

## General theory of the electrical resistivity of the alkali metals at low temperatures

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A complete analysis is presented for the temperature dependence of the electrical resistivity of the alkali metals at low temperatures. New results are found for the temperature dependence of the umklapp-scattering term. We find one expression appropriate to the low-temperature limit and a different expression appropriate to somewhat higher temperatures. These results are used to explain the reported  $T^5$  behavior for the low-temperature-resistivity data. It is found that the temperature below which  $T^5$  behavior is reported is proportional to the lower transverse velocity of sound in the [110] direction, in excellent agreement with experiment for all the alkalis. For still lower temperatures, phonon drag is shown to play a decisive role on the temperature dependence of the resistivity, leading to an exponential decrease with temperature, rather than a power-law dependence. Finally, the restriction of the above analysis to the alkali metals is explained in terms of Matthiessen's rule and the requirement of a spherical Fermi surface.

### I. INTRODUCTION

With the advent of quantum mechanics, one of the first problems to which solid-state theoreticians turned their attention was the calculation of the temperature-dependent part of the dc electrical resistivity  $\rho(T)$  of pure metals, particularly at low temperatures. The principal result of this early work was the Bloch-Grüneisen formula,<sup>1</sup> leading to the well-known Bloch  $T^5$  law to describe  $\rho(T)$  at low temperature,  $T \ll \Theta$ , where  $\Theta$  is the Debye temperature of the metal. Later, more complete calculations<sup>2</sup> confirmed the Bloch law. In fact, until very recently,<sup>3</sup> the  $T^5$  law was the cornerstone of the theory of the low-temperature resistivity. It had been almost universally believed that one can completely describe the low-temperature data for  $\rho(T)$  for all the simple metals by determining the coefficient of the  $T^5$  term, as well as the temperature below which  $T^5$  behavior occurs. This point of view seemed to be well supported by an examination of the data,<sup>4</sup> which show that for an impressively large number of metals, including all the alkalis,  $T^5$  behavior is indeed reported for the low-temperature regime.

This idyllic situation was very recently upset, both experimentally<sup>5-7</sup> and theoretically.<sup>3,8,9</sup> Very careful measurements by Ekin and co-workers<sup>5,6</sup> of  $\rho(T)$  for potassium in the range 2-20 °K revealed that the low-temperature behavior of  $\rho_{\text{expt}}(T)$  is quite complicated and, in fact, does not exhibit a  $T^5$  dependence. Furthermore, as a result of a very careful experimental study of  $\rho(T)$  for potassium in the range 2-4 °K, Guban<sup>7</sup> reported that  $\rho_{\text{expt}}(T)$  decays exponentially with temperature below 4 °K. Concurrent with these recent experiments, calculations<sup>8,9</sup> for  $\rho(T)$  for potassium at low temperatures have been carried out. Although these calculations constitute a significant improve-

ment over earlier calculations, they failed to yield the observed<sup>7</sup> exponential decay of  $\rho(T)$ .

It is the goal of this paper to derive analytically the complex temperature dependence of  $\rho(T)$  for all the alkali metals throughout the low-temperature regime,  $T < 0.2\Theta$ . Our expression for  $\rho(T)$  yields an exponential temperature dependence at very low temperature and a dependence closely approximating  $T^5$  at somewhat higher temperatures, both results being in precise agreement with experiment.<sup>4-7</sup> We also analyze in detail the relationship between the Bloch  $T^5$  law and the reported<sup>4</sup>  $T^5$  dependence for  $\rho(T)$ , showing why the older data yielded a low-temperature  $T^5$  dependence for all the alkalis and also showing why for Na, at still lower temperatures, a  $T^6$  dependence was found.<sup>10</sup> In addition to being able to predict the different temperature dependences observed in various temperature ranges, we determine where each temperature range begins for each of the alkalis in terms of the macroscopic properties of the metal, in particular, the velocity of sound in the [110] direction. The agreement with experiment<sup>4</sup> is excellent.

An important feature of our results is that they are derived without any computer calculations whatsoever. Our analysis is based on the recognition that for low temperatures, a relatively small portion of the Brillouin zone in the vicinity of the [110] direction makes the dominant contribution to all the  $\vec{k}$ -space resistivity integrals. By expanding all the integrands around the dominant [110] direction, we are able to obtain analytical expressions for the vitally important umklapp contribution to  $\rho(T)$ . This in turn permits a completely analytic treatment of the temperature dependence of  $\rho(T)$  for both the very-low-temperature, exponential, phonon-drag regime, as well as the somewhat higher-temperature, approximate,  $T^5$

regime.

Although all the above results are obtained without the need for computer calculations, it is clear that a detailed quantitative comparison between theory and experiment requires a separate computer calculation for each metal. In the following paper,<sup>11</sup> we present such a comparison for potassium and show that complete agreement is obtained for the measured<sup>5,6</sup> temperature range, 2–20 °K. Such quantitative agreement with experiment complements the qualitative picture presented in this paper.

In Sec. II we discuss the assumptions needed to derive the expression for  $\rho(T)$ , including phonon drag, and explain how these assumptions limit the validity of the resulting expression to the alkali metals. In Sec. III we analyze the expression for  $\rho(T)$  and point out the simplifying features at low

temperatures which enable us to derive analytic expressions for the low-temperature behavior of the umklapp contribution to  $\rho(T)$ . The relationship between the Bloch  $T^5$  law and the  $T^5$  behavior widely reported for  $\rho_{\text{ext}}(T)$  at low temperature is discussed in Sec. IV. In Sec. V, we analyze the contribution to  $\rho(T)$  due to phonon drag and show how phonon drag dominates the limiting low-temperature behavior for  $\rho(T)$ , leading to an exponential temperature dependence in the lowest-temperature regime. The role of Matthiessen's rule in the analysis is discussed in Sec. VI. The summary follows in Sec. VII.

## II. FORMALISM

When Matthiessen's rule is valid, the temperature-dependent part of the electrical resistivity  $\rho(T)$  can be obtained by a variational solution<sup>1</sup> of the Boltzmann equation,

$$\rho(T) = \frac{\pi\Omega_0 \iint [dS(\vec{K}_1)/u(\vec{K}_1)] [dS(\vec{K}_2)/u(\vec{K}_2)] [\phi_{e1}(\vec{K}_1) - \phi_{e1}(\vec{K}_2) - \phi_{ph}(\vec{q})]^2 P(\vec{K}_1, \vec{K}_2)}{2e^2\hbar^3 \left\{ \int d^3K u(\vec{K}) \phi_{e1}(\vec{K}) [\partial f_0(\vec{K})/\partial E(\vec{K})] \right\}^2}, \quad (2.1)$$

where  $\Omega_0$  is the atomic volume,  $E(\vec{K})$  and  $\vec{u}(\vec{K})$  are the electron energy and velocity, respectively, and the surface integrals are taken over the Fermi surface, with  $\vec{K}_1$  and  $\vec{K}_2$  being the wave vectors of the initial and final states of the electron which is scattered by a phonon of wave vector  $\vec{q}$ . The function  $P(\vec{K}_1, \vec{K}_2)$  is proportional to the transition probability for scattering an electron through  $\vec{k} = \vec{K}_2 - \vec{K}_1$  from state  $\vec{K}_1$  to state  $\vec{K}_2$ . The trial functions  $\phi_{e1}(\vec{K})$  and  $\phi_{ph}(\vec{q})$  are proportional to the deviation, caused by the electric field, of the electron and phonon distribution functions  $f(\vec{K})$  and  $n(\vec{q})$  from their equilibrium values  $f_0(\vec{K})$  and  $n_0(\vec{q})$ , respectively,

$$\begin{aligned} f(\vec{K}) &= f_0(\vec{K}) - \phi_{e1}(\vec{K}) \left( \frac{\partial f_0(\vec{K})}{\partial E(\vec{K})} \right), \\ n(\vec{q}) &= n_0(\vec{q}) - \phi_{ph}(\vec{q}) \left( \hbar^{-1} \frac{\partial n_0(\vec{q})}{\partial \omega(\vec{q})} \right), \end{aligned} \quad (2.2)$$

where  $\hbar\omega(\vec{q})$  is the phonon energy.

The trial functions  $\phi_{e1}(\vec{K})$  and  $\phi_{ph}(\vec{q})$  are to be chosen consistent with each other and such that  $\rho(T)$  is minimized. The form of the trial functions plays a decisive role in the subsequent analysis because the structure of the resulting resistivity integral is entirely different for different trial functions. For each of the alkali metals, and only for the alkali metals, the following three important simplifications are valid.

(i) The Fermi surface is spherical,<sup>12</sup> (ii) a single plane wave suffices to represent the pseudo-wave-function, and (iii) the function  $P(\vec{K}_1, \vec{K}_2)$  factors into the product  $\mathfrak{s}(\vec{k})v^2(k)$ , where  $\mathfrak{s}(\vec{k})$  and  $v(k)$  are the structure factor<sup>13</sup> and form factor,

respectively. When these three simplifications are valid, it can be shown (details presented in Appendix A) that the correct electron trial function is given to a good approximation by the following simple form

$$\phi_{e1}(\vec{K}) \propto \vec{K} \cdot \vec{F}, \quad (2.3)$$

where  $\vec{F}$  is the applied electric field.

