

tial used to process the neutron data. A set of force constants (WSM) has been found which reproduces the observed peak structure in  $\alpha^2(\omega)F(\omega)$ . Two very different empty-core model pseudopotentials have been obtained which give very similar  $\alpha^2(\omega)F(\omega)$ 's; and very good agreement with experiment is obtained. We have included band-structure effects only in an average way through the band effective mass. It should be noted that inclusion of the actual Fermi surface may modify the agree-

ment somewhat. These two pseudopotentials take different band-mass values and thus give different specific-heat effective masses.

We point out that Figs. 7 and 8 indicate that thallium is a case where  $\alpha^2(\omega)$  shows a strong increase in the low-energy region above its value near the high-energy end of the spectrum. This is significant since it may not always be justified, even as a first approximation, to ignore the energy dependence of  $\alpha^2(\omega)$  when comparing  $\alpha^2(\omega)F(\omega)$  to  $F(\omega)$ .

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## Temperature and Volume Dependence of the Electrical Resistivity of Sodium and Potassium\*

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The temperature dependence of the electrical resistivity of sodium and potassium is calculated both at constant pressure and at constant volume for the following extensive temperature range: for sodium from 50 °K to the melting point, and for potassium from 20 °K to the melting point. Excellent agreement with experiment is obtained. It is found that the significant difference between the constant-pressure and the constant-volume temperature dependences of the resistivity is completely explained by explicitly taking into account anharmonic effects on the phonon spectrum and on the polarization vectors. The contribution due to the volume dependence of the screened electron-ion-interaction matrix elements is also included.

### I. INTRODUCTION

One of the fundamental problems of solid-state physics is the calculation of the temperature dependence of the dc electrical resistivity  $\rho$  of metals. The problem has received serious attention from many workers since the advent of quantum mechanics. Among the most important early contributions are those of Bloch,<sup>1</sup> Bardeen,<sup>2</sup> Ziman,<sup>3</sup> and Bailyn.<sup>4</sup> An excellent and detailed account of these papers, as well as all progress up to about 1960, is given by Ziman.<sup>5</sup> Since 1960, interest in the problem has not lessened, as evidenced by the many recent

calculations<sup>6-15</sup> of  $\rho(T)$  just for Na and K.

Of particular interest is a comparison between the temperature dependence of the resistivity at constant pressure  $\rho_p(T)$  and at constant volume  $\rho_v(T)$ . Only the very recent paper by Hayman and Carbotte<sup>15</sup> reports a calculation of both  $\rho_p(T)$  and  $\rho_v(T)$ . However, such a calculation requires a better treatment of anharmonic effects than that presented by Hayman and Carbotte. The goal of this paper is to predict quantitatively for Na and K both  $\rho_p(T)$  and  $\rho_v(T)$  by a careful analysis which takes proper account of anharmonic effects on the phonon spectrum as well as on the polarization

vectors. We achieve our goal in that for both metals our calculations for both  $\rho_p(T)$  and  $\rho_v(T)$  are in excellent agreement with the measured values. The discrepancy never exceeds 5%, and is usually much less, throughout the following extensive temperature range for which the accurate data of Dugdale and Guban<sup>16</sup> are available—for K, from 20 °K to room temperature, and for Na, from 50 °K to room temperature. Below these temperatures, there is no distinction between  $\rho_p(T)$  and  $\rho_v(T)$ .

In Sec. II we describe the formalism we used to calculate  $\rho(T)$ . The resulting expression contains the structure factor (discussed in Sec. III, with

anharmonic effects considered in Sec. IV) and the screened electron-ion-interaction matrix elements (discussed in Sec. V). We present the results of our calculations in Sec. VI. In Sec. VII we give a critical discussion of previous work. The summary follows in Sec. VIII.

## II. FORMALISM

For our calculations, we use the weak-coupling theory<sup>5</sup> to describe the electron-phonon interaction and the Boltzmann equation<sup>5</sup> to describe the transport theory. The variational solution<sup>5,9</sup> of the Boltzmann equation gives, for a cubic metal,

$$\rho(T) = \frac{\pi\Omega_0 \int \int [dS(\vec{k}_1)/u(\vec{k}_1)][dS(\vec{k}_2)/u(\vec{k}_2)][\Phi(\vec{k}_1) - \Phi(\vec{k}_2)]^2 P(\vec{k}_1, \vec{k}_2)}{2e^2 \hbar^3 \int \int d^3k' u(\vec{k}') \Phi(\vec{k}') [\partial f_0(\vec{k}')/\partial E(\vec{k}')]^2}, \quad (2.1)$$

where  $\Omega_0$  is the atomic volume 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 scattered electron, having energy  $E(\vec{k}')$  and velocity  $u(\vec{k}')$  in state  $\vec{k}'$ . The function  $\Phi(\vec{k}')$  is proportional to the deviation caused by the electric field on the Fermi distribution function  $f(\vec{k}')$  from its equilibrium value  $f_0(\vec{k}')$ ,

$$f(\vec{k}') = f_0(\vec{k}') - \Phi(\vec{k}') \frac{\partial f_0(\vec{k}')}{\partial E(\vec{k}')} . \quad (2.2)$$

The variational principle states that the function  $\Phi(\vec{k}')$  which minimizes the right-hand side of Eq. (2.1) gives the exact Boltzmann-equation solution for  $\rho$ .

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  $\vec{k}_2$ . For the case of a general Bloch electron, this function is quite complicated and we shall not bother to write it down. Instead, we shall discuss only the much simpler cases of Na and K, whose very nearly spherical Fermi surfaces imply that, for the calculation of  $\rho$ , one plane wave correctly represents the pseudo-wave-function. When this is so,  $P(\vec{k}_1, \vec{k}_2)$  factors into the product  $s(\vec{k})v^2(k)$ , where  $s(\vec{k})$  and  $v(k)$  are structure factor and form factor, respectively. The resulting simplifications were the primary motivation for choosing Na and K for the resistivity calculations. The properties of  $s(\vec{k})$  and  $v(k)$  will be the subject of Secs. III–V.

To proceed further in the calculation for  $\rho$ , we must make a choice for  $\Phi(\vec{k})$ . The standard (simplest) choice<sup>5</sup> for a trial function is  $\Phi(\vec{k}) \propto \vec{k} \cdot \vec{F}$ , where  $\vec{F}$  is the applied electric field. At high temperatures the electron scattering is effectively elastic and for elastic scattering the standard trial function is exact. However, even at low tempera-

tures where the inelasticity of the scattering becomes important, we have found<sup>17</sup> that the same choice for  $\Phi(\vec{k})$  is still an excellent approximation. Inserting this  $\Phi(\vec{k})$  into Eq. (2.1) and exploiting the spherical symmetry of the Fermi surface yields

$$\rho(T) = \frac{m^2}{12\pi^3 e^2 \hbar^3 n^3} \int_0^{2k_F} dk k^3 v^2(k) S(k), \quad (2.3)$$

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

$$S(k) = (4\pi)^{-1} \int d\Omega_{\vec{k}} s(\vec{k}). \quad (2.4)$$

The expression for  $\rho(T)$  given in Eqs. (2.3) and (2.4) and indeed even the more general expression Eq. (2.1) ignore phonon drag.<sup>5</sup> That is, it is assumed that the phonon distribution equilibrates quickly compared with the electron-phonon relaxation time, and therefore the electrons are always scattered by the thermal-equilibrium distribution of phonons. We have calculated the contribution of phonon drag to  $\rho(T)$  for all temperatures and we find<sup>17</sup> that, although it is a very important effect at very low temperatures ( $\lesssim 3$ – $4$  °K for Na and K), phonon drag may be safely ignored over the temperature range considered here.

