PHYSICAL REVIEW B VOLUME 36, NUMBER 18 15 DECEMBER 1987-II

Transport properties of Rb in high magnetic fields

R. Fletcher and I. B. Verma
Physics Department, Queen's University, Kingston, Ontario, Canada K7L 3N6
(Received 19 June 1987)

We have obtained a reasonably complete set of transport coefficients (electrical, thermal, and thermoelectric) for two Rb samples in magnetic fields up to 8 T in the liquid-^{4}He temperature range. The results are similar to those for K and are generally consistent with Rb being a simple free-electron-like metal with a spherical Fermi surface. However, in contrast to K, the lattice thermal conductivity of Rb is not anomalous; possible reasons for this difference are suggested.

I. INTRODUCTION

Of the alkali metals, only K has been extensively studied with reference to a complete set of transport properties at high magnetic fields.[1] Of particular interest in that study was the use of high fields to extract the lattice thermal conductivity λ_g. This was done using conventional rectangular geometry, but it has been recently repeated[2] using Corbino geometry with essentially the same outcome. The results on λ_g so obtained are far larger than theory[3] had initially led us to expect, even though theoretical estimates had proved quite accurate for other metals, in particular the noble metals,[4] and In and Al.[5] The discrepancy was traced to the fact that K is very free-electron-like and has a Fermi surface which does not intersect any Brillouin zone boundaries. A one–orthogonalized-plane-wave (1 OPW) approximation provides an excellent model for K, but in such an approximation the electron-phonon coupling is zero for purely transverse phonons (provided their wave vector is small enough that only normal processes are allowed) and hence these phonons can make a large contribution to λ_g. This is the case only if phonon-phonon scattering is relatively weak so that phonon momentum cannot be redistributed to other phonons, which in turn can be scattered by electrons, but this seems to be the case for K at low temperatures. So far demonstration of this behavior has been unique to K though other alkali metals might behave similarly. Na also has a very spherical Fermi surface but is not a promising candidate because it undergoes an incomplete martensitic phase transformation at low temperatures. This is likely to leave extensive damage in the crystal structure, which, if our recent experiences[6] with the plastic deformation of K can be used as a guide, will strongly reduce λ_g. The next most spherical Fermi surface is Rb. Although there has been a recent suggestion[7] that this metal may undergo a phase transformation at 1 K, the situation is not yet clear, especially in view of the original strong evidence[8] that no phase transformation occurs, even in heavily cold-worked samples, at 5 K.

The intent of the present work was to produce a set of data for Rb similar to that for K so that we can gauge whether K is likely to remain a unique case or whether its behavior is mirrored by the other alkali metals.

II. EXPERIMENTAL TECHNIQUES

Rb is much softer than K and is chemically more reactive. All sample handling was carried out under argon gas in a glovebox which could maintain freshly cut Rb in good condition for at least 30 min, and often for considerably longer. In the case of K we have used both rolling and casting to produce samples. The former technique proved to be impractical for Rb, for although the clean material is very easy to roll, the thin sheets are difficult to handle, especially after cutting out the required shapes. Hence we resorted to casting using a mold made of high-density polyethylene and polypropylene. The mold was made vacuum tight with O rings except for the loading funnel at the top. A piece of clean Rb was inserted into the funnel and the mold placed in an evacuated can and heated. When the Rb had melted, clean argon gas was allowed into the can to force the Rb into the mold. (A 1-mm-diam constriction in the funnel prevented this happening before the gas pressure was applied.) Most of the many samples so made were reasonably free of surface defects and surface oxidation. Two of the best were used for these experiments; each was made from stock bought at different times.[9] There were no significant differences in their properties. The samples had an "active" region of about $16\times5\times1.7$ mm^3. The actual thickness of the samples was taken from the mold dimensions because the samples were too soft for the thickness to be measured by normal techniques (see Ref. 1 for sample shapes).

The experimental techniques, though different in many details, were close enough to those in Ref. 1 that no further explanation is required. However, the signal-to-noise ratio for the chopper amplifier (which was used mainly to measure thermoelectric voltages) was much improved in the present set of measurements, and even at the highest magnetic fields we could resolve 10 pV with an averaging time of 10 sec. This means that the thermoelectric measurements are much more precise than was previously the case for K.

