Phonon-Assisted Impurity Scattering in Gold Alloys*

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(Received 25 September 1967; revised manuscript received 5 February 1968)

Measurements of the electrical resistivity of a number of gold alloys containing Pt, Cu, and In solutes were made between 1.5 and 40°K. Below 20°K the difference between the measured resistivity and the value predicted by Matthiessen's rule is separated into two components, one associated with the "two-band effect" and one associated with phonon-assisted impurity scattering. Above 20°K, only the two-band effect seems to be important. The two-band effect is analyzed in the manner of Dugdale and Basinski; it is smaller in these gold alloys than in their copper and silver alloys. It is shown theoretically that the strength of the phonon-assisted impurity scattering depends on the departure of the conduction-electron wave functions from free-electron-like behavior and on the distortion of the impurity potential by the phonons. The absence of this scattering at high temperature is attributed to the destruction of the temporal coherence of the electron states by the electron-phonon interaction. The ideal resistivity of gold is tabulated from 10 to 500°K.

I. INTRODUCTION

THE electrical resistivity of metals and alloys, as stated by Matthiessen's rule, is of the form

$$\rho(T) = \rho_0 + \rho_i(T), \qquad (1)$$

where ρ_0 is independent of temperature T, depends on the impurities and defects of the specimen, and vanishes for an ideally pure and structurally perfect metal, while the ideal resistivity $\rho_i(T)$ vanishes at $T=0$, and is the same for all specimens of a particular metal and alloys having that metal as major constituent. Theoretically, this rule is based on the assumption that there are two scattering mechanisms acting on the conduction electrons: scattering by impurities and defects, leading to ρ_0, and scattering by lattice vibrations, leading to ρ_i.

In practice there are always deviations from Matthiessen's rule, so that

$$\rho(T) = \rho_0 + \rho_i(T) + \Delta(T), \qquad (2)$$

where the deviation $\Delta(T)$ generally depends on the nature and concentration of defects and impurities in a complicated manner. These deviations can arise, theoretically, from three causes:

(1) changes in the electronic band structure and phonon spectrum on alloying;

(2) the fact that two or more groups of electrons may contribute to the conductivity, and that phonon and impurity scattering of one group may contribute to its partial resistivity in a different proportion than they do to the partial resistivity of the other group (two-band effect);

(3) scattering processes which involve phonons and impurities simultaneously, and are thus included neither in $\rho_i(T)$ nor in ρ_0 (phonon-assisted impurity scattering).

The present work aims to investigate deviations due to the last-named cause. Since deviations from the other causes are also present, the various deviations have to be identified and separated. The two major effects will be deviations due to the two-band effect and deviations due to phonon-assisted impurity scattering.

The possibility of phonon-assisted impurity scattering appears to have been considered first by Koshino.[1] He considered scattering to arise from the fact that an impurity is periodically displaced by a lattice wave. This theory has been criticized by Taylor,[2] who showed the periodic displacement does not lead to additional scattering. Although his result only holds under restricted conditions, one would, nevertheless, expect phonon-assisted impurity scattering to be considerably weaker than predicted by Koshino. The same process was also considered by Klemens,[3] with the important difference being that he considered the perturbation to arise not from the rigid displacement of an impurity potential, but from the change of form of the impurity potential owing to the strain of the surrounding lattice. Such an effect cannot be transformed away, but since it is proportional to strain rather than to displacement, the scattering is weaker at low temperatures than suggested by Koshino, and varies as T^4 instead of T^2. This point will be discussed in some detail in Sec. II.

In order to search for phonon-assisted impurity scattering, we have investigated deviations from Matthiessen's rule of a series of gold alloys at low temperatures. These deviations Δ are comparable to ρ_i below, say, 40°K. By confining ourselves to dilute alloys, so that the change in electron concentration is less than 5%, we have reason to believe that Δ_1, deviations due to changes in the band structure and the phonon spectrum, are an order of magnitude smaller than the observed deviations. By studying the dependence of Δ on temperature and solute concentration, it is possible to separate the observed deviation Δ into a component Δ_2 due to the two-band effect or its general-

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

[2] P. L. Taylor, Proc. Phys. Soc. (London) A80, 755 (1962); Phys. Rev. 135, A1333 (1964).

[3] P. G. Klemens, J. Phys. Soc. Japan 18, Suppl. II, 77 (1963).

ization and a component Δ_3 due to phonon-assisted impurity scattering.

The component Δ_3 thus found does indeed vary as T^4 at very low temperatures, increases less rapidly at temperatures approaching 20°, and seems to be negligible compared to Δ_2 at higher temperatures. Such behavior is to be expected if one considers that the coherence time of the electrons must exceed the reciprocal of the phonon frequency in order for phonon-assisted impurity scattering to have the value calculated from perturbation theory. As the temperature is increased and the lifetime of the electron states is decreased, this requirement is progressively violated.

Phonon-assisted impurity scattering at lowest temperatures depends essentially on the strain sensitivity of the impurity potential, and on the modulation of the free-electron wave function. It will be seen from the present results that the apparent strain sensitivity of the impurity potential, or Δ_3/ρ_0, is almost the same irrespective of the solute atom, and seems to be determined by the nature of the parent metal.

The present investigations were conducted on gold alloys because the major deviations occur in a temperature region easily accessible to cryogenic techniques. It remains to be seen whether alloys of other metals will show similar behavior, and whether there will be systematic differences between different parent metals.

Deviations of Matthiessen's rule of noble-metal alloys have also been studied recently by Dugdale and Basinski[4] and Stewart and Huebener.[5] These authors interpret their results above 20 to 30°K in terms of the two-band mechanism, and do not need to invoke phonon-assisted impurity scattering. In the case of gold alloys[5] the data below 20°K are not sufficiently extensive to test the presence of Δ_3. In the case of copper and silver alloys[4] the low-temperature data have been presented in a manner that does not make it clear whether a component Δ_3 is present.

