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Deviations from Matthiessen's rule for dilute alloys of polyvalent and noble metals

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An analysis is presented of the low-temperature deviations from Matthiessen's rule (DMR) for the polyvalent and noble metals. For these metals, the Fermi surface intersects the Brillouin-zone boundaries, leading to an enormous enhancement, at low temperatures, of the electron-phonon scattering probability for the electrons near the Brillouin-zone intersections. An electron distribution function is introduced which takes explicit account of these localized regions of extremely strong electron-phonon scattering. This electron distribution function is shown to provide the basis for understanding (i) the large magnitude of the low-temperature DMR, (ii) their temperature dependence, (iii) their dependence on residual resistivity, and (iv) their variation from metal to metal. Moreover, it is found that by including the contribution of the interference term, one may explain the observed lack of saturation of the DMR for large values of the residual resistivity. Finally, it is demonstrated that normal electron-phonon scattering constitutes a large part of the total calculated DMR.

I. INTRODUCTION

Since 1970, a vast body of experimental data[1,2] has established the existence of large deviations from Matthiessen's rule for the low-temperature electrical resistivity of the polyvalent and noble metals. Concurrent with the many experiments, considerable theoretical effort has been directed to understanding the observed deviations from Matthiessen's rule (DMR). Bass[1] has described and critically reviewed the various theoretical approaches to account for the DMR. The present approach is based on the fact that, at low temperatures, the electron-phonon scattering probability is very anisotropic over the Fermi surface. In recent years, it has become increasingly recognized[3-19] that such an approach is particularly appropriate for the polyvalent and noble metals because these metals are characterized by an unusually large anisotropy of the electron-phonon scattering probability.

The key to the physical picture lies in the recognition that for the polyvalent and noble metals at low temperatures, the electrons occupying a relatively small portion of the Fermi surface are scattered very much more strongly than the electrons on the rest of the Fermi surface. The small regions in question are the immediate vicinity of the various intersections of the Fermi surface and the Brillouin-zone boundaries. The existence of such small regions of extremely strong electron-phonon scattering is by itself sufficient to imply large DMR.

The explanation for the DMR is conveniently formulated in terms of the deviation of the electron distribution function from its thermal equilibrium value, which may be called the deviation distribution function. Consider first a pure metal, for which the dominant scattering process is electron-phonon scattering. Since electron-phonon scattering is highly anisotropic over the Fermi surface, the resulting deviation distribution function will also be very anisotropic. In fact, for the strong-scattering regions of the Fermi surface, the deviation distribution function will vanish because these electrons are very rapidly scattered back to their thermal-equilibrium distribution, and hence do not contribute to the resistivity. This implies that the main contribution to the conductivity arises from the electrons which are scattered much more weakly. The result is a relatively high conductivity, and thus a low resistivity.

Consider now a very impure metal, for which the dominant scattering process is electron-impurity scattering. Since electron-impurity scattering is nearly isotropic over the Fermi surface, the resulting deviation distribution function will also be relatively isotropic. This immediately implies that all the electrons must contribute to the resistivity, with the electrons in the strong-scattering regions of the Fermi surface making an enormous contribution at low temperatures. Thus, at low temperatures, the strong-scattering regions of the Fermi surface constitute the dominant contribution to the resistivity for impure metals, but contribute almost nothing to the resistivity for pure metals. This is the basic cause for the large DMR at low temperatures. We shall show that the development of these ideas provides an explanation for the magnitude of the DMR, for their variation from metal to metal, for their temperature dependence, and for their dependence on residual resistivity.

The most useful theoretical tool for analyzing the phenomena associated with the large DMR is the variational formulation[20] of the Boltzmann equation. We use this powerful method to carry out a detailed analysis of the low-temperature DMR for the polyvalent and noble metals. The results are in complete agreement with experiment.[1,2]

Although the present analysis is performed without a computer calculation, it is clear that a detailed quantitative comparison between theory and experiment requires a separate computer calculation for each metal. In the following paper,[21] we present such a comparison for aluminum and show that agreement is obtained for the measured low-temperature DMR. Such quantitative agreement with experiment complements the qualitative picture presented here.

In Sec. II, the variational formulation of the Boltzmann equation is used to derive an expression for the DMR. Based on this expression for the DMR, a new deviation distribution function is introduced in Sec. III, which incorporates explicitly the extremely large anisotropy over the Fermi surface of the electron-phonon scattering probability. This deviation distribution function is shown to form the basis for the explanation of the very large DMR that are observed at low temperatures for the polyvalent and noble metals. In Sec. IV, the interference term is introduced and an analysis is presented of the behavior of the DMR for large values of the residual resistivity for different temperature ranges. In Sec. V, the principal experimental features of the DMR are explained qualitatively in terms of the electron distribution function and the interference term. Normal electron-phonon scattering is discussed in Sec. VI and its importance is established for quantitative calculations of the DMR. The summary follows in Sec. VII.

II. MATTHIESSEN'S RULE AND THE VARIATIONAL FORMULATION

A study of the DMR deals with the electrical resistivity ρ arising from the simultaneous presence of electron-impurity scattering and of electron-phonon scattering. We denote by ρ_0 the residual resistivity arising from electron-impurity scattering in the absence of electron-phonon scattering, and we denote by ρ_i the ideal resistivity arising from electron-phonon scattering in the absence of electron-impurity scattering. The experimental data are traditionally presented in terms of $\Delta\rho$, defined by

$$\Delta\rho = \rho_{\text{tot}} - \rho_0 , \tag{2.1}$$

where ρ_{tot} is the total resistivity. Matthiessen's rule states that ρ_{tot} is the sum of ρ_0 and ρ_i, or equivalently, that $\Delta\rho$ is independent of ρ_0. However, experiment[1,2] shows that for polyvalent metals at low temperatures, $\Delta\rho$ exhibits a very marked dependence on ρ_0, implying very large DMR. For example, for Al at 14 K, $\Delta\rho$ increases[1,2] by a factor of about 6 as ρ_0 increases from 0.1 to 1000 nΩ cm. Another phenomenon requiring explanation is that for bulk samples at fixed temperatures, $\Delta\rho$ appears[1,2] to depend almost solely on the value of ρ_0, without regard to the source of ρ_0, be it electron scattering by various types of impurities or electron scattering by various types of lattice imperfections.

To describe the scattering of the electrons by both phonons and impurities, we introduce the total scattering operator $\hat{P}_{\text{tot}}$, which may be written

$$\hat{P}_{\text{tot}} = \hat{P}_{\text{ph}} + \hat{P}_{\text{imp}} + \hat{P}_{\text{int}} , \tag{2.2}$$

where the operator $\hat{P}_{\text{ph}}$ describes the scattering of the electrons by phonons, and hence depends on temperature through the phonon occupation numbers, the operator $\hat{P}_{\text{imp}}$ describes the scattering of the electrons by impurities, and hence depends linearly on the (dilute) concentration of impurities, and the operator $\hat{P}_{\text{int}}$ is an "interference" term which depends both on temperature and on the concentration of impurities. For most ranges of temperature and residual resistivity, say, up to about 1 $\mu\Omega$ cm, $\hat{P}_{\text{int}}$ contributes but little to $\Delta\rho$ and may be safely ignored. When one considers very large values of residual resistivity, one must include explicitly the contribution of $\hat{P}_{\text{int}}$ to $\Delta\rho$. However, for our present discussion, it is sufficient to assume that for a given electron scattering event, the total probability for scattering is given by the sum of the individual probabilities for scattering by phonons and by impurities.

