Electronic transport properties of thin potassium wires below 1 K. II. Thermoelectric ratio G

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Measurements are reported of the thermoelectric ratio G for thin K wires with diameters as small as 0.06 mm at temperatures from 4 K down to 0.1 K. The phonon-drag component of G becomes less negative as the wires become thinner, whereas the electron-diffusion component becomes more negative. The low-temperature limits of G for almost all of the samples are consistent, to within an experimental uncertainty of 0.2 V^{-1}, with values of $G_0^s = -0.6$ V^{-1} and $G_0^i = 0$ V^{-1}. G_0^s is the surface contribution to the low-temperature limit of the electron-diffusion component of G, and G_0^i is the impurity contribution. The surface contribution is compatible with completely diffuse surface scattering. The phonon-drag component of G varies at low temperatures approximately as T^2 and ρ_0^{-1}.

I. INTRODUCTION

In the process of studying the low-temperature electrical resistivity $\rho(T)$ of thin potassium (K) wires,[1,2] we also measured the thermoelectric ratio G of these same wires. In this paper we describe the results we obtained, which shed additional light upon the behavior of thin K wires. As we discuss below, G provides information complementary to that obtained from $\rho(T)$.

We know of only one prior set of studies of the low-temperature thermoelectric properties of thin K wires, the pioneering measurements by MacDonald and co-workers. MacDonald, Pearson, and Templeton[3] measured the thermopower S of K wires with diameters ranging from $d = 0.8$ to 0.07 mm. These samples were not made from the same stock, and they found no systematic variation of properties of S with d. We will summarize their results below.

This paper is organized as follows. In Sec. II we review the results obtained by MacDonald et al. on the low-temperature thermoelectric properties of high-purity K and describe the expected behavior for G. In Sec. III we present and analyze our data. Section IV contains a summary and conclusions.

II. REVIEW OF PREVIOUS WORK AND BACKGROUND INFORMATION

MacDonald et al.[3] fit their thermopower data for high-purity K below about 3 K to the equation

$$S = AT + BT^3 + C \exp(-\Theta/T) . \tag{1}$$

The form of this equation was based upon the predicted behavior for a simple, free-electron metal with a spherical Fermi surface that does not contact the Brillouin-zone boundary.[4] The first term was attributed to the electron-diffusion component of S, the second term to the normal portion of the phonon-drag component, and the third term to the umklapp portion of the phonon-drag component. They found values of $A = (+0.5$ to

$-1.0) \times 10^{-8}$ V/K^2 and $B = (-0.15$ to $-0.30) \times 10^{-8}$ V/K^4 for samples with $\mathcal{R}$'s ranging from 4000 to 10 000 and $0.07 \leq d \leq 0.8$ mm. Above about 1.5 K, both the second and third terms in Eq. (1) are significant, and they combine to produce a minimum in G at ~ 3.3 K. Below 1 K, where we will examine our data quantitatively, the third term in Eq. (1) is completely negligible.

The thermoelectric ratio G is related to S by the equation

$$G = S/LT \tag{2}$$

where L is the Lorenz ratio.[4] Experimentally we have found[5] that L is equal to L_0 (the Sommerfeld value of the Lorenz ratio, 2.44×10^{-8} V^2/K^2), only at temperatures below 1 K. For quantitative analysis of G we thus concentrate upon $T \leq 1$ K.

From Eqs. (1) and (2) we expect G to have the low-temperature form[4]

$$G = G_0 + DT^2 , \tag{3}$$

where $G_0 = A/L_0$ and $D = B/L_0$. The data of MacDonald et al. described above gave $G_0 \approx +0.2$ to -0.4 V^{-1} and $D = -0.06$ to -0.12 $V^{-1}K^{-2}$.