II. THEORY OF PHONON-ASSISTED IMPURITY SCATTERING

Consider an impurity, and the associated impurity potential $V(\mathbf{r})$; let the impurity be displaced through a distance $\mathbf{u}$. According to Koshino[1] the corresponding perturbation Hamiltonian linking electron states $\mathbf{k}$ and $\mathbf{k}'$ is given by

$$H''_{\mathbf{k}',\mathbf{k}} = \int \psi_{\mathbf{k}'}{}^* \mathbf{u} \cdot \frac{\partial V}{\partial \mathbf{r}} \psi_{\mathbf{k}} d\mathbf{r}, \qquad (3)$$

where $\psi_{\mathbf{k}}$ denotes the electron wave function. The displacement $\mathbf{u}$ of a lattice site $\mathbf{x}$ can be expressed as a superposition of lattice waves

$$\mathbf{u}(\mathbf{x}) = G^{-1/2} \sum_{\mathbf{q},j} \boldsymbol{\varepsilon}_j e^{i\mathbf{q}\cdot\mathbf{x}} a_j(\mathbf{q}) + \text{H.c.}, \qquad (4)$$

[4] J. S. Dugdale and Z. S. Basinski, Phys. Rev. **157**, 552 (1967).
[5] R. G. Stewart and R. P. Huebener (private communication).

where G is the number of atoms in the crystal, $\mathbf{q}$ the wave vector and j the polarization index of each wave, $\boldsymbol{\varepsilon}$ the (unit) polarization vector and $a(\mathbf{q})$, $a^*(\mathbf{q})$, respectively, are the phonon annihilation and creation operators. If (4) is substituted into (3), each term corresponds to a process where an electron is scattered from $\mathbf{k}$ to $\mathbf{k}'$ with the absorption or emission of a phonon $\mathbf{q}$. If $V(\mathbf{r})$ and $\partial V/\partial\mathbf{r}$ are of short range compared to the dominant phonon wavelength, the corresponding scattering probability is proportional to $\langle u^2 \rangle$, the mean-square thermal displacement, and is thus proportional to T^2 at low temperatures.

However, the choice of (3) as perturbation Hamiltonian does not take account of all the effects of the displacement. Consider the perturbation Hamiltonian of the static impurity potential

$$H'_{\mathbf{k}',\mathbf{k}} = \int \psi_{\mathbf{k}'}{}^* V(\mathbf{r}) \psi_{\mathbf{k}} d\mathbf{r}. \qquad (5)$$

Taylor[2] points out that the displacement reduces the scattering due to (5) by an amount which just about compensates for the phonon-assisted impurity scattering due to (3). This is because a rigidly displaced impurity potential gives a perturbation Hamiltonian which can be written as

$$H'(\mathbf{u}) = \int \psi_{\mathbf{k}'}{}^*(\mathbf{r}) V(\mathbf{r}-\mathbf{u}) \psi_{\mathbf{k}}(\mathbf{r}) d\mathbf{r}$$

$$= \int \psi_{\mathbf{k}'}{}^*(\mathbf{r}+\mathbf{u}) V(\mathbf{r}) \psi_{\mathbf{k}}(\mathbf{r}+\mathbf{u}) d\mathbf{r}. \qquad (6)$$

If now the electrons are free, so that $\psi_{\mathbf{k}}(r) \propto e^{i\mathbf{k}\cdot\mathbf{r}}$,

$$H'(\mathbf{u}) = e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{u}} H'(0), \qquad (7)$$

where $H'(0)$ is the undisplaced perturbation Hamiltonian (5). The magnitude of the perturbation Hamiltonian is therefore unaffected by the displacement; Taylor pointed out that this leaves the total electrical resistivity essentially unchanged.

Taylor's conclusions depend upon two premises: The electrons are free and the impurity potential is not changed in form by a lattice wave, but is rigidly displaced.

Consider first the possibility that the impurity potential is changed in shape by a lattice wave. This effect occurs because the immediate surroundings of the impurity ion are deformed; one would thus expect this change to be proportional to strain. We may write phenomenologically that the change in impurity potential by a local strain e is

$$\delta V(r) = AeV(r), \qquad (8)$$

so that

$$H''_{\mathbf{k},\mathbf{k}'} = AeH'_{\mathbf{k},\mathbf{k}'}, \qquad (9)$$

where H' is given by (5). Therefore, there is a one-to-

one correspondence between each elastic scattering process due to the static impurity potential and each phonon-assisted scattering process due to H'', so that the additional electrical resistivity can be expressed in the form[3]

$$\Delta_3 = A^2 \rho_0 \langle e^2 \rangle, \qquad (10)$$

where $\langle e^2 \rangle$ is the square of the thermal-strain amplitude and can be expressed as

$$\langle e^2 \rangle = E(T)/Mv^2, \qquad (11)$$

where $E(T)$ is the thermal energy per atom, M is the atomic mass, and v is the sound velocity. At ordinary temperatures $\langle e^2 \rangle \propto T$ and at low temperatures $\langle e^2 \rangle \propto T^4$.

Equation (10) was obtained by treating the strain of the lattice waves classically. A quantum-mechanical treatment is given in the Appendix, leading to Eq. (A9), which exceeds (10) at low temperatures by a factor of 4.

In the derivation of (10) it was assumed that the electron wave functions are coherent over a large period of time as compared to the period of the lattice wave. If this condition is not satisfied, the electron wave would not sense the timelike periodicity of the strain field, and scattering would be elastic and depend on the instantaneous shape of the impurity potential. Since the interaction takes place over a limited region of space, the important factor is the timelike coherence of the electron waves; this is not affected by elastic impurity scattering. Thus the criterion for the applicability of (10) is that

$$\omega \tau_i > 1, \qquad (12)$$

where ω is the angular frequency of the important thermal phonons (i.e., $\omega \sim 4kT/\hbar$), while τ_i is the ideal (or phonon-limited) electron relaxation time. Since phase coherence rather than correlation in direction of flow is involved here, the relaxation time τ_i is not the relaxation time governing the ideal electrical resistance, but is comparable to the relaxation time governing the ideal thermal resistance,[6] and smaller than the former by a factor of order $(T/\theta)^2$.

The lack of coherence of the electron wave functions at high temperatures may account for the fact that in a previous investigation[7] we failed to find effects ascribable to phonon-assisted impurity scattering involving local modes.

In addition to changes of $V(\mathbf{r})$ with strain, which leads to phonon-assisted impurity scattering, there may also be a contribution due the modulation of the electron wave functions. Writing the electron wave function as

$$\psi_k(r) \propto \varphi_k(\mathbf{r}) e^{i k \cdot r}, \qquad (13)$$

one obtains from (6)

$$H'(\mathbf{u}) = e^{i(k-k') \cdot \mathbf{u}} \int e^{i(k-k') \cdot \mathbf{r}} V(\mathbf{r}) \varphi_{k'}{}^*(\mathbf{r}+u)$$
$$\times \varphi_k(\mathbf{r}+\mathbf{u}) d\mathbf{r}. \qquad (14)$$

In the free-electron case, when $\varphi = 1$, one recovers Taylor's result [Eq. (7)]. More generally, expanding (14) to first power in $\mathbf{u}$, one obtains

$$H'(\mathbf{u}) = e^{i(k-k') \cdot \mathbf{u}} H'(0) + e^{i(k-k') \cdot \mathbf{u}} \mathbf{u} \cdot \int \frac{\partial}{\partial \mathbf{r}} (\varphi_{k'}{}^* \varphi_k)$$
$$\times e^{i(k-k') \cdot \mathbf{r}} V(\mathbf{r}) d\mathbf{r}. \qquad (15)$$

The displacement $\mathbf{u}$ can be expressed in terms of phonon operators by means of (4), so that the second term contributes to phonon-assisted impurity scattering.

