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Mathiessen's Rule and Anisotropic Relaxation Times

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Departures from Matthiessen's rule were measured for dilute alloys of copper with gold, tin, or germanium, and of silver with gold or tin; and for strained copper and silver. The concentration of alloyed elements ranged from 0.01 to 1 at.%; residual resistivities per atomic percent impurity are estimated to be known within better than 1% accuracy and were compared with Linde's values. In evaluating the deviations, corrections were applied for the volume dependence of the residual resistivity due to thermal expansion and the ideal resistivity due to alloying. The results were interpreted on a simple two-band model as due to different anisotropies of the relaxation times associated with different scattering processes; the expected temperature dependence of the anisotropy of phonon scattering was taken into account. At temperatures where the residual resistivity dominates, deviations from Matthiessen's rule become comparable to or greater than the ideal resistivity, making experimental determination of the ideal resistivity in this region open to criticism.

INTRODUCTION

According to Matthiessen's rule the resistivity of a metal which contains impurities or imperfections is given at any temperature, T, by the relationship

$$\rho_{\text{tot}}=\rho_{\text{ph}}+\rho_0\,,$$

where ρ_{tot} is the resistivity of the impure metal at temperature T, ρ_{ph} (the "ph" stands for phonons) is the resistivity that a pure, perfect crystal of the metal would have at this temperature, and ρ_0 is the resistivity that the impure metal has at very low temperatures where the resistivity has ceased to depend on temperature. Basically, this rule assumes that the scattering of electrons by phonons and by impurities are independent of each other and that effectively a single relaxation can characterize each type of scattering. Departures from Matthiessen's rule can arise for a number of reasons. Some of the most important (for nonmagnetic impurities) are as follows:

1. The phonon spectrum of the metal may be changed by the addition of impurities. In the simplest cases this means that the θ_D value of the lattice is altered.[1]
2. The phonon distribution under current-carrying conditions may be perturbed by the added impurity.
3. The Fermi surface (or more generally the electronic band structure of the metal) may be altered by the impurity.
4. The relaxation times for phonon and impurity scattering may have different anisotropies.[2]

In addition, there are effects associated with inelastic scattering from impurities. This problem has been studied both theoretically[3–5] and experimentally. Some experiments[6] appear to show positive results at very low temperatures (below about 20°K) but further experiments[7] looking for effects associated with local modes have been unsuccessful. The present situation is obscure and although it is not possible to rule out effects of this kind, we shall ignore them in our subsequent discussion.

We shall be concerned with dilute alloys, the maximum impurity content being 1 at.%. For this reason we believe we can neglect any changes in the band structure of the metal; furthermore, by comparing results for impurities of different mass we shall find that the effects of changes in the phonon spectrum and phonon distribution are not important. Our attention is thus focused on (4) the anisotropies of τ; wherever such different anisotropies exist, there must be departures from Matthiessen's rule. We shall argue that, in the alloys discussed here, this is the main effect.

EXPERIMENTAL

The specimens were prepared by melting together pure parent material (American Smelting and Refining Company 99.999% Cu and 99.999% Ag, and Canadian Mint 99.99+ % Au) with the requisite amount of alloying element in a sealed quartz tube, and then quenched. The alloys were homogenized at 940°C for 3 weeks. After drawing down the ingots to the required diameter, the specimens were cut to approximately the right length and annealed at 550°C for 18 h. To minimize preferential evaporation of one of the constituents the anneal was made in close-fitting Pyrex tubes. The same treatment was given to pure Cu samples to check whether the melting procedure resulted in the pickup of any impurity. The residual resistance ratio of the melted pure Cu samples did not show any increase

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[1] S. B. Das and A. N. Gerritsen, Phys. Rev. **135**, A1081 (1964).

[2] J. M. Ziman, Phys. Rev. **121**, 1320 (1961).

[3] S. Koshino, Progr. Theoret. Phys. (Kyoto) **24**, 484 (1960); **24**, 1049 (1960).

[4] P. L. Taylor, Proc. Phys. Soc. (London) **80**, 755 (1962); and Phys. Rev. **135**, A1333 (1964).

[5] P. G. Klemens, J. Phys. Soc. Japan **18**, Suppl. 11, 77 (1963).

[6] D. H. Damon and P. G. Klemens, in *Proceedings of the Ninth International Conference on Low Temperature Physics, Columbus, Ohio, 1964*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965).

[7] D. H. Damon and P. G. Klemens, Phys. Rev. **138**, A1390 (1965).

over that of wires drawn without melting, suggesting that unintentional alloy pickup was negligible. The intended compositions of the alloys were checked by determining the change of lattice parameters with respect to that of the pure parent metal.

Residual resistivities versus nominal composition are shown in Figs. 1 and 2 for two sets of copper and silver alloys. For most of the specimens the residual resistivity is very accurately proportional to the composition. We estimate that the resistivity per atomic percent impurity is known to an accuracy of better than 1%. A comparison with Linde's[8] value is made in Table I.

To measure departures from Matthiessen's rule over a wide range of temperature it is necessary to determine the absolute resistivities of the specimens. This means that we have had to measure the *shape factors* of the specimens, i.e., in addition to the resistance of the specimens one has to measure their cross-sectional area and the distance between the potential leads.

The specimens consisted of rods about 15 cm long drawn down to about 1 mm in diameter. The cross-sectional areas were calculated from the weight, length' and density, accurate alloy densities being obtained from crystallographic data.[9] The ends of the specimens were cut at right angles to the axis by spark erosion and an accurate length measurement made with a traveling microscope.

TABLE I. $\Delta\rho$ and ρ_0 in $\mu\Omega$-cm per atomic percent impurity.