To describe the phenomena associated with the DMR, we employ the variational formulation,[20] according to which ρ_{tot} is given in terms of matrix elements of the scattering operators

$$\rho_{\text{tot}} = \frac{\langle \Phi | \hat{P}_{\text{tot}} | \Phi \rangle}{|\langle \Phi | X \rangle|^2} = \frac{\langle \Phi | \hat{P}_{\text{ph}} | \Phi \rangle + \langle \Phi | \hat{P}_{\text{imp}} | \Phi \rangle}{|\langle \Phi | X \rangle|^2} , \tag{2.3}$$

where X is the electric field term[20] and the function $\Phi(\vec{K})$ describes the deviation, caused by the electric field, of the electron distribution function $f(\vec{K})$ from its equilibrium value $f_0(\vec{K})$,

$$f(\vec{K}) = f_0(\vec{K}) - \Phi(\vec{K})[\partial f_0(\vec{K})/\partial E(\vec{K})] . \tag{2.4}$$

For much of the discussion, it is not necessary to know the exact form of the scattering matrix elements in (2.3). Nevertheless, to avoid the appearance of undue abstraction, we write down their explicit form. The procedure for reducing the scattering matrix elements of (2.3) to double surface integrals has been lucidly described by

Ziman,[20] leading to the following expressions:

$$\langle\phi|\hat{P}_{\text{ph}}|\phi\rangle = A\iint [dS(\vec{K}_1)/v(\vec{K}_1)][dS(\vec{K}_2)/v(\vec{K}_2)] \times[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2 \times\sum_{\lambda}\int d^3q\, P_{\text{ph}}^{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)\,, \tag{2.5}$$

$$\langle\Phi|\hat{P}_{\text{imp}}|\Phi\rangle = A\iint [dS(\vec{K}_1)/v(\vec{K}_1)][dS(\vec{K}_2)/v(\vec{K}_2)] \times[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2 P_{\text{imp}}(\vec{K}_1,\vec{K}_2), \tag{2.6}$$

$$\langle\Phi|X\rangle = B\int dS(\vec{K})\,\hat{v}(\vec{K})\Phi(\vec{K})\,, \tag{2.7}$$

where A and B are known[20] constants, $v(\vec{K})$ is the velocity of the electron in state $\vec{K}$, and the wave vectors $\vec{K}_1$ and $\vec{K}_2$ characterize the initial and final states, respectively, of the electron being scattered by an impurity or by a phonon of wave vector $\vec{q}$, polarization λ, and frequency $\omega_\lambda(\vec{q})$. The double surface integrals are to be evaluated over the true anisotropic Fermi surface of the polyvalent or noble metal. It should be noted that the transition probability for electron-phonon scattering $P_{\text{ph}}^{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$ contains the contributions both of normal scattering $(\vec{K}_2-\vec{K}_1=\vec{q})$ and of umklapp scattering $(\vec{K}_2-\vec{K}_1=\vec{q}+\vec{G}$, where $\vec{G}$ is a reciprocal-lattice vector). The transition probability for electron-impurity scattering $P_{\text{imp}}(\vec{K}_1,\vec{K}_2)$ is proportional to the (dilute) concentration of impurities and is temperature independent, whereas the transition probability for electron-phonon scattering $P_{\text{ph}}^{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$ depends strongly on the temperature through the phonon occupation numbers.

To facilitate the discussion, it is convenient to introduce the following notation:

$$\begin{aligned}\rho_i(\Phi) &\equiv \langle\Phi|\hat{P}_{\text{ph}}|\Phi\rangle/|\langle\Phi|X\rangle|^2\,,\\ \rho_0(\Phi) &\equiv \langle\Phi|\hat{P}_{\text{imp}}|\Phi\rangle/|\langle\Phi|X\rangle|^2\,.\end{aligned} \tag{2.8}$$

In this notation, (2.3) becomes

$$\rho_{\text{tot}} = \rho_i(\Phi)+\rho_0(\Phi)\,. \tag{2.9}$$

Moreover, we introduce the notation $\phi_{\text{ph}}(\vec{K})$ and $\phi_{\text{imp}}(\vec{K})$ for the solutions to the Boltzmann equation corresponding to the case of only electron-phonon scattering $(\hat{P}_{\text{imp}}=0)$ and of only electron-impurity scattering $(\hat{P}_{\text{ph}}=0)$, respectively. In this notation, the ideal resistivity ρ_i equals $\rho_i(\phi_{\text{ph}})$ and the residual resistivity ρ_0 equals $\rho_0(\phi_{\text{imp}})$. Note that the variational principle asserts that $\rho_i(\Phi)>\rho_i$ and that $\rho_0(\Phi)>\rho_0$; using the incorrect distribution function always increases the calculated resistivity. Combining (2.1), (2.8), and (2.9) leads to

$$\Delta\rho = \rho_{\text{tot}}-\rho_0 = \rho_i(\Phi)+\rho_0(\Phi)-\rho_0(\phi_{\text{imp}})\,. \tag{2.10}$$

Matthiessen's rule states that

$$\Delta\rho = \rho_i = \rho_i(\phi_{\text{ph}})\,. \tag{2.11}$$

The condition for the validity of Matthiessen's rule is readily seen to be that $\phi_{\text{ph}}(\vec{K})\propto\phi_{\text{imp}}(\vec{K})$. If these two functions are proportional to each other, then the solution $\Phi(\vec{K})$ of the Boltzmann equation must satisfy $\Phi(\vec{K})\propto\phi_{\text{ph}}(\vec{K})\propto\phi_{\text{imp}}(\vec{K})$, and it immediately follows that the general result (2.10) reduces to (2.11). In general, however, $\phi_{\text{ph}}(\vec{K})$ is not proportional to $\phi_{\text{imp}}(\vec{K})$ and then DMR are present.

We now evaluate (2.10) for the two limiting cases. For very large ρ_0, we shall soon see that $\Phi(\vec{K})\to\phi_{\text{imp}}(\vec{K})$, implying that the last two terms of (2.10) cancel. For very small ρ_0, both terms are negligible compared with $\rho_i(\Phi)$. Since the last two terms of (2.10) cancel for large ρ_0 and are negligible for small ρ_0, it is adequate for the purpose of our discussion to ignore these two terms for all ρ_0. This leads to the key result

$$\Delta\rho \simeq \rho_i(\Phi)\,. \tag{2.12}$$

In the presence of both electron-phonon scattering and electron-impurity scattering, the functional form of the exact $\Phi(\vec{K})$ depends on the relative probabilities for electron-phonon scattering and for electron-impurity scattering. For a given probability of electron-phonon scattering, i.e., for a given temperature, the function $\Phi(\vec{K})$ depends on the probability of electron-impurity scattering, i.e., on c, the concentration of impurities and/or lattice imperfections. Therefore, it follows that at a fixed temperature, the function $\Phi(\vec{K})$ changes as c changes. However, since ρ_0 is proportional to c, a dependence on c is equivalent to a dependence on ρ_0. Thus, the form of the function $\Phi(\vec{K})$ depends on the value of ρ_0. According to (2.12), this dependence of $\Phi(\vec{K})$ on ρ_0 leads to a dependence of $\Delta\rho$ on ρ_0. Indeed, the large observed DMR, i.e., the marked dependence of $\Delta\rho$ on ρ_0 at low temperatures, can be accounted for almost completely in terms of the dependence of $\Phi(\vec{K})$ on ρ_0. This idea will be developed in detail in the next section.

III. DEVIATIONS FROM MATTHIESSEN'S RULE

Although the exact functional form of $\Phi(\vec{K})$ is unknown for arbitrary values of ρ_0, one can nevertheless arrive at important conclusions from general considerations. Consider a series of samples, all at a fixed temperature but with each sample having a different concentration of impurities, i.e., a different value of ρ_0. As one takes samples with progressively larger values of ρ_0, electron-impurity scattering increases until it completely dominates electron-phonon scattering. When this limit is reached, $\Phi(\vec{K})$ is determined solely by electron-impurity scattering. In other words, in the limit of large ρ_0, $\Phi(\vec{K})$ approaches the exact solution to the Boltzmann equation in the presence of electron-impurity scattering only. Thus, we have that $\Phi(\vec{K}) \rightarrow \phi_{\text{imp}}(\vec{K})$ for very large ρ_0. One may call this the "dirty limit." We now make the analogous argument for samples in the "pure limit," defined as the limit of vanishingly small values of ρ_0. Thus, we have that for sufficiently small ρ_0, $\Phi(\vec{K})$ approaches $\phi_{\text{ph}}(\vec{K})$, the exact solution to the Boltzmann equation in the presence of electron-phonon scattering only. Combining these results, one obtains that for fixed temperature, as ρ_0 increases from the pure limit (vanishingly small ρ_0) to the dirty limit (very large ρ_0), $\Phi(\vec{K})$ varies from $\phi_{\text{ph}}(\vec{K})$ to $\phi_{\text{imp}}(\vec{K})$. This shows how the functional form of $\Phi(\vec{K})$ depends on the value of ρ_0. Note that once a sample is within the pure limit or within the dirty limit, the functional form of $\Phi(\vec{K})$ no longer varies with ρ_0, but rather remains $\phi_{\text{ph}}(\vec{K})$ or $\phi_{\text{imp}}(\vec{K})$, respectively.