If two different scatterers are present, e.g., impurities (i) and the sample surface (s), then from the Gorter-Nordheim equation[4] we expect the value of G_0 to be

$$G_0 = (\rho_i/\rho_0)G_0^i + (\rho_s/\rho_0)G_0^s . \tag{4a}$$

Here G_0^i and ρ_i are, respectively, the bulk thermoelectric ratio and resistivity due to residual impurities, G_0^s and ρ_s are the thermoelectric ratio and resistivity due to surface scattering, and $\rho_0 = \rho_i + \rho_s$. We can eliminate the variable ρ_s from Eq. (4a) and rewrite it as

$$G_0 = G_0^s + (\rho_i/\rho_0)(G_0^i - G_0^s) . \tag{4b}$$

Since G_0^s, G_0^i, and ρ_i are assumed constant for a set of thin samples from a given batch of K, a plot of G_0 versus $1/\rho_0$ should yield a straight line with intercept G_0^s and

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slope $\rho_i(G_0^i - G_0^s)$.

Equations (3) and (4b) will form the basis for analysis of our experimental data. Although Eq. (3) was initially derived from a simple model involving a free-electron diffusion term plus phonon drag, we now know that its form is also appropriate to more modern analyses of low-temperature thermopower involving many-body contributions such as the Nielsen-Taylor effects[4,6] and electron-phonon mass enhancement.[4,7] Nielsen and Taylor showed that a many-body contribution which they labeled "virtual recoil" provided a qualitative understanding of the impurity thermopowers produced by Na, Rb, and Cs impurities in K. Another contribution which they labeled "phony-phonon-drag," produced a diffusion thermopower in pure metals that mimicked the temperature dependence of phonon drag. These effects complicate the analysis of experimental data, especially in a case such as ours where the total residual impurity content is small and its detailed composition is not known. We thus concentrate upon presenting our experimental results, deriving values of the quantities in Eq. (4b), and showing that the contribution of surface scattering to the thermopower is what would be expected if such scattering is completely diffuse. We continue to refer to the two terms in Eq. (3) as electron-diffusion and phonon-drag components, although the second term in Eq. (3) may contain a contribution from "phony-phonon-drag."

For a metal with an essentially spherical Fermi surface, like K, one should be able to write the low-temperature diffusion term in the thermoelectric ratio to good approximation as[4]

$$G = (e/E_F)\{[d \ln(nv)/d \ln E] - (d \ln l /d \ln E)\}_{E=E_F} \cdot$$

(5a)

Here e is the electronic charge, n the electronic density of states, v the Fermi velocity, l the electron mean free path, and the logarithmic derivatives are to be evaluated at the Fermi energy E_F. If the nv term is evaluated for a free-electron model, we obtain

$$G = -0.5(1 + d \ln l /d \ln E)_{E_F} \ V^{-1} .$$

(5b)

We will use Eqs. (4b) and (5b) to find values of $d \ln l /d \ln E$ for both residual impurities in our samples and the sample surface.

Equation (1) of Ref. 1 and Eq. (4) of the present paper demonstrate both the complementary nature of ρ and G, and an important fundamental difference between them. Equation (1) of Ref. 1 shows that the contributions to ρ from two different sources of scattering are additive. For each scatterer, ρ increases linearly with the concentration of that scatterer, until the two concentrations become so large that the individual scatterers interact. In contrast, we see from Eq. (4) above that, when one scatterer is strongly dominant, the value of G becomes independent of the concentration of both that scatterer and any minority scatterer.

III. EXPERIMENTAL DATA

We have measured G on a variety of samples, as described in Ref. 1. Following Ref. 1, we categorize the samples as follows. Three sets were prepared and cooled in He gas; these sets are designated as K(7300), K(4800), and K(1700), where the numbers refer to the measured residual resistance ratios $[\mathscr{R} = R(295 \text{ K})/R(0 \text{ K})]$ of bulk samples from each set. The fourth set contains samples of material from K(7300), but which were either prepared and cooled in Ar gas, or prepared in He and cooled in vacuum. They will be designated by the symbols Ar or V, respectively.

Figure 1 shows the G values for the K(7300) samples. The values of $d\rho/dT$ for these samples are given in Fig. 1 of Ref. 1. If we examine first the data for the thickest— $d = 1.5$ mm—samples (crosses), we find a relatively large, negative phonon-drag minimum with a magnitude > 3 V^{-1} at its lowest point at about 3.3 K. Below 3.3 K, the data rise smoothly to a low-temperature limiting value which is close to zero and usually slightly negative. As the samples become thinner, G changes systematically; the phonon-drag minimum becomes shallower, and the low-temperature limit G_0 becomes more negative.

