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Righi-Leduc and Hall coefficients of the alkali metals *

R. Fletcher
Physics Department, Queen's University, Kingston, Ontario, Canada K7L3N6

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We have extended our previous investigations on Na and K to Li and Rb. The Hall and Righi-Leduc coefficients (R and A_m) have been determined at a field of 0.95 T over the temperature range 2–120 K. When plotted as a function of reduced variables, the A_m results for all the alkali metals are strikingly similar and show a characteristic peak at low temperatures. We also present further data on the field and temperature variation of R and A_m in the ^{4}He temperature range for a pure K sample. Although R is independent of field and temperature, A_m shows a rapid increase near 4 K as the magnetic field is reduced.

I. INTRODUCTION

In a previous paper,[1] to be referred to as I, we presented results on the Righi-Leduc and Hall coefficients of Na and K. The available theories have suggested that these two coefficients would be simply related by the Sommerfeld value of the Lorenz number ($L_0 = 2.44_3 \times 10^{-8}$ V^2 K^{-2}) apart from a correction term due to the lattice thermal conductivity. The experimental results agreed with this prediction only in the low-temperature high-magnetic-field limit. Unexpectedly, the Righi-Leduc coefficient showed a pronounced peak at intermediate temperatures, the origin of which is not known. We have now extended these results to Rb and Li and report them in this paper. We also present some further data on the magnetic field dependence of the Righi-Leduc coefficient of K; the previous data were taken on a rather impure K sample and became inaccurate below 4 K, so we have attempted to remedy both of these deficiencies.

In Sec. II. we shall outline the experimental techniques (where these differ from those in I) and present the data on Li and Rb. Section III is devoted to a discussion of the new results as well as to a comparison with the previous results on Na and K. We shall also present our new data on K in that section.

II. EXPERIMENTAL TECHNIQUES AND RESULTS

Lithium, being the least reactive of the alkalis, is a relatively easy material to work with. Although the metal is harder than Na and K, it was possible to roll thin sheets using a stainless-steel roller and block in the same manner as outlined in I. Oil was not required to keep the sample in a clean condition, if the atmosphere in the glove box was maintained in a reasonably inert condition. A razor blade (broken so that the blade was pointed) and template were used to produce samples of a similar size and shape to those described in I. Two samples were made from the same starting material[2] and although the electrical resistivity was not determined for either one, the measured thermal conductivities could be used to estimate the residual resistivity ratios ($\rho_{293\text{K}}/\rho_{4.2\text{K}}$) as 850. The thickness of each sample was about 0.75 mm and its measurement is the major source of absolute uncertainty for the present data; our previous experience with the much softer Na and K suggested that the thickness can be measured to about 3% with a micrometer and we expect at least an equal accuracy on the much harder Li. In fact the absolute measurements on the two Li samples agree with each other to 2% over the whole temperature range.

A different technique was required for Rb since it was found to be impossible to roll satisfactorily thin sheets of this metal under oil, and the glove-box atmosphere was never good enough to allow us to dispense with the oil. When prepared by rolling, the samples tended to flake and were clearly not homogeneous. The samples were finally made by casting molten Rb into a mold constructed of polyethylene and polypropylene. More than enough Rb to fill the mold was placed in a polyethylene syringe with the plunger in position, but leaving ample space for the metal. The tip of the syringe (without the needle) had a stainless-steel insert pressed in; a No. 60 hole was drilled through this insert, this being found to be sufficiently small to prevent molten Rb dripping through under gravity. The tip was inserted into the mold, and the whole placed in an evacuable container. All the parts of the mold, as well as the syringe and Rb, had a very light coating of paraffin oil and the whole operation took place inside the glove box. The container was evacuated using a two-stage rotary pump (a small hole in the side of the syringe allowed the gas to escape from the mold) and heated to above the melting point of Rb. After 25–30 min, a time long enough to ensure complete melting of the Rb and warming of the mold, clean argon gas was allowed into the container to force the Rb into the mold. The samples prepared in this way appeared to be homogeneous, but often had surface imperfections due to tiny oil droplets. Many samples were made before acceptable ones were produced. Two samples, to be referred to as Rb(1) and Rb(2), were judged good enough for investigation. The starting materials were obtained from Mackay[3] [Rb(1)] and M. S. A.[4] [Rb(2)] and had very similar residual resistivity ratios, being 489 for the former and 441 for the latter. We estimated the thickness of the samples (about 1.7 mm) from the mold dimensions and expect this to be accurate to about 3%.

