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## Electrical Resistivity of Potassium from 1 to 25 °K<sup>†</sup>

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Low-temperature electrical-resistivity data are presented for pure and impure potassium samples [ $8000 \gtrsim \rho(20^\circ\text{C})/\rho(0^\circ\text{K}) \gtrsim 100$ ] and compared with theory. The experimental and theoretical results are tabulated, interpreted, and compared with the work of others. In particular, the resistivity data of the impure samples exhibited only relatively minor deviations from Matthiessen's rule and did not differ appreciably in temperature dependence from the resistivity data of the pure samples. Experimental details are presented and a short study of quenching effects has been made.

### I. INTRODUCTION

The temperature and impurity dependence of the electrical resistivity of a metal can act, in many cases, as a definitive test for establishing the state of our present theoretical understanding of low-temperature transport mechanisms. In particular, questions concerning electron-phonon umklapp scattering processes and electron-impurity scattering processes have prompted this study of the low-temperature electrical resistivity of potassium. Previous treatments of these scattering mechanisms have been mostly qualitative and many discrepancies between theoretical prediction and experimental observation have emerged.

Recently, we reported the first detailed agreement between theory and experiment as concerns our understanding of the role of umklapp processes in determining the low-temperature electrical resistivity of potassium in particular and more generally of the ideal monovalent metals.<sup>1</sup> This paper presents additional resistivity data on less-pure samples, an explicit tabulation of the earlier reported results, and a more extensive discussion of other aspects of these results.

The details of sample preparation, cryostat design, and instrumentation are discussed in Sec. II. In Sec. III the experimental results are presented: The results of a short study of quenching effects are reported in Sec. III A; the experimental results of the purer potassium samples are tabulated and compared with the work of others in Secs. III B and III C; and in Sec. III D results from measurements on less-pure samples and alloys are discussed along with some of their more general implications as regards deviations from Matthiessen's rule. Last, in Sec. IV the theoretical results are summarized, tabulated, and several interpretive remarks are presented.

### II. EXPERIMENTAL RESULTS

#### A. Sample Preparation

Prior to extrusion of the polycrystalline wire samples, an etching solution of 2% secondary butyl alcohol in xylene was used to remove surface contamination from the bulk material. Extrusion was done at room temperature under dehydrated paraffin oil. Wire diameters were maintained at approximately ten times the maximum low-temperature electron mean free path and in no case were sig-

nificant size effects observed.

During the extrusion process, the bare wires were wound on bakelite formers and electrical connections made. Fine copper wire potential contacts wetted with a very thin film of mercury were inserted in the potassium at least five sample diameters from the current contacts. After extrusion all samples were annealed one week at room temperature under pumped paraffin oil, rinsed in xylene, and the sample assembly mounted in the cryostat in an argon atmosphere for immediate slow cooling to liquid-helium temperatures.

#### B. Cryostat Design

A schematic drawing of the cryostat is presented in Fig. 1. An inner chamber containing the sample and mount was separated by a (cryogenically pumped) vacuum jacket from the reference bath (liquid helium or liquid nitrogen depending on the desired temperature range). A radiation shield in the vacuum jacket minimized the effect of differential radiant cooling of this inner chamber at higher temperatures, insuring an isothermal sample environment. The inner chamber was also filled with a small amount of helium exchange gas to maintain good thermal equilibrium along the entire length of the approximately 1-m-long wire samples. In addition all electrical leads to the cryostat from the room-temperature instrumentation were triply heat sunk to bring them accurately to sample temperature before connection. Above about 10°K, the temperature gradient across the sample was monitored by a gold-cobalt alloy vs copper thermocouple; the observed gradient never exceeded 10 mK.

Below 100°K, the absolute temperature was measured with a Cryocal CR2500H germanium resistance thermometer in good thermal contact with the sample and above 100°K a platinum resistance thermometer was employed. A convenient four-terminal ac bridge circuit<sup>2</sup> was used to read thermometer resistances  $R$ , with an absolute accuracy of 0.02%. Absolute error in these temperature readings was determined by the thermometer calibration which was always better than 0.25% of reading. A multiple parameter least-squares fit of the calibration data to the function

$$(T)^{-1} = \sum_{i=-n}^{n+1} c_i (\ln R)^i$$

allowed convenient and accurate interpolation.

Maintaining a constant temperature for long periods of time over a wide temperature range required good thermal isolation of the sample chamber in order to minimize power input to the helium bath. Except for the current leads, all connections between the helium bath and sample chamber could easily be made to have high thermal resistance.

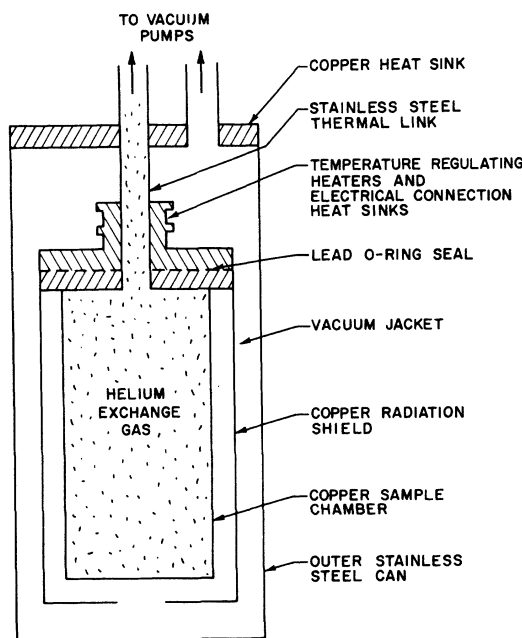


FIG. 1. Design of cryostat.

At low temperatures where fairly large measuring currents were required, good isolation was maintained by making the current leads out of relatively fine silver-clad superconducting ribbon.

Very high temperatures were easily obtained by only partially immersing the system in liquid helium. Since all heat sinking was performed at the top of the outer stainless steel can, a large variable thermal resistance to the helium bath was obtained by simply raising the top slightly out of the helium bath thereby adjusting the amount of stainless steel between the bath and the heat sinks. The absolute temperature was controlled automatically by means of two (high and low power) constantan wire heaters. Temperature stability was better than 0.01% and the temperature could be varied continuously from 1 to 300°K by changing the liquid refrigerant from helium to nitrogen at about 150°K.

#### C. Instrumentation

In low-temperature resistivity studies such as this, it is necessary to measure the temperature-dependent part of the resistivity in the presence of a residual resistivity background that is usually much larger than the temperature-dependent portion. Even in the purest potassium available, the residual resistivity becomes 100 times the ideal resistivity by about 2½°K. Consequently, to measure the temperature-dependent part to within a few percent it is necessary to make resistivity measurements with an accuracy of at least a few parts in ten thousand.