Impurity	$\Delta\rho$ (Linde)	ρ_0 (present experiments)
	Parent metal: copper	
none	...	0.00060
Au	0.55	0.49
Ge	3.75	3.6$_6$
Sn	2.85	2.8
	Parent metal: silver	
none	...	0.0020
Au	0.38	0.36$_5$
Sn	4.32	4.3$_5$

For resistance measurements, current and potential leads were attached to the specimen by means of spring clips with knife-edge contacts at right angles to the axis of the specimens. The inner pair of these contacts was used for the potential measurements and the distance between them was subsequently measured by a travelling microscope from the distance between the imprints of the knife edges on the specimens.

In this way, *absolute* resistivities could be measured with an accuracy better than one in a thousand. It should perhaps be emphasized that there is no way of avoiding absolute measurements without making some assumption about Matthiessen's rule or the form of departures from it. Krautz and Schultz[10] for example, assumed that Δ [see Eq. (1)] must become independent of temperature at high temperatures.

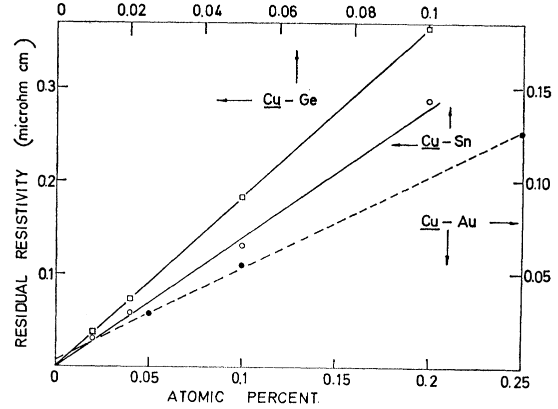

FIG. 1. Residual resistivity versus nominal composition in *Cu*-Au, *Cu*-Ge, and *Cu*-Sn alloys. The appropriate scales are indicated by the arrows.

The temperature dependence of the resistivities was measured in an apparatus built on the principle of an adiabatic calorimeter. The specimens and thermometers were enclosed in a copper vessel containing exchange gas. This vessel was mounted in a vacuum enclosure entirely surrounded by a shield kept at the same temperature as the vessel. All the leads going to the specimens and thermometers were first carefully anchored to the shield so that when the shield and vessel were at the same temperature there was no heat influx into the latter. The relative temperature of shield and vessel was measured by means of a thermocouple and the temperature of the two kept the same by means of a heater on the shield. Outside the shield the walls of the vacuum en-

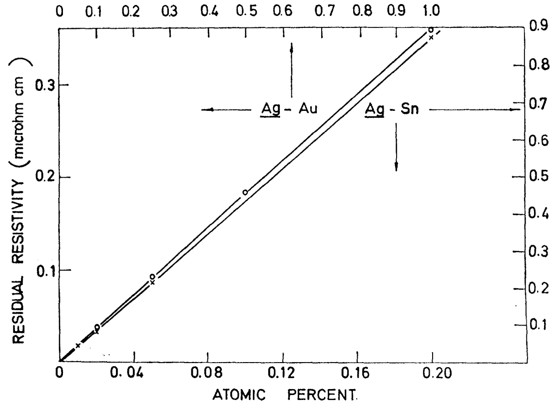

FIG. 2. Residual resistivity versus nominal composition in *Ag*-Au and *Ag*-Sn alloys. The appropriate scales are indicated by the arrows.

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[8] J. O. Linde, Ann. Physik. **15**, 239 (1932).

[9] W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958).

[10] E. Krautz and H. Schultz, Z. Naturforsch. **12a**, 719 (1952).

closure were kept cool by liquid helium or liquid nitrogen according to the temperature range of the experiments.

By controlling the heat input to the shield manually it was found possible to keep the temperature in the vessel containing the specimens constant to about 0.01°K during the time required for a measurement. This was typically about twenty minutes, which was sufficient to make two sets of readings on six specimens and the thermometer. At temperatures up to 20°K there was some difficulty in maintaining the temperature constant because the thermal capacity of the vessel is small in this region; however, this range of temperatures was not very important to us.

The thermometers used were a calibrated platinum resistance thermometer, which could operate between about 10°K and room temperature, and a carbon thermometer for the region between 4.2 and 20°K.

The main limitation on the accuracy of the resistance measurements was due to the heating effects of the measuring current. The spring clips which made contact with the specimens were made of beryllium-copper which has a rather high resistivity even at low temperatures and although the greater part of the clip was shorted out by a copper lead, the remaining resistivity was high enough to give appreciable heating at low temperatures if the measuring current exceeded about 50 mA. The resistances were measured by a potentiometer with a chopper amplifier and pen recorder as the detector. In this way, potentials could be measured with an accuracy of about 0.01 μV.

EXPERIMENTAL RESULTS

From our measurements we were able to calculate the resistivities of the alloys, the deformed metals and the pure annealed metals as a function of temperature between 4.2°K and room temperature. In order to compare these with the predictions of Matthiessen's rule, we define a quantity Δ by the relation

$$\Delta=\rho_{\mathrm{tot}}-(\rho_{\mathrm{ph}}+\rho_0)\,, \tag{1}$$

where ρ_0 is the resistivity of the specimen as measured at 4.2°K.