In contrast to the case of Na and K, crystallites were never observable in either the Li or Rb even when stored under oil.

The Li sample was mounted in a frame in exactly the same way as the Na and K samples.[1] However, Rb was found to be too soft to produce reliable crimp contacts for the leads and a different method was used. Small copper blocks were attached to the nylon support rods of the sample holder. The Rb limbs were compressed onto the blocks using plates which were screwed down with small screws. To improve the contact, the blocks had a grid pattern chiselled across the contact area. The thermocouples were held in soft copper crimps about 15 mm long (being insulated by cigarette paper and G. E. 7031 varnish) which had previously been soldered to the copper blocks. The grid pattern was also chiselled into the heater and sink connections; the quality of these contacts can be gauged by the fact that no observable heating of the sample occurred for a current of 0.5 A through the end contacts, which enables us to put an upper limit of about 10 mΩ on the contact resistances. The results on K, which we will present later, were taken using a similar mounting procedure with the exception that all temperatures and temperature differences were measured with carbon thermometers which were inserted into the blocks. All of the samples were supported only by their ends.

Our experiences in I showed that the Hall and Righi-Leduc coefficients should be taken on the same samples to eliminate uncertainties due to the thickness when comparisons between the coefficients are made. The heavy current lead required for the Hall measurements could not be left in position for the Righi-Leduc experiments since it provided too large a heat leak. For both Li and Rb, the first sample [Li(1) and Rb(1)] was used to determine A_m, the Righi-Leduc coefficient, after which the heavy current lead was attached and the Hall coefficient R was measured. The second samples [Li(2) and Rb(2)] as well as the K, were investigated in the reverse order. The uncertainties in the Li and Rb data arising from thermocouples and other calibrations are the same as those discussed in I.

The K data were taken and analyzed in the same manner as described previously[5] and the actual sample was in fact the same as that labeled K3 in that previous paper. It has a residual resistivity ratio of 6050.

The samples were allowed to sit overnight in the cryostat (under high vacuum) at room temperature before slowly cooling.

The Rb results are shown in Fig. 1 and those on Li are reproduced in Fig. 2. Several comments relevant to these results are in order before proceeding to the discussion. Li, like Na, undergoes a martensitic phase transformation at low temperatures. On cooling, Li begins to transform from the bcc to hcp phase at temperatures of 65–80 K, though 70–75 K seems appropriate to pure samples.[6] By helium temperatures, up to 50% of the sample may have undergone the transformation. With subsequent warming, the sample reverts to bcc beginning at perhaps 100 K with most of the process being completed by about 120 K. With this in mind, the data on Li was taken cyclically starting at about 130 K, cooling to 2 K, and subsequently warming to 130 K again. The whole cycle took 4–5 days to complete in the case of A_m and perhaps 2–3 days for R.

A further point concerning the results of Fig. 2 is that the data on Li (2) have been systematically shifted by a constant percentage to increase the clarity of the hysteresis curves. The intercepts of R as $T \to 0$ were determined as -1.45×10^{-10} and -1.48×10^{-10} m^3/C for Li(1) and Li(2), respectively, the difference presumably reflecting uncertainties in the thickness. All the data for Li(2) (i.e., for both R and A_m) were reduced by the factor $\frac{145}{148}$.

Finally it should be mentioned that all the data for Li and Rb have been corrected for thermal expansion using smooth curves connecting the available lattice parameter data[7] for the bcc phases. The hcp phase of Li has an atomic volume some 1% larger than the bcc phase at 77 K; this corresponds to a difference of about 0.3% in linear dimensions which is not significant for the present measurements. The magnetic field used in all cases was about 0.95 T. Some data were taken on Li at 0.5 T which will not be reproduced, but will be referred to later.