This was accomplished by using a stable nanovolt

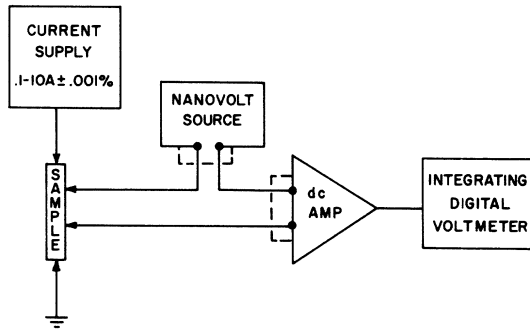


FIG. 2. Instrumentation. The dashed lines indicate low thermal emf electrical connections. A Keithley 148 nanovoltmeter was used for the dc voltage amplifier and a Keithley 260 for the nanovolt source. The integrating digital voltmeter was a Hewlett Packard 2401C operated at an integration time of 1 sec.

source to balance most of the large constant residual component at low temperatures, thereby allowing direct detection of the temperature-dependent portion with a relatively low accuracy nanovoltmeter, as shown in Fig. 2. A current supply was constructed to provide measuring currents from 100 to 10 A with a stability of a few parts in  $10^5$ . Although heating and magnetoresistive effects were negligible at higher currents, the data in this study were obtained with measuring currents limited to less than 1 A. Simultaneous reversal of the measuring current and nulling potential permitted cancellation of thermoelectric offset voltages. These thermal voltages were kept small and constant by using continuous potential leads and temperature-stabilized connections to the room-temperature instrumentation. The net result was a system capable of measuring resistivities with an absolute accuracy of  $\pm 1\%$  and a relative accuracy of about  $\pm 0.01\%$  at the lowest temperatures.

### III. EXPERIMENTAL RESULTS

#### A. Quenching Studies

During the course of this work it was found that the slow cooling of a pure potassium sample from room temperature to liquid-helium temperatures led to considerably lower resistivity values than were obtained when the sample was cooled rapidly. It should be remembered (see Sec. II) that the samples were bare polycrystalline wires, freely mounted on a bakelite former. Rapid cooling was accomplished by directly quenching the bare potassium sample in a liquid-nitrogen bath; slow cooling was accomplished by mounting the sample in the inner chamber of the cryostat at room temperature and cooling via the weak thermal link to the outer can (see Fig. 1). Unless stated otherwise, all data in this article were obtained from measurements on slow-cooled samples.

TABLE I. Quenching study.

Sample treatment	Resistivity at 4.2 °K ( $10^{-9} \Omega \text{ cm}$ )
1-week anneal at 22 °C	1.18
10-h slow cool <sup>a</sup>	
Quench <sup>b</sup>	2.35
1-week further anneal at 22 °C	1.26
10-h slow cool	
Quench	2.32
10-h slow cool	1.23
Quench	$\sim 2.3$
1-h slow cool	1.23

<sup>a</sup>The time durations indicate the approximate number of hours for the sample to cool from room temperature to liquid-helium temperatures.

<sup>b</sup>After warming to room temperature, the bare potassium sample was immersed directly in liquid nitrogen and subsequently in liquid helium.

Measurements of quench-induced changes in the resistivity showed several general properties. For the purest samples, quenching more than doubled the residual resistivity. This change in resistivity was found to be reversible; that is, as shown in Table I, the effects of quenching could be removed. Further long-term (one week) annealing was not necessary to restore the former low resistivity of a specimen; slow cooling over a relatively short period of time ( $\sim 1$  h) was all that was required. Also, it did not matter whether this cooling process was carried out in a vacuum or in the presence of an inert-exchange-gas atmosphere.

The quench-induced changes in the resistivity,

$$\Delta\rho \equiv \rho(4.2 \text{ °K})^{\text{quenched}} - \rho(4.2 \text{ °K})^{\text{slow cooled}},$$

were also found to depend on the temperature  $T_q$  from which the potassium sample was quenched. If it is assumed that

$$\Delta\rho \propto e^{-E/k_B T_q},$$

where  $k_B$  is the Boltzmann constant, then the activation energy  $E$  is on the order of 0.2 eV. It appears that rapid quenching of a well-annealed polycrystalline potassium specimen from high temperatures freezes in thermally activated defects which contribute significantly to the residual resistivity. Of principal importance for low-temperature resistivity studies is that slow cooling of potassium is required to minimize such defects when high resistance ratios are desired.

#### B. High-Purity Results

Resistance data were obtained at more than 40 different temperatures in the 1–25 °K range and at room temperature using samples having residual-

TABLE II. Electrical resistivity of potassium. Values in this table were obtained by averaging the temperature-dependent part of the resistivity ( $\rho_T \equiv \rho - \rho_0$ ) for the purer-potassium samples [ $\rho_0 = (0.902, 0.954, \text{ and } 1.587) \times 10^{-9} \Omega \text{ cm}$ ]. The uncertainty in  $\rho_T$  is the greater of  $\pm 1\%$  and  $\pm 2 \times 10^{-13} \Omega \text{ cm}$ ; the former is the absolute error, the latter extrapolation error in  $\rho_0$ .

$T$ (°K)	$\rho_T$ ( $\Omega \text{ cm}$ )	$\rho_T/T^5$ ( $10^{-14} \Omega \text{ cm } ^\circ\text{K}^{-5}$ )	$T$ (°K)	$\rho_T$ ( $\Omega \text{ cm}$ )	$\rho_T/T^5$ ( $10^{-14} \Omega \text{ cm } ^\circ\text{K}^{-5}$ )
2.00	$1.6 \times 10^{-12}$	5.2	8.00	$5.42 \times 10^{-9}$	16.5
2.25	4.1	7.1	8.50	6.82	15.4
2.50	8.5	8.7	9.00	8.43	14.3
2.75	$1.72 \times 10^{-11}$	10.9	9.50	$1.02 \times 10^{-8}$	13.2
3.00	3.25	13.4	10.00	1.23	12.3
3.25	5.64	15.6	11.00	1.70	10.6
3.50	9.22	17.6	12.00	2.27	9.11
3.75	$1.42 \times 10^{-10}$	19.2	13.00	2.93	7.90
4.00	2.08	20.3	14.00	3.70	6.88
4.25	2.94	21.2	15.00	4.58	6.03
4.50	4.03	21.8	16.00	5.57	5.31
4.75	5.36	22.2	17.00	6.67	4.70
5.00	6.95	22.2	18.00	7.86	4.16
5.50	$1.10 \times 10^{-9}$	21.9	19.00	9.16	3.70
6.00	1.65	21.2	20.00	$1.06 \times 10^{-7}$	3.30
6.50	2.34	20.1	22.00	1.36	2.64
7.00	3.18	18.9	24.00	1.69	2.12
7.50	4.21	17.7			

resistance ratios [ $r_R \equiv \rho(20^\circ\text{C})/\rho(0^\circ\text{K})$ ] ranging from about 100 to 8000. The resistance data were converted to absolute resistivity values assuming a room-temperature ( $22^\circ\text{C}$ ) resistivity<sup>3</sup> of  $7.19 \mu\Omega \text{ cm}$ . The temperature-dependent part of the resistivity,  $\rho_T$ , was then obtained by subtracting the observed value of the residual resistivity ( $\rho_T \equiv \rho - \rho_0$ ).

