Momentum Nonconservation and the Low-Temperature Resistivity of Alloys

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The temperature-dependent part of the electrical resistivity of a dilute alloy at low temperatures is generally much larger than that of the pure host metal. A simple calculation based on the relaxation of the usual conservation requirements for electron-phonon scattering in the alloy leads to a formula which contains no free parameters and which agrees well with experiment for a wide variety of alloy systems.

In dilute nonmagnetic alloys experiment generally shows that the electrical resistivity ρ_T is greater than the sum of the residual resistivity ρ_0 and the phonon resistivity of the pure solvent ρ_T^{pure}.[1-8] This deviation from Matthiessen's rule can be large at low temperatures, and a number of mechanisms have been proposed, including impurity-induced changes in the phonon spectrum, anisotropy of the conduction-electron relaxation time over the Fermi surface,[9] and energy dependence of the impurity cross section.[10,11]

Recent experiments by Caplin and Rizzuto[1] on the low-temperature resistivity of aluminum-based alloys show the following: (i) The deviation Δ_T (defined by $\Delta_T=\rho_T-\rho_0-\rho_T^{\text{pure}}$) varies as T^3 at low temperatures, whereas ρ_T^{pure} varies as T^5; for even the purest available material, Δ_T dominates ρ_T^{pure} below 10°K (Fig. 1). (ii) At a given low temperature $\rho_T-\rho_0$ is a slowly increasing function of the residual resistivity (approximately as $\ln\rho_0$) and is independent of the impurity species causing the residual resistivity. These results cannot be reconciled with any of the above explanations and we suggest that the origin of this breakdown of Matthiessen's rule is the relaxation of the conservation-of-momentum requirement in electron-phonon scattering, brought about by the loss of translational symmetry in an impure metal.

We now use a simple physical argument to estimate the phonon resistivity in this situation. In the well-known Bloch-Grüneisen approach, in which momentum and energy conservation at collisions is assumed, the phonon resistivity is given by[12]

$$\rho_T^{\text{pure}}=A(T/\theta)^5\int_0^{\theta/T}[z^5e^z(e^z-1)^{-2}]dz, \qquad (1)$$

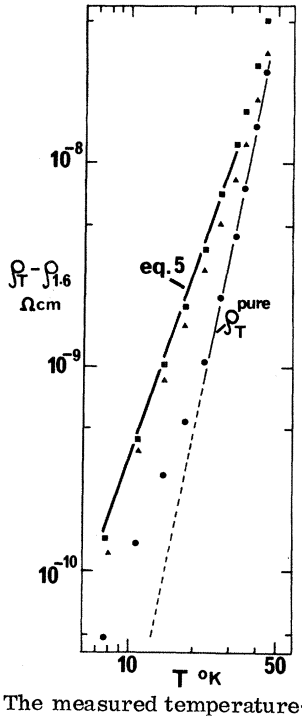

FIG. 1. The measured temperature-dependent part of the resistivity for a series of Al-based alloys, from Caplin and Rizzuto, Ref. 1. The alloy residual resistivities are closed squares, 560 nΩ cm; closed triangles, 25 nΩ cm; and closed circles, 0.8 nΩ cm. The bold line is our Eq. (5) calculated with $\theta=380$°K and with $(d\rho/dT)_{T\geq\theta}=11.2$ nΩ cm/°K. The ideal resistivity ρ_T^{pure} (thin line) is obtained in a manner described in Ref. 1; the broken portion at low temperatures is an extrapolation. Note that at 10°K the alloy resistivities are up to thirty times larger than the ideal resistivity.

where A is a constant and θ is the Debye temperature. $z=\hbar\omega/kT$, where ω is the phonon frequency. Suppose now that at low temperatures we have a high enough concentration of impurities for the sample to be in a dirty limit such that (i) the uncertainty in momentum of any electron state $|k\rangle$ is so great that it can be scattered through large angles by a phonon of any wave vector q; and (ii) on an energy scale $\sim\hbar\omega$, energy is not conserved at electron-phonon collisions because of frequency impurity scattering (this condition does not imply that overall energy is not conserved).[13] The first condition eliminates a small-angle scattering factor $(Q^2/2k_F^2)(T/\theta)^2z^2$ in the Bloch-Grüneisen integral where Q and k_F are the Debye and Fermi radii, and the second removes a factor $ze^z(e^z-1)^{-1}$. We are then left with

$$R_T=B(T/\theta)^3\int_0^{\theta/T}[z^2(e^z-1)^{-1}]dz \qquad (2)$$

(which, as it turns out, is exactly proportional to the number of phonons).