Strictly speaking, Matthiessen's rule can be applied only if ρ_{tot}, ρ_{ph}, and ρ_0 are all measured at the same atomic volume. In practice, however, alloying changes the volume slightly, and, since the measurements are made at constant pressure, different temperatures also alter the volume of the specimens. To allow for this, we have made corrections to ρ_{ph} and ρ_0 from the pressure derivatives of these quantities. We have assumed that the thermal expansion of the alloy is the same as that of the parent metal; consequently ρ_{ph} has been corrected for a fixed change of colume at all temperatures, i.e., for the volume change produced on alloying.[11,12] ρ_0, on the other hand, which is measured at 4.2°K, has been corrected for the change due to thermal expansion of the metal at all temperatures.[13,14] The corrections to ρ_{ph} and ρ_0 can have a large influence on the value of Δ. At room temperature, where the corrections to ρ_{ph} have their greatest influence, we have the following values for the most concentrated alloy in each of the copper series:

		$\delta\rho_{\mathrm{ph}}/\rho_{\mathrm{ph}}$	$\delta\rho_{\mathrm{ph}}/\Delta$
0.25%	*Cu*-Au	30×10^{-4}	0.5
0.1%	*Cu*-Ge	48×10^{-4}	0.1
0.1%	*Cu*-Sn	25×10^{-4}	0.36

The largest correction to Δ (in *Cu*-Au) is thus about $\frac{1}{3}$ of the uncorrected value. However, the size of the correction falls off at lower temperatures because ρ_{ph} falls off, whereas Δ actually increased until quite low temperatures. (In *Ag*-Au this correction is always very small because addition of gold has little effect on the lattice parameter of silver).

The corrections to ρ_0 are biggest at the highest temperatures, where the thermal expansion is greatest. At room temperature the values are as follows:

		$\delta\rho_0/\rho_0$	$\delta\rho_0/\Delta$
0.25%	*Cu*-Au	-0.7×10^{-2}	0.1
0.1%	*Cu*-Ge	$+0.6\times10^{-2}$	0.1
0.1%	*Cu*-Sn	$+0.9\times10^{-2}$	0.2

These corrections are smaller than those due to ρ_{ph} but still appreciable at the highest temperatures; at lower temperatures, however, they fall off rather quickly.

Although the corrections involve assumptions and approximations, we believe that they have to be included if we wish to compare our results with theoretical predictions.

The results corrected in this way are shown in Figs. 3, 4, and 5 for the copper alloys, Figs. 6 and 7 for the

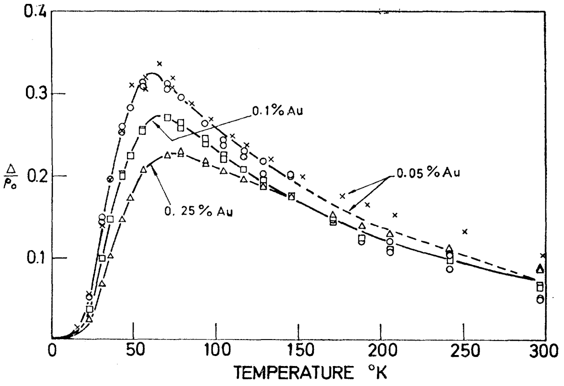

FIG. 3. Δ/ρ_0 versus temperature for the *Cu*-Au alloys. The crosses are the results of a repeated set of measurements (including the shape factor) on the 0.05% alloy.

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[11] J. S. Dugdale and D. Gugan, Proc. Roy. Soc. (London) **A241**, 397 (1957).

[12] K. Okumura (unpublished).

[13] J. O. Linde, Arkiv. Mat. Astron. Fys. **36A**, No. 10 (1949).

[14] J. S. Dugdale and D. Phillips (to be published).

silver alloys and in Fig. 8 for the strained specimens. The general features shown by the graphs of Δ/ρ_0 versus temperature are that in the dilute alloys there is a pronounced maximum at roughly $\theta/5$ (above 50°K for copper-based alloys and below 50°K for the silver-based alloys). The size of the maximum diminishes with increasing concentration while the temperature of the maximum tends to increase; at high enough concentration the maximum may disappear (cf. Figs. 6 and 7). Krautz and Schultz[10] found such a maximum in their measurements of Δ in dilute gold-silver and silver-gold alloys but its existence was subsequently questioned by Alley and Serin,[15] who found no evidence for it from their measurements on aluminum, tin, and copper alloys. There is, however, now no doubt about its existence at least in the dilute alloys measured here.

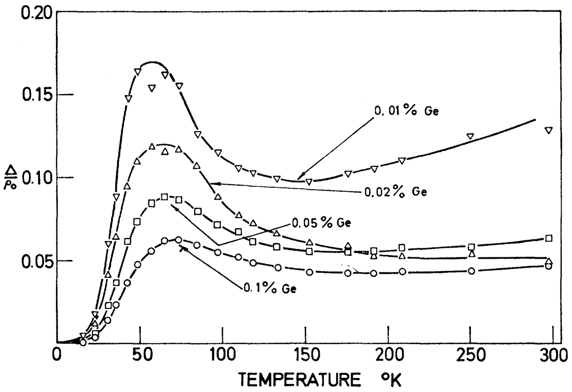

FIG. 4. Δ/ρ_0 versus temperature for the *Cu*-Ge alloys. There is probably a systematic error (from the shape factor) in the results for the 0.01% alloy.

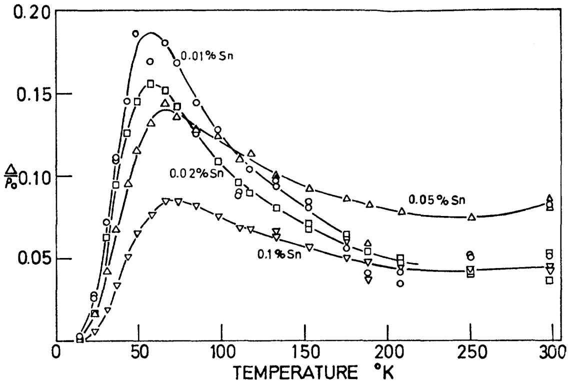

FIG. 5. Δ/ρ_0 versus temperature for the *Cu*-Sn alloys.