High-purity samples were extruded from potassium obtained from Mine Safety Appliances Ltd. (MSA), Callery, Pa. Values of  $\rho_T$  for these purer samples ( $4500 \lesssim r_R \lesssim 8000$ ) showed no systematic scaling with residual resistivity; all values were identical and reproducible to within  $\pm 1\%$ . These results, which were reported in Ref. 1, are tabulated in Table II and plotted in Fig. 3.<sup>4</sup> It is to be emphasized that these data were neither smoothed nor adjusted in any way. This is believed to be the most accurate and complete set of low-temperature resistivity data available for potassium.

Note that the errors indicated in Table II are not the usually quoted relative uncertainties, which are significantly smaller (see Sec. II C). Rather,  $\pm 1\%$  is an absolute figure which indicates the extent to which  $\rho_T$  could be reproduced from run to run and sample to sample, and  $\pm 2 \times 10^{-13} \Omega \text{ cm}$  is a realistic estimate of the uncertainty in  $\rho_0$  due to extrapolation errors. Extrapolation errors are the principal source of error in determining  $\rho_T$  at low temperatures where  $\rho_0$  severely dominates  $\rho_T$ . Typical practice is to reduce the uncertainty in  $\rho_0$  by making fine adjustments in its value to obtain the best fit to a pure  $T^5$  temperature dependence for  $\rho_T$  at

very low temperatures. The errors inherent in such a procedure are obvious. For this reason values of  $\rho_T$  in Table II have been purposely omitted at temperatures below  $2^\circ\text{K}$  where the uncertainty in  $\rho_0$  dominates data evaluation in this form. In Sec. III C, the very-low-temperature data will be presented in a form which is independent of any

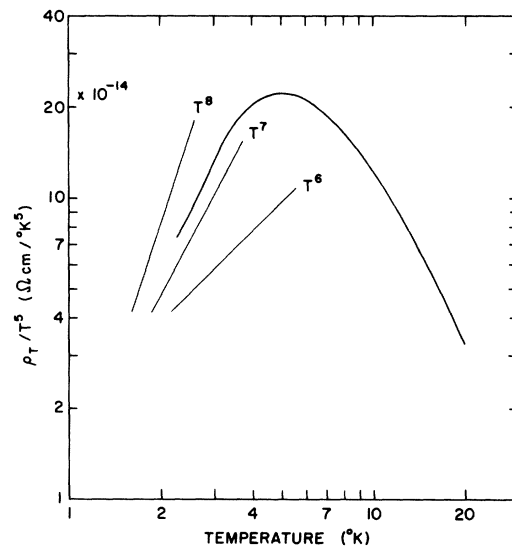


FIG. 3. Temperature dependence of the temperature-dependent part of the resistivity ( $\rho_T \equiv \rho - \rho_0$ ) for the purer potassium samples [ $\rho_0 = (0.902, 0.954, \text{ and } 1.587) \times 10^{-9} \Omega \text{ cm}$ ] reported in Ref. 1. Scatter in the data was less than the width of the line depicting the results.

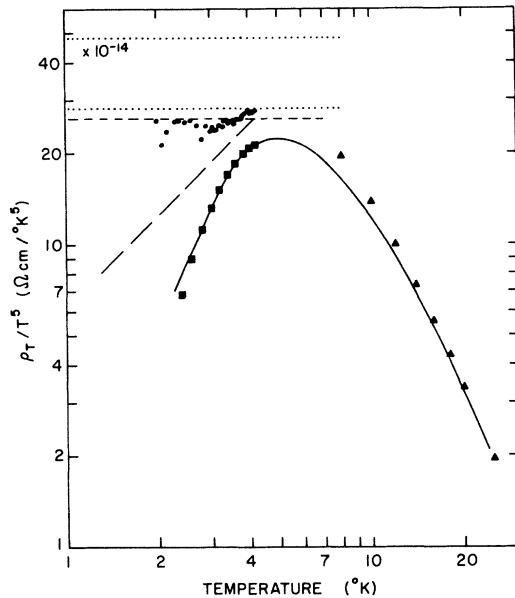


FIG. 4. Comparison of the results of Fig. 3 (solid curve) with the work of other investigators: dotted lines,  $T^5$  dependence reported below about 8 °K by Ref. 5 [upper line, sample K2 ( $r_R=512$ ); lower line, sample K1 ( $r_R=532$ ) and K4 ( $r_R=324$ )]; short dashed line,  $T^5$  dependence reported below about 7 °K by Ref. 6 ( $1400 \lesssim r_R \lesssim 2800$ ); circles, data of Ref. 7 ( $r_R=3800$ ); long dashed line,  $T^5$  dependence reported in the interval 1.3–4.2 °K by Ref. 8 ( $r_R=5300$ ); squares, data for sample K3(c) of Ref. 9 ( $r_R=8180$ ); and triangles, data of Ref. 10 ( $r_R=1400$ ).

extrapolation errors in  $\rho_0$  arising from curve fitting.

### C. Comparison with Other Measurements

The results for high-resistance-ratio samples are compared with the work of other investigators<sup>5–10</sup> in Fig. 4. As can be seen, there is considerable disagreement at low temperatures between this work and previous measurements where a  $T^5$  temperature dependence extending to quite high temperatures ( $T \approx 5$  °K or more) was usually reported. A low-temperature  $T^5$  behavior is in sharp contrast to this work where we observe a rather complex temperature dependence. The discrepancy with these earlier measurements<sup>5–8</sup> is due principally to greater uncertainty in  $\rho$  and curve-fitting errors in determining  $\rho_0$ .

Recent measurements below 4.2 °K by Gugan<sup>9</sup> have provided independent experimental confirmation of a steep (greater than  $T^5$ ) low-temperature behavior. The results for his purest sample ( $r_R \approx 8200$ ), represented in Fig. 4 by squares, are in quite good agreement with this work (solid line) in the liquid-helium temperature range. However, extrapolation uncertainties in Gugan's results ( $\pm 1 \times 10^{-13}$   $\Omega \text{ cm}$ ) are comparable to those of this work and, again, values of  $\rho_T$  retain full signifi-

cance only at higher temperatures (above about  $2\frac{1}{2}$  °K).

Uncertainties in  $\rho_0$  do not enter into a determination of the temperature derivative. An evaluation of the low-temperature data in this manner is limited only by the relative accuracy. In Fig. 5 we compare the low-temperature derivative obtained from our results with that of Gugan. The derivative is taken in such a way that a horizontal line on the graph corresponds to a pure  $T^5$  temperature dependence [a line of positive slope corresponds to a temperature dependence greater than  $T^5$  ( $T^{n>5}$ ) and a negative slope on this plot corresponds to a temperature dependence less than  $T^5$  ( $T^{n<5}$ )].