Many metals seem to approximate quite well to the free-electron model, so that $\varphi_k(\mathbf{r})$ should be almost constant over most of the atomic cell. One would thus expect the second term in (15) to be small. However, the impurity potential $V(\mathbf{r})$ is usually confined to the atomic core,[8] where the spatial dependence of $\varphi_{k'}{}^* \varphi_k$ is largest. The second term in (15) is clearly very sensitive to the details of the electronic wave functions, and we have no good way of estimating this term at present.

If we include the effect of strain on the impurity potential, we can write the total perturbation Hamiltonian in the form

$$H'(\mathbf{u}) = H'(0) + \mathbf{u} \cdot H'' + AeH'(0). \qquad (16)$$

The first term leads to elastic scattering. The second term leads to the effect predicted by Koshino, but reduced in magnitude, since its existence depends on the modulation of the wave functions. Since $\langle u^2 \rangle \propto T^2$ at low temperatures, this term by itself should lead to a resistivity component proportional to impurity concentration (or ρ_0) and to T^2. The third term, as discussed earlier, should lead to a resistivity contribution proportional to $\rho_0 T^4$.

Since the scattering probabilities depend on $|H'(\mathbf{u})|^2$, we must also consider interference terms between the three components of (16). We can disregard interference terms between $H'(0)$ and the other two, because $H'(0)$ does not contain a phonon operator and the others do, so that the former links different states. The same conclusion would hold if the lattice waves are treated classically, as $\mathbf{u}$ and e vanish in the average and only second-order terms in these quantities can contribute to $|H'|^2$. However, we must allow for possible interference between the second and third term, since both contain the same phonon operators, or alternatively, since ue does not vanish in the average.

There is also a question of whether $\mathbf{u}$ in (16) should be the absolute displacement, or the displacement of

[6] See, for example, P. G. Klemens, Handbuch der Physik, edited by S. Flügge (Springer-Verlag, Berlin, 1965), Vol. 14.
[7] D. H. Damon and P. G. Klemens, Phys. Rev. 138, A1390 (1965).
[8] N. F. Mott and H. Jones, Theory of Properties of Metals and Alloys (Oxford University Press, New York, 1936).

the impurity relative to the surrounding atoms. This depends on whether the electron wave functions adjust themselves to a large-scale displacement of the lattice. Intuitively, one would expect that a uniform displacement should not give rise to electron scattering: Thus, the displacement **u** in the second term of (16) should denote the displacement of the impurity relative to the surrounding crystal rather than the absolute displacement. This would imply that the electron wave functions adjust themselves adiabatically to large-scale motion of the crystal, but not to any motion of the impurity relative to its surroundings. Here again we face a theoretical question without being able to provide a solution. We shall see in fact that a T^2 component to Δ_3 has not been observed. This would indicate either that $\mathbf{H}''$ is intrinsically small, or that the electron wave functions adjust themselves to large-scale motion of the crystal around the impurity.

In summary, we can expect to find: (1) a component of Δ_3, proportional to T^4, owing to the effect of strain on the impurity potential [from the third term of Eq. (16), see also Eqs. (8)–(11)]; (2) a component that varies either as T^2 or T^4, arising from the modulation of the electron wave functions [from the second term of Eq. (16)]; and (3) a component of Δ_3 varying either as T^3 or T^4, arising from interference between the second and third terms of (16). All these components should be proportional to impurity concentration, i.e., to ρ_0 in a given alloy series.

III. EXPERIMENTAL PROCEDURE

The alloys that we investigated were alloys of gold, with platinum, copper, and indium in concentrations from 0.2 to 2.6 at.%. The specimens were wires of 0.7 to 2.5×10^{-2} cm diam and about 20 cm long. Before measurements of the electrical resistance were made, the wires were annealed at 750°K for times varying from 8 to 24 h. Potential probes were spot-welded to the wires that were then loosely wound on a 1.5-cm-diam lava sample holder. The holder was mounted and sealed in a heavy copper sample chamber which was evacuated and then filled with helium gas at a pressure of a few cm of Hg. Between 1.5 and 4.2°K and between 14 and 20°K, measurements were made with the sample chamber immersed in liquid helium or hydrogen. In order to reach other temperatures the sample chamber, fitted with a cold finger, was raised above a liquid-helium bath. The temperature was controlled by balancing the heat produced by an electrical heater against the heat conducted to the bath. The temperature difference between the top and bottom of the sample chamber, shielded from room-temperature radiation by a Styrofoam plug, was measured with a Au–2.7 at.% Co versus Cu thermocouple and was found not to exceed 0.15°K. A comparison of the resistivity of two gold specimens measured together showed that the

temperature differences over the sample holder did not exceed 0.05°K.

Measurements of resistance were made from 1.5 to about 40°K. In each run, one or more alloy specimens were measured together with a gold wire ($\rho_0 < 10^{-8}$ Ω cm). Measurements of the temperature above 4.2°K were first made with a Au–2.7 at.% Co versus Cu thermocouple with its cold junction in the helium bath at ~ 4.2°K. However, after four runs, this thermocouple showed a significant change in its thermoelectric power, as indicated by failure to reproduce the resistance-temperature values of gold between 14 and 20°K, determined from the measurements with liquid hydrogen. Subsequent runs were made using either a Au–0.2 at.% Fe versus Cu thermocouple or a calibrated Ge resistance thermometer, purchased from Cryo-Cal, Inc., of Rivera Beach, Fla. In the course of this investigation, well over 100 measurements of the resistivity of gold were made between 1.5 and 40°K. A comparison of the measurements made on three different specimens with these various thermometers showed that the accuracy of the temperature measurements is equal to or better than ±0.1°K over the entire temperature range. Between 20 and 14°K the accuracy is ±0.02°K and from 10 to 14°K about ±0.05°K.

Table I lists the samples used in this investigation. Samples 9, 12, and 13 were prepared from the same materials used for samples 6, 2, and 3, respectively, of Ref. 7. The procedures used to establish accurate values of the resistivity are described in detail in that paper. As will be shown below, it is not as important for this investigation to obtain very accurate values of the geometrical form factors of the specimens as it had been for our previous study of the deviations from Matthiessen's rule at high temperatures. Nevertheless, when comparing different samples it is necessary to be concerned with questions of absolute accuracy. The accuracy of the values of the total resistivity reported in this paper is ±0.3% and is mainly determined by the accuracy in the measurement of the form factors. This accuracy is quite adequate for our purposes, but at low temperatures the accuracy on the resistance measurements themselves turns out to be the most serious

TABLE I. Solute content and residual resistivity of samples.