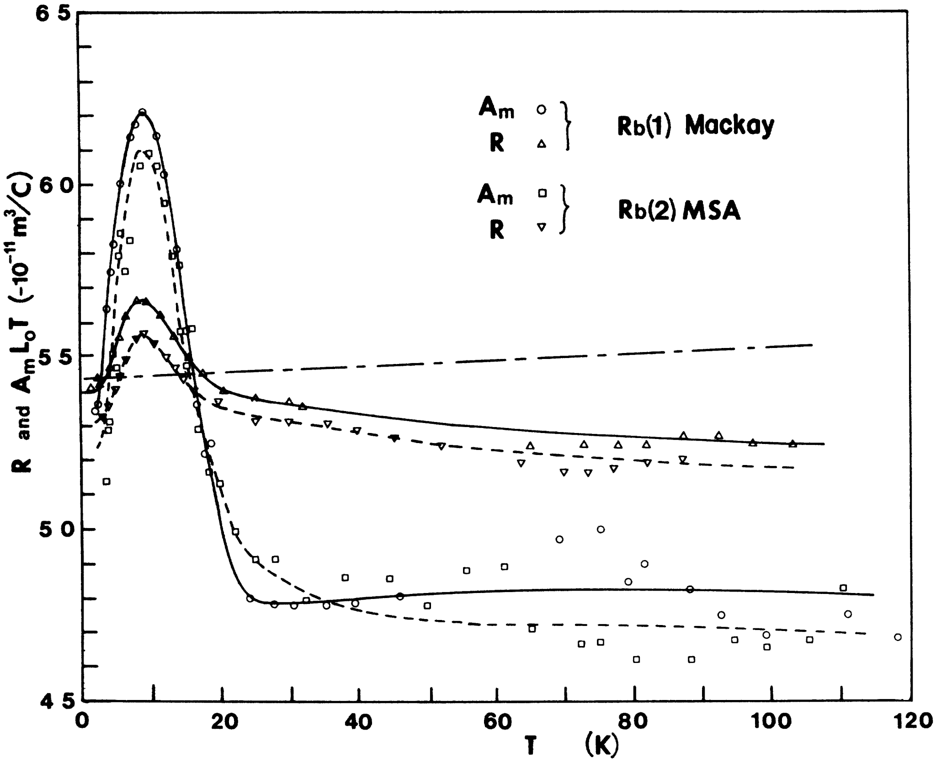

FIG. 1. Hall R and Righi-Leduc A_m coefficients of the two Rb samples; A_m has been multiplied by L_0T for comparison with R. The chain line gives the variation of $(ne)^{-1}$ corrected for thermal expansion.

III. DISCUSSION

A. Hall coefficients

The temperature dependence of R for Rb has not been previously reported. It will be seen from Fig. 1 that R shows a marked, though relatively small, peak near 10 K. The peak is presumably the result of the anisotropic scattering of electrons by phonons,[1,8-10] but it will be recalled that this mechanism is only effective in the low-field regime, i.e., $\omega\tau \ll 1$, where ω is the cyclotron frequency and τ the relaxation time. At the lowest temperatures the Rb samples are entering the high-field regime with $\omega\tau \simeq R\sigma B \simeq 2$ near 4 K (σ is the conductivity and B the magnetic field). In the high-field limit, R should tend[11] to the free-electron value of $(ne)^{-1}$ (n being the number of electrons per unit volume and e the negative electronic charge)