In order to evaluate R_T we note that at high temperatures ($T\gg\theta$), even in the absence of impurities, (i) all phonons can scatter through large angles; and (ii) the electron energy spread kT is greater than the maximum phonon energy. These are just the same conditions as the dirty limit at low temperatures, so Eq. (2) should again apply. We conclude that the resistivities in the low-temperature dirty limit and at high temperatures should be in the ratio of the R_T integrals in the two cases.

At low temperatures, using a Debye model and free electrons, Eq. (2) reduces to

$$R_T=2.4B(T/\theta)^3. \qquad (3)$$

The high-temperature limit is often not easily attainable, but the temperature coefficient of resistivity becomes constant for T of the order of θ. In this region,

$$dR_T/dT=0.5B/\theta. \qquad (4)$$

Combining (3) and (4), we have immediately a formula for the low-temperature resistivity in the dirty limit:

$$\rho_T^{\,d}-\rho_0=[4.8/\theta^2(d\rho/dT)_{T\simeq\theta}]T^3. \qquad (5)$$

For Al, θ is 380°K[14] and $d\rho/dT$ at room temperature is 11.2 nΩ cm/°K,[15] so Eq. (5) predicts $\rho_T^{\,d}-\rho_0=3.7\times10^{-13}T^3$ Ω cm. Caplin and Rizzuto[1] found for their most impure sample $\rho_T-\rho_0=3.3\times10^{-13}T^3$ Ω cm between 4 and 20°K (Fig. 1). Seth and Woods's[2] data for Al:Ag and Al:Mg show excellent agreement with those of Caplin and Rizzuto. The experiments show that the dirty limit (as defined above) is reached when ρ_0 is of the order of 1 μΩ cm or greater; the measured phonon resistivities are then within about 10% of those predicted by our heuristic argument, which must be regarded as remarkable when it is remembered that it is difficult to obtain even order-of-magnitude agreement between measured and calculated resistivities of pure metals at similarly low temperatures (see, for example, Reich's[4] discussion of his own results).

Only rather less complete information is available on other alloy systems, but qualitatively the same features are apparent: For a given host metal at a fixed temperature, $\rho_T-\rho_0$ is a slowly increasing function of ρ_0; if $\rho_T-\rho_0$ is fitted at the lowest temperatures by a T^n law, n is usually found to be between 3 and 4, and decreases towards 3 as ρ_0 increases. Reich[4] measured the resistivity of single-crystal Ga along the (001) axis between 1 and 4°K and fitted the data for his most impure sample ($\rho_0=404$ nΩ cm) by $\rho_T-\rho_0=(1.3\times10^{-11})T^3$ Ω cm. With the parameters of Ga [$\theta=240$°K,[14] $(d\rho/dT)_{(001)}=160$ nΩ cm/°K[15]], Eq. (5) predicts that $\rho_T-\rho_0=1.4\times10^{-11}T^3$ Ω cm. Because of the incompleteness of some of the data, the comparison for other elements has been made (Table I) between the measured resistivity of the most impure alloy of each metal at a temperature low enough for $\rho_T-\rho_0$ to be much less than ρ_0 (so that the sample can be taken as approaching the dirty limit) and the limiting resistivity $\rho_T^{\,d}-\rho_0$ calculated from Eq. (5) with accepted high-temperature values of the Debye temperature[14] and the temperature coefficient of resistivity.[15] For the hexagonal metals the value of θ deduced from specific-heat measurements varies with temperature; we have not taken this into account, but allowing for it would bring the calculated values more into line with the experimental results.

To summarize, it appears that for alloys where ρ_0 is of the order of 1 μΩ cm the usual conservation requirements are removed; this in turn indicates the failure of the adiabatic approximation[12,13] in these alloys at low temperatures.

