# Sample Dependence of the Electron-Electron Contribution to the Electrical Resistivity of Sodium and Potassium

B. Levy, M. Sinvani, and A. J. Greenfield
*Department of Physics, Bar-Ilan University, Ramat-Gan, Israel*

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Measurements of the temperature dependence of the electrical resistivity of sodium and potassium give $\rho=\rho_0+AT^n$, with $n=2.0\pm0.1$ below 2.1 K for sodium and below 1.4 K for potassium, where $\rho_0$ is the residual resistivity. It was found that $A$ is sample dependent, varying linearly with $(\rho_d/\rho_0)^2$, where $\rho_d$ is the contribution to $\rho_0$ arising from electron-dislocation scattering.

The temperature dependence of the electrical resistivity $\rho(T)$ of potassium at low temperatures has been the subject of extensive experimental interest in recent years.[1-4] For sufficiently low temperatures, the standard theory[5] predicts that for the simple metals, $\rho(T)=\rho_0+AT^n$, where $\rho_0$ is the residual resistivity and the second term arises from electron-electron scattering, with $n=2$ and $A$ being a sample-independent constant. However, recent experiments[1,2] for K have cast doubt on these predictions. It was found that $1.5\lesssim n\lesssim 2$ and that $A$ depends strongly on the sample, being roughly proportional to $\rho_0$. In line with these findings,[1,2] a theory[6] has recently been proposed to account for the sample dependence of $A$. Rather than being dependent on $\rho_0$, however, according to this theory $A$ depends on the ratio $\rho_d/\rho_0$, where $\rho_d$ is the contribution to $\rho_0$ arising from electron-dislocation scattering.

In this Letter, we report the results of a series of measurements on two different alkalis, Na and K. The measurement of $\rho(T)$ for Na, reported here for the first time, allows for a very accurate determination of the exponent $n$ because of the large temperature range over which $\rho(T)$ varies as $T^2$. A statistical analysis of the data yields that for both sodium and potassium, $n=2.0\pm0.1$, in complete accord with the standard theory. As for $A$, our results differ from the prediction of the standard theory.[5] We find that $A$ is a linear function of $(\rho_d/\rho_0)^2$, in accord with the recent theory.[6] The dependence of $A$ on $\rho_d/\rho_0$ has been demonstrated with use of an experimental procedure which allows one to vary $\rho_0$ without changing $\rho_d$, thus allowing one to establish the ratio $\rho_d/\rho_0$ for each sample.

The present experimental results were obtained with use of a flux-gate null detector to measure the sample resistance against a standard reference. The double current source (master and slave) is especially designed for long-term stability of better than 1 ppm for currents of about 0.9 A. The sensitivity achieved, one to a few ppm, is limited by both the detector and the current source. The details of the measuring apparatus will be published separately.[7]

The electrical resistivity of a series of samples of Na and K was measured as a function of temperature from 1.1 to 4.2 K. A definite $T^2$ temperature dependence was found below 2.1 K for sodium and below 1.4 K for potassium. The results for a number of these samples are shown in Fig. 1. Above these temperatures, there are deviations from $T^2$ behavior resulting from the onset of a significant contribution to $\rho(T)$ arising from the electron-phonon scattering term $\rho_{\text{el-ph}}(T)$. One expects that the magnitude of $\rho_{\text{el-ph}}(T)$ will scale with temperature as the Debye temperature $\theta_D$. An examination of Fig. 1 shows that, indeed, for both metals and for all samples, the onset of the deviations from $T^2$ behavior occurs for $T\simeq\theta_D/70$.

The data were analyzed by assuming them to be of the form $\rho(T)=\rho_0+AT^n$. A least-squares analysis was developed to determine the best values for $\rho_0$, $A$, and $n$. The error found for $A$ (corresponding to one standard deviation) is about $\pm0.01$ p$\Omega$ cm/deg$^2$ for each of the measured samples. The values of $n$ quoted above correspond to the average value of all the measured samples for each metal and the quoted errors are the rms deviations.