Number	Samples	Solute (at.%)	ρ_0 (10^{-6} Ω cm)
1	Au	pure	0.00779
2	Au	pure	0.00910
3	Au	pure	0.00907
4	Au+In	0.29	0.3309
5	Au+In	0.58	0.6530
6	Au+In	0.86	0.9693
7	Au+In	1.15	1.254
8	Au+Cu	0.63	0.2715
9	Au+Cu	2.6	1.136
10	Au+Pt	0.22	0.2230
11	Au+Pt	0.49	0.4943
12	Au+Pt	1.0	0.9239
13	Au+Pt	1.6	1.576

TABLE II. $\rho_i(T)$ for gold from 10 to 40 and 80 to 480°K.

From 10 to 40°K		From 80 to 480°K	
T (°K)	$10^8 \times \rho_i$ (Ω cm)	T (°K)	$10^8 \times \rho_i$ (Ω cm)
10.0	6.1 $\times 10^{-2}$	80	$0.448_4 \times 10^2$
11.0	9.2 $\times 10^{-2}$	100	$0.617_4 \times 10^2$
12.0	1.38 $\times 10^{-1}$	120	$0.785_9 \times 10^2$
13.0	1.96 $\times 10^{-1}$	140	$0.951_0 \times 10^2$
14.0	2.72 $\times 10^{-1}$	160	1.115 $\times 10^2$
16.0	4.80 $\times 10^{-1}$	180	1.277 $\times 10^2$
18.0	7.80 $\times 10^{-1}$	200	1.435 $\times 10^2$
20.0	1.205 $\times 10^0$	220	1.594 $\times 10^2$
22.0	1.755 $\times 10^0$	240	1.754 $\times 10^2$
25.0	2.825 $\times 10^0$	260	1.915 $\times 10^2$
30.0	5.210 $\times 10^0$	280	2.076 $\times 10^2$
35.0	8.39 $\times 10^0$	300	2.238 $\times 10^2$
40.0	1.200 $\times 10^1$	320	2.401 $\times 10^2$
		340	2.565 $\times 10^2$
		360	2.730 $\times 10^2$
		380	2.896 $\times 10^2$
		400	3.064 $\times 10^2$
		420	3.234 $\times 10^2$
		440	3.404 $\times 10^2$
		460	3.575 $\times 10^2$
		480	3.748 $\times 10^2$

limitation to our analysis. For example, between 4 and 10°K the resistance of samples 10 and 13 changed by 0.4 and 0.1%, respectively.

The voltages were measured with a Leeds and Northrup K-3 potentiometer; its calibration was checked in the Westinghouse Standards Laboratory. The measuring current was supplied by a North Hills Precision Current Source, model CS-12, which over short periods of time can maintain a current constant to ±0.005%. The current was measured as the voltage developed across an NBS-type 0.1-Ω standard resistor, which was kept in an oil bath to maintain temperature stability. The measured voltages ranged from 1 to 5 mV and changes of 0.2 μV could be detected. The potentiometer was balanced for no deflection on reversal of the galvanometer leads. Thermal emfs, i.e., the difference between the voltages measured for two current directions, were about 1 μV. At the lowest temperatures, the resistances of the samples with the largest residual resistivities were very nearly equal to the resistance of the standard resistor so that in comparing them to the standard only slight changes in the potentiometer dials were necessary. Under these conditions the accuracy of the resistance measurements should be 0.01%. The resistance of the other samples at the lowest temperature, particularly the pure gold specimens, were smaller than the resistance of the standard and such accuracy cannot be expected. Of course, the high accuracy is not as important for the resistance of the specimens that are more sensitive to temperature.

Measurements of the resistance were made for several values of the measuring current and no heating effects were observed except for the gold sample No. 1. The resistance of this sample was about $\frac{1}{10}$ that of sample Nos. 2 and 3 since its diameter was about three times larger than the diameters of the latter two specimens.

Corrections for the heating were made and the results were in excellent agreement with those found for the samples with smaller diameters.

IV. RESULTS

Table I also gives the relevant characteristics of the samples. The residual resistivities were obtained by extending the measurements down to 1.5°K. For the gold specimen the measured values of $(\rho - \rho_0)$, which may be identified with the ideal resistivity $\rho_i(T)$, agreed very well with the results of previous workers. In Table II we have listed $\rho_i(T)$ obtained from the gold specimens in the temperature ranges 10–40 and 80–480°K.

The total resistivity ρ of the alloy specimens behaved regularly as a function of temperature except for the sample No. 10, which showed a slight minimum, so
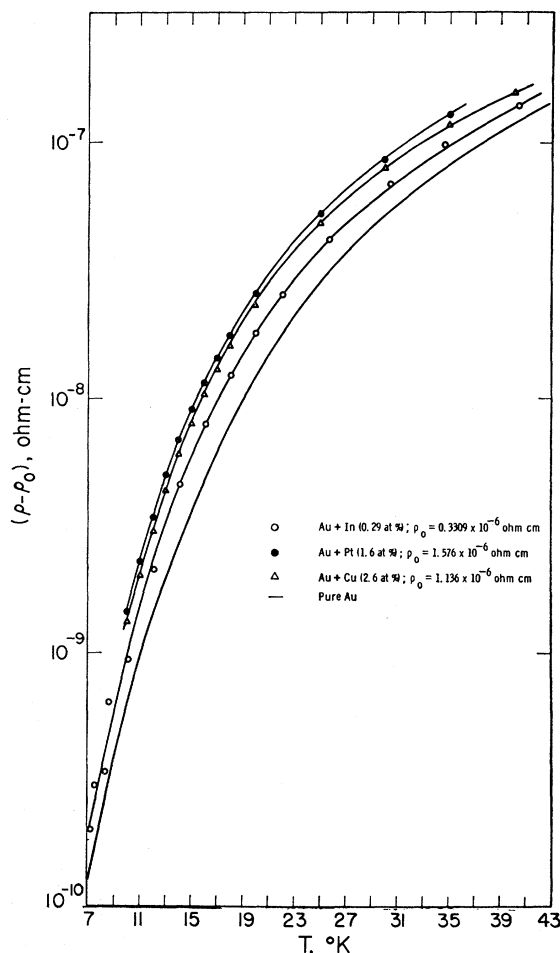

FIG. 1. Values of $\rho - \rho_0$ versus T. A log scale is used for $\rho - \rho_0$ and a linear scale for T only for convenience in displaying the results. The lowest curve shows the behavior of the pure gold specimens. The upper curves show the results of the different alloy systems (Au+Pt, Au+Cu, Au+In) and are distinguished in the legend. As discussed in the text, the values of ρ_i shown here may be significantly larger than the true values at the lowest temperatures.

