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Electronic transport properties of thin potassium wires below 1 K.
I. Derivative of electrical resistivity, $d\rho/dT$

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Previous measurements below 1 K of the temperature-dependent resistivities of thin potassium wires prepared and cooled in He gas have been extended to samples of different lengths and different bulk purities. The new data all show "size-effect anomalies" similar in temperature dependence to those previously reported. The anomalies appear to be affected by surface corrosion, the complete effect and role of which is not yet clear. The anomalies do not generally depend upon sample length, and for a given size of the anomaly the temperature dependence is independent of all parameters studied, including sample length, bulk purity, and the atmosphere in which the sample is prepared and/or cooled. The variation of the anomaly with sample diameter d is different for the old data and the new; the old data varied approximately as $d^{1/2}$, while the new vary as a power between d and d^2. The anomalies for wires of different bulk purity are of similar size only for the thinnest wires studied. The data do not appear to be explained by the Gurzhi effect, or by current theories of interference between electron-electron scattering and surface scattering, reduction in surface scattering due to electron-phonon scattering, localization effects combined with charge-density waves (CDW), or simple CDW behavior. Some additional experiments which might clarify the situation are proposed.

I. INTRODUCTION

We recently published[1] measurements of the temperature-dependent electrical resistivities $\rho(T)$ below 1 K of thin, high-purity potassium (K) wires prepared and cooled to low temperatures in the presence of He gas. As shown in Fig. 1, wires thinner than diameter $d \approx 1$ mm showed anomalous deviations from the simple T^2 variation expected for electron-electron scattering. Wires thinner than the elastic bulk mean free path for impurity scattering ($l \approx 0.2$ mm) displayed negative values of $d\rho/dT$, the temperature derivative of the resistivity. When Rb was added to the K to reduce l to ~ 0.02 mm, a $d = 0.25$ mm wire of the dilute alloy showed a much smaller anomaly, as we discuss below. We concluded that we were seeing a size effect, and tentatively attributed the anomalous behavior to the Gurzhi effect,[2] a reduction in electron-surface scattering due to normal electron-electron scattering. It was noted[1] that wires prepared and cooled in Ar gas, or prepared in He but cooled in vacuum, displayed anomalies having the same form as those prepared and cooled in He, but with magnitudes generally representative of thicker wires and with more variation from wire to wire of a given thickness. This somewhat different behavior, illustrated in Fig. 2, was rationalized[3] as being due to the different atmospheres. Indeed, part of the stimulus for the investigation in Ref. 1 of the behavior of thin K wires cooled in He gas was the apparent contradiction between observations by Rowlands *et al.*[4] of anomalous behavior in $d = 0.8$ mm K wires cooled in He, and those by Lee *et al.* of little or no such anomalies in $d = 0.9$ mm K wires cooled in Ar.[5]

The measurements of Ref. 1 stimulated proposals of three alternative models for the anomalous behavior: (1) localization effects;[6] (2) reduction in electron-surface scattering due to electron-phonon scattering;[7] and (3) interference between electron-surface scattering and electron-electron scattering.[8] The authors of these models, as well those of a more recent paper,[9] all challenged the applicability of the Gurzhi effect to the data of Ref. 1.

Of particular interest was the localization model,[6] which predicted that when $d\rho/dT < 0$, the anomalous behavior should be proportional to L^2, the square of the length of the wire, provided that a parameter ν, defined as the number of distinct conduction channels in the thin wire, is constant. This model stimulated us to make new measurements on thin wires with diameter $d \leq 0.1$ mm, but with different lengths. The new samples had bulk resistance ratios $\mathcal{R} = R(295\text{ K})/R(0\text{ K})$ which differed from that for the old samples. We were thus able to investigate the effects of different bulk electron mean free paths on the behavior of thin K wires. This paper is a report of the results of our measurements. In addition to our measurements of $d\rho/dT$, we also routinely measured the thermoelectric ratio G of our samples, which provides information that complements $d\rho/dT$. The behavior of G is generally compatible with the patterns described in the current paper. Details of the behavior of G are given in the following paper.[10]

This paper is organized as follows. In Sec. II we briefly review the various models proposed to explain the original size-effect data on $d\rho/dT$. In Sec. III we discuss experimental details, focusing upon sample characterization and modifications of previous procedures. In Sec. IV we present our data and some data analysis. Section V contains a summary of the most important features of the data and a more detailed analysis, as well as comparisons with various theories. Section VI contains our conclusions.

II. THEORETICAL BACKGROUND

For a simple nearly-free-electron metal such as K [neglecting, for the moment, the possibility of a charge-density-wave (CDW) ground state[11]], we would expect[1] the very-low-temperature electrical resistivity of a thick sample to have the form

$$\rho=\rho_i+\rho(T)=\rho_i+AT^2+B\rho_iT^2+\rho_{e-\mathrm{ph}} . \tag{1}$$

Here ρ_i is the temperature-independent residual resistivity due to impurities in the sample and $\rho(T)$ is composed of an electron-electron component AT^2, an inelastic electron-impurity component $B\rho_iT^2$, and an electron-phonon component $\rho_{e\text{-ph}}$ that drops off exponentially with decreasing temperature.[12] In bulk K, $\rho_{e\text{-ph}}$ is negligibly small below about 1 K.

We can eliminate the unknown constant term ρ_i by measuring $d\rho/dT$, the temperature derivative of ρ. If we neglect $\rho_{e\text{-ph}}$, then from Eq. (1) we expect $d\rho/dT$ to have the form

$$d\rho/dT=2(A+B\rho_i)T , \tag{2}$$

so that a plot of $d\rho/dT$ versus T should yield a straight line passing through the origin. Indeed, as illustrated by the + symbols in Fig. 1, Eq. (2) is closely obeyed for bulk samples of high-purity K. However, for thin wires we find large deviations from this equation. It is these deviations which we call the "anomaly."

The model originally proposed to explain the data in Fig. 1 is the Gurzhi effect.[2] In this effect, normal electron-electron scattering (NEES) (which, by itself, cannot contribute to the electrical resistivity in a metal with

