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Magnetothermal Resistivity of Potassium*

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This Letter reports the results of an investigation of the magnetothermal resistivity of potassium aimed at measuring the contribution of the lattice to the thermal current. The observed behavior of the lattice conductivity is contrary to that expected, possibly suggesting other contributions to the thermal current.

If one assumes that the electronic thermal conductivity tensor $\bar{\lambda}_e$, in the presence of a magnetic field along the z axis, is of the form

$$\bar{\lambda}_e = \begin{vmatrix} \lambda_{xx} & \lambda_{xy} & 0 \\ -\lambda_{xy} & \lambda_{xx} & 0 \\ 0 & 0 & \lambda_{zz} \end{vmatrix}$$

and that the phonon conductivity is simply $\lambda_g \bar{I}$, where \bar{I} is a unit matrix, then taking the thermal resistivity $\bar{\gamma}$ to be the inverse of $\bar{\lambda}_e + \lambda_g \bar{I}$ and assuming thermoelectric terms to be negligible one can show¹ after some manipulation that the measured transverse thermal resistivity γ_{xx}^m measured under the condition $\partial T / \partial y = 0$ is given by

$$\gamma_{xx}^m = \gamma_{xx}^e \left(\frac{\alpha + \lambda_g (\gamma_{yx}^e)^2 (\gamma_{xx}^e)^{-1}}{\alpha^2 + (\lambda_g \gamma_{yx}^e)^2} \right).$$

In this equation γ_{xx}^e and γ_{yx}^e are the transverse and Righi-Leduc thermal resistivities that the electrons would exhibit if $\lambda_g = 0$, and $\alpha = (1 + \gamma_{xx}^e \lambda_g)$. For uncompensated metals in not too high fields the equation reduces, to an excellent approximation, to

$$\gamma_{xx}^m = \gamma_{xx}^e + (\gamma_{yx}^e)^2 \lambda_g. \quad (1)$$

It is also possible to show, with the same assump-

tions, that γ_{yx}^e differs insignificantly from the measured value γ_{yx}^m so that Eq. (1) provides a simple and convenient method of obtaining λ_g . Potassium is an excellent material for study since it can be obtained with high purity (thus γ_{xx}^e is small) and γ_{yx}^m is large.² We report here our investigations, prompted by the foregoing predictions, on γ_{xx}^m for several samples of pure potassium.

All the samples were obtained from Mine Safety Appliances Ltd.³ The preparation and handling of similar samples has already been outlined,² but in the present case there are some modifications. The samples were approximately $50 \times 4 \times 1$ mm³ in size and were cut from a rolled sheet using a simple sharp-edged mold. Limbs were provided to measure the longitudinal temperature difference ΔT_l appropriate to γ_{xx}^m and, in the case of sample No. 3 (K3) only, transverse limbs were incorporated to determine the temperature difference appropriate to γ_{yx}^m . Heater powers of 1–10 mW produced $\Delta T_l / T \sim 0.2$ – 0.5% , T being the mean temperature of the sample. The small ΔT were determined with carbon thermometers using ac excitation powers of 1 nW at 4 K decreasing to 30 pW at 1.5 K; these showed magnetoresistance

but this was completely negligible at the fields used ($\Delta R/R \approx 0.1\%$ at 4 K and 1 T). During each run the resistors were calibrated against the vapor pressure of He⁴ using points spaced 0.1–0.2 K apart, and least-mean-squares fits were made with functions of the form $T^{-1} = \sum_n a_n (\ln R)^n$ and $\ln \Delta R = \sum_n a_n (\ln R)^n$, with n typically running up to 5 or 6; here ΔR is the zero-heat difference between pairs of thermometers used to measure temperature differences. Since all the samples showed thermal magnetoresistance, the mean temperature of the sample changed as the field was increased. Such changes directly influence the sensitivity (dR/dT) of the thermometers, and although these effects were relatively small they were taken into account in the analysis of the data. Fields were measured with a Hall probe to 0.5%, though the linearity is better than this.