DISCUSSION

We now have a detailed picture of the Fermi surfaces of the noble metals. In addition, we have an appreciable amount of information about the cyclotron effective masses in these metals so that we know how the velocities of the conduction electrons vary over the Fermi surface. At present, however, we have very little knowledge about how the relaxation time, $\tau(k)$, varies over the Fermi surface. Ziman[2] has given a very lucid discussion of this question from a theoretical point of view. He emphasizes the difficulty of defining a unique relaxation time for each point on the Fermi surface even when one is considering only one type of transport

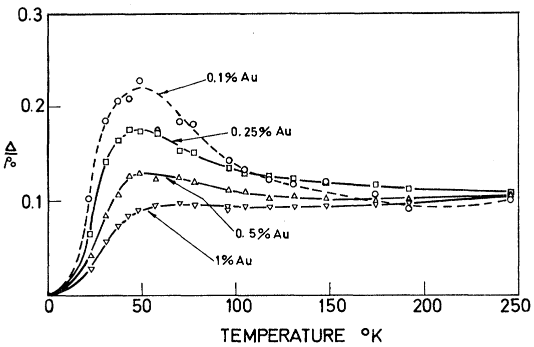

FIG. 6. Δ/ρ_0 versus temperature for the *Ag*-Au alloys.

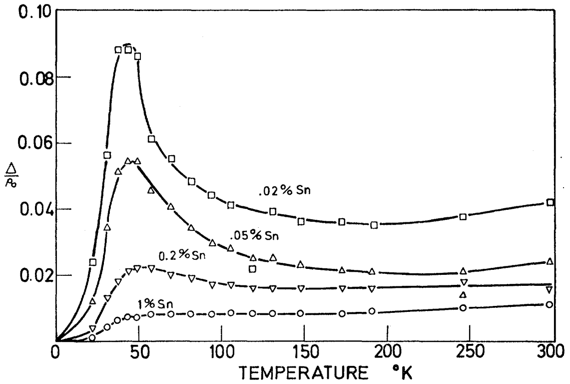

FIG. 7. Δ/ρ_0 versus temperature for the *Ag*-Sn alloys. Note the absence of a maximum in the most concentrated alloy.

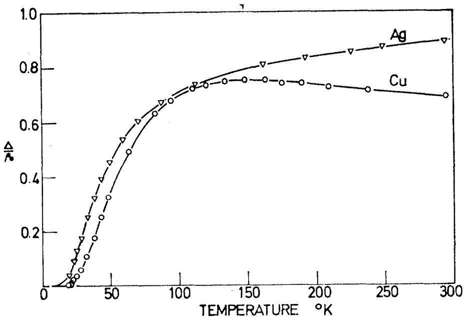

FIG. 8. Δ/ρ_0 versus temperature for strinaed Cu and strained Ag

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[15] P. Alley and B. Serin, Phys. Rev. 116, 334 (1959).

property, for example, electrical resistivity. Nevertheless, he suggests that something like a relaxation time must exist at each such point and we shall adopt this point of view.

In his analysis, Ziman attempts to make some estimate of the anisotropy of τ for both phonon and impurity scattering in a noble metal. To do this he considers two extreme groups of electrons on the Fermi surface: (1) The belly electrons which are associated with the more or less spherical parts of the Fermi surface, and have something of the character of free electrons; and (2) The neck electrons which are associated with those regions of the Fermi surface which are in contact with, or close to, the {111} Brillouin zone boundaries. These electrons require at least two orthogonalized plane waves to describe their wave functions; moreover these functions, theory shows, have p-like symmetry. This means that the electron wave functions have their greatest amplitudes between the ions in contrast to the s-like functions which have their greatest amplitude *at* the ions. Physically this means that the p-like electrons tend to move along the channels between ions and this fact is important for certain kinds of impurity scattering.

In considering phonon scattering Ziman argues that the belly electrons will have a relaxation time τ_B which will tend to increase rapidly at low temperatures since umklapp processes (which could cause wide-angle scattering) will die out with falling temperature. On the other hand, the relaxation time of the neck electrons τ_N will not increase so rapidly because in the neck regions of the Fermi surface, where the curvature is large, quite small phonons can still cause appreciable changes in the electron velocity. At high temperatures where there is an abundance of phonons with large wave number we may expect that the scattering will be more or less isotropic, i.e., $\tau_N/\tau_B \simeq 1$. Thus we expect τ_N/τ_B to diminish as the temperature falls.

In discussing impurity scattering Ziman distinguishes between impurities with the *same* valence (e.g., Ag in Au) which thus perturb the lattice potential over a comparatively short range and those which differ markedly in valence from the host (e.g., Ge in Cu). The scattering by the former tends to have predominantly s-like symmetry; this implies that the perturbation by the impurity is largely confined to the immediate neighborhood of that impurity. But, as we saw above, the neck electrons tend to move between the ions and so would scarcely be scattered by such impurities. On the other hand the belly electrons are scattered in the usual way so that τ_N/τ_B is large for this kind of impurity. This situation is reflected in the Hall coefficient of the *Ag*-Au alloy series.[16]

In contrast to uncharged impurities the scattering from strongly charged impurities tends, according to Ziman, to be more isotropic and to have τ larger on the bellies than on the necks. Direct measurements of τ have, to some extent, confirmed these predictions[17,18] about the difference between "charged" and "uncharged" impurities.

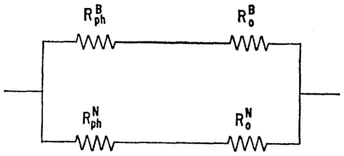

FIG. 9. Schematic representation of a metal consisting of two groups of charge carriers subject to two kinds of scattering process.