We close this section by emphasizing that the simplicity of Eq. (2.3) for  $\rho$  is only apparent. In reality the expression for  $\rho$  contains complicated 3-dimensional integrals even for the simplest cases of Na and K, and one can obtain reliable numerical results only by detailed computer calculations.

## III. STRUCTURE FACTOR

For Na and K, for the structure factor<sup>18</sup>  $s(\vec{k})$  we use the one-phonon harmonic approximation

$$s(\vec{k}) = \frac{\hbar^2}{Mk_B T}$$

$$\times \sum_{\lambda} \frac{[\vec{k} \cdot \hat{\xi}_{\lambda}(\vec{q})]^2}{\{\exp[\hbar\omega_{\lambda}(\vec{q})/k_B T] - 1\} \{1 - \exp[-\hbar\omega_{\lambda}(\vec{q})/k_B T]\}}, \quad (3.1)$$

where  $M$  is the ionic mass and  $\omega_{\lambda}(\vec{q})$  and  $\hat{\xi}_{\lambda}(\vec{q})$  are the frequency and polarization vector, respectively, of a phonon of branch  $\lambda$  and wave vector  $\vec{q}$ . 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 one of the reciprocal-lattice vectors. For a given  $\vec{k}$ , there are a unique  $\vec{q}$  and  $\vec{G}_n$  that satisfy (3.2).

Evaluation of  $s(\vec{k})$  involves overcoming two difficulties. First one must know  $\omega_{\lambda}(\vec{q})$  and  $\hat{\xi}_{\lambda}(\vec{q})$  for each phonon of each branch throughout the entire Brillouin zone. Second, for each  $\vec{k}$ , one must determine which  $\vec{G}_n$  is needed to reduce  $\vec{k}$  to  $\vec{q}$ . These two difficulties are both overcome by the Born-Von Karman analysis,<sup>19</sup> according to which  $\omega_{\lambda}(\vec{q})$  and  $\hat{\xi}_{\lambda}(\vec{q})$  are the eigenvalues and eigenvectors, respectively, of the dynamical matrix  $\bar{A}(\vec{q})$ . The matrix elements of  $\bar{A}(\vec{q})$  are given by

$$A_{ij}(\vec{q}) = \sum_m \theta_{ij}(\vec{R}_m) e^{i\vec{q} \cdot \vec{R}_m}, \quad (3.3)$$

where the interatomic force constant  $\theta_{ij}(\vec{R}_m)$  is the force in direction  $i$  acting on an atom at the origin as a result of a displacement in direction  $j$  of an atom at lattice site  $\vec{R}_m$ . Thus,  $\omega_{\lambda}(\vec{q})$  and  $\hat{\xi}_{\lambda}(\vec{q})$  satisfy

$$\sum_j [A_{ij}(\vec{q}) - M\omega^2(\vec{q})\delta_{ij}] \xi_j(\vec{q}) = 0. \quad (3.4)$$

The first advantage of the Born-Von Karman method is that an experimental determination of  $\theta_{ij}(\vec{R}_m)$  enables one to calculate  $\omega_{\lambda}(\vec{q})$  and  $\hat{\xi}_{\lambda}(\vec{q})$  for all  $\vec{q}$  throughout the Brillouin zone. The force constants out to five nearest neighbors have been measured by means of neutron scattering for both sodium<sup>20</sup> (at  $T = 90^\circ\text{K}$ ) and potassium<sup>21</sup> (at  $T = 9^\circ\text{K}$ ). The second advantage is that  $\bar{A}(\vec{q})$  is periodic in  $\vec{G}_n$  as is clear from (3.3). Therefore, from Eq. (3.4), it follows that for the Born-Von Karman method the very important periodicity properties of the phonon frequencies and polarization vectors are automatically satisfied:

$$\begin{aligned} \omega_{\lambda}(\vec{k}) &= \omega_{\lambda}(\vec{q} + \vec{G}_n) = \omega_{\lambda}(\vec{q}), \\ \hat{\xi}_{\lambda}(\vec{k}) &= \hat{\xi}_{\lambda}(\vec{q} + \vec{G}_n) = \hat{\xi}_{\lambda}(\vec{q}). \end{aligned} \quad (3.5)$$

Hence, for any given  $\vec{k}$ , we can calculate exactly the phonon frequency and polarization vector even for umklapp processes without having to know which  $\vec{G}_n$  is needed to reduce  $\vec{k}$  into the first Brillouin zone. The computational advantages of the Born-Von Karman method can hardly be overestimated.

The bulk of the numerical work comes in performing the angular integration of Eq. (2.4), because  $s(\vec{k})$  is a highly anisotropic function. Typical

curves for  $S(k)$  are given in Fig. 1 for K at  $T = 50$  and  $280^\circ\text{K}$ . Note that the shapes of the two curves are rather similar, though they differ radically in magnitude. As  $k$  increases from 0 to  $k_F$ ,  $S(k)$  increases by less than a factor of 2, whereas, as  $k$  increases from  $k_F$  to  $2k_F$ ,  $S(k)$  increases by nearly a factor of 20. [It should be pointed out that at very low temperatures ( $T \lesssim 10^\circ\text{K}$ ), which we do not discuss in this paper, the curves for  $S(k)$  look very different from Fig. 1.]

The explanation for the rapid increase of  $S(k)$  with  $k$  is the following: In almost every direction,  $\omega_{\lambda}(\vec{q})$  increases as  $\vec{k}$  increases until  $\vec{k}$  passes through the Brillouin-zone boundary and umklapp-scattering becomes possible. Then  $\omega_{\lambda}(\vec{q})$  decreases as  $\vec{k}$  increases. When  $|\vec{k}| \rightarrow 2k_F$ ,  $\omega_{\lambda}(\vec{q})$  becomes relatively small. Therefore, as  $|\vec{k}| \rightarrow 2k_F$ , the denominator of Eq. (3.1) is rapidly decreasing while the numerator is increasing, leading to the rapid increase of  $S(k)$  for large  $k$ . Since large  $k$  dominates the integral in Eq. (2.3), one can understand why an exact treatment of umklapp scattering is crucial for a reliable quantitative calculation of  $\rho(T)$ .

It should be mentioned that, if  $\vec{k} = \vec{G}_n$ , then  $\vec{q} = 0$  according to (3.2), and the denominator of (3.1) vanishes. However, there is no actual singularity in the transition probability  $P(\vec{k}_1, \vec{k}_2)$ . When  $\vec{k} \rightarrow \vec{G}_n$  one must use at least two plane waves for the pseudo-wave-function and  $P(\vec{k}_1, \vec{k}_2)$  no longer simplifies into the factorized form  $s(\vec{k})v^2(k)$ . Instead, one must use the more general form, which

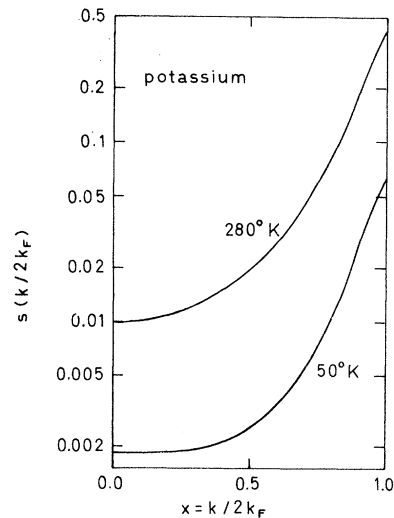


FIG. 1. Quantity  $S(k)$  for K at  $T = 50^\circ\text{K}$  and at  $T = 280^\circ\text{K}$ , where the temperature has been increased at constant volume. The two curves are very similar in shape. They differ only by a scale factor, as is evident by the constant vertical difference between the curves on a log scale.

remains finite for  $\vec{k}_2 - \vec{k}_1 = \vec{G}_n$ . For Na and K, this situation never arises because in every direction in the Brillouin zone  $|\vec{k}| = 2k_F$  is significantly shorter than the relevant  $\vec{G}_n$ . Therefore, for all  $\vec{k}$ , we expect one plane wave to suffice for the pseudo-wave-function. We have explicitly verified this by calculating the correction to  $P(\vec{k}_1, \vec{k}_2)$  obtained by using two plane waves for the pseudo-wave-function. We find that, except for very low temperatures which we do not consider here, using a single plane wave leads to a negligible error in  $\rho$  of less than 1%.

