substances with vanishing shear modulus, i.e., fluids. For solids the equations are modified by terms involving Poisson's ratio, which depends generally on the elastic constants and the external pressure. However, the effect of this correction on the isotopic mass dependence of the Debye temperature is negligible. I am grateful to Professor G. A. Stewart for bringing this correction to my attention.

[10] We have assumed that the structures of the He^3 and He^4 films are the same, but changes in θ due to structure differences would not affect the qualitative conclusions. Based on the behavior in 3D, He^3 tends to a more open structure, i.e., square rather than triangular. Since $\theta_{bcc}(He^3) < \theta_{hcp}(He^3)$ (Ref. 8), we would expect $\theta_{sq}(He^3) < \theta_{tri}(He^3)$. Therefore the observed ratios in the films are minimum values for monolayers having identical structures.

[11] L. H. Nosanow, Phys. Rev. 146, 120 (1966).

[12] B. H. Brandow, Ann. Phys. (New York) 74, 112 (1972).

[13] A. D. Novaco, Phys. Rev. A 8, 3065 (1973).

[14] See, e.g., J. S. Dugdale, in *Physics of High Pressure and the Condensed Phase*, edited by A. van Itterbeck (North-Holland, Amsterdam, 1965), p. 358.

Explanation for the Deviations from Matthiessen's Rule for the Low-Temperature Electrical Resistivity of the Simple Metals

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A new type of trial function is introduced which explains both the large deviations from Matthiessen's rule observed for the low-temperature electrical resistivity of the polyvalent metals, as well as the absence of such deviations for the alkali metals. Excellent quantitative agreement between theory and experiment is obtained for the resistivity of aluminum, both as a function of temperature and as a function of residual resistivity.

The observed[1-3] large deviations from Matthiessen's rule[4] (DMR) for the low-temperature electrical resistivity of the polyvalent metals, typified by aluminum, have recently been the subject of extensive theoretical investigation.[5-14] In this Letter, we show that one can obtain quantitative agreement with the measured[1-3] DMR data for Al by the use of a new type of trial function for the variational solution[15] of the Boltzmann equation. The essential feature of the analysis is the introduction of a trial function that takes explicit account of the anisotropy of the Fermi surface and therefore is appropriate to polyvalent metals.

Calculating the electrical resistivity with an improved solution to the Boltzmann equation was previously proposed by Klemens and Jackson,[16] although by a method completely different from that proposed here. The Klemens-Jackson[16] calculation for a pure metal was subsequently generalized by Ehrlich[17] to include impurity scattering, an important generalization for the calculation of the DMR. The Ehrlich analysis[17] contains the assumption that in the absence of umklapp scattering, Matthiessen's rule would be obeyed. However, our explicit calculation for Al shows that for the low temperatures considered here, normal scattering by itself is responsible for a large part of the observed DMR. This surprising result stems from the fact that even for normal scattering, a one-orthogonalized-plane-wave state vector is inadequate and a two-orthogonalized-plane-wave state vector must be used for the electron states.

Matthiessen's rule states that $\Delta\rho$ is independent of the residual resistivity ρ_0, where $\Delta\rho \equiv \rho_{tot} - \rho_0$ and ρ_{tot} is the total resistivity. Our calculation provides an explanation for the following experimental observations regarding $\Delta\rho$: (1) At low temperatures, the DMR for the polyvalent metals are extremely large. For Al at $T = 14^\circ K$, $\Delta\rho$ increases[1,2] by a factor of 6 as ρ_0 increases from 0.1 to 1000 nΩ cm. For lower temperatures, the effect is much greater. (2) In marked contrast to the polyvalent metals, the alkali metals exhibit[18,19] very small DMR at all temperatures.
(3) The temperature dependence of $\Delta\rho$ for Al is found[3] to be approximately T^3 over a significant range of T in the low-temperature regime.
(4) The impurity dependence of $\Delta\rho$ is found[1,2] for Al to be expressible as a universal function of ρ_0, independent of the type of impurity. The universal function varies approximately as $\ln(\rho_0)$ over a significant range of ρ_0.