We now turn to the phonon trial function  $\phi_{ph}(\vec{q})$ . A nonzero  $\phi_{ph}(\vec{q})$  is the source of the negative contribution to  $\rho(T)$  due to phonon drag. This takes account of the fact that the phonon system does not return to thermal equilibrium between electron-phonon collisions. We make the standard<sup>1</sup> choice

$$\phi_{ph}(\vec{q}) \propto \vec{q} \cdot \vec{F}. \quad (2.4)$$

Having chosen both  $\phi_{e1}(\vec{K})$  and  $\phi_{ph}(\vec{q})$ , one is in a position to evaluate  $\rho(T)$ . The resistivity is conveniently separated into

$$\rho(T) = \rho_{\text{eq}}(T) - \rho_g(T) = \rho_{\text{eq}}(T) [1 - X(T)], \quad (2.5)$$

where  $\rho_{\text{eq}}(T)$  is the resistivity obtained by assuming that the phonons equilibrate rapidly between electron-phonon collisions, i. e.,  $\phi_{ph}(\vec{q}) = 0$ , and  $\rho_g(T)$  is the contribution due to phonon drag, i. e.,  $\phi_{ph}(\vec{q}) \propto \vec{q} \cdot \vec{F}$ . Reducing<sup>1,14,15</sup> the multiple integral for  $\rho(T)$  appearing in Eq. (2.1) yields

$$\rho_{\text{eq}}(T) = \frac{m^2}{12\pi^3 e^2 \hbar^3 n^3} \int_0^{2k_F} dk k^3 v^2(k) S(k), \quad (2.6)$$

where  $n$  is the density of electrons,  $m$  is the electron mass,  $k_F$  is the Fermi momentum, and  $S(k)$  is the angular average of the structure factor

$$S(k) = (4\pi)^{-1} \int d\Omega_{\vec{k}} \mathfrak{s}(\vec{k}). \quad (2.7)$$

A similar procedure<sup>1,14</sup> yields

$$X(T) = P_{1L}^2 / P_{11} P_{LL} \quad (2.8)$$

where

$$\begin{aligned} P_{11} &= C \int d^3k k^{-1} s(\vec{k}) v^2(k) k^2, \\ P_{1L} &= C \int d^3k k^{-1} s(\vec{k}) v^2(k) \vec{k} \cdot \vec{q}, \\ P_{LL} &= C \int d^3k k^{-1} s(\vec{k}) v^2(k) q^2. \end{aligned} \quad (2.9)$$

Here,  $C$  is a known constant,  $\vec{q}$  is the wave vector  $\vec{k}$  "folded back" into the first Brillouin zone, and the integration is taken over the sphere  $|\vec{k}| \leq 2k_F$ . Note that  $P_{11}$  is proportional to the triple integral for  $\rho_{\text{eq}}$  given in Eqs. (2.6) and (2.7).

We close this section by emphasizing that Eqs. (2.6)–(2.9) for  $\rho(T)$  apply only to the alkali metals and are totally inappropriate for the polyvalent and noble metals. The reason for this is that for the polyvalent and noble metals, none of the three previously mentioned simplifications are valid and, consequently, Eq. (2.3) is an extremely poor approximation to the trial function  $\phi_{\text{el}}(\vec{K})$ . The resulting theory of  $\rho(T)$  for the polyvalent metals is radically different from that for the alkali metals, as will be discussed in Sec. VI. We note here that the analysis to be presented in Secs. III–V is based on Eqs. (2.6)–(2.9) and therefore limited to the alkali metals.

### III. LOW-TEMPERATURE BEHAVIOR OF UMKLAPP CONTRIBUTION TO $\rho_{\text{eq}}(T)$

The key to our analysis lies in the low-temperature behavior of the structure factor<sup>13</sup>  $s(\vec{k})$ . In the one-phonon harmonic approximation we have

$$s(\vec{k}) = \frac{\hbar^2}{Mk_B T} \sum_{\lambda} \frac{[\vec{k} \cdot \xi_{\lambda}(\vec{q})]^2}{(e^{\hbar\omega_{\lambda}(\vec{q})/k_B T} - 1)(1 - e^{-\hbar\omega_{\lambda}(\vec{q})/k_B T})} \quad (3.1)$$

where  $M$  is the ionic mass and  $\omega_{\lambda}(\vec{q})$  and  $\xi_{\lambda}(\vec{q})$  are the frequency and polarization vector, respectively, of a phonon of branch  $\lambda$  and wave vector  $\vec{q}$ . As before, the vector  $\vec{q}$  is just the scattering vector  $\vec{k}$  "folded back" into the first Brillouin zone,

$$\vec{q} = \vec{k} - \vec{G}_n, \quad (3.2)$$

where  $\vec{G}_n$  is the appropriate reciprocal-lattice vector. For a given  $\vec{k}$ , there is a unique  $\vec{q}$  and  $\vec{G}_n$  that satisfy (3.2).

In order to understand the low-temperature behavior of  $s(\vec{k})$ , we plot in Fig. 1,  $\omega_{T_2}(\vec{q})$  for potassium as a function of  $\vec{k}$  for the [110] direction, the subscript  $T_2$  denoting the lower transverse-phonon branch. We see that, for  $T < 10^\circ\text{K}$ ,  $k_B T < \hbar\omega_{T_2}(\vec{q})$  for all  $\vec{k}$  except near  $k = 0$ . Therefore, for  $k$  not too small, the argument of the exponents in the expression (3.1) for  $s(\vec{k})$  exceeds unity. Since the lower transverse-phonon branch in the [110] direction has the lowest frequency of any  $\omega_{\lambda}(\vec{q})$ , it is a good approximation, when  $k$  is not too small, to

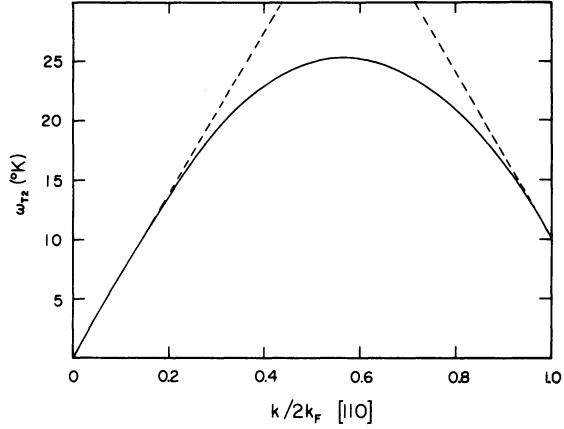


FIG. 1. Lower transverse-phonon branch in the [110] is plotted in units of temperature as a solid curve. The dashed line is the Debye approximation with the appropriate velocity of sound. In the [110] direction, the Brillouin-zone boundary is reached at  $k/2k_F = 0.57$ .

drop both the negative exponential and the unity to obtain

$$s(\vec{k}) = \frac{\hbar^2}{Mk_B T} \sum_{\lambda} [\vec{k} \cdot \xi_{\lambda}(\vec{q})]^2 e^{-\hbar\omega_{\lambda}(\vec{q})/k_B T} \quad (3.3)$$

Let us now turn to  $\rho_{\text{eq}}(T)$ , given by the integrals in Eqs. (2.6) and (2.7). Because of the exponential dependence of  $s(\vec{k})$  on  $\omega_{\lambda}(\vec{q})$ , at low temperatures there will be a significant contribution to the integral for  $\rho_{\text{eq}}(T)$  only for  $k$  very near zero and  $k$  very near  $2k_F$ . Therefore, it is not necessary to know the entire phonon spectrum  $\omega_{\lambda}(\vec{q})$ . Indeed, the Debye approximation

$$\omega_{\lambda}(\vec{q}) = v_{\lambda}(\hat{q})q, \quad (3.4)$$

given by the dashed line in Fig. 1, is a quite adequate approximation to  $\omega_{\lambda}(\vec{q})$  for determining  $\rho(T)$  at low  $T$ , where  $v_{\lambda}(\hat{q})$  means the velocity of sound in the direction  $\hat{q}$  for polarization  $\lambda$ .

It follows from the above discussion that there is an unambiguous separation of the integral for  $\rho_{\text{eq}}(T)$  into the normal (low- $k$ ) contribution  $\rho_N(T)$  and the umklapp (high- $k$ ) contribution  $\rho_U(T)$ . We shall see in the course of the discussion that  $\rho_U(T)$  is of particular interest. Because of the exponential dependence of  $s(\vec{k})$  on  $\omega_{\lambda}(\vec{q})$ , given in (3.3), only the smallest  $\omega_{\lambda}(\vec{q})$  contribute significantly to  $\rho_U(T)$ . Near  $k = 2k_F$ , the smallest  $\omega_{\lambda}(\vec{q})$  lie on the lower transverse branch ( $T_2$ ) in the neighborhood of the [110] direction. The  $\omega_{\lambda}(\vec{q})$  corresponding to all other directions or other branches are at least 3 times as large. Since  $s(\vec{k})$  depends exponentially on  $\omega_{\lambda}(\vec{q})$ , we may restrict our attention to the  $T_2$  branch, with  $\vec{k}$  lying within a small solid angle around the [110] direction in the vicinity of  $2k_F$ . The relevant geometry in the  $k_x$ - $k_y$  plane is pre-

sented in Fig. 2. In precisely the [110] direction,  $\vec{k}$ ,  $\vec{q}$ , and  $\vec{G}_{110}$  are all parallel to each other and perpendicular to the polarization vector  $\hat{\xi}_{T_2}(\vec{q})$ . Thus, there is no contribution to  $s(\vec{k})$  because  $\vec{k} \cdot \hat{\xi}_{T_2}(\vec{q})$  vanishes. However, as  $\vec{k}$  changes direction slightly,  $\vec{k}$  is no longer perpendicular to  $\hat{\xi}_{T_2}(\vec{q})$  and  $s(\vec{k})$  no longer vanishes. These  $\vec{k}$  values, in the neighborhood of the [110] direction, give rise to the dominant contribution to  $S(k)$  and hence to  $\rho_U(T)$ .

