without first having a good deal of information about the Fermi surface, and would be even if the phonons were isotropic. (See, for example, the denominator of β'.) Thus a neat separation of phonon from Fermi-surface effects is not in general possible.

Notice that the weighting w'' in Eq. (A15) is different from the w' in Eq. (A10). The difference consists mainly in an extra factor $|\rho_q|^{-1}$ in the former. This may at first glance seem surprising, but if it is noted that Eq. (A14) contains an integral over the Fermi *surface* whereas Eq. (A9) has one only over a *line* of tangency, we can see the connection. If, in fact, we performed part of the surface integral in Eq. (A14) we would get another factor $|\rho_q|$ which would cancel the $|\rho_q|^{-1}$ already present. Thus if we seek the contribution to S_{gi} from some particular phonon (direction), then the weighting along a line of tangency should not include the magnitude $|\rho_q|^{-1}$ but only the sign, $\mathrm{sgn}\rho_q$.

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Anisotropy of Relaxation Times and Phonon Drag in the Noble Metals

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The effect of impurities on the phonon-drag part S_g of the thermoelectric power at very low temperatures is examined for alloys of copper, silver, and gold. S_g is separated into three terms corresponding to: (1) the neck regions in the ⟨111⟩ directions, (2) the convex belly regions around the ⟨100⟩ directions, and (3) the concave belly regions around the ⟨110⟩ directions. We find that in gold the concave belly region is most important and in silver the necks are most important. The sign of the neck contribution is examined through the behavior of the ⟨110⟩ phonons at the zone boundary, and it is found that the positive contributions dominate there. The experimental results for three types of impurities, (A) uncharged, (B) charged, and (C) transition-metal, are discussed, and qualitative agreement with the theory is found.

1. INTRODUCTION

IN what follows we wish to apply the results obtained in the previous paper[1] (henceforth referred to as I) to a particular example, that of phonon-drag S_g in the noble metals at very low temperatures.

Recent experiments[2–4] have shown very strikingly that the magnitude and even, in some cases, the sign of S_g in the noble metals varies with the kind of impurity which dominates the electron scattering. For example, in silver S_g is positive down to the lowest temperatures in all the samples so far studied.[2] Where, however, the scattering is by 'uncharged' impurities (Au or Cu in Ag), S_g is much larger than when the scattering is by 'charged' impurities (e.g., Ge, In). In gold, it has recently been found that although S_g is normally positive it becomes negative at low temperatures when the scattering is by Pt impurity.

Explanations of this dependence of S_g on the type of impurity scattering have already been put forward.[3,5] Here we extend and to some extent modify these ideas inthe light of I.

We saw, in I, that the sign of the contribution to S_g from a transition along a particular strip of the Fermi surface depended at very low temperatures on its concavity or convexity with respect to the occupied states. In the noble metals we can distinguish three regions which differ in this respect: (1) the convex belly regions associated roughly with ⟨100⟩ directions (2) the *concave* belly regions centered mainly around the ⟨100⟩ directions, and (3) the neck regions, (in the ⟨111⟩ directions) where the principal radii of curvature have opposite signs.

For simplicity it is often assumed that apart from the necks, the Fermi surfaces of the noble metals are nearly spherical. There are, however, substantial concave regions which are particularly conspicuous in Cu and Au. These can be seen clearly in the diagrams given by Segall[6] and by Roaf[7] and even more strikingly

[1] M. Bailyn, preceding paper, Phys. Rev. **157**, 480 (1967); hereafter referred to as I.
[2] A. M. Guénault, Phil. Mag. **133**, 17 (1967).
[3] C. Van Baarle, Physica **33**, 424 (1967).
[4] C. Van Baarle and R. Huebener, Phys. Letters **23**, 189 (1966).
[5] R. Fletcher and J. S. Dugdale, in Proceedings of the International Low-Temperature Conference, Moscow, 1966 (to be published).
[6] B. Segall, Phys. Rev. **125**, 109 (1961).
[7] D. J. Roaf, Phil. Trans. Rov. Soc. London **255**, 135 (1962).