To relate these results to the DMR, i.e., to the calculation of $\Delta\rho$ as a function of ρ_0, one refers to Eq. (2.12), which gives the expression for $\Delta\rho$. In the dirty limit, one has $\Phi(\vec{K}) = \phi_{\text{imp}}(\vec{K})$, implying that $(\Delta\rho)_{\text{dirty}} = \rho_i(\phi_{\text{imp}})$. Similarly, in the pure limit, one has $\Phi(\vec{K}) = \phi_{\text{ph}}(\vec{K})$, implying that $(\Delta\rho)_{\text{pure}} = \rho_i(\phi_{\text{ph}})$. Thus, as ρ_0 increases from very small values to very large values, $\Delta\rho$ increases monotonically from $\rho_i(\phi_{\text{ph}})$ to $\rho_i(\phi_{\text{imp}})$. The fact that $\Delta\rho$ increases as a function of ρ_0 follows directly from applying the variational principle to (2.12). The variational principle states[20] that $\rho_i(\Phi) > \rho_i(\phi_{\text{ph}})$ for any $\Phi(\vec{K})$, including $\phi_{\text{imp}}(\vec{K})$. Thus $(\Delta\rho)_{\text{dirty}}$ must be larger than $(\Delta\rho)_{\text{pure}}$.

It is useful to illustrate these ideas by means of a graph. In Fig. 1, we plot schematically $\Delta\rho$ as a function of ρ_0 on a logarithmic scale for fixed temperature, based on (2.12). If Matthiessen's rule were valid, then $\Delta\rho$ would be independent of ρ_0, as indicated in the figure by the horizontal dashed line labeled "Matthiessen's rule." However, since Matthiessen's rule is not valid, $\Delta\rho$ increases as the value of ρ_0 increases. The values for $\Delta\rho$ in the pure limit and in the dirty limit are indicated in the figure. Note that in the dirty limit, $\Delta\rho$ exhibits Matthiessen-rule-like behavior in that $\Delta\rho$ is independent of ρ_0. We shall defer discussion of the importance of this last result until Sec. IV.

The above analysis establishes that the general behavior of $\Delta\rho$ is as given in Fig. 1. However, an important aspect of any discussion of the DMR concerns their magnitude. The magnitude of the DMR may be characterized quantitatively by the expression

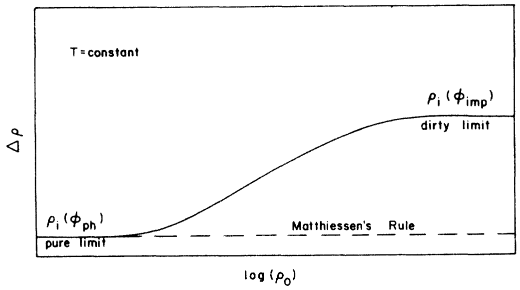

FIG. 1. Schematic plot of $\Delta\rho$ as a function of $\log(\rho_0)$ for constant temperature. The dashed horizontal line depicts the constant value of $\Delta\rho$ that would be obtained if Matthiessen's rule were valid. The solid curve depicts the increase in $\Delta\rho$ from the small-ρ_0 (pure) limit to the large-ρ_0 (dirty) limit. The theoretical expression for $\Delta\rho$ is given for each limit.

$$R(\text{DMR}) = \frac{(\Delta\rho)_{\text{dirty}}}{(\Delta\rho)_{\text{pure}}} - 1 = \frac{\rho_i(\phi_{\text{imp}})}{\rho_i(\phi_{\text{ph}})} - 1 , \tag{3.1}$$

where the last equality is based on (2.12). The unity has been subtracted to insure that $R(\text{DMR})$ vanishes when there are no DMR. The calculation of $R(\text{DMR})$ thus reduces to comparing the relative magnitudes of $\rho_i(\phi_{\text{imp}})$ and $\rho_i(\phi_{\text{ph}})$. A large value of $R(\text{DMR})$ results if $\rho_i(\phi_{\text{imp}})$ is much larger than $\rho_i(\phi_{\text{ph}})$. To investigate $R(\text{DMR})$ for the polyvalent and noble metals at low temperatures, one examines $\rho_i(\phi_{\text{imp}})$. For concreteness, one may write the approximate expression

$$\phi_{\text{imp}}(\vec{K}) \propto \vec{v}(\vec{K}) \cdot \vec{E} , \tag{3.2}$$

where $\vec{v}(\vec{K})$ is the velocity of the electron in state $\vec{K}$ and $\vec{E}$ is the applied electric field. The important point is that $\phi_{\text{imp}}(\vec{K})$ is almost isotropic over the Fermi surface, except of course for the dependence on the electric field direction. Therefore, in the dirty limit, one obtains at once from the near isotropy of $\phi_{\text{imp}}(\vec{K})$ that *all* electrons contribute to $\rho_i(\phi_{\text{imp}})$.

The importance of this result lies in the fact that, at low temperatures, almost the entire contribution to $\rho_i(\phi_{\text{imp}})$ arises from the vicinity of the intersections of the Fermi surface and the Brillouin-zone boundaries. In Fig. 2, we depict a totally schematic plot of the Fermi surface of a polyvalent metal containing its principal feature, namely, that the Fermi surface (solid curves) intersects the Brillouin-zone boundaries (dashed lines) which are a distance G apart, where G is the magnitude of the relevant reciprocal-lattice vector. The shaded portions correspond to the vicinity of the intersections of the Fermi surface and the Brillouin-zone boundaries; these portions of the Fermi surface shall be denoted collectively as the

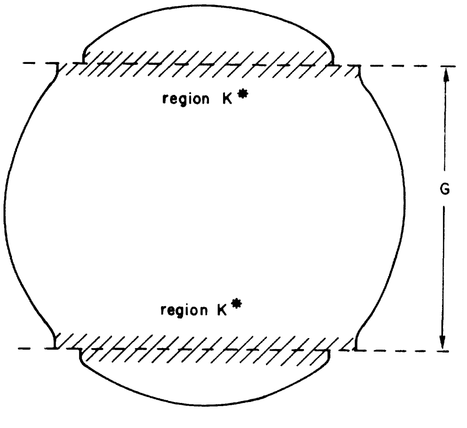

FIG. 2. Schematic plot of a cross section of the Fermi surface of a polyvalent metal, showing the intersections between the Fermi surface (solid curves) and the Brillouin-zone boundaries (dashed lines), which are separated by a reciprocal-lattice vector G. The hatched regions K^* denote those portions of the Fermi surface near the Brillouin-zone boundaries.

region K^*. The region K^* has the crucial property that when both initial electron state $\vec{K}_1$ and final electron state $\vec{K}_2$ lie in region K^*, then the electron-phonon scattering probability is enormously enhanced, by orders of magnitude at low temperatures, over its value when $\vec{K}_1$ and $\vec{K}_2$ lie elsewhere on the Fermi surface. This enhancement occurs both for umklapp scattering ($\vec{K}_2 - \vec{K}_1 = \vec{q} + \vec{G}$) and for normal scattering ($\vec{K}_2 - \vec{K}_1 = \vec{q}$).

For umklapp scattering, geometrical considerations show that only for both $\vec{K}_1$ and $\vec{K}_2$ in region K^* can the value of $|\vec{q}|$ be very small. The phonon occupation numbers in the integrand of $\rho_i(\phi_{\text{imp}})$ lead to exponentials of the form $\exp[-\hbar\omega_\lambda(\vec{q})/k_B T]$. At low temperatures, unless $|\vec{q}|$ is very small, such exponentials are totally negligible. Therefore, only for both $\vec{K}_1$ and $\vec{K}_2$ in the region K^* will there be a non-negligible contribution to the umklapp-scattering term $\rho_i^U(\phi_{\text{imp}})$.

For the normal-scattering term $\rho_i^N(\phi_{\text{imp}})$, the above discussion does not apply, because everywhere on the Fermi surface, normal-scattering processes are possible with arbitrarily small $|\vec{q}|$. Nevertheless, $\rho_i^N(\phi_{\text{imp}})$ is also enormously enhanced when both $\vec{K}_1$ and $\vec{K}_2$ lie in region K^*. The two sources of enhancement will be summarized here and discussed in detail in Sec. VI. Both sources of enhancement of $\rho_i^N(\phi_{\text{imp}})$ stem from the fact that for $\vec{K}$ in region K^*, the electron pseudo-wave-function must be represented by a linear combination of at least two plane waves,[22] whereas for $\vec{K}$ elsewhere on the Fermi surface, a single-plane-wave pseudo-wave-function is sufficient. The first large enhancement (two orders of magnitude for Al) of $\rho_i^N(\phi_{\text{imp}})$ arises from the factor $[\phi_{\text{imp}}(\vec{K}_1) - \phi_{\text{imp}}(\vec{K}_2)]^2$ in the integrand of Eq. (2.5). The second large enhancement (one order of magnitude for Al) of $\rho_i^N(\phi_{\text{imp}})$ arises from scattering by transverse phonons. Only for $\vec{K}_1$ and $\vec{K}_2$ in region K^*, where a two-plane-wave pseudo-wave-function is required, do the transverse phonons scatter electrons in normal processes. Since $\omega_T(\vec{q})$ is much smaller than $\omega_L(\vec{q})$ for small $|\vec{q}|$, there is a large enhancement of $\rho_i^N(\phi_{\text{imp}})$.