In order to derive an analytic expression for the temperature dependence of  $\rho_U(T)$  in the limit  $T \rightarrow 0$ , we expand  $\omega_{T_2}(\vec{q}) = \omega_{T_2}(\vec{k})$  around the [110] direction, corresponding to a value of  $\vec{k}$  having components

$$\begin{aligned} k &= 2k_F, \quad \theta = \frac{1}{2}\pi, \quad \text{and} \quad \phi = \frac{1}{4}\pi, \\ \omega_{T_2}(\vec{q}) &\simeq \omega_0 + \omega_q(2k_F - k) + \frac{1}{2}\omega_{\theta\theta}(\theta - \frac{1}{2}\pi)^2 \\ &\quad + \frac{1}{2}\omega_{\phi\phi}(\phi - \frac{1}{4}\pi)^2, \end{aligned} \quad (3.5)$$

where  $\omega_0 \equiv \omega_{T_2}(2k_F, \frac{1}{2}\pi, \frac{1}{4}\pi)$ ,  $\omega_q \equiv \partial\omega/\partial q = -\partial\omega/\partial k$ ,  $\omega_{\theta\theta} \equiv \partial^2\omega/\partial\theta^2$ , and  $\omega_{\phi\phi} = \partial^2\omega/\partial\phi^2$ , with all partial derivatives evaluated at  $\vec{k} = (2k_F, \frac{1}{2}\pi, \frac{1}{4}\pi)$ . The

linear terms in the  $\theta$  and  $\phi$  expansions must vanish because  $\omega_{T_2}(\vec{k})$  has a minimum in the [110] direction. Let us designate by  $\gamma_0$ ,  $\delta_0$ , and  $k_0$ , the small angles and small wave numbers defined so that the expansion (3.5) is valid for  $|\theta - \frac{1}{2}\pi| < \gamma_0$ , for  $|\phi - \frac{1}{4}\pi| < \delta_0$ , and for  $k > 2k_F - k_0$ .

The structure factor  $s(\vec{k})$  also contains the factor  $[\vec{k} \cdot \hat{\xi}_{T_2}(\vec{q})]^2$ . It can be seen from Fig. 2 that for small changes in  $\theta$  from the [110] direction, the vector  $\vec{k}$  rotates around the  $\hat{\xi}_{T_2}$  axis but remains perpendicular to it. Therefore, we need only consider small changes in  $\phi$  with  $\theta$  fixed at  $\frac{1}{2}\pi$ , i. e., small rotations of  $\vec{k}$  in the  $k_x$ - $k_y$  plane. The relevant geometry is presented in Fig. 3. It is seen from the figure that for small changes in  $\phi$ , the angle  $\delta = \phi - \frac{1}{4}\pi$  is proportional to the angle  $\delta_0$ , and therefore  $\vec{k} \cdot \hat{\xi}_{T_2}(\vec{q}) \propto \delta$  for small  $\delta$ . Hence, we have

$$[\vec{k} \cdot \hat{\xi}_{T_2}(\vec{q})]^2 \propto (\phi - \frac{1}{4}\pi)^2. \quad (3.6)$$

Inserting all these results into Eqs. (2.6) and (2.7) yields

$$\begin{aligned} \omega_{T_2}\rho_U(T) &\propto T^{-1} e^{-\hbar\omega_0/k_B T} \int_{2k_F-k_0}^{2k_F} dk e^{-\hbar\omega_q(2k_F-k)/k_B T} \int_{\pi/2-\gamma_0}^{\pi/2+\gamma_0} d\theta e^{-\hbar\omega_{\theta\theta}(\theta-\pi/2)^2/2k_B T} \\ &\quad \times \int_{\pi/4-\delta_0}^{\pi/4+\delta_0} d\phi (\phi - \frac{1}{4}\pi)^2 e^{-\hbar\omega_{\phi\phi}(\phi-\pi/4)^2/2k_B T}. \end{aligned} \quad (3.7)$$

For sufficiently low temperature, the integrands are negligible outside the indicated limits of integration. Note that we have evaluated the product  $k^3 v^2(k)$  at  $k = 2k_F$  and taken it outside the integral. Letting the argument of the exponent be a new variable in each integral and extending the limits to infinity gives

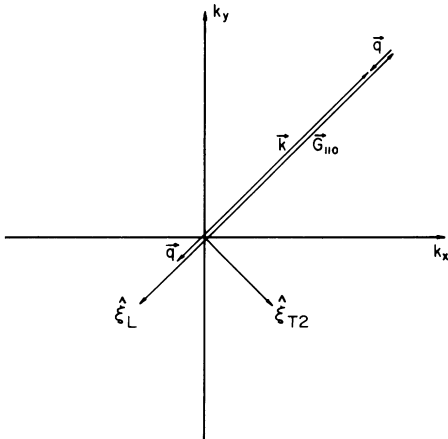


FIG. 2. For  $\vec{k}$  in the [110] direction and having magnitude  $2k_F$ , the vector  $\vec{q}$  is depicted as well as the two polarization vectors  $\hat{\xi}_\lambda(\vec{q})$  in the  $k_x$ - $k_y$  plane.

$$\begin{aligned} \rho_U(T) &= AT^{-1} e^{-\hbar\omega_0/k_B T} [(T)(T^{1/2})(T^{3/2})] \\ &= AT^2 e^{-\hbar\omega_0/k_B T}, \end{aligned} \quad (3.8)$$

where each of the three integrals contributes the indicated power of  $T$ . The constant  $A$  contains  $v^2(2k_F)$  and also the partial derivatives  $\omega_q$ ,  $\omega_{\theta\theta}$ , and  $\omega_{\phi\phi}$ . Of particular interest is  $\omega_0$ , which is given by the velocity of sound in the [110] direction and contains the combination of elastic constants  $c_{11} - c_{12}$ . The values for  $\omega_0$  for each of the alkali metals are presented in the second column of the Table I. Not only  $\omega_0$ , but the partial derivatives as well are readily determined functions of the three elastic constants of the metal. Therefore, the only parameter in  $A$  is the square of the form factor evaluated at  $2k_F$ .

At somewhat higher temperatures the limits on the  $\phi$  integral must be extended, leading to a breakdown of the expansion of  $\omega_{T_2}(\vec{k})$  in  $\phi$ . However, as shown in Appendix B, we may then make a different expansion for  $\phi$  which leads to

$$\rho_U(T) = BT^{7/2} e^{-\hbar\omega_1/k_B T}, \quad (3.9)$$

where  $\omega_1 \simeq 0.8\omega_0$ , as shown in Appendix B. As with the previous expansion, the ratio  $B/v^2(2k_F)$  is readily derived in terms of the elastic constants of the metal.

It is appropriate to point out the new features of the low-temperature expressions for  $\rho_U(T)$

given in (3.8) and (3.9). First of all, the power of  $T$  multiplying the exponent differs significantly from the standard result<sup>1</sup> of  $T^{-1}$ . Second, we have obtained explicit expressions for the arguments of the exponentials,  $\omega_0$  and  $\omega_1$ . We will show in Secs. IV and V how these results can be used to explain the observed low-temperature behavior of  $\rho(T)$ .

#### IV. BLOCH $T^5$ LAW

The widely quoted result<sup>1</sup> for the low-temperature behavior of  $\rho(T)$  is the Bloch  $T^5$  law

$$\rho_{\text{Bloch}}(T) = CT^5, \quad T < T_c. \quad (4.1)$$

Indeed, the low-temperature experimental data for  $\rho(T)$  for many metals have been presented<sup>4</sup> by simply reporting two parameters, the coefficient  $C$  and the temperature  $T_c$  below which (4.1) applies. In particular, except for the recent highly accurate measurements for potassium, the data for  $\rho(T)$  for all the alkalis<sup>4,16</sup> appear to exhibit  $T^5$  behavior below some temperature  $T_c$ .

Equation (4.1) is of course based on a calculation of  $\rho(T)$  that ignores  $\rho_U(T)$ . Although it has long been known that  $\rho_U(T)$  is larger than  $\rho_N(T)$  for high temperatures, it had generally been assumed that the reason the data exhibit  $T^5$  behavior below  $T_c$  is that at such low temperatures,  $\rho_U(T)$  has already become negligible because of its exponential decrease with temperature. Moreover, at such low temperatures, the Bloch approximation to  $\rho_N(T)$  becomes very good and thus one may confidently expect that (4.1) will accurately describe the data for  $\rho(T)$ .