On the whole there is excellent agreement at low temperatures. Note especially that below about 4 °K Fig. 5 clearly shows a steep temperature dependence ( $T^{n>5}$ ) in both sets of data persisting down to at least  $1\frac{1}{2}$  °K. The only difference occurs in the region below about  $1\frac{1}{2}$  °K; Gugan's results indicate a smaller low-temperature  $T^5$  coefficient (the ordinate) than we observe. However, as indicated by error bars in Fig. 5, the errors at about  $1\frac{1}{2}$  °K are relatively large for both sets of data. At higher temperatures the magnitude of such uncertainties rapidly becomes smaller, at lower temperatures rapidly larger.

For purposes of comparison we have also plotted in Fig. 4 the high-temperature ( $T > 8$  °K) results of Dugdale and Gugan<sup>10</sup> obtained in less-pure potassium samples ( $r_R \approx 1400$ ). Above 20 °K the agreement is good, but differences are significant at lower temperatures. These are most likely a result of impurity scattering effects in their samples. Differences between this work and that of Dugdale and Gugan increase to about 15% of  $\rho_T$  and are not inconsistent with those observed in our

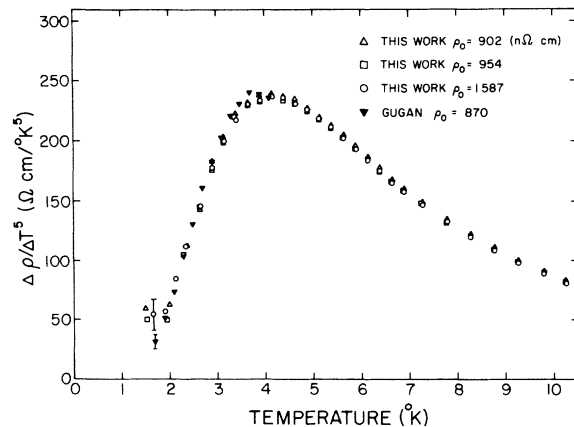


FIG. 5. Temperature derivative of the data; comparison of this work with that of Gugan (Ref. 10). Here  $\Delta\rho/\Delta T^5 \equiv (\rho_i - \rho_j)/(T_i^5 - T_j^5)$  with  $i$  and  $j$  any two adjacent data points; also note that  $n\Omega \text{ cm} \equiv 10^{-9} \Omega \text{ cm}$ .

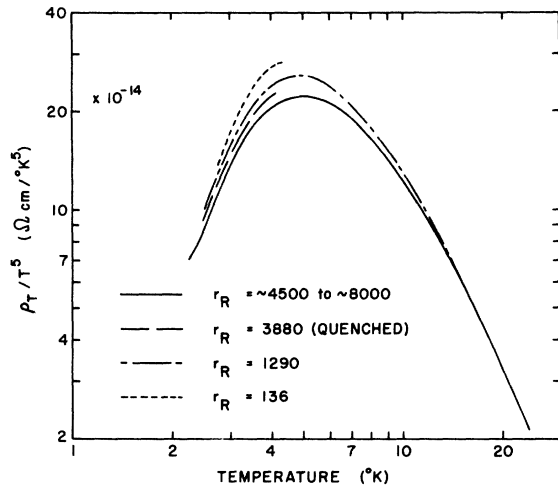


FIG. 6. Comparison of the temperature-dependent part of the resistivity ( $\rho_T \equiv \rho - \rho_0$ ) in pure and impure samples of potassium: solid curve,  $\rho_0 = (0.902, 0.954, \text{ and } 1.587)$  n $\Omega$  cm; long dashes,  $\rho_0 = 1.836$  n $\Omega$  cm; long and short dashes,  $\rho_0 = 5.53$  n $\Omega$  cm; and short dashes,  $\rho_0 = 52.2$  n $\Omega$  cm.

less-pure samples; these data are presented in Sec. III D.

#### D. Low-Purity Results and Deviations from Matthiessen's Rule

Data presented so far are the averaged results of  $\rho_T$  for the purest samples ( $4500 \lesssim r_R \lesssim 8000$ ). Whereas the values of  $\rho_T$  for these purer samples differed by less than the experimental error, a significant purity dependence of  $\rho_T$  was observed in less-pure samples. A study of the purity dependence of  $\rho_T$  in potassium shows two important points; first, the deviations are relatively small (amounting to only  $\sim 30\%$  of  $\rho_T$  in the least-pure sample,  $r_R = 136$ ) and second, the general features of the temperature dependence of  $\rho_T$  in the impure samples is essentially unchanged from that in pure samples.

The results for several such impure samples are compared with the results for the pure samples in Fig. 6. The sample having  $r_R = 3880$  was obtained by quenching one of the high-purity MSA potassium samples; the sample having  $r_R = 1290$  was extruded from 99% nominal purity potassium obtained from Allied Chemical Corporation (the principal impurity being sodium), and the sample having  $r_R = 136$  was an alloy of 0.05 wt% sodium with high-purity MSA potassium (where nominal impurity levels were in the order of 10 ppm).

While undoubtedly Matthiessen's rule is not strictly obeyed at the lowest temperatures even in the most pure specimens, the comparison between the results of pure and impure samples in Fig. 6 indicates that deviations from Matthiessen's rule

are comparatively small in potassium. Neither the magnitude nor the temperature dependence of  $\rho_T$  is seriously effected. This is in contrast to what is observed for some other metals. In particular, there is no evidence for the marked change to an approximate  $T^3$  temperature dependence for  $\rho_T$  that is observed in aluminum when impurity scattering begins to dominate.<sup>11,12</sup> Recently it has been suggested<sup>13,14</sup> that such a  $T^3$  behavior is very general and represents a breakdown of momentum conservation due to high concentrations of chemical impurities in the host metal. Yet no such effect is observed in potassium. For the most-impure potassium sample ( $r_R = 136$ ),  $\rho_T$  at the lowest temperatures (where the dirty limit is approached most closely) exhibits the same rather complicated temperature dependence as is observed in the purest samples. If the temperature dependence of  $\rho_T$  were to be characterized by a  $T^n$  law, then  $n$  would be a rapidly varying function of temperature with values markedly different from 3; see Fig. 6. As shown in Fig. 7, a similar temperature dependence is exhibited by the deviations directly<sup>15</sup> ( $\Delta\rho_T \equiv \rho_T^{\text{impure}} - \rho_T^{\text{pure}}$ ).

#### IV. THEORETICAL COMPARISON AND DISCUSSION

Both the implications of this work as concerns our theoretical understanding of electron-phonon umklapp processes and the details of our theoretical calculations have been previously presented.<sup>1,16</sup> Here we shall tabulate, compare and comment only on the more important aspects of these results.