As a check on the techniques, an aluminum sample with residual resistivity ratio of about 3000 ($\rho_{293}/\rho_{4.2}$) was examined. Such a sample should show no observable B^2 contribution attributable to $\lambda_g(\gamma_{yx}^m)^2$, assuming $\lambda_g \sim 1 \text{ W m}^{-1} \text{ K}^{-1}$,⁴ and this was found to be the case. The relative change in the electrical resistivity with field, $\Delta\rho_{xx}/\rho_{xx}$, was compared to the relative change of the thermal resistivity, $\Delta\gamma_{xx}^m/\gamma_{xx}^m$, and the two quantities were found to agree to an accuracy of about 1% over the whole temperature and field range. (Impurity scattering completely dominates both ρ_{xx} and γ_{xx}^m .) In addition the *absolute* values were compared using the Lorenz number L_0 and it was found that $\rho_{xx} = \gamma_{xx}^m L_0 T$ and $\rho_{yx} = \gamma_{yx}^m L_0 T$ to within $\pm 5\%$ at all temperatures and fields.

The variation of γ_{xx}^m with B for a typical set of potassium data is shown in Fig. 1. It will be noticed that, at the higher temperatures, γ_{xx}^m is approximately linear in B , though a positive deviation from linearity is clearly observed at higher fields. As the temperature is reduced the deviation from linearity becomes more pronounced. The form of the data suggests fitting with equations of the form $\gamma_{xx}^m = a_0 + a_1 B + a_2 B^2$ and this has been done using least-mean-squares procedures; the equations are found to reproduce the data extremely well (usually to 1% or better) and examples are shown in Fig. 1. However it was often found that the zero-field value of γ_{xx}^m was the only point that did not lie on such curves, within the experimental uncertainty, especially at lower temperatures. The reason for this is not clear but may be connected with the fact that the zero-field value is the only point for which the samples are not in high-field conditions.

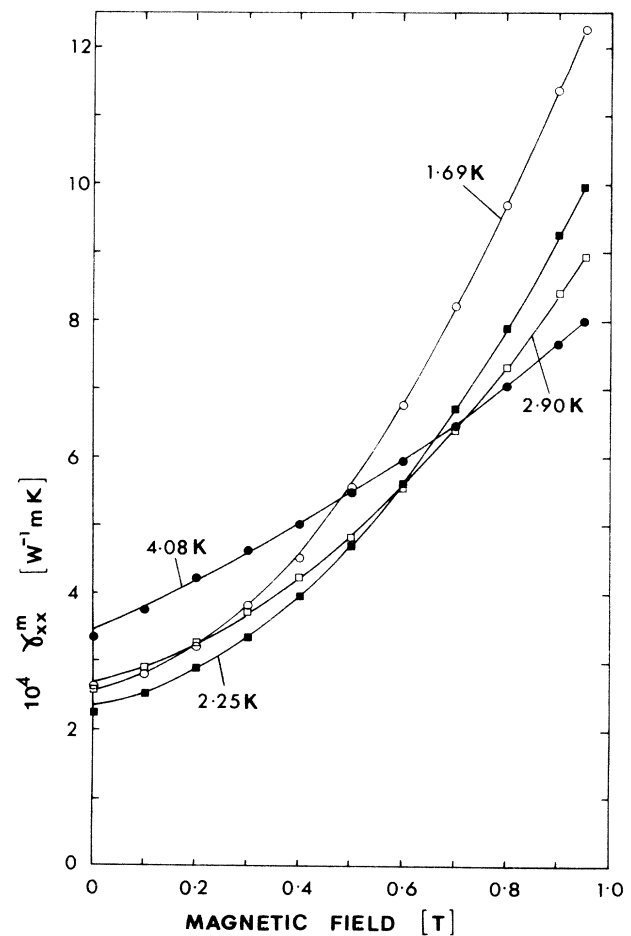


FIG. 1. Measured thermal resistivity γ_{xx}^m of K5 as a function of magnetic field at four different temperatures. The full lines show the results of least-mean-squares fits of the data with $\gamma_{xx}^m = a_0 + a_1 B + a_2 B^2$.