We now turn to the calculation of  $S(k)$  for small  $k$ . It should be recognized that we cannot use the compressibility sum rule<sup>22</sup>

$$S(0) = nk_B T \chi, \quad (3.6)$$

where  $\chi$  is the isothermal compressibility. The sum rule is *not* satisfied because a metal in the solid phase is not a homogeneous system, a requirement for the applicability of the sum rule. To see this explicitly, let us consider an elastically isotropic cubic metal (*not* Na or K, which are elastically quite anisotropic) for which the three elastic constants are related by  $c_{12} = c_{11} - 2c_{44}$ . Then, for small  $k$ , expanding Eq. (3.1) gives

$$S(k) = s(\vec{k}) = \frac{k_B T}{M} \sum_{\lambda} \frac{[\vec{k} \cdot \hat{\xi}_{\lambda}(\vec{q})]^2}{[\omega_{\lambda}(\vec{q})]^2}. \quad (3.7)$$

Since our system is imagined to be elastically isotropic, we may conveniently choose  $\vec{k} = \vec{q}$  in the [100] direction. Then the sum over  $\lambda$  gives only the term  $k^2/\omega_1^2 = v_1^2 = nM/c_{11}$ , where  $v_1$  is the longitudinal sound velocity in the [100] direction. Finally, noting that for an elastically isotropic solid the inverse compressibility or bulk modulus  $B = c_{11} - \frac{4}{3}c_{44}$  and the shear modulus  $Y = c_{44}$ , we obtain

$$S(0) = nk_B T (B + \frac{4}{3}Y)^{-1}, \quad (3.8)$$

which does not satisfy the sum rule because of the presence of the  $Y$ .

For Na and K, the deviation between  $S(0)$  and the sum-rule result  $nk_B T \chi$  is about 80 and 50%, respectively, depending somewhat on the temperature. Moreover, even the more general expression (3.8) is valid only for an elastically isotropic solid and hence not appropriate to Na and K. One can appreciate how highly anisotropic Na and K are by comparing  $s(\vec{k})$  in different directions of  $k$  for  $|\vec{k}| \rightarrow 0$ . For K, for example, for low  $k$ , the ratio of  $s(\vec{k})$  in the [111] direction to  $s(\vec{k})$  in the [110] direction is 2.65.

#### IV. ANHARMONIC EFFECTS

The harmonic one-phonon approximation for  $s(\vec{k})$ , given by Eq. (3.1), can be improved in two ways. First, we can ascribe a finite lifetime  $1/\Gamma_{\lambda}(\vec{q})$  to the phonons. Numerical evaluation shows

that, even with the generous estimate  $\Gamma_{\lambda}(\vec{q})/\omega_{\lambda}(\vec{q}) \approx 0.2$ , this improvement changes  $\rho$  by only a few percent at all temperatures. Furthermore, this lifetime effect is almost independent of temperature. Therefore, in our study of the temperature dependence of  $\rho(T)$  we may neglect entirely the finite lifetime of the phonons.

The second improvement to  $s(\vec{k})$  is to include the temperature dependence of the phonon frequencies:  $\omega_{\lambda}(\vec{q}) \rightarrow \omega_{\lambda}(\vec{q}, T)$ . This effect is not only numerically significant, but is of particular importance for an accurate calculation of  $\rho(T)$  over a wide temperature range. Moreover, including the temperature dependence of  $\omega_{\lambda}(\vec{q})$  is vital for distinguishing between  $\rho_p(T)$  and  $\rho_v(T)$ , the constant-pressure and constant-volume temperature dependences, respectively.

When we consider temperature increases at constant pressure (generally atmospheric pressure  $\approx$  zero pressure),  $\omega_{\lambda}(\vec{q})$  changes for two reasons. First, there is a volume effect, i. e., the lattice constant increases with temperature. In essence, we obtain a different crystal at every temperature. This volume effect always reduces  $\omega_{\lambda}(\vec{q})$  because the farther apart the ions are, the weaker the force constants and hence the lower the frequencies.

Second,  $\omega_{\lambda}(\vec{q})$  changes owing to an amplitude effect; i. e., with increasing temperature the amplitude of the vibrating ions increases. Since there are anharmonic (i. e., higher than second order) terms in the expansion of the interionic potential as a power series in the amplitude, the frequencies depend on the amplitude of vibration. One cannot say *a priori* whether the amplitude effect will increase or decrease  $\omega_{\lambda}(\vec{q})$ . In fact, some of the  $\omega_{\lambda}(\vec{q})$  increase with temperature, whereas others decrease.

Of these two effects, the volume effect is considerably more important than the amplitude effect. Therefore, we expect and find that for temperature changes at constant pressures, where both volume and amplitude effects occur, the temperature dependence of  $\omega_{\lambda}(\vec{q})$  is several times greater than for temperature changes at constant volume, where only the amplitude effect occurs.

In principle, one can determine the temperature dependence of the  $\omega_{\lambda}(\vec{q})$  for all  $\vec{q}$  from neutron-scattering measurements of the force constants  $\theta_{ij}(\vec{R}_m)$  carried out at two different temperatures. Since the  $\theta_{ij}(\vec{R}_m)$  vary linearly with temperature above about 50°K, we immediately obtain the  $\theta_{ij}(\vec{R}_m)$  and hence  $\omega_{\lambda}(\vec{q}, T)$  for all temperatures. Unfortunately, for both Na and K neutron-scattering measurements sufficiently detailed to obtain the  $\theta_{ij}(\vec{R}_m)$  have been performed at only a single temperature (90°K for Na and 9°K for K). Therefore, for these metals we must calculate the temperature dependence of  $\omega_{\lambda}(\vec{q})$ .

For low  $q$  there is no problem. One may use

macroscopic elasticity theory to express the  $\omega_\lambda(\vec{q})$  in terms of the three independent elastic constants  $c_{11}$ ,  $c_{12}$ , and  $c_{44}$ . From the measured temperature and pressure dependence of the  $c$ 's (data displayed in Table I), one may calculate  $[\partial\omega_\lambda(\vec{q}, T)/\partial T]_p$  and  $[\partial\omega_\lambda(\vec{q}, T)/\partial T]_V$  for all polarizations and directions in the low- $q$  region. The result is that the proportional frequency change  $[\omega_\lambda(\vec{q}, T)]^{-1} \times [\partial\omega_\lambda(\vec{q}, T)/\partial T]$  is independent of  $|\vec{q}|/q_{\max}$ , where  $q_{\max}$  is the distance to the Brillouin-zone boundary in the direction under consideration and the temperature derivative is understood to be taken at constant  $q/q_{\max}$ , rather than at constant  $q$ .<sup>23</sup> For high  $q$ , we assume that the proportional frequency change exhibits the same behavior; i. e., we assume that throughout the Brillouin zone  $[\omega_\lambda(\vec{q}, T)]^{-1}[\partial\omega_\lambda(\vec{q}, T)/\partial T]$  is independent of the magnitude of  $|\vec{q}|/q_{\max}$ . However, this quantity does have a strong dependence on the direction of  $q$  and on the polarization  $\lambda$ . This assumption is made very plausible in the Appendix. There do exist some measurements<sup>24</sup> for  $\omega_\lambda(\vec{q})$  for K at higher temperatures, and these few measurements are indeed consistent with our calculation of  $[\partial\omega_\lambda(\vec{q}, T)/\partial T]_p$ .