in the work of Morse, Myers and Walker[8,9] on gold. Segall explicitly states (Ref. 6, p. 118) that the Fermi surface of copper is pushed *in* the ⟨110⟩ directions. He emphasizes that this inward distortion in the ⟨110⟩ directions arises because "the conduction bands are selectively 'repelled' by the d-band states of the same symmetry through an admixture of d component in their wave functions···. The states for the ⟨110⟩ direction··· will interact fully with the d bands all the way out to the zone surface."[6] This admixture of d character which is therefore associated with these concave regions will be of great importance in relation to impurity scattering, as we shall see below. We may also note that in the neck region the wave functions have a large p component and this too, as Ziman[10] has emphasized, is very important in determining the response of these electrons to scattering by certain impurities. The electrons of the convex region we assume are predominantly s-like in character, in particular having little d admixture. In gold, however, the convex regions have a curvature so different from that of the free-electron sphere that we anticipate some departure from free-electron character even here.

We see, therefore, that the three regions of the Fermi surface which differ from each other in curvature are also distinguished by the character of the associated wave functions.

In order to assess the effect of the contributions from these different types of surfaces we shall employ the formal result of Eq. (9) of I and suppose that the sum over the regions i consists of three terms corresponding to the three regions mentioned above: convex belly (abbreviated cv), concave belly (cc), and neck (n). Thus

$$S_g=\frac{\sigma_{\rm cv}}{\sigma}S_{g,{\rm cv}}+\frac{\sigma_{\rm cc}}{\sigma}S_{g,{\rm cc}}+\frac{\sigma_n}{\sigma}S_{g,n}. \tag{1}$$

The usefulness of Eq. (1) rests primarily on the fact that phonon-electron interactions can, at least in the temperature ranges we wish to consider (~1°K), be separated from the electron-impurity interactions. This comes about by making the basic assumption that the impurity-dominated $\tau(k)$ are fairly constant within a given region (but may differ from one region to another) so that τ actually cancels out in S_{gi}.

When this cancellation is effected, S_{gi} (i=cv, cc, n) depends exclusively [through the factors α in Eqs. (6) and (A1) of I] on the interactions involving phonons, in particular, on the electron-phonon interaction. Further, for low enough temperatures, the relative importance of phonon-impurity interactions to phonon-electron interactions in the α's is completely negligible since only the very long-wave phonons are of importance and these long waves at about 1°K will not see even the strain fields in any significant way. We have, in fact, the remarkable result that experiments on phonon drag at these low temperatures can reveal effects due to the electron-phonon interaction even though the electron scattering is dominated by impurities.[11]

Another aspect of Eq. (1) is that once the cancellation of the τ's in S_{gi} is performed, and the phonon-impurity scattering in the α's neglected, the resultant S_{gi}'s depend exclusively on the properties of the host material. The effect of adding one type of impurity as opposed to another is contained entirely in the σ_i/σ which because of the low temperatures need themselves contain no reference to the electron-phonon scattering.[11]

A final point about Eq. (1). If in a given region the electron-phonon scattering is large, then S_{gi} becomes large (in magnitude). But if the electron-impurity scattering is large, then σ_i/σ becomes *small*. Thus the two types of scattering act in quite the opposite manner as far as enhancing the influence of a given region is concerned. Note also that at these low temperatures electron-phonon scattering requires small $\mathbf{k}\rightarrow\mathbf{k}'$ jumps, whereas no such restriction is present in electron-impurity scattering.

It is clear that our discussion falls naturally into two parts: the electron-phonon effect in the S_{gi}'s and the electron-impurity effect in the σ_i/σ's. We now discuss these in turn.