Fact (1) can be explained in terms of the new

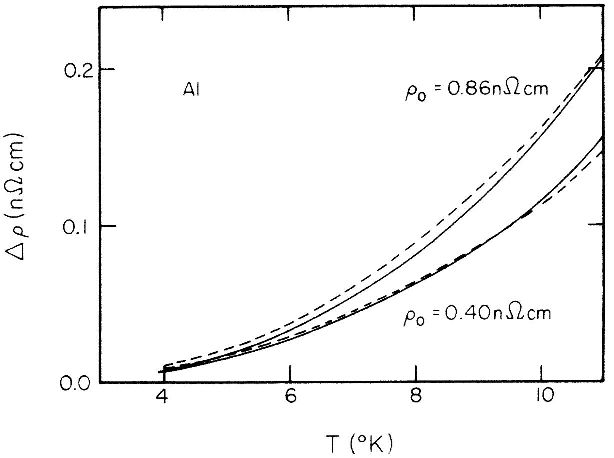

FIG. 1. Calculated (solid lines) and measured (dashed lines) values of $\Delta\rho$ as a function of T for the two indicated values of ρ_0.

trial function even without calculating $\Delta\rho$. Whenever two scattering mechanisms are present, Matthiessen's rule is valid[15] only if the same trial function is appropriate to calculate the contribution to the resistivity from each of the two scattering mechanisms. We find that at low temperatures the standard[15] trial function, which is very good for describing electron-impurity scattering, overestimates electron-phonon scattering by 1–2 *orders of magnitude.* This is sufficient to ensure that there will be large DMR.

Fact (2) can be explained by noting that the new trial function differs from the standard trial function only when the Fermi surface is anisotropic. Since the Fermi surface of the alkali metals is spherical, both the new and the standard trial functions are identical. Therefore, for the alkalis we predict no DMR at all. This is indeed observed[18,19] to be the case for high-purity samples of potassium. The small DMR found[18,19] for low-purity samples arise from a different mechanism and will be the subject of a separate publication.

In Fig. 1, we compare the calculated curves (solid lines) for the temperature dependence of $\Delta\rho$ for Al with the detailed measurements of Ekin[3] (dashed lines) for two values of ρ_0 (0.40 and 0.86 nΩ cm). The agreement between theory and experiment is evident. Both theory and experiment exhibit nearly a T^3 behavior for $\Delta\rho$ for both values of ρ_0.

In Fig. 2, we compare the calculated curve (solid line) for the ρ_0 dependence of $\Delta\rho$ for Al at the fixed temperature of 14°K with the data[20] (solid circles) reported by Caplin and Rizzuto[1,2] and by Bass.[3] Again, there is clear agreement between theory and experiment. Note that $\Delta\rho$ varies almost logarithmically with ρ_0 over more than 2 orders of magnitude, as ρ_0 increases from about 0.2 to about 50 nΩ cm.

We see from Fig. 2 that at 14°K, the "pure" limit $\rho_{\rm pure}(T)$, in which Matthiessen's rule is valid, is not reached until ρ_0 is less than 0.1 nΩ cm. The "dirty" limit begins at about $\rho_0 \gtrsim 100$ nΩ cm. Above this value of ρ_0, $\Delta\rho$ is independent of ρ_0 and Matthiessen-rule-like behavior is observed. We may characterize the magnitude of the DMR by the ratio $(\rho_{\rm dirty} - \rho_{\rm pure})/\rho_{\rm pure}$. From Fig. 2, we see that this ratio equals 5 for Al at 14°K.

For lower temperatures, the calculated curves resemble Fig. 2 qualitatively, but there are two important quantitative differences. First, the magnitude of the DMR greatly increases, with $(\rho_{\rm dirty} - \rho_{\rm pure})/\rho_{\rm pure}$ reaching 40 at $T = 4$°K. Second, there is a shift in the values of ρ_0 marking the onset of the pure and dirty limits. At 4°K, the pure limit is not reached until $\rho_0 \simeq 10^{-4}$ nΩ cm, whereas the dirty limit is already reached at $\rho_0 \simeq 1$ nΩ cm.

Our calculation of $\Delta\rho$ is based on the variation-

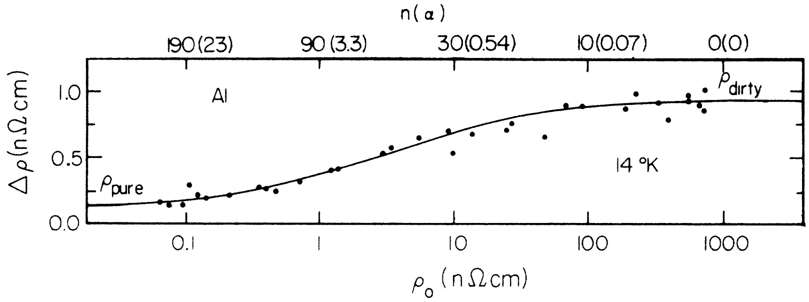

FIG. 2. Calculated (solid line) and measured (filled circles) values of $\Delta\rho$ as a function of ρ_0 at the fixed temperature of 14°K. On the upper abscissa are given the calculated values of n and α (in parentheses) as a function of ρ_0 at 14°K.