As the temperature increases, not only the  $\omega_\lambda(\vec{q})$  but also the polarization vectors  $\hat{\xi}_\lambda(\vec{q})$  change. The procedure for calculating this temperature dependence  $\hat{\xi}_\lambda(\vec{q}, T)$  is analogous to the procedure used for calculating  $\omega_\lambda(\vec{q}, T)$ . We use the elastic constants to compute  $[\partial\hat{\xi}_\lambda(\vec{q}, T)/\partial T]_p$  and  $[\partial\hat{\xi}_\lambda(\vec{q}, T)/\partial T]_V$  for small  $q$  and assume that throughout the Brillouin zone these derivatives depend only on the direction of  $\vec{q}$  and on  $\lambda$ , but not on the magnitude of  $|\vec{q}|/q_{\max}$ . This effect of including  $\hat{\xi}_\lambda(\vec{q}, T)$  is rather small, being an order of magnitude less important than  $\omega_\lambda(\vec{q}, T)$  in the calculation of the temperature dependence of  $\rho$ . The reason for this is that along the symmetry direction the phonons must be either pure longitudinal or pure transverse. Hence, the  $\hat{\xi}_\lambda(\vec{q})$  are temperature independent along the symmetry direction. For a cubic crystal there is no region in the Brillouin zone that is very far from one of the symmetry directions. Therefore,

the temperature dependence of the  $\hat{\xi}_\lambda(\vec{q})$  must be weak for all  $\vec{q}$ .

What is relevant to our calculation of  $\rho(T)$  is, of course, the effect on  $S(k)$  resulting from the temperature dependence of  $\omega_\lambda(\vec{q})$  and of  $\hat{\xi}_\lambda(\vec{q})$ . From the integral for  $\rho(T)$ , Eq. (2.3), we see that the upper limit  $2k_F$  also depends on temperature. It is convenient to eliminate this temperature dependence by changing the variable of integration to  $x = k/2k_F$ . We therefore define  $\Delta S(x)$  as the change in  $S(x)$  due to the temperature dependence of  $\omega_\lambda(x)$  and  $\hat{\xi}_\lambda(x)$  only<sup>25</sup>:

$$\Delta S(x) = S(x, T, \omega(x, T), \hat{\xi}(x, T)) - S(x, T, \omega(x, T - \Delta T), \hat{\xi}(x, T - \Delta T)). \quad (4.1)$$

Note that in the definition of  $\Delta S(x)$ , we do not include the change with temperature of the factor  $k_F^2$  which arises from  $S(x) \propto k_F^2 x^2$ . In Fig. 2 we plot both  $[\Delta S(x)]_p/S(x)$  and  $[\Delta S(x)]_V/S(x)$  as functions of  $x$  for Na for  $\Delta T = 200^\circ\text{K}$  from 90 to 290 °K.

We may understand qualitatively the behavior of these curves by examining the expression  $\Delta s(x)/s(x)$  for a single polarization in a general direction. We make a high-temperature expansion of Eq. (3.1), valid at  $T = 290^\circ\text{K}$ , to obtain

$$\frac{\Delta s(x)}{s(x)} = -2 \left[ 1 + \frac{1}{12} \left( \frac{\hbar\omega_\lambda(x)}{k_B T} \right)^2 \right] \frac{\Delta\omega_\lambda(x)}{\omega_\lambda(x)}. \quad (4.2)$$

Consider first the region  $0 < x \leq 0.6$ , where only normal scattering occurs. The ratio  $\Delta\omega_\lambda(x)/\omega_\lambda(x)$  is independent of  $x$  (and always negative, except for certain directions at constant volume), but  $\omega_\lambda^2(x)$  increases with  $x$ , explaining the increase of the curves up to  $x = 0.6$ . Another significant effect in the low- $x$  region is the change of the direction of the  $\hat{\xi}_\lambda$  as a function of temperature in the off-symmetry directions of the Brillouin zone. This implies a temperature dependence to the extent to which transverse phonons contribute to  $\Delta S(x)/S(x)$  because of the factor  $[\vec{k} \cdot \hat{\xi}_\lambda(\vec{q})]^2$ . This is particularly striking for the constant-volume case for which in many regions of the Brillouin zone the transverse

TABLE I. Measured values and temperature and pressure derivatives of the elastic constants of Na and K. The units for  $c$  and  $\partial c/\partial T$  are  $10^9 \times \text{cgs}$  and  $\partial c/\partial p$  is dimensionless. The values given for  $c$  refer to room temperature;  $(\partial c/\partial p)_T$  is independent of temperature;  $(\partial c/\partial T)_p$  and  $(\partial c/\partial T)_V$  are nearly independent of temperature above about 100 °K. Below 100 °K,  $(\partial c/\partial T)_p$  and  $(\partial c/\partial T)_V$  decrease somewhat below the given values.

	Sodium <sup>a, b</sup>			Potassium <sup>c, d</sup>		
	$c_{11}$	$c_{12}$	$c_{44}$	$c_{11}$	$c_{12}$	$c_{44}$
$c$	$771 \pm 10$	$648 \pm 10$	$435 \pm 10$	$370 \pm 10$	$314 \pm 10$	$188 \pm 10$
$(\partial c/\partial T)_p$	$-0.41 \pm 0.02$	$-0.31 \pm 0.02$	$-0.66 \pm 0.04$	$-0.21 \pm 0.02$	$-0.17 \pm 0.02$	$-0.38 \pm 0.03$
$(\partial c/\partial p)_T$	$4.2 \pm 0.2$	$3.7 \pm 0.2$	$1.7 \pm 0.1$	$4.3 \pm 0.2$	$3.8 \pm 0.2$	$1.6 \pm 0.1$
$(\partial c/\partial T)_V$	$+0.14 \pm 0.02$	$+0.16 \pm 0.02$	$-0.42 \pm 0.02$	$+0.19 \pm 0.02$	$+0.20 \pm 0.02$	$-0.23 \pm 0.01$

<sup>a</sup>R. H. Martinson, Phys. Rev. **178**, 902 (1969).

<sup>b</sup>W. B. Daniels, Phys. Rev. **119**, 1246 (1960).

<sup>c</sup>W. R. Marquardt and J. Trivisonno, J. Chem. Phys.

Solids **26**, 273 (1965).

<sup>d</sup>P. A. Smith and C. S. Smith, J. Phys. Chem. Solids **26**, 279 (1965).

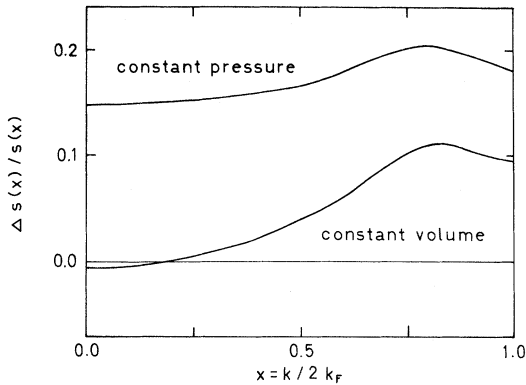


FIG. 2. Relative change in  $S(x)$  for Na owing to the temperature dependence of  $\omega_\lambda(\vec{q})$  and  $\xi_\lambda(\vec{q})$ , at both constant pressure and constant volume.

$\omega_\lambda(\vec{q})$  have a temperature dependence opposite in sign to that of the longitudinal  $\omega_\lambda(\vec{q})$ . Therefore, changing the direction of the  $\xi_\lambda$ , and hence the relative contribution of transverse and longitudinal phonons, may even change the sign of  $\Delta S(x)/S(x)$ . This explains the negative values for  $[\Delta S(x)]_V/S(x)$  for  $x < 0.2$ .