Data were taken at a number of fixed temperatures for both directions of magnetic field $\pm B$, typically at ten points between 0 and 8 T. Suitable averages of the $\pm B$ data were taken to produce the final results.

III. RESULTS

A. Electrical coefficients

The resistance ratios ($\rho_{295\,K}/\rho_{1.2\,K}$) of the two samples were similar at 465 (Rb 1) and 410 (Rb 2). These are an order of magnitude lower than for pure K, but are not atypical of the best Rb available commerically. For our purposes, the most appropriate measure of purity is the product of the cyclotron frequency ω_c and the electronic relaxation time τ; we estimate $\omega_c\tau \sim 1$ at about 0.5 T at the lowest temperatures, so most of the data presented here corresponds to high-field conditions.

Figure 1 shows the transverse electrical resistivity ρ_{xx} as a function of B at 1.2 and 4.2 K from which it is seen that for higher fields the relationship appears to be linear, as seems to be the case for all uncompensated metals (see Refs. 2 and 10 for reviews of previous work). The Kohler slopes $-\Delta\rho/R_H\Delta B$, where R_H is the Hall coefficient, are 0.010 and 0.0047 for Rb 1 and Rb 2, respectively, at 1.2 K; there was no obvious difference between the two samples which could lead to this variation. Although the zero-field resistivity increases by over 20% between 1.2 and 4.2 K, there was no significant temperature dependence of the Kohler slopes.

The Hall constants R_H ($=\rho_{yx}/B$), Fig. 2, appear to be well behaved and show no appreciable field dependence at the higher fields (i.e., when $\omega_c\tau \gg 1$). Any differences

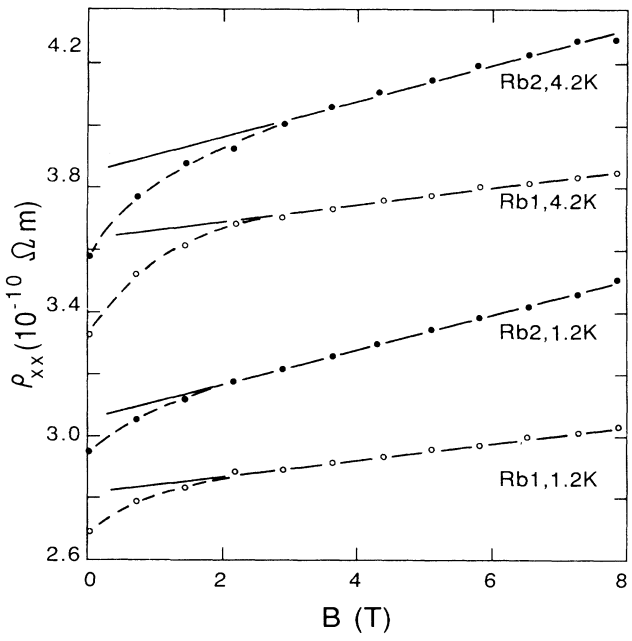

FIG. 1. The electrical resistivity ρ_{xx} of Rb 1 and Rb 2 as a function of magnetic field at 1.2 and 4.2 K.

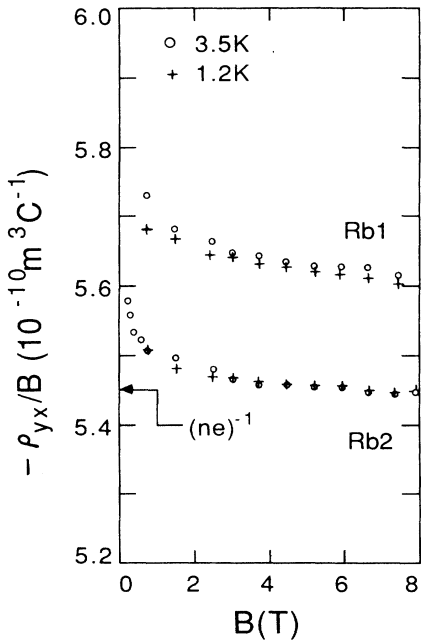

FIG. 2. The Hall coefficients ($=\rho_{yx}/B$) as a function of magnetic field for the two samples. The expected high-field limit is $(ne)^{-1}$, where n is the electron density and e the electronic charge. The gain of the chopper amplifier is usually slightly field dependent; some of the slow decrease in $-\rho_{yx}/B$ ($\lesssim 0.25\%$) might be attributable to this cause. The absolute errors could be $\simeq 5\%$.