According to the standard picture of phonon drag in K, the phonon-drag minimum at ~ 3.3 K involves a competition between a negative "normal" component and a positive "umklapp" component.[4] In this picture, the fact that the phonon-drag minimum becomes shallower with decreasing wire thickness and concurrent increase in ρ_0 indicates that the additional surface scattering in the thinner wires reduces either the normal component alone, or both the normal and umklapp components together. As we noted above, many-body contributions to the temperature-dependent portion of the thermopower may complicate this interpretation.

The shift toward more negative values of G_0 with decreasing sample thickness indicates (a) that the dominant scatterer in the samples is changing from impurity scattering to surface scattering (possibly including effects of surface corrosion) as the sample thickness decreases
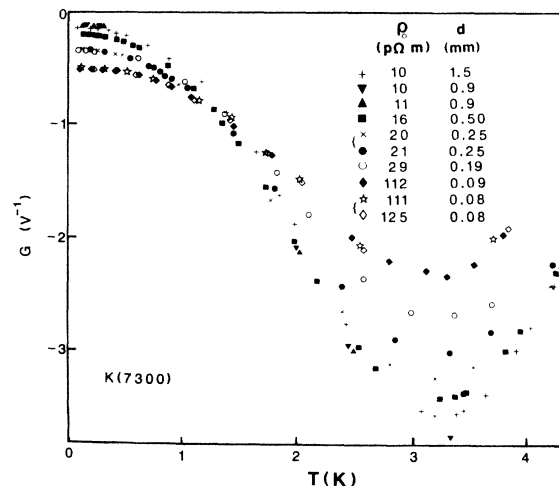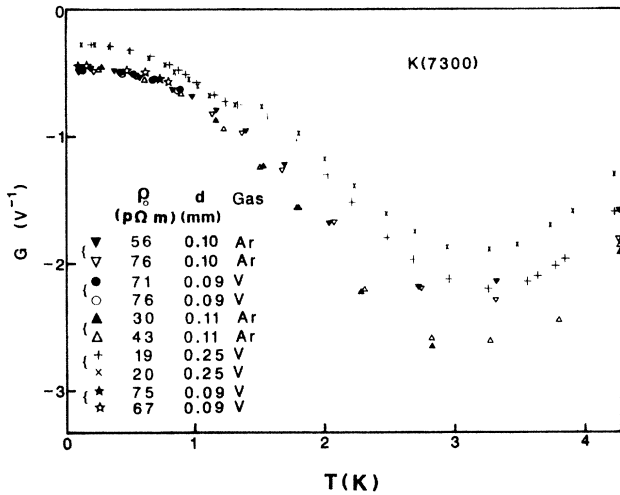

FIG. 1. G vs T for He-cooled K(7300).

FIG. 2. G vs T for Ar- and vacuum-cooled K. For the vacuum-cooled samples, about 10 μm Hg of residual He gas was left in the sample can at room temperature to ensure that the samples would cool properly. This gas affected the G data above 1 K, which is thus not as reliable as the remainder of the data in this paper.

and (b) that surface scattering produces a negative contribution to G_0.

Similar behavior is shown in Fig. 2—Ar and vacuum, cooled, Fig. 3—K(1700), and Fig. 4—K(4800). The behaviors of $d\rho/dT$ for these same samples are shown in Figs. 2, 5, and 6, respectively, in Ref. 1. Comparison of Fig. 2 in the current paper with Figs. 1, 3, and 4, shows that the general behavior of G for samples prepared or cooled in Ar and vacuum differs little from that for samples of the same diameter and purity prepared and cooled in He.