For  $x > 0.6$ , umklapp scattering becomes important and the transverse phonons  $\omega_{T1}$  and  $\omega_{T2}$  become as important as the longitudinal phonons  $\omega_L$ . The combination of elastic constants entering  $\omega_{T1}$ ,  $\omega_{T2}$ , and  $\omega_L$  is such that, for most  $\vec{q}$ , the  $\omega_{T1}$  and  $\omega_{T2}$  have a much stronger temperature dependence than  $\omega_L$ . This explains the relatively sharp rise of the curves in the region  $0.6 \lesssim x \lesssim 0.8$ . For  $x \gtrsim 0.8$  the curves again drop. This occurs because for  $x \gtrsim 0.8$  the dominant contribution to  $S(x)$  comes from the vicinity of the  $[110]$  direction and, in these directions,  $\Delta S(x)/S(x)$  is small. This occurs first because the phonons that contribute most have a rather small temperature dependence, and second because  $\omega_\lambda(x)$  itself is decreasing as  $x$  approaches unity.

In summary, not only can one calculate quantitatively the anharmonic effects on the structure factor, but one can also understand all these effects qualitatively. It is worth emphasizing that a complete understanding of these effects is important not only for the calculation of  $\rho(T)$ , but for the temperature dependence of the other transport coefficients as well.

## V. ELECTRON-ION-INTERACTION MATRIX ELEMENTS

We now turn to the determination of the form factor  $v(k)$  for the matrix elements of the electron-ion interaction. We use the pseudopotential formulation in which  $v(k)$  is just the pseudopotential form factor. Although  $v(k)$  is a function only of the magnitude of  $k$ , this formulation includes in full

its nonlocality. This can be seen in the following way. We require the matrix element of the pseudopotential between plane-wave pseudo-wave-functions  $\langle \vec{k}_1 | \hat{v} | \vec{k}_2 \rangle = v(\vec{k}_1, \vec{k}_2)$ . This matrix element is a function of  $\vec{k}_1$  and  $\vec{k}_2$  separately, and not just of their difference  $\vec{k}$ , because the pseudopotential is an operator and not merely a function. Because the screened ion is spherically symmetric, the matrix element is actually a function of only three independent variables, rather than six,  $v(\vec{k}_1, \vec{k}_2)$

$-v(k, k_1, k_2)$ . The expression for  $\rho(T)$  contains only matrix elements describing scattering processes where both the initial state  $\vec{k}_1$  and the final state  $\vec{k}_2$  lie on the Fermi surface. Since the Fermi surface is spherical for Na and K, we have  $k_1 = k_2 = k_F$  and thus  $v(k, k_1, k_2) = v(k, k_F, k_F) \equiv v(k)$ , where  $k$  is restricted to be smaller than  $2k_F$ . Therefore, although our expression for the form factor  $v(k)$  is written as a function of a single variable  $k$ , it includes in full the nonlocality of the pseudopotential. These matters are discussed more fully in the recent review article by Wiser and Greenfield.<sup>26</sup>

While there exist various calculations of  $v(k)$ , it has become clear<sup>27</sup> that none of these is sufficiently accurate for calculating  $\rho(T)$ . Therefore, we have taken an empirical approach. We use the phenomenological potential of Harrison<sup>28</sup> and fix its single parameter  $\beta$  by equating  $\rho_{\text{calc}}(T_0)$  to  $\rho_{\text{expt}}(T_0)$  at a specific temperature  $T_0$ . This completely determines  $v(k)$  and enables us to calculate  $\rho_p(T)$  and  $\rho_V(T)$  at all temperatures.

The phenomenological potential of Harrison is

$$v(k) = \frac{-(4\pi e^2/k^2) + \beta}{\Omega_0 \epsilon(k)}, \quad k \leq 2k_F \quad (5.1)$$

where  $\Omega_0$  is the atomic volume. For the screening function  $\epsilon(k)$  we use the Hartree dielectric function

$$\epsilon(k) = 1 + \frac{1}{\pi k_F a_0 x^2} \left( \frac{1-x^2}{4x} \ln \left| \frac{1+x}{1-x} \right| + \frac{1}{2} \right), \quad (5.2)$$

where  $x = k/2k_F$  and  $a_0$  is the Bohr radius. The first term in the numerator of Eq. (5.1) is the Fourier transform of a (monovalent) point-ion Coulomb potential and the second term ( $\beta$ ) represents deviations from this simple potential. These deviations arise from the effective repulsive potential that is central to the pseudopotential formulation, from corrections to the point-ion Coulomb potential in the interior of the ion core, from the approximate and local nature of the Hartree dielectric function, and from other smaller effects.

The phenomenological potential (5.1) differs from the true potential in several respects. First of all, one obtains (5.1) by normalizing the plane-wave pseudo-wave-functions to unity. However, the scattering amplitude theorem of Austin, Heine, and Sham<sup>29</sup> shows that it is the true wave function and not the pseudo-wave-function which must be

normalized to unity. Inserting the proper normalization factor<sup>29</sup> would require us to divide the  $v(k)$  of (5.1) by  $1 - \sum_c |\langle \vec{k}_F | c \rangle|^2$ , where  $|\vec{k}_F\rangle$  is a normalized plane wave of wave number  $k_F$  and  $|c\rangle$  is an ionic core wave function. The sum over all core wave functions (call it  $\Sigma$ ) requires performing three integrals for Na and five integrals for K. The integrals were carried out by Harrison<sup>28</sup> for a series of metals and he found that the value of  $\Sigma$  is typically about 0.1, being somewhat smaller for Na and somewhat larger for K.

The second approximation contained in (5.1) is that the constant  $\beta$  is properly a function of  $k$ . The point of using the phenomenological potential is to account for both the normalization constant  $\Sigma$  and the  $k$  dependence of  $\beta(k)$  by means of suitably chosen constant  $\beta_{\text{eff}}$ :

$$\frac{-4\pi e^2/k^2 + \beta(k)}{1 - \Sigma} \rightarrow \frac{-4\pi e^2}{k^2} + \beta_{\text{eff}}. \quad (5.3)$$

We shall now justify using this simple form for  $v(k)$  to calculate  $\rho(T)$ . Let us first consider high temperatures  $T \gg \Theta_D$  ( $\Theta_D$  is the Debye temperature). For high temperature, one can readily see from Eq. (3.1) that  $S(k)$  factors into  $T \times F(k)$ , where  $F(k)$  contains no explicit temperature dependence. Then, Eq. (2.3) can be written

$$\rho(T) \propto T \int_0^{2k_F} dk k^3 v^2(k) F(k) \propto T \int_0^1 dx x^3 v^2(x) F(x), \quad (5.4)$$

where  $x = k/2k_F$ . Aside from the slight volume dependence of  $v^2(x)$ , the only temperature dependence of the integrand lies in the implicit temperature dependence of  $F(x)$ , arising from the anharmonic effects on  $\omega_\lambda(x)$  and the  $\xi_\lambda(x)$ . We have already plotted in Fig. 2 the relative temperature change in  $F(x)$ , since  $\Delta F(x)/F(x) = \Delta S(x)/S(x)$ . From the figure we see that, both at constant pressure and at constant volume,  $\Delta F(x)/F(x)$  is nearly independent of  $x$  for  $x \approx 0.6$ . However, it is only in this region of  $x$  that the various proposed forms<sup>25</sup> for  $v(x)$  differ from each other; for lower  $x$ , all proposed forms are equivalent. Therefore, for the calculation of  $\rho(T)$  at high temperatures, the precise functional form of  $v(x)$  is actually irrelevant, as long as it contains one parameter chosen to give the correct value of the integral in Eq. (5.4).