from the expected value of -5.45×10^{-10} m^{3}C^{-1} [as evaluated from the lattice constant at 5 K (Ref. 8)] are within experimental error; we would not be surprised to see discrepancies of up to 5% resulting from the thickness determinations of the samples. The results are corrected for thermal expansion.[8]

B. Thermal coefficients

Over the range 1.5–4.2 K, the zero-field thermal resistivities $\gamma_0(T)$ of both samples are well represented by (to $\lesssim 2\%$)

$$\gamma_0(T)=(\rho_0/L_0T)+\beta T^2 , \tag{1}$$

where ρ_0 is the measured resistivity of each sample ($\pm 2\%$) and the slope β is 8.8×10^{-5} ($\pm 5\%$) m W^{-1} K^{-1} for both samples. (L_0 is the Sommerfeld value of the Lorenz number.) This value for β is in good agreement with that quoted by MacDonald *et al.*[11] at 9.3×10^{-5} m W^{-1} K^{-1}.

In a magnetic field the relevant components of the thermal resistivity tensor $\vec{\gamma}^m$ (the superscript m meaning the measured value) are modified by the presence of the lattice conductivity λ_g and are given by[12]

$$\gamma^m_{xx}=\gamma^e_{xx}(\alpha+\lambda_g\gamma^{e\,2}_{yx}\gamma^{-1}_{xx})/[\alpha^2+(\lambda_g\gamma^e_{yx})^2] , \tag{2a}$$

$$\gamma^m_{yx}=\gamma^e_{yx}/[\alpha^2+(\lambda_g\gamma^e_{yx})^2] , \tag{2b}$$

where $\alpha = 1 + \gamma^e_{xx}\lambda_g$, the superscript e signifying the value the component would have if $\lambda_g = 0$. The denominator in both expressions is close to unity and varies from 1.01–1.02 at $B = 0$, to 1.02–1.04 at 8 T for the present measurements. For the purposes of analyzing γ^m_{xx} we take the denominator to be unity and with α also taken to be unity (valid to within 1%), then Eq. (2a) becomes

$$\gamma^m_{xx} = \gamma^e_{xx} + \lambda_g \gamma^{e\,2}_{yx} \ . \tag{3}$$

We expect $\gamma^e_{yx} = \rho_{yx}/L_0 T$ (see the following sections) and we take $\rho_{yx} = R_H B$ where $R_H = (ne)^{-1}$. For K, γ^e_{xx} is well represented[13] by $\gamma_0(T) + A_1(T)B$ where $A_1(T)$ is a coefficient whose physical origin is uncertain but is presumably connected with the Kohler slopes mentioned in Sec. III A. If the same is true for Rb, then Eq. (3) becomes

$$\gamma^m_{xx} = \gamma_0(T) + A_1(T)B + A_2(T)B^2 \ , \tag{4}$$

where $A_2(T) = \lambda_g (R_H/L_0 T)^2$. Our data fit this equation very well, especially if we allow $\gamma_0(T)$ to be a variable, say $A_0(T)$, rather than fixing it according to Eq. (1). In this case the fits reproduce the experimental data at the level of 1% but $A_0(T)$ is usually larger than $\gamma_0(T)$ by 2–4%. The last term is relatively large and enables us to extract λ_g, the results of which are shown in Fig. 3. The differences between Rb 1 and Rb 2 are probably not particularly significant, being typically less than 10%, and experimental uncertainties will be at a similar level, but it is interesting that Rb 1 produced observably higher values of λ_g after cycling to room temperature even though other properties showed no change. This kind of behavior was not noticed with K.