To determine G_0^s and G_0^i as defined in Eq. (4), we plot G_0 versus $1/\rho_0$ in Fig. 5. Aside from three data points,[8] the data for the four sets of K fall on three straight lines, with most of the Ar and vacuum data falling on the same line as the He data from the K(7300) batch of K. As ex-
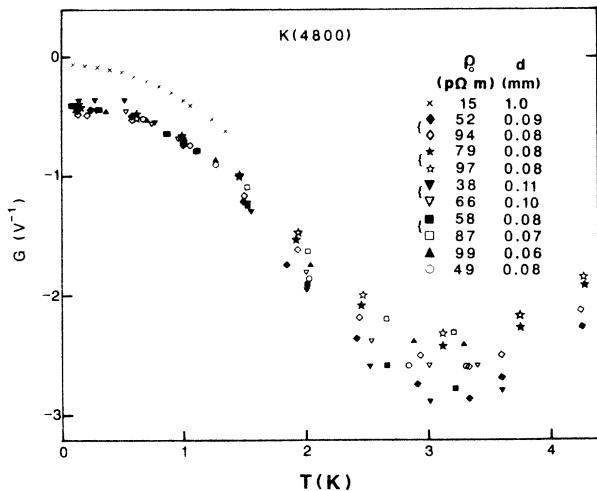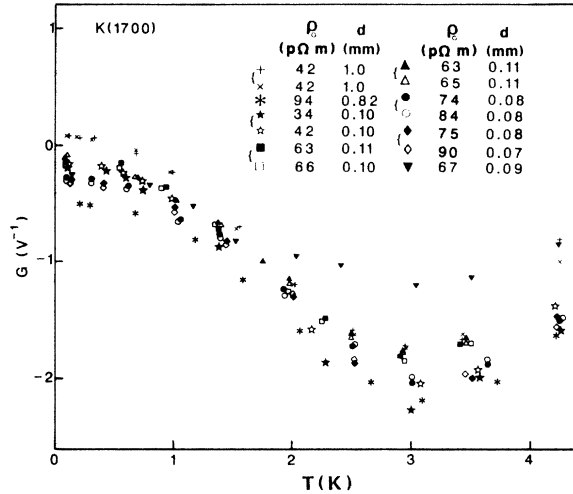

FIG. 4. G vs T for He-cooled K(1700).

pected from Eq. (4), the slopes of these lines are in proportion to the values of ρ_i for the different sample sets. Within experimental uncertainties, the data for the K(7300) and K(4800) samples determine the same values of G_0^s and G_0^i, namely $G_0^s \approx -0.55 \pm 0.1$ V^{-1} and $G_0^i \approx -0.1 \pm 0.1$ V^{-1}. The data for the K(1700) samples determine the slightly different values $G_0^s = -0.65 \pm 0.1$ V^{-1} and $G_0^i = +0.1 \pm 0.1$ V^{-1}. Within their mutual uncertainties, both sets of data are consistent with the common values $G_0^s = -0.6 \pm 0.2$ V^{-1} and $G_0^i = 0 \pm 0.2$ V^{-1}, which we take as our best estimates for G_0^s and G_0^i. We note that this value of G_0^i falls within the range of the values estimated from the data of MacDonald et al.[3]

If we insert these estimates for G_0^i and G_0^s into Eq. 5(b), we find that
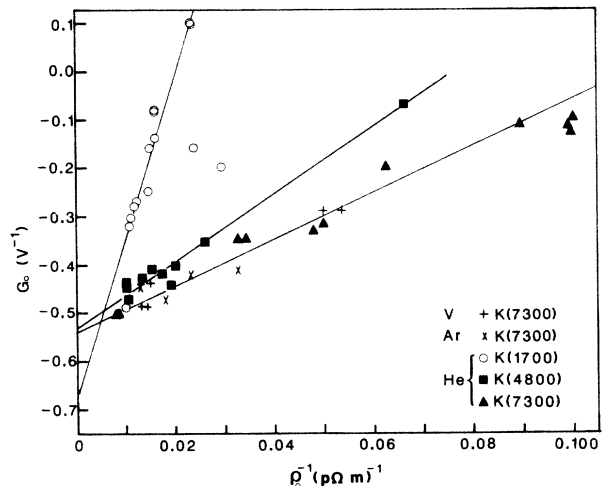
$$(d \ln l^i / d \ln E)_{E_F} = -1 \pm 0.3 \tag{6a}$$
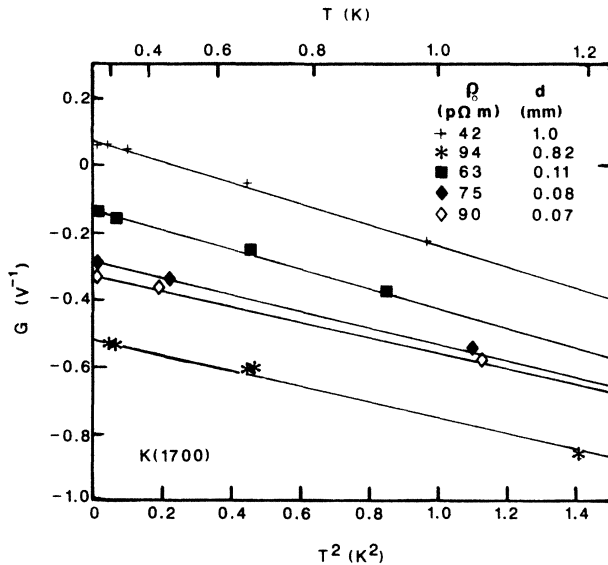
and