● Au + Pt Alloys
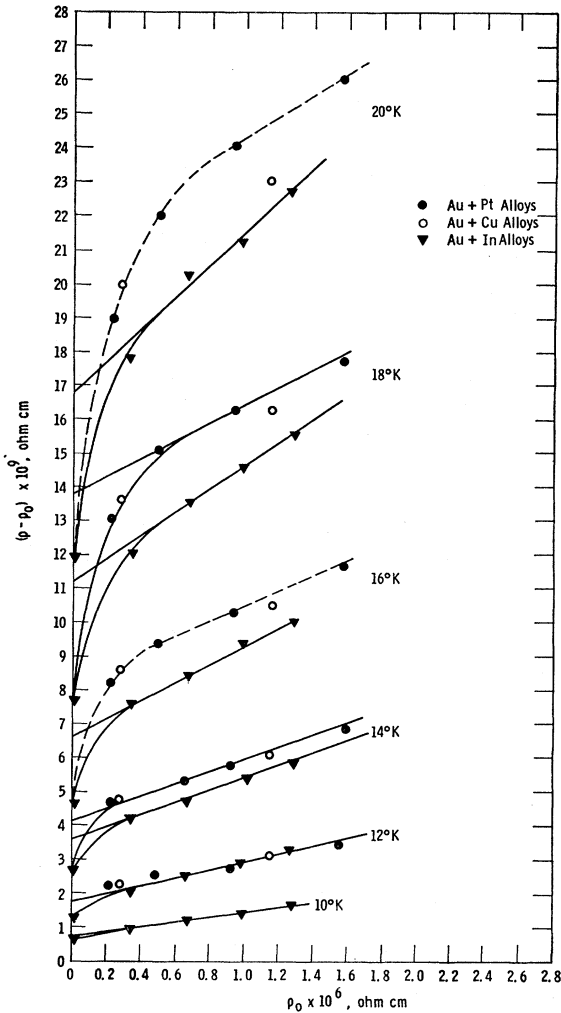○ Au + Cu Alloys
▼ Au + In Alloys

FIG. 2. Values of $\rho-\rho_0$ plotted against ρ_0 at different temperatures for different alloy systems as distinguished in the legend. The values of α and β are obtained from Eq. (17). At large values of ρ_0 the slope of $\rho-\rho_0$ versus ρ_0 gives β and α as obtained from the intercept at $\rho_0=0$.

phonon spectrum. We expect these changes to yield a deviation Δ_1 such that Δ_1/ρ_i is comparable to the fractional change in electron density or the fractional impurity content. The observed deviations are an order of magnitude bigger. Furthermore, the observed deviations do not show any regular dependence, either on electron concentration or on impurity mass, as one would have expected from such mechanisms.

In the presence of deviations due to the two-band effect and due to phonon-induced impurity scattering, the temperature-dependent component of the resistivity should have the form

$$\rho-\rho_0=\alpha(\rho_0,T)+\beta(T)\rho_0, \qquad (17)$$

where $\alpha=\Delta_2+\rho_i$ and should, on the basis of the two-band model, attain a value $\alpha^0(T)$, independent of ρ_0, in the limit $\rho_0\gg\rho_i$. The second term, due to phonon-assisted impurity scattering, is of the form suggested by Eq. (10). Thus, $\rho-\rho_0$ should tend towards a linear dependence on ρ_0 for large values of ρ_0, though this limit is rapidly pushed towards high values of ρ_0 as T, and therefore ρ_i, is increased.

Figure 2 shows plots of $(\rho-\rho_0)$ against ρ_0 at several temperatures. As expected, there is indeed a linear relationship; from the slopes and the intercepts of the lines, one can deduce α and β up to a temperature of 16°K. The above analysis seems to be adequate below 16°K but at higher temperatures the separation becomes highly uncertain. This can be seen from the 18 and 20°K plots. The difficulty is probably due to the fact that the condition $\rho_0\gg\rho_i$ is not satisfied here. Another interesting feature is that at 12°K there seems to be no distinction between the different solute atoms. However, at higher temperatures the behavior of Cu and Pt solutes is still similar but that of In solutes differs somewhat. Above 18°K all solutes behave differently and none of them follows the linear dependence with ρ_0.

Figure 3 shows the plot of β as a function of temperature T. Below $T=15°$K, β varies as T^n, where $n=4$ for

that its ρ_0 is somewhat uncertain. The minimum in ρ for this particular alloy appears at about 5.5°K and is about 99.7% of the resistivity at 1.4°K. The value of ρ_0 for this sample was obtained by extrapolating $\rho(T)$ above the minimum to the lowest temperatures. The other samples, however, presented no such difficulty.

Figure 1 shows the measured values of $(\rho-\rho_0)$ as a function of temperature T for the gold samples and for one representative sample from each alloy system. It is clear that $\rho-\rho_0$ for the alloys is substantially larger than ρ_i. Within each alloy system $\rho-\rho_0$ increases with ρ_0 at all temperatures.

The observed deviations from Matthiessen's rule, $\Delta(T)$ of Eq. (1), can be attributed to three causes, as mentioned in the Introduction. We shall disregard the first effect, changes in $\rho_i(T)$ on alloying because of changes in the electronic band structure and in the

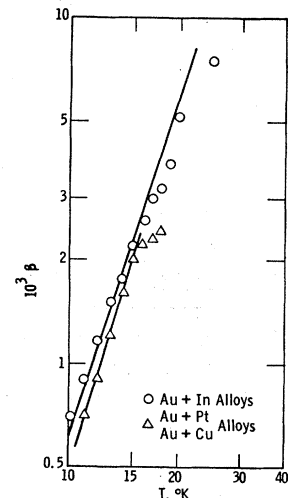
FIG. 3. Values of β versus T for the different alloy systems. The T^4 dependence in Au+Pt and $T^{3.6}$ in Au+In are observed. At $T>16°$K, there is a departure from these temperature dependences. Values of β(In) are greater than β(Pt) at any temperature.

○ Au + In Alloys
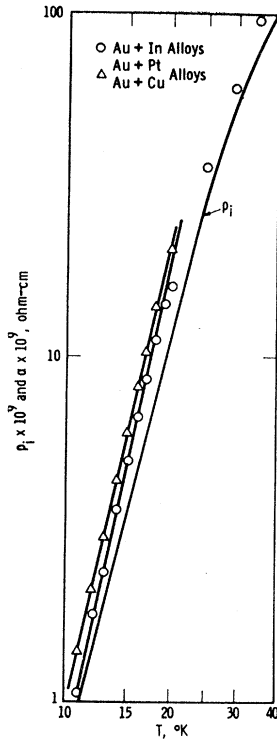△ Au + Pt Alloys
○/△ Au + Cu Alloys

Fig. 4. Values of α [see Eq. (17)] and ρ_i against T. α(Pt) is greater than α(In) and α varies as T^5.