In summary, for both $\rho_i^U(\phi_{\text{imp}})$ and $\rho_i^N(\phi_{\text{imp}})$, the dominant contribution to the resistivity integrals occurs for both $\vec{K}_1$ and $\vec{K}_2$ lying in the region K^* of strong electron-phonon scattering.

Thus far, we have been discussing the dirty limit, for which $\Phi(\vec{K}) \to \phi_{\text{imp}}(\vec{K})$. Let us now turn to the pure limit, for which electron-impurity scattering is very small and it is electron-phonon scattering that determines the electron distribution function. Since the probability for electron-phonon scattering (both normal and umklapp) is enormously enhanced by orders of magnitude for $\vec{K}_1$ and $\vec{K}_2$ in region K^*, the electrons in this region are rapidly scattered back to their thermal-equilibrium distribution via electron-phonon scattering. In other words, $\phi_{\text{ph}}(\vec{K})$ must vanish for $\vec{K}$ in region K^*. These considerations show that $\phi_{\text{ph}}(\vec{K})$ must closely resemble the following form:

$$\begin{aligned} &\phi_{\text{ph}}(\vec{K}) \simeq 0 \quad \text{for } \vec{K} \text{ in region } K^*, \\ &\phi_{\text{ph}}(\vec{K}) \simeq \phi_{\text{imp}}(\vec{K}) \quad \text{for } \vec{K} \text{ not in region } K^*. \end{aligned} \tag{3.3}$$

Of course, expression (3.3) for $\phi_{\text{ph}}(\vec{K})$ is not the only possible choice. Indeed, it is not difficult to construct other forms[9,21] for $\phi_{\text{ph}}(\vec{K})$ which do not have the aesthetic defect of being a discontinuous function of $\vec{K}$. The only important requirement of a suitable $\phi_{\text{ph}}(\vec{K})$ for the pure limit is that the function be negligible in the strong-scattering region K^* and be almost unchanged from $\phi_{\text{imp}}(\vec{K})$ elsewhere on the Fermi surface.

If one inserts the $\phi_{\text{ph}}(\vec{K})$ given by (3.3) into $\rho_i(\phi_{\text{ph}})$, it is clear that the resulting value of $\Delta\rho$ will be very much reduced from $\rho_i(\phi_{\text{imp}})$. The region K^*, which made the dominant contribution to $\rho_i(\phi_{\text{imp}})$, does not contribute at all in the pure limit. Since the magnitude of R(DMR) is basically the ratio $\rho_i(\phi_{\text{imp}})/\rho_i(\phi_{\text{ph}})$, according to (3.1), and since $\rho_i(\phi_{\text{ph}})$ is very much smaller than $\rho_i(\phi_{\text{imp}})$, one obtains large DMR. This is the basic reason for the existence of large DMR for the polyvalent and noble metals at low temperatures.

The choice (3.3) for $\phi_{\text{ph}}(\vec{K})$ was justified above on physical grounds. However, it is instructive also to justify (3.3) on mathematical grounds by appealing to the variational theorem. The variational theorem asserts[20] that the exact $\phi_{\text{ph}}(\vec{K})$ is that function $\Phi(\vec{K})$ that minimizes $\rho_i(\Phi) = \langle\Phi|\hat{P}_{ph}|\Phi\rangle / |\langle\Phi|X\rangle|^2$ of Eqs. (2.5) and (2.7). Thus, one may construct a good approximation to $\phi_{ph}(\vec{K})$ *solely* on its ability to reduce $\rho_i(\Phi)$. A function $\Phi(\vec{K})$ that drastically reduces $\rho_i(\Phi)$ is automatically a good candidate for $\phi_{ph}(\vec{K})$. It has already been emphasized that at low temperatures, almost the entire contribution to the integral of Eq. (2.5) arises from the region K^*. This implies that eliminating the small region K^* from the integral will drastically reduce $\rho_i(\Phi)$. The functional form given by (3.3) has precisely this desired property of vanishing in the region K^*, and thus must be a good approximation to $\phi_{ph}(\vec{K})$ according to the requirement of the variational theorem.

It is satisfying that the same functional form for $\phi_{ph}(\vec{K})$, given by (3.3), is dictated both by physical requirements [vanishingly small $\phi_{ph}(K)$ in the region of extremely strong electron-phonon scattering] and by mathematical requirements [$\phi_{ph}(\vec{K})$ minimizes $\rho_i(\Phi)$]. In Sec. V, it will be shown that this approximate function for $\phi_{ph}(\vec{K})$ can be used to explain a number of experimental findings associated with the DMR.

IV. LARGE-ρ_0 BEHAVIOR OF $\Delta\rho$

The theoretical picture presented thus far leads to saturation for $\Delta\rho$, i.e., for large values of ρ_0, $\Delta\rho$ is predicted to approach its dirty-limit value $\rho_i(\phi_{imp})$ and become independent of ρ_0. The data are not in accord with this prediction. Although the results vary somewhat for different metals, the extensive data[1] for Al at 20 K are typical. Whereas our calculation[9,21] predicts the onset of saturation for $\Delta\rho$ at $\rho_0 \simeq 1000$ nΩ cm, the large-ρ_0 data[1,2,23,24] show that $\Delta\rho$ continues to increase with increasing ρ_0 up to 11 $\mu\Omega$ cm, the highest measured value.

This discrepancy with experiment results from the neglect thus far of the interference term $\hat{P}_{int}$. Denote by $\Delta\rho_{int}$ the contribution to $\Delta\rho$ arising from $\hat{P}_{int}$. As long as one considers values of ρ_0 below about 1 $\mu\Omega$ cm, it is justified to neglect $\Delta\rho_{int}$. However, for ρ_0 in the $\mu\Omega$ cm-range, the contribution of $\Delta\rho_{int}$ to $\Delta\rho$ is no longer negligible and must be included.

There is another important reason for the need to include $\Delta\rho_{int}$ at large ρ_0. For temperatures below $\Theta_D/20$, the dirty limit occurs for $\rho_0 < 1$ $\mu\Omega$ cm. Therefore, for low temperatures, if one neglects $\Delta\rho_{int}$, the values for $\Delta\rho$ saturate at large ρ_0 and $\Delta\rho$ no longer increases with increasing ρ_0. As a result, $\Delta\rho_{int}$ is the *only* contribution to the increase in $\Delta\rho$ when ρ_0 is in the $\mu\Omega$ cm-range. Hence, it is not possible to explain the large-ρ_0 data for $\Delta\rho$ without taking $\Delta\rho_{int}$ into account.

The quantitative theory of $\Delta\rho_{int}$ for polyvalent and noble metals, based on the pioneering work of Kagan and Zhernov,[25] will be presented in the following paper.[21] However, we briefly summarize here the results for the ρ_0 dependence and the magnitude of $\Delta\rho_{int}$. For the alloys under consideration, $\Delta\rho_{int}$ is proportional to the concentration of impurities. As pointed out earlier, this is equivalent to $\Delta\rho_{int}$ being proportional to ρ_0, since ρ_0 is proportional to the concentration of impurities. The magnitude of $\Delta\rho_{int}$ varies with the type of impurity, but is of the order of 10–50% of $\Delta\rho$ at $\rho_0 \simeq 10$ $\mu\Omega$ cm.

To see how the inclusion of $\Delta\rho_{int}$ alters Fig. 1, it is necessary first to discuss the dirty limit in some more detail. Denote by $(\rho_0)_{dirty}$ the value of ρ_0 which marks the onset of the dirty limit. The value of $(\rho_0)_{dirty}$ is a strong function of temperature, because the dirty limit refers to values of ρ_0 much larger than $\rho_i(\phi_{imp})$, and $\rho_i(\phi_{imp})$ in turn is a strong function of temperature. For concreteness, consider the case of Al. One obtains by direct calculation[9,21] that $(\rho_0)_{dirty} \simeq 10^3$ nΩ cm for $T = 20$ K $= \Theta_D/20$.