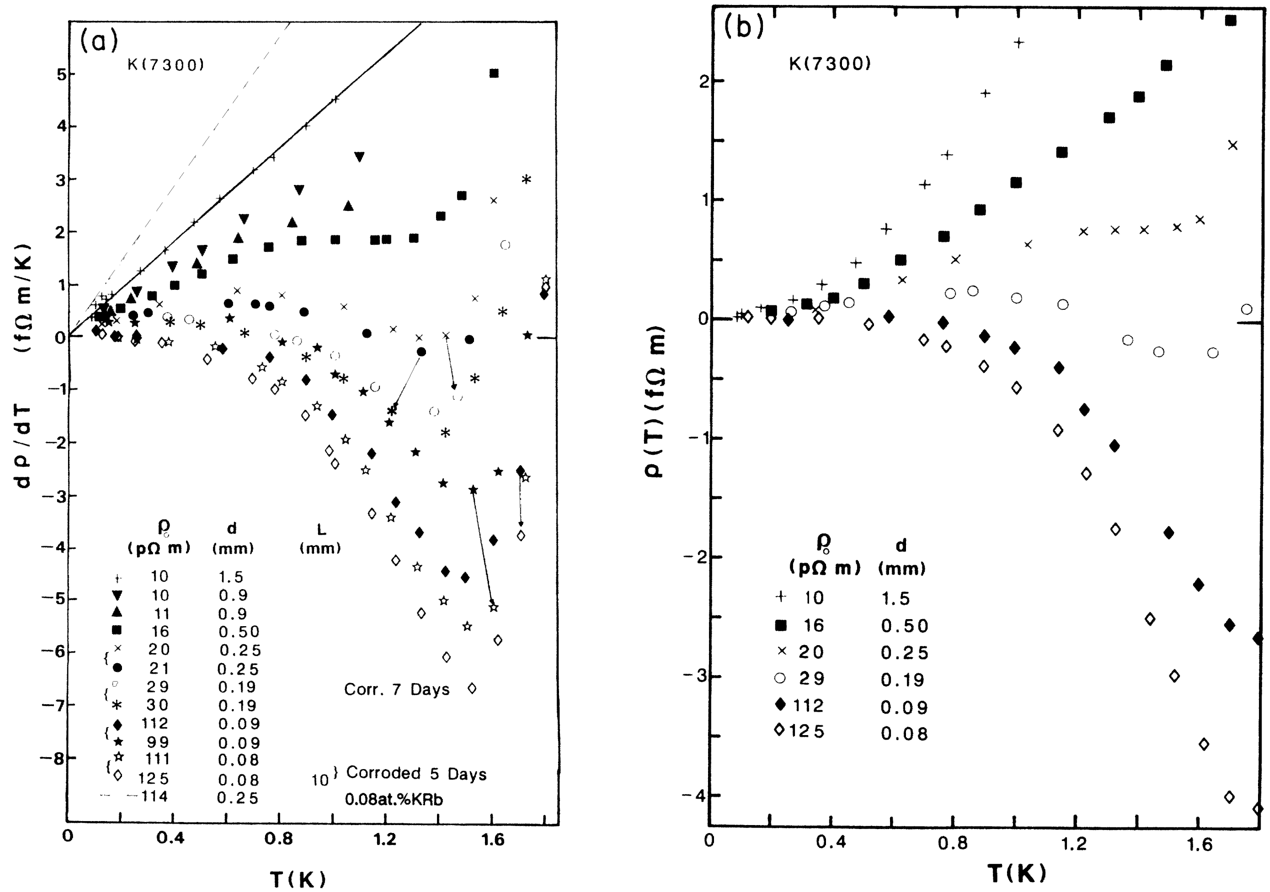

FIG. 1. (a) $d\rho/dT$ vs T for the K(7300) samples, which were prepared and cooled in a He atmosphere. This figure is taken from Ref. 1, but the data have been renormalized as described in the text, a few plotting errors have been corrected, some of the nominal sample diameters have been revised as described in the text, and some additional samples from Ref. 3 have been added. Two nearly identical samples were always prepared and measured together; for the samples in this figure, the data for both wires in a pair were always fairly close. For simplicity, we omit the pairs of the thicker samples; paired samples are indicated by brackets. Two pairs of samples were annealed at room temperature to thin them further after their initial measurements; the arrows indicate the changes which occurred due to these annealings. (b) $\rho(T)$ vs T for selected data from (a); the data of (a) were integrated by hand. Note that the integrated data have qualitatively similar form to the data of (a).

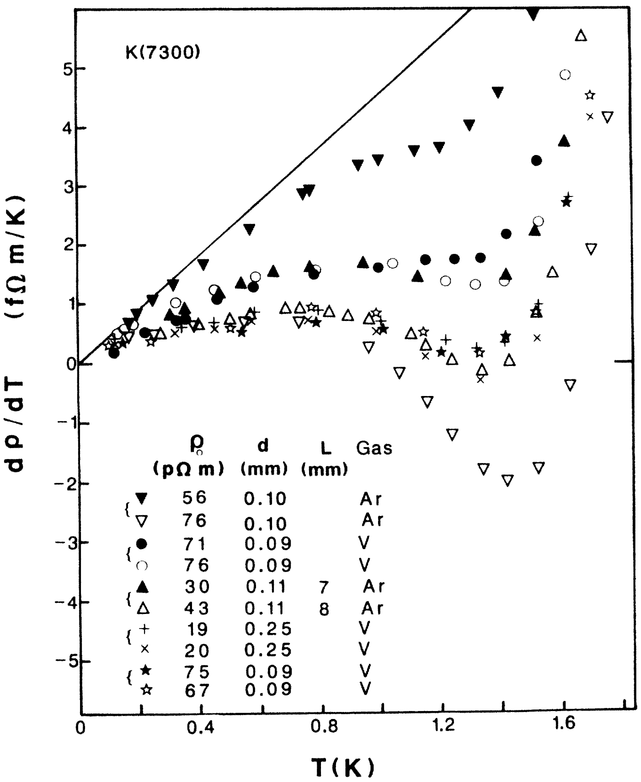

FIG. 2. $d\rho/dT$ vs T for thin K(7300) wires cooled in an Ar atmosphere or in partial vacuum. This figure is taken from Ref. 3, but the data have been renormalized as described in the text. The straight line indicating bulk behavior is the same line as in Fig. 1. The samples connected by brackets were prepared and measured together.

a spherical Fermi surface and isotropic scattering) reduces the probability that a typical electron will reach the sample surface where it is diffusely scattered, compared to this probability in the absence of NEES. In Ref. 1, we noted that our data were not in the regime where the Gurzhi effect predominates, but we suggested that the effect might persist down to where our data lay. Subsequent theoretical work, both numerical[9] and analytical,[13] has shown that this suggestion is incorrect.

The next model, proposed by DeGennaro and Rettori,[8] involved an interference between NEES and surface scattering. This model predicted an anomaly in $\rho(T)$ that was proportional to T^2, and that passed through a maximum value as a function of l/d at $l/d \approx 1$. The anomaly was a complex function of l/d, the form of which had to be determined numerically for the range of values of l/d of interest. The predicted T^2 temperature dependence disagreed with the data of Fig. 1. In addition, recent theoretical analysis[9] calls into question the validity of this model.

Kaveh and Wiser[7] proposed an alternative explanation for the anomaly in terms of a reduction in the effectiveness of electron-surface scattering due to electron-phonon scattering. This model predicted the form

$$\rho_{\mathrm{anom}}(T) \propto -3(\rho_0^2/\rho_s\rho_i)(2l/d)T^5 \ , \tag{3}$$

where ρ_s is the residual resistivity due to surface scattering, and $\rho_0 = \rho_i + \rho_s$ is the total residual resistivity of the wire. In the "thin wire" limit we expect $\rho_s \propto \rho_i(l/d)$, and this model predicts $\rho_{\mathrm{anom}} \propto (1+l/d)^2$, provided that no contaminants are introduced into the sample during thinning. The predicted temperature dependence of T^5 was much too rapid to explain the data of Fig. 1.

Finally, Farrell *et al.*[6] proposed that the data of Ref. 1 were due to a combination of charge-density-wave effects for thicker wires,[14] plus localization effects for sufficiently thin, high-purity wires. The CDW model was used to describe the data when $d\rho/dT > 0$, and the localization effects were assumed to take over for $d\rho/dT < 0$. This model predicted that localization would predominate for $l/d > 1$, provided that certain other conditions were also satisfied. The model also predicted a variation of $d\rho/dT$ with L^2 in the localization regime, provided that the number of parallel conducting channels remained constant. Our new data allow us to investigate whether two different phenomena are present, but we were not able to obtain enough data on samples with different lengths *and negative values of* $d\rho/dT$ to convincingly test for an L^2 variation of the anomaly under the conditions predicted.

III. SAMPLE CHARACTERIZATION AND EXPERIMENTAL PROCEDURE

A. Samples and sample preparation

The samples were prepared from high-purity (99.95%) K purchased from the Mine Safety Appliances (MSA) Division of Gallard Schlesinger Corp. The K was supplied in 5- or 20-g glass ampoules filled with argon gas. Different batches of K from MSA contain different amounts of trace impurities, as shown by the different impurity tables supplied by the manufacturer. For example, the Na content of the K studied in Ref. 1 and the purer K in the present study were both listed as containing 15 ppm Na, while the less pure K in the present study was listed as 48 ppm Na. The typical bulk $\mathcal{R} = R(295\ \mathrm{K})/R(0\ \mathrm{K})$ (or bulk residual resistivities ρ_i) for the three different batches of K were also different. To account for these differences, we compare the data for thin samples against data for thick ("bulk") samples prepared from the same batch. This procedure is not perfect, since thick samples prepared from different ampoules can show different values of ρ_i, as can, in some cases, even samples prepared from the same ampoule. Variations from within a single ampoule are normally only 10–20% (see Table 3.1 in Ref. 3), but variations between ampoules can be much larger. These variations can produce significant scatter in the inferred thin sample behavior.