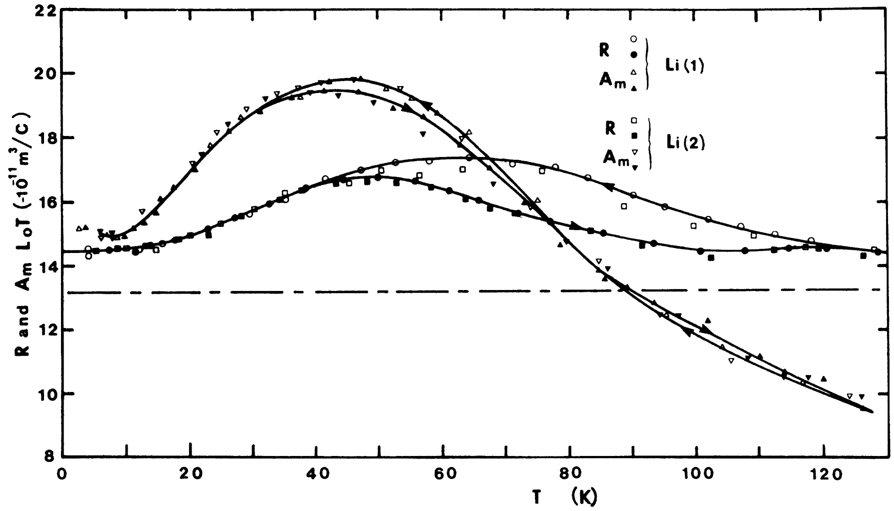

FIG. 2. Hall R and Righi-Leduc coefficients of the two Li samples; A_m has been multiplied by L_0T for comparison with R. The chain line gives $(ne)^{-1}$ evaluated using lattice parameters appropriate to the bcc phase. All the data for Li (2) have been reduced by the factor $\frac{145}{148}$ for clarity. The open symbols refer to decreasing temperature and the closed symbols to increasing temperature; note that, contrary to the case of Na, the hysteresis is much larger for R than for A_m.

since Rb has a simple closed Fermi surface. The chain line on Fig. 1 gives $(ne)^{-1}$ corrected for thermal expansion and it is seen that R does tend to $(ne)^{-1}$ at the lowest temperatures to within experimental error; the expected value is $-5.4_4 \times 10^{-10}$ $\mathrm{m^3C^{-1}}$, which is to be compared with the mean experimental value of $-5.3_5 \times 10^{-10}$ $\mathrm{m^3C^{-1}}$. The precise position of the peak and its absolute magnitude are not too important since they are field dependent and reflect the low- to high-field transition.

At high temperatures (the Debye temperature Θ_D of Rb is only 56 K)[12], the electronic scattering should become isotropic and R should then be a measure of the average curvature of the Fermi surface.[13] A particularly noticeable feature of the data in Fig. 1 is that R is consistently lower than $(ne)^{-1}$ for $T \gtrsim \Theta_D$. If it is assumed that the low-temperature value of R should be $(ne)^{-1}$, then the observed value at 100 K is about 4% lower than $(ne)^{-1}$. Having noticed this for Rb, an examination of the previous data on Na and K shows that a discrepancy also exists for K but not for Na. The case of K is particularly important in that the results were obtained on high-purity samples, many of which had $\omega\tau > 10$ at low temperatures, and the Fermi surface is known to be simple so that the limiting valve of R should be exactly $(ne)^{-1}$. (Even for a material as complicated as Al, the high-field value of R has been accurately reached[14] by $\omega\tau \sim 10$.) This may be used as a reference to normalize the data and, if this is done, then it is seen that R is about 2% low at $T \sim \Theta_D$ ($\Theta_D \sim 90$ K for K)[12]. Any discrepancy for Na is at most 1% by 110 K, though we note that this is well below Θ_D(~ 153 K)[12].

It seems likely that the discrepancies may be a result of departures of the Fermi surfaces from spherical. The Rb Fermi surface is much more distorted[15] than that of K, which in turn is more distorted than that of Na. (Only the bcc phase of Na is present at high temperatures so complications due to the unknown electronic structure of the hcp phase do not arise.) Previous work[16] suggests that distortion will usually reduce the value of R below $(ne)^{-1}$.

Another feature of the data in I, which was not pointed out previously, is that it is not immediately clear that the low-temperature high-field limiting value of R for Na should indeed be $(ne)^{-1}$ as was observed to be the case. Since a substantial fraction of the sample is in the hcp phase, one might have expected to see a departure from $(ne)^{-1}$ if the Fermi surface of the hcp phase were not closed. The surface should be intersected by the hexagonal faces of the first Brillouin zone,[17] so presumably the energy gaps across these faces are either very small or zero.