We now include the contribution due to $\Delta\rho_{int}$. Since $\Delta\rho_{int}$ ceases to be negligible at about $\rho_0 \simeq 1$ $\mu\Omega$ cm, one has that $\Delta\rho_{int}$ begins to contribute precisely at the onset of the saturation region of Fig. 1. Thus, for Al at $T = \Theta_D/20$, the effect of $\Delta\rho_{int}$ is to eliminate entirely the saturation region, with $\Delta\rho$ continuing to increase as a function of ρ_0. These results are plotted schematically in Fig. 3. For $\rho_0 \lesssim 10^3$ nΩ cm, the curve for $\Delta\rho$ is unchanged from Fig. 1. In discussing the additional contribution of $\Delta\rho_{int}$ in the large-ρ_0 region, recall that the abscissa is traditionally taken as $\log(\rho_0)$, rather than ρ_0, to indicate the slow increase of $\Delta\rho$ with ρ_0. Since $\Delta\rho_{int} \propto \rho_0$, the additional term $\Delta\rho_{int}$ increases rapidly on a $\log(\rho_0)$ scale, reaching a magnitude of about 20–40% of $\Delta\rho$ at $\rho_0 \simeq 10$ $\mu\Omega$ cm. It should be emphasized that the magnitude of $\Delta\rho_{int}$ depends strongly on the type of impurity, varying by as much as a factor of 2. This is indicated by the hatched area in Fig. 3.

To see how Fig. 3 compares with experiment, it is instructive to replace the theoretical curve for $\Delta\rho$ beyond the pure limit ($\rho_0 > 1$ nΩ cm) with simulated "experimental" data points. The simulated experimental data points are obtained by adding to the theoretical values for $\Delta\rho - \rho_i$ a random scatter corresponding to a maximum deviation of ±20%. Such a scatter is a quite reasonable description of the expected dependence of $\Delta\rho$ on the type of impurity. That is, for a given value of ρ_0, the value of $\Delta\rho - \rho_i$ will vary by up to ±20% for different samples having different types of impurities present. These simulated points are plotted in Fig. 4.

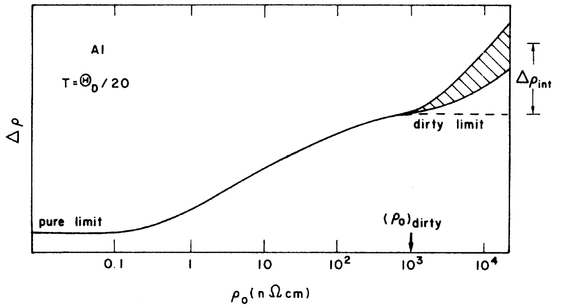

FIG. 3. Semilog plot of $\Delta\rho$ for Al as a function of ρ_0 for $T=\Theta_D/20$, including the contribution of the interference term $\Delta\rho_{\text{int}}$. The onset of the dirty limit is denoted by $(\rho_0)_{\text{dirty}}$, which for this temperature occurs just about where $\Delta\rho_{\text{int}}$ begins to contribute to $\Delta\rho$. The values for $\Delta\rho_{\text{int}}$ are uncertain to about a factor of 2 because of the dependence of $\Delta\rho_{\text{int}}$ on the type of impurity present. This is indicated by the hatched area. The dashed line denotes the values of $\Delta\rho$ without taking $\Delta\rho_{\text{int}}$ into account.

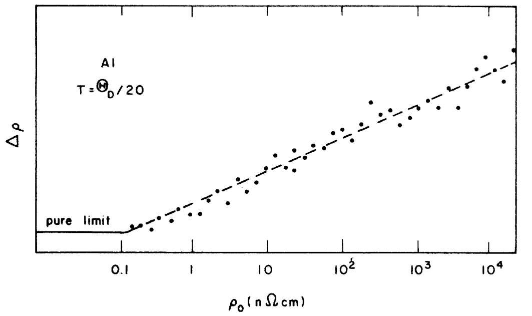

FIG. 4. Semilog plot of $\Delta\rho$ for Al as a function of ρ_0 for $T=\Theta_D/20$. The points are simulated "experimental" points, which are related to the theoretical curve as described in the text. The dashed line is a smooth empirical fit to the points, showing apparent straight-line behavior.

If one wishes to fit the experimental data points of Fig. 4 to an empirical curve, it is quite natural to try a straight line. Indeed, the points fit the straight line quite nicely, as shown by the dashed curve in Fig. 4. The fit is, in fact, so good that it is not hard to understand why such straight-line fits to the $\Delta\rho$-vs-$\log(\rho_0)$ data have become a common procedure.[2] However, the above analysis shows that the experimental data are really derived from the curve in Fig. 3, and are unrelated to a straight line. Moreover, the curve in Fig. 3 has a sound theoretical foundation, whereas the various attempts to justify theoretically a straight-line fit to the data have all been refuted.[1,6,26-28]

The above discussion dealt with temperatures for which $(\rho_0)_{\text{dirty}} \simeq 1\ \mu\Omega\,\text{cm}$ ($T=\Theta_D/20$ for Al). In discussing other temperatures, it is natural to focus attention on the experimentally accessible range $10^{-1} < \rho_0 < 10^4\ \text{n}\Omega\,\text{cm}$. It has not proved possible to prepare samples having values of ρ_0 significantly outside this range. For higher temperatures, $(\rho_0)_{\text{dirty}}$ increases rapidly until it reaches values larger than $10^4\ \text{n}\Omega\,\text{cm}$. Thus, for higher temperatures, the dirty limit is not experimentally accessible. Hence, even the $\mu\Omega\,\text{cm}$ range of ρ_0, where $\Delta\rho_{\text{int}}$ is no longer negligible, lies within the transition region of ρ_0 between the pure limit and the dirty limit. However, within the transition region, the increase of $\Delta\rho$ aside from $\Delta\rho_{\text{int}}$ is much larger than the contribution due to $\Delta\rho_{\text{int}}$. Therefore, including $\Delta\rho_{\text{int}}$ at higher temperatures does not qualitatively change Fig. 1, even for ρ_0 in the $\mu\Omega\,\text{cm}$ range. The dirty limit is simply never reached experimentally and $\Delta\rho$ always increases even without the contribution of $\Delta\rho_{\text{int}}$.

Of greater interest is the low-temperature regime. For low temperatures, the dirty limit is already reached for quite low values of ρ_0 and it is the pure limit that is never reached experimentally. For example, for Al at 4 K, one finds by direct calculation[9,21] that $(\rho_0)_{\text{dirty}} \simeq 1\ \text{n}\Omega\,\text{cm}$. Recall that $\Delta\rho_{\text{int}}$ is negligible below $\rho_0 \simeq 10^3\ \text{n}\Omega\,\text{cm}$. Therefore, at 4 K for Al, Fig. 1 is unchanged by the presence of $(\Delta\rho)_{\text{int}}$, inasmuch as $\rho_0 = 10^3\ \text{n}\Omega\,\text{cm}$ is off the scale of the figure. As a result, for ρ_0 in the range 1–1000 $\text{n}\Omega\,\text{cm}$, one would expect to find saturation for $\Delta\rho$, that is, no increase in $\Delta\rho$ with increasing ρ_0. This is indeed what the 4-K data[2] for Al show. For $\rho_0 > 1\ \text{n}\Omega\,\text{cm}$, the data for $\Delta\rho$ are constant to within experimental error over two decades of ρ_0, up to the largest measured values of ρ_0. This result is in complete accord with Fig. 1. Experimental evidence for saturation for Ga, with $(\rho_0)_{\text{dirty}} \simeq 20\ \text{n}\Omega\,\text{cm}$, has recently been reported[29] for single-crystal samples of Ga at $T=4.2$ K. These results for Ga are also in accord with Fig. 1.

We close this section by pointing out that not every metal fits the picture presented here as nicely as do Al and Ga. Barber and Caplin[30] have emphasized that their data for $\Delta\rho$ for Ag at 4.2 K do not exhibit saturation even for the range of ρ_0 where the above considerations would suggest that saturation should occur. It therefore follows that for Ag, there are additional contributions to the DMR than those considered here. The theory of the low-temperature DMR for Ag will be the subject of a separate publication.[31]

V. DISCUSSION OF EXPERIMENTAL FINDINGS

A. Variation of DMR from metal to metal

The magnitude of the DMR are observed to vary significantly for different classes of metals for a given reduced temperature T/Θ_D, where Θ_D is the

Debye temperature of the metal in question. Consider the following four examples: typical polyvalent metal (Al), typical noble metal (Cu), K, and Li. In Table I, we list the experimental values[1,2] for R(DMR) for these four metals at the reduced temperature $T=\Theta_D/20$. For those metals for which $\Delta\rho$ has not saturated in the large-ρ_0 region, because of the presence of $\Delta\rho_{\rm int}$, we take $\rho_0 \simeq 10^3$ nΩ cm to be a rough estimate for the onset of the dirty limit.

The large value of about 5-6 for R(DMR) for Al may be viewed as the standard for comparison. The comparable value of about 3–4 for Cu is expected because the same arguments that apply to Al apply also to Cu. For both metals, the Fermi surface intersects the Brillouin-zone boundaries, and that is sufficient for the applicability of the arguments that predict large DMR.