The theoretical resistivity values<sup>17</sup> are tabulated in Table III and the respective pseudopotentials are listed in Table IV. Above 8  $^\circ\text{K}$  our results for the total resistivity (normal plus umklapp) agree to within 10% with those of Hasegawa,<sup>18</sup> who has calculated the resistivity of potassium at these higher temperatures. The slight disagreement can easily be accounted for in terms of the difference in phonon spectra and integration procedures that were used. More recently, Rice and Sham<sup>19</sup> have calculated the total resistivity of potassium above 2  $^\circ\text{K}$  using a number of different pseudopotentials. To facilitate comparison with the work of Rice and Sham, we have used the same pseudopotentials (except for the Bardeen pseudopotential, where we have used Hasegawa's parameters). Provided a correction factor of  $\frac{2}{3}$  is applied to their resistivity values,<sup>20</sup> the agreement between the two sets of results where they overlap is quite good. Very recently, Kaveh and Wiser<sup>21</sup> have also reported a theoretical evaluation of the low-temperature electrical resistivity of potassium, in which they see a change from  $T^6$  behavior to  $T^5$  behavior at  $T \approx 3$   $^\circ\text{K}$ , in accordance with the experimental data of Ref. 7 (see Fig. 4). Such a result differs

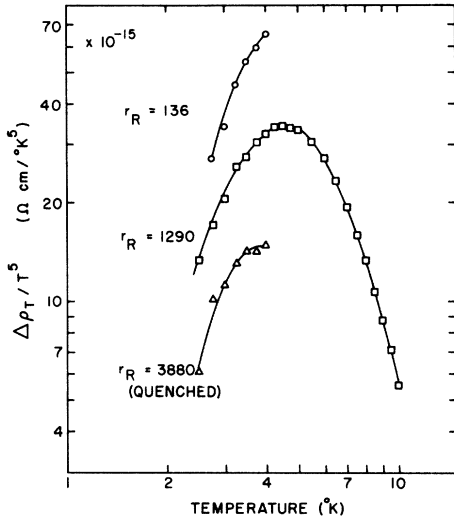


FIG. 7. Temperature dependence of the differences in resistivity between pure and impure samples of potassium,  $\Delta\rho_T \equiv \rho_T^{\text{impure}} - \rho_T^{\text{pure}}$ ;  $\rho_0^{\text{pure}} = 0.902 \text{ n}\Omega \text{ cm}$ ;  $\rho_0^{\text{impure}} = 52.2 \text{ n}\Omega \text{ cm}$  (circles),  $5.53 \text{ n}\Omega \text{ cm}$  (squares), and  $1.836 \text{ n}\Omega \text{ cm}$  (triangles).

markedly from this work, where both our experimental and theoretical results exhibit a rather complicated temperature dependence which ranges from a  $T^4$  temperature dependence at  $T \approx 8 \text{ }^\circ\text{K}$  to

something greater than a  $T^7$  dependence at  $T \approx 3 \text{ }^\circ\text{K}$  (with the  $T^{n>5}$  temperature dependence persisting down to at least  $\sim 1\frac{1}{2} \text{ }^\circ\text{K}$ ).

Figure 8 compares our theoretical results with our experimental data shown previously in Fig. 6. Three points should be emphasized. (i) The agreement between theory and experiment in both temperature dependence and absolute value is quite good. Using no free parameters, the results for the various pseudopotentials straddle the experimental  $\rho_T$  resistivity data over five orders of magnitude. It should also be stressed that the parameters appearing in the pseudopotentials themselves were determined independent of resistivity measurements; in most cases they were fitted to Fermi-surface data deduced from de Haas-van Alphen studies. (ii) The umklapp component is quite sensitive to the precise form of the pseudopotential particularly the magnitude of the pseudopotential in the region corresponding to changes of electron wave number of  $2k_F$  ( $k_F$  being the Fermi wave number). The normal component, on the other hand, depends on the small wave-number region and is nearly independent of pseudopotential form at low temperatures. (iii) A comparison of the umklapp and normal contributions to the resistivity shows clearly that the steep temperature dependence ( $T^{n>5}$ ) of the experimental data below  $4 \text{ }^\circ\text{K}$  is a result of the rapid disappearance of the umklapp component

TABLE III. Electrical resistivity of potassium as calculated using several different pseudopotentials. The total resistivity has been separated into normal and umklapp components. In each case the resistivity has been divided by the fifth power of the temperature, the units being  $10^{-14} \text{ } \Omega \text{ cm}/^\circ\text{K}^5$ .

T (°K)	Bardeen pseudopotential			Lower Lee-Falicov pseudopotential			Ashcroft pseudopotential		
	Normal	Umklapp	Total	Normal	Umklapp	Total	Normal	Umklapp	Total
1.00	3.54	0.009	3.55	3.54	0.004	3.55	3.54	0.006	3.55
1.25	3.57	0.075	3.65	3.58	0.032	3.61	3.57	0.047	3.62
1.50	3.61	0.37	3.98	3.61	0.16	3.77	3.61	0.23	3.84
1.75	3.65	1.21	4.86	3.66	0.51	4.17	3.66	0.68	4.34
2.00	3.71	2.79	6.50	3.72	1.19	4.91	3.72	1.47	5.19
2.25	3.78	5.15	8.93	3.79	2.22	6.01	3.80	2.54	6.34
2.50	3.85	8.1	12.0	3.87	3.53	7.40	3.88	3.76	7.64
2.75	3.94	11.4	15.3	3.96	4.99	8.95	3.97	4.98	8.95
3.00	4.02	14.8	18.8	4.04	6.5	10.5	4.06	6.1	10.2
3.25	4.10	17.9	22.0	4.12	7.9	12.0	4.14	7.1	11.2
3.50	4.16	20.7	24.9	4.19	9.2	13.4	4.20	7.8	12.0
3.75	4.21	23.1	27.3	4.24	10.4	14.6	4.26	8.4	12.6
4.00	4.25	25.0	29.3	4.27	11.3	15.6	4.29	8.7	13.0
4.50	4.26	27.5	31.8	4.28	12.6	16.9	4.31	9.0	13.3
5.00	4.19	28.5	32.7	4.22	13.2	17.4	4.25	8.9	13.2
6.00	3.91	27.5	31.4	3.93	13.0	16.9	3.96	8.0	12.0
8.00	3.11	21.1	24.2	3.12	10.4	13.5	3.15	5.84	8.99
10.00	2.41	15.2	17.6	2.41	7.7	10.1	2.44	4.23	6.67
12.00	1.91	10.9	12.8	1.90	5.73	7.63	1.92	3.16	5.08
14.00	1.54	7.90	9.44	1.53	4.29	5.82	1.55	2.41	3.96
16.00	1.26	5.83	7.09	1.25	3.25	4.50	1.27	1.87	3.14
18.00	1.04	4.37	5.41	1.03	2.49	3.52	1.04	1.46	2.50
20.00	0.85	3.33	4.18	0.84	1.93	2.77	0.85	1.16	2.01

TABLE IV. Pseudopotentials used in calculating the resistivity values of Table III. Potential values are expressed in units of  $\frac{2}{3} E_F$  (where  $E_F$  is the Fermi energy); wave numbers are expressed in units of  $2k_F$  (where  $k_F$  is the Fermi wave number).