For completeness, the coefficient $A_1(T)$ is plotted in Fig. 4 in the form $A_1(T)L_0 T$ so that the slope of the ρ_{xx} data can also be shown on the same graph. We do not pursue this coefficient further except to remark that it behaves in a similar manner to that of K (Ref. 13) and such behavior has not yet been plausibly explained.

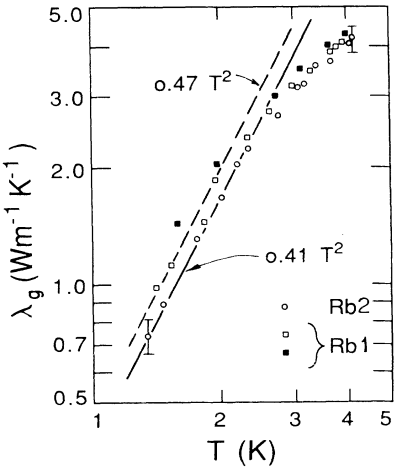

FIG. 3. The lattice conductivity of the two samples as a function of temperature. The uncertainties shown are typical. In the case of Rb 1 the open and solid squares correspond to different runs with a warming to room temperature between them.

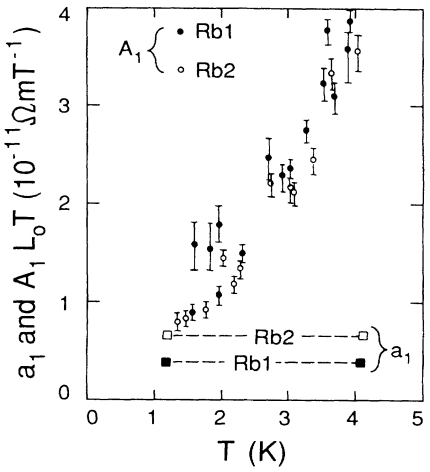

FIG. 4. The coefficient a_1 in the expression $\rho_{xx} = a_0 + a_1 B$ (see Fig. 1 at high fields) and the coefficient A_1 in $\gamma_{xx} = A_0 + A_1 + A_2 B^2$ [Eq. (4)], both as a function of T. The latter is multiplied by $L_0 T$ for comparison with a_1. The error bars are those obtained from least-mean-squares fits to the data.

The Righi-Leduc coefficient γ^m_{yx} is shown in Fig. 5 for Rb 1 and is plotted in the form $\gamma^m_{yx} L_0 T/B$ so that comparison with ρ_{yx}/B is possible. We can use Eq. (2b) to

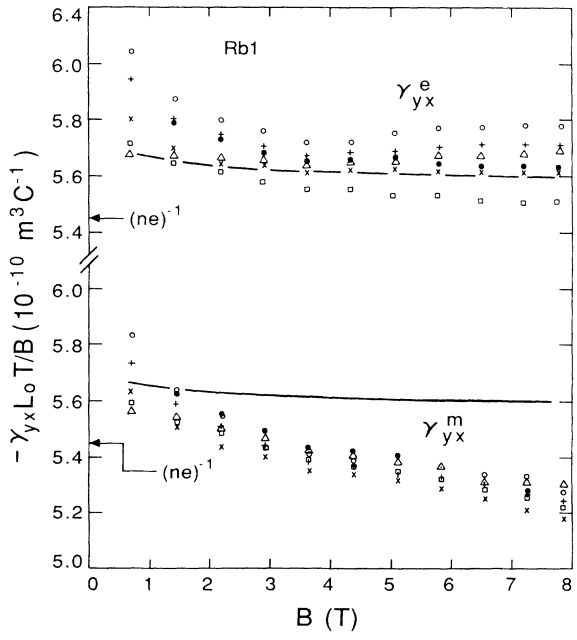

FIG. 5. The measured data on $\gamma^m_{yx} L_0 T$ (lower data set) and the coefficient corrected for λ_g, i.e., $\gamma^e_{yx} L_0 T$ (upper data set) for Rb 1. The symbols correspond to ○, 3.92 K; +, 3.64 K; × 3.07 K; ●, 2.65 K; □, 1.96 K; △, 1.54 K. Relative accuracies should be ≤ 2–3%. The solid line is ρ_{yx}/B (cf. Fig. 2). Rb 2 shows a similar behavior.