Now consider K. There is no intersection between the spherical Fermi surface and the Brillouin-zone boundaries, and hence no region of strong electron-phonon scattering. Of course, the electron-phonon scattering probability is still anisotropic. However, the absence of a well-localized, strong-scattering region of the Fermi surface implies that R(DMR) must be relatively small, in accord with experiment.

In fact, the contrast between K on the one hand and the polyvalent and noble metals on the other hand is even greater than that shown by the values of R(DMR) given in Table I, for the following reason. There exists a small contribution to R(DMR) that arises from the energy dependence[32-37] of $\phi_{\rm ph}(\vec{K})$, an effect not considered in the present paper because of its small magnitude. The energy dependence of $\phi_{\rm ph}(\vec{K})$ contributes[32] about 0.2 to R(DMR) for K and a comparable value[37] for Al and Cu. Therefore, it is instructive to compare for various metals the values of a "reduced" R(DMR), by which one means the value for R(DMR) that arises solely from the angular dependent of $\phi_{\rm ph}(\vec{K})$, without the contribution due to the energy dependence of $\phi_{\rm ph}(\vec{K})$. To obtain the values for the reduced R(DMR) of Al, Cu, and K, one simply subtracts ~0.2 from the values given in the first line of Table I. It is clear that this subtraction has a negligible effect for Al and Cu, whereas for K, the reduced R(DMR) has the extremely small value of ~0.1. The dramatic contrast between the values of the reduced R(DMR) at $T=\Theta_D/20$ for K (~0.1) and for the polyvalent and noble metals (~3–6) finds a natural explanation in terms of the absence (for K) or the presence (for Al and Cu) of a well-localized region on the Fermi surface of extremely strong electron-phonon scattering.

TABLE I. Values for R(DMR) and "reduced" R(DMR) for different metals at the temperature $T=\Theta_D/20$.

Metal	Al	Cu	K	Li
R(DMR)	~5–6	~3–4	~0.3	~1
"reduced" R(DMR)	~5–6	~3–4	~0.1	

Now consider the intermediate case of Li. The value[35,36] for R(DMR) is several times larger than for K but several times smaller than for the polyvalent and noble metals. As with the case of K, the Fermi surface of Li is very nearly spherical, with no special region K^*, and hence one might expect very small DMR. However, Li has a relatively large value[38] for $w(2k_F)$, where $w(k)$ is the electron-ion pseudopotential matrix element. This leads to a very large contribution to $\rho_i(\phi_{\rm imp})$ for the vicinity of the [110] direction. This direction thus plays a role analogous to the strong-scattering region K^*. Although the effect is of course weaker than for the polyvalent and noble metals, direct calculation[35,36] for Li shows that the effect is sufficiently strong to lead to R(DMR)$\simeq 1$ for Li. By contrast, K has a much smaller value[38] of $w(2k_F)$. It is this difference between Li and K that causes the DMR to be significantly larger for Li than for K.

B. Approximate log(ρ_0) dependence of $\Delta\rho$

For a given temperature, the data[1,2] for $\Delta\rho$ appear to exhibit a log(ρ_0) dependence over a large range of ρ_0. More precisely, $\Delta\rho$ increases very slowly with increasing ρ_0, such that a log(ρ_0) dependence fits the data well. This result follows from the fact that $\Delta\rho$ varies with ρ_0 because of the dependence of $\Phi(\vec{K})$ on ρ_0. Moreover, the variation of $\Phi(\vec{K})$ with ρ_0 is very slow. For $\Phi(\vec{K})$ to vary from the small-ρ_0 limiting expression of $\phi_{\rm ph}(\vec{K})$ to the large-ρ_0 limiting expression of $\phi_{\rm imp}(\vec{K})$, the value of ρ_0 must increase from $\rho_0 \ll \rho_i(\phi_{\rm ph})$ to $\rho_0 \gg \rho_i(\phi_{\rm imp})$. Taking much smaller or larger to imply an order of magnitude smaller or larger gives two orders of magnitude, and recalling that $\rho_i(\phi_{\rm imp})$ is several times larger than $\rho_i(\phi_{\rm ph})$ gives nearly an additional order of magnitude.

Thus one has that $\Delta\rho$ is independent of ρ_0 for very small ρ_0 and requires about a three-order-of-magnitude increase in ρ_0 to go from the small-ρ_0 limit to the large-ρ_0 limit. Such behavior for $\Delta\rho$ implies a very slow increase with increasing ρ_0, closely resembling a log(ρ_0) dependence over a wide range of ρ_0, as is observed. Moreover, for ρ_0 in the $\mu\Omega$ cm-range, the values for $\Delta\rho$ continue to increase, even in the dirty limit, because of the contribution of $\Delta\rho_{\rm int}$, as explained in Sec.

IV. As a result, $\Delta\rho$ increases as approximately $\log(\rho_0)$ over about five decades of ρ_0.

C. Universal curve for $\Delta\rho$ vs ρ_0, independent of type of impurity

For a given temperature and given ρ_0, the measured dependence of $\Delta\rho$ on the type of impurity present is generally quite weak,[1,2] hardly beyond the experimental scatter of the data. Therefore, to good approximation, the data for $\Delta\rho$ as a function of ρ_0 can be plotted on a universal curve, independent of the type of impurity that gives rise to ρ_0. This can be understood by recalling that $\Delta\rho = \rho_i(\Phi)$ and that $\rho_i(\Phi)$ depends on ρ_0 because $\Phi(\vec{K})$ varies with ρ_0. However, once the sample corresponds to either the pure limit or the dirty limit, $\Phi(\vec{K})$ equals either $\phi_{ph}(\vec{K})$ or $\phi_{imp}(\vec{K})$, respectively, and no longer depends on electron-impurity scattering. Since $\Delta\rho$ is completely independent of the type of impurity both in the pure limit ($\Delta\rho \ll \rho_0$) and in the dirty limit ($\Delta\rho \gg \rho_0$), it is not surprising to find only a weak dependence for $\Delta\rho$ on the type of impurity in the intermediate region ($\Delta\rho \simeq \rho_0$). Direct calculation[21] shows that the dependence of $\Delta\rho$ on the type of impurity does not generally exceed ±20%.

This estimate of ±20% applies also to the $\mu\Omega$ cm range of ρ_0 where $\Delta\rho_{int}$ is important. The variation of $\Delta\rho_{int}$ with type of impurity is much larger than for the other contribution to $\Delta\rho$, being about 50–100% for polyvalent metals.[21] However, since $\Delta\rho_{int}$ itself is only about 20–40% of the total $\Delta\rho$, a 50–100% variation in $\Delta\rho_{int}$ with type of impurity corresponds to only about a 20% variation in the total $\Delta\rho$. Therefore, for all ranges of ρ_0, the values for $\Delta\rho$ should fit reasonably well (±20%) on a universal curve of ρ_0, in accord with the data.

Although the existence of universal curves for $\Delta\rho$ vs ρ_0 is well established experimentally,[1,2] there are certain exceptions that should be mentioned. The data[1] for thin-film samples, for which ρ_0 is caused primarily by boundary scattering, do not fit on the universal curve for $\Delta\rho$. This is hardly surprising because the considerations which lead to the prediction of a universal curve for $\Delta\rho$ vs ρ_0 implicitly deal with bulk properties of the metal. Size effects are not considered here. However, even for bulk samples, there are exceptional metals. Barber and Caplin[30] found that for dilute alloys of Ag, significantly different values were obtained for $\Delta\rho$ for the same value of ρ_0 for samples containing different types of impurities. In particular, for a given value of ρ_0, Pd impurity in Ag yielded a much smaller value of $\Delta\rho$ than did Pt or Au impurity in Ag. This feature of the DMR exhibited by Ag is quite atypical and suggests that further experiments on dilute alloys of Ag containing different types of impurities should prove to be very instructive.