Wave number	Bardeen <sup>a</sup>	Lower Lee-Falicov <sup>b</sup>	Ashcroft <sup>c</sup>
0.00	-1.000	-1.000	-1.000
0.05	-0.994	-0.994	-0.994
0.10	-0.976	-0.977	-0.977
0.15	-0.946	-0.948	-0.949
0.20	-0.906	-0.909	-0.911
0.25	-0.857	-0.862	-0.864
0.30	-0.801	-0.806	-0.809
0.35	-0.740	-0.745	-0.748
0.40	-0.675	-0.679	-0.683
0.45	-0.608	-0.610	-0.615
0.50	-0.541	-0.540	-0.544
0.55	-0.476	-0.470	-0.474
0.60	-0.412	-0.402	-0.403
0.65	-0.352	-0.336	-0.334
0.70	-0.296	-0.274	-0.268
0.75	-0.245	-0.217	-0.204
0.80	-0.198	-0.167	-0.143
0.85	-0.157	-0.123	-0.086
0.90	-0.121	-0.087	-0.032
0.95	-0.090	-0.060	+0.018
1.00	-0.064	-0.040	+0.066

<sup>a</sup>J. Bardeen, Phys. Rev. **52**, 688 (1937); apart from the lattice parameter (5.225 Å), the parameters in this model are those given by Hasegawa, Ref. 18.

<sup>b</sup>M. J. G. Lee and L. M. Falicov, Proc. Roy. Soc. (London) **A304**, 319 (1968); we are grateful to L. J. Sham for providing a tabulation of this pseudopotential; for details see Ref. 19.

<sup>c</sup>N. W. Ashcroft, Phys. Letters **23**, 48 (1966).

in this regime. This conclusion is independent of the pseudopotential used. The umklapp contribution prevails over that of normal processes for temperatures above about  $2\frac{1}{2}$  °K, but decreases rapidly for temperatures below this. In the remainder of this section, detailed aspects of each of these points will be considered.

#### A. Experimental-Theoretical Agreement

With respect to the first point, it is worth noting that better than order-of-magnitude agreement between measured and calculated resistivities of pure metals at low temperatures is unusual. In this work, the detailed agreement between theory and experiment is due primarily to several ideal characteristics of potassium. The important features are that there is no complicating effect of a martensitic transformation, the Fermi surface is reasonably spherical, and electrons on this surface are relatively well described by simple one plane-wave states. This greatly facilitates an accurate theoretical determination of the resistivity; the

principle considerations are now an accurate pseudopotential and phonon spectrum.

Not all the approximations of the calculation have been theoretically justified, however. In particular, phonon drag effects have not been taken into account and these may become important at those low temperatures where umklapp processes are frozen out. Yet the agreement with experiment seems not to be appreciably affected by this approximation at temperatures above  $1\frac{1}{2}$  °K.

#### B. Sensitivity of the Umklapp Component to Pseudopotential Form

As regards the second point, the sensitivity of the umklapp component to the precise form of the pseudopotential can be seen easily in the case of the Ashcroft<sup>22</sup> pseudopotential. By varying the single parameter appearing in this pseudopotential (the core radius  $R_{\text{core}}$ ) by as little as 1%, changes of over 20% are produced in the umklapp contribution to the resistivity. These magnified changes in the umklapp component can be used as a very sensitive means of determining this parameter.

To demonstrate this, we have adjusted the core radius in the Ashcroft pseudopotential to obtain a best fit with the experimental resistivity data of Table II<sup>23</sup> (instead of taking  $R_{\text{core}}$  to be fixed by Fermi-surface data as was done for the Ashcroft pseudopotential results given in Table III and Fig. 8 where  $R_{\text{core}}$  was set equal to<sup>22</sup> 1.13 Å). Also, an exchange-correlation corrected form for the dielectric function appearing in the Ashcroft pseudopotential was used.<sup>24</sup> The best fit with this correction applied is presented in Fig. 9 and is obtained using  $R_{\text{core}} = 1.126$  Å. Because of the sensitivity of the umklapp component to minor changes in the pseudopotential, this value could be determined to within a few tenths of a percent. Also it should be noted that this result compares quite favorably with the above value of 1.13 Å obtained from a Fermi-surface fit.<sup>22</sup>

#### C. Disappearance of the Umklapp Component at Low Temperatures

The third point raises a question concerning our qualitative understanding of the role of umklapp processes at low temperatures. We have shown that the umklapp component of the resistivity rapidly becomes smaller than the normal component for temperatures less than  $\sim 2\frac{1}{2}$  °K, but predominates for temperatures above this.<sup>1</sup> Prior to this work, it was generally expected that any rapid decrease in the umklapp component should be readily observable at higher temperatures. Why is it that the umklapp contribution persists to such low temperatures?

In particular, the umklapp component is frozen out with an approximate exponential dependence<sup>25</sup>



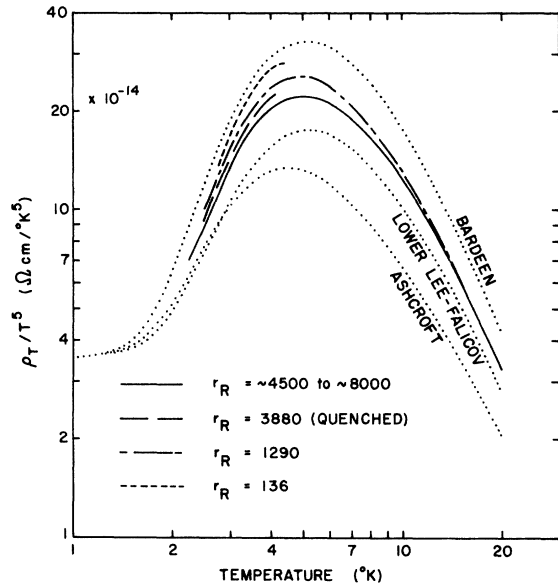


FIG. 8. Comparison of experimental and theoretical results for the electrical resistivity of potassium. Dotted curves represent the theoretical results of Table III; dashed curves represent the experimental results of Fig. 6 (same curve codes as Fig. 6).

