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Hall Coefficients in the Alkali Metals[†]

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We have calculated the effect of the anisotropy in the electron-phonon interaction on the temperature dependence of the Hall constant in the alkali metals. We find that the effective number of carriers n^* decreases with temperature in qualitative agreement with experiment. At low temperatures, we find a minimum in n^*.

I. INTRODUCTION

Robinson and Dow[1] have computed the Hall coefficient for the alkali metals at room temperature. They employed Heine-Abarenkov[2] pseudopotentials for the electron-ion form factor and took the phonons from inelastic-neutron-scattering data. From this information they compute the scattering times for electrons at three points of high symmetry on the Fermi surface. These scattering times are then averaged in an appropriate way to get the Hall coefficient. In this paper we report on new and more extensive calculations of the Hall coefficient in the alkali metals. The improvements over the previous work are several. We are able to compute scattering times at a large number of points on the ir-

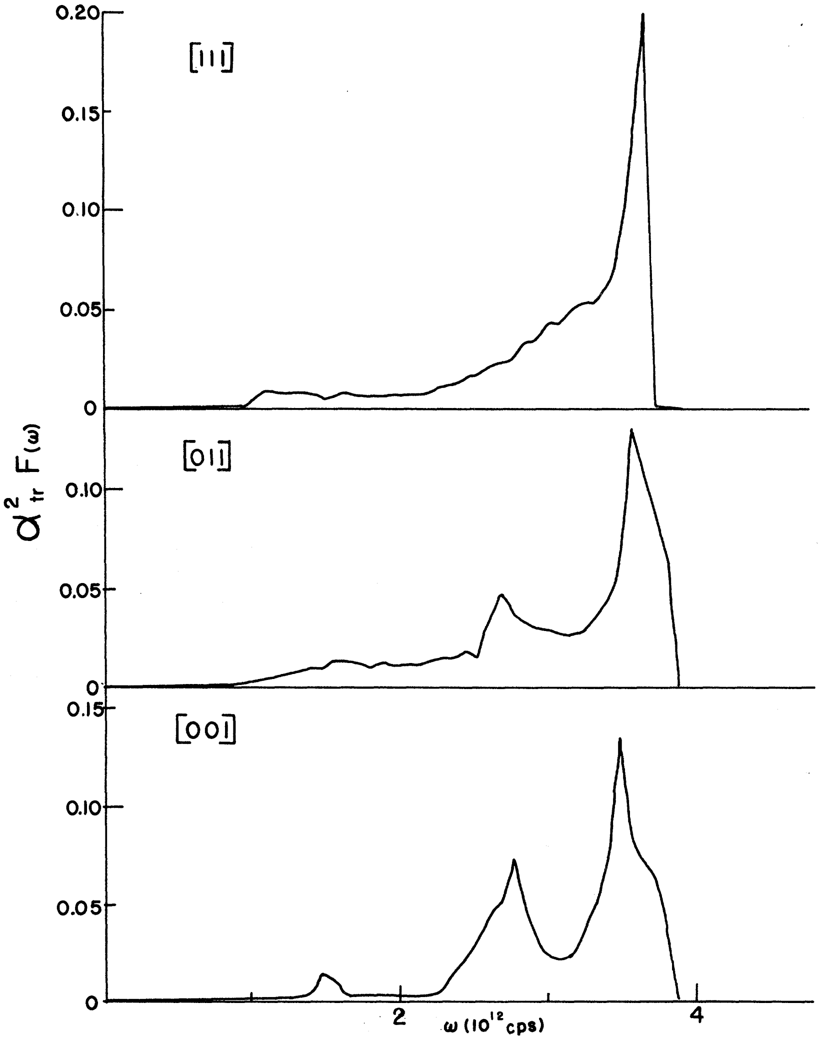

FIG. 1. Electron-phonon "transport frequency distribution" $\alpha^2_{\mathrm{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ for $\vec{k}$ in three high-symmetry directions. The curves refer to Na. The function $\alpha^2_{\mathrm{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ is dimensionless and the frequency ω is in units of 10^{12} cps.

reducible $\frac{1}{48}$ of the Fermi surface. By formulating the theory in terms of a "transport frequency distribution," instead of the overlap of a temperature-dependent structure factor and a pseudopotential, it is possible to extend the calculations to all temperatures with no added difficulty. This is important since, experimentally, the effective number of carriers per atom is observed to decrease with decreasing temperature. In potassium we carry out calculations for several commonly used pseudopotentials so as to determine the sensitivity of our results to this quantity. Since the form factor is found to be of quantitative although not qualitative importance, we carry out all further calculations using the form factor previously developed by us[2] for the alkalis. These pseudopotentials are known to fit very well the resistivity of the solid over a wide temperature range. The resistivity is, of course, closely related to the Hall coefficient.

In Sec. II, we give the formula for the Hall coefficient and discuss the ingredients needed for its evaluation. Section III describes our calculations and presents intermediate results while in Sec. IV, we present and discuss our results for the effective number of charge carriers as a function of temperature. In Sec. V we draw conclusions.