The origin of a_1 is not understood and space does not allow a detailed discussion of the data. We noticed a significant reduction of a_1 as T was decreased. The results for the coefficient a_2 are shown in Fig. 2. Although there appears to be a spread for the various samples, it will be noticed from Fig. 2 that the residual resistivities of the samples are widely different. Thus near 2 K, for example, the zero-field value of γ_{xx}^m for K5 is roughly five times smaller than that for K1. This means that the first term of Eq. (1) varies widely among the samples and in view of this the reproducibility of a_2 can be considered as good. K2 was mounted with Perspex supports so that ρ_{xx} could be determined as a function of B for comparison purposes. To within the experimental error of about 2%, ρ_{xx} could be accurately reproduced by $\rho_{xx} = b_0 + b_1 B$, where b_0 was temperature

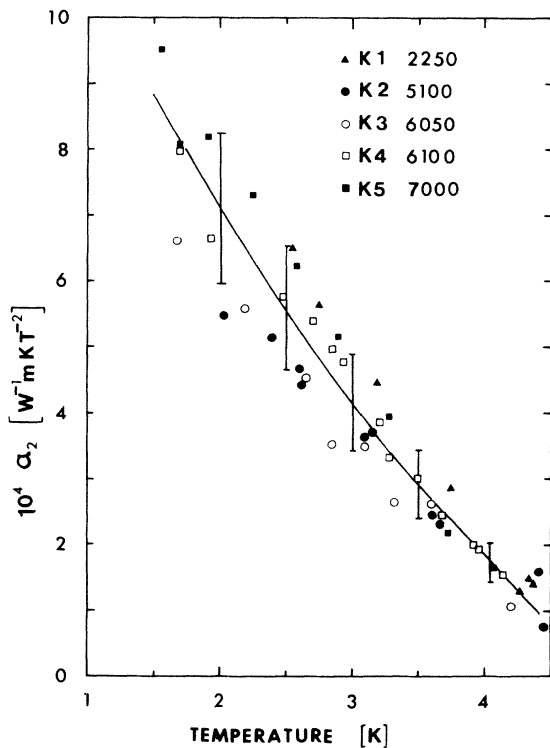


FIG. 2. Coefficient a_2 as a function of temperature for all the samples. The solid line has been used to evaluate λ_g (shown in Fig. 3), and the error bars are simply a guide to the spread of the data and are equivalent to those appearing in Fig. 3. The numbers in the key at the top right give the residual resistivity ratios of the samples ($\rho_{293}/\rho_{4.2}$). The resistivity significantly decreased below 4.2 K for most samples.

dependent, but b_1 appeared to be almost constant. (The magnitude of the $b_1 B$ term was roughly 15% of b_0 at a field of 1 T, but the term linear in B in γ_{yx}^m is relatively much larger than this except at the lowest temperatures where it appears to be similar in magnitude.) Assuming the term $a_2 B^2$ is to be associated with $\lambda_g (\gamma_{yx}^m)^2$ of Eq. (1), then we need to evaluate γ_{yx}^m in order to obtain λ_g . This was done using K3 and it was found that $\gamma_{yx}^m = B(neL_0 T)^{-1}$ at the higher fields to within about 3%, this being well within the estimated errors due to sample dimensions; here n is the number of electrons per unit volume and e the negative electronic charge. At low fields the absolute value of γ_{yx}^m/B increases above that obtained at high fields. The effect is worst at the higher temperatures and amounts to about 10% near 4 K, but by 1.5 K this field variation has practically disappeared. We have ignored such variations and evaluated λ_g using $\lambda_g = a_2 (neL_0 T)^2$. Taking the sol-

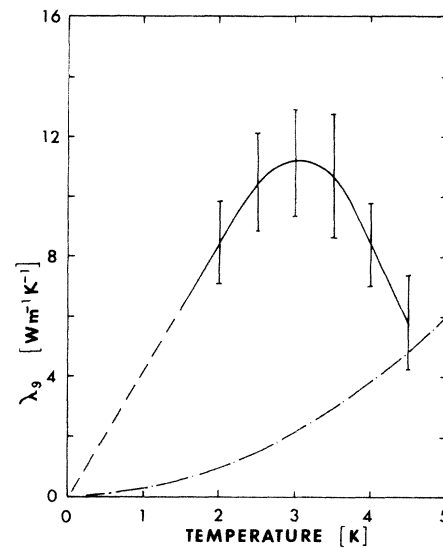


FIG. 3. The solid line shows the λ_g which are calculated using the line through the data of Fig. 2. The error bars show the spread of the data and are equivalent to the error bars of Fig. 2. The dashed line is a tentative extrapolation to $T=0$. The dash-dotted line is that calculated by Ekin (Ref. 5).