evaluate γ^e_{yx} by taking γ^e_{xx} from λ_g from the experimental data on γ^m_{xx}. The results are also plotted in Fig. 5 and are seen to agree with ρ_{yx}/B to an accuracy of 2–3 %, this resulting discrepancy likely being due only to errors in thermometer calibration. The data for Rb 2 are very similar. This demonstrates that the decrease of $\gamma^m_{yx}L_0T/B$ with field is well accounted for by λ_g and the corrected values, i.e., $\gamma^e_{yx}L_0T/B$, have the expected behavior.[14]

C. Thermoelectric coefficients

Figure 6 shows the (adiabatic) thermopower S^a of Rb 2 at zero field and at 8 T as a function of temperature, and Fig. 7 shows the variation of S^a as a function of field at various fixed temperatures. The insensitivity to magnetic field is quite striking and similar to the behavior of K. The data for Rb 1 are very similar to those for Rb 2 but are generally larger by up to 10%. Figure 8 reproduces our results on the Nernst-Ettingshausen coefficient (see Ref. 1 for detailed definitions). Above $B \sim 2$ T, P^a/B is independent of field (to accuracies $\lesssim 3\%$) and so we have not presented the field dependence.

IV. DISCUSSION

The general behavior of the coefficients ρ_{yx}, γ^e_{yx}, S^a, and P^a as a function of magnetic field is consistent with Rb having a free-electron-like Fermi surface which does not contact the Brillouin zone boundaries, and is similar to that observed for K. This behavior should be contrasted with that of Al (Refs. 15 and 16) or In (Ref. 17) whose Fermi surfaces intersect many zone boundaries leading to a strong field dependence of all the

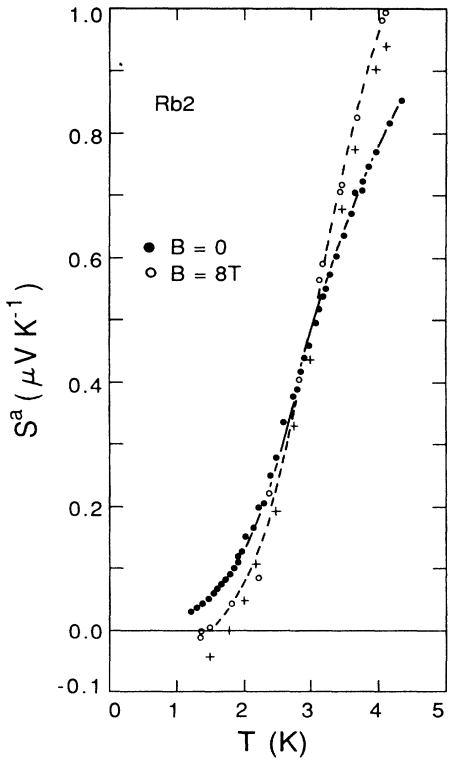

FIG. 6. The thermopower of Rb 2 as a function of T at $B=0$ and $B=8$ T. The crosses are calculated according to $-P^a/\gamma^m_{yx}$ at 8 T. Rb 1 is similar.