The samples in Ref. 1 were made from material taken from several different 5-g ampoules purchased at the same time. The data of Ref. 3 show that the bulk $\mathcal{R}$ varied somewhat from ampoule to ampoule. Based upon all of the available data, we assume a bulk $\mathcal{R} = 7300$ for both the samples prepared in He and those prepared in Ar. The samples used in the current study were made from two different sets of K. The first set of new samples was fabricated from a single 20-g ampoule. The data from this set are shown below in Fig. 6. Measurements on one thick sample from this ampoule gave $\mathcal{R}=4800$, which we take as the bulk $\mathcal{R}$. The second set of new samples was fabricated from several 5-g ampoules purchased together at a later time. The data from this set are shown in Fig. 5 below. From measurements on two different samples which were in close agreement, the bulk $\mathcal{R}$ for the set is taken as $\mathcal{R}=1700$. We show in Ref. 10 that the behavior of G supports this division of our samples into batches having three different bulk purities. For simplicity, we refer to samples as being from batches labeled by K(7300), K(4800), and K(1700).

From Eq. (2), we would expect the T^2 coefficient of $\rho(T)$ for bulk samples to vary linearly with ρ_i (i.e., inversely with $\mathcal{R}$). Such behavior is illustrated in Fig. 3 for samples prepared in both He and Ar. Note especially the substantial variations in ρ_i (and the associated values of $A+B\rho_i$) for the samples of K(7300) from different ampoules. The solid symbols in Fig. 3 indicate the values of $A+B\rho_i$ used as the reference "bulk" behavior in Figs. 1, 2, 5, and 6.

The sample wires were extruded at room temperature from stainless-steel presses through stainless-steel dies. As in Ref. 1, two wires were extruded and mounted together in a sample can inside a He filled glove box. The sample can was sealed with an In O-ring and transferred to a dilution refrigerator, with which the samples were cooled. When the sample can was filled with He gas at atmospheric pressure, molecular sieve was used to absorb the residual He gas in the can at low temperatures. In the current measurements, the sieve was freshly baked in vacuum at 300 °C for each sample pair, except in one case noted below. To better clean the sieve, this temperature was 100 °C higher than that used in Ref. 1.

Although the surfaces of the samples were still shiny when the sample can was sealed, by the time the thin samples had been measured and brought back up to room temperature their surfaces were normally covered with a thin film of white material. To check whether this white material was essential to the anomalous behavior, for the last few thin samples studied we further cleaned the atmosphere in the sample can by wrapping a thin copper foil freshly coated with K around the inside surface of the can. This foil was inserted into the can along with the freshly baked sieve and the can was initially sealed a day before the samples were extruded and mounted. The large area of fresh K cleaned the He atmosphere in the sample can both before and after the samples were mounted. For the first time, this procedure yielded surfaces of thin wires ($d \leq 0.1$ mm) that were still shiny when the samples were warmed back to room temperature after being measured.

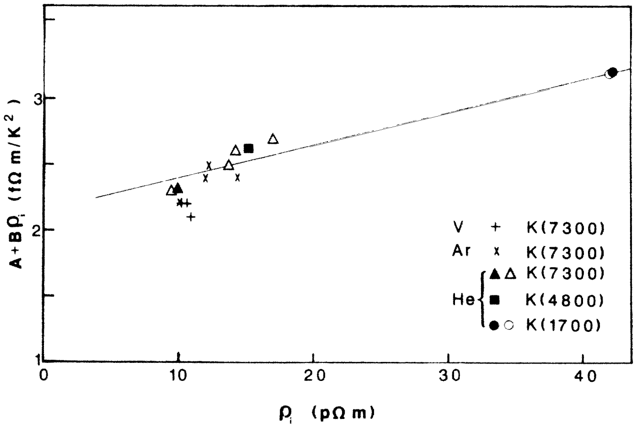

FIG. 3. The T^2 coefficient $A+B\rho_i$ for "bulk" ($d \geq 1$ mm) samples of K as a function of residual resistivity ρ_i. The solid symbols indicate the data used to determine bulk behavior for K(7300), K(4800), and K(1700) (for definitions see text) in Figs. 1, 2, 5, and 6, respectively. The K(7300) wires had $d=1.5$ mm, the K(4800) and K(1700) wires had $d=1.0$ mm. The straight line is a best fit to all of the data. Its slope of 2.5×10^{-5} K^{-2} is somewhat larger than those for Rb (1.3×10^{-5} K^{-2}) and Na (0.8×10^{-5} K^{-2}) impurities in K.

The lengths of the thinnest wires in Ref. 1 were about 10 mm, although length measurements were not generally recorded. The carefully measured lengths of the new wires varied from 2 to 14 mm. For wires of diameter $d \geq 0.25$ mm, the sample length was determined by two K potential leads of the same diameter as the sample. Thinner wires were connected between 1-mm-diam wires as described in Ref. 1.

B. Measuring system and procedures

The basic measuring system and procedures are described elsewhere.[1,15] We note here only one important improvement upon previous procedure, namely that we were able to extend our experimental resolution from a part in 10^7 to a few parts in 10^8 using computer averaging of the last digit of our current comparator.

C. Sample thickness determination

It is important for this study to know the diameters of the samples. For samples with $d \geq 0.25$ mm, measurements of sample length L (with an uncertainty of $<10\%$) and room-temperature resistance R(295 K) (with an uncertainty of $<1\%$), combined with the known ρ(295 K) for K, showed that the diameters of the sample wires were closely equal to the diameters of the dies through which the samples were extruded. For samples with $d \leq 0.1$ mm, however, surface corrosion usually caused the effective diameter of the sample to decrease between the time when the sample was mounted on the sample holder in the glove box and when it was cooled to liquid-nitrogen temperature. We estimated the diameters of these thinnest samples as follows.

For the samples of Ref. 1, where the sample lengths were not generally recorded, there is no independent way to evaluate the diameters of most of the thinnest wires. We thus retain the values listed in Ref. 1, except for one sample pair where the lengths are known, and for those samples where the room-temperature resistance R(295 K) changed significantly before and after measuring. In these latter cases, we reduced the diameter listed in Ref. 1 by the ratio $[\bar{R}(295)/R(295\text{ K})]^{1/2}$. Here R(295 K) is the resistance before the low-temperature measuring run, and $\bar{R}(295)$ is the average of the resistances before and after the run. This procedure assumes that the samples thinned somewhat due to corrosion between the time they were mounted and when they were measured at low temperatures.

For our new samples, we defined d by the equation

$$d=[4\rho(295\ \mathrm{K})L/\pi\bar{R}(295\ \mathrm{K})]^{1/2}\ , \qquad (4)$$

where $\rho(295\ \mathrm{K})=71.9\ \mathrm{n\Omega\,m}$. $R(295\ \mathrm{K})$ normally changed by $\leq 10\%$ over a single cooling cycle, but changes of 20–50%—and once even 90%—were occasionally observed. Large changes were always observed when the samples were held at room temperature for several days or weeks before being cooled down again. We note that the use of Eq. (4) is strictly valid only when the sample diameter is uniform along the sample length. To check for uniformity of corrosion, we cut open some highly corroded thick samples, and found that the corrosion was *not* uniform along the sample length, as will be discussed in more detail below. Nonuniformities are likely to be largest in the thinnest samples and in those which were corroded most. The effect of nonuniform corrosion should be to produce an anomaly characteristic of a sample thinner than the diameter given by Eq. (4).