2. S_{gi} AND THE ELECTRON-PHONON INTERACTION

We are concerned now with the evaluation of S_{gi}. We take as the starting point the expression (A14) of I rewritten as follows:

$$S_{gi}=-\frac{k}{|e|}\frac{1}{A_iv_i}\int_i dS_{\rm k}\int d\phi_{\rm q}\sum_j\frac{1}{v(\mathbf{k})\rho_q(\mathbf{k})}\times\left(\frac{T}{\theta(\hat{q})}\right)^3 p(\mathbf{k},\hat{q},j), \tag{2}$$

$$p(\mathbf{k},\hat{q},j)=k_F{}^3\frac{|\mathbf{I}\cdot\xi|^2}{\displaystyle\int_{{\rm LT}(q)}dl\,|\mathbf{I}\cdot\hat{\xi}|^2\rho_{\rm q}(l)\sin(\mathbf{q},dl)v(l)^{-2}}. \tag{3}$$

Here $dS_{\rm k}$ is an integral over the ith region of the Fermi surface, of area A_i, and on which the average of $v(\mathbf{k})$ is v_i. $d\phi_{\rm q}$ is an integral over all phonon directions tangent to the Fermi surface at the point $\mathbf{k}$, $\rho_{\rm q}(\mathbf{k})$ is the algebraic radius of curvature of the normal section containing $\mathbf{q}$, and $\theta(\hat{q})$ and k_F are defined in Eqs. (A11) and (A12),

[8] R. W. Morse, A. Myers, and C. T. Walker, J. Acoust. Soc. Am. **33**, 699 (1961).

[9] The most dramatic evidence for concavity in gold we have found is in Fig. 28 of C. T. Walker's Ph.D. thesis, Brown University, 1961 (unpublished); available in microfilm.

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

[11] In the alloys contemplated here, the electron mean free path is still greater than the phonon wavelength (at 1°K, say). In more concentrated alloys, or at temperatures greatly below 1°K, the Pippard effect [J. Phys. Chem. Solids **3**, 175 (1957)] could be important and cause a concentration dependence of S_g.

respectively, of I. Finally, the integral in the denominator of $p(\mathbf{k}\hat{q}j)$ is over the lines on the Fermi surface where $\mathbf{q}$ is tangent (see Appendix of I). This line integral is not restricted to the region i. In obtaining this formula from I, we have assumed that $\tau(\mathbf{k})$ is constant within each region.

Let us consider the main factors in Eq. (2).

$dS_k/(A_i v_i)$: The $1/(A_i v_i)$ came from the denominator of Eq. (11a) of I, and the A_i part of it exactly cancels the integrated value of dS_k. There is thus a factor $1/v_i$ left over, which will favor the neck regions. Shoenberg[12] has found that the ratio of the velocity on the neck at the zone boundary (its lower limit) to that on the bellies is about 1:2 in Cu and Au and 1:4 in silver. We have an average, not the extremes, so that the ratios of v_n to v_{cv} or v_{cc} is probably more nearly $1:\sqrt{2}$ for Cu and Au, and 2 for Ag. This factor in any case significantly weights the necks in silver compared to the other noble metals.

$1/v(\mathbf{k})\rho_q(\mathbf{k})$: The $1/v(\mathbf{k})$ here came from three sources in Eq. (11a) of I: the density of k states, the factor $v(\mathbf{k})-v(\mathbf{k}+\mathbf{q})$, and the α factor. The $1/\rho_q$ came from the $v(\mathbf{k})-v(\mathbf{k}+\mathbf{q})$ factor. This combination, $1/v\rho$, will generally serve to emphasize the necks over the other regions. In the heading above, we have discussed how the velocities go. The magnitudes of the radii of curvature can be roughly inferred from Roaf's[7] Fig. 3. Very crudely, we estimate that the ratios $1/\rho v$ from belly to extreme neck regions (near the zone boundary) go as 1:10 in Cu, 1:30 in Ag and 1:12 in Au. These figures are very rough, but they do emphasize the conspicuous position of silver.