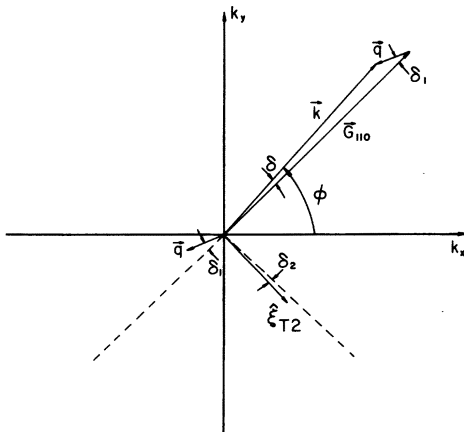


FIG. 3. For  $\vec{k}$  in the  $k_x$ - $k_y$  plane, the directions are given for  $\vec{q}$  and  $\xi_{T2}$ . The direction of  $\vec{k}$  deviates from the [110] direction by a small angle  $\delta$ . The corresponding deviations in the directions of  $\vec{q}$  and  $\xi_{T2}$  are designated by the small angles  $\delta_1$  and  $\delta_2$ , respectively, both of which are of course proportional to  $\delta$ .

TABLE I. For each of the alkali metals, we list  $\omega_0$  and  $\omega_1$  (in units of temperature) and  $(T_c)_{\text{expt}}$ . The frequency  $\omega_0$  lies on the lower transverse-phonon branch in the [110] direction at  $q = G_{110} - 2k_F$  and constitutes the lowest frequency in the Brillouin zone participating in umklapp scattering. As explained in the text,  $\omega_1 = 0.8\omega_0$  corresponds to the temperature  $(T_c)_{\text{expt}}$  at which the onset of the observed  $T^5$  behavior for  $\rho(T)$  occurs.

Metal	$\hbar\omega_0/k_B$ (°K)	$\hbar\omega_1/k_B$ (°K)	$(T_c)_{\text{expt}}$ (°K)
Li <sup>a</sup>	35	28	>20 <sup>f</sup>
Na <sup>b</sup>	20	16	15
K <sup>c</sup>	10.0	8.0	8
Rb <sup>d</sup>	6.0	4.8	5
Cs <sup>e</sup>	4.3	3.5	3.1

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<sup>d</sup>E. J. Gutman and J. Trivisonno, J. Phys. Chem. Solids **28**, 805 (1967).

<sup>e</sup>F. J. Kollarits and J. Trivisonno, J. Phys. Chem. Solids **29**, 2133 (1968).

<sup>f</sup>Although the value quoted in Ref. 16 is 15°K, it is clear from Fig. 3 of Ref. 16 that  $(T_c)_{\text{expt}}$  definitely exceeds 20°K.

The above explanation for the observed  $T^5$  behavior of  $\rho(T)$  is not correct.<sup>3</sup> In fact, even at temperatures considerable below  $T_c$ ,  $\rho_U(T)$  still exceeds  $\rho_N(T)$  and can by no means be ignored. To understand the reported  $T^5$  behavior for  $\rho(T)$  for the alkalis,<sup>16</sup> let us write

$$\rho(T) \approx \rho_{\text{eq}}(T) = \rho_N(T) + \rho_U(T). \quad (4.2)$$

Note that we have ignored the phonon-drag contribution  $\rho_g(T)$ . This is an appropriate approximation for a qualitative discussion since we are considering temperatures not too far below  $T_c$ . For the term  $\rho_N(T)$ , (4.1) is certainly adequate at low temperatures. Finally, we use Eq. (3.9) for  $\rho_U(T)$ . The lower-temperature form for  $\rho_U(T)$ , given in Eq. (3.8), is valid only for temperatures considerably below  $T_c$  [where  $\rho_g(T)$  must also be taken into account] and we discuss such low temperatures only in Sec. V.

Inserting (4.1) and (3.9) into (4.2) yields

$$\rho(T) = CT^5 [1 + (B/C)T^{-3/2} e^{-\hbar\omega_1/k_B T}]. \quad (4.3)$$

The expression in the brackets has a broad maximum centered at

$$T_{\text{max}} = \hbar\omega_1/1.5k_B. \quad (4.4)$$

Therefore, very near  $T_{\text{max}}$  to a good approximation  $\rho(T) \propto T^5$ . The important question is over what temperature range do the observed values of

$\rho_{\text{expt}}(T)$  continue to closely approximate a  $T^5$  dependence. The answer depends of course on the quality of the experimental data. One may illustrate this point by examining  $\rho(T)/CT^5$  as a function of the reduced temperatures  $T/T_{\text{max}}$ . For concreteness, we shall choose the ratio  $B/C$  so that at  $T = T_{\text{max}}$   $\rho_U = 2\rho_N$ , a value typical of the alkalis. Our conclusions are insensitive to the value chosen for  $B/C$ . In Fig. 4, the dashed line represents Eq. (4.3). The "experimental" values of  $\rho(T)/CT^5$  have been simulated by adding to the values calculated from (4.3) a random scatter corresponding to a standard mean deviation of  $\pm 3\%$ . This is a rather modest estimate of the experimental error for a typical measurement of  $\rho(T)$  at low temperatures.<sup>17</sup> Note that the points fit quite nicely to the horizontal line over the range  $0.7 \lesssim T/T_{\text{max}} \lesssim 1.5$ . This implies that experimental data will appear to have reached the  $T^5$  limit at about  $1.5 T_{\text{max}} = \hbar\omega_1/k_B$ , i. e., at  $T_c \approx 1.5 T_{\text{max}}$  and will appear to maintain  $T^5$  behavior down to about  $\frac{1}{2} T_c$ . We may compare these ideas with experiment by listing in the fourth column of Table I the experimental<sup>16</sup> values of  $T_c$ . The agreement between the third column (theoretical) and the fourth column (experimental) is seen to be very good. Furthermore, the low-temperature deviations from  $T^5$  behavior shown in Fig. 4 will be noticed only if the measurements are continued down to temperatures below  $\frac{1}{2} T_c$ . Of the measurements for the alkalis reported by Meaden,<sup>4</sup> only for Na was this done and, indeed, for Na it was found that below 8°K, the data of  $\rho(T)$  resemble  $T^6$  rather than  $T^5$ . Thus, we have a rather complete experi-

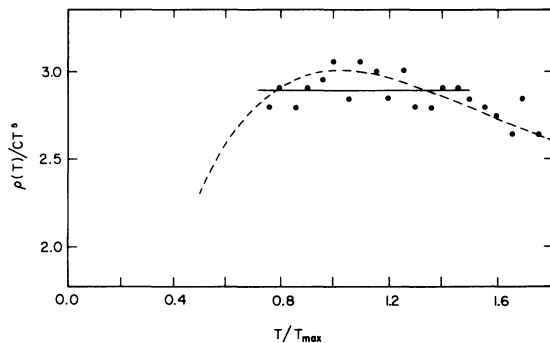


FIG. 4. Plot of  $\rho(T)/CT^5$  as a function of the reduced temperature  $T/T_{\text{max}}$ , where  $T_{\text{max}}$  is the temperature at which the curve has its maximum. The points are simulated experimental points which are related to the true dashed curve as described in the text. The solid line is a smooth fit through the points, showing the apparent  $T^5$  behavior (horizontal line) for  $\rho(T)$  over the range  $0.7 \lesssim T/T_{\text{max}} \lesssim 1.5$ . The Bloch-Grüneisen theory predicts a horizontal line passing through unity, which is below the range of the figure.

mental confirmation of our analysis.

The true behavior for  $\rho(T)$ , given qualitatively by (4.3), will be revealed only with very accurate data having a scatter corresponding to a standard mean deviation of considerably less than  $\pm 3\%$ . Such accurate data have been obtained<sup>6,7</sup> only very recently and only for K. Examination of these data for K makes it clear that, in fact, a true  $T^5$  dependence for  $\rho(T)$  never occurs. Instead, one sees<sup>6</sup> a maximum for  $\rho_{\text{expt}}(T)/T^5$  at  $T \approx 5^\circ\text{K}$ , in excellent agreement with the value of  $T_{\text{max}}$  predicted by (4.4).