It is in terms of this sort of picture we shall now discuss our results. We have seen that at least at low temperatures phonon scattering and impurity scattering may produce very different anisotropies in τ. Thus in an alloy at a temperature where both scattering mechanisms operate we would not expect the total scattering to be simply the sum of the two separately as is implied by Matthiessen's rule. (Indeed, we should then expect that the other rules that assume simple additivity would also fail, e.g., the Gorter-Nordheim rule in thermoelectric power.) Under these conditions we may get some idea of the effect by assuming a simple two-band model in which the two bands are, say, the belly electrons and the neck electrons. The neck electrons (those near the necks) are presumably quite small in number. Obviously this division into two groups is a gross oversimplification, but we may hope to see from this model the qualitative effects caused by the different anisotropies of τ.

It is simplest at this stage to work in terms of the conductivities, σ_B and σ_N, associated, respectively, with the belly and neck regions. Suppose that the ratio $\sigma_N{}^{\mathrm{ph}}/\rho_B{}^{\mathrm{ph}}$ (call it α) represents the ratio of the neck to belly conductivities when the scattering is due to phonons and that $\sigma_N{}^0\sigma_B{}^0$ (call it β) represents the same quantity when the scattering is entirely due to impurity.

Our two-band model can be represented schematically by the circuit in Fig. 9 and it is then not difficult to show that on this model Δ is given by the following expression:

$$\frac{\Delta}{\rho_0}=\frac{\rho_{\mathrm{ph}}(\beta-\alpha)^2}{\alpha\rho_0(1+\beta)^2+\beta\rho_{\mathrm{ph}}(1+\alpha)^2}. \qquad (2)$$

Here ρ_{ph} is the resistivity that arises when only phonon scattering is present, and ρ_0 that when only impurity scattering is allowed. α and ρ_{ph} thus depend on temperature while ρ_0 depends only on concentration. β is fixed for a given impurity in a given parent metal.

If A_N, v_N, and τ_N represent, respectively, the area of the neck region, the velocity of the neck electrons and their relaxation time, while A_B, v_B, and τ_B are the cor-

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[16] V. Heine, Phil. Mag. **12**, 53 (1965).

[17] B. C. Deaton and J. D. Gavenda, Phys. Rev. **129**, 1990 (1963).

[18] P. E. King-Smith, Phil. Mag. **12**, 1123 (1965).

responding quantities for the bellies, then

$$\frac{\sigma_N}{\sigma_B}=\frac{A_N v_N \tau_N}{A_B v_B \tau_B}. \tag{3}$$

This means that ultimately we can interpret the ratio of conductivities in terms of relaxation time provided we can make reasonable assumptions about the relative areas and velocities to be associated with the neck and belly regions. Equation (3) also implies that the ratios α and β differ from each other only if the ratio of relaxation times for scattering by phonons differs from that for scattering by impurities. Thus in *a given parent metal* the ratio of the conductivities reflects directly the ratio of the relaxation times.

In expression (2) there are two factors that determine how Δ/ρ_0 depends on temperature: One is the relative amounts of the two kinds of scattering (i.e., the ratio ρ_{ph}/ρ_0; the other is the temperature dependence of α itself. To a first approximation these two effects can be separated to show how Δ/ρ_0 depends both on temperature and on concentration (i.e., the value of ρ_0). Let us now consider each in turn.

Figure 10(a) shows how according to Eq. (2) Δ/ρ_0 would vary with temperature if both α and β were independent of temperature. The curve is then monotonic and its steepest slope occurs where $\rho_{\text{ph}}\sim\rho_0$. The limiting value at high temperatures is the same for all concentrations of impurity (all ρ_0). This is the form of departure from Matthiessen's rule which has frequently been discussed.[19]

Now let us take account of the variation with temperature of α. Figure 11 shows how we would expect α to vary with temperature; it is small at all temperatures since the necks have a relatively small area and the electrons there have smaller velocities than on the bellies (cf. Eq. 3). At high temperatures where we expect the relaxation times due to scattering by phonons to be roughly isotropic, α has its largest value: At low temperatures it falls off to perhaps $\frac{1}{4}$ or $\frac{1}{3}$ of this value because, according to the arguments already outlined, the neck electrons are relatively much more strongly scattered at low temperatures than are the belly electrons. At the lowest temperatures α will probably cease to change much with temperature (i.e., when all the scattering is small angle scattering and its effectiveness for a given phonon wave number depends roughly on the inverse ratio of the radii of curvature of belly and neck).

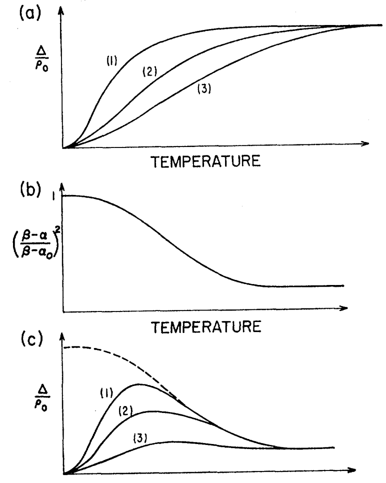

FIG. 10. Schematic (a) Δ/ρ_0 versus temperature in a two-band model with α and β constant [see Eq. (2)]. (b) $\{(\beta-\alpha)/(\beta-\alpha_0)\}^2$ versus temperature in the case where $\beta>\alpha$ at all temperatures. (c) Δ/ρ_0 versus temperature when α varies with temperature.

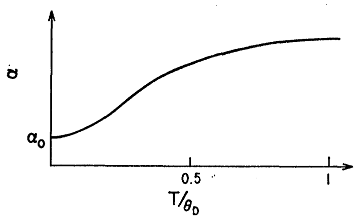

FIG. 11. The variation of α (the anisotropy parameter for scattering of electrons by phonons) with temperature in a noble metal (schematic).

