

## Electronic transport in $\text{ReO}_3$ : dc conductivity and Hall effect\*

T. P. Pearsall<sup>†</sup> and C. A. Lee

*Department of Electrical Engineering, Cornell University, Ithaca, New York 14850*

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The dc resistivity and low-field Hall effect of the transition-metal oxide  $\text{ReO}_3$  have been measured as a function of temperature. The samples used were oriented single crystals which were large enough for measurements to be made by a conventional four-point probe method. The samples of  $\text{ReO}_3$  showed metallic conductivity with a resistance ratio  $\rho(300)/\rho(4.2)$  between 50 and 70. At 300 °K resistivity is  $(8.95 \pm 0.03) \times 10^{-6} \Omega \text{ cm}$ , and the Hall coefficient at 300 °K is  $(-3.28 \pm 0.10) \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$ . The experimental results show that  $\text{ReO}_3$  behaves like a simple metal with one free electron per unit cell. A least-squares fitting routine is used to compare the resistivity data to a model involving electron-phonon and electron-electron scattering.

### I. INTRODUCTION

While it has been known for some time that the transition-metal oxide  $\text{ReO}_3$  has metallic conductivity,<sup>1</sup> reports of measured resistivity,<sup>2,3</sup> with the exception of a paper by Phillips and Shanks,<sup>4</sup> have been limited to data taken at only a few temperatures, usually 4.2 and 300 °K. In this paper we report some results of an experimental program to characterize electronic transport in  $\text{ReO}_3$ . The resistivity has been measured from 4.2 to nearly 500 °K. The Hall effect in the low-field limit has been measured from 4.2 to 300 °K and is reported here for the first time. In Sec. III we compare the resistivity data to a model of acoustic-phonon scattering and electron-electron scattering by a least-squares fit. The fitting procedure is used to determine a value of  $\Theta_R$ , the Debye temperature which appears in the acoustic-phonon scattering term. We show that this model cannot be made to fit the data at all points within the experimental error. This failure indicates the need for a better theoretical model. In particular, we feel that the simultaneous processes of electron-electron and electron-phonon scattering lead to a larger resistance than one obtains by simply summing the separate contributions.

### II. EXPERIMENTAL PROCEDURES AND RESULTS

#### A. Sample preparation

The electrical transport properties of  $\text{ReO}_3$  were measured on single-crystal samples grown by chemical vapor transport. The details of crystal growth are reported elsewhere.<sup>5</sup> The growth habit of the  $\text{ReO}_3$  crystals varied with the concentration and type of transport agent. In the case of iodine, we found that a concentration of iodine of  $12 \text{ mg cm}^{-3}$  produced crystals of  $\text{ReO}_3$  with  $\{100\}$  growth faces exposed, while a concentration of  $6 \text{ mg cm}^{-3}$  resulted in  $\{110\}$  faces. The largest products of crystal growth were of  $10\text{-mm}^3$  volume.

Using the growth property described above, we avoided much cutting and polishing in obtaining single crystals of tetragonal geometry whose dimensions were large compared with the resistivity-probe size. We were thus able to overcome the difficulties of uncertain sample geometry and small sample size which have plagued earlier authors.<sup>1-4</sup>

The growth product was checked for impurity content and dislocation density. A spark mass-spectrographic analysis showed that the principal contaminant, calcium, was present in a concentration of 100 ppm. All other impurity concentrations were on the order of 1 ppm. The crystals used in the experiments showed a residual-resistance ratio  $\rho(300)/\rho(4.2)$  between 50 and 70. The dislocation density was measured by Berg-Barrett x-ray topography and by an etch. Both techniques showed a density of less than  $10^4$  lines  $\text{cm}^{-2}$ .

Current contacts to the sample were made by sandwiching the sample between two copper blocks approximately the size of the sample. A gasket of gold tape was put between the polished copper face and the  $\text{ReO}_3$  crystal to achieve a more uniform contact. The four voltage probes were fashioned from 0.2-mm tungsten wire, electropolished to a  $10\text{-}\mu\text{m}$  tip diameter.

A great deal of care was taken in the selection of contact materials. Even though  $\text{ReO}_3$  shows metallic conductivity and even though a four-point probe method was used, contact difficulties did occur. Evaporated contacts proved troublesome because the heat of the evaporant caused decomposition of the  $\text{ReO}_3$  surface. Gallium-indium solder was used to form the current contact but was unsatisfactory. While it seemed to wet the surface uniformly, it alloyed with the  $\text{ReO}_3$  forming a harder compound on various parts of the surface. The contacts which we used gave satisfactory service throughout the course of the experiment. We achieved uniform current streaming and avoided thermal transients which might result from a nonuniform or point-contact current lead.