D. Temperature dependence of the DMR

The measured[1] temperature dependence of $\Delta\rho$ for Al for fixed ρ_0 is close to T^3. Apparently spurred on by this simple temperature dependence for Al, some of the earlier theories[1] of the DMR predicted that a T^3 dependence for $\Delta\rho$ was a general result for all metals. However, the more recent data show that each alloy system exhibits its own characteristic temperature dependence for $\Delta\rho$. The dependence may be integral powers other than 3 [e.g., Ag (Ref. 30), In (Ref. 39)], fractional powers (e.g., Mg, Cd),[40] or a temperature dependence that is not a power law at all. (e.g., Cu).[41]

Direct calculation[9,21] for Al does lead to a nearly-T^3 temperature dependence for $\Delta\rho$ over a wide range of temperature and of ρ_0, in accord with experiment. However, this result for Al is by no means general. For each metal, one must evaluate the integrals Eqs. (2.5)–(2.7) to obtain the numerical values for $\Delta\rho$. To a good approximation, the temperature dependence of both the normal-scattering term $\rho_N(T)$ and the umklapp-scattering term $\rho_U(T)$ follow power laws.[7,21] The absence of exponential temperature dependence for $\rho_U(T)$ at low temperature for polyvalent and noble metals, in contrast to the alkali metals, results of course from the intersections of the Fermi surface and the Brillouin-zone boundaries. These intersections imply that all phonons may participate in umklapp scattering, even those having $q \to 0$, which leads directly to power-law behavior.[7] However, the power-law behavior deduced for $\rho_U(T)$ and $\rho_N(T)$ does not imply that the temperature dependence of $\Delta\rho$ will also exhibit power-law behavior, for two reasons.

First, power-law behavior is found for $\rho_N(T)$ and $\rho_U(T)$ only if one assumes that the entire temperature dependence of the resistivity integral (2.5) arises from the temperature dependence of the transition probability for electron-phonon scattering $P_{ph}^{\vec{q}\lambda}(\vec{K}_1, \vec{K}_2; T)$, which contains the temperature-dependent phonon occupation numbers. This assumption is indeed appropriate to describe the dirty limit, for which $\Phi(\vec{K})$ is independent of temperature. However, for that range of temperature that spans the transition region, one has that $\Phi(\vec{K})$ varies from the dirty-limit value $\phi_{imp}(\vec{K})$ (low-temperature limit, for which $\Delta\rho \ll \rho_0$) to the pure-limit value $\phi_{ph}(\vec{K})$ (high-temperature limit, for which $\Delta\rho \gg \rho_0$). Thus, for temperatures in the transition region, $\Phi(\vec{K})$ also depends on temperature, and in a complex manner. As a result, the temperature dependence of the resistivity integral, (2.5), and of $\Delta\rho$, need not follow a simple power law. There is also a second reason for expecting a non-power-law temperature dependence for $\Delta\rho$. The power laws obeyed by $\rho_N(T)$ and $\rho_U(T)$ are not the same. Since the relative contribution of $\rho_N(T)$ and $\rho_U(T)$ to $\Delta\rho$ varies with temperature and with ρ_0, one can readily understand the non-power-law temperature behavior for the resultant $\Delta\rho$.

In summary, the theory predicts that there is no simple temperature dependence for $\Delta\rho$ that appears as a general feature of all metals. Therefore the theory is completely consistent with the data in that the temperature dependence of $\Delta\rho$ varies from metal to metal, in some cases being quite simple whereas for other cases being quite complex.

For all metals, the measured DMR decrease rapidly with increasing temperature. Already at 50 K, the value of R(DMR) for Al is much smaller than unity, reminiscent of K. This general experimental result is readily explained in terms of the electron-phonon transition probability. The dramatic effect of large R(DMR) at low temperatures occurs primarily because of the phonon occupation numbers, which contain exponentials of the form $\exp[-\hbar\omega_\lambda(\vec{q})/k_BT]$. At low temperatures, unless $|\vec{q}|$ is very small, such exponentials are negligible. However, at higher temperatures, even relatively large values of $|\vec{q}|$ yield a small argument $\hbar\omega_\lambda(\vec{q})/k_BT$, and hence, a sizable probability for electron-phonon scattering. Since large values of $|\vec{q}|$ are important, it follows that almost all portions of the Fermi surface contribute significantly to the resistivity integral (2.5). Therefore, at higher temperatures, the region K^* of strong electron-phonon scattering is no longer well localized to a small portion of the Fermi surface. As a result, the entire effect is weakened and R(DMR) is much reduced. In other words, at higher temperatures, Al behaves not much differently from K.

The measured DMR are commonly plotted[1,42] in terms of the quantity Δ, which is defined as follows:

$$\Delta \equiv \rho_{\text{tot}} - \rho_i - \rho_0 = \Delta\rho - \rho_i \,. \tag{5.1}$$

Thus, Δ gives a measure of the DMR and vanishes when the DMR vanish. A graph of Δ as a function of temperature for given ρ_0 invariably exhibits a maximum, called a "hump," at a specific temperature $T_{\max}$. Moreover, $T_{\max}$ varies with ρ_0. This phenomenon has been studied very extensively for Al, with detailed data[42] available for many different types of impurity.

The existence of a hump in Δ as a function of temperature can be related directly to the variation of $\Phi(\vec{K})$ with temperature for fixed ρ_0. Since $\Delta\rho$ decreases rapidly with decreasing temperature, for any given ρ_0, a low enough temperature corresponds to the dirty limit $\Delta\rho \ll \rho_0$. Similarly, for given ρ_0, sufficiently high temperatures correspond to the pure limit $\Delta\rho \gg \rho_0$. Thus, as the temperature increases for a given value of ρ_0, the sample passes from the dirty limit to the pure limit. It is precisely this passage of $\Phi(\vec{K})$ through the transition region from its dirty-limit value to its pure-limit value as the temperature increases that leads to the hump in Δ. Indeed, direct calculation[21] of Δ as a function of temperature agrees quantitatively with the data for Al.

Finally, it should be emphasized that the theory presented here is not limited to low temperatures and the associated large DMR. For higher temperatures as well, for which the DMR are very small, the integrals can be evaluated and the resistivity calculated. In this high-temperature regime, direct calculation of $\Delta\rho$ for Al leads to values in agreement with experiment. It is quite satisfying to find that the same theoretical framework and numerical calculations account both for the large DMR at low temperatures, as well as the temperature dependence of the resistivity at high temperatures.

VI. ROLE OF NORMAL SCATTERING

The analysis of the normal-scattering term $\rho_N(T)$ merits special consideration for the case of the polyvalent and noble metals. It is not generally appreciated how important is the role played by $\rho_N(T)$ for these metals. There are striking differences between $\rho_N(T)$ for the alkali metals on the one hand and for the polyvalent and noble metals on the other hand. In particular, the following assumptions regarding $\rho_N(T)$ are appropriate *only* to the alkali metals: (i) that the Bloch approximation $\rho_{\text{Bloch}}(T)$ is reasonable for $\rho_N(T)$ at low temperatures, at least to within a factor of 2 or 3, and (ii) that $\rho_N(T)$ makes only a negligible contribution to the DMR.

The facts are quite otherwise for the polyvalent and noble metals. Regarding the first assumption, we shall presently see that the calculated values for $\rho_N(T)$ at low temperatures are *orders of magnitude* larger than $\rho_{\text{Bloch}}(T)$. Moreover, whereas $\rho_{\text{Bloch}}(T)$ is negligible compared with $\rho_U(T)$ at all temperatures, the calculated values for $\rho_N(T)$ are comparable with $\rho_U(T)$ at low temperatures in the dirty limit and are much larger than $\rho_U(T)$ in the pure limit.[9,11,21] It follows from these results that no calculation of $\Delta\rho$ for the polyvalent and noble metals can be reliable unless the contribution of

$\rho_N(T)$ is properly taken into account. Regarding the second assumption, $\rho_N(T)$ in fact makes a very important contribution to the calculated DMR, given quantitatively by the ratio R(DMR) of Eq. (3.1). Indeed, if one were to ignore $\rho_U(T)$ altogether and only take $\rho_N(T)$ into account, one would still obtain a large value for R(DMR) at low temperatures for the polyvalent and noble metals.