Let us now consider the coefficient of the apparent  $T^5$  term for  $\rho(T)$ . For all the alkalis, the observed<sup>16</sup> coefficient  $C_{\text{expt}}$  is considerably larger than the value  $C$  predicted by the Bloch theory. One can readily understand this if one rewrites (4.3):

$$\rho(T)/T^5 \equiv C_{\text{expt}} = C[1 + (\rho_U/\rho_N)_{\text{max}}] \quad (4.5)$$

where the subscript "max" denotes the value of  $\rho_U/\rho_N$  at  $T_{\text{max}}$ . Taking the typical value of about 2 for  $(\rho_U/\rho_N)_{\text{max}}$  gives

$$C_{\text{expt}} = 3C \quad (4.6)$$

One may wonder why more attention was not paid to this large discrepancy between  $C_{\text{expt}}$  and  $C$  by those who attributed the observed  $T^5$  behavior for  $\rho(T)$  to the Bloch  $T^5$  law. The reason may lie in the fact that the expression for  $C$  consists<sup>1</sup> of known constants and  $\Theta$ , the Debye temperature, which is, of course, not a uniquely defined parameter. In fact, one often<sup>18</sup> defines a temperature-dependent function  $\Theta_R(T)$  as the value of the parameter needed at each temperature to make the Bloch-Grüneisen<sup>1</sup> expression  $\rho_{\text{BG}}(T)$  be equal to  $\rho_{\text{expt}}(T)$ . A weak temperature dependence for  $\Theta_R(T)$  is then taken as evidence that the Bloch-Grüneisen theory is a good approximation to  $\rho(T)$ . The danger of employing this procedure at low temperatures is that  $C \propto \Theta_R^{-6}$ . The high power of  $\Theta_R$  which appears implies that one can obtain large changes in  $C$  by relatively small changes in  $\Theta_R$ . For example, if one needed to triple  $C$  to obtain agreement with  $C_{\text{expt}}$ , as indicated in (4.6), one would have to reduce  $\Theta_R$  by only 20%. The required change in  $\Theta_R$  looks quite modest on a plot of  $\Theta_R(T)$  vs  $T$ , as shown in Fig. 3 of Ref. 18, effectively concealing the large discrepancy between  $C_{\text{expt}}$  and  $C$  by means of temperature-dependent  $\Theta_R(T)$ .

To summarize, it is the temperature dependence of both  $\rho_U(T)$  and  $\rho_N(T)$ , and not of  $\rho_N(T)$  alone, which explains the  $T^5$  behavior reported for the low-temperature resistivity data for the alkali metals. Similarly, the magnitude of the coefficient of the  $T^5$  term is primarily determined by

$\rho_U(T)$ , which is about twice as large as  $\rho_N(T)$  at these temperatures.

### V. PHONON DRAG

We shall now derive the expression for  $\rho(T)$  for the alkali metals for temperatures much lower than  $T_{\max}$ , i. e., considerably below the apparent  $T^5$  region shown in Fig. 4. For such low temperatures, the phonon-drag contribution  $\rho_g(T)$  to the resistivity is very important.<sup>14</sup> The existence of  $\rho_g(T)$  has long been recognized.<sup>1</sup> However, with the exception of the incorrect calculation by Sondheimer,<sup>19</sup>  $\rho_g(T)$  has invariably been neglected in actual calculations of  $\rho(T)$  at low temperatures.

Ignoring  $\rho_g(T)$  leads to the widely quoted (incorrect) result that the umklapp scattering contribution to the resistivity  $\rho_U(T)$  disappears exponentially at very low temperatures, leaving only the normal scattering term  $\rho_N(T)$ ,

$$\rho(T) = \rho_N(T) + \rho_U(T) \xrightarrow{T \rightarrow 0} \rho_N(T) \propto T^5 \quad (5.1)$$

In fact, as we shall show, for the alkali metals precisely the opposite is true. At very low temperatures,  $\rho_g(T)$  cancels  $\rho_N(T)$  almost completely leaving only  $\rho_U(T)$ :

$$\rho(T) = \rho_N(T) + \rho_U(T) - \rho_g(T) \xrightarrow{T \rightarrow 0} \gamma \rho_U(T) \quad (5.2)$$

where  $\gamma$  is a constant of order unity. The limiting low-temperature expression for  $\rho_U(T)$  is given by Eq. (3.8). Therefore, we obtain the low-temperature result

$$\rho(T) \propto T^2 e^{-\hbar\omega_0/k_B T} \quad (5.3)$$

showing that the resistivity drops exponentially<sup>20</sup> to zero with decreasing temperature.

Equation (5.3) is based on the expression for  $\rho_g(T)$ , or equivalently for  $X(T)$ , given in Eqs. (2.8) and (2.9). The expression for  $P_{LL}$  assumes that the only important mechanism for phonon equilibration is phonon-electron scattering, thus neglecting the contribution to  $P_{LL}$  arising from phonon-impurity scattering and from phonon-phonon scattering. For the ultra pure samples currently available, having residual resistivity ratios of nearly 10 000, it is certainly justified to neglect phonon-impurity scattering relative to phonon-electron scattering as a mechanism for equilibrating the phonons. The role of phonon-phonon scattering in achieving phonon equilibrium is also clear. At sufficiently low temperatures, phonon-phonon scattering may be ignored. This follows from the general theory<sup>1</sup> of the phonon-phonon interaction, which predicts an exponential temperature decay of the effectiveness of phonon-phonon scattering as a mechanism for achieving phonon equilibration. By contrast, the effectiveness of phonon-electron scattering decreases much more slowly with temperature, having a power-law tem-

perature dependence. In summary, for the low temperatures and high-purity samples considered here, both phonon-phonon scattering and phonon-impurity scattering make negligible contributions to  $P_{LL}$ .

We now turn to the derivation of (5.2). For each of the three  $P_i$  integrals ( $i=11, 1L, LL$ ) appearing in Eq. (2.9), there is an unambiguous separation at low temperature between the normal contribution  $P_i^N$  and the umklapp contribution  $P_i^U$ . It is convenient to define  $\alpha_{1L}(T)$  and  $\alpha_{LL}(T)$  by

$$\begin{aligned} \dot{P}_{1L}^U &= -\alpha_{1L}(T) P_{11}^U \quad , \\ P_{LL}^U &= +\alpha_{LL}(T) P_{11}^U \quad . \end{aligned} \quad (5.4)$$

As was the case with  $\rho_U \propto \rho_{11}^U$ , the dominant contribution to both  $P_{1L}^U$  and  $P_{LL}^U$  comes from the  $T_2$  phonon branch in the vicinity of the [110] direction. Therefore, Figs. 2 and 3 are relevant to the analysis of each of the  $P_i^U$  integrals. It is easy to see that both  $\alpha_{1L}(T)$  and  $\alpha_{LL}(T)$  must be positive. For  $P_{11}^U$  and  $P_{LL}^U$ , the integrand is positive for all  $k$ , whereas for  $P_{1L}^U$ , the integrand is negative because  $\vec{k} \cdot \vec{q} < 0$  for values of  $\vec{k}$  that contribute significantly (see Figs. 2 and 3). Also, it is readily seen that both  $\alpha_{1L}(T)$  and  $\alpha_{LL}(T)$  are small compared to unity. This follows from the fact that  $P_{1L}^U$  and  $P_{LL}^U$  contain  $\vec{k} \cdot \vec{q}$  and  $q^2$ , respectively, in place of the  $k^2$  that appears in  $P_{11}^U$ . A glance at Figs. 2 and 3 shows that  $q \ll k$ . As  $T$  decreases, the dominant contributions to the  $\theta$  and  $\phi$  integrals come from angles increasingly closer to the [110] direction. In the limit  $T \rightarrow 0$ , the values for  $\alpha_{1L}$  and  $\alpha_{LL}$  are given by taking  $\vec{k}$  parallel to  $\vec{G}_{110}$  with  $k = 2k_F$  (see Fig. 2). This corresponds to the geometry of Fig. 3 with  $\delta = 0$ . Then,  $\vec{k} \cdot \vec{q} = -kq = -0.14 k^2$  and  $q^2 = (0.14 k)^2 = 0.02 k^2$ , leading to

$$\alpha_{1L}(0) = 0.14, \quad \alpha_{LL}(0) = 0.02 \quad (5.5)$$

We recall that the contribution to  $g(\vec{k})$  from the  $T_2$  phonon branch vanishes for  $\vec{k}$  exactly in the [110] direction. Therefore, for  $T > 0$ , the correct geometry is that of Fig. 3 with a nonzero angle  $\delta$ , implying that  $|\vec{k} \cdot \vec{q}|$  is somewhat smaller than  $kq$  and that  $q^2$  is larger than  $0.02 k^2$ . Nevertheless, the  $T=0$  values of  $\alpha_{1L}$  and  $\alpha_{LL}$  listed in (5.5) are sufficiently accurate for the purposes of our discussion.

Inserting  $P_i^N + P_i^U$  into Eq. (2.8) for  $X(T) = \rho_g(T)/\rho_{\text{eq}}(T)$  gives

$$X(T) = \frac{(P_{1L}^N)^2 [1 + (P_{1L}^U/P_{1L}^N)]^2}{P_{11}^N P_{LL}^N [1 + (P_{11}^U/P_{11}^N)] [1 + (P_{LL}^U/P_{LL}^N)]} \quad (5.6)$$

For  $P_{1L}^N$  and  $P_{LL}^N$ ,  $\vec{q} = \vec{k}$  and therefore  $P_{1L}^N = P_{LL}^N = P_{11}^N$ . Furthermore, since  $\rho_{\text{eq}}(T) \propto P_{11}$ , we have  $P_{11}^U/P_{11}^N = \rho_U/\rho_N$ . Using these results together with Eq. (5.6) yields

$$X(T) = \frac{[1 - \alpha_{1L}(\rho_U/\rho_N)]^2}{[1 + (\rho_U/\rho_N)][1 + \alpha_{LL}(\rho_U/\rho_N)]} \quad (5.7)$$

The products  $\alpha_{1L}(\rho_U/\rho_N)$  and  $\alpha_{LL}(\rho_U/\rho_N)$  are quite small at low temperatures, even though the ratio  $\rho_U/\rho_N$  exceeds unity. Therefore, for low temperatures, we may expand the numerator and the second term in the denominator to obtain

$$X(T) \approx \frac{1 - (2\alpha_{1L} + \alpha_{LL})(\rho_U/\rho_N)}{1 + (\rho_U/\rho_N)} \quad (5.8)$$

Finally, inserting (5.8) into (2.5) gives the desired result,

$$\rho(T) = [1 + 2\alpha_{1L}(T) + \alpha_{LL}(T)]\rho_U(T) \equiv \gamma(T)\rho_U(T) \quad (5.9)$$

Since  $\alpha_{1L}(T) \ll 1$  and  $\alpha_{LL}(T) \ll 1$ ,  $\gamma(T)$  is independent of temperature to within a few percent. If we now insert the low-temperature exponential temperature dependence of  $\rho_U(T)$ , we obtain (5.3) for low temperatures. An exponential temperature dependence for  $\rho_{\text{expt}}(T)$  below 4 °K has, in fact, been recently reported by Guban<sup>7</sup> for potassium, in complete agreement with (5.9).