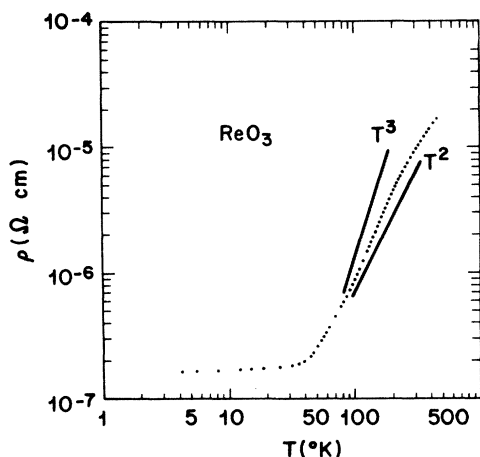


FIG. 1. Resistivity of  $\text{ReO}_3$  as a function of temperature. These data were taken at a current of 100 mA. Some points have been omitted for the sake of clarity where the density of measurements was high.

#### B. dc resistivity

The resistivity of  $\text{ReO}_3$  was measured between 4.2 and 470 °K using a standard four-point probe technique. The voltage-detection instrument was a Keithley model 147 nanovoltmeter which was tested and calibrated at the factory directly before these measurements were made. The current source was variable from  $10^{-4}$  to 10 A, corresponding to current densities in the sample of  $10^{-3}$ – $10^2$   $\text{A cm}^{-2}$ .

The resistivity was measured at approximately 3 °K intervals between 4.2 and 77 °K. Between 77 and 470 °K, resistivity was measured at 50 temperatures spaced evenly over the range. There were several specific temperatures which could be maintained to  $\pm \frac{1}{2}$  °K for 30–40 min (4.2, 42, 50, 63, 77, 140, and 300 °K). At these temperatures the resistivity was measured as a function of current at 40 points covering four orders of magnitude. Otherwise, the resistivity was measured at 100 mA where the signal was strong, but no heating effects were detected. The sample dimensions and probe separation were measured to better than three significant figures using a calibrated microscope.

In Fig. 1 we show the resistivity as a function of temperature for our largest sample, which had a resistance ratio  $\rho(300)/\rho(4.2) = 53$ . At 300 °K,  $\rho = (8.95 \pm 0.03) \times 10^{-6}$   $\Omega \text{ cm}$ . This crystal was oriented with the current in the [100] direction and the voltage probes on the (010) face. Between 470 and 250 °K,  $\rho$  varies as  $T^{1.5}$ . In the neighborhood of 100 °K,  $\rho$  varies as  $T^x$ , where  $3 > x > 2$ . The residual resistance region, which characterizes the resis-

tivity between 4.2 and 30 °K, is the result of impurities and not dislocations as the dislocation density was found to be low. That the resistivity varies faster than  $T^2$  can be seen more clearly if Matthiessen's rule<sup>6</sup> is used to subtract the residual resistivity from the data. The resulting ideal resistivity is plotted in Fig. 2.

Resistivity measurements were made on three other crystals. Two of these crystals were oriented with the current in the [110] direction and the voltage probes on the  $(\bar{1}\bar{1}0)$  face. The remaining crystal was oriented in the  $\langle 100 \rangle$  directions. The resistivity data for these crystals reproduced the results of Fig. 1 within  $\pm 3\%$  over the entire temperature range with the exception, of course, that the value of the residual resistivity varied between  $1.25 \times 10^{-7}$  and  $1.65 \times 10^{-7}$   $\Omega \text{ cm}$  depending upon the purity. Because  $\text{ReO}_3$  is a cubic crystal, no orientational dependence of the conductivity was expected or seen.

#### C. Low-field Hall effect

The Hall effect was measured at the seven temperatures (see Sec. II B) between 4.2 and 300 °K. At each temperature, the Hall effect was measured as a function of current over three orders of magnitude and as a function of field magnitude between 1 and 10 kG. At 4.2 °K, the high-field region where  $\omega_c \tau > 1$  begins at 30 kG, so that all the Hall-effect data correspond to the low-field limit.

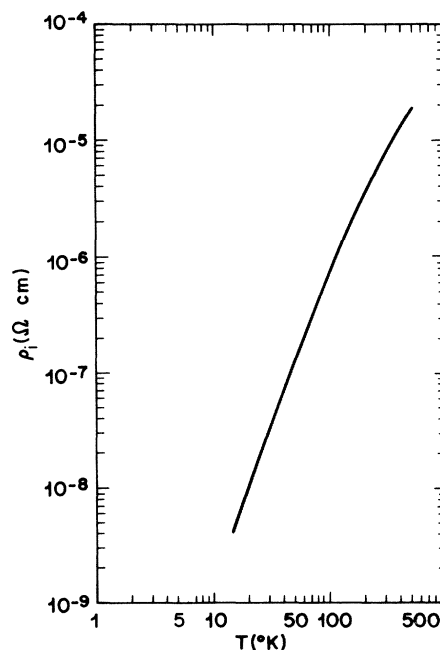


FIG. 2. Ideal resistivity of  $\text{ReO}_3$  as a function of temperature. These data are those in Fig. 1 with the residual resistivity subtracted out.