A check for internal consistency of the sample thicknesses inferred from Eq. (4) can be obtained from a plot of ρ_0 versus $1/d$ as shown in Fig. 4. If surface scattering is purely diffuse, if the sample diameter is uniform, and if no additional contamination is introduced during sample thinning, then the residual resistivities of thin wires of a given bulk purity should be given to good approximation by the Nordheim Equation[16]

$$\rho_0=\rho_i+\tfrac{3}{4}(\rho_i l/d)\ , \qquad (5)$$

where for K we expect[16] $\rho_i l=2.9\times 10^{-14}\ \Omega\,\mathrm{m}$.

For the new, K(1700) samples, all but three of the thicker wire data points fall around the expected line down to about $d=0.08$ mm, and the data for thinner wires rise only slightly above this line. Perhaps the two K(1700) samples which fall below the nominal bulk values came from an ampoule with lower residual impurity content. This is, however, only speculation, since, as we show below and in Ref. 10, both the $d\rho/dT$ anomaly and the thermoelectric properties of these two samples are indistinguishable from those for similar samples from this batch with values of ρ_0 that fall on the expected line. For the $d=0.8$ mm K(1700) sample corroded in air, we believe that portions of the sample have cross sections much less than the average diameter, as we discuss below. For the new K(4800) samples, the data for wires thicker than 0.1 mm fall around the expected line, but for $d \leq 0.1$ mm the data rise well above this line. For the old K(7300) samples, the data for $d \geq 0.25$ mm fall around the expected line, but for thinner wires the data begin to rise above this line, and by $d=0.1$ mm, the data lie well above the line. The data for the Ar- and vacuum-cooled K(7300) samples approximately follow those for the He K(7300) samples. It appears from Fig. 4 that the purer the starting K, the thicker the wire for which the data begin to rise above the expected line. Finally, we note that the data in Fig. 4 for wires with shiny surfaces (indicated by the letter *s*) are similar to those for wires of equivalent diameter with white surfaces.

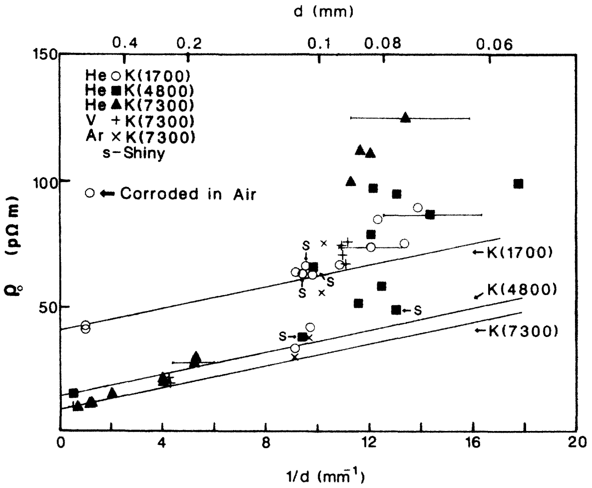

FIG. 4. ρ vs $1/d$ for K wires of different diameter and different bulk purity. The solid lines have a slope taken from Ref. 16. The letter *s* indicates samples with shiny surfaces.

Taken together, these data show that independent measurements of sample length and room-temperature resistance permit reasonably accurate determinations of the diameters of the extruded thin K wires down to $d\approx 0.1$ mm. Below this value, the samples must either be thinner than we estimate—because of nonuniform corrosion, or else their values of ρ_0 must be higher due to internal contamination leading to shortening of the bulk mean free path. If we assume that they are only thinner, then we should get an estimate of the correct diameters by moving the high data points in Fig. 4 to the right until they lie on the appropriate full lines. From Eq. (5) we see that this is equivalent to defining a new inverse diameter, $1/d'=\frac{4}{3}[(\rho_0-\rho_i)/\rho_i l]\propto\rho_0-\rho_i$. Below we will analyze our data in terms of both $1/d$ and $\rho_0-\rho_i\propto 1/d'$.

IV. EXPERIMENTAL DATA AND ANALYSIS

A. Data from Ref. 1

Figure 1(a) contains the data from Fig. 1 of Ref. 1 [along with some additional samples of K(7300) not shown in Ref. 1], replotted as $(\rho_0/\rho)\Delta\rho/\Delta T$ instead of the original $(\rho_{4.2\ \mathrm{K}}/\rho)\Delta\rho/\Delta T$. This replotting eliminates a sample-dependent normalization factor $\rho_{4.2\ \mathrm{K}}/\rho_0$ present in Ref. 1. For the temperature range considered in this paper, we have $(\rho-\rho_0)/\rho_0<0.1\%$. Thus the quantity plotted in Fig. 1 and the other figures is essentially $d\rho/dT$, and for simplicity we use $d\rho/dT$ to label the ordinates of our figures. For ease of comparison, the symbols of Fig. 1 of Ref. 1 have been retained. In Fig. 1(b), we replot selected data from Fig. 1(a) in integrated form to give $\rho(T)$.

For bulk, high-purity K, in which simple electron-electron scattering with $\rho=AT^2$ is dominant, we would expect $d\rho/dT=2AT$, corresponding to a straight line passing through the origin. The + symbols in Fig. 1 indicate that the behavior of the 1.5-mm-thick sample chosen as the reference wire for this set of samples conforms to this expectation. However, very different behavior is found as the wire thickness decreases below 1 mm, and for $d \leq 0.2$ mm we find negative values of $d\rho/dT$. The arrows show how the sizes of the anomalies increased when the wires were thinned inside the sample can by surface corrosion. To see whether substantially shortening the electron mean free path would eliminate the anomaly, we prepared a $d = 0.25$ mm wire of K-0.08-at. % Rb with $l \approx 0.02$ mm. As illustrated by the dashed curve of Fig. 1, because of inelastic impurity scattering, the value of $A + B\rho_i$ for this wire was larger than that for the thick pure K wires. It was, however, only a little smaller than the value for a thick wire of the same Rb concentration (not shown), and showed no evidence of deviations from straight line behavior. Any anomaly was thus quite small (see Figs. 8–11 below).

Figure 2 contains data similar to that in Fig. 1, but for wires prepared and cooled in Ar, or prepared in He and cooled in partial vacuum ($\approx$10–100 μm of He) without molecular sieve. These data were noted but not shown in Ref. 1. Figure 2 contains data from both samples of all of the pairs studied, and we have retained the symbols used in Fig. 4.8 of Ref. 3 for the three sample pairs shown there. We see that the data of Fig. 2 display the same anomalous form as those in Fig. 1. However, while the data for the pair of $d = 0.25$ mm wires show the same size anomaly as $d = 0.25$ mm wires in Fig. 1, the data for the $d \leq 0.1$ mm samples show smaller anomalies than in Fig. 1, and also much more variation from wire to wire, especially for the wire pair designated by inverted triangles. This pair of wires was unusual, in that instead of the normal few minutes between the mounting of the two paired samples, the sample designated by the open inverted triangles was mounted an hour before its pair. Additional surface corrosion of this sample as it sat in the glove box certainly contributed to its larger anomaly. As noted in the Introduction, the somewhat different behavior between the thinnest samples in Fig. 2 and those in Fig. 1 was originally[1] attributed to differences in the atmospheres. We shall see below that most of these anomalies in Fig. 2 agree rather well with the anomalies for our new sample sets K(4800) and K(1700).