$e^{-\theta^*/T}$ , where  $\theta^*$ , the characteristic decay temperature, is approximately 20 °K in the Debye approximation (using a Debye temperature of  $\sim 100$  °K). With such a high expected decay temperature and with the umklapp resistivity contribution scarcely three times larger than the normal contribution above liquid-helium temperatures, why does the umklapp contribution not disappear below the normal component at temperatures significantly higher

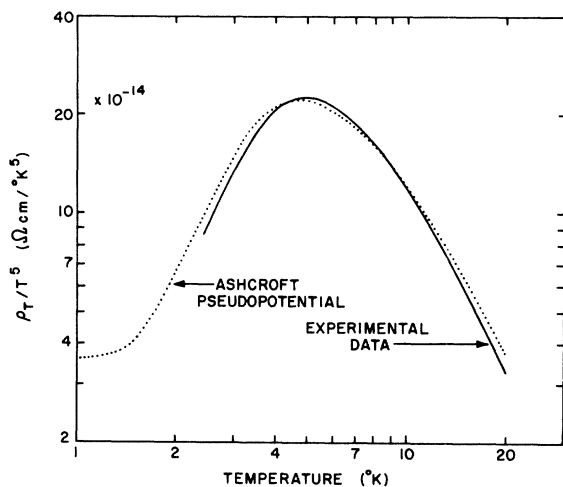


FIG. 9. Fit of the one parameter Ashcroft pseudopotential form (dotted line) to the experimental resistivity data of Table II (solid line).

than  $2\frac{1}{2}$  °K?

The usual answer is that the phonon spectrum of potassium is nondegenerate in the  $\langle 110 \rangle$  directions (the directions of the nearest Bragg planes) and that in these directions the slow shear mode has the low value of 11 °K for  $\theta^*$  (for the fast shear mode,  $\theta^* = 35$  °K, and for the longitudinal mode,  $\theta^* = 48$  °K). With its relatively low decay temperature, the slow shear mode does not freeze out until well after the others; for example, our calculations show the slow shear umklapp contribution at 3 °K to be more than 50 times greater than that from the other two modes. However, this is only part of the answer as to why the umklapp contribution persists to such low temperatures since a  $\theta^*$  of 11 °K applies only to the *least* energetic phonon capable of participating in an umklapp process. Actually, most umklapp scattering events at liquid-helium temperatures involve phonons more energetic than this. An analysis of the umklapp component in the form of  $e^{-\theta^*/T}$  is given in Fig. 10 [using the two theoretical curves (Bardeen and lower Lee-Falicov), which immediately straddle the experimental curves, see Fig. 8]. At liquid-helium temperatures,  $\theta^*$  is in the order of 20 °K or more (in contrast to 11 °K), so we are still without a satisfactory explanation for the umklapp component's low disappearance temperature.

However, there is a second reason for the persistence of the umklapp component to such low temperatures. The umklapp contribution to the resistivity has an inherently slower temperature dependence than that of the normal and this tends to counteract the effect of the exponential freeze out.

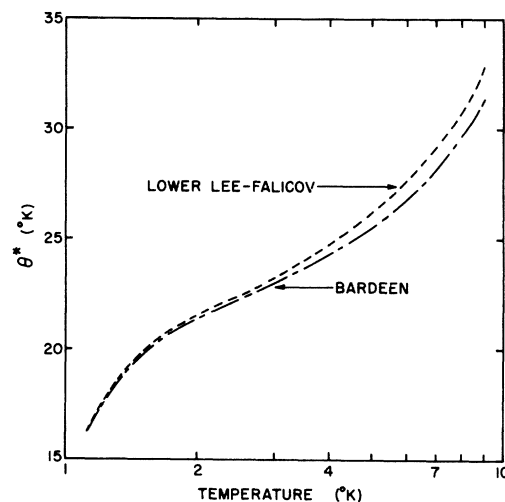


FIG. 10. Temperature dependence of the characteristic temperature  $\theta^*$ .  $\theta^*$  was determined from the umklapp component (see Table III) of the Bardeen and lower Lee-Falicov pseudopotentials, assuming for this component an exponential dependence,  $e^{-\theta^*/T}$ .

More specifically, consider the usual Kohler variational expression for the resistivity due to electron phonon scattering<sup>16,27</sup>:

$$\rho_T \propto \frac{1}{T} \times \int_{\text{Fermi surface}} \int \frac{(\vec{k}' - \vec{k})^2 [(\vec{k}' - \vec{k}) \cdot \hat{\epsilon}] W(|\vec{k}' - \vec{k}|)^2}{(e^{\hbar\omega/k_B T} - 1)(1 - e^{-\hbar\omega/k_B T})} d^2k' d^2k,$$

where  $W$  is the pseudopotential, and  $\vec{k}'$  and  $\vec{k}$  are the electron wave vectors before and after the absorption (or creation) of a phonon of frequency  $\omega$  and polarization vector  $\epsilon$ . If one neglects the phonon distribution factor in the denominator (which is responsible for the freezing out of umklapp processes) and concentrates instead on the numerator, the source of this slower temperature dependence for the umklapp contribution is immediately apparent. Factors involving the change in electron wave vector,  $(\vec{k}' - \vec{k})$ , which scale with temperature in the case of normal processes, remain large and nearly temperature independent for umklapp processes at low temperatures [where  $(\vec{k}' - \vec{k}) \approx \vec{G}$ , a reciprocal-lattice vector]. This difference in temperature dependence of the numerator tends to

balance the effect of the exponential factor in the denominator, delaying until quite low temperatures any rapid decrease of the umklapp component below that of the normal.

In summary, careful measurements of the low-temperature electrical resistivity of potassium are in excellent detailed agreement with a theoretical evaluation of the resistivity due to electron-phonon interaction. In particular, it is found that the umklapp contribution disappears below the normal at a temperature of about  $2\frac{1}{2}^\circ\text{K}$  but plays a dominant role in determining the resistivity of potassium at higher temperatures. Deviations from Matthiessen's rule, while present, are comparatively small and do not appreciably alter the temperature dependence of the resistivity for even the least-pure sample ( $r_R = 136$ ).

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<sup>2</sup>J. W. Ekin and D. K. Wagner, Rev. Sci. Instr. **41**, 1109 (1970).

<sup>3</sup>The precision of this value is about 1%; J. S. Dugdale and D. Guban, Proc. Roy. Soc. (London) **A270**, 186 (1962).

<sup>4</sup>One of the residual resistivities in the figure captions of Ref. 1 should have been labeled  $1.587 \times 10^{-9} \Omega \text{ cm}$  as in Figs. 3 and 5, rather than  $5.531 \times 10^{-9} \Omega \text{ cm}$ .

<sup>5</sup>D. K. C. MacDonald, G. K. White, and S. B. Woods, Proc. Roy. Soc. (London) **A235**, 358 (1956).

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<sup>8</sup>V. S. Tsoi and V. F. Gantmakher, Zh. Eksperim. i Teor. Fiz. **56**, 1232 (1969) [Sov. Phys. JETP **29**, 663 (1969)].