As can be seen from Fig. 1, our samples span a large range of values of $A$, the coefficient of the $T^2$ term. This sample dependence of $A$ is one of the main subjects of this investigation. Particular attention was paid to the contribution of $\rho_d$ to the total residual resistivity $\rho_0$. With use of a special procedure,[7] samples of potassium were successfully prepared having a very low value for both $\rho_d$ and $\rho_0$. This was achieved by carefully casting the sample in a meticulously clean, precoiled polyethylene tube. For our first sample, $\rho_0$ had an initial value of 0.503 n$\Omega$ cm, consisting

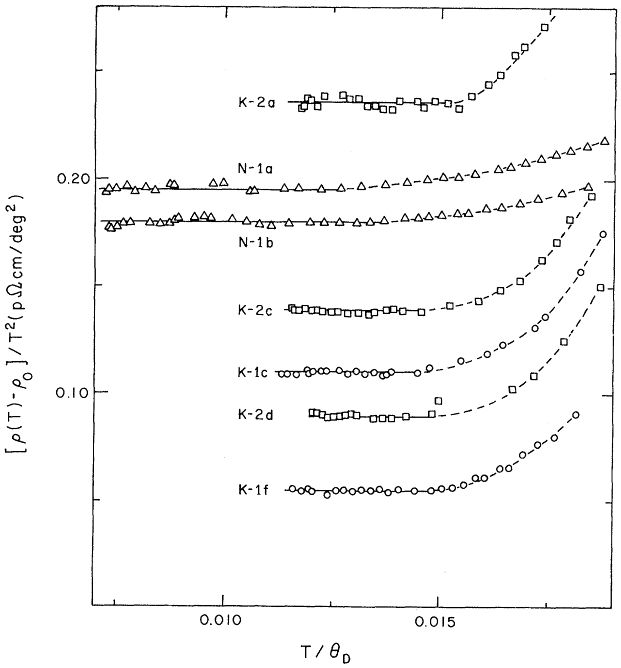

FIG. 1. Plot of $[\rho(T)-\rho_0]/T^2$ vs reduced temperature $T/\theta_D$, where the Debye temperatures are taken to be 160 K for sodium and 100 K for potassium. A horizontal line is drawn through the flat portion of the data to show the value of $A$ obtained for each sample. The dashed lines showing the deviations from $T^2$ behavior is drawn free hand amonst each set of points to guide the eye. The triangles (△), circles (○), and squares (□) give the results, respectively, for the measurements of Na, sample 1 of K, and sample 2 of K.

of about 80% $\rho_d$ and 20% $\rho_i$, where $\rho_i$ is the contribution to $\rho_0$ arising from electron-impurity scattering ($\rho_0=\rho_i+\rho_d$). This was established by a separate experiment.[8] Subsequently, a series of treatments was performed on the same sample and $\rho(T)$ was remeasured after each successive treatment. These treatments were designed to increase only $\rho_i$ while leaving $\rho_d$ unchanged.

The initially cast potassium sample, denoted K-1*a*, was measured as cast after slow cooling to 4.2 K. Samples K-1*b*, K-2*c*, and K-1*d* were obtained by exposing the original, polyethylene-clad sample K-1*a* to contamination at room temperature for the period of time shown in Table I. This treatment increased only $\rho_i$ in each case, since the sample was not mechanically disturbed in any way throughout the process. It should be noted that the first day of annealing in a vacuum (sample K-1*b*) left the value of $\rho_0$ unchanged. This is important evidence that the relatively small density of dislocations produced by our sample preparation method are not readily annealed out. This is in marked contrast to extended wire samples[1,3] for which two days of annealing of the much higher density of dislocations reduces $\rho_0$ by about a factor of 2.

At this point, sample K-1*d* was subjected to a series of further treatments designed to increase sharply the impurity content. Sample K-1*e* was obtained by light cold working of sample K-1*d* sufficient to bring the surface impurities into intimate contact with the purer bulk metal inside. The resulting increase in $\rho_0$ is large and thus any small increase in dislocation density from the cold working is expected to be unimportant compared with the large increase in $\rho_0$ arising from the increase of $\rho_i$. This result was anticipated in view of the previous observation[9] of the quick recovery of potassium from the deformation caused by cold work. As can be seen from Table I, the measured value of $A$ for sample K-1*e* has dropped markedly, which is entirely consistent with the assumption that the increase in $\rho_0$ is due only to the increase in $\rho_i$ but not $\rho_d$.

The final treatment for this sample was to subject K-1*e* to further heavier cold working, followed by annealing which included a 2-h heating period at 50 °C. This process further increased $\rho_i$ substantially because at high temperature, there is an increased solubility and diffusion rate for the impurities mixed into the bulk by the cold work. Moreover, the high-temperature annealing process assures that the final dislocation density is about equal to the original value before the cold working. The sample is now denoted as K-1*f* in Table I. The measured value of $A$ has further decreased, consistent with the expectation that only $\rho_i$ has increased but not $\rho_d$.