FIG. 3. G vs T for He-cooled K(4800).

FIG. 5. G_0 vs $1/\rho_0$ for the data of Figs. 1–4.

FIG. 6. Test of $G(T) = G_0 + DT^2$ below 1 K for selected data from Fig. 4.

FIG. 7. The T^2 coefficient D from Fig. 6, vs ρ_0^{-1}, for the data of Figs. 1–4.

$$(d \ln l^s / d \ln E)_{E_F} = +0.2 \pm 0.3 \ . \tag{6b}$$

Here l^i and l^s are the electron mean free paths for scattering from impurities and the sample surface, respectively.

The sign of the impurity term [Eq. 6(a)] is opposite to that expected for simple elastic scattering of electrons by impurities.[4] This sign discrepancy argues for the presence of the many-body contributions of Nielsen and Taylor.[6]

To within experimental uncertainty, the surface term [Eq. 6(b)] is consistent with the value zero. This is exactly what would be expected for completely diffuse surface scattering, in which an electron hitting the sample surface is scattered into a random direction independent of its incoming energy.

According to Eq. (3), we expect $G(T)$ to vary as T^2 for temperatures below the phonon-drag peak. This expectation is valid, to within experimental uncertainties, as illustrated in Fig. 6 with a subset of samples chosen to have minimal overlap of data. We have checked how the coefficient D varies with various parameters such as residual resistivity ρ_0, nominal sample diameter d, etc. The best systematic variation was found to be with ρ_0^{-1}, as shown in Fig. 7.
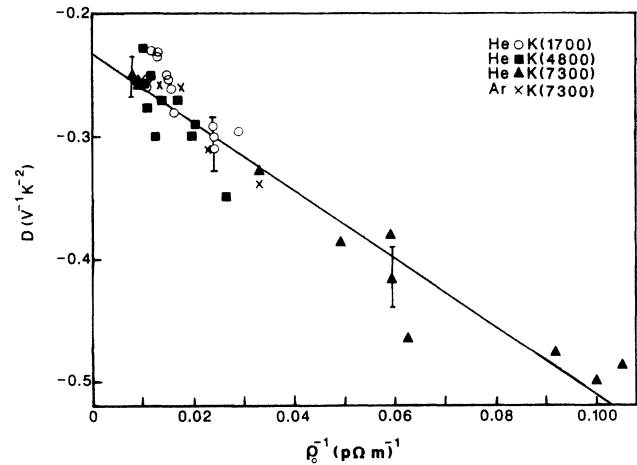
IV. SUMMARY AND CONCLUSIONS

From the foregoing data and analysis, we are able to draw the following conclusions. (1) The general form of G remains the same as samples are thinned, but the phonon-drag minimum generally becomes less negative and the low-temperature electron-diffusion limiting value G_0 becomes more negative. (2) The data for all four sets of samples are consistent with the Gorter-Nordheim rule, and mostly fall on the three different straight lines, one for each bulk sample purity. These lines determine values of G_0^i and G_0^s which are the same for the K(4800) and K(7300) samples, but slightly different for the K(1700) samples. To within an experimental uncertainty of ± 0.2 V^{-1}, the data for all four sample sets are consistent with the values $G_0^s \approx -0.6 \pm 0.2$ V^{-1} and $G_0^i \approx 0 \pm 0.2$ V^{-1}. This value for the surface term is compatible with completely diffuse surface scattering. (3) Below 1 K, G varies approximately as DT^2, as expected from Eq. (3), and the coefficient D varies approximately as ρ_0^{-1}.

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