Pt solute and 3.6 for In solute. Since only two samples with Cu as solute were measured, we cannot get α, β for them but it seems that Cu solute behaves more like Pt than In. The β values for In solute are larger than for Pt or Cu solutes, indicating corresponding differences in the values of A of Eq. (10).

Figure 4 shows α as a function of temperature. It varies roughly as T^5 for all solutes up to a temperature of 20°K; above 20°K the temperature dependence of $\alpha(T)$ decreases continuously. One also notes that α is larger for Pt solutes than for In.

V. DISCUSSION

Before we can discuss the physical significance of our results, it is important to be aware of the limitations of experimental errors. Values of Δ have been obtained from plots of $\rho - \rho_0$ versus T, but to consider the accuracy of these values it is best to write

$$\Delta(T) = (R(T) - R_0)f - (R_P(T) - R_{P0})f_P, \quad (18)$$

where $R(T)$ is the resistance of an alloy specimen, R_0 its residual resistance, and f its geometrical form factor; $R_P(T)$ is the resistance of the pure specimen, R_{P0} its residual resistance, and f_P its geometrical form factor. The error in Δ arises both from the resistance measurements and from the form factors. Following Alley and Serin,[9] the fractional error in Δ due to errors in the f's

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

may be written

$$\frac{\delta\Delta}{\Delta} = \frac{\delta f}{f} + \frac{\rho_i}{\Delta}\left(\frac{\delta f}{f} - \frac{\delta f_P}{f_P}\right). \quad (19)$$

If ρ_i/Δ is large, as is the case at high temperatures, then this may be a serious source of error. For the present measurements ρ_i/Δ is of order unity. For example, from the resistivity of the Au–Pt alloy with $\rho_0 \approx 0.27 \times 10^{-6}$ Ω cm, one finds $\Delta \approx 0.9 \times 10^{-9}$ Ω cm and $\rho_i \approx 1.3 \times 10^{-9}$ Ω cm at 12°K and $\Delta \approx 8 \times 10^{-9}$ Ω cm and $\rho_i \approx 12 \times 10^{-9}$ Ω cm at 20°K. Therefore, $\rho_i/\Delta \leq 1.5$ and is nearly independent of temperature below 20°K. The contribution of the error in the f's to the errors in Δ is at most 1.2% and, of greatest importance, this error will not introduce a spurious temperature dependence of Δ.

For the gold specimens $R_P(T) - R_{P0} \approx 0.16R_{P0}$ at 12°K and the errors in these measurements give rise to less than 1% error in Δ. Most of the error in Δ is traceable to the error in measuring values of $R(T) - R_0$. We have previously described the care that was taken in making these measurements. For the Au–Pt alloys at 12°K, $\rho - \rho_0$ increases from $\sim 2.3 \times 10^{-9}$ Ω cm for $\rho_0 = 3 \times 10^{-7}$ Ω cm to $\sim 3.4 \times 10^{-9}$ Ω cm for $\rho_0 = 1.5 \times 10^{-6}$ Ω cm. The resulting values of Δ should therefore be accurate within 10% at this temperature. These values of Δ change by slightly more than a factor of 2 over this range of values of ρ_0. Noting that at 12°K four points determine the value of β for both the Au–Pt and Au–In alloys, these considerations suggest that the accuracy of both α and β should be about 10%. This conclusion seems well substantiated by the scatter of the data points shown in Fig. 2. At higher temperatures the accuracy of the values of Δ improves substantially but the separation of Δ into Δ_2 and Δ_3 according to Eq. (17) becomes increasingly uncertain. Although the values of β for the Au–Pt alloys are consistently smaller than those for the Au–In alloys, this difference cannot be said to be beyond experimental error. Moreover, the difference between $T^{3.6}$ and T^4 is not unambiguous. On the other hand, the difference between the values of α for the Au–Pt and Au–In alloys is beyond experimental error.

In Sec. IV it has been shown that part of the deviation of the resistivity from Matthiessen's rule is proportional to ρ_0 and T^4. The remaining deviation Δ_2 must be identified with the two-band effect. Figure 4 shows that $\alpha = \Delta_2 + \rho_i$ is very nearly proportional to ρ_i as would be predicted by the two-band model. Dugdale and Basinski[4] have studied the deviations from Matthiessen's rule in a number of dilute alloys based on Cu and Ag solvents. They explained their results in terms of the two-band effect alone without invoking phonon-assisted impurity scattering. They also found no significant effects that could be associated with changes in the Fermi surface and the phonon spectrum. In Sec. II we have suggested that the effect of phonon-

assisted impurity scattering should become of decreasing importance as the phonon scattering of the electrons becomes stronger. We have assumed that the deviations of the resistivity from Matthiessen's rule in our gold alloys above 20°K are solely due to the two-band effect and have followed Dugdale and Basinski's analysis. This is reasonable because $\omega\tau_i \sim 2$ at 20°K and decreases as $1/T^2$ with increasing temperature.

Briefly, in using this model one assumes that the roles of the two bands are played by different parts of the Fermi surface, and in view of the known structure of the Fermi surface[10] we think of these two bands as the electrons on the belly and on the necks. Both the phonon and the impurity scattering may be quite different from these two groups of electrons. If σ_N^0 and σ_B^0 are the contributions to the conductivity of the neck and belly electrons, respectively, when only impurity scattering is important, and similarly σ_N^i and σ_B^i are the same quantities when only phonon scattering is important, then an expression for Δ_2 can be written in terms of ρ_0, ρ_i, σ_N^0/σ_B^0, and σ_N^i/σ_B^i, namely,[11]

$$\Delta_2 = \left(\frac{\sigma_N^0}{\sigma_B^0} - \frac{\sigma_N^i}{\sigma_B^i}\right)^2 \rho_0 \bigg/ \left[\frac{\sigma_N^i}{\sigma_B^i}\left(1+\frac{\sigma_N^0}{\sigma_B^0}\right)^2 \frac{\rho_0}{\rho_i}\right.$$
$$\left. + \frac{\sigma_N^0}{\sigma_B^0}\left(1+\frac{\sigma_N^i}{\sigma_B^i}\right)^2\right]. \quad (20)$$

Given the measured values of Δ, ρ_0, and ρ_i, this expression is then fitted to the data by chosing values of σ_N^0/σ_B^0 and σ_N^i/σ_B^i. As discussed in detail by Dugdale and Basinski, one expects σ_N^0/σ_B^0 to be different for each solute, whereas σ_N^i/σ_B^i should be the same for all gold alloys. The value of σ_N^i/σ_B^i should increase from a limiting low-temperature value $(T\ll\theta)$ to a high-
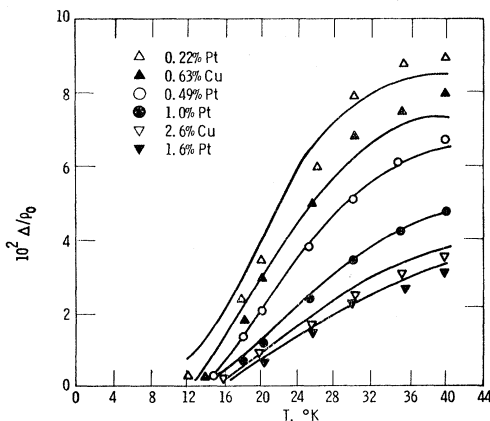

FIG. 5. Values of Δ_2/ρ_0 plotted against T for Pt alloys. The points represent the measured values and the lines represent the theoretical curves from Eq. (20) for the different alloys.