The variation of R with temperature for Li has previously been investigated by Alderson and Farrell,[18] though they were not able to determine the full hysteresis curve. Over the range of overlap, the present and previous results are very similar, but the absolute values cannot be compared since the earlier data was normalized to $(ne)^{-1}$ at room temperature. Li has the most distorted Fermi surface by far of all the alkalis,[15] as well as having the most anisotropic electronic scattering[9] (even up to $\Theta_D \simeq 335$ K), so the normalization cannot be expected to be reliable for Li though the temperature variation should be accurate. Our mean value of R as $T \to 0$ is $(-1.46_5 \pm 0.03_0) \times 10^{-10}$ $\mathrm{m^3C^{-1}}$, which is to be compared with $(ne)^{-1}$ values in the range $-1.31_3 \to -1.32_7 \times 10^{-10}$ $\mathrm{m^3C^{-1}}$ (for the bcc and hcp phases, respectively). We estimate $\omega\tau \sim 1.3$ for both samples and this is low enough to throw some doubt on whether the difference is due mainly to distortion of the bcc and hcp Fermi surfaces from spherical, or if it is due to an open surface in the hcp phase.

If we normalize the previous data[18] to our value at 4 K, which is not unreasonable since the sources and purities of the samples seem to be the same, then we estimate a room-temperature value of R of $(-1.38 \pm 0.03) \times 10^{-10}$ $\mathrm{m^3C^{-1}}$ to be compared with a value for $(ne)^{-1}$ of $-1.34_8 \times 10^{-10}$ $\mathrm{m^3C^{-1}}$. These values are in substantial agreement, but this may be coincidental. The distortions of the Fermi surface should decrease R below $(ne)^{-1}$, but the anisotropic electronic scattering, being non-negligible at room temperature, may increase R again (this last is not clear, though R would be certainly raised for anisotropic scattering and a simple spherical surface).

The peaks in R for both decreasing and increasing temperature are presumably attributable to anisotropic scattering and not to the phase transformation. The reason is that the peaks are already in evidence before the transformation gets underway, either from bcc to hcp for decreasing temperature or from hcp to bcc for increasing temperature. The large peaks are consistent with theory.[9]

B. Righi-Leduc coefficients

As was found to be the case for Na and K, the limiting low-temperature experimental values of R and $A_m L_0 T$ are in agreement for the Rb samples. There seems to be a discrepancy of (3–4)% in the case of Li, but this is not far enough outside the expected errors of about 2% to be convincing.

The overall behavior of $A_m L_0 T$ as a function of T for both Li and Rb is very similar to that for Na and K. Indeed when we plot all the data using the reduced quantities $A_m L_0 T\, ne$ and T/Θ_D (Fig. 3),

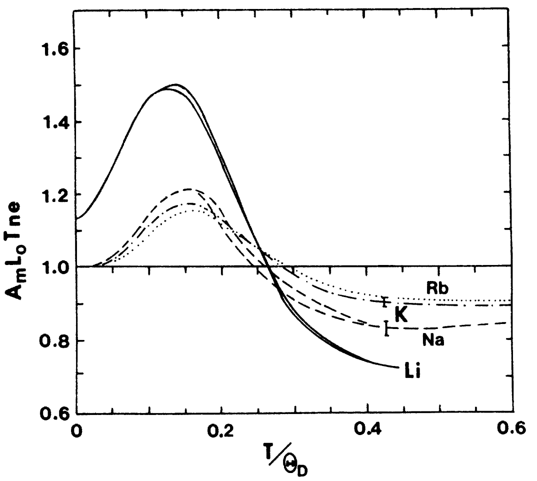

FIG. 3. Data on A_m for all the alkalis plotted as a function of reduced variables. The free-electron value of A_m would be $1/L_0Tne$.

the similarities become striking (all the data except those for Li are normalized by assuming the limiting low-temperature value of A_mL_0T is $1/ne$). The reduced quantities A_mL_0T/R and T/Θ_D do not produce as consistent a series (Fig. 4). Of particular note is the fact that the hysteresis curves in R and A_mL_0T for both Na and Li do not show the same behavior, i.e., for Li, A_mL_0T hardly shows hysteresis at all, whereas it is a large effect in R; the opposite is true for Na. These facts lead us to the conclusion that the peaks in A_mL_0T and R are probably due to different causes. If we believe that the peaks in R originate in the anisotropic electronic scattering, then we must find some other mechanism to account for the behavior of A_mL_0T. However, the strong correlation of $A_mL_0T\,ne$ with T/Θ_D leaves no doubt (even for Li) that the peak is connected with electron-phonon scattering.