The conventional criterion for this approximation to hold is that $q\lambda\gg1$ where q is the phonon wave vector and λ the electron mean free path. At 10°K in Al, for example, typical phonons have $q\sim2\times10^6$ cm^{-1}, and even with $\rho_0\sim1$ μΩ cm, λ is about 10^{-5} cm, so this condition is always well satisfied; consequently we suggest that it is, in

Table I. A comparison of the measured low-temperature resistivity of a number of alloy systems with the dirty-limit resistivity of our Eq. (5). For each system the most concentrated alloy has been chosen, and the comparison made at the lowest temperature at which the measurements retain significant accuracy; under these conditions the dirty limit should be approached, and the measured $\rho_T - \rho_0$ for the alloy is expected to be considerably greater than $\rho_T{}^{\text{pure}}$ (cf. Fig. 1).

Solvent	θ[a] (°K)	$(d\rho/dT)_{T \gtrsim \theta}$[b] (nΩ cm/°K)	Alloy ρ_0 (nΩ cm)	T (°K)	$(\rho_T - \rho_0)$ meas. (nΩ cm)	$(\rho_T{}^{d} - \rho_0)$ calc. (nΩ cm)
Cd	170	29	1000[c]	10	15	5.0
Mg	320	73	3900[c]	18.5	9.8	22
Ag	225	6.5	800[d]	12.0	1.3	1.1
Sn	160	54	23[e]	5	1.2	1.2
Be	920	40	930[e]	77	50	95
Cu	310	6.7	970[f]	20	2.6	2.7
Au	185	8.3	1250[g]	12	3.0	2.0
Zn	240	24	260[h]	10	4.0	2.0
In	110	30	260[i]	4.2	2.5	0.9

[a]See Ref. 14.
[b]See Ref. 15.
[c]See Ref. 2.
[d]See Refs. 2 and 3.
[e]See Ref. 4.
[f]See Ref. 5.
[g]See Ref. 6.
[h]See Ref. 7.
[i]See Ref. 8.

fact, insufficiently stringent to ensure validity of the adiabatic approximation. A substantially stronger condition may be derived from a qualitative uncertainty-principle argument: The real-space volume swept out by an electron between collisions is λ multiplied by the electron cross section, which is about equal to the square of the Fermi wavelength $\lambda_F{}^2$; the volume of k space associated with the diffuseness of electron momentum in an impure system is therefore of the order $(2\pi)^3/(\lambda\lambda_F{}^2)$; this is directly proportional to ρ_0, which is physically correct, and is characterized by a real-space length $(\lambda\lambda_F{}^2)^{1/3}$. We suggest that the correct condition for the adiabatic approximation to hold may instead involve $q(\lambda\lambda_F{}^2)^{1/3}$ which, for the example cited above, would be only of the order of 10^{-1}.

There are, no doubt, other contributions to the breakdown of Matthiessen's rule arising from the effects mentioned earlier, but our analysis indicates that the dominant mechanism at low temperatures is a more general one involving the nature of electron-phonon collisions in systems lacking translational symmetry, and the resulting resistivity can then be calculated with surprising accuracy by a simple argument. Very recently Mills[16] has given formal justification for the physical picture used here, and derived a contribution to the resistivity from interference between electron-phonon and electron-impurity scattering equal to our Eq. (5), apart from a numerical factor close to 1. Mills's term adds to $\rho_T{}^{\text{pure}}$ and should therefore correspond to Δ_T $(=\rho_T - \rho_0 - \rho_T{}^{\text{pure}})$ rather than to $\rho_T - \rho_0$ alone. The quantity that is measured experimentally is $\rho_T - \rho_0$ and, because $\rho_T{}^{\text{pure}}$ is difficult to establish at low temperatures,[1] the subtraction to obtain Δ_T is necessarily somewhat uncertain. However, in the limit of large ρ_0 and low temperatures, $\rho_T{}^{\text{pure}}$ is so much smaller than $\rho_T - \rho_0$, as is shown for Al in Fig. 1, that $\Delta_T \approx \rho_T - \rho_0$ and the quantitative comparison of measured resistivities with Eq. (5) is scarcely affected. Analysis of the higher temperature data for Al[1] and for Ag[3] suggests that Mills is probably correct, and Eq. (5) does describe an additional scattering process.