[10] D. Shoenberg, Phil. Trans. Roy. Soc. London **A255**, 85 (1962).
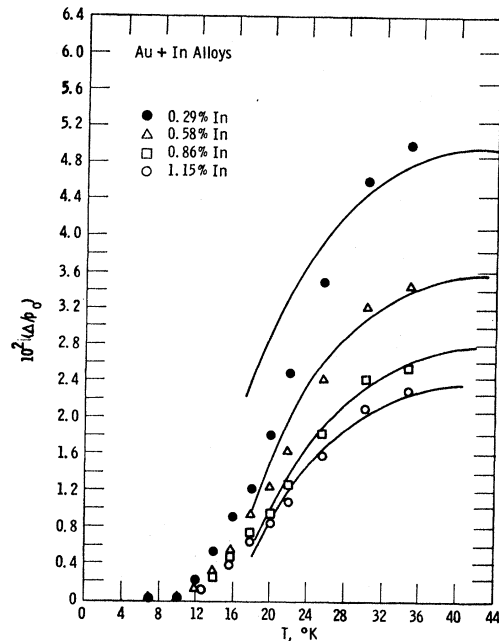[11] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., pp. 310–313.

FIG. 6. Values of Δ_2/ρ_0 plotted against T for In alloys. The points represent the measured values and the lines represent the theoretical curves from Eq. (20) for the different alloys.

temperature value $(T>\theta)$, whereas σ_N^0/σ_B^0 should be independent of temperature.

Figures 5 and 6 show the fit of this formula to our data for the gold alloys. The curves have been calculated from Eq. (20), using $\sigma_N^0/\sigma_B^0 = 0.15$, 0.13, and 0.12, respectively, for the Pt, Cu, and In solutes. We found σ_N^i/σ_B^i to be about 0.01 at 20°K; its value increases to about 0.02 at 40°K. We have taken its value to be 0.01, independent of T, below 20°K. The values shown by the points in the figures were calculated from the total Δ above 20°K, and from the values of $\Delta_2 = \alpha - \rho_i$ determined from plots such as those shown in Fig. 2 below 20°K. At the higher temperatures these curves give a good account of the data, but at the lower temperatures discrepancies are found. These could be removed if one were willing to allow σ_N^i/σ_B^i to assume a minimum value of 0.01 at 18°K and then increase to a value of about 0.017 at 12°K. The necessity for this can be seen most clearly in Fig. 4, where it is seen that $\alpha = \rho_i + \Delta_2$ increases slightly faster than ρ_i with temperature between 10 and 18°K. This appears to be inconsistent with the two-band model, but it may simply be a spurious result. At 12°K, ρ_i is only about 20% of ρ_0 for our purest gold specimen. The deviation of the resistivity from Matthiessen's rule in the pure specimens could therefore be a significant fraction of ρ_i at the lowest temperatures (perhaps as much as 20% at 12°K). This would make our calculated values of Δ for the gold alloys too small at the lowest temperatures and bring about the discrepancies shown in Figs. 5 and 6. It should be noted that this possible error will in no way interfere

with the determination of the term $\beta\rho_0$, since it does not affect $\alpha=\Delta_2+\rho_i$. It is significant that we find α to vary as T^5, as it should if $\Delta_2\propto\rho_i$.

These values of σ_N^0/σ_B^0 and σ_N^i/σ_B^i for the gold alloys are considerably smaller than the values of these quantities for the Ag and Cu alloys found by Dugdale and Basinski. Although the differences between the values of these quantities for gold and silver alloys are somewhat greater than the differences between their values for the silver and copper alloys, the systematic decrease in these quantities as one proceeds from Cu to Ag to Au alloys is marked. The deviation of the resistivity from Matthiessen's rule due to the two-band effect is therefore smaller in the gold alloys than in either the Cu or Ag alloys for the same values of ρ_i/ρ_0. Even if the effect of inelastic impurity scattering were to be comparable in the three alloy systems, it would contribute a smaller fraction of the total deviation in the Ag and Cu alloys and thus be more difficult to observe. However, it is also possible that the coefficient A^2 in Eq. (10) is smaller for copper and silver alloys than for gold alloys. Even though information on Δ_3 in copper and silver alloys is probably more difficult to obtain, it would be most interesting to see if there is a systematic trend in A^2.

We have succeeded in separating the measured values of Δ into two parts, one associated with the two-band effect which, although smaller than that found in Ag and Cu alloys, is in other ways very similar, and one proportional to T^4 and ρ_0. Let us note explicitly that the two-band effect cannot be used to explain the dependence of Δ and ρ_0 shown in Fig. 2. For example, at 15°K with $\sigma_N^i/\sigma_B^i=0.01$ and $\sigma_N^0/\sigma_B^0=0.15$ for the Au–Pt alloys one expects Δ_2 to increase by 15% as ρ_0 is increased from 2×10^{-7} to 1.5×10^{-6} whereas, we observe an increase of more than a factor of 2 in Δ. Qualitatively, the term $\beta\rho_0$ that we have found to represent a significant fraction of the deviation of the resistivity from Matthiessen's rule in gold alloys is well explained by inelastic impurity scattering.

According to the results of Sec. II and the Appendix, β is given by

$$\beta=A^2\langle e^2\rangle=4A^2E(T)/Mv^2. \tag{21}$$

To obtain an estimate of $E(T)/Mv^2$ we have taken

$$E(T)=\int_0^T C_v dT,$$

with $C_v=1944(T/\Theta)^3$ J per mole per deg, and v to be the velocity of the transverse modes. With $\Theta=164°$K and $\beta=6\times10^{-4}$ °K^{-4} at 10°K, one obtains $A^2=40$.