II. FORMALISM

The Hall coefficient R can be written in terms of an effective density of charge carriers n^*,

$$R = -\frac{1}{n^* |e| c}\ , \tag{1}$$

where e is the electron charge and c the velocity of light. Following, for example, Robinson and Dow,[1] we write

$$\frac{n^*}{n} = \frac{\langle \tau(\vec{k}, T)\rangle^2}{\langle \tau^2(\vec{k}, T)\rangle}\ , \tag{2}$$

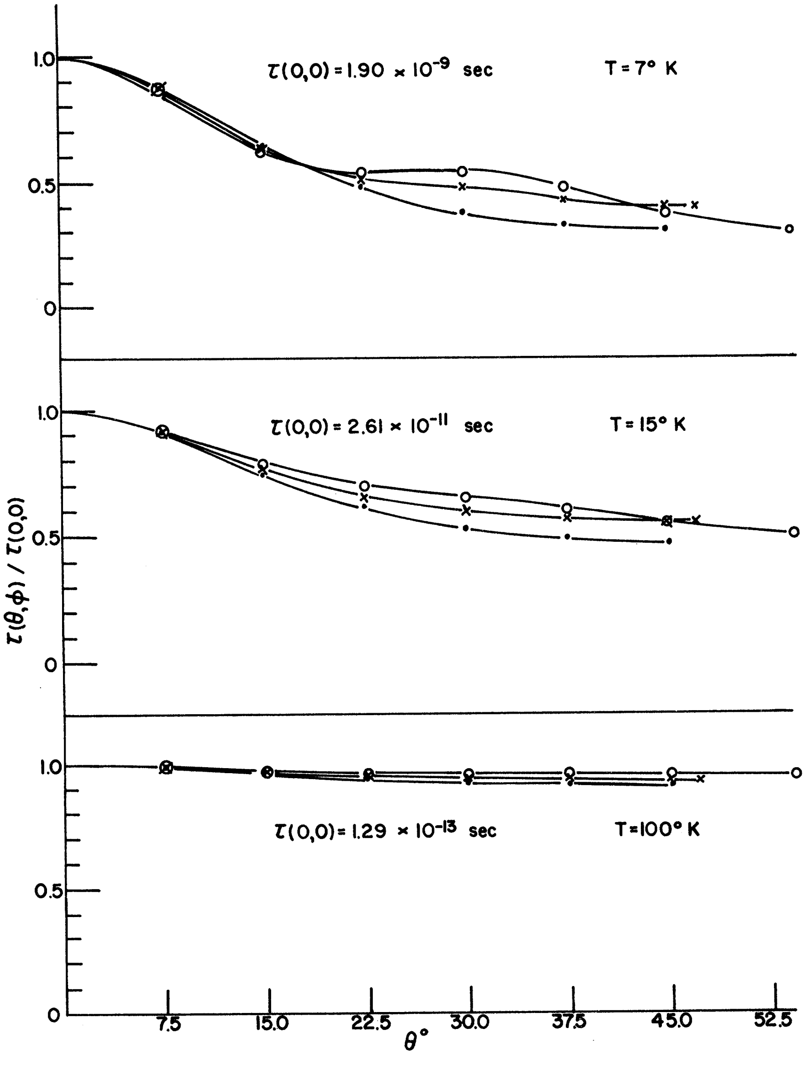

FIG. 2. Scattering time $\tau(\vec{k}, T)$ for three different temperatures in Na as a function of position on the irreducible $\frac{1}{48}$ th of the Fermi surface. For $\vec{k} \equiv (\theta, \phi, k_F)$, the results for the three arcs $\phi = 0°$, $22\frac{1}{2}°$ and $45°$ are to be distinguished as follows: •, $\phi = 0°$; ×, $\phi = 22\frac{1}{2}°$; o, $\phi = 45°$. The results are normalized to the value of τ at $\theta = 0$ and $\phi = 0$. For each temperature, $\tau(0, 0)$ is entered on the graph.

where n is the number of free electrons per unit volume and $\tau(\vec{k}, T)$ is the scattering time for an electron in the state $|\vec{k}\rangle$ at temperature T. The average indicated in (2) by the brackets $\langle\ \rangle$ is over the Fermi surface which we will take to be a sphere. Hayman and Carbotte[2] have shown how, at least for certain purposes, the ordinary formula for the electrical resistivity can be rewritten in a more convenient way in terms of a transport frequency distribution which they denote by $\overline{\alpha}^2(\omega)F(\omega)$. The variable ω is a phonon frequency. Once this quantity is known, the resistivity at any temperature follows by a simple quadrature over thermal factors and $\overline{\alpha}^2(\omega)F(\omega)$. Allen,[3] in his discussion of the infrared properties of metals, has also introduced an effective frequency distribution which he denotes by $\alpha^2_{\mathrm{tr}}(\omega)F(\omega)$. To within a multiplicative constant, $\alpha^2_{\mathrm{tr}}(\omega)F(\omega)$ is equal to $\overline{\alpha}^2(\omega)F(\omega)/\omega$. In what follows, we will employ Allen's notation because, as he has it defined, $\alpha^2_{\mathrm{tr}}(\omega)F(\omega)$ has the convenient property of being a dimensionless quantity. Here, tr stands for transport.