At lower temperature  $T \lesssim \Theta_D$ , the factorization of  $S(k)$  into  $T \times F(k)$  is no longer valid, and the functional form of  $v(k)$  is very important. The appropriateness of our choice for  $v(k)$  is demonstrated by the fact that we obtain excellent agreement with experiment for both  $\rho_p(T)$  and  $\rho_v(T)$  over the entire temperature range we are here considering, i. e., down to 50 °K for Na and down to 20 °K for K. However, we wish to emphasize that at still lower temperatures our potential becomes inadequate to calculate  $\rho(T)$ . Indeed, it can be shown<sup>17</sup> that every

one-parameter potential becomes inadequate to calculate  $\rho(T)$  at sufficiently low temperatures. In our analysis of the very-low-temperature regime,<sup>17</sup> we show how to generalize (5.1) to obtain a potential valid over the entire temperature range, from the melting point down to absolute zero.

We now turn to the volume or  $k_F$  dependence of  $\beta$  which results from the nonlocality of the pseudo-potential.<sup>26</sup> Harrison's explicit calculations<sup>28</sup> demonstrated that this dependence is negligible for Al. Our calculations for  $\rho(T)$  and, in particular, its volume derivative  $\partial(\ln\rho)/\partial(\ln V)$  show that one may safely ignore this effect for Na and K as well. The validity of ignoring this  $k_F$  dependence of  $\beta$  has also been established in previous calculations of  $\rho(T)$  for liquid Na, where it was found<sup>30</sup> that the effect of including the  $k_F$  dependence of the  $A_l(E_F)$  parameters of the Abarenkov-Heine model potential<sup>31</sup> was completely negligible. These  $A_l(E_F)$  parameters are analogous to  $\beta(k_F)$  in the Harrison potential.

In summary, we find that the phenomenological potential of Harrison, Eq. (5.1), is perfectly adequate for calculating  $\rho(T)$  for both Na and K from  $T \approx \frac{1}{4}\Theta_D$  to melting point. The single constant  $\beta_{\text{eff}}$  is the *only* parameter in the calculation of  $\rho(T)$  throughout the entire temperature range considered, both at constant pressure and at constant volume.

It remains to determine the parameter  $\beta_{\text{eff}}$  by selecting a temperature  $T_0$  at which to equate  $(\rho_v)_{\text{calc}}$  with  $(\rho_v)_{\text{expt}}$ . The best over-all fit to the  $\rho(T)$  data is obtained by choosing  $T_0 = 200$  °K for both Na and K. For this choice we find, in units of Ry (Bohr-radius)<sup>3</sup>, the values

$$\begin{aligned} \beta_{\text{eff}} &= 27.0 \text{ for Na} \\ &= 42.7 \text{ for K.} \end{aligned} \quad (5.5)$$

A change in  $\beta_{\text{eff}}$  of 0.3 and 0.4 for Na and K, respectively, corresponds to a change in  $\rho(T)$  of 3%. This is the maximum change in  $\rho(T)$  that is compatible with the data, as we shall see in Sec. VI. These changes in  $\beta_{\text{eff}}$  correspond to changes in  $v(2k_F)$  of only 0.0008 and 0.0006 Ry for Na and K, respectively.

We plot in Fig. 3 the curves for  $v(k)$  for Na and K at the density corresponding to room temperature. We see that for both Na and K  $v(k)$  is very nearly zero at  $2k_F$ , being slightly negative for Na and slightly positive for K.

## VI. CALCULATIONS AND RESULTS

Having determined both the structure factor  $s(\vec{k})$  and the form factor  $v(k)$ , we are ready to perform the triple integral for  $\rho(T)$  prescribed in Eqs. (2.3) and (2.4). All calculations were performed on the IBM 360/50 system of the Computation Center of Bar-Ilan University.

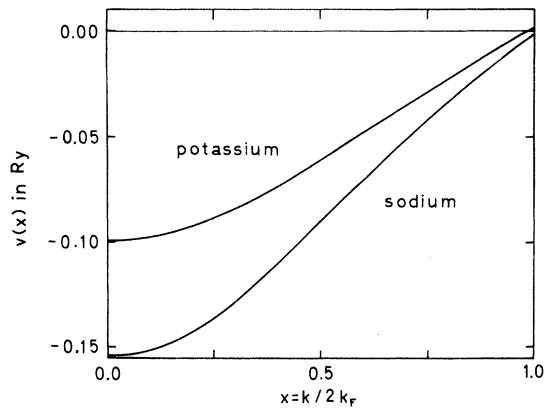


FIG. 3. Form factor  $v(k)$  for Na and K at the density corresponding to room temperature.

In making comparisons with experiment we are fortunate in having available the accurate data of Dugdale and Guban,<sup>16</sup> who measured both  $\rho_p(T)$  and  $\rho_V(T)$ . For Na and K, there is no distinction between  $\rho_p(T)$  and  $\rho_V(T)$  below 50 and 20 °K, respectively. Over the short temperature range from room temperature to the melting point, data for  $\rho_V(T)$  do not exist for either Na or K.

Our results for  $\rho_p(T)$  and  $\rho_V(T)$  for Na and K are presented in Tables II and III. The third and fifth columns of each table give the percentage discrepancy between calculated values and experiment. We see that for both Na and K the results are excellent, with the discrepancy between theory and experiment never exceeding 5% for any temperature, either for  $\rho_p(T)$  or for  $\rho_V(T)$ . The quality of this agreement can be appreciated by noting the very large change in  $\rho(T)$  over this temperature range.

Of primary interest in this work is the distinction between  $\rho_p(T)$  and  $\rho_V(T)$ . In the sixth and seventh columns of Tables II and III, we compare

the experimental and the calculated values of  $(\rho_p - \rho_V)/\rho_V$ . We see that at room temperature  $\rho_p(T)$  and  $\rho_V(T)$  differ appreciably, by 22% for Na and by 36% for K. Our calculated values for the percentage differences are in excellent agreement with experiment over the entire temperature range.

There are four contributions to the difference between the calculated values of  $\rho_p(T)$  and  $\rho_V(T)$ . The first two result from the different temperature dependence of  $\omega_\lambda(\vec{q})$  and  $\xi_\lambda(\vec{q})$  at constant pressure and at constant volume. The third and fourth contributions are the explicit volume dependences appearing in  $v(k)$  and in the factor<sup>32</sup>  $k_F^{-3}$  which are present in  $\rho_p(T)$  but absent in  $\rho_V(T)$ . The contribution of each effect is listed in Table IV, where  $\Delta\rho/\rho$  means the percentage change in  $\rho_{\text{calc}}(T)$  resulting solely from the change in the listed quantity with temperature and/or volume over the range from  $T = 90^\circ\text{K}$  to  $T = 290^\circ\text{K}$ . For example,  $\Delta\rho/\rho$  corresponding to  $\omega_\lambda(\vec{q}, T)$  means  $[\rho_{290^\circ\text{K}}(\omega(290^\circ\text{K})) - \rho_{290^\circ\text{K}}(\omega(90^\circ\text{K}))]/\rho_{290^\circ\text{K}}(\omega(290^\circ\text{K}))$ , where by  $\rho_{290^\circ\text{K}}(\omega(90^\circ\text{K}))$  we mean the resistivity calculated with all the temperature-dependent quantities evaluated at 290 °K, with the exception of the  $\omega_\lambda(\vec{q}, T)$ , for which we use their value at 90 °K. We see from Table IV that by far the greatest contribution to  $\Delta\rho/\rho$  comes from the  $\omega_\lambda(\vec{q}, T)$ . Even at constant volume, the temperature dependence of the  $\omega_\lambda(\vec{q}, T)$  makes a significant contribution to  $\rho(T)$ . Therefore, all those previous calculations that ignored the temperature dependence of the phonon frequencies have a built-in error whose magnitude is evident from Table IV.