$(T/\Theta)^3$: This came essentially from the $\partial N_0/\partial T$ factor of Eq. (11a) of I. It takes into account the anisotropy of the phonons. For one of the transverse modes this factor varies in the ratio $1:\frac{1}{2}:\frac{1}{8}$ in going from the ⟨110⟩ to the ⟨111⟩ to the ⟨100⟩ directions. Between this transverse ⟨110⟩ and the longitudinal modes generally, the factor is about 10^{-2}. Thus we assume that the transverse modes dominate provided that the p factor, which we discuss next, does not override the effect. The $(T/\Theta)^3$ factors does not, as far as we can see, favor any particular region of the Fermi surface.

$p(\mathbf{k},j,\hat{q})$: This represents the relative strength of phonon interaction between the electron at $\mathbf{k}$ and between the electrons elsewhere on the lines of tangency of $\mathbf{q}$. It comes from and preserves the relative probability character of the α factor of Eq. (11a) of I.

There is one central aspect of p that must be brought out. The cosine in the dot-production between $\hat{\xi}$ and $\mathbf{I}$ can be extremely small for transverse phonons when the wave function at $\mathbf{k}$ is free-electronlike, for then $\mathbf{I}$ is in the direction of $\mathbf{q}$. Thus the factor p tends to discriminate against the parts of the Fermi surface which are free-electronlike. (But note that in the unlikely event that the *whole* of the lines of tangency of $\mathbf{q}$ were free-electronlike, then p would not be particularly small because even if the numerator is everywhere small, so also is the denominator.) Thus we expect the p factor to discriminate against the convex region very strongly in the quite free-electronlike surface of silver, slightly less so in Cu, and still less so in Au. The degree of discrimination may lie between one and two orders of magnitude. At the upper limit (silver) we then expect that in the convex region the longitudinal phonons will vie with the transverse for supremacy, but the region will, in any case, be of almost negligible significance.

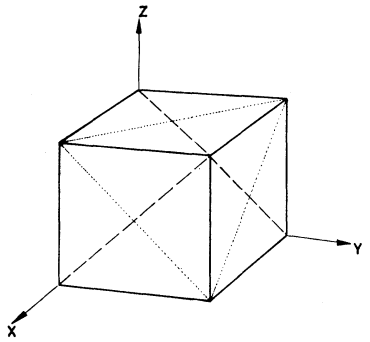

FIG. 1. The ⟨110⟩ directions in relation to the 111 direction. The ⟨110⟩ directions are dotted or dashed. The dashed ones tend to form concave connections on the 111 neck, the dotted ones tend to form convex connections on the 111 neck.

It remains to discuss the signs of S_{gi}. As discussed in I, the signs of the convex and concave regions are clear but that of the neck is, as yet, indeterminate. Now the preceding paragraphs have shown that $S_{g,n}$ (the value of S_g at the necks) is large; it is unlikely that even a heavy cancellation of sign could cut down the relative contribution by more than a factor of 2, so that the neck $S_{g,n}$'s will almost certainly have by far the largest values.

To estimate the sign of $S_{g,n}$ we shall consider in detail how the ⟨110⟩ phonons behave on a neck. Because of the $(T/\Theta)^3$ factor, these phonons are the most important, and, because of the $1/\rho v$ factor, they will make their most significant contribution when $\mathbf{k}$ is at the zone boundary.

Figure 1 shows the various ⟨110⟩ directions on a cube. There are six directions in all, which, with two senses for each, give the usual twelve ⟨110⟩'s. Now half of these six tend to form convex connections on the 111 neck, and the other half will tend to form concave connections. The former are indicated by dotted lines, the latter by dashed lines.