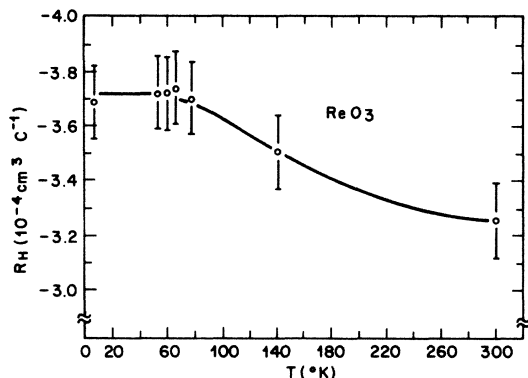


FIG. 3. Low-field Hall constant of  $\text{ReO}_3$  as a function of temperature. This graph is a composite of all the data taken. The solid bars represent two standard deviations about the mean.

Under such experimental conditions, the Hall voltage should be linear with magnetic field and current, and not dependent on crystal orientation. These properties were observed to be the case.

The Hall data were not as accurate as the resistivity data because of fluctuations in the magnetic field. Results were consistent within  $\pm 5\%$  throughout the experimental program (9 months) and this figure is taken as a measure of experimental accuracy.

In Fig. 3, the Hall constant is plotted as a function of temperature. The seven points on this curve represent a composite of all the data taken. The bars correspond to two standard deviations about the mean, which is indicated by the small circles. For completeness, in Fig. 4 we show the results of Hall voltage as a function of current and magnetic field at  $77^\circ\text{K}$ .

The measured Hall constant at  $300^\circ\text{K}$  is  $-3.28 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$ . It increases monotonically to  $-3.72 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$  at  $4.2^\circ\text{K}$ . This sort of behavior is common to many metals.<sup>7</sup> Using one electron per unit cell, the free-electron model gives  $-3.28 \times 10^{-4} \text{ cm}^3 \text{ C}^{-1}$ . The sign of the Hall constant indicates electrons as the predominant carrier, although the band structure of Mattheiss<sup>8</sup> indicates that hole states do play some part in conduction.

### III. ANALYSIS OF THE RESISTIVITY DATA

#### A. Modeling the resistivity

In forming a model for the resistivity, it is necessary to consider the way in which contributions to the resistivity from various scattering mechanisms combine to form the total resistivity. The first-order approximation is to treat the constituent scattering mechanisms as mutually independent. Such an approach is not justified, strictly speaking,

from a theoretical point of view.<sup>9</sup> It implies the existence of a relaxation time for each of the scattering processes which is independent of any of the others. There is not general agreement that this is the case in metals. A proper evaluation of individual scattering mechanisms is best done by analyzing the resistivity in a temperature regime where one kind of scattering predominates. Unfortunately, we were restricted to our temperature range because  $\text{ReO}_3$  becomes chemically unstable at elevated temperatures, and impurities kept us from the advantage of very low temperatures.

The scattering model was picked to be as simple as reason could permit. With a suitably large number of scattering mechanisms, a model could be made to fit the data arbitrarily well. Scattering by acoustic phonons is certainly present, and the general shape of the temperature-resistivity curve suggests the Block-Grüneisen term:

$$\rho_{e-p} = C \left( \frac{T}{\Theta_R} \right)^5 J_5 \left( \frac{\Theta_R}{T} \right), \quad (1)$$

where  $\Theta_R$  is the Debye temperature for acoustic phonons and  $J_5$  is defined as

$$J_5 \left( \frac{\Theta_R}{T} \right) = \int_0^{\Theta_R/T} \frac{Z^5 dZ}{(e^Z - 1)(1 - e^{-Z})}. \quad (2)$$

Because  $\text{ReO}_3$  is a metal, electron-electron Coulomb scattering must be considered. The temperature dependence of this type of scattering is given by Fermi statistics and results in a resistivity which varies at  $T^2$ :