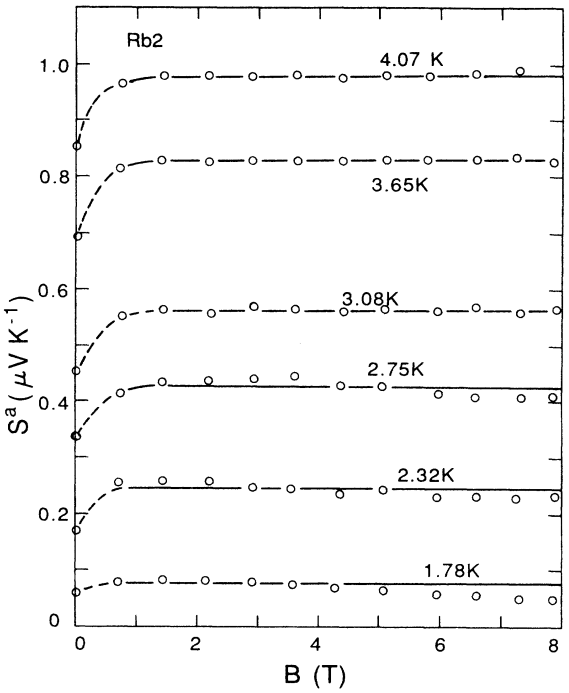

FIG. 7. The thermopower of Rb 2 as a function of magnetic field.

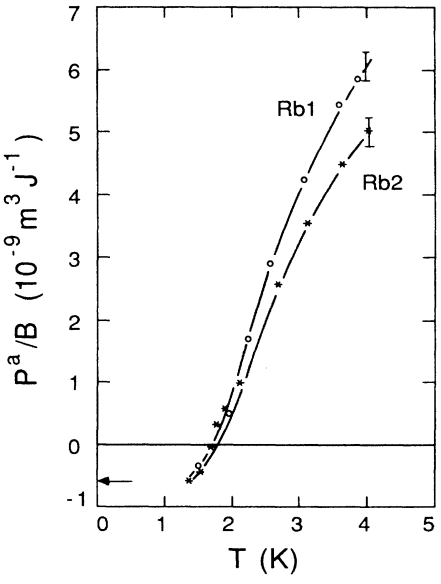

FIG. 8. The Nernst-Ettingshausen coefficient P^a (divided by B) as a function of temperature for both samples. The arrow at -0.61×10^{-9} m^3 J^{-1} is the calculated low-temperature limit (using the electronic specific-heat coefficient, cf. Ref. 1).

coefficients. The contrast is reinforced by a simple relationship that can be derived between P^a/B and S^a and which is valid, at least approximately, only for simple spherical Fermi surfaces. In terms of the thermoelectric tensor $\vec{\epsilon}''$ defined by the relationship $\mathbf{J}=\rho^{-1}\mathbf{E}+\vec{\epsilon}''\nabla T$, where $\mathbf{J}$ is the electric current density produced by an electric field $\mathbf{E}$ and temperature gradient ∇T, one finds ($\mathbf{B}$ is always taken to be parallel to z)

$$S^a=-\vec{\epsilon}''_{xx}(\rho_{xx}-\gamma_{yx}\rho_{yx}/\gamma_{xx}) +\vec{\epsilon}''_{yx}(\rho_{yx}+\gamma_{yx}\rho_{xx}/\gamma_{xx}) , \tag{5a}$$

and

$$P^a=\vec{\epsilon}''_{yx}(\rho_{xx}\gamma_{xx}-\gamma_{yx}\rho_{yx})+\vec{\epsilon}''_{xx}(\rho_{yx}\gamma_{xx}+\gamma_{yx}\rho_{xx}) \tag{5b}$$

(we drop the superscript m on γ but all the coefficients are those actually measured). One can see that S^a and P^a are complicated combinations of many coefficients, all varying as a function of B. In Eq. (5a) the term $\rho_{yx}\vec{\epsilon}''_{yx}$ is dominant at high fields and is independent of B. The first term is negligible, but the second and last are both significant for these samples and would be expected to lead to a relatively strong field dependence of S_{xx} (due to the γ_{xx} appearing in the denominator.) However for free electrons, and assuming only entropy contributions to $\vec{\epsilon}''_{xx}$ and $\vec{\epsilon}''_{yx}$ (i.e., ignoring any relaxation-time effects in the diffusion components and assuming only normal electron-phonon scattering contributes to the phonon-drag term), then one finds[17] that

$$\vec{\epsilon}''_{xx}\rho_{yx}+\vec{\epsilon}''_{yx}\rho_{xx}=0 \tag{6}$$

so that the second and last terms would cancel. Now the rapid temperature dependence of P^a and S^a, as well as their signs, point to them being dominated by electron-phonon umklapp processes and the validity of the relationship that we are about to derive strongly suggest that Eq. (6) must also be valid under these conditions for free electrons. Thus at high B we find