Suppose that now we calculate Δ/ρ_0 with α constant and equal to its extreme low temperature value, α_0. For different concentrations of a particular alloy this will give a set of curves for Δ/ρ_0 as a function of temperature as in Fig. 10(a). The curves all start from zero at $T=0$ and have the same limiting high temperature value; the temperature at which the curve has its maximum slope depends, for given values of α and β, only on the ratio ρ_{ph}/ρ_0. To convert these curves approximately to the correct ones in which α changes with temperature, we must multiply them all by $[(\beta-\alpha)/(\beta-\alpha_0)]^2$ at each temperature. [The approximation involved in this procedure lies in ignoring changes in the α in the denominator of (2). Over most of the range this does not introduce any appreciable error but obviously the approximation breaks down if the first term in the denominator is large where α is changing rapidly.]

To see how the factor $[(\beta-\alpha)/(\beta-\alpha_0)]^2$ changes with temperature we must specify the kind of residual scattering involved. Let us therefore consider the different kinds of residual scattering in turn.

"Uncharged" Impurities

Consider first the case of the "uncharged" impurities (Au in Ag, say) where we expect $\beta>\alpha$ even at high temperatures. Then $[(\beta-\alpha)/(\beta-\alpha_0)]^2$ starts at low temperatures with the value 1 (by the definition of α_0) and then, because α increases, it diminishes as the temperature goes up. Notice that the curve is the same for all concentrations for a given parent metal [see Fig. 10(b)]. To obtain (very closely) the final dependence of Δ/ρ_0 on T, the curves in 10(a) (which correspond to different values of ρ_0) must be multiplied by the curve in 10(b). This shows why the resulting curves have a

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[19] M. Kohler [Z. Physik **126**, 495 (1949)] has discussed departures from Matthiessen's rule from this point of view. He, of course, envisaged that the anisotropies could be temperature-dependent but this fact has often been neglected since.

maximum and why, the more dilute the alloy, the bigger is the maximum and the lower its temperature. See Fig. 10(c). If, however, ρ_0 is so large that ρ_{ph} and ρ_0 become comparable only at temperatures where α is effectively constant, then there will be no maximum in Δ. This explains why in concentrated alloys such a maximum is not generally found.

It is also clear from this procedure that a very dilute alloy is most valuable in revealing the dependence of α on temperature. This is because, starting at very low temperatures and allowing the temperature to increase, we very quickly reach in such an alloy the region where $\rho_{\text{ph}}\gg\rho_0$. Here Δ/ρ_0 no longer changes significantly because of the change in the proportions of different kinds of scattering: It changes only because α itself is changing [See Eq. (2)]. Moreover alloys in which $\beta\gg\alpha$ will be most useful in this respect, because in them we shall most quickly reach the region where the second term of the denominator of Eq. (2) completely dominates the first. For this reason the dilute *Ag*-Au alloys are particularly suited to reveal how α changes with temperature in silver. Correspondingly among the copper alloys measured here, dilute *Cu*-Au is the best. If we had an "infinitely dilute" alloy $(\Delta/\rho_0)^{1/2}$ would reflect directly the variation of $(\beta-\alpha)$ with temperature over the whole temperature range.

Dislocations

To interpret the form of the departures from Matthiessen's rule in deformed specimens[20] we will assume that the main defects responsible for scattering, i.e., dislocations, produce an anisotropy of τ which is similar to that of low temperature phonons. Thus $(\beta-\alpha)^2$ is very small at low temperatures and increases steadily as α increases. In that case we would expect that the curves would be monotonic and that Δ/ρ_0 would be large at high temperatures (because $(\beta-\alpha)^2$ becomes large there). As in the previous case the temperature dependence of $(\Delta/\rho_0)^{1/2}$ should, once $\rho_{\text{ph}}\gg\rho_0$, reflect directly the temperature dependence of α. If this model is correct, then Δ/ρ_0 at high temperatures should be independent of the concentration of dislocations; this could be used as a test of the model. As we mention below, there are other ways of accounting for the departures from Matthiessen's rule in strained specimens: The one proposed here can at present only be regarded as a possibility.

Charged Impurities

Ziman estimates the anisotropy ratio τ_N/τ_B for scattering by, say, germanium in copper to be about 0.6–0.7. This would therefore be the same as the corresponding ratio for phonon scattering in copper at about 60°K. If over the Fermi surface $\tau(k)$ for the two scattering mechanisms became truly *identical* then of course Δ would vanish. It is virtually certain that this exact agreement could never be achieved but we might expect that a *similarity* in the two distributions of $\tau(k)$ would produce a minimum in the Δ/ρ_0 versus temperature curve. We see a broad minimum in the curves for the *Cu*-Ge alloys at much higher temperature round about 150–200°K and this might have some such origin; however, it would be unwise to place too much reliance on the shape of the curves here in view of the size of the corrections that have to be applied (see our earlier discussion of this) and the errors that arise from determining the shape factors of the specimens.

A comparison between the *Cu*-Ge and the *Cu*-Sn results shows that the magnitude of Δ/ρ_0 for a given concentration of impurity is about the same in the two. (Δ/ρ_0 is a bit bigger in the corresponding *Cu*-Sn alloy but this probably reflects the slightly smaller scattering of the Sn ion). The shape of the curves is very similar and the maxima at corresponding concentrations occur at the same temperature. So it seems reasonable to conclude that the relative mass difference $\Delta M/\bar{M}$, which is about 13% in *Cu*-Ge and about 60% in *Cu*-Sn, is not an important factor in the phenomenon. This rules out changes in the phonon spectrum or disequilibrium of the phonons as major causes of the departures from Matthiessen's rule found here.