Consider then the contrast between a typical dashed and a typical dotted ⟨110⟩ direction at the zone boundary. The dotted one will have a radius of curvature that is precisely the neck radius, call it r. Now consider the dashed one. In Fig. 2 we have drawn a section of the neck, point P being the point of tangency for this ⟨110⟩, which, however, makes an angle of $\sin^{-1}(1/\sqrt{3})$ with the [111] direction. If r_1 $(=r)$ and r_2 (<0) are the principle radii of curvature[13] at P, then the radius

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

[13] This presupposes that the neck intersects the zone boundary prependicularly.

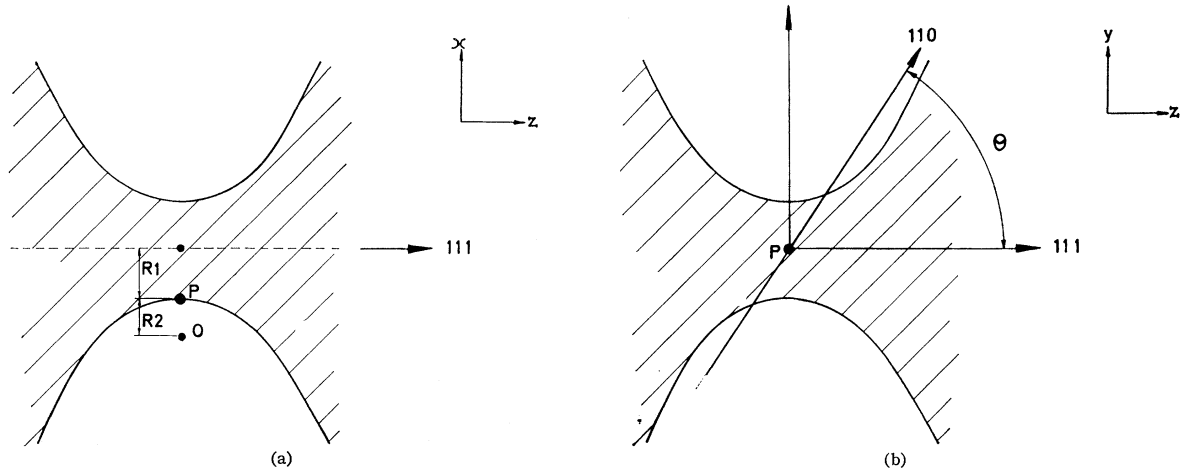

FIG. 2. Two views of a neck, displaying a concave 110 connection, and the principle radii of curvature r_1 and r_2, at the zone boundary discussed in the text. In Fig. 2(a) the two radii of curvature are displayed, and the q-vector in the 110 direction is tangent at the point P and therefore in a plane perpendicular to the page. Fig. 2(b) is a view of the neck seen from the point 0 of Fig. 2a. The points P are the same in both (a) and (b). The angle θ in Eq. (4) is shown in Fig. 2b. The x, y, z axes drawn here are to indicate the relative orientations of the views in (a) and (b) and are not the cube axes. These drawings have assumed that the neck is symmetrical across the zone boundary. The orientation of the 110 vector in Fig. 2(b) is schematic.

of curvature ρ_q we are interested in is given by

$$\frac{1}{\rho_q}=\frac{\cos^2\theta}{r_1}+\frac{\sin^2\theta}{r_2}=\frac{1}{3r_1}+\frac{2}{3r_2}, \tag{4}$$

where θ is the angle between $\mathbf{q}$ and the direction in which the radius of curvature is r_1. To estimate r_2, we approximate the boundaries between the filled and empty regions of Fig. 2 by hyperbolas, and determine the parameters in the hyperbola formula from the points nearest contact given by Roaf[7] in his Tables 4 and 5. (Table 5 defines the point right at the boundary.) We deduce that r_2/r_1 is approximately -0.4, -0.3_5, and -0.4 for copper, silver, and gold, respectively. (Roaf's tables give rise to two hyperbolas, in the $\phi=45°$ column: one "above" contact, the other "below". The results, however, are not very different, and the numbers we have just cited are an average of the two.) From Eq. (3), above, we compute that the corresponding values of ρ_q/r are -0.7_5, -0.6, and -0.7_5. Thus we find that the radius of curvature for the concave $\langle 110\rangle$ connection is considerably smaller than that for the convex connection at the place of greatest interest.