$$S^a\simeq\vec{\epsilon}''_{yx}\rho_{yx} . \tag{7a}$$

In an analogous manner [though Eq. (6) is not really necessary now] we have

$$P^a\simeq-\vec{\epsilon}''_{yx}\gamma_{yx}\rho_{yx} . \tag{7b}$$

Combining these last two equations gives the final result $S^a=-P^a/\gamma_{yx}$. We have plotted $-P^a/\gamma_{yx}$ in Fig. 6 and the agreement with S^a at high B is seen to be excellent. The only serious discrepancies are at low temperatures where the assumptions leading to the derivation of the relationship are not well founded. In particular, we expect diffusion terms to begin to dominate the thermoelectric coefficients and relaxation-time contributions to the diffusion terms cannot be ignored without incurring errors of the order of a factor of 2 in $\vec{\epsilon}''_{xx}$. It is also of interest that S^a ($B\rightarrow 0$) is given by $-\vec{\epsilon}''_{xx}\rho_{xx}$ and the equivalence of this term with the right-hand side of Eq. (7a) is expected to hold only for the same condition of a simple spherical Fermi surface.[17] The same results hold for K (Ref. 1) but not for other metals that have been investigated (i.e., Cu, Ag, Au, In, and Al of the simpler ones). It is interesting to note that $S^a=-P^a/\gamma_{yx}$ corresponds to $E_x/(\partial T/\partial x)=E_y/(\partial T/\partial y)$.

So far the correspondence between K and Rb has been very close, but the behavior of λ_g for each of these metals does appear to be different. A way of bringing out this difference is to use the expression due to Klemens[4] which relates λ_g and the coefficient β of Eq. (1). If one takes $\lambda_g=\alpha T^2$, as would be appropriate at low temperatures if electron-phonon scattering were the dominant process limiting the mean free path of the phonons, then one finds

$$\alpha=313/\beta\theta_D^4 z^{4/3} , \tag{8}$$

where θ_D is the Debye temperature and z the valence of the metal. Although the result has been generalized to more complex metals by Butler and Williams,[18] the equation retains this form for simple metals. Equation (8) works well for the noble metals,[4] Al and In,[5] and Sn,[19] giving agreement to no worse than a factor of 2. For K, taking[20] $\beta=1.7\times10^{-5}$ m W^{-1} K^{-1} and $\theta_D=90$ K, one finds $\alpha=0.28$ W m^{-1} K^{-3} or a value of λ_g at 2 K of about 1.1 W m^{-1} K^{-1}. For reasonably unstrained samples the experimental result is about 10 W m^{-1} K^{-1} at 2 K.[1,2,6] In other words the relationship fails badly. With a calculation devoted specifically to K, Ekin[3] found λ_g at 2 K to be 0.96 W m^{-1} K^{-1} in substantial agreement with Eq. (8). The resolution of this problem has been outlined in Sec. I and involves the purely transverse phonons along high-symmetry directions that cannot be scattered by the electrons if a 1 OPW approximation is appropriate. Ekin[3] used a variational approach which can give only a lower limit to λ_g and much the same physics is implicit in Eq. (8). Nevertheless when we apply Eq. (8) to Rb using the value of β mentioned earlier (8.8×10^{-5} m W^{-1} K^{-1}) and $\theta_D=55$ K, we find $\lambda_g=0.36T^2$ W m^{-1} K^{-1} which agrees rather well with our data. The line drawn through the low-temperature data of Rb 2 in Fig. 2 obeys $\lambda_g=0.41T^2$ W m^{-1} K^{-1} with the data for Rb 1 being slightly higher at $0.47T^2$ W m^{-1} K^{-1}.