id line through the data of Fig. 2 as the variation of a_2 with T , we reproduce the evaluated λ_g in Fig. 3, the error bars in Fig. 3 showing the spread of the data of Fig. 2. The variation of λ_g with T so found is contrary to that expected. Ekin⁵ has calculated λ_g as a function of temperature. His calculation indicates that λ_g should be proportional to T^2 and his result is shown as the dash-dotted line in Fig. 3. There would clearly be interest in extending the experimental data to higher temperatures. Higher fields than 1 T would be required for such work unless λ_g begins to increase rapidly above 4 K. The calculations of Ekin⁵ and the experiments of Fletcher and Friedman² and Newrock and Maxfield⁶ appear to have laid to rest doubts about any grossly unusual behavior of λ_g that have previously been expressed in the literature.^{7,8} However it should be borne in mind that the ratio of λ_g to the electronic thermal conductivity is typically 0.3% in the present work, i.e., the present experiments show a much higher resolution than any previous data. However in view of the unexpected behavior of λ_g it is tempting to speculate that we are really observing some other contribution to the heat current. It will be clear that heat transport by any uncharged excitation can lead to a similar behavior of λ_{xx}^m and presumably spin- and charge-density waves

would be equally effective. It would be of interest to have informed theoretical comment on this suggestion.

To the author's knowledge there is no other mechanism reported in the literature capable of producing a B^2 contribution to γ_{xx}^m . After this work had been submitted for publication, Newrock and Maxfield⁹ published data on γ_{xx}^m for potassium which is similar to that presented here. Being unaware of the effect of λ_g , they examined the available theories and concluded, in agreement with the present opinion, that there appeared to be no other possible explanation of the B^2 contribution.

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A Priori Prediction of the Cohesive Energy of One-Dimensional Metallic Hydrogen*

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Ab initio wave functions and properties have been calculated for 14-, 26-, 38-, 50-, and 62-membered rings of hydrogen atoms. The properties converge rather quickly (with respect to the number of atoms in the ring) to those expected for one-dimensional metallic hydrogen. Electron correlation is explicitly considered by way of extensive configuration interaction. The cohesive energy is predicted to be 1.73 ± 0.2 eV per hydrogen atom.

For more than forty years, the hydrogen molecule has served as a prototype for theoretical studies of the electronic structure of molecules. Since the work of James and Coolidge,¹ who in essence solved the problem *ab initio*, most of the calculations carried out on H_2 have had as their purpose the testing of some particular method for the description of electronic structure. Unfortunately, there has been no comparable prototype for studies of the electronic structure of solids. This problem of course arises from the fact that, prior to the very recent work of Harris and co-workers,^{2,3} there had been no truly *ab initio* calculations carried out on solids. It has been suggested many times⁴ that the most logical prototype for the electronic structure of solids would be a one-dimensional array of hydrogen atoms. It seems clear that accurate *ab initio* calculations on one-dimensional hydrogen would fill the need for a benchmark with which to compare approximate methods for the calculation of energy bands and other electronic properties of solids. In addition it should be pointed out that in

recent years a significant amount of interest⁵⁻⁷ has developed in the properties of the thus-far hypothetical substance, metallic hydrogen.

In the present research we have attempted to treat one-dimensional hydrogen as a large molecule. It is clear⁴ that if one takes a finite chain of hydrogen atoms and increases n in H_n , the behavior of the system will ultimately approach that of one-dimensional hydrogen to within any specified tolerance. However, the very important question of "at what point" does this large molecule take on the properties of an infinite chain has never, to our knowledge, been investigated *ab initio*. In addition to completing self-consistent-field (SCF) calculations on systems as large as H_{62} , we are able to report a detailed calculation taking account of electron correlation for H_{14} .

Our first step was to carry out SCF computations on successively larger rings of hydrogen atoms. The spacings between each adjacent pair of atoms were constrained to be equal. A single $1s$ Slater function, $(\zeta^3/\pi)^{1/2} \exp(-\zeta r)$, where ζ is