_0-3.290\overline{W}_1\rho_0(T/\Theta)^2+124.4\rho_1(T/\Theta)^5. \tag{6}$$

It is clear that the "dressed" resistivities do not obey Matthiessen's rule, and that $\rho(0)$ is not the same thing as $\rho_0$. In the same way Eq. (5) may be rewritten for high $T$:

$$\rho(T)\cong\rho_0+(\rho_1-0.02\rho_0)(T/\Theta)$$

$$\equiv\rho_0+\alpha\rho(293\,^\circ\mathrm{K})T, \tag{7}$$

where $\alpha$ is called the temperature coefficient of resistivity at room temperature and has meaning when the variation of $\rho(T)$ is linear.

Examining Eq. (7), we see that for samples having $\rho_0$ smaller than or comparable to $\rho_1$, then $\rho(T)$ increases monotonically at high $T$ with a large coefficient $\alpha$. For these samples Eq. (6) says that their dominant behavior at low $T$ consists of residual resistivity plus a $T^5$ term. This is the behavior observed for all "normal" samples, which are those for which the ideal resistivity becomes comparable to the residual resistivity at $T$ near or even very much below room temperature.

However, for "anomalous" samples having $\rho_0$ much larger than $\rho_1$, i.e., highly resistive metal alloys, interesting predictions follow. At high $T$ the coefficient $\alpha$ is comparatively small and may even be negative, providing $\rho_0>50\rho_1$; in other words, $\rho_0\gg\rho_1$ by a factor of two orders of magnitude, allowing for uncertainty in our estimate. At low $T$ $\rho(T)$ has a minimum which is not of the logarithmic form, such as occurs in the Kondo system, but is instead a polynomial in $T$. To estimate where the minimum occurs in $\rho(T)$, let us set $\alpha=0$ in Eq. (7), which has the effect of setting $\rho_0\overline{W}_1=\frac{1}{2}\rho_1$ in Eq. (6). Then

$$\rho(T)\cong0.995\rho_0-1.645\rho_1(T/\Theta)^2+124.4\rho_1(T/\Theta)^5. \tag{8}$$

This expression possesses a minimum at a value of $T$ a certain fraction of $\Theta$, namely at $T_{\min}\simeq0.18\Theta$. Thus if $\Theta\approx300$ °K, then $T_{\min}\approx54$ °K. The value of $\rho_{\min}$ is $\simeq0.9945\rho_0$, so that the relative depth of the minimum $[\rho(0)-\rho_{\min}][\rho(0)]^{-1}$ is a constant $\simeq0.0005$. By extending this analysis, we can easily show that $\alpha$ decreases with $\rho_0$ while $T_{\min}$ and the depth of $\rho_{\min}$ increase.

## III. DISCUSSION

We wish now to numerically compare $\rho_0$ to $\rho_1$ for actual metallic alloys, in order to decide which ones are expected to show the predicted behavior. We will use experimental results for $\rho_0$, since its sensitive structure dependence makes theoretical estimate uncertain. However, owing to the way contributions to $\rho_1$ are normalized, i.e., because it is multiplied by powers of $T/\Theta$ in the various formulas, we can easily estimate $\rho_1$ using Ziman's theory of high-temperature resistivity.[1]

We have for the ideal resistivity $\rho_i$, in terms of an ideal mean free path $\Lambda_i$,

$$\rho_i = \frac{\hbar k_F}{ne^2\Lambda_i} = \rho_1 \frac{T}{\Theta}$$

with $n$ being the density of electrons and $k_F$ their Fermi wave vector. Now a fair estimate of $\Lambda_i$ is

$$\Lambda_i \approx 50aT_m/T,$$

where $a$ is the lattice parameter and $T_m$ is the melting temperature. Thus

$$\rho_1 \approx \hbar k_F \Theta / 50ne^2aT_m$$

and we estimate for typical materials that these relations hold:

$$T_m \approx 3\Theta, \quad k_F \approx \pi/a, \quad n \approx 2/a^3, \quad a \approx 2\times 10^{-8}\ \text{cm}.$$

This yields $\rho_1 \approx 10^{-18}$ sec. Since the conversion between cgs and mks units has $1\ \Omega = 1.139\times 10^{-12}$ sec/cm, we have $\rho_1 \approx 10^{-6}\ \Omega\,\text{cm}$.