It is possible without detailed calculations to obtain a reliable value for the magnitude of the phonon-drag contribution to  $\rho(T)$  at various temperatures. According to Eq. (2.5), the reduction of  $\rho_{\text{eq}}(T)$  due to  $\rho_g(T)$  is given by  $1 - X(T)$ . From (5.8), we have

$$1 - X(T) = \frac{\gamma(\rho_U/\rho_N)}{1 + (\rho_U/\rho_N)} \quad (5.10)$$

For  $\gamma(T)$ , we may take the  $T = 0$  value of 1.3. Since  $\alpha_{1L}(T) < \alpha_{1L}(0)$  and  $\alpha_{LL}(T) > \alpha_{LL}(0)$ , it follows that  $\gamma(T)$  is only weakly dependent on temperature. In fact,  $\gamma(T) \approx \gamma(0)$  to within 10% up to  $T_{\text{max}}$ . At  $T = T_{\text{max}}$ , taking the typical value of 2 for  $\rho_U/\rho_N$  yields

$$1 - X(T_{\text{max}}) \approx 0.9 \quad (5.11)$$

Thus, phonon drag decreases  $\rho_{\text{eq}}(T)$  by only about 10% at  $T_{\text{max}}$ . This justifies our neglect of  $\rho_g(T)$  in our discussion of the apparent  $T^5$  region for  $\rho_{\text{expt}}(T)$  presented in Sec. IV. We may also determine when phonon drag cuts  $\rho_{\text{eq}}(T)$  in half. Equating  $1 - X(T)$  to  $\frac{1}{2}$  leads to  $\rho_U/\rho_N = 0.6$ , which occurs at about  $T \approx \frac{1}{3} T_{\text{max}}$  (see Fig. 4). Ignoring phonon drag for such low temperatures is clearly unjustified.

## VI. MATTHIESSEN'S RULE

We have already emphasized that the analysis presented in this paper applies only to the alkali metals. One reason for this limitation lies in the applicability of Matthiessen's rule. In general, the electrical resistivity of a metal results from the scattering of electrons both by impurities and by phonons. Therefore, the total resistivity  $\rho_{\text{total}}$  is

the sum of three terms:

$$\rho_{\text{tot}}(T) = \rho_{\text{imp}} + \rho_{\text{pure}}(T) + \Delta(T, \rho_{\text{imp}}) \quad (6.1)$$

where  $\rho_{\text{imp}}$  is the temperature-independent residual resistivity due to impurity scattering,  $\rho_{\text{pure}}(T)$  is the temperature-dependent resistivity of the pure metal due to phonon scattering [our previous  $\rho(T)$ ], and  $\Delta(T, \rho_{\text{imp}})$  is a coupling term arising from the fact that the two scattering mechanisms influence each other. If  $\Delta \ll \rho_{\text{pure}}$ , the metal is said to obey Matthiessen's rule, and one may calculate the temperature dependence of the resistivity by treating the contribution due to impurity scattering as a temperature-independent constant. If Matthiessen's rule is not valid, one may not even speak of the temperature-dependent contribution of the resistivity without also specifying the residual resistivity of the particular specimen.

Our analysis is appropriate only when Matthiessen's rule is valid. This is the case for high-purity samples of the alkali metals. For example, for high-purity samples of K, no measurable deviation from Matthiessen's rule was observed,<sup>5-7</sup> even for the lowest measured temperatures ( $\approx 2$  °K). Thus, even though  $\rho_{\text{pure}}(T)$  is decreasing exponentially with temperature, it was found<sup>5-7</sup> that  $\Delta$  is negligible compared with  $\rho_{\text{pure}}$  at all temperatures. Since we may ignore  $\Delta$ , the entire temperature dependence of the resistivity for high-purity samples of the alkalis is contained in  $\rho_{\text{pure}}(T)$ , which we may designate as  $\rho(T)$  without the subscript "pure." Whenever Matthiessen's rule is valid, it follows<sup>21</sup> directly from the variational analysis that Eqs. (2.6)–(2.9) apply to  $\rho_{\text{pure}}(T)$ , including the phonon-drag contribution, regardless of the presence of  $\rho_{\text{imp}}$ . This is true<sup>21</sup> even at very low temperatures, where  $\rho_{\text{imp}} \gg \rho_{\text{pure}}(T)$ . Indeed, this is the meaning of the validity of Matthiessen's rule.

For the polyvalent and noble metals, typified by Al, the experimental results are radically different from the results for K. It is found<sup>22,23</sup> that Matthiessen's rule totally fails for Al in the low-temperature regime, even for ultrapure samples having residual resistivity ratios of nearly 10 000. Instead of  $\Delta \ll \rho_{\text{pure}}$ , as is the case for K, low-temperature experiments<sup>22,23</sup> for Al show that  $\Delta \gg \rho_{\text{pure}}$  to the extent that one may ignore  $\rho_{\text{pure}}$  entirely and obtain the temperature dependence of  $\rho_{\text{tot}}$  solely from the temperature dependence of  $\Delta$ . Thus, the entire analysis presented here is, of course, not relevant to Al.

We should point out that there is another important difference between the alkali metals and the polyvalent and noble metals. None of the three simplifying features listed in Sec. II applies to the polyvalent or noble metals. Therefore, not only does Matthiessen's rule break down for polyvalent and noble metals, but also the reduction of the re-



sulting resistivity integrals must follow a different path. This leads to integrals having a much different structure from those of Eqs. (2.6)–(2.9). Since the analysis we have presented is based on the structure of integrals (2.6)–(2.9), our conclusions would not apply to the polyvalent metals even if Matthiessen's rule were valid. The considerably more complex analysis appropriate to the polyvalent metals will be presented in a subsequent paper.

### VII. SUMMARY

We have presented a detailed discussion of the temperature dependence of the electrical resistivity of the alkali metals at low temperatures. We find that it is possible, without any computer calculations, to obtain complete understanding of the relatively complicated low-temperature behavior of the resistivity. Our principal results are the following.

(i) Explicit expressions are derived for  $\rho_V(T)$ , one valid in the limit  $T \rightarrow 0$  and the other valid in the temperature regime where  $T^5$  behavior has been reported for  $\rho_{\text{expt}}(T)$ .

(ii) It is demonstrated that although  $\rho_V(T)$  decreases exponentially with decreasing temperature, there exists no range of temperature in which it is justified to ignore  $\rho_V(T)$  and to retain only  $\rho_N(T)$ , as is done in the Bloch theory.

(iii) The reported  $T^5$  behavior for  $\rho_{\text{expt}}(T)$  at low temperatures has been explained and shown to be unrelated to the Bloch  $T^5$  law. The temperature below which  $T^5$  behavior occurs has been explicitly derived in terms of the lower transverse velocity of sound in the [110] direction.

(iv) Phonon drag is shown to play a decisive role, both quantitatively and qualitatively, in determining the low-temperature behavior of  $\rho(T)$ , leading to an exponential rather than a power-law temperature dependence for  $\rho(T)$ .

(v) It is pointed out that the failure of Matthiessen's rule for the polyvalent metals and the crucial requirement of sphericity of the Fermi surface limit all the above results to the alkali metals.

### ACKNOWLEDGMENTS

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### APPENDIX A

Even for the simple case of the alkali metals, the choice of the trial function given in Eq. (2.3) is not exact. Equation (2.3) would be exact only if two conditions were met, namely, that the scattering be elastic and that the structure factor  $s(\vec{k})$

be isotropic. It is easy to show there is no difficulty even though the first condition is not fulfilled. Corrections to  $\phi_{\text{e1}}(\vec{k})$  to account for the inelasticity of electron-phonon scattering lead to negligible corrections<sup>1</sup> in  $\rho(T)$  of order  $(k_B T/E_F)^2$ . However, the second condition requires discussion in view of the fact that  $s(\vec{k})$  is a highly anisotropic function for all the alkalis.

Before presenting our analysis, we point out that Greene and Kohn<sup>24</sup> checked this question numerically for Na at high temperatures by considering trial functions having a more complicated angular dependence than (2.3). They found that the use of an improved  $\phi_{\text{e1}}(\vec{k})$  decreased  $\rho(T)$  by only 2–4%, the result depending slightly on the temperature, thus confirming the choice (2.3) for  $\phi_{\text{e1}}(\vec{k})$ .