These results suggest that the transverse phonons in Rb are not as effective as those in K in carrying a heat current. The simplest interpretation of this is that Rb is sufficiently non-free-electron-like, as compared to K, that the electron-phonon coupling is able to keep the transverse phonons in equilibrium. In this context it is also of interest that recent experiments[6] on K have failed to establish phonon scattering by dislocations as the process which finally limits the heat conductivity of the transverse phonons, as was originally suggested[1] to be the case. It is possible that, in K too, it is the departure from 1 OPW behavior which finally limits the lattice conductivity to the observed values. These experimental deductions should be amenable to theoretical testing.

There is one point which could cloud our interpretation of λ_g, and this is the possibility of a martensitic transformation in Rb; this would introduce internal damage and reduce λ_g, presumably leaving the agreement obtained above as a fortuitous coincidence. The recent evidence which favors such a transformation[7] was

obtained near 1 K and although this evidence is indirect, it is convincing. On the other had, the original work indicating no transformation, even after considerable cold work, was carried out at 5 K and is equally convincing. As we mentioned in Sec. III, our data on λ_g for Rb 1 were not quite reproducible after cycling to room temperature, a fact which is difficult to explain unless the sample became in some way different between the two sets of data, e.g., because of a transformation in one case. At the moment, we consider this only speculation and await further experiments concerning the possibility of a transformation.

V. SUMMARY

All of the present results, except possibly those on the lattice thermal conductivity, are consistent with what one would expect from a simple metal, i.e., one in which the Fermi surface is spherical and does not intersect any zone boundaries. In this respect the results are quite similar to those obtained for K.[1] The only difference between K and Rb is the behavior of λ_g. For K we find λ_g to be an order of magnitude more than simple models predict, whereas for Rb the predictions are approximately correct. It will be interesting to determine whether the increased distortions of the Fermi surface of Rb compared to K are sufficient to account for this difference.

ACKNOWLEDGMENTS

Conversations with Dr. C. R. Leavens of the National Research Council of Canada are gratefully acknowledged. The work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

[1]M. R. Stinson, R. Fletcher, and C. R. Leavens, Phys. Rev. B **20**, 3970 (1979).
[2]R. J. M. van Vucht, H. van Kempen, and P. Wyder, Rep. Prog. Phys. **48**, 853 (1985).
[3]J. W. Ekin, Phys. Rev. B **6**, 371 (1972).
[4]P. G. Klemens, in *Solid State Physics*, edited by E. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1958), Vol. 7, pp. 1–98.
[5]T. Amundsen, O. Furuseth, and R. P. Sovik, J. Phys. F **7**, L159 (1977).
[6]R. Fletcher, Phys. Rev. B **36**, 3042 (1987).
[7]I. M. Templeton, J. Phys. F **12**, L121 (1982).
[8]C. S. Barrett, Acta. Cryst. **9**, 671 (1956).
[9]Mine Safety Appliances Ltd., Pittsburgh, Pa.
[10]R. Fletcher, Can. J. Phys. **60**, 679 (1982).
[11]D. K. C. MacDonald, G. K. White, and S. B. Woods, Proc. R. Soc. London, Ser. A **235**, 358 (1956).
[12]R. Fletcher, J. Phys. F **4**, 1155 (1974).
[13]R. S. Newrock and B. W. Maxfield, J. Low. Temp. Phys. **23**, 119 (1976).
[14]M. Ia Azbel', M. I. Kaganov, and I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **32**, 1188 (1957) [Sov. Phys.—JETP **5**, 967 (1957)].
[15]*Thermoelectric Power of Metals*, F. J. Blatt, P. A. Schroeder, C. L. Foiles, and D. Greig (Plenum, New York, 1976).
[16]T. Amundsen, Philos. Mag. **20**, 166 (1969).
[17]B. J. Thaler and R. Fletcher, J. Low Temp. Phys. **30**, 773 (1978).
[18]W. H. Butler and R. K. Williams, Phys. Rev. **18**, 6483 (1978).
[19]M. C. Karamargin, C. A. Reynolds, F. P. Lipshultz, and P. G. Klemens, Phys. Rev. B **6**, 3624 (1972).
[20]R. S. Newrock and B. W. Maxfield, Phys. Rev. B **7**, 1283 (1973).