Observations over many years have shown that $\rho_0$ is much smaller than this estimate of $\rho_1$ for crystalline metals, while $\rho_0$ is at most of order $\rho_1$ for highly doped crystalline alloys. Therefore, these materials should exhibit "normal" behavior, something which they are known to do. The type of system for which $\rho_0$ is much greater than $\rho_1$ is the amorphous metal alloy, also known as the metallic glass. This material should exhibit "anomalous" behavior. It is known to do this,[3] but the question is: Are the observed anomalies in agreement with the predicted ones?

The metallic glass systems most studied contain a significant fraction of one or more transition metals, including Pd-Ni-P,[3] Pt-Ni-P,[4] and a number of others for which the relative proportions of constituents may be varied within limits. Their room-temperature resistivities, as also their residual resistivities, take values generally in the range $(100-300)\times 10^{-6}\ \Omega\,\text{cm}$, in other words 100–300 times $\rho_1$ (if $\Theta$ is approximately equal to the room temperature). These are metallic materials with $\rho_0 \gg \rho_1$ by a factor of two orders of magnitude. The theory presented above predicts that, for these materials, at high $T$ $\rho(T)$ is linear with coefficient $\alpha$ small and of either sign, while at low $T$ there is a resistivity minimum of polynomial form.

Boucher[3] has published detailed results of measurements of $\rho(T)$ for the metallic glass system $(\text{Pd}_{50}\text{-Ni}_{50})_{100-x}\text{P}_x$ with $x$ varying from 15 to 27.5 at.%. Indeed he finds that at high temperature $\rho(T)$ does vary linearly, with small coefficient which may be of either sign and which depends systematically on concentration $x$ in such a way that $\alpha = 0$ at $x \approx 24$. He also finds a resistivity minimum whose characteristics depend systematically upon $x$, with $T_{\text{min}}$ in the range 10–30 °K and relative depth $\approx 0.001$. These numerical values are different from but not far off the values estimated above. Moreover, theory and experiment are in agreement in finding that $T_{\text{min}}$ and depth of minimum increase with $\rho_0$ while $\alpha$ decreases.

However, it must quickly be added that closer inspection of the data reveals temperature dependences ($\log T$ at low $T$ and combinations of $T$ and $T^2$ terms in slightly higher temperature ranges)[5] which disagree in important ways with our predictions. Furthermore, there are two serious criticisms in principle of the application of our theory to this type of system. First, these materials have such short mean free paths that a model of nearly free electrons interacting with defects and lattice vibrations may not be valid. It may be invalid both for the electrons and for the phonons, and the concepts relied upon, such as mean free path and wave vector, may lose their meaning. Second, there are expected effects from the $d$ electrons and from the amorphous "structure." Several have been predicted[5,6] and presumably some have been detected in the experiments which measure the $T$ dependences.[5] Possibly the predictions of this paper are present experimentally but are partially masked by these stronger effects.

## ACKNOWLEDGMENT

Thanks go to L. Kabacoff and W. Hines for valuable discussions of principles and experimental observations, and to J. Budnick for inspiration and support.

---

[1] J. M. Ziman, *Principles of the Theory of Solids*, 2nd ed. (Cambridge U.P., United Kingdom, 1972). See Secs. 2.9 and 7.5. (a) *ibid.*, Eq. (2.111), p. 64.

[2] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963). See Chap. 20.

[3] B. Y. Boucher, J. Non-Cryst. Solids 7, 277 (1972).

[4] A. K. Sinha, Phys. Rev. B 1, 4541 (1970).

[5] R. Hasegawa and C. C. Tsuei, Phys. Rev. B 2, 1631 (1970); Phys. Rev. B 3, 214 (1971); R. Hasegawa and J. A. Dermon, Phys. Lett. A 42, 407 (1973).

[6] R. Hasegawa, Phys. Lett. A 36, 425 (1971); Phys. Lett. A 38, 5 (1972); G. L. Tangonan, Phys. Lett. A 54, 307 (1975); R. W. Cochrane, R. Harris, J. O. Ström-Olsen, and M. J. Zuckermann, Phys. Rev. Lett. 35, 676 (1975).