It is worth noting that  $\Delta\rho/\rho$  resulting from the volume change of  $v^2(k)$  is positive for both Na and K. To understand this, it is convenient to write the volume change of  $v^2(k)$  as the product  $2v(k)\Delta v(k)$ . In the range of  $k$  that dominates the integral for  $\rho(T)$ ,  $\Delta v(k)$  is always negative.<sup>30</sup> For both Na and K,  $v(k)$  is also negative throughout

TABLE II. Comparison between the calculated and experimental values for Na for  $\rho_p(T)$ ,  $\rho_V(T)$ , and the difference between them.

$T$ (°K)	$[\rho_p(T)]_{\text{expt}}$ ( $\mu\Omega\text{ cm}$ )	$\left(\frac{\rho_{\text{calc}} - \rho_{\text{expt}}}{\rho_{\text{expt}}}\right)_p$ (%)	$[\rho_V(T)]_{\text{expt}}$ ( $\mu\Omega\text{ cm}$ )	$\left(\frac{\rho_{\text{calc}} - \rho_{\text{expt}}}{\rho_{\text{expt}}}\right)_V$ (%)	$\left(\frac{\rho_p - \rho_V}{\rho_V}\right)_{\text{calc}}$	$\left(\frac{\rho_p - \rho_V}{\rho_V}\right)_{\text{expt}}$
50	0.317	+5.0	0.314	+4.5	0.01	0.01
60	0.475	+1.5	0.469	+2.0	0.01	0.01
80	0.805	-2.5	0.788	-2.0	0.02	0.02
100	1.146	-3.5	1.108	-3.0	0.03	0.04
120	1.484	-3.0	1.416	-3.5	0.05	0.05
160	2.166	-0.5	2.001	-1.5	0.09	0.08
200	2.874	+0.0	2.566	+0.0	0.12	0.12
240	3.626	+1.0	3.123	+1.0	0.16	0.16
280	4.432	+3.0	3.676	+2.0	0.22	0.21
295	4.750	+4.0	3.882	+2.5	0.24	0.22



TABLE III. Comparison between the calculated and experimental values for K for  $\rho_p(T)$ ,  $\rho_V(T)$ , and the difference between them.

$T$ (°K)	$[\rho_p(T)]_{\text{expt}}$ ( $\mu\Omega$ cm)	$\left(\frac{\rho_{\text{calc}} - \rho_{\text{expt}}}{\rho_{\text{expt}}}\right)_p$ (%)	$[\rho_V(T)]_{\text{expt}}$ ( $\mu\Omega$ cm)	$\left(\frac{\rho_{\text{calc}} - \rho_{\text{expt}}}{\rho_{\text{expt}}}\right)_V$ (%)	$\left(\frac{\rho_p - \rho_V}{\rho_V}\right)_{\text{calc}}$	$\left(\frac{\rho_p - \rho_V}{\rho_V}\right)_{\text{expt}}$
20	0.107	-5.0	0.107	-5.0	0.00	0.00
30	0.285	-4.0	0.283	-4.0	0.01	0.01
40	0.496	-4.0	0.490	-3.5	0.01	0.01
60	0.944	-4.0	0.921	-3.5	0.02	0.02
80	1.389	-4.0	1.329	-3.5	0.04	0.05
100	1.836	-4.0	1.716	-3.5	0.07	0.07
120	2.294	-2.5	2.102	-3.0	0.10	0.09
160	3.250	-1.0	2.824	-2.0	0.16	0.15
200	4.281	+1.0	3.543	+0.0	0.22	0.21
240	5.418	+1.5	4.264	+1.0	0.28	0.27
280	6.673	+2.5	4.991	+2.0	0.35	0.34
295	7.190	+3.0	5.272	+2.5	0.37	0.36

this range of  $k$ , leading to a positive  $\Delta\rho/\rho$ .

Dugdale and Guban<sup>16</sup> also reported their values for the volume derivative of the resistivity  $\partial(\ln\rho)/\partial(\ln V)$  at constant temperature. This quantity is of special significance because it measures directly the difference between  $\rho_p(T)$  and  $\rho_V(T)$ . In Table V we make comparison between our calculated values and experiment. From the excellent agreement we may draw an important conclusion. The major contribution to the volume derivative of  $\rho$  arises from the volume derivative of the  $\omega_\lambda(\vec{q})$ . Since this derivative has not been measured, we computed it in the same approximation used to compute the temperature derivative of  $\omega_\lambda(\vec{q})$ . From the fact that the calculated volume derivative of  $\rho$  is in excellent agreement with the measured value, we may conclude that the approximation used to determine the volume derivative of the  $\omega_\lambda(\vec{q})$  is very good. Furthermore, precisely the same approximation was used to determine the temperature derivative of the  $\omega_\lambda(\vec{q})$ . This lends further support to the argument presented in the Appendix to justify our approximation.

TABLE IV. Contribution to the temperature dependence of  $\rho(T)$  for Na and K from quantities having an implicit temperature or volume dependence. The ratio  $\Delta\rho/\rho$  denotes the percentage contribution to  $\rho(T)$  arising solely from the listed quantity over the temperature range from  $T=90^\circ\text{K}$  to  $T=290^\circ\text{K}$ .

Temperature or volume dependence	Na		K	
	$(\Delta\rho/\rho)_p$ (%)	$(\Delta\rho/\rho)_V$ (%)	$(\Delta\rho/\rho)_p$ (%)	$(\Delta\rho/\rho)_V$ (%)
$\omega_\lambda(\vec{q})$	+18.0	+8.5	+25.0	+6.0
$\xi_\lambda(\vec{q})$	-1.0	-1.0	-1.5	-1.0
$v^2(k)$	+4.5	...	+3.0	...
$k_F^3$	+3.5	...	+4.5	...
Total	+25.0	+7.5	+31.0	+5.0

Finally, we see here confirmation in our procedure, which neglects the volume dependence due to nonlocality of the parameter  $\beta_{\text{eff}}$ . If its volume dependence were significant, it would surely contribute to the volume derivative of the resistivity, and prevent us from obtaining the good agreement that we in fact find.

One sees from Table V that  $\partial(\ln\rho)/\partial(\ln V)$  is larger at lower temperatures. The reason for this can be understood by examining the functional dependence of  $s(\vec{k})$  on  $\omega_\lambda(\vec{q})$  as given in Eq. (3.1). For high temperatures [ $k_B T \gtrsim \hbar\omega_\lambda(\vec{q})$ ], expanding the exponentials gives  $s(\vec{k}) \propto [\omega_\lambda(\vec{q})]^{-2}$ , whereas for low temperatures [ $k_B T \ll \hbar\omega_\lambda(\vec{q})$ ], dropping the negative exponential and the unity gives  $s(\vec{k}) \propto \exp[-\hbar\omega_\lambda(\vec{q})/k_B T]$ . Since the exponential dependence of  $s(\vec{k})$  on  $\omega_\lambda(\vec{q})$  is much more sensitive than the inverse-square dependence, we find that for low temperatures the derivative of  $s(\vec{k})$ , and hence  $\rho$ , with respect to  $\omega_\lambda(\vec{q})$  is appreciably larger. Recalling that the major contribution to  $\partial(\ln\rho)/\partial(\ln V)$  arises from  $\partial\omega_\lambda(\vec{q})/\partial V$ , we can see why the volume derivative of  $\rho$  is larger at lower temperatures.

TABLE V. Calculated and experimental values for Na and K for the volume derivative of the resistivity at low temperatures and at high temperatures. The uncertainty in the calculated values results from the experimental error in the pressure and temperature derivatives of the elastic constants (see Table I).