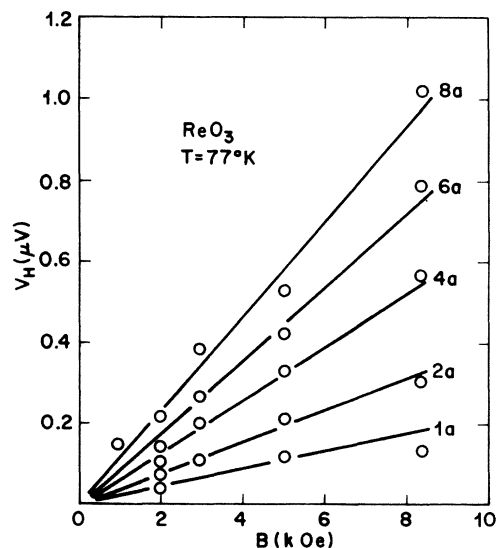


FIG. 4.  $\text{ReO}_3$ : Hall voltage as a function of current and magnetic field at  $77^\circ\text{K}$ .

$$\rho_{e-e} = B \left( \frac{T}{\Theta_R} \right)^2. \quad (3)$$

We considered the "s-d" scattering model of Mott which is often used to explain the resistivity of transition metals.<sup>10</sup> We did not include it in this calculation because it is especially difficult to argue for the existence of *d* bands in  $\text{ReO}_3$ . On the basis of group-theoretical arguments, the conduction bands in  $\text{ReO}_3$  are principally of *p* symmetry. The band structure shows no "flat" or "narrow" bands at the Fermi surface.<sup>8</sup>

Our model of the resistivity was as follows:

$$\rho(T) = A + B \left( \frac{T}{\Theta_R} \right)^2 + C \left( \frac{T}{\Theta_R} \right)^5 J_5 \left( \frac{\Theta_R}{T} \right). \quad (4)$$

The constant term *A* is the residual resistivity.

#### B. Least-squares fit to the data

We fit the resistivity model, Eq. (4), to the data using a least-squares method which minimized the total rms percentage deviation between the model and the data. This procedure determined *A*, *B*, and *C* in Eq. (4) for a given value of  $\Theta_R$ . We repeated this calculation incrementing  $\Theta_R$  by 20 °K from 300 to 900 °K to determine the value of  $\Theta_R$  for the best fit. The results of this fit are

$$A = 0.1680 \mu\Omega \text{ cm},$$

$$B = 13.4 \mu\Omega \text{ cm},$$

$$C = 83.1 \mu\Omega \text{ cm},$$

$$\Theta_R = 720 \text{ }^\circ\text{K}.$$

The convergence of the fit is shown in Fig. 5. Total rms deviation is plotted against  $\Theta_R$ . The fit approximated the data well except for the tempera-

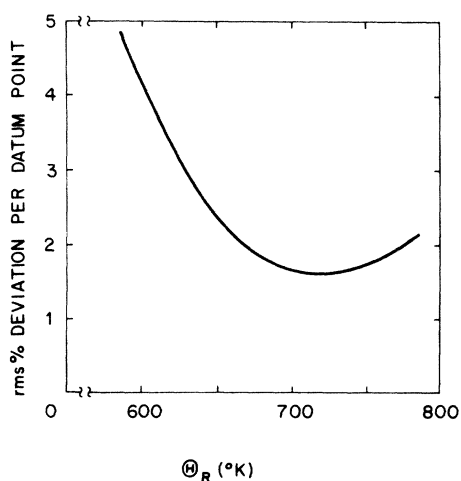


FIG. 5. rms percent deviation per datum point as a function of  $\Theta_R$ . The value  $\Theta_R = 720$  °K gives the least deviation of the fit from all the data.

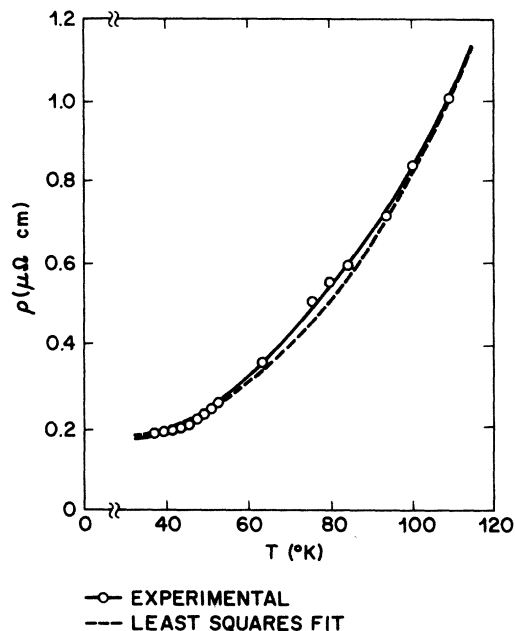


FIG. 6. Comparison between the fitted curve (dashed line) and the data (solid line) for  $\text{ReO}_3$ . The largest deviations between the fit and the data occur in the temperature range shown.

ture range  $50 < T < 100$  °K. A comparison between the data (solid line) and fit (dashed line) is shown in Fig. 6. It can be seen that the calculated dependence is well outside the limit of experimental error ( $\pm 3\%$ ). For