Some Numerical Estimates

We have seen that the general *qualitative* features of the model correspond with those found experimentally. The model is too crude to give reliable numerical values but the following comparisons between silver and copper as parent metals and between different kinds of scattering do show that the model gives physically reasonable values for the parameters in Eq. (2).

Consider first the dependence of ρ_0/Δ on ρ_0/ρ_{ph} at a fixed temperature. We see from Eq. (2) that if α is constant (as we expect at constant temperature and low concentration) ρ_0/Δ should depend linearly on ρ_0/ρ_{ph}. At low temperatures, where the results are most reliable and require the smallest corrections, we have tested this and found it to be valid for the *Ag*-Au and *Ag*-Sn alloys. It is also approximately valid for the copper alloys. From these comparisons we have derived values of α at low temperatures and of β for different kinds of impurity. It should be noted that, if the model is to be consistent, the value of α, which refers to phonon scattering, should be the same for all alloys of given parent metal. This turns out to be the case; the values of α for scattering by phonons at low temperatures that we quote in Table II fit quite well the data on all three copper alloy series and on both the silver alloy series.

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[20] Departures from Matthiessen's rule in strained copper have also been measured by Powell *et al.* [R. L. Powell, H. M. Roder, and W. J. Hall, Phys. Rev. **115**, 314 (1959)] and interpreted as due to anisotropy of relaxation times. They also give references to related work.

TABLE II. Approximate values for relative conductivities and relaxation times of neck and belly regions in Cu and Ag.

Type of scattering	Copper as parent metal σ_N/σ_B	Copper as parent metal τ_N/τ_B	Silver as parent metal σ_N/σ_B	Silver as parent metal τ_N/τ_B
Phonons at low temperatures (~25°K)	0.06_5	0.4	0.04	0.3
Phonons at high temperatures (~300°K)	0.2	1.2	0.13	1.0
Au as impurity	0.4_6	2.7	0.34	2.7
Ge as impurity	0.3	2		
Sn as impurity	0.3_5	2	0.2	1.6
Dislocations	0.03	0.2	0.02	0.2

At high temperatures, where $\rho_{\text{ph}} \gg \rho_0$, the value of Δ/ρ_0 should, according to the model, become independent of concentration. For the *Cu*-Au and *Ag*-Au series this is true.[21] Consequently we can then use the high temperature value of Δ/ρ_0 together with the appropriate value of β already deduced to evaluate α at high temperatures.

As a final step we can then use these values of α and the magnitude of Δ/ρ_0 for dislocations at high temperatures to determine β for scattering by dislocations. The results are summarized in Table II.

Also listed in Table II are values of τ_N/τ_B for the various kinds of scattering. These were obtained directly from the values of σ_N/σ_B by using Eq. (3). To use this equation we need to know the ratios $\bar{v}_N/\bar{v}_B$ and A_N/A_B for both copper and silver; these were estimated as follows.

The ratios of the velocities for neck and belly electrons were deduced from results quoted by Shoenberg[22]; these were obtained both from his own de Haas–van Alphen work and from that of Kip *et al.*[23] on cyclotron resonance. In copper the ratio v_N/v_B is about $\frac{1}{2}$ and in silver about $\frac{1}{4}$. Since these refer to the extreme group of neck electrons, we have assumed, taking averages, that $\bar{v}_N/\bar{v}_B$ has the value $\sim\frac{2}{3}$ in Cu and $\sim\frac{1}{2}$ in Ag.

From the diagrams of sections of the Fermi surfaces of Cu and Ag given by Roaf[24] we have estimated, that in both Cu and Ag A_N/A_B is about $\frac{1}{4}$ (i.e., the neck areas constitute about 20% of the total). This figure is necessarily rather arbitrary because of our rather arbitrary division of the electrons into two groups; nevertheless this is probably a reasonable figure.

On the basis of these factors we now have that in Cu $\tau_N/\tau_B \simeq 6\sigma_N/\sigma_B$ and in Ag $\tau_V/\tau_B \simeq 8\sigma_N/\sigma_B$. In this way the ratio of relaxation times was estimated. What is notable in the table is that the ratio, τ_N/τ_B, for a given kind of scatterer is about the same in both Cu and Ag. Moreover the high temperature phonon scattering appears to be roughly isotropic in both metals.

If we restrict ourselves to comparison of anisotropies for a given parent metal we eliminate the arbitrariness and uncertainty involved in the above estimates of area and velocity. We then see that the anisotropy due to phonon scattering in both Cu and Ag changes by a factor of three between high and low temperatures in the sense predicted by Ziman. Also in accordance with Ziman's predictions is the fact that gold as impurity causes a large anisotropy in the opposite sense to that of phonons at low temperatures. On the other hand, the difference in anisotropy between Au as scatterer (an *uncharged* impurity) and Ge or Sn (*charged* impurities) is not very marked. From our numbers we would have to conclude that even at room temperature the anisotropy due to phonon scattering, although comparable, has not reached or surpassed the value due to the charged impurities; consequently the minimum in Δ/ρ_0 as a function of temperature shown in figures could not be ascribed to this cause.

Table II indicates that, if the departures from Matthiessen's rule in strained samples are due to the mechanism discussed here, then the anisotropy of τ due to scattering by dislocations is about twice as extreme as that of phonons at low temperatures. This implies that the scattering of the neck electrons by dislocations must relatively be very severe and there is some evidence for this from direct measurements of τ by de Haas–van Alphen techniques. On the other hand an alternative mechanism for departures from Matthiessen's rule in strained specimens has recently been put forward by Barbee *et al.*[25] This depends on the nonuniform distribution of the dislocations in strained specimens; effects due to this may indeed be important.