We shall now show why improving  $\phi_{\text{e1}}(\vec{k})$  decreases  $\rho(T)$  by so little even at low temperatures. Consider the two functions

$$\phi_1(\vec{k}) = K_z F, \quad \phi_2(\vec{k}) = K_z f(\vec{k}) F, \quad (\text{A1})$$

where  $\phi_1(\vec{k})$  is the trial function given in (2.3), with the electric field  $\vec{F}$  in the  $z$  direction, and  $f(\vec{k})$  is any function consistent with the cubic symmetry of the metal. The improved trial function will be

$$\phi_{\text{e1}}(\vec{k}) = \eta_1 \phi_1(\vec{k}) + \eta_2 \phi_2(\vec{k}), \quad (\text{A2})$$

where the parameters  $\eta_1$  and  $\eta_2$  are chosen to minimize  $\rho(T)$ . Ziman<sup>1</sup> has lucidly described the procedure and we follow his notation. It is convenient to cast the final result in the following form:

$$\rho(T) = \rho_1(T) Z(T), \quad (\text{A3})$$

where  $\rho_1(T)$  is the result obtained with only  $\phi_1(\vec{k})$  for  $\phi_{\text{e1}}(\vec{k})$  and

$$Z(T) = \frac{1 - P_{12}^2/P_{11}P_{22}}{1 + (J_2/J_1)^2 (P_{11}/P_{22}) - 2(J_2/J_1) (P_{12}/P_{22})}. \quad (\text{A4})$$

The ratio  $J_2/J_1$  is independent of  $s(\vec{k})$  and is readily evaluated for any given  $\phi_2(\vec{k})$ . The important feature of the  $P_i$  integrals ( $i = 11, 12, 22$ ), which are explicitly defined in Ref. 1, is that each contains  $s(\vec{k})$  in the integrand. The point is that the anisotropy of  $s(\vec{k})$  affects each of the three  $P_i$  integrals in a similar way, so that the ratios that appear in (A4) are not much affected. If  $s(\vec{k})$  were strictly isotropic, we would have  $P_{12}/P_{11} = J_2/J_1$ , leading immediately to  $Z(T) = 1$  and hence to  $\rho(T) = \rho_1(T)$ . In other words, for an isotropic  $s(\vec{k})$ ,  $\phi_1(\vec{k})$  is the exact solution to the Boltzmann equation. The anisotropy of  $s(\vec{k})$  may be expressed by writing

$$P_{12}/P_{11} = (1 - \epsilon) J_2/J_1, \quad (\text{A5})$$

where we anticipate that  $\epsilon$  will be small. Inserting (A5) into (A4) and defining  $\alpha$  by  $Z(T) = (1 + \alpha)^{-1}$  leads to

$$\alpha = \frac{\epsilon^2(\rho_1/\rho_2)}{1 - (\rho_1/\rho_2)(1 - \epsilon)^2}, \quad (\text{A6})$$

where  $\rho_1 = P_{11}/J_1^2$  and  $\rho_2 = P_{22}/J_2^2$  are the resistivities one would obtain using only  $\phi_1(\vec{k})$  and only  $\phi_2(\vec{k})$ , respectively, for  $\phi_{e1}(\vec{k})$ .

The variational principle tells us that  $\rho_1/\rho_2 < 1$ , since  $\phi_1(\vec{k})$  is clearly a better trial function than  $\phi_2(\vec{k})$ . If  $\phi_2(\vec{k})$  leads to a resistivity similar to that obtained with  $\phi_1(\vec{k})$ , i. e., if  $\rho_1/\rho_2 \approx 1$ , then  $\epsilon$  will be quite small, say  $\lesssim 0.1$ . Then, (A6) leads to  $\alpha < \frac{1}{2}\epsilon$ . On the other hand, if  $\epsilon$  is not small, then we will find that  $\phi_2(\vec{k})$  is a very poor trial function, i. e.,  $\rho_1/\rho_2 \ll 1$ . In that case, (A6) gives  $\alpha \ll 1$ . Therefore, in all cases,  $\alpha$  is very small, implying that  $Z(T) \approx 1$  and  $\rho(T) \approx \rho_1(T)$ . This justifies the choice (2.3) for  $\phi_{e1}(\vec{k})$  even though  $s(\vec{k})$  is a highly anisotropic function.

It is instructive to illustrate the preceding discussion by a numerical example. We take  $\phi_2(\vec{k}) = K_z(K_z^2)$ , for which  $J_2/J_1 = \frac{3}{5}$ . Performing the  $P_i$  integrals for potassium<sup>25</sup> at  $T = 5^\circ\text{K}$  yields  $P_{12}/P_{11} = 0.537$ , rather close to the value for  $J_2/J_1$ . This yields, from (A5), the value  $\epsilon = 0.105$ . For the ratio  $P_{11}/P_{22}$ , we obtain 2.57, leading to  $\rho_1/\rho_2 = 0.925$ . Thus, for  $\rho_1/\rho_2 \approx 1$ , we find  $\epsilon \approx 0.1$ . Inserting these values into (A6) yields  $Z = 0.96$ , showing that the resistivity would be reduced by only 4% by using the improved trial function (A2), instead of (2.3).

#### APPENDIX B

We here consider the range of validity of the  $\phi$  integral of Eq. (3.7). We first perform the  $k$  integration and the  $\theta$  integration as described in the text, and change variables in the  $\phi$  integral from  $\phi$  to  $\delta = \phi - \frac{1}{4}\pi$  to obtain

$$\rho_U(T) \propto T^{1/2} e^{-\hbar\omega_0/k_B T} \int_{-\delta_0}^{+\delta_0} d\delta \delta^2 e^{-\hbar\omega_{\phi\phi}\delta^2/2k_B T}, \quad (\text{B1})$$

where  $\delta_0$  denotes the range of validity of the quadratic expansion, Eq. (3.5), of  $\omega_{T_2}(\vec{k})$  in  $\delta$ . The integral over  $\phi$  differs from the integral over  $\theta$  in (3.7) in that the  $\theta$  integrand takes its maximum value at the midpoint  $\theta = \frac{1}{2}\pi$  and rapidly decreases thereafter. By contrast, the  $\phi$  integrand vanishes at the midpoint  $\phi = \frac{1}{4}\pi$  and exhibits a maximum at

$$\delta_{\max} = \phi_{\max} - \frac{1}{4}\pi = (2k_B T/\hbar\omega_{\phi\phi})^{1/2}. \quad (\text{B2})$$

Therefore, the range of the integration is much larger than for the  $\theta$  integration. For  $T$  sufficiently small so that  $\delta_{\max} \ll \delta_0$ , the  $\phi$  integrand is negligible beyond  $\delta_0$ . Then, the expansion of Eq. (3.5) is valid throughout the range of integration and we obtain Eq. (3.8). However, as  $T$  increases, eventually  $\delta_{\max} \approx \delta_0$ , and we may no longer restrict the limits of integration to  $\pm\delta_0$ . Thus, the  $\phi$  part of the expansion (3.5) breaks down.

For this higher temperature range, where  $\delta_{\max} \geq \delta_0$ , we expand  $\omega_{T_2}(\vec{k})$  around  $\delta_{\max}$ , which is now large enough to make the expansion in  $\delta$  linear:

$$\omega_{T_2}(\vec{k}) \approx \omega(\delta_{\max}) + \omega_{\phi}(\delta_{\max})(\delta - \delta_{\max}) + \omega_{\phi\phi}(2k_F - k) + \frac{1}{2}\omega_{\phi\phi\phi}(\theta - \frac{1}{2}\pi)^2, \quad (\text{B3})$$

where  $\omega(\delta_{\max})$  denotes  $\omega_{T_2}(\vec{k})$  evaluated at  $k = 2k_F$ ,  $\theta = \frac{1}{2}\pi$ , and  $\phi = \frac{1}{4}\pi + \delta_{\max}$ , and where  $\omega_{\phi}(\delta_{\max})$  means that the partial derivative is to be evaluated at  $\delta_{\max}$ . The  $k$  integration and the  $\theta$  integration are performed exactly as before. Moreover, it is not hard to show from Fig. 3 that Eq. (3.6) for  $[\hat{\xi}_{T_2}(\vec{q})]^2$  remains valid for a large range of  $\delta$ , a range extending considerably beyond  $\delta_{\max}$ . Therefore, we may insert (B3) and (3.6) into the integral for  $\delta$  and extend the limits to infinity to obtain Eq. (3.9),

$$\rho_U(T) \propto T^{1/2} e^{-\hbar\omega_1/k_B T} \int_{-\infty}^{+\infty} d\delta \delta^2 e^{-\hbar\omega_{\phi}(\delta_{\max})\delta/k_B T} \propto T^{7/2} e^{-\hbar\omega_1/k_B T}, \quad (\text{B4})$$

where

$$\omega_1 = \omega(\delta_{\max}) - \delta_{\max}\omega_{\phi}(\delta_{\max}). \quad (\text{B5})$$