All the above arguments refer only to the dirty limit; however, experiments show that over a very wide concentration range below the dirty limit (of the order of 10^4 in Al[1]), a T^3 term with a lower coefficient is still found. The coefficient appears to vary approximately as $\ln\rho_0$, the pure limit ($\rho_T - \rho_0$ independent of ρ_0) being attained only when $\rho_0 \lesssim \rho_T$. This behavior implies that the quenching of the conservation requirement as impurities are added to the pure metal is exceedingly gradual.

In conclusion we emphasize that it is essential to include this impurity-induced term in any analysis of the temperature dependence of the resistivity for even the purest metal samples, and, a fortiori, for alloys.

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[1]A. D. Caplin and C. Rizzuto, J. Phys. C: Proc. Phys. Soc., London 3, L117 (1970).

[2]R. S. Seth and S. B. Woods, Phys. Rev. B 2, 2961 (1970).

[3]R. J. Tainsh, J. G. Collins, and G. K. White, to be published.

[4]R. Reich, thesis, Université de Paris, 1965 (unpublished).

[5]B. Lengeler, W. Schilling, and H. Wenzl, J. Low-Temp. Phys. 2, 59 (1970).

[6]D. H. Damon, M. P. Mathur, and P. G. Klemens Phys. Rev. 176, 876 (1968).

[7]M. R. Cimberle, S. Ledda, and C. Rizzuto, to be published.

[8]H. Meissner and R. Zdanis, Phys. Rev. 109, 681 (1958).

[9]J. S. Dugdale and Z. S. Basinsky, Phys. Rev. 157, 552 (1967).

[10]M. J. Rice, Phys. Rev. Lett. 23, 1108 (1969).

[11]H. Smith and J. W. Wilkins, Phys. Rev. Lett. 24, 221 (1970).

[12]J. M. Ziman, *Electrons and Phonons* (Oxford Univ., London, 1960).

[13]R. E. Peierls, *Quantum Theory of Solids* (Oxford Univ., London, 1955), 1st ed., p. 124.

[14]G. K. White, *Experimental Techniques in Low Temperature Physics* (Oxford Univ., London, 1968), 2nd ed., Table E, p. 374.

[15]*Landolt-Börnstein: Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik,* edited by K.-H. Hellwege and A. M. Hellwege (Springer, Berlin, 1959), 6th ed., Vol. II, Pt. 6.

[16]D. L. Mills, following Letter [Phys. Rev. Lett. 26, 242 (1971)].

Temperature Dependence of the Contribution to the Transport Properties from Electron-Phonon Scattering in Dilute Alloys

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A mechanism is suggested to explain the temperature dependence and magnitude of a contribution to the electrical resistivity observed in a number of alloys.

The temperature dependence of the electrical resistivity ρ of pure, nonmagnetic metals should be accurately described by the Bloch-Grüneisen theory.[1] This theory predicts that $\Delta\rho = \rho(T) - \rho(0)$ should vary with temperature like T^5 when $T \ll \Theta_D$, the Debye temperature.

Recently, Caplin and Rizzuto[2] have completed a careful study of $\Delta\rho$ for a number of dilute alloys of Al with nonmagnetic transition-metal impurities. They find a contribution $\Delta(T)$ to ρ with the following properties:

(a) At low temperatures, $\Delta(T) = BT^3$.

(b) The magnitude of B seems independent of the type of impurity present in the alloy. However, B was observed to have a very weak dependence on the residual resistivity ρ_0 of the sample. This dependence is slight; as ρ_0 varies over four orders of magnitude, B changes by less than one order of magnitude. Caplin and Rizzuto suggest that in Al, B is proportional to $\ln\rho_0$.

(c) As ρ_0 is decreased, the range of temperatures over which the T^3 behavior is observed tends to become smaller. As the temperature increases, $\Delta(T)$ appears to become independent of T, but scatter in the data makes this conclusion tentative.

(d) Campbell, Caplin, and Rizzuto[3] have presented a heuristic argument based on the breakdown of wave-vector conservation which leads to an empirical formula that relates B to the high-temperature value of ρ in a number of alloys. They propose that

$$\Delta(T)|_{\text{low } T} = \frac{K}{\Theta_D^2}\left(\frac{d\rho}{dT}\right)_\infty T^3 \qquad (1)$$

with $K = 4.8$ accounts for the magnitude of B for