Magnitude of ρ_{ph} at Low Temperatures

There is a further important consequence of the low temperature measurements. Taking the *Cu*-Au series as an example, at the lowest temperatures Δ/ρ_0 becomes roughly equal to ρ_{ph}/ρ_0 so that $\Delta \simeq \rho_{\text{ph}}$. This means that if we were making measurements of resistivity in the residual resistance range and using Matthiessen's rule to deduce ρ_{ph} we would get the right *temperature* dependence for ρ_{ph} but the magnitude of ρ_{ph} would be too high by a factor of 2 (in the *Ag*-Au series it would be nearly 3). This point could therefore be of crucial importance when for example the coefficient of the T^5 term in electrical resistivity is being discussed quantitatively.

Dislocation Scattering in Alloys

A similar effect can occur with dislocation scattering. If a measurement of the resistivity due to dislocations, $\Delta\rho_{\text{dis}}$, is made in an alloy, say *Ag*-Au, of residual re-

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[21] In the *Cu*-Ge and *Cu*-Sn alloys, this also appears to be approximately true. (There are probably errors in the shape factor which obscure the issue.) In *Ag*-Sn, however, there seems to be a systematic dependence on concentration at all temperatures.

[22] D. Shoenberg, Phil. Trans. Roy. Soc. (London) **255**, 85 (1962).

[23] A. F. Kip, P. N. Langenberg, and T. W. Moore, Phys. Rev. **124**, 359 (1961).

[24] D. J. Roaf, Phil. Trans. Roy. Soc. (London) **255**, 85 (1962).

[25] T. W. Barbee, R. A. Huggins, and W. A. Little, Phil. Mag. **14**, 255 (1966).

sistivity $\rho_0(\gg\Delta\rho_{\text{dis}})$ and if this is now compared with the scattering due to dislocations in the *pure* parent metal, the results, according to the data of Table II, would differ by a factor of about 4, just because of the different anisotropies in the scattering.

CONCLUSIONS

The departures from Matthiessen's rule that we have observed in dilute alloys of Cu and Ag can all be attributed to different anisotropies of the phonon and impurity scattering. The departures found in strained specimens can likewise be accounted for. This explanation gives a qualitative account of the maximum and its concentration dependence. Some approximate quantitative estimates of the anisotropy of τ are consistent with the general theoretical picture except that they do not show any very great difference in the anisotropy due to charged and uncharged impurities.

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Low-Temperature Specific Heat of Arsenic and Antimony†

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The specific heats of arsenic and antimony have been measured from 0.7 to 4.0°K and 0.5 to 4.0°K, respectively. For the electronic contributions we find 0.194 ± 0.007 mJ/mole °K^2 in arsenic, and 0.112 ± 0.005 mJ/mole °K^2 in antimony. Both values are in agreement with de Haas–van Alphen measurements on these semimetals. The lattice specific heat for arsenic is found to be $C_L=0.0880T^3+0.55\times10^{-3}T^5$ mJ/mole °K with $\Theta_D(0)=280.5\pm1.0$°K. For antimony $C_L=0.206T^3+0.0033T^5$ mJ/mole °K with $\Theta_D(0)=211.3\pm1.5$°K.

I. INTRODUCTION

The semimetals arsenic, antimony, and bismuth make up a family of elements in which there are close resemblances. They all crystallize in rhombohedral *A*7 structures; they show metallic conduction, but much less than normal metals; they all have small Fermi surfaces made up of sets of hole and electron surfaces; and they all have at least one abundant naturally occurring isotope with a nuclear hyperfine structure due to an electric quadrupole interaction.

Phillips[1] has already measured the specific heat of bismuth below 2.0°K. He found (1) a small electronic specific heat due to the small pieces of Fermi surface, (2) a Debye temperature which is not constant at temperatures below $\Theta_D/50$ as is normally found in most metals, and (3) a nuclear specific heat due to the nuclear electric quadrupole interaction at very low temperatures.

Since arsenic and antimony have the same general electronic, lattice, and nuclear hyperfine structures, it is expected, and indeed we find, that the contributions to their specific heat at low temperatures are quite similar to those for bismuth.

The rest of this paper will deal with the expected behavior of the specific heat of arsenic and antimony in Sec. II and the measurement of the specific heat in Sec. III. The results are presented and discussed in the light of theory and other experimental results in Sec. IV.

II. COMPONENTS OF THE OBSERVED C_p

The electronic specific heat C_E obeys a linear temperature law, $C_E=\gamma T$, where

$$\gamma=(\pi^2/3)k^2N(E)\,, \tag{1}$$

and $N(E)$ is the density of electronic states at the Fermi surface. $N(E)$, and therefore γ, can be calculated from the geometry of the Fermi surface if one assumes parabolic energy bands. For an ellipsoidal Fermi surface the maximal areas can be measured by de Haas–van Alphen oscillations in a reciprocal magnetic field, which can be then converted to the effective-mass components α_{ii}. The Fermi energy is obtained from cyclotron-resonance data and the density of states can then be calculated from

$$N(E)=\left(\frac{8\pi V_m}{h^3}\right)\frac{(2E_F)^{1/2}m^{3/2}}{(\alpha_{11}\alpha_{22}\alpha_{33})^{1/2}}\,. \tag{2}$$

Here V_m is the molar volume and m is the electronic mass.

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† Based on work performed under the auspices of the U. S. Atomic Energy Commission. A preliminary report of this work was given at the Chicago meeting of the American Physical Society, October, 1965 [Bull. Am. Phys. Soc. **10**, 1104 (1965)].

[1] N. E. Phillips, Phys. Rev. **118**, 644 (1960).