Although this treats only the most important $\langle 110\rangle$ tangencies, we shall assume that it is characteristic of all the directions of phonons on the zone boundary so that the part of the $dS_\mathbf{k}$ integral near the zone boundary provides a positive contribution to $S_{g,n}$. As we proceed from the zone boundary to the belly, we may expect this positive type of contribution to get smaller, and even to become negative very near the belly where the concave $\langle 110\rangle$ connections could disappear. Nevertheless, the positive parts are weighted heavily by the $1/v(\mathbf{k})\rho$ factor; this weighting is very much enhanced in silver, where the $1/v(\mathbf{k})$ is particularly large, and where the neck concavities seem to be particularly pronounced. It is at the very least consistent with the data here to regard silver as having a (*large*) *positive* $S_{g,n}$ and the other noble metals as having a smaller positive or (remotely possible) negative $S_{g,n}$.

We shall now sum up the qualitative description to give an overall extremely crude estimate of how the various S_{gi}'s might relate in the various metals.

In copper, $S_{g,n}$ should be about 3 times bigger than $S_{g,cc}$ which in turn should be about an order of magnitude larger than $S_{g,cv}$.

Silver has a small and shallow concave region, but a very important neck. The smallness of the concave belly area does not affect $S_{g,cc}$ since area factors cancel, but the shallowness does, since that means the $1/\rho_q$ is smaller. The neck $S_{g,n}$ on the other hand will have an enormous value, and a crude estimate on the basis of the preceding discussion gives the neck S_{gn} as *two orders of magnitude* larger than $S_{g,cv}$ and between one and two orders of magnitude larger than $S_{g,cc}$.

Gold has a pronounced convexity, and a pronounced concavity in the belly, so that $S_{g,cv}$ and $S_{g,cc}$ have larger values relative to $S_{g,n}$ than in copper. Furthermore, the necks are not in any case so important as in silver because of the factors of $1/v_i$ and $1/\rho v$. We estimate S_{gn} as about twice as large as $S_{g,cc}$, and $S_{g,cc}$ about three times as large as $|S_{g,cv}|$.

3. σ_i/σ AND THE ELECTRON IMPURITY INTERACTION

We now return to Eq. (1) and consider the σ_i/σ factors. It is possible as we shall see below to estimate these directly by experiment but in this section we shall discuss these ratios in their component parts, using

the formula

$$\frac{\sigma_i}{\sigma}=\frac{\langle v\rangle_i A_i \tau_i}{\langle v\rangle A\tau}. \tag{5}$$

The factors $A_i v_i$ just cancel similar factors in S_{gi}, and will obviously discriminate against the necks, thus helping to balance the influences from the various sections. The convex and concave areas combine to give what is called the belly area. Roughly, we shall assume $A_{cv}=A_{cc}$ except in silver, where A_{cc} is probably very small.

We now turn to the τ_i/τ factor. Ziman[10] in discussing the anisotropy of relaxation times in the noble metals has shown that the character of the electron wave functions on different parts of the Fermi surface influences how the electrons on these parts respond to scattering by different kinds of impurity. For example, he notes that because the neck electrons have strong p character they are not much scattered by uncharged impurities since these produce highly localized perturbations of the potential (characterized by a large s phase shift). We make use of this sort of effect to explain how the different kinds of electrons scattering will alter S_g.

We distinguish here three kinds of impurity: (A) the uncharged impurity strongly localized, (B) the charged impurity, and (C) the transition-metal impurity. We assume that (A) has mainly s character (large s phase shift,[10] for scattering at E_F), (B) because of its comparatively long range (a screened Coulomb potential) it has roughly equal s and p phase shifts, and smaller but not negligible d shifts at E_F,[14] and (C), because of the unfilled d shell has a strong d character in its scattering at E_F (Friedel[15] has emphasized that in such impurities the d phase shift is particularly big.)