al formulation,[15] according to which the total resistivity is given by the expression

$$[\langle\Phi|\hat{P}_{\mathrm{imp}}+\hat{P}_{\mathrm{ph}}|\Phi\rangle]/[\langle\Phi|X\rangle]^2, \tag{1}$$

with the exact trial function $\Phi(\vec{K})$ being that function which minimizes (1). The scattering operators $\hat{P}_{\mathrm{imp}}$ and $\hat{P}_{\mathrm{ph}}$ describe electron-impurity scattering and electron-phonon scattering, respectively, and X is the electric field term.[15] The procedure for reducing the electron-phonon scattering matrix element $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$ to a double surface integral has been lucidly described by Ziman,[21] leading to the expression

$$\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle = AT^{-1}\iint[dS(\vec{K}_1)/v(\vec{K}_1)][dS(\vec{K}_2)/v(\vec{K}_2)][\Phi(\vec{K}_2)-\Phi(\vec{K}_1)]^2\textstyle\sum_\lambda|M_{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)|^2, \tag{2}$$

where A is a known[21] constant; $v(\vec{K})$ is the velocity of the electron in state $\vec{K}$; the wave vectors $\vec{K}_1$ and $\vec{K}_2$ characterize the initial (1) and final (2) states of the electron being scattered by a phonon of wave vector $\vec{q}$, polarization λ, and frequency $\omega_\lambda(\vec{q})$; and the double surface integral is to be performed over the true anisotropic Fermi surface of Al.[22] It should be emphasized that both normal scattering ($\vec{K}_2-\vec{K}_1=\vec{q}$) and umklapp scattering ($\vec{K}_2-\vec{K}_1=\vec{q}+\vec{G}$, $\vec{G}$ = reciprocal lattice vector) make significant contributions to $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$ throughout the low-temperature regime.

For a polyvalent metal, the temperature-dependent scattering function $M_{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$ must be calculated using the two-plane-wave pseudo wave functions appropriate to each point $\vec{K}_1$ and $\vec{K}_2$. For the low temperatures considered here, the one-plane-wave approximation to $M_{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$ is worst for precisely those values of $\vec{K}_1$ and $\vec{K}_2$ that dominate the integral (2), and its use would lead to a significant error in $\Delta\rho$ for both normal and umklapp scattering. For example, for Al at $T=7°\mathrm{K}$ and $\rho_0=10$ nΩ cm, the resulting error in $\Delta\rho$ would exceed a factor of 2. Sham and Ziman[23] present the details of the two-plane-wave calculation of $M_{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$. For the effective electron-ion potential appearing in $M_{\vec{q}\lambda}(\vec{K}_1,\vec{K}_2;T)$, we used the Ashcroft model potential.[24] Therefore, once one has chosen the trial function $\Phi(\vec{K})$, the calculation of $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$ contains no free parameters.

The matrix element $\langle\Phi|\hat{P}_{\mathrm{imp}}|\Phi\rangle$ is evaluated in the same way[15] as $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$, leading to a double-surface integral analogous to Eq. (2). For $\hat{P}_{\mathrm{imp}}$, we used a screened Coulomb potential. The screening function contains a parameter, independent of both ρ_0 and T, which was chosen to give the best overall fit of the calculated $\Delta\rho$ to experiment. This is the only adjustable parameter in the calculation of $\Delta\rho$.

For electron-impurity scattering, it is justified to use the standard[15] trial function

$$\Phi_{\mathrm{imp}}(\vec{K})=\vec{v}(\vec{K})\cdot\vec{F}, \tag{3}$$

where $\vec{F}$ is the electric field. However, for electron-phonon scattering, using (3) for the trial function and performing the double surface integral of (2) shows that at low temperatures, for both umklapp and normal scattering almost the entire contribution arises from the immediate vicinity of the intersections of the Fermi surface with the Brillouin zone boundaries, i.e., the vicinity where the anisotropy of the Fermi surface is greatest. A trial function which minimizes these large contributions, $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$, will constitute a very significant improvement over (3). Consider the form

$$\Phi_n(\vec{K})=[v(\vec{K})/v_{\mathrm{F}}]^n\vec{v}(\vec{k})\cdot\vec{F}, \tag{4}$$

where the Fermi velocity v_{F} is included as a normalizing factor so that for the spherical portions of the Fermi surface, the quantity in brackets equals unity.

Near the intersection of the Fermi surface with the Brillouin zone boundaries, the true velocity $v(\vec{K})$ is considerably smaller[22] than v_{F}. This behavior is characteristic of all polyvalent metals. Therefore, by using a high power of n, we eliminate almost entirely the large contribution of these regions to $\langle\Phi|\hat{P}_{\mathrm{ph}}|\Phi\rangle$. The power n is determined by the requirement that (1) be minimized at each temperature. Therefore, n depends on T and is typically 100–200 for pure Al. Note that the impurity-scattering trial function (3) corresponds to (4) with $n=0$. Thus, $\Phi_{\mathrm{imp}}(\vec{K})=\Phi_0(\vec{K})$, implying that $\langle\Phi_0|\hat{P}_{\mathrm{imp}}|\Phi_0\rangle/(\langle\Phi_0|X\rangle)^2=\rho_0$.

We now turn to the calculation of the DMR by taking into account both $\hat{P}_{\mathrm{imp}}$ and $\hat{P}_{\mathrm{ph}}$. For the trial function, we take a linear combination of $\Phi_0(\vec{K})$ and $\Phi_n(\vec{K})$,

$$\Phi(\vec{K})=\Phi_0(\vec{K})+\alpha\Phi_n(\vec{K}), \tag{5}$$

where the value of α is determined[15] by the requirement that ρ_{tot} be minimized. For each value of ρ_0 and T, we calculated the values of n and α that minimized (1). In Fig. 2, we present the calculated values for both n and α as a function of ρ_0 for $T=14^\circ\mathrm{K}$. Inserting these values of n and α into (4) and (5), combined with the values[22] of $v(\vec{K})$ for Al, gives explicitly the variation of the trial function over the anisotropic Fermi surface.

In summary, we have calculated the deviations from Matthiessen's rule for Al using a new trial function that takes proper account of the anisotropy of the Fermi surface. Other essential features of the calculation are the use of a two-orthogonalized-plane-wave function for both normal and umklapp scattering and the performing of all surface integrals over the true anisotropic Fermi surface of Al. Including all these features in the calculation leads to quantitative agreement with experiment for $\Delta\rho$ for Al, both as a function of ρ_0 and as a function of temperature.

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

[2] A. D. Caplin and C. Rizzuto, Aust. J. Phys. 24, 309 (1971).

[3] J. W. Ekin, Ph.D. thesis, Cornell University, Ithaca, New York, 1971 (unpublished). The data of Ekin are reproduced in Fig. 36 of J. Bass, Advan. Phys. 21, 431 (1972). Note that the vertical scale is incorrectly labeled. It should be $\Delta\rho/T^3$ (10^{-14} Ω cm/deg^3).

[4] A comprehensive review article has been written by J. Bass (Ref. 3). This encyclopedic work lucidly presents a detailed account of the entire field.

[5] I. A. Campbell, A. D. Caplin, and C. Rizzuto, Phys. Rev. Lett. 26, 239 (1971).

[6] D. Mills, Phys. Rev. Lett. 26, 242 (1971).

[7] L. Dworin, Phys. Rev. Lett. 26, 1244 (1971).

[8] D. A. Smith, J. Phys. C: Proc. Phys. Soc., London 4, L145 (1971).

[9] D. Sherrington, Phys. Lett. 35A, 399 (1971).

[10] F. Napoli and D. Sherrington, J. Phys. F: Metal Phys. 1, L53 (1971).

[11] Yu. Kagan and A. P. Zhernov, Zh. Eksp. Teor. Fiz. 60, 1832 (1971) [Sov. Phys. JETP 33, 990 (1971)].

[12] D. Schotte and U. Schotte, Solid State Commun. 10, 131 (1972).

[13] W. E. Lawrence and J. W. Wilkins, Phys. Rev. B 6, 4466 (1972).

[14] A. D. Caplin, F. Napoli, and D. Sherrington, J. Phys. F: Metal Phys. 3, L93 (1973).

[15] J. M. Ziman, *Electrons and Phonons* (Clarendon Press, Oxford, England, 1960), Chap. VII.

[16] P. G. Kelmens and J. L. Jackson, Physica (Utrecht) 30, 2031 (1964).

[17] A. C. Ehrlich, Phys. Rev. B 1, 4537 (1970).

[18] D. Gugan, Proc. Roy. Soc., Ser. A 325, 223 (1971).

[19] J. W. Ekin and B. W. Maxfield, Phys. Rev. B 4, 4215 (1971).

[20] The data are reproduced from a photograph of Fig. 9 of the review article by Bass (Ref. 3). We have not included the size-effect data of $\Delta\rho$ since, as Bass explained, only data for the bulk metal lie on the universal curve of $\Delta\rho$ versus ρ_0. Bass had added several data to those originally presented by Caplin and Rizzuto (Refs. 1 and 2).

[21] See Ref. 15, Sec. 9.5.

[22] N. W. Ashcroft, Phil. Mag. 8, 2055 (1963).

[23] L. J. Sham and J. M. Ziman, Solid State Phys. 15, 221 (1963), Sec. 11.

[24] N. W. Ashcroft, Phys. Lett. 23, 48 (1966).