By our method of separating Δ into a component which saturates with increasing ρ_0 and one which continues to increase linearly with ρ_0, we have demonstrated the existence of a resistive component which has the general characteristics expected from phonon-assisted impurity scattering. There are two physical mechanisms that can give rise to this effect: changes in the impurity potential because of strain, and effects that depend on the modulation of the electron wave function. In the absence of a detailed theory of these effects, we do not know to what extent these two mechanisms contribute to phonon-assisted impurity scattering, or even whether the observed magnitude of the empirical coefficient A^2 is at all reasonable from a theoretical point of view. The relative insensitivity of A^2 to the nature of the impurity requires some explanation.

If our interpretation of the data in terms of phonon-assisted impurity scattering is correct, there should be observable effects not only on electronic-conduction properties but also on phonon transport properties, namely, the lattice thermal conductivity and the phonon-drag component of the thermoelectric power. Existing measurements do not cover the optimum temperature and concentration ranges to test the existence of such effects. The present results provide the information needed to predict the lattice thermal-conductivity changes to be expected from this mechanism, and such measurements should then provide a test of the concept.

Clearly the phonon-assisted impurity scattering raises a number of questions related to the details of the impurity potential and the wave functions. We believe that we have demonstrated the existence of the effect, which had been first proposed by Koshino. It is still necessary to understand it in detail and to acquire systematic information about it.

ACKNOWLEDGMENTS

APPENDIX

Expression (10) was obtained by treating the strain of the lattice waves classically. The corresponding quantum-mechanical treatment, which leads to a numerical correction, is given below. For simplicity we shall only consider the case of a highly localized impurity potential, leading to isotropic scattering both for the elastic and the phonon-assisted processes. The treatment closely parallels that of the usual electron-phonon interaction.[12]

The rate of change of the electron distribution function $f(\mathbf{k})$ due to a static impurity potential of

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[12] A. Sommerfeld and H. Bethe, in *Handbuch der Physik*, edited by H. Geiger and Karl Scheel (Julius Springer, Berlin, 1933).

matrix elements (5) is given by

$$-\frac{df}{dt}=\sum_{\mathbf{k}'} 2\pi(H')^2[g(\mathbf{k})-g(\mathbf{k}')]\delta(E-E'), \quad \text{(A1)}$$

where $g(\mathbf{k})$ is the deviation of $f(\mathbf{k})$ from equilibrium f^0. Assuming isotropic scattering, so that $\sum (H')^2 g(\mathbf{k}')=0$, the relaxation time becomes in the usual way

$$\frac{1}{\tau}=-\frac{1}{g}\frac{df}{dt}=\sum_{\mathbf{k}'} 2\pi(H')^2\delta(E-E'). \quad \text{(A2)}$$

This may now be compared with the scattering due to a perturbation of the form (9). One can express e, the strain at the impurity, in terms of the strain due to the lattice waves (4), and express the displacements $a^*(\mathbf{q})$ and $a(\mathbf{q})$ in terms of the usual phonon creation and annihilation operators. One thus obtains

$$\frac{df}{dt}=2\pi A^2 \sum_{\mathbf{k}',\mathbf{q}} q^2\frac{\hbar}{2M\omega}(H')^2\delta(E+\hbar\omega-E')$$

$$\times[(1-f)f'(N+1)-f(1-f')N], \quad \text{(A3)}$$

where N is the average number of phonons in mode $\mathbf{q}$ and the summation is over all modes and also over the cases when scattering from $\mathbf{k}$ to $\mathbf{k}'$ leads to the emission of a phonon, formally taken account of by changing the sign of ω and interchanging the position of the factors N and $N+1$.

Expanding the square bracket in (A3), one obtains $(f'-f)N-ff'+f'$. This factor vanishes when f, f', and N are in equilibrium. Writing $f=f^0+g$, etc., and assuming N to have the equilibrium value, this factor becomes $(g'-g)N-gf'-fg'+g'$, where f and f' now denote equilibrium values. Because of the simplification that $\sum_{\mathbf{k}'} (H')^2 g(\mathbf{k}')=0$, one needs only to retain terms in g, so that one finally obtains for the relaxation time

$$\frac{1}{\tau}=2\pi A^2 \sum_{\mathbf{k}',\mathbf{q}} q^2\frac{\hbar}{2M\omega}(H')^2[(N+f')\delta(E+\hbar\omega-E')$$

$$+(N+1-f')\delta(E-\hbar\omega-E')], \quad \text{(A4)}$$

where now the summation is over positive values of ω only. In the classical approximation when $N\gg1$, one can compare (A4) with (A2) to obtain Eq. (10).

The relaxation rate $1/\tau$ is clearly a function of the reduced energy of the electron $\mathbf{k}$, i.e., of $\epsilon=(E-\zeta)/KT$. In the electrical-conduction problem we are, however, not interested so much in the functional form of $\tau(\epsilon)$ but in the average rate of momentum removal from a group of states of a given direction of $\mathbf{k}$ about the Fermi energy. Writing g in the form $g(\mathbf{k})=k_x(df^0/d\epsilon)\alpha$, the constant α is obtained in terms of an average relaxation rate:

$$\left(\frac{1}{\tau}\right)_{\text{av}}=-\int\frac{g}{\tau}d\epsilon\Big/\int\frac{df^0}{d\epsilon}d\epsilon. \quad \text{(A5)}$$

The first term in the square brackets of (A4) makes a contribution to this average relaxation time proportional to

$$-\int\frac{df^0}{d\epsilon}[N+f']d\epsilon$$

$$=\int d\epsilon\frac{e^\epsilon}{(e^\epsilon+1)^2}\left[\frac{1}{e^x-1}+\frac{1}{e^{\epsilon+x}+1}\right], \quad \text{(A6)}$$

where $x=\hbar\omega/kT$ is the reduced phonon energy. As shown in standard works, for example, Ref. 12, this factor is equal to $xe^x/(e^x-1)^2$; similarly for the second term in (A4). Hence, while the classical approximation contains a factor

$$\sum_{\mathbf{q}}\frac{N\hbar\omega}{Mv^2}\propto T^4\int\frac{x}{(e^x-1)}x^2\,dx, \quad \text{(A7)}$$

the quantum-mechanical result contains a factor

$$\sum_{\mathbf{q}}\frac{\hbar\omega}{Mv^2}\frac{xe^x}{(e^x-1)^2}\propto T^4\int\frac{x^2e^x}{(e^x-1)^2}x^2\,dx. \quad \text{(A8)}$$

In the low-temperature limit expression (A8) exceeds (A7) by a factor of 4. Hence Eq. (10) becomes, more properly, at very low temperatures

$$\Delta_3=A^2\rho_0 4E(T)/Mv^2, \quad \text{(A9)}$$

where Δ_3 is proportional to T^4.

If the impurity scattering is anisotropic, there is no simple relation between Δ_3 and ρ_0. It is expected, however, that the qualitative aspects of (A9) will still be retained.