B. New data

In Figs. 5 and 6 we present collected data for the new pairs of K wires examined in this study, most of which were extruded through 0.1 mm dies. These two figures contain a wealth of data, which must be considered in detail to develop an understanding of the behavior of thin K. Wires prepared together are indicated by brackets. For these two figures, in each wire pair the sample designated by the open symbol was prepared first. The figures contain listings of the sample diameters d, lengths L, and values of ρ_0, as well as brief notes with other important information. These samples were all prepared and cooled in He gas. The + and × symbols in each figure represent assumed bulk behavior (see solid symbols in Fig. 3), determined as described above.

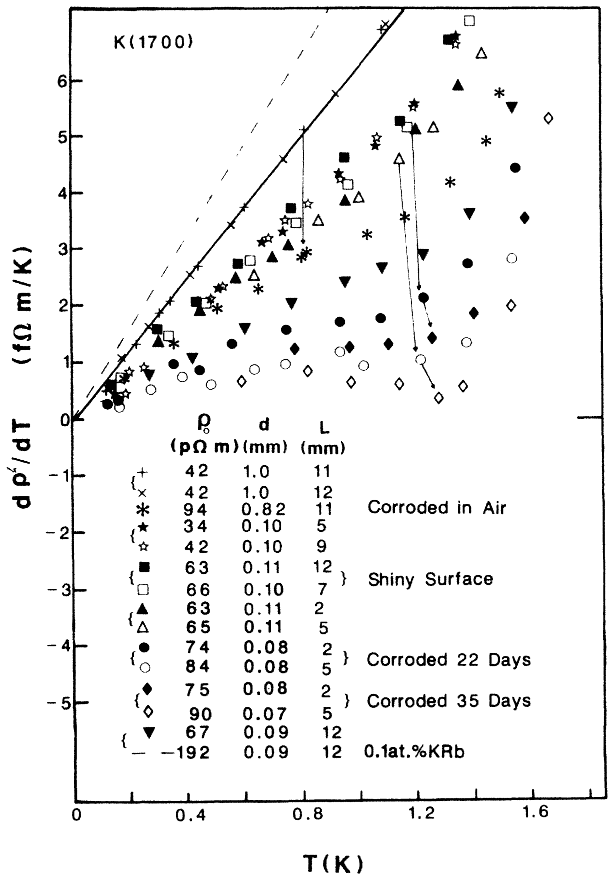

FIG. 5. $d\rho/dT$ vs T for the K(1700) samples. Pairs of samples prepared together are designated by identical symbols, with the open symbol designating the sample prepared first. Note that in each pair the anomaly is always larger for the sample prepared first, and the anomaly is independent of sample length. After their initial cooling, some of the samples were given room-temperature anneals and then cooled and measured again. The progression of behavior after such anneals is indicated by the arrows.

1. K(1700)

Figure 5 contains data for the thin K(1700) samples. Their bulk $\mathcal{R}$ corresponds to an elastic mean free path of $l \approx 0.05$ mm, about half the $d \approx 0.1$ mm of our smallest die. Three pairs of $d \approx 0.1$ mm wires were prepared; they are designated by stars, squares, and triangles, and are listed on the figure in the order measured. As initially extruded, all six samples showed only relatively small anomalies. These anomalies were essentially independent of sample length, and approximately the same size for all six samples, independent of their values of ρ_0. The stars and squares were measured in two different sample cans; we thus conclude that the sample can is not a major issue.

To see whether, and how, these anomalies increased in size as the samples became still thinner, we thinned one pair of samples (the triangles) two times by surface corrosion at room temperature. The circles are after corrosion for 22 days, and the diamonds are after a total of 35 days. As indicated by the arrows, the anomalies in both samples became larger by similar amounts as the sample diameters decreased.

To test whether surface corrosion would affect a thicker wire, we corroded a $d=1$ mm sample (+'s) until its apparent average diameter decreased by 20%. As shown by the arrow, a significant anomaly appeared. Since this sample was thick, it was possible to section it and check the uniformity of corrosion with a microscope. The corrosion was highly nonuniform; in some places, the surface was deeply corroded and fingers of corrosion extended into the center of the sample; in other places, the corrosion was so great that the sample could best be described as three or four thin cylinders of K embedded in a wire of corroded material.

To check whether the presence of some surface corrosion is essential to the appearance of an anomaly, we cleaned the atmosphere in the sample can with a large area of fresh K on a Cu foil, as described above. This procedure yielded, for the first time, $d \leq 0.1$ mm samples which remained shiny when reexamined after being measured. For the K(1700) sample set, the samples with shiny surfaces (squares in Fig. 5) showed anomalies similar in magnitude to those for samples with the typical white surfaces. This means either that surface corrosion is not essential to the anomaly, or that only an extremely thin film of surface corrosion is sufficient to produce an anomaly if the wire is sufficiently thin. Since we see little or no anomaly in thick high-purity wires, or in thin wires of dilute K-Rb alloys, surface corrosion alone apparently cannot produce an anomaly.

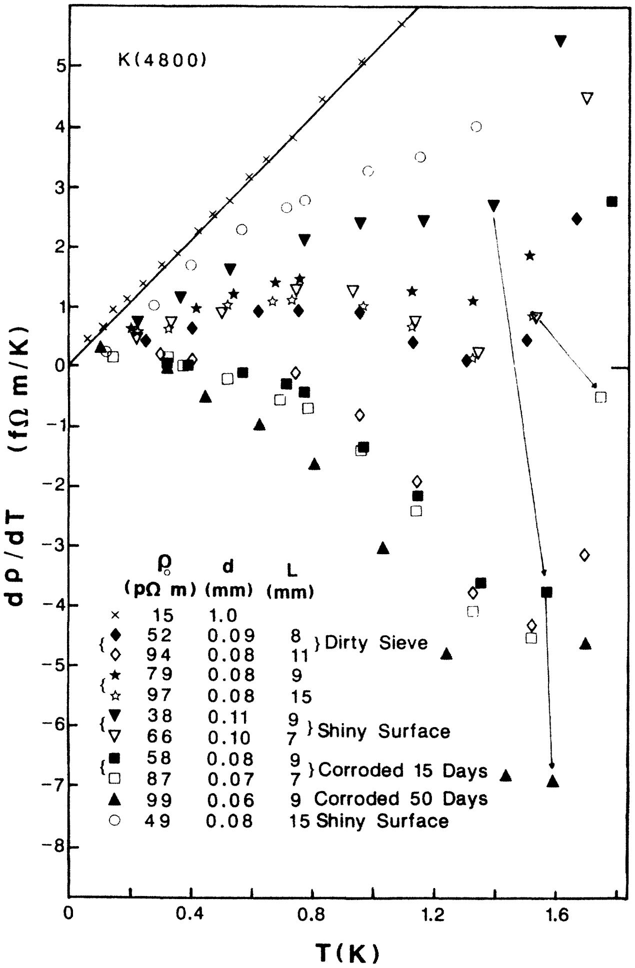

FIG. 6. $d\rho/dT$ vs T for the K(4800) samples. Pairs of samples prepared together are designated by identical symbols, with the open symbol designating the sample prepared first. Note that in each pair the anomaly is always larger for the sample prepared first, and the anomaly is independent of sample length, except for the sample pair denoted by diamonds. This pair was the only one that showed a length dependence approximately proportional to L^2. After their initial cooling, some of the samples were given room-temperature anneals and then cooled and measured again. The progression of behavior after such anneals is indicated by the arrows.

To recheck that greatly reducing l does indeed greatly reduce the anomalous behavior, we measured a K–0.1-at.% Rb sample made from K(1700) material. In agreement with our previous results (see Fig. 1 and Figs. 8–10 below), the data were very close to bulk behavior for such a dilute alloy.