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<sup>11</sup>A. D. Caplin and C. Rizzuto, Proc. Phys. Soc. (London) **3**, L117 (1970).

<sup>12</sup>J. W. Ekin (unpublished). In a separate communication, our observations of deviations from Matthiessen's rule in aluminum will be contrasted with those in potassium and some general implications explored.

<sup>13</sup>I. A. Campbell, A. D. Caplin, and C. Rizzuto, Phys.

Rev. Letters **26**, 239 (1971).

<sup>14</sup>D. L. Mills, Phys. Rev. Letters **26**, 242 (1971).

<sup>15</sup>In this work, a four nearest-neighbor Aitken-Lagrange interpolation scheme was used to interpolate the experimental data to even temperature values so that differences between the resistivity values of different samples could be accurately determined.

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<sup>17</sup>For details, see Ref. 16.

<sup>18</sup>A. Hasegawa, J. Phys. Soc. Japan **19**, 504 (1964).

<sup>19</sup>T. M. Rice and L. J. Sham, Phys. Rev. B **1**, 4546 (1970).

<sup>20</sup>T. M. Rice and L. J. Sham, Phys. Rev. B **4**, 674 (1971).

<sup>21</sup>M. Kaveh and N. Wiser, Phys. Rev. Letters **26**, 635 (1971).

<sup>22</sup>N. W. Ashcroft, Phys. Letters **23**, 48 (1966).

<sup>23</sup>It should be mentioned here that a fit to the low-purity data might be more appropriate than a fit to the high-purity results of Table II at low temperatures. This is due to the assumption of an isotropic relaxation time in the standard trial function used in the calculations (see Refs. 1 or 16). The calculational results would thus be best applicable not to ideally pure potassium, but rather to the case, for instance, where isotropic impurity scattering dominated the resistivity. Such considerations can become important in a metal such as aluminum, see Ref. 12; in potassium, however, the difference between the high- and low-purity results is relatively small.

<sup>24</sup>L. Hedin and B. Lundqvist, J. Phys. C (to be published); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133-8 (1965). The specific form (suggested by Hedin and Lundqvist) is based on a Kohn-Sham local density scheme and is given by  $g(x) = 1 - \gamma(q/2k_F)^2$  with  $\gamma = 1 +$

$[(0.7734 r_s)/(21+r_s)]$ . Here  $g(x)$  is a multiplicative correction to the usual Lindhard dielectric function,  $r_s$  is the electron spacing in Å, and  $q$  is the magnitude of the change in electron wave number. This parametrization of  $\gamma$  was determined from the electron gas compressibility in the long-wavelength limit; it should be reasonably valid for  $q < 2k_F$ , but it is questionable for larger  $q$ . In the

case of potassium,  $\gamma=1.084$ .

<sup>25</sup>See, for example, J. M. Ziman, *Electrons and Photons* (Oxford U.P., Oxford, England, 1960), Chap. 9, pp. 369 and 370; or F. J. Blatt, *Physics of Electronic Conduction in Solids* (McGraw-Hill, New York, 1968), Chap. 7, p. 193.

## Effect of Pressure on the Diffusion of Gold in Lead to 50 kbar\*†

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We have measured the diffusion of gold in lead to pressures of 46 kbar and temperatures of 420 °C using a radioactive-tracer technique. The data were analyzed assuming a single effective mechanism of diffusion with a temperature- and pressure-dependent activation volume. The earlier data on the diffusion of silver in lead by Curtin, Decker, and Vanfleet were also analyzed in a similar manner. The activation energy and activation volume at the melting point and atmospheric pressure are, respectively,  $\Delta H=9.48 \pm 0.30$  kcal per mole,  $\Delta V/V_0=0.28 \pm 0.03$  for Au in Pb;  $\Delta H=14.63 \pm 0.24$  kcal per mole,  $\Delta V/V_0=0.34 \pm 0.04$  for Ag in Pb. Although no definite conclusion as to the specific nature of the diffusion mechanism can be drawn, the results are not inconsistent with an interstitial-substitutional double mechanism.

### I. INTRODUCTION

The diffusion of noble metals in lead has been of interest since the early work of Roberts-Austen<sup>1</sup> and Seith and Keil.<sup>2</sup> It was noted that these materials diffuse in lead at a rate which is several orders of magnitude more rapid than the self-diffusion of lead and that the activation energy for the diffusion of noble metals in lead is very small. The question to be considered is then by what mechanism does this rapid diffusion take place.

Nowick<sup>3</sup> suggested that the high rate of diffusion for gold and silver in lead was due to diffusion along internal surfaces. However, Ascoli<sup>4</sup> and Kidson<sup>5</sup> demonstrated that there is no important contribution to the diffusion of gold in lead from grain boundaries, dislocations, or the crystalline surface for diffusion anneals above 190 °C.

Because of the rapidity of the diffusion, Wagner<sup>6</sup> proposed that gold dissolved in lead interstitially and diffused via an interstitial mechanism. Ascoli and Damask<sup>7</sup> proposed that gold dissolves substitutionally in lead and diffuses by a vacancy mechanism with a strong binding between the gold atoms and the vacancies. Kidson<sup>5</sup> considered both of these models and concluded that neither of them is consistent with the experimental observations. He suggested, along the lines of that proposed by Frank and Turnbull<sup>8</sup> for the diffusion of copper in germanium, that gold dissolved in lead both substitutionally and interstitially and that the interstitial component diffuses very rapidly. His analysis as-

sumes also that the concentration of substitutional gold is much larger than the concentration of interstitial gold. Curtin *et al.*<sup>9</sup> made a similar proposal of a possible double mechanism to interpret their data on the diffusion of silver in lead at high pressures. Dyson, Anthony, and Turnbull<sup>10</sup> concluded that rapid diffusion of copper and silver in lead must be principally due to interstitial diffusion with both substitutional and interstitial noble-metal atoms present.

Measurements of the effect of pressure on these diffusion couples adds another dimension of information which should help to distinguish between the proposed mechanisms. Pressure dependence on self-diffusion in lead was studied by Nachtrieb, Resing, and Rice<sup>11</sup> to 8 kbar and also by Hudson and Hoffman<sup>12</sup> to 33 kbar. The latter results are somewhat clouded by their pressure calibration which is greatly in error at the higher pressures, but from these results we see that the activation volume of self-diffusion in lead is  $0.66 \pm 0.07$  atomic volumes. This value can be considered as typical of diffusion by a vacancy-controlled mechanism. Curtin *et al.*<sup>9</sup> measured the effect of hydrostatic pressure on the diffusion of silver in lead to 40 kbar. Their results indicated a reduction of the activation volume from 0.5 atomic volumes at atmospheric pressure to 0.38 atomic volumes at and above 12 kbar. They felt that this indicated a change from one diffusion mechanism to another as one progressed to higher pressures. Ascoli *et al.*<sup>13</sup> measured the effect of pressure on the dif-