$T$ (°K)	Na		K	
	50°K	290°K	30°K	290°K
$\left(\frac{\partial(\ln\rho)}{\partial(\ln V)}\right)_{\text{expt}}$	6.3 ± 0.1	4.4 ± 0.1	7.3 ± 0.1	5.7 ± 0.1
$\left(\frac{\partial(\ln\rho)}{\partial(\ln V)}\right)_{\text{calc}}$	6.5 ± 0.5	4.6 ± 0.4	7.4 ± 0.3	5.8 ± 0.2

## VII. DISCUSSION OF PREVIOUS WORK

The only previous calculation for any metal of both  $\rho_p(T)$  and  $\rho_v(T)$ , permitting a comparison between them, is that of Hayman and Carbotte (HC).<sup>15</sup> The calculation consists of two steps. The first step is to calculate the temperature dependence of the resistivity at constant volume and without anharmonic effects. There is, at this stage, no difference between  $\rho_p(T)$  and  $\rho_v(T)$ . The second step is to include the anharmonic effects, as well as all explicit volume dependences. The first step of the HC calculation is very similar in spirit to our own work, and the results are quite comparable. However, we are here interested in the difference between  $\rho_p(T)$  and  $\rho_v(T)$ , which results exclusively from the second step of the calculation. Both our analysis and our results for this second step are completely different from those of HC.

There are four contributions to the difference between  $\rho_p(T)$  and  $\rho_v(T)$ . These are listed in Table IV. A glance at the table shows that by far the largest contribution arises from the anharmonic effects on the phonon frequencies  $\omega_\lambda(\vec{q})$ . To calculate this, HC used a Grüneisen-type approach,

$$\omega_\lambda(\vec{q}, V) = \omega_\lambda(\vec{q}, V_0)[1 + \gamma(V - V_0)/V_0], \quad (7.1)$$

where  $\gamma$  is the Grüneisen constant,  $V_0$  is a reference volume, and  $V$  is the volume at temperature  $T$ . This approach is equivalent to the following two approximations. First, anharmonic effects on  $\rho_v(T)$  are completely neglected. Second, the temperature dependence of the  $\omega_\lambda(\vec{q})$  is assumed to be the same for all  $\vec{q}$  and for all  $\lambda$ . For low  $\vec{q}$ , one may test these approximations explicitly by calculating both the constant-volume and the constant-pressure temperature dependence of the  $\omega_\lambda(\vec{q})$  by means of macroscopic elasticity theory. Performing such a calculation shows that each of these approximations seriously underestimates the temperature dependence of the  $\omega_\lambda(\vec{q})$ . The argument given in the Appendix suggests that (7.1) will be similarly inadequate throughout the Brillouin zone. We have calculated  $(\Delta\rho/\rho)_p$  due to  $\omega_\lambda(\vec{q})$  for both Na and K according to the approximation (7.1) and we obtain 8% for Na and 11% for K. This is less than half of our result (18% for Na and 25% for K), which is based on a treatment that includes anharmonic effects exactly for low  $q$  and to very good approximation throughout the Brillouin zone.

In summary, we see that anharmonic effects on the phonon spectrum constitute a large contribution to the temperature dependence of the resistivity. Therefore, one cannot make a meaningful comparison between  $\rho_p(T)$  and  $\rho_v(T)$  without a proper treatment of this important effect.

## VIII. SUMMARY

In this paper, we have compared the constant-pressure and constant-volume temperature dependences of the resistivity for Na and K. This was achieved by incorporating into the calculation the constant-pressure and constant-volume temperature dependences of the phonon frequencies and polarization vectors, as well as the volume dependence of the  $k_F$  factors and of  $v(k)$ . Excellent agreement was obtained with experiment. We also computed the volume derivative of the resistivity at constant temperature and again obtained complete agreement with experiment.

We conclude from these results that it is possible to achieve excellent agreement with experiment for both  $\rho_p(T)$  and  $\rho_v(T)$  over the entire temperature range in the solid, provided that proper account is taken of anharmonic effects on phonon frequencies and polarization vectors.

We are presently extending our calculations to include the polyvalent metals to see whether similar good agreement can be achieved for this significantly more difficult problem.

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## APPENDIX

We wish to demonstrate that for all  $\vec{q}$  it is reasonable to obtain the temperature dependence of the  $\omega_\lambda(\vec{q})$  by assuming that  $[\omega_\lambda(\vec{q}, T)]^{-1}[\partial\omega_\lambda(\vec{q}, T)/\partial T]$  is independent of the magnitude of  $|\vec{q}|/q_{\max}$ , where the temperature derivative is understood to be taken at constant  $q/q_{\max}$ . Let us first consider the symmetry directions. For each symmetry direction (and only for the symmetry directions), for each polarization the phonon frequency can be expressed<sup>20</sup> in terms of the interplanar force constants  $\Phi_n(T)$  by means of

$$\omega^2(T) = M^{-1} \sum_{n=1}^N \Phi_n(T)[1 - \cos(n\pi q/q_{\max})], \quad (A1)$$

where  $M$  is the mass of the atom, the sum over  $n$  is taken out of  $N$  planes of atoms, and  $q_{\max}$  is the distance to the Brillouin-zone boundary in the direction under consideration.

It turns out that for each polarization, in each of the three symmetry directions ([100], [110], [111]), one term dominates the sum over  $n$ , since one of the  $\Phi_n(T)$  [call it  $\Phi_m(T)$ ] is about 10 times larger than any of the others. Thus, to a very good approximation, we may write

$$\omega^2(T) \approx M^{-1}\Phi_m(T)[1 - \cos(m\pi q/q_{\max})]. \quad (A2)$$

The approximation given in (A2) is especially good

in the important [110] direction, where for Na the largest  $\Phi_m(T)$  is 36, 67, and 1660 times larger than the next largest  $\Phi_n(T)$  for the longitudinal and two transverse polarizations, respectively.<sup>20</sup>

From (A2) it immediately follows that

$$\frac{1}{\omega(T)} \frac{\partial \omega(T)}{\partial T} = \frac{1}{2\omega^2(T)} \frac{\partial \omega^2(T)}{\partial T} = \frac{1}{2\Phi_m(T)} \frac{\partial \Phi_m(T)}{\partial T}, \quad (\text{A3})$$

independent of  $q/q_{\max}$ .

For a bcc lattice, there is no region in the Brillouin zone which is very far from one of the symmetry directions. Therefore, it is reasonable to expect that for all directions, not just for the symmetry directions, our procedure for obtaining the temperature dependence of the  $\omega_\lambda(\vec{q})$  is a very good approximation.

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<sup>18</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  $[\hbar\omega/k_B T]/[\exp(\hbar\omega/k_B T) - 1]$  and integrated over  $\omega$ .  
<sup>19</sup>See, for example, Ref. 9, Sec. III.  
<sup>20</sup>A. D. B. Woods, B. N. Brockhouse, R. H. March, A. T. Stewart, and R. W. Bowers, *Phys. Rev.* **128**,

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<sup>23</sup>Note that  $q_{\max} \propto a^{-1}$  ( $a$  = lattice constant), and thus the temperature derivative of  $\omega_\lambda(\vec{q}, T)$  is understood to be taken at constant  $qa$ , suppressing the volume dependence of  $a$ . The reason for this is most easily seen by considering periodic boundary conditions, for which  $q = 2\pi n/Na$ , where  $N$  is the number of atoms and  $n = (n_1^2 + n_2^2 + n_3^2)^{1/2}$ , the  $n_i$  being integers. Then  $qa = 2\pi n/N$  does not depend on volume and hence has no temperature dependence.

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<sup>25</sup>Note that  $\omega_\lambda(x)$  contains no explicit  $k_F$  dependence because  $q$  always appears in the combination  $qa$  ( $a$  = lattice constant) and  $qa = 2(k_F a)x$ ; the product  $k_F a$  is of course independent of volume.

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<sup>32</sup>The factor  $k_F^{-3}$  arises as follows. The factor  $n^{-3}$  in Eq. (2.3) gives a factor  $k_F^{-3}$ . Changing variables from  $k$  to  $x = k/2k_F$  gives a factor  $k_F^4$ , and we recall that  $S(x)$  contains an explicit factor  $k_F^2$ .