There are some features of Figs. 3 and 4 which should be borne in mind if a theoretical comparison is to be made at some future date. The first is that A_m should be corrected for the effects of the lattice thermal conductivity λ_g if one requires the Righi-Leduc coefficient "intrinsic" to the electronic system,[1] say A. For this reason the absolute values of A_mL_0T should all be raised except at the lowest temperatures where the correction is negligible. The correction factor is $\alpha = (1+\lambda_g/\lambda_e)^2 \sim 1+2\lambda_g/\lambda_e$, where λ_e is the electronic thermal conductivity. It seems possible, at first sight, that the dip of A_mL_0T below unity above about $\Theta_D/3$ may be accounted for in this manner. However, if one uses the theoretical estimates[19] of λ_g (taking the Grüneisen parameter to be 2 in all cases since we were not able to find any experimental data on this quantity), and our experimental results for λ_e, we estimate $\lambda_g/\lambda_e \sim 0.005(\Theta_D/T)$, $0.02(\Theta_D/T)$, $0.02(\Theta_D/T)$, and $0.03(\Theta_D/T)$ for Li, Na, K, and Rb, respectively. In all cases, and especially for Li, the correction factor is too small to account for the depression of $A_mL_0T\,ne$ at high temperatures (say $T/\Theta_D \sim 0.5$).

Another important point is that the temperatures at which the peaks appear in Figs. 3 and 4 can be lowered by reducing the magnetic field; this also has the effect of increasing the peak heights. In I we have reported some observations on this effect for Na and K. An investigation for Li showed a similar effect is present here too. A series of measurements on A_mL_0T for Li showed that the peak increases in height by (2–3)% and shifts down in temperature by about 3 K when the field is lowered from 0.95 to 0.5 T. At temperatures just 5 K (i.e., $\Delta T \sim 0.015\Theta_D$) above the 0.95 T peak position for Li, decreasing the field below 0.95 T has less than a 1% effect on A_m. These results, and similar ones on Na and K, show that the data on the high-temperature side of the peak can be taken to be representative of low-field conditions ($\omega\tau \ll 1$).

We have previously investigated the effect on R and A_mL_0T of changing the field over the whole temperature range of 2–100 K for Na and K. The data became very inaccurate at low temperatures and low fields because of the low sensitivity of the thermocouples. We have since examined A_mL_0T over the ranges 0.1–1 T and 1.5–4.2 K for a pure K sample (residual resistivity ratio 6050) using carbon thermometers; these results are much more accurate than the previous and are repro-

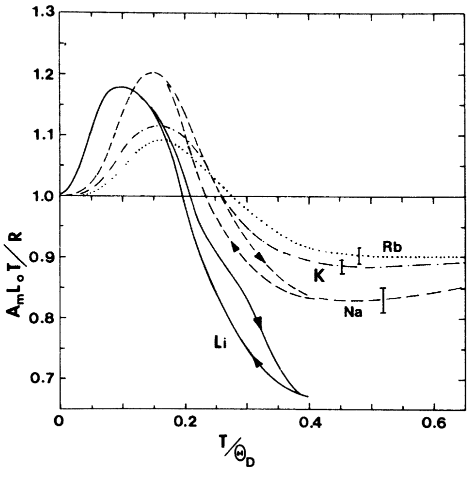

FIG. 4. Ratio A_mL_0T/R as a function of reduced temperature. The curves do not correlate as well as those in Fig. 3.

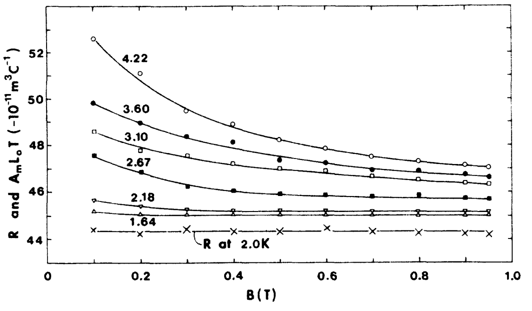

FIG. 5. Hall R and Righi-Leduc A_m coefficients of a pure K sample plotted as a function of magnetic field B for temperatures in the ^{4}He range. The crosses give R measured at 2.0 K but this coefficient showed essentially no temperature variation up to 4 K. All the other data give A_mL_0T for various temperatures. The expected result for R at these temperatures and fields is $(ne)^{-1}$ which has a value of -4.45×10^{-10} m^{3}C^{-1} (corrected for thermal expansion).