The basic rule is then the following: Large scattering (small σ_i) occurs when an impurity of a certain character interacts with wave functions strong in the *same* character. Thus the s-like uncharged impurity A interacts most strongly with the s-like convex part. The charged impurity B will interact less strongly in the d-like concave part than in the convex and neck regions. And the d-like transition-metal impurity C will interact most strongly with the d-like concave regions.

Now large scattering in region i means small τ_i, and therefore small contribution from the corresponding term in the sum in Eq. (1). The conclusions are then the following:

I. An uncharged impurity will favor scattering with s waves, and hence with the convex part of the Fermi surface. This will *decrease* σ_{cv} and hence will promote a more *positive* character to the total S_g.

II. A charged impurity type B will scatter relatively more in s and p like regions (cv and n) and less in d-like ones (cc). Thus τ_{cc} is much larger than τ_{cv} and τ_n. The initial effect of such impurities is therefore to promote again a more *positive* over-all S_g. (See below, however).

III. A transition-metal impurity will favor interactions with the concave regions and hence will decrease the (positive) cc term of Eq. (1).

It should be realized here, however, that σ_i/σ is a relative conductivity. Thus if σ_{cc}/σ goes *down*, as in III above, then σ_n/σ and/or σ_{cv}/σ must go *up*. The effect stemming from a change in σ_n/σ or σ_{cv}/σ may then be larger than that from the change from σ_{cc}/σ, if, for example, S_{gn} is very large. (Cf. the discussion on silver below.)

4. COMPARISON WITH EXPERIMENT

Let us now consider the three metals in turn in the light both of experimental results and of our interpretation.

Silver

From our previous discussion, $S_{g,n}$ is so much larger than $S_{g,cc}$ and $S_{g,cv}$ in silver that it would take a very small σ_n/σ to offset this. The ratio σ_n/σ has recently been estimated by experiments on departures from Matthiessen's rule[16] (using a two-band neck-belly model, which is adequate[17] for the present argument), and it is found to be of the order of magnitude 1 which does not drastically cut down the neck contribution. Thus as a very good approximation, we may rewrite Eq. (1) for silver as

$$S_g\simeq(\sigma_n/\sigma)S_{g,n}. \tag{6}$$

The experimental results with which we shall make comparison are those of Guénault,[2] who among other things compared the S_g of an uncharged impurity (type A), namely gold, with that of a charged impurity (type B), namely germanium. Let us call the former $S_g(A)$ and the latter $S_g(B)$. He found $S_g(A)/S_g(B)$ equal to about 2.

Now to interpret this, we refer to Eq. (6) and note that a simple change of impurity will affect only the factor σ_n/σ. In fact, we can write approximately

$$\frac{S_g(A)}{S_g(B)}=\frac{(\sigma_n/\sigma)_A}{(\sigma_n/\sigma)_B}\cdots\text{Ag alloys}. \tag{7}$$

The experiments of Basinski and Dugdale[18] indicate that this ratio is about 1.7, so that the considerations

[14] F. Blatt, Phys. Rev. **101**, 285 (1957); **101**, 1204 (1957).
[15] J. Friedel, Can. J. Phys. **34**, 1190 (1956).
[16] J. S. Dugdale and Z. S. Bazinski, this issue, Phys. Rev. **157**, 552 (1967).
[17] We have already pointed out that in silver the concave regions are neither extensive nor with a great degree of concavity. They would therefore seem in any case to be unimportant, and could be lumped with the convex regions (also unimportant as far as phonon drag goes) to form a belly. Such an approximation we believe to be quite good for silver, but not very good for copper, and not at all good for gold.
[18] See Ref. 16. In Ref. 16, *Ag*–Sn was used. The results of *Ag*–Sn should be similar to those of *Ag*–Ge, studied by Guénault (Ref. 2).

given here are in reasonable agreement with the experimental results of Guénault. [That the ratio in Eq. (7) is greater than 1 is consistent with the discussion of the preceding section, in which the larger scattering in the neck region for the B type impurity will decrease σ_n/σ.]