Finally, to see what effect introducing corroded material into the body of a sample would have, we first corroded some K(1700) material, and then mixed the white product with new pure K(1700), all in an *Ar*-filled glove box. Ar was chosen to eliminate the need for sieve. A $d=1$ mm wire extruded in Ar from this composite material had an $\mathcal{R}$ of 1800, and its anomaly fell between bulk behavior and that found for $d=0.1$ mm wires (see Fig. 5). Corrosion in the body of the sample thus apparently produced a small anomaly in the Ar atmosphere. We then corroded the surface of this wire by taking it out into the air. Its ρ_i increased by 60%, and the magnitude of $A+B\rho_i$ *increased* approximately as expected for the observed increase in the *bulk* ρ_i (see Fig. 3). The effect of surface corrosion on this $d=1$ mm wire prepared and measured in Ar was thus quite different from that of the $d=1$ mm wire prepared and measured in He described above.

2. K(4800)

Figure 6 contains data for the K(4800) samples, for which $l \approx 0.15$ mm. Here the anomalies in freshly prepared $d=0.1$ mm samples were generally slightly larger than those in Fig. 5, but not as large as those in Fig. 1. Again data are shown for several sample pairs of different lengths, and for one pair subjected to additional corrosion. The sample designated first by an open inverted triangle and then by an open square, broke before it became an open erect triangle; it was replaced by a fresh sample, which is designated by the open circle. K(4800) samples with shiny surfaces also showed anomalies, but these were smaller than for white-surfaced samples.

C. Synthesis of information
from Figs. 1, 2, 5, and 6

We ask first whether the anomalous behavior we see can be due to a combination of two different phenomena. If these phenomena had different temperature dependences, then we would expect the temperature dependence of an anomaly of a given magnitude to change when different conditions led to different ratios of the two phenomena. Figure 7 shows, however, that for an anomaly of a given size, very different samples produce data having exactly the same temperature dependence—independent of sample length, sample diameter, or whether the samples were prepared in He or Ar. This fact strongly suggests that our "size effects" are the result of a single physical phenomenon.

Since the temperature dependence of an anomaly of a given size is unique, it is worth parametrizing. We focus upon the data below 1.2 K, since here electron-phonon scattering should be very small. Most of the published theories assume that the anomaly simply adds to the bulk T^2 behavior predicted by Eq. (2). We thus take $\rho(T)$ to consist of a T^2 term plus an anomaly which varies as T^n. Neither additivity nor a power-law dependence is necessarily correct, but requiring both behaviors makes the parametrization unique. When we plotted $d\rho/dT - 2(A+B\rho_i)T$ versus T^{n-1}, and looked for a value of n that led to straight lines, we found, in agreement with Ref. 3, a best fit of $n \approx 2.33$ for all anomaly sizes. The solid curves going through the data in Fig. 7 were determined with this form. Both $n=2$ and $n=2.5$ gave significantly worse fits. Note that the fits go above the minima in the various curves. This suggests the need for an additional negative contribution before the rapidly rising, positive umklapp electron-phonon term sets in.

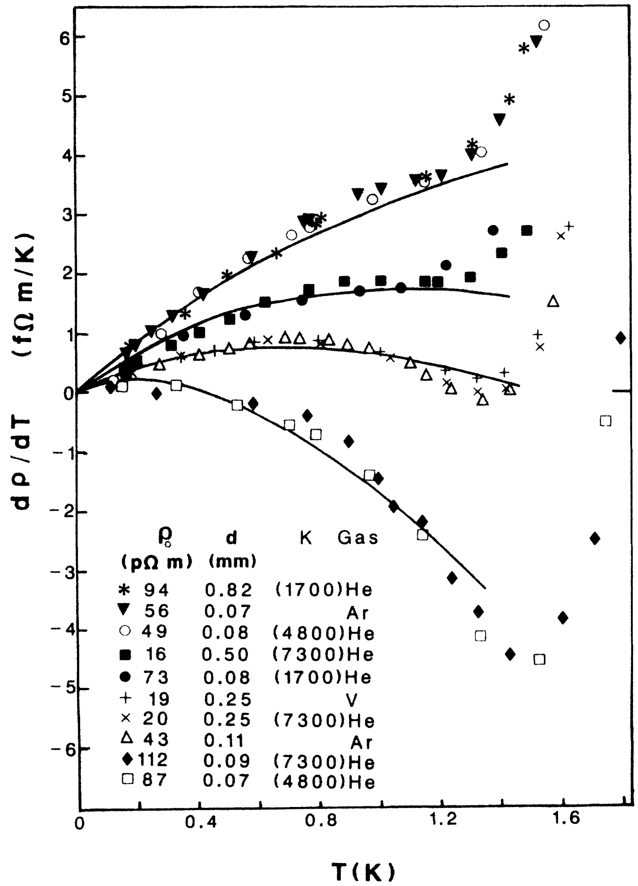

FIG. 7. Intercomparison of data sets with four different size anomalies involving wires having different thicknesses, different bulk $\mathscr{R}$'s, and/or cooled in different gases. The curves through the low-temperature data are fits up to 1.2 K to an equation of the form $\rho(T)=(A+B\rho_i)T^2-CT^{7/3}$, where $A+B\rho_i$ is determined by the behavior of thick K wires.

The second major feature of interest is that, with only one exception (the open and solid diamonds in Fig. 6), the size of the anomaly in a given sample pair does *not* vary significantly with the sample length. Rather, for a given pair, the anomaly is practically independent of sample length, and a larger anomaly always occurs in the sample prepared first. We attribute this latter behavior to extra surface corrosion in the sample prepared first, since this sample sat unprotected in the glove box for several minutes while the second sample was extruded and mounted. The only case where a longer sample had a substantially larger anomaly than its shorter mate (the diamonds in Fig. 6), occurred when the molecular sieve was not freshly cleaned before the samples were mounted. Both the room-temperature resistance and ρ_0 for the longer sample (which was mounted first) indicate that it corroded considerably more than the shorter one. We believe that additional thinning of the longer sample due to surface corrosion contributed importantly to its larger anomaly.

The next important issue is whether we are seeing a size effect. To try to answer this question quantitatively, we define the quantity Δ as the difference at $T=1.0$ K between the value of $d\rho/dT$ for a given thin sample and the value of $d\rho/dT$ for the reference bulk sample for the same batch of K. 1.0 K was chosen as the highest temperature for which we can safely neglect effects of electron-phonon scattering. Because of the uncertainties noted above concerning the thicknesses of our thinnest samples, we analyze the data in two different ways, one involving the inverse diameters $1/d$ determined from the diameters of the extrusion dies and measurements of the sample lengths and room-temperature resistances as described above, and the other involving the "effective" inverse diameter, $\rho_0-\rho_i \propto 1/d'$, defined via Eq. (5). This latter alternative "corrects" the sample diameters of thin wires which do not fall on the straight lines in Fig. 4.

If the anomaly is due primarily to surface scattering, then for each sample set, Δ should increase as $1/d$ increases. We see from Fig. 8 that this is true—with two obvious exceptions[17]—within modest scatter for each of the K(7300), K(4800), and K(1700) sample sets. The only possible alternative explanation for an increase of Δ with increasing $1/d$ is that of increasing bulk contamination as the wires become thinner. From Eq. (2), which is confirmed by our data for thin wires of dilute *K*Rb alloys, we know that adding substitutional impurities to K *increases* the T^2 coefficient $A+B\rho_i$, and thus produces a change in $d\rho/dT$ that is *opposite* to the anomaly we see. We can thus rule out such contamination as the source of our anomalies. More complex is the possibility that surface corrosion extends into the body of the sample and contributes to the anomalies we see. We consider this alternative further below.