In Fig. 2, the solid circles denote the results for sample 1. The measured value of $A$ is seen to be a linear function of $(\rho_d/\rho_0)^2$, as predicted by the recent theory.[6]

Another sample, denoted K-2*a*, was prepared in the same way as K-1*a*, except that K-2*a* was kept at room temperature in an argon atmosphere for a period of four days after casting. This waiting period resulted in an initial value for $\rho_0$ of 0.571 n$\Omega$ cm which is only slightly higher than for K-1*a*. Sample K-2*a* received a series of subsequent treatments, as given in Table I, resulting in the increase by stages in $\rho_0$, with the intermediate stages denoted by K-2*b*, K-2*c*, K-2*d*, and K-2*e*. In order to be absolutely certain that no dislocations were introduced, this sample was not subjected to any mechanical disturbance at

TABLE I. Results of resistivity measurements for two potassium samples and one sodium sample. Each measurement was performed after the treatment indicated alongside the data. Note that the environment invariably included some admixture of air.

| Sample | $\rho_0$ (n$\Omega$ cm) | $\rho_i$ (n$\Omega$ cm) | $(\rho_d/\rho_0)^2$ | $A$ (p$\Omega$ cm/K$^2$) | Treatment (Time) | Treatment (Temp.) | Treatment (Envir.) |
|---|---|---|---|---|---|---|---|
| K-1*a* | 0.503 | 0.103 | 0.63 | 0.292 | Measured as cast | | |
| K-1*b* | 0.509 | 0.109 | 0.62 | 0.285 | 1 d[a] | 25 °C | vac |
| K-1*c* | 0.691 | 0.291 | 0.34 | 0.140 | 38 d | 25 °C | argon |
| K-1*d* | 0.703 | 0.303 | 0.32 | 0.161 | 1 d[a] | 25 °C | He |
| K-1*e* | 1.058 | 0.658 | 0.14 | 0.110 | 2 h[b] | 25 °C | air |
| K-1*f* | 3.64 | 3.24 | 0.01 | 0.055 | 2 h[b] | 50 °C | oil |
| K-2*a* | 0.571 | 0.171 | 0.49 | 0.236 | 4 d | 25 °C | argon |
| K-2*b* | 0.598 | 0.198 | 0.45 | 0.198 | 2 h | 51 °C | oil |
| K-2*c* | 0.736 | 0.336 | 0.30 | 0.139 | 2 d | 50 °C | oil |
| K-2*d* | 1.20 | 0.80 | 0.11 | 0.089 | 10 d | 56 °C | oil |
| K-2*e* | 2.36 | 1.96 | 0.03 | 0.058 | 42 d | 56 °C | oil |
| N-1*a* | 0.916 | 0.34 | 0.40 | 0.195 | 5 d | 25 °C | argon |
| N-1*b* | 0.787 | 0.34 | 0.33 | 0.180 | 14 d | 55 °C | oil |
| N-1*c* | 0.828 | 0.34 | 0.35 | 0.190 | Cycled from 4.2 K | | |

[a] Followed by fast cooling to 4.2 K.

[b] Treatment after cold work.

any stage. The increase of $\rho_0$ by substantial amounts was achieved by heating the sample at elevated temperatures for the period of time indicated in Table I.

The results for $A$ versus $(\rho_d/\rho_0)^2$ for sample 2 are plotted in Fig. 2 as the five solid squares. Thus, one sees that for both sample 1 and sample 2, $A$ increases linearly with increasing $(\rho_d/\rho_0)^2$. Note that we find $A$ *increases* with *decreasing* $\rho_0$, whereas previous experiments[1,2] found that $A$ decreases with decreasing $\rho_0$. The resolution of this seeming contradiction lies in the fact that $\rho_0$ is not the relevant parameter for determining the value of $A$. Rather, $A$ is determined by the ratio of $\rho_d/\rho_0$, as predicted by the recent theory of Kaveh and Wiser.[6]

The previous data of Rowlands, Duvvury, and Woods[1] and van Kempen *et al.*[2] are completely consistent with the present results. In each case, the sample[1,2] was successively annealed for long periods of time with a resultant drop in the value of $A$. Since annealing tends both to decrease $\rho_d$ and to increase $\rho_1$ through oxidation, with each annealing period, there is a decrease in the ratio $\rho_d/\rho_0=(1+\rho_1/\rho_d)^{-1}$. Thus, one expects a decrease in the value of $A$ with each annealing period. This is exactly what was found by both Rowlands, Duvvury, and Woods[1] and van Kempen *et al.*[2].