Guénault also measured S_g in alloys of silver with palladium a transition-metal impurity (type C). He finds that S_g in *Ag*–Pd, call it $S_g(C)$, is still positive, but larger than in *Ag*–Ge. Once again we ascribe the effect to the relative conductivities:

$$\frac{S_g(C)}{S_g(B)}=\frac{(\sigma_n/\sigma)_C}{(\sigma_n/\sigma)_B}\cdots\text{Ag Alloys}, \tag{8}$$

but unfortunately there are no experiments determining the σ_i/σ in the *Ag*–Pd case. The results of Guénault are, however, qualitatively understandable by the considerations of the preceding section. For there it was shown that a transition-metal impurity will *raise* σ_n/σ. Thus the ratio in Eq. (8) should go up, as in fact Guénault's experiments indicate.

Finally a word about the situation where no impurities are present, and phonon scattering dominates the σ_n/σ ratio. According to the Matthiessen's-rule results,[16] it is found that phonon scattering reduces the relative conductivity of the neck electrons in silver very markedly (by an order of magnitude compared to scattering by gold as impurity) so that Eq. (6) is no longer a good approximation. However, the size of $S_{g,n}$ is so large that we expect that S_g even in this case will still be dominated by the necks, and therefore remain positive, although much smaller in magnitude.

Gold

In our examination of the experimental results for silver and gold alloys, an outstanding feature was that when a transition metal impurity was added to silver, it *increased* the magnitude of an already positive S_g, whereas when a transition-metal impurity was added to gold, it actually made S_g go *negative*. (See the experimental results of van Baarle and Huebner[4] on *Au*–Pt.) This difference in behavior can at once be understood in terms of the discussion in the previous sections. We showed there that the results in silver were attributable to an S_g more or less completely neck-dominated, and to a rise in σ_n/σ as the transition-metal impurity is added. The fact that σ_{cc}/σ must go down is of no particular significance in silver, because the cc contribution is in any case small.

But in gold, just the opposite occurs. If the relaxation time were approximately isotropic, there would be comparable contributions to S_g from all three regions, with however the concave belly contribution definitely dominant. The primary positive contribution to S_g in gold comes, not from the necks, but from the cc belly region. Hence when a transition metal impurity is added, the decrease in σ_{cc}/σ is all important.

If we suppose that the cc contribution is quenched altogether by the transition metal impurity then the final sign of S_g depends on a competition between the contributions from the neck and cv belly regions. We have already indicated that the cv region in gold is relatively more important than in the other noble metals because of its large deviation from free-electron curvature; it is therefore not surprising that the negative cv region ultimately wins out. To go beyond this plausibility argument, however, would require a detailed numerical calculation beyond the scope of this paper.

Copper

In copper we have estimates of σ_n/σ and σ_b/σ for *Cu*–Au *Cu*–Ge, *Cu*–Sn and also Cu dominated by phonon scattering.[16] Here again the analysis has been made on the basis of a two-band model although we believe that in discussing Cu three bands are really needed. If, however, we assume that in terms of conductivity the convex and concave belly regions are quite similar and contribute equally to the conductivity we can estimate σ_n/σ, σ_{cv}/σ and σ_{cc}/σ from these experimental results. It then turns out that if we combine these values with our estimates of the S_{gi}, the convex regions with their relatively small value of S_{gcv} are unimportant. S_g is thus positive and would remain so even if the scattering were due to a transition metal. In *Cu*–Ni, for example, we would expect S_g to become small but still positive. There are as yet no experiments in the relevant temperature range to test this.

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