If we now consider the general patterns in Fig. 8, we see that the K(1700) Δs seem to fall slightly below the

K(4800) Δs, but these two sets of data are mutually consistent for all $1/d$ to within their experimental uncertainties. In contrast, the K(7300) Δs, and the Δs for one pair of wires prepared in Ar, fall well above the other data for $1/d < 10$. On the other hand, for $1/d > 12$ the K(7300) Δs approach the others. The remainder of the Ar- and vacuum-cooled data fall among the overlapping K(4800) and K(1700) data sets. If each set of data is separately fit to the form $(1/d)^n$, then the K(7300) data suggest $n \approx \frac{1}{2}$, while the K(4800) and K(1700) data seem to give $1 \leq n \leq 2$. The Δs for $d = 0.25$ mm K−0.1 at. % Rb and $d = 0.1$ mm K−0.08 at. % Rb are the smallest in Fig. 8, and both are consistent with no anomaly at all. Aside from its slightly higher purity, the only treatment of the K(7300) sample set which we know differed from that for the K(4800) and K(1700) sets was the 100 °C lower temperature at which the molecular sieve was baked. Perhaps this lower baking temperature led to greater surface contamination of the K(7300) samples which, in turn, led to larger anomalies in thick samples. The data of Fig. 4 are consistent with somewhat greater surface corrosion in the K(7300) samples.

Since Kaveh and Wiser[7] have predicted that Δ should vary with l/d, we replot Δ versus l/d in Fig. 9. This plot rescales each data set along the abscissa, but leaves the ordinate of each point unchanged. Figure 9 brings the K(7300) and K(4800) data closer together than in Fig. 8, but separates the K(4800) and K(1700) data.

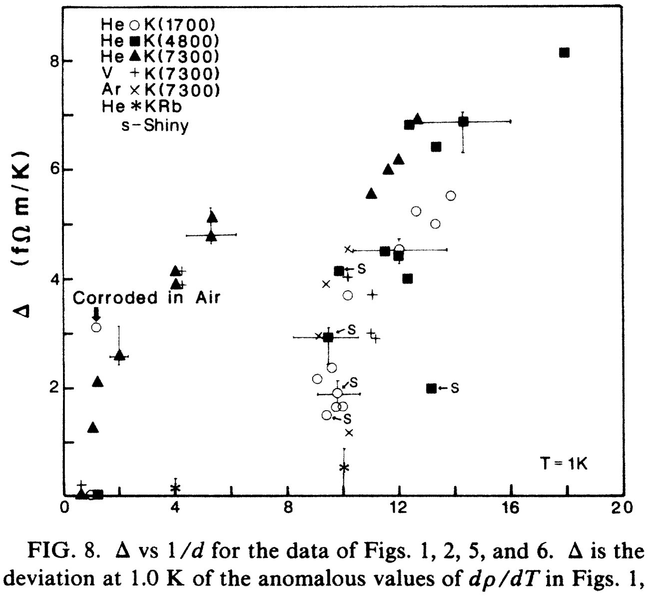

FIG. 8. Δ vs $1/d$ for the data of Figs. 1, 2, 5, and 6. Δ is the deviation at 1.0 K of the anomalous values of $d\rho/dT$ in Figs. 1, 2, 5, and 6 from the bulk behavior shown in each figure. The letter s indicates samples with shiny surfaces.

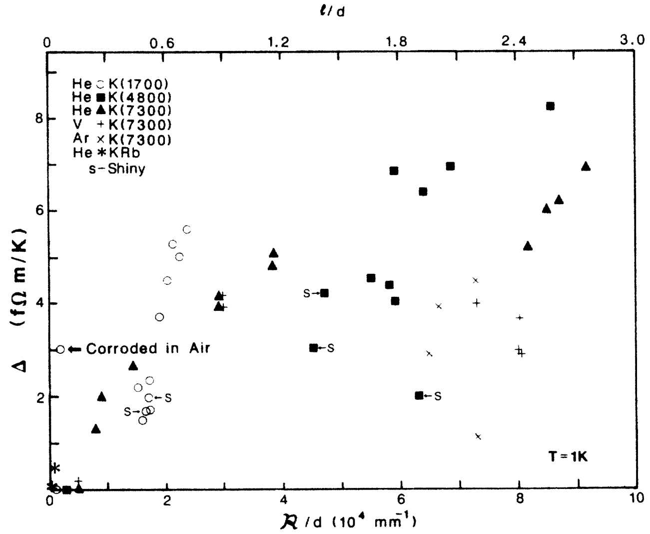

FIG. 9. Δ vs $\mathcal{R}/d$ for the data of Figs. 1, 2, 5, and 6. The scale for Δ vs l/d is given at the top of the graph. The letter s indicates samples with shiny surfaces.

Because the residual resistivities of the samples in each set are not simple functions of $1/d$ (see Fig. 4), we examine in Fig. 10 how Δ varies with "corrected" sample diameter, $\rho_0 - \rho_1 \propto 1/d'$. If the increase in ρ_0 is due mainly to nonuniform thinning of the samples, then the data should vary more nearly as $1/d'$ than as $1/d$. The data for the different samples in Fig. 10 overlap rather like those in Fig. 8. However, the data for the thinner samples clearly lie more to the right in Fig. 10 than in Fig. 8 relative to the thicker sample data, and the data for the purer samples—K(7300) and K(4800)—lie to the right of the data for the least pure samples—K(1700). There are two alternative interpretations of the data in Figs. 8 and 10. (1) The higher than expected values of ρ_0 in Fig. 4 are due primarily to nonuniform diameters, in which case Fig. 10 indicates that Δ increases less rapidly than linearly with $1/d'$ and may even be "saturating" for the thinnest wires. (2) The higher than expected values of ρ_0 for the thinnest samples are due in large measure to internal contamination of the thinner wires, leading to less rapid than expected increases in Δ wire $1/d'$. To test this latter alternative, we compared the increases in Δ for wires thinned by extrusion through smaller dies with the increases due to explicit surface corrosion—as indicated by the arrows in Figs. 11(a) and 11(b). We conclude that changes in Δ due to corrosion are generally indistinguishable from those due to thinning. The one obvious excep-

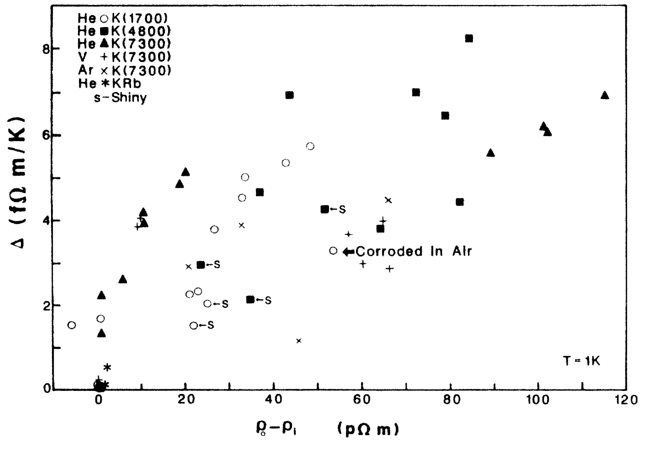

FIG. 10. Δ vs $\rho_0 - \rho_i$ for the data of Figs. 1, 2, 5, and 6. The letter s indicates samples with shiny surfaces.