To understand the reason for these results, consider the integrand of the resistivity integral (2.5). In particular, consider the factor $[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2$. It has been shown[43] that the expression $\vec{v}(\vec{K})\cdot\vec{E}$ is a good approximation for $\phi_{\text{imp}}(\vec{K})$, certainly sufficient for our purposes. Thus, in the dirty limit, one may use this expression for $\Phi(\vec{K})$ and exploit the cubic symmetry of the metal to average over the electric field direction $\hat{E}$. This yields

$$[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2=\tfrac{1}{3}[\vec{v}(\vec{K}_1)-\vec{v}(\vec{K}_2)]^2. \qquad (6.1)$$

When considering regions of the Fermi surface not in K^*, i.e., not near the intersections of the Fermi surface and the Brillouin-zone boundaries, then it is sufficient to take the single-plane-wave expression for $\vec{v}(\vec{K})$. Inserting $\vec{v}(\vec{K})=\hbar\vec{K}/m$ into (6.1) yields immediately, for normal scattering $(\vec{K}_2-\vec{K}_1=\vec{q})$,

$$[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2_{1\text{-pw}}=(\hbar^2/3m^2)q^2. \qquad (6.2)$$

On the other hand, when one considers $\vec{K}$ in the region K^*, a single plane wave is no longer an adequate representation for the pseudo-wave-function and one must use the appropriate linear combination of two plane waves.[22] Rather than writing down the general two-plane-wave expression for $\vec{v}(\vec{K})$ for arbitrary $\vec{K}$, we at once turn to the scattering events of greatest physical interest at low temperatures, namely, those for which both $\vec{K}_1$ and $\vec{K}_2$ lie in the region K^* and $|\vec{q}|$ is small. For this case, one obtains[22]

$$[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2_{2\text{-pw}}=(\hbar^2/3m^2)[\hbar^2G^2/4m\,|w(G)|]^2q^2, \qquad (6.3)$$

where G is the magnitude of the reciprocal-lattice vector that enters the two-plane-wave pseudo-wave-function and $w(G)$ is the corresponding matrix element of the screened electron-ion pseudopotential. Equations (6.2) and (6.3) differ by the factor $[\hbar^2G^2/4m\,|w(G)|]^2$. For Al, for the reciprocal-lattice vector G_{111}, this factor is of order 10^3. In other words, the two-plane-wave expression for $[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2$, which is relevant to the region K^*, is 3 orders of magnitude larger than the one-plane-wave expression, which is relevant to the remainder of the Fermi surface. The effect on the integral of using the two-plane-wave integrand is of course reduced because the region K^* constitutes only a small portion of the total Fermi surface over which the resistivity integral, (2.5), is to be performed. Nevertheless, employing the correct dirty-limit expression for $[\Phi(\vec{K}_1)-\Phi(\vec{K}_2)]^2$ increases the normal contribution to the resistivity integral by 2 orders of magnitude for Al. By contrast, the Bloch result $\rho_{\text{Bloch}}(T)$ is equivalent to using a single-plane-wave expression for $\vec{v}(\vec{K})$ for all $\vec{K}$, even for $\vec{K}$ in the region K^*. Therefore the error introduced by using the Bloch approximation to $\rho_N(T)$ is clear.

It should be admitted that Al is somewhat of an extreme case in that $w(G_{111})=0.0179$ Ry is unusually small.[44] Nevertheless, even for Cu, for which $w(G_{111})\simeq 0.2$ Ry is rather large,[44] the factor $[\hbar^2G^2/4m\,|w(G)|]^2$ is still of order 10^2. Thus, it is never justified for the calculation of $\rho_N(T)$ to ignore the two-plane-wave character of the pseudo-wave function in the region K^*.

The above discussion does not complete the analysis of $\rho_N(T)$. There is a second reason, related to phonon polarization, why $\rho_N(T)$ is much larger than $\rho_{\text{Bloch}}(T)$ for polyvalent and noble metals. The point is best illustrated by considering an isotropic phonon spectrum. For small q, as is relevant at low temperatures, this situation corresponds closely to Al. For $\vec{K}_1$ and $\vec{K}_2$ not in the region K^*, a single plane wave accurately represents the pseudo-wave-function. For this case, it is well known[20] that transverse phonons cannot lead to normal electron-phonon scattering. This result derives from the polarization-vector factor $(\vec{q}\cdot\hat{\xi}_{\vec{q}\lambda})^2$ appearing in $P^{\vec{q}\lambda}_{\text{ph}}(\vec{K}_1,\vec{K}_2;T)$, where $\hat{\xi}_{\vec{q}\lambda}$ is the polarization vector of the phonon of wave vector $\vec{q}$ and polarization λ. For an isotropic phonon spectrum, as we are considering here, for both the transverse modes $(\lambda=T)$, the factor $(\vec{q}\cdot\hat{\xi}_{\vec{q}T})$ vanishes, and hence there is no electron scattering from transverse phonons. However, for $\vec{K}_1$ and $\vec{K}_2$ in the region K^*, this result is no longer true because one must use the two-plane-wave expression for the polarization-vector factor. In the limit $q\to 0$, the two-plane-wave polarization factor for transverse phonons has the form[22]

$$(\vec{G}\cdot\vec{q})^2[(\vec{G}\cdot\hat{\xi}_{\vec{q}T1})^2+(\vec{G}\cdot\hat{\xi}_{\vec{q}T2})^2], \qquad (6.4)$$

where $T1$ and $T2$ denote the fast and slow transverse phonons, respectively, and $\vec{G}$ is the reciprocal-lattice vector that enters the two-plane-wave pseudo-wave-function. The expression (6.4) clearly does not vanish except for special directions of $\vec{q}$ relative to $\vec{G}$. Therefore, the transverse phonons *do* scatter electrons in the region K^*.

The importance of this result lies in the fact that the frequency of the slow transverse phonon $\omega_{T2}(\vec{q})$ is much lower than the frequency of the longitudinal phonon $\omega_L(\vec{q})$. For a given value of $\vec{q}$, the value of $\omega_{T2}(\vec{q})$ is typically about half that of $\omega_L(\vec{q})$. Therefore, the argument $\hbar\omega_\lambda(\vec{q})/k_BT$ of the exponential appearing in the phonon occupation number is halved for transverse phonons. At low temperatures, this leads to a very large enhancement of the normal electron-phonon scattering probability. For Al at $T = 10$ K, the resulting[21] enhancement exceeds an order of magnitude.

In summary, the overall enhancement of $\rho_N(T)$ at low temperatures due to scattering events for which both $\vec{K}_1$ and $\vec{K}_2$ lie in the region K^* is three orders of magnitude for Al. Of this total enhancement, two orders of magnitude result from the expression $[\Phi(\vec{K}_1) - \Phi(\vec{K}_2)]^2$ and one order of magnitude results from the scattering by transverse phonons. The Bloch approximation to $\rho_N(T)$ is equivalent to using single-plane-wave pseudowave functions for the entire Fermi surface, including the region K^*, and is thus seen to be in error by three orders of magnitude. Therefore it is clear that relying on the Bloch expression for $\rho_N(T)$, which is in fact equivalent to discarding $\rho_N(T)$ altogether, is totally without justification.

As important as the large magnitude of $\rho_N(T)$ is the fact that the dominant contribution to $\rho_N(T)$ arises from the very restricted region K^* of the Fermi surface, just as is the case for $\rho_U(T)$. Therefore, the pure-limit function $\phi_{\text{ph}}(\vec{K})$, given by Eq. (3.3), leads to a very much smaller value of $\rho_N(T)$ than does the dirty-limit function $\phi_{\text{imp}}(\vec{K})$, given by Eq. (3.2). This is sufficient to assure that the analysis of the DMR presented in Sec. III applies equally well to $\rho_N(T)$ and to $\rho_U(T)$. In particular, it follows immediately that $\rho_N(T)$ by itself gives rise to large DMR, even without the presence of $\rho_U(T)$. Indeed, a plot of $\Delta\rho$ as a function of ρ_0 arising from $\rho_N(T)$ alone would look remarkably similar to Fig. 1, which includes both $\rho_N(T)$ and $\rho_U(T)$. More specifically, at low temperatures, normal electron-phonon scattering accounts for a significant part of the total calculated DMR. Any calculation which assumes that $\rho_U(T)$ is the only source of the DMR cannot be quantitatively correct.

VII. SUMMARY

We have presented a detailed discussion of the deviations from Matthiessen's rule for the polyvalent and noble metals. These metals, in contrast to the alkalis, are characterized by having a Fermi surface that intersects the Brillouin-zone boundaries. As a result of these intersections, the electrons on a very small portion of the Fermi surface are scattered much more strongly than the electrons on the rest of the Fermi surface. Using this fact as the cornerstone, it is possible to obtain a complete qualitative understanding of the DMR. Our principle results are the following:

(i) The variational formulation of the Boltzmann equation is used to obtain a simple expression for the magnitude of the DMR, which is a good approximation for all values of ρ_0.

(ii) A new expression is introduced for the electron distribution function, which permits one to account for most of the experimental findings associated with the DMR, without performing any computer calculations. The form of the approximate distribution function is justified both on physical grounds and on mathematical grounds.

(iii) The behavior of $\Delta\rho$ for large values of ρ_0 (dirty limit) is analyzed for different ranges of temperature. In particular, the contribution of the interference term is shown to account for the observed lack of saturation of $\Delta\rho$ in the dirty limit.

(iv) The theoretical framework developed here is shown to provide a natural explanation for the magnitude for the DMR, their temperature dependence, their variation from metal to metal, and the approximate $\log(\rho_0)$ dependence of $\Delta\rho$, independent of the type of impurity.

(v) It is shown that the contribution to $\Delta\rho$ from normal electron-phonon scattering is by no means negligible. In fact, for the polyvalent and noble metals, the normal-scattering contribution to the DMR is comparable in magnitude to the umklapp-scattering contribution.

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