Measurements of the sample dependence of $A$ have also been carried out for sodium. Because of the much lower reactivity of sodium, it is more difficult to increase $\rho_i$. In fact, for Na, the value of $\rho_0$ decreased with time in going from sample N-1*a* to N-1*b*. Since $\rho_i$ cannot decrease with time, the decrease in $\rho_0$ must be due to a corresponding decrease in $\rho_d$ because of annealing. For our

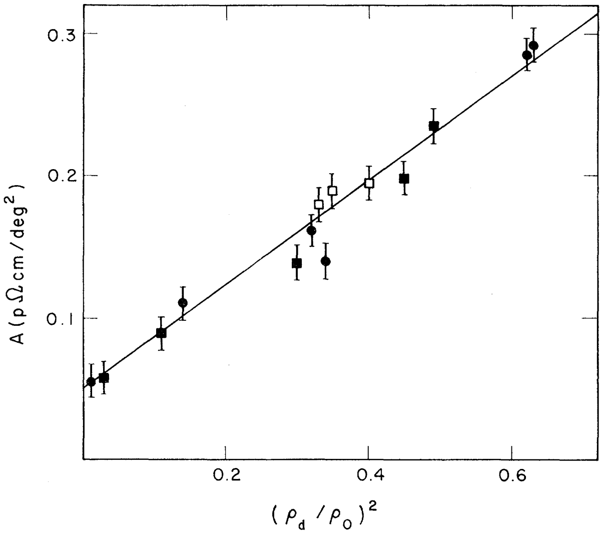

FIG. 2. Plot of $A$ vs $(\rho_d/\rho_0)^2$ for the six treatments of sample K-1 (closed circles) and the five treatments of sample K-2 (closed squares) for potassium, and the three treatments of sample N-1 of sodium (open squares). The straight line is from the theory.

sample preparation technique, the annealing of the cast sodium samples reduced $\rho_d$, whereas the annealing of the cast potassium samples did not. This difference between the two is undoubtedly due to the low-temperature martensitic phase transformation of sodium which produces samples having an unstable array of strains.

To test the effect of the martensitic phase transformation on our results, sample N-1*b* was cycled to room temperature and back. The results for the sample, now denoted as N-1*c*, show a 5% increase in both $\rho_0$ and $A$. This is, of course, due to the increase in $\rho_d$ caused by the additional strain introduced by cycling through the phase transformation, a phenomenon previously observed by Dugdale and Gugan.[10]

With the assumed starting ratio $\rho_d/\rho_0 = 0.36$, samples N-1*b* and N-1*c* (open squares) are seen to follow the same general behavior as K. This is in accordance with the expectation that electron-electron scattering should be quite similar for both Na and K.

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[8] In a separate experiment, with use of a technique which produces virtually strain-free samples, a potassium sample taken from the same stock of starting material was prepared having $\rho_0 = 0.1$ nΩ cm. This value for $\rho_0$ remained constant to within 3% upon thermal cycling of the sample including warming, further annealing, and recooling. Therefore, the value for $\rho_i$ in both samples taken from this stock cannot be much larger than about 0.1 nΩ cm unless the preparatory process introduces additional impurities. Our technique for sample preparation is not expected to introduce significant amounts of further impurities. Since the present results are not very sensitive to the precise value of $\rho_i$, it was sufficient to prepare only a single such virtually strain-free sample. A detailed description of the preparation of our samples will be published separately (see Ref. 7).

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# Anomalous Conduction-Electron Polarization in Superconducting $YRh_4B_4$

P. K. Tse, A. T. Aldred, and F. Y. Fradin
*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439*

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NMR and magnetization measurements in $Y_{1-x}Er_xRh_4B_4$ indicate a strong conduction-electron–local-moment interaction with only a weak depression of the superconducting transition temperature $T_c$. The appearance of large hyperfine interactions below $T_c$ indicates that a grossly uncompensated conduction-electron spin state exists in the superconducting phase of $YRh_4B_4$. These results are discussed in terms of both itinerant electron antiferromagnetism and non-*s*-wave Cooper pairing.

Since the discovery of re-entrant superconductivity in the ternary compound $ErRh_4B_4$ by Fertig *et al.*,[1] there have been extensive studies of superconductivity and magnetic order in this class of rhodium-boride compounds containing a rare earth with a localized moment. One of the surprising features of this phase is the weak depression of $T_c$ in the presence of localized magnetic moments, even though there is no obvious crystallographic isolation of the rare-earth ion from the transition metal atoms as there is in the Chevrel-phase ternary superconducting compounds.[2] In the present investigation $^{11}$B NMR and static magnetization results are reported for the normal and superconducting states of $Y_{1-x}Er_xRh_4B_4$ ($x \leq 0.1$). These results show, for the first time, that the conduction electrons in $YRh_4B_4$ strongly couple to the local moments, yet there is an ex-