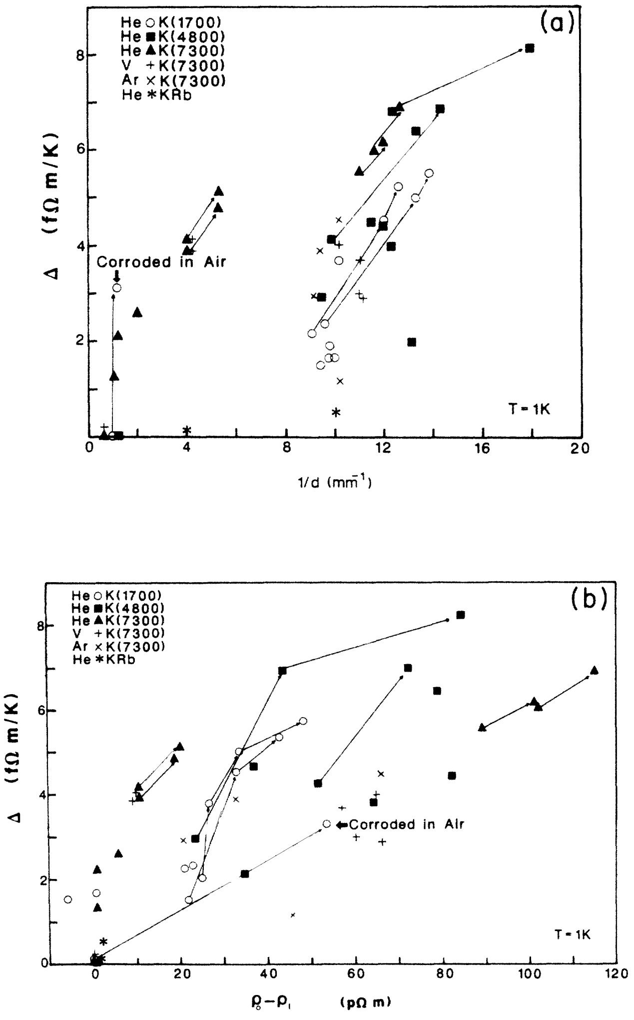

FIG. 11. (a) Figure 8 with arrows indicating changes in Δ which occur upon corrosion. (b) Figure 10 with arrows indicating changes in Δ which occur upon corrosion.

tion is the $d=0.8$ mm sample, for which the effect of corrosion is unusually large in the plot versus $1/d$, but unusually small in the plot versus $\rho_0-\rho_i$. Both behaviors are compatible with highly nonuniform thinning, leading to an effective average diameter much smaller than the nominal one.

In the following paper,[10] we examine the behavior of the thermoelectric ratio G of these same samples. We see from Fig. 5 in Ref. 10 that most of our data points fall on three separate lines on a Gorter-Nordheim plot, in a manner consistent with the separation into three different sample sets that we have been assuming in the current paper. Only three data points deviate significantly from the three expected lines in Fig. 5 of Ref. 10. Two are for the K(1700) samples which have unusually low values of ρ_0 in Fig. 4. The deviation in Fig. 5 of Ref. 10 is due primarily to these unusual values of ρ_0. The third is the corroded $d=0.8$ mm sample of K(1700)—the six-pointed star in Fig. 5 of the current paper. Its G_0 is consistent with a much smaller effective diameter, as we have just argued.

V. SUMMARY OF BEHAVIOR AND COMPARISON WITH THEORIES

From the foregoing experimental data, we summarize the behavior of $d\rho/dT$ as follows. (1) All of our pure K samples thinner than $d=1$ mm show anomalies. (2) The anomalies are generally larger the thinner the wires and the purer the host material, but there are some large variations for thin wires of a given diameter. (3) Both white and shiny surfaces yield anomalies, but anomalies associated with the former are usually larger. (4) If l is greatly reduced by adding small amounts of Rb, the anomalies become too small to reliably isolate. (5) The anomalies all have the same temperature dependence for a given anomaly size, independent of wire thickness, bulk resistivity, or the gas in which the wire is prepared and cooled. (6) Surface corrosion both thins the wires and increases the sizes of the anomalies—as a corollary, the anomaly is invariably larger in the sample mounted first in a given sample pair. (7) There is no systematic length dependence of anomalies for which $d\rho/dT$ remains positive. We do not have enough data to draw conclusions about length dependence for anomalies for which $d\rho/dT$ becomes negative. (8) The variation of the anomaly size with $1/d$ apparently has a different form for the K(7300) samples from that for the K(4800) and K(1700) samples. (9) The data are not unique functions of any of the following variables: $1/d$, l/d, or $\rho_0-\rho_i$. (10) Below about 1.2 K, where electron-phonon scattering is small, the anomaly can be parametrized as $\rho(T)\alpha T^{7/3}$ independent of the anomaly size. This form seems to require an additional negative contribution to $d\rho/dT$ for data in the vicinity of 1.2 K.

We now consider whether any of the proposed models can describe these results. We omit the Gurzhi effect, which can be ruled out on theoretical grounds.[6–9,13]

A combination of CDW effects with localization seems unlikely because, as illustrated in Fig. 7, the temperature dependence of the anomaly follows a single pattern. We thus do not seem to have a combination of two quite different phenomena—a CDW effect for thicker samples and localization for thinner ones—which just accidentally smoothly match together.

The model of interference effects between normal electron-electron scattering and surface scattering makes two predictions: (1) a T^2 variation of the anomaly; and (2) that the magnitude of the anomaly passes through a maximum value at $l/d\approx 1-2$. The first prediction is at variance with the temperature-dependent behavior shown in Fig. 7. The second prediction could be compatible with the behavior shown in Fig. 10 if the maximum occurs for the largest values of l/d we have been able to produce, i.e., $l/d\approx 2.5$. We note that this model has recently been criticized theoretically.[9]

Reduction of the effectiveness of surface scattering by normal electron-phonon scattering can be ruled out as the primary source of the anomaly by the temperature dependence of the data illustrated in Fig. 7. The anomaly varies approximately as $T^{7/3}$, rather than the T^5 variation predicted by this model. If this $T^{7/3}$ term is taken as reliable, then there *is* need for a small additional negative contribution to $d\rho/dT$ in the vicinity of 1.2 K, which could be due to this T^5 term.

Finally, we consider what alternatives exist to these models. If we combine the separate contributions of interference effects plus reduction of surface scattering by normal electron-phonon scattering, we can generate a temperature dependence of about $T^{2.33}$. But we have the claim[9] that the interference effect model is incorrect. The possibility of a complete explanation in terms of a CDW state coupled with scattering from the sample surface cannot be ruled out. A CDW-based model has the advantages that (1) it provides for unexpected variations from sample to sample due to differences in orientation of the CDW domains, and (2) it provides for deviations from simple T^2 behavior. It has the disadvantages that (1) no CDW-based model without localization yet predicts a negative $d\rho/dT$; (2) it is hard to see why the data for a given bulk purity fall into such generally nice patterns for a given sample purity if the anomaly is sensitively dependent upon the CDW domain structure, and (3) there appears to be no need for a CDW model to explain the behavior of either bulk K or dilute K-based alloys.[1,5]

VI. CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

We have summarized the results of our measurements in the numbered items in the preceding section. We conclude that there does appear to be an anomalous size effect in thin K wires, the nature of which is not yet clear. Especially unclear is the contribution and role of surface corrosion. We know of no theory that seems able to adequately describe all of our data.

Additional measurements which might help clarify the situation include the following. (1) Measurements on still thinner wires with both shiny and corroded surfaces. Such measurements are not easy, because very thin wires take heavy pressure and long times to extrude, so that extrusion is difficult and the wire surfaces will invariably corrode. (2) Measurements with still higher-purity bulk K. This will require additional purification of commercial K by vacuum distillation. (3) Incorporating white, corroded material into the body of K wires prepared and cooled in He, to clearly establish whether or not introducing such material into K produces an anomaly.

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[17] The two exceptions to the pattern of increasing Δ with increasing $1/d$ in Fig. 8 are the corroded $d = 0.8$ mm K(1700) wire and one shiny K(4800) wire. As noted above, we believe that the $d = 0.8$ mm K(1700) wire has portions much thinner than its average diameter. The reason for the unexpectedly small Δ for the one shiny K(4800) wire is less clear, but may involve accidental internal contamination.