We now turn to the evaluation of  $\omega_1$ . We use the fact, shown schematically in Fig. 5, that the expansion of  $\omega(\phi)$  around  $\frac{1}{4}\pi$  is quadratic up to  $\delta_0$  and linear thereafter. This gives immediately

$$\omega(\delta_{\max}) = \omega_0 + \frac{1}{2}\omega_{\phi\phi}\delta_0^2 + \omega_{\phi}(\delta_{\max})(\delta_{\max} - \delta_0),$$

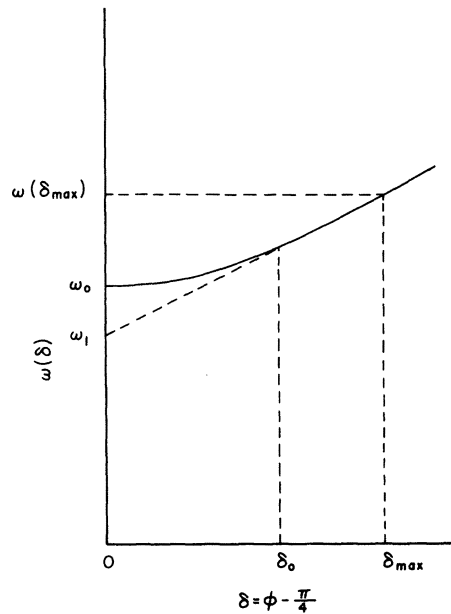


FIG. 5. Schematic plot of  $\omega_{T_2}(\vec{k})$  as a function of angle  $\delta$  from the [110] direction. The frequency is quadratic in  $\delta$  until  $\delta_0$  and linear in  $\delta$  thereafter. At the angle  $\delta_{\max}$ , the integrand in Eq. (B4) attains its maximum value.

$$\omega_{\phi}(\delta_{\max}) = \omega_{\phi}(\delta_0) = \omega_{\phi\phi} \delta_0 \quad (B6)$$

Inserting (B6) into (B5) yields

$$\omega_1 = \omega_0 - \frac{1}{2} \omega_{\phi\phi} \delta_0^2, \quad (B7)$$

which shows that  $\omega_1 < \omega_0$ .

We evaluate  $\omega_{\phi\phi} \delta_0^2$  as follows. For small  $\delta$ , only even powers of  $\delta$  can appear in the expansion of  $\omega_{T_2}(\vec{k})$  around its minimum value in the [110] direction. Therefore, we may write

$$\omega_{T_2}(\vec{k}) = \omega_0 f(\delta^2) + \omega_q(2k_F - k) + \frac{1}{2} \omega_{\theta\theta}(\theta - \frac{1}{2}\pi)^2, \quad (B8)$$

where the function  $f(\delta^2)$  has the properties  $f(0) = 1$  and  $[df(\delta^2)/d(\delta^2)]_0 = f'_0 > 0$ . We shall see later that  $f''(0) = [d^2f(\delta^2)/d(\delta^2)^2]_0 = f''_0 < 0$ . Expanding  $f(\delta^2)$  in powers of  $\delta^2$  gives

$$\omega_{T_2}(\vec{k}) = \omega_0 [1 + f'_0 \delta^2 - \frac{1}{2} |f''_0| \delta^4] + \omega_q(2k_F - k) + \frac{1}{2} \omega_{\theta\theta}(\theta - \frac{1}{2}\pi)^2. \quad (B9)$$

This gives immediately that  $\omega_{\phi\phi} = \partial^2 \omega / \partial \delta^2 = 2f'_0 \omega_0$ . Since the third term in the expansion in  $\delta^2$  is negative, it tends to cancel the effect of the second (quadratic) term. Therefore, the expansion of

$\omega_{T_2}(\vec{k})$  will be essentially quadratic in  $\delta$  only as long as the magnitude of the third term is very small compared to the second term, their ratio being about 0.1. This condition determines  $\delta_0$  and leads to  $\delta_0^2 \approx 0.2f'_0/|f''_0|$ . Thus, we have

$$\frac{1}{2} \omega_{\phi\phi} \delta_0^2 \approx 0.2\omega_0(f'_0)^2/|f''_0|. \quad (B10)$$

Since  $k \approx 2k_F$  in the [110] direction corresponds to small  $q$ , we may use macroscopic elasticity theory. We obtain the function  $f(\delta^2)$  explicitly by solving the equations of motion<sup>26</sup> for the lower transverse velocity of sound in the direction corresponding to  $\delta$ . This yields

$$f(\delta^2) = [1 + C \sin^2(\alpha \delta)]^{1/2}, \quad (B11)$$

where  $C$  is a combination of elastic constants which we need not write down and  $\alpha$  is a geometrical factor relating the angles  $\delta$ ,  $\delta_1$ , and  $\delta_2$  shown in Fig. 3. The derivatives are easily obtained,  $f'_0 = \alpha^2 C/2$  and  $f''_0 = -\alpha^4 C^2/4$  (negative, as promised). Inserting these results into (B10) and (B7) yields

$$\omega_1 \approx 0.8 \omega_0 \quad (B12)$$

independent of  $C$  and  $\alpha$ , thus proving the result quoted immediately after Eq. (3.9).

<sup>1</sup>J. M. Ziman, *Electrons and Phonons* (Oxford U. P., Oxford, England, 1962).

<sup>2</sup>J. M. Ziman, Proc. R. Soc. Lond. A **226**, 436 (1954).

<sup>3</sup>M. Kaveh and N. Wisner, Phys. Rev. Lett. **26**, 635 (1971).

<sup>4</sup>G. T. Meaden, *The Electrical Resistance of Metals* (Plenum, New York, 1965).

<sup>5</sup>J. W. Ekin, Phys. Rev. Lett. **26**, 1550 (1971).

<sup>6</sup>J. W. Ekin and B. W. Maxfield, Phys. Rev. B **4**, 4215 (1971).

<sup>7</sup>D. Guban, Proc. R. Soc. Lond. A **325**, 223 (1971).

<sup>8</sup>T. M. Rice and L. J. Sham, Phys. Rev. B **1**, 4546 (1970); **4**, 674E (1971).

<sup>9</sup>P. N. Trofimenkoff and J. W. Ekin, Phys. Rev. B **4**, 2392 (1971).

<sup>10</sup>S. B. Woods, Can. J. Phys. **34**, 223 (1956).

<sup>11</sup>M. Kaveh and N. Wisner, following paper, Phys. Rev. B **9**, 4060 (1974).

<sup>12</sup>M. J. G. Lee, Phys. Rev. **178**, 953 (1969).

<sup>13</sup>Strictly speaking, what we loosely call the "structure factor"  $S(\vec{k})$  is really the dynamical structure factor (space and time Fourier transform of the time-dependent pair correlation function) multiplied by  $(\hbar\omega/k_B T)/(e^{\hbar\omega/k_B T} - 1)$  and integrated over  $\omega$ .

<sup>14</sup>M. Kaveh and N. Wisner, Phys. Rev. Lett. **29**, 1374 (1972).

<sup>15</sup>M. Kaveh and N. Wisner, Phys. Rev. B **6**, 3648 (1972).

<sup>16</sup>D. K. C. MacDonald, G. K. White, and S. B. Woods, Proc. R. Soc. Lond. A **235**, 358 (1956).

<sup>17</sup>By examining Fig. 4 of the paper of Ekin and Maxfield (Ref. 6), one can readily be convinced that a realistic estimate of the experimental error would correspond

to a standard mean deviation considerably larger than  $\pm 3\%$ . In this figure, a summary is presented of previous low-temperature data for  $\rho(T)$  for K, and it is quite clear that the discrepancies between the various measurements are very significant.

<sup>18</sup>See, for example, J. S. Dugdale and D. Guban, Proc. R. Soc. Lond. A **270**, 186 (1962).

<sup>19</sup>The earlier work of E. H. Sondheimer [Can. J. Phys. **34**, 1246 (1956)] vastly overestimated  $\rho_g(T)$ . Sondheimer based his calculation on the incorrect assumption that the principal mechanism for phonon equilibration is phonon-impurity scattering. He obtains, for example, for Na,  $\rho_g/\rho_{eq} = 0.3$  at  $T = 10^\circ\text{K}$ , which is an order of magnitude too large.

<sup>20</sup>The expectation of an exponential decrease in the resistivity was previously suggested by M. Bailyn [Phys. Rev. **112**, 1587 (1958)] using general arguments.

<sup>21</sup>See, for example, Ref. 1, Sec. 9.13. Note that if  $\Delta(T, \rho_{imp})$  is negligible, then our Eq. (6.1) is precisely Ziman's Eq. (9.13.6), which follows directly from the general expression Eq. (9.13.3).

<sup>22</sup>A. D. Caplin and C. Rizzuto, J. Phys. C **2**, L117 (1970).

<sup>23</sup>I. A. Campbell, A. D. Caplin, and C. Rizzuto, Phys. Rev. Lett. **26**, 239 (1971).

<sup>24</sup>M. P. Greene and W. Kohn, Phys. Rev. **137**, A513 (1965).

<sup>25</sup>The integrals were performed using the  $v(\vec{k})$  described in Sec. III of Ref. 11.

<sup>26</sup>C. Kittel, *Introduction to Solid State Physics*, 3rd ed. (Wiley, New York, 1966), Chap. 4.