duced in Fig. 5. To put the data in perspective, we notice that even at the lowest fields we have used, the sample has $\omega\tau > 1$. Using $\omega\tau \simeq R\sigma B$, we estimate $\omega\tau \gtrsim 40B$ at all temperatures below 4 K for this sample. We expect, and observe, no significant departures of R from $(ne)^{-1}$ for all fields we have used. Presumably an estimate of $\omega\tau$ more appropriate to thermal quantities can be made using $\omega\tau \simeq \lambda RB/L_0T$, where λ is the measured thermal conductivity (we have ignored the relatively small differences between R and A_mL_0T). Using the measured value of $\lambda \simeq 3000$ Wm^{-1}K^{-1} at 4 K, we estimate $\omega\tau \simeq 14B$. Thus, even for the thermal measurements at 4 K, the sample should be tending to high-field conditions at our lowest field of 0.1 T. Presumably then, the limiting low-field value of A_mL_0T could be very high at 4 K if the present data in Fig. 5 can be taken as a guide. The previous data on K reported in I was taken on a much lower purity sample (residual resistance ratio ~ 1005) and did not exhibit the spectacular rise in A_mL_0T between 1.6 and 4.2 that we find here. The only obvious difference in the two samples is that the electronic scattering in the earlier one was impurity dominated at 4 K, but it is phonon dominated in the present one. This again suggests that the rise in A_mL_0T above $(ne)^{-1}$ is closely related to the actual scattering of the electrons by phonons.

In I we examined various possible origins of the peak and showed that none appeared plausible. We would like to add a few more comments concerning the most obvious (though, we believe, still incorrect) explanation. One might argue that since the normal resistivities do not obey the Wiedemann-Franz relation, then there seems to be no reason why the Hall and Righi-Leduc resistivities should. Indeed if we evaluate the usual Lorenz number $L = \rho/WT$, where ρ and W are the electrical and thermal resistivities, and a Lorenz number defined by $L_T = R/A_mT$, then both L and L_T have a similar temperature dependence and show a minimum at intermediate temperatures. We tried to give a simple physical argument in I to show that this explanation is not correct. The idea is that a steady current, say electrical, produces a particular electronic distribution which, under the influence of a weak magnetic field, is rotated on an average through some angle $\omega\tau_\sigma$, where τ_σ is the relaxation time appropriate to electrical conduction. This produces a Hall current which of course is not allowed to flow in an isolated sample. Instead, an electric field is established such that this field produces an equal and opposite electrical current to the Hall current. The relevant parameter in the argument is τ_σ, which disappears (to first order) from the final result for R. A similar argument can be made in the case of the Righi-Leduc effect where the relevant parameter is τ_λ, the relaxation time associated with thermal scattering. This argument is reinforced when one realizes that, although τ_σ might increase a factor 10^3–10^4 for a pure sample cooled from room to helium temperature, the Hall coefficient does not vary by more than a few percent. The insensitivity of R to τ_σ is remarkable and of course is directly opposite to the sensitivity of ρ to τ_σ. It is only because there is a direct connection between ρ and τ_σ, and W and τ_λ that the usual Lorenz number shows the dip. It follows then that we expect no dip for L_T.

IV. SUMMARY

As was found for Na and K, the Hall coefficient of Rb deviates little from the free-electron value, but there does seem to be a significant difference at high temperatures; the difference is also noticeable for K, and the differences may be a result of departures of the Fermi surfaces from precisely spherical. The data on Li does not extend to high enough temperatures to draw any conclusions in this respect. However, Li shows very pronounced deviations from free-electron behavior at intermediate and low temperatures compared with the other alkalis. This is consistent with calculations based on anisotropic scattering of the electron by phonons.

The results on the Righi-Leduc coefficients of all the alkalis show remarkable similarities when scaled by the free-electron values and plotted as a function of reduced temperature. This, together with the observed behavior of the coefficient for an impure and pure K sample as a function of field, suggests that the electron-phonon scattering is responsible for the characteristic peaks that we observe in the Righi-Leduc coefficient. As yet there have been no theoretical explanations of these results.

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