The quantity of central importance in our work is a directional $\alpha^2_{\mathrm{tr}}(\omega)F(\omega)$ which we will denote by $\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)$. Averaging over the Fermi sphere gives the average quantity, i.e.,

$$\alpha^2_{\mathrm{tr}}(\omega)F(\omega) = \langle \alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)\rangle$$

$$\equiv \int (d\Omega_{\vec{k}}/4\pi)\, \alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)\,,$$

where the angular average $d\Omega_{\vec{k}}$ is on the Fermi sphere. The formula for $\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)$ is[2,3]

$$\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega) = \frac{\hbar}{2}\frac{N(0)}{P_F^2}\sum_{\lambda=1}^{3}\langle g^2_{\vec{k}\vec{k}'\lambda}(\vec{k}-\vec{k}')^2 \times \delta(\omega - \omega_\lambda(\vec{k}-\vec{k}'))\rangle, \quad (3)$$

where $N(0)$ is the single-spin density of states at the

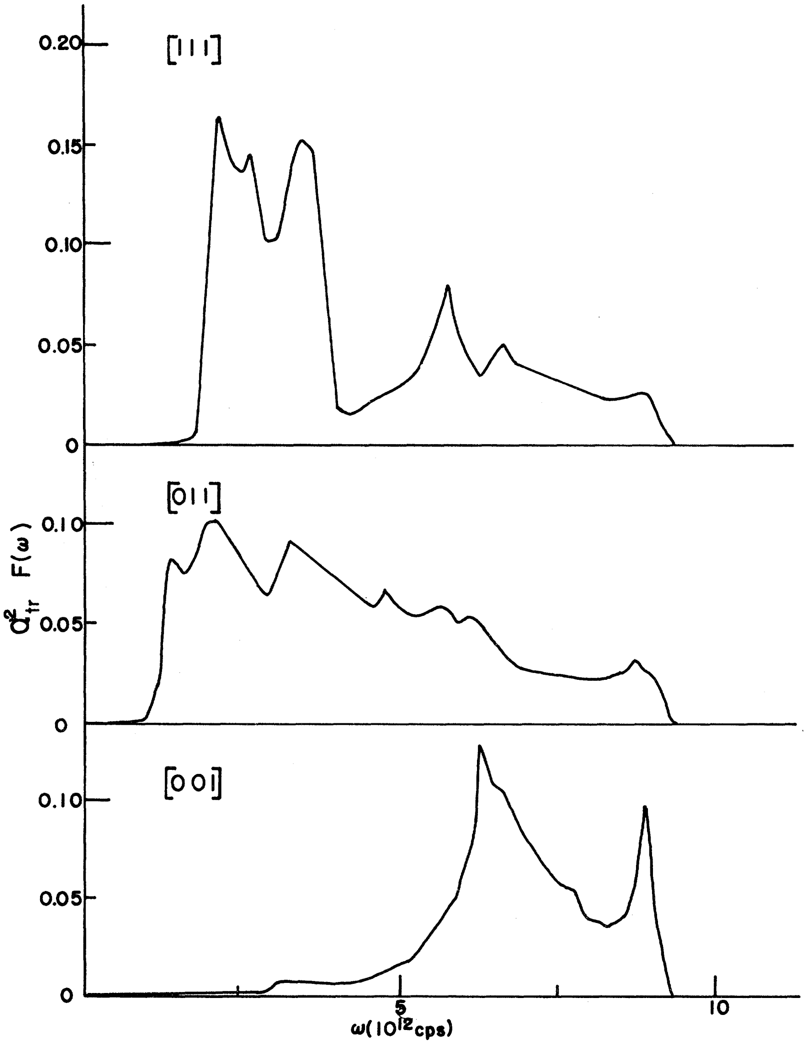

FIG. 3. Electron-phonon "transport frequency distribution" $\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)$ for $\vec{k}$ in three high-symmetry directions. The curves refer to Li. The function $\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)$ is dimensionless and the frequency ω is in units of 10^{12} cps.

Fermi level, per unit volume, P_F is the Fermi momentum and $g_{\vec{k}\vec{k}'\lambda}$ is the electron-phonon coupling for scattering from $|\vec{k}\rangle$ to $|\vec{k}'\rangle$. The index λ denotes the phonon polarization branches and $\omega_\lambda(\vec{k})$ is the frequency of the $\vec{k}\lambda$th mode. Finally, $\hbar$ is Planck's constant over 2π. The electron-phonon coupling can be written

$$g_{\vec{k}\vec{k}'\lambda} = -i\left(\frac{\hbar}{2\omega_\lambda(\vec{k}-\vec{k}')MN}\right)^{1/2}(\vec{k}-\vec{k}')\cdot\vec{\epsilon}_\lambda(\vec{k}-\vec{k}') \times W(\vec{k}-\vec{k}'), \qquad (4)$$

with N the number of ions per unit volume; M, the ion mass; $\vec{\epsilon}_\lambda(\vec{k}-\vec{k}')$, the phonon polarization vector; and $W(\vec{k}-\vec{k}')$, the pseudopotential form factor.

The scattering time $\tau(\vec{k}, T)$ for the state $|\vec{k}\rangle$ is given by

$$\frac{1}{\tau(\vec{k}, T)} = 4\pi\beta\hbar\int_0^\infty \frac{d\omega\,\omega\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)}{(e^{\hbar\beta\omega}-1)(1-e^{-\beta\omega\hbar})}, \qquad (5)$$

where m is the electron mass and $\beta^{-1} \equiv k_BT$ with k_B, the Boltzmann constant and T, the absolute temperature.[4] It should be clear from (5) that having computed the transport frequency distribution $\alpha^2_{\mathrm{tr}\vec{k}}(\omega)F_{\vec{k}}(\omega)$ as a function of frequency for a large number of points on the irreducible $\frac{1}{48}$ of the Fermi surface, there is no difficulty in determining from this information $\tau(\vec{k}, T)$ at any temperature. We turn now to an evaluation of this function.

III. CALCULATIONS

To evaluate (3), we need to know the pseudopotential form factor $W(q)$ for scattering from one point of the Fermi sphere to another, i.e., for momentum transfer $q\epsilon(0, 2k_F)$. Besides this, information about the lattice dynamics is needed. This latter information can be taken from the inelastic-neutron-scattering data on the phonons which are usually analyzed on a Born–von Kármán model to yield the interatomic force constants. These force constants completely determine the phonon frequencies and polarization vectors.

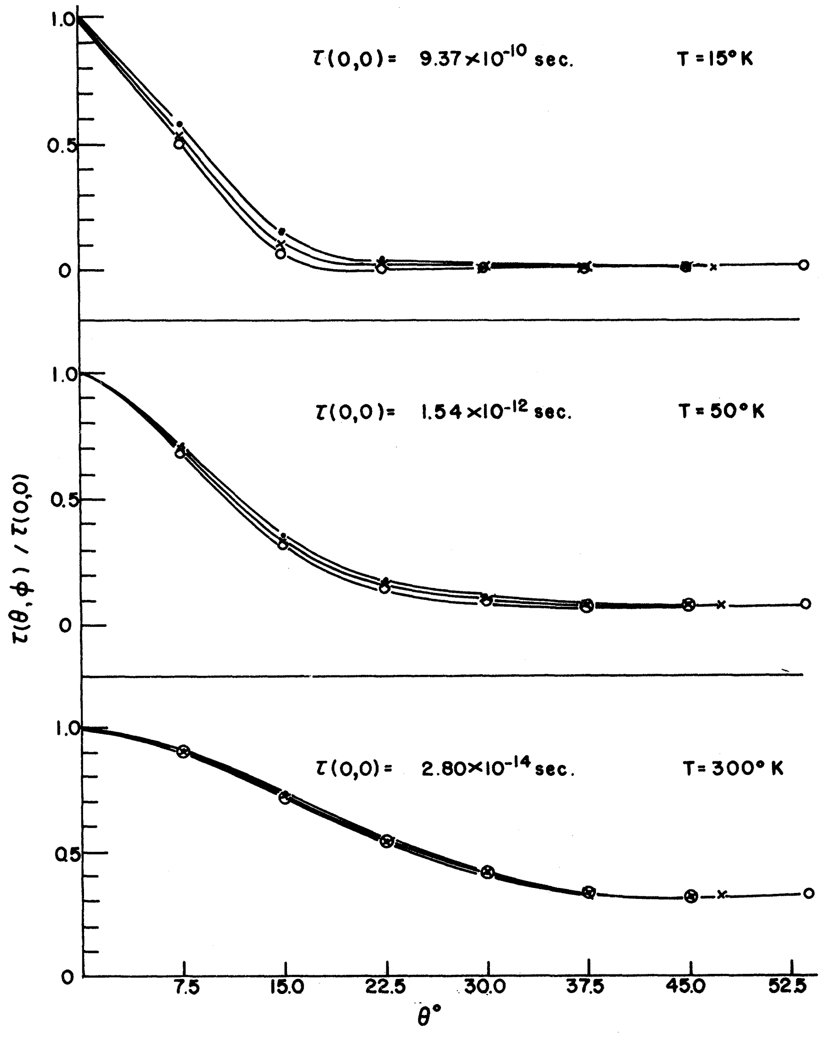

FIG. 4. Scattering time $\tau(\vec{k}, T)$ for three different temperatures in Li as a function of position on the irreducible $\frac{1}{48}$th of the Fermi surface. For $\vec{k} \equiv (\theta, \phi, k_F)$, the results for the three arcs $\phi = 0°$, $22\frac{1}{2}°$, and 45° are to be distinguished as follows: •, $\phi = 0°$; ×, $\phi = 22\frac{1}{2}°$; ○, $\phi = 45°$. The results are normalized to the value of τ at $\theta = 0$ and $\phi = 0$. For each temperature, $\tau(0, 0)$ is entered on the graph.

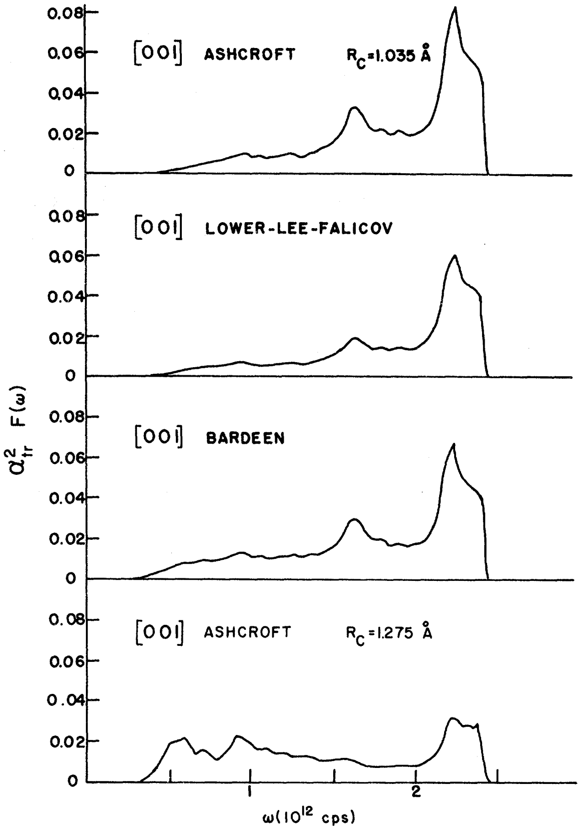

FIG. 5. Electron-phonon "transport frequency distribution" $\alpha^2_{\text{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ for $\vec{k}$ in the [001] direction. Results for the four different pseudopotentials discussed in the text are compared. The function $\alpha^2_{\text{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ is dimensionless and the frequency ω is in units of 10^{12} cps.

From this, (3) can easily be evaluated on a computer. The technique is now well established[5]–[7] and it would be repetitive to give more details. It is sufficient to present results.

In Fig. 1, we compare $\alpha^2_{\text{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ for $\vec{k}$ in the [001], [011], and [111] directions. A considerable amount of anisotropy is displayed in these figures. The plots are for Na. The pseudopotential used is the Ashcroft form developed in Ref. 2 and the Born–von Kármán force constants are from Woods *et al.*[8] In Fig. 2, we show the variation in $\tau(\vec{k}, T)$ as a function of position on the irreducible $\frac{1}{48}$ of the Fermi surface, which results from integrating (5) at three different temperatures. We see that at the lowest temperature considered, the variation is greatest while the variation tends to be reduced with increasing T. This is not unexpected. For fairly low temperatures ($T \approx 7$ °K) the thermal factors in (5) are fairly sharply peaked around $\omega = 0$. This implies that the low-frequency part of the "transport frequency distribution" will be the most important. We note that, at those frequencies where $\alpha^2_{\text{tr}\,\vec{k}}(\omega)F_{\vec{k}}(\omega)$ becomes significant in Fig. 1, the differences between the three directions shown are quite marked. As the temperature is increased, these differences are emphasized much less as more of the entire distribution is sampled in (5).

The distributions obtained for Li are distinctively different from those in Na. They are shown in Fig. 3 for the same three high-symmetry directions.[9] We note that for the [011] and [111] distributions, there is considerable weight at the low frequency as opposed to what is found in Na. In Fig. 4 we show scattering times as a function of position on the irreducible $\frac{1}{48}$th of the Fermi surface. The amount of anisotropy that remains even for $T = 300$ °K is not unexpected considering the distributions of Fig. 3.

It is of some interest and importance to know how sensitive the transport frequency distribution is to the form of the electron-ion pseudopotential. In Fig. 5, we compare results for four pseudopotentials. One is the Lee-Falicov[10,11] form, which is obtained from a fit to the Fermi-surface data; another is the Bardeen matrix element[11] and the others are two Ashcroft forms developed by Hayman and Carbotte.[2] Only the distributions in the [001] direction are compared. Differences are certainly evident in this figure. In particular, the low-frequency end of the distribution is very much more important for the Ashcroft form with $R_c = 1.275$ Å. The Bardeen matrix element also gives considerable weight to this region. A more striking way of presenting the differences is to show $\tau(\vec{k}, T)$. In Fig. 6 we present results for $\tau(\vec{k}, T)$ for $T = 4$ °K and for the four different forms mentioned for the electron-ion pseudopotential. The four form factors are compared in Fig. 7. The lower Lee-Falicov, the Bardeen, and the Ashcroft forms with $R_c = 1.0353$ Å are all similar. The Ashcroft form with $R_c = 1.2753$ Å is considerably different. It has a node for a momentum transfer before 1.0, in units of $2k_F$, and is quite large around $2k_F$. This implies that umklapp processes will be emphasized more in this case. This leads to the relatively greater importance of the low-frequency end in the "transport frequency distribution," which was previously noted (Fig. 5). It also leads to the greatest amount of anisotropy in $\tau(\vec{k}, T)$ at $T = 4$ °K, as can be seen in Fig. 6. It is clear from this figure that the form of the pseudopotential is of considerable importance in determining the variation of τ on the Fermi surface. Also, the absolute value of the scattering times can be strongly affected.

IV. RESULTS AND DISCUSSION

Once the scattering times are known at a large number of points on the irreducible $\frac{1}{48}$th of the

Fermi surface, it is not difficult to compute the averages indicated in Eq. (2) to obtain n^*/n. We begin by showing results for K, for which case several different pseudopotentials were considered. Potassium was singled out for this purpose because of the considerable amount of recent activity related to its low-temperature resistivity.[10,11] In Fig. 8, we have plotted n^*/n as a function of temperature in the most interesting range below ≈20 °K. Curve 1 is obtained from the Ashcroft form with a core-radius value of $R_c = 1.035$ Å. This value of R_c leads to very good results for the temperature variation of the resistivity in K.[2] Curve 2 applies for the Lee-Falicov pseudopotential while curve 3 is for the Bardeen form factor as described by Trofimenkoff and Ekin,[11] with reference to a discussion of the low-temperature resistivity $\rho(T)$ of K. The final curve labeled 4 is for an Ashcroft form with $R_c = 1.275$ Å which does fit the resistivity at 90 °K, but was rejected by Hayman and Carbotte,[2] because it failed at lower temperatures. It is included in Fig. 8 to show an extreme case. We see that the shape of the curves obtained is qualitatively the same whatever the pseudopotential used. Quantitatively, however, the results are very sensitive to the form of $W(q)$. On the other hand, it is encouraging that curves 1 and 2 are not very different. Both are obtained from empirical pseudopotentials fitted to experimental data. Since curve 1 is obtained from the resistivity data, we would tend to prefer it to curve 2 although we should stress again that, at the moment, we are more interested in the general qualitative features of our results.

It is important to note the minimum at roughly 4 °K in all these curves. This minimum correlated well with the maximum observed by Ekin[10] in a plot of $\rho(T)/T^5$ vs T. This author observes a maximum at ≈5 °K, which he correlates with the onset of umklapp processes at this temperature.

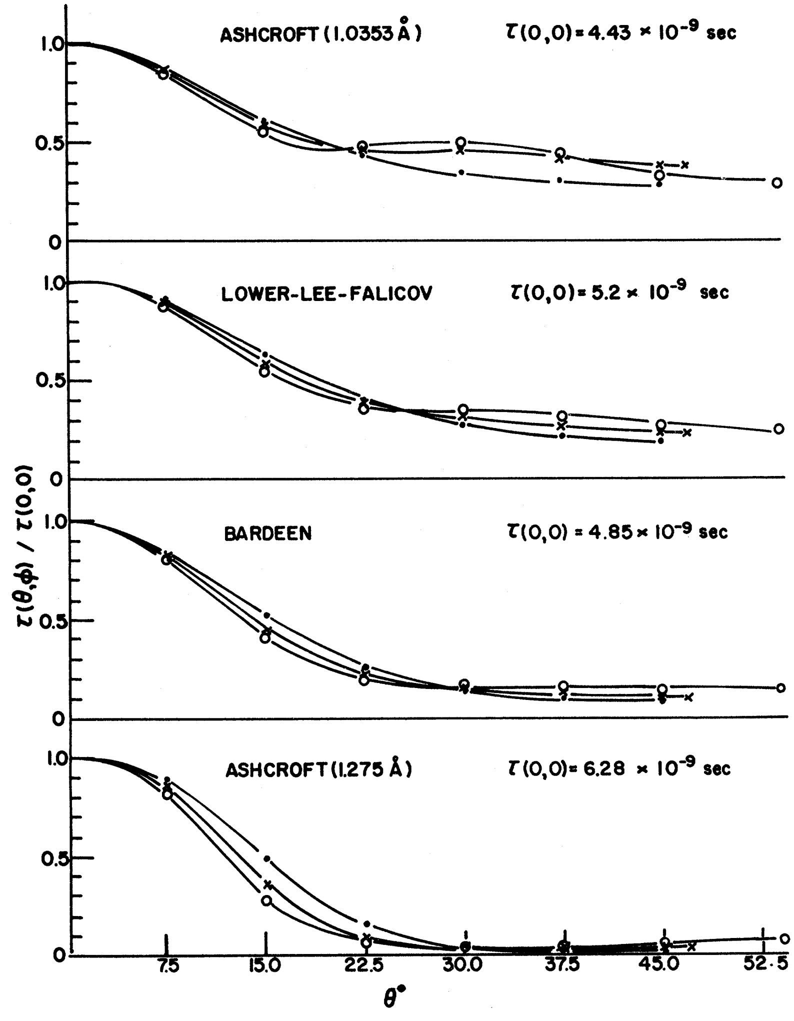

FIG. 6. Scattering times in K at 4 °K as a function of position on the irreducible $\frac{1}{48}$th of the Fermi surface. Results for various possible choices of pseudopotentials are compared. On each graph the value of $\tau(\vec{k})$ for $\vec{k} = (0, 0, k_F)$ is entered and all results are normalized to this value. For $\vec{k} \equiv (\theta, \phi, k_F)$, the results for the three arcs $\phi = 0°$, $22\frac{1}{2}°$, and 45° are to be distinguished as follows: •, $\phi = 0°$; ×, $\phi = 22\frac{1}{2}°$; o, $\phi = 45°$.

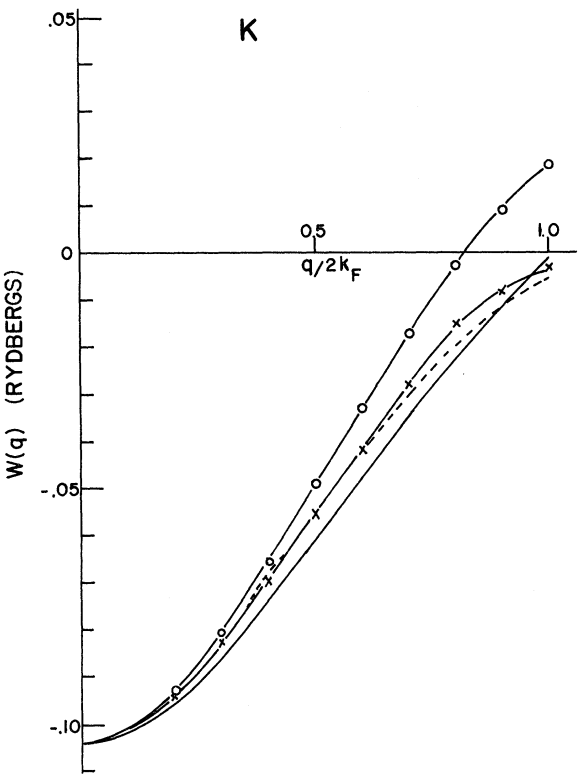

FIG. 7. Comparison of various form factors $W(q)$: Bardeen(----), lower Lee-Falcov (x-x-x), Ashcroft $R_c = 1.27$ Å (o-o-o), and Ashcroft $R_c = 1.04$ Å (—).

We believe the minimum in n^*/n to have the same origin. In Fig. 9, we show results for Na, Rb, and Li. These curves are all based on pseudopotentials which fit the resistivity well.[2,9] We see that, in all cases, as T decreases, n^*/n also decreases. It then reaches a minimum at a few degrees kelvin and starts increasing again. For Rb and Na, deviations of n^*/n from 1.0 seem to become of some significance only at the very lowest temperatures. For Li, the effect is quite large even at room temperature. This is not unexpected since Li has by far the most anisotropy.

Robinson and Dow[1] quote room-temperature experimental results for n^*/n of 0.87 (0.79) in Li, 0.95 (1.17) in Na, 0.95 (1.11) in K, and 0.94 in Rb. The numbers in parentheses are other experimental numbers which are included to indicate to the reader the uncertainty that seems to exist at the present time. For lithium we get 0.87 while for the other alkalis we get slightly less than 1. We consider the agreement satisfactory although more experimental work would certainly be of interest.

Recently, Alderson and Farrell[12] have measured n^*/n in Li, Na, and K over the temperature range 6–300 °K. It is observed that n^*/n decreases slowly with T in qualitative agreement with our calculations. Na and K show the least variations while that in Li is much more pronounced again in

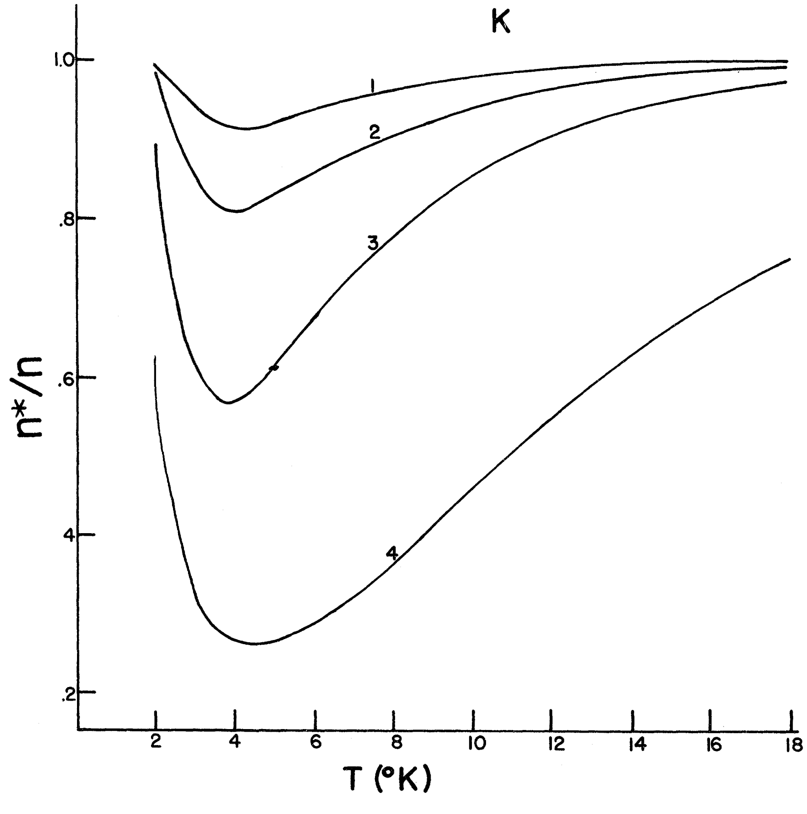

FIG. 8. Effective number of carriers n^*/n as a function of temperature for various choices of $W(q)$ in K.

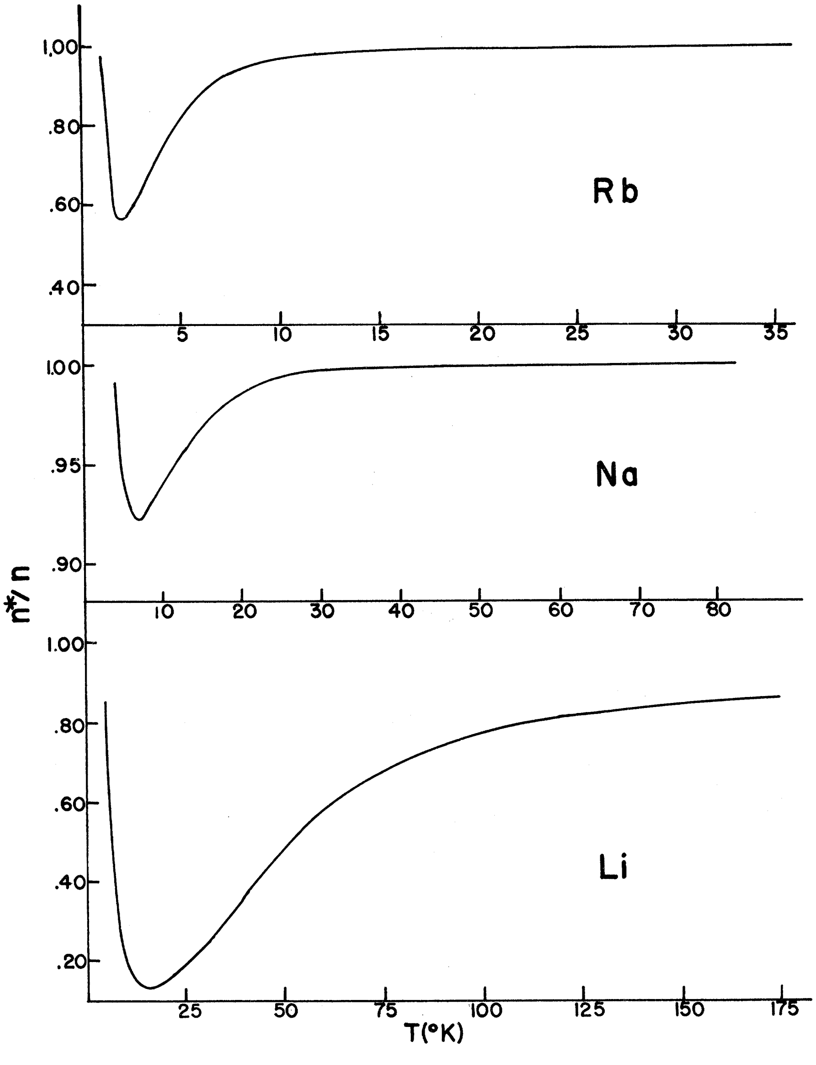

FIG. 9. Effective number of carriers n^*/n as a function of temperature for Na, Rb, and Li. In all cases the pseudopotential form factors developed by Hayman and Carbotte have been employed since they fit the resistivity data well.

general agreement with our work. At the lower temperature end, the experimental results in Li and Na are complicated by a Martensitic transformation. In K, if we ignore the minimum observed around ≈ 20 °K because its origin is not well known, we estimate roughly a 8% decrease from high to low temperature. This is in reasonable accord with our results (see curve 1, Fig. 8).

V. CONCLUSION

We have calculated the effective number of charge carriers n^*/n in the alkali metals. We ignore Fermi-surface anisotropy but include the anisotropy in the scattering time, due to anisotropy in the electron-phonon interaction. We find that the data of Alderson and Farrell on the temperature variation of n^*/n can be understood qualitatively on the basis of our calculations. We find further that at very low temperatures a minimum occurs in our theoretical curves which we believe to be due to the onset of umklapp processes. A similar effect has recently been observed by Ekin in the low-temperature resistivity of K. We find that at low T, n^*/n is very sensitive to the form of the pseudopotential form factor. The Hall coefficient is another method to get information on this quantity. It is hoped that the present study will stimulate more experiments on the temperature variation of the Hall constant.

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Low-Field Magnetoresistance of Palladium Alloys[*]

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Observations are reported of a negative contribution to the magnetoresistance of a paramagnetic transition metal, palladium, with nonmagnetic impurities. The longitudinal magnetoresistance of some polycrystalline palladium alloys which show a resistance minimum is compared with the magnetoresistance of palladium alloys with no resistance minimum. Kondo scattering in these alloys cannot account for the results, but we suggest that the energy dependence of Mott *s-d* scattering, used successfully to explain the temperature dependence of resistivity of these alloys, is also responsible for the negative magnetoresistance. A positive contribution to the magnetoresistance which, unlike the negative component, obeys Kohler's rule is also present. We attribute this component to anisotropy of scattering on the Fermi surface. It proves to be surprisingly sensitive to the impurity type, suggesting that this may be a profitable way to study the anisotropy of scattering in other paramagnetic transition metals.

INTRODUCTION

In a recent letter Rowlands *et al.*[1] described experiments on the electrical resistivity of dilute *Pd*-Rh[2] alloys which showed a resistance minimum. Other workers[3] have found resistance minima in some concentrated *Pd*-Ag alloys. However, no minimum is seen in dilute *Pd*-Ag or *Pd*-Pt alloys. Rowlands *et al.* explained these results on the basis of the energy dependence of Mott *s-d* scattering, which gives rise to a resistance of the form

$$\rho_T = \rho_0(1 - AT^2), \tag{1}$$

where A is a term related to the energy dependence of the density-of-states curve.

This mechanism was first applied to impurity resistivity by Coles and Taylor,[4] who successfully explained the peculiar concentration dependence of the room-temperature resistivity of *Pd*-Ag alloys on this basis. It was extended and applied to other electronic properties by Dugdale and Guenault.[5]

There is no evidence that the impurity exhibits a local moment in any of the alloys we have mentioned[6]; therefore, the Kondo effect can be ruled out. Rowlands and Greig[7] in a forthcoming paper discuss further evidence to support the contention that even in some *Pd*-Cr and *Pd*-Np alloys, where it is possible that the impurity is magnetic, the resistance minimum that has been observed is due to a virtual bound state with a strongly energy-dependent density of states. If the energy dependence of the final *d* states in our alloys is responsible for the resistance minimum, then the effect of a magnetic field on the alloys should also be marked. A component of the magnetoresistance, which we shall call "band" magnetoresistance will arise from the splitting of the *d* band into two spin bands. The band magnetoresistance may be evaluated from the density-of-states curves for pure palladium derived from magnetic-susceptibility data. It turns out that it is negative and proportional to the solute concentration for sufficiently dilute alloys. "Anisotropy" magnetoresistance, arising from the anisotropy of scattering processes on the Fermi surface,[8] is the other component to be expected in these alloys. In alloys where the band component is small, it is demonstrated experimentally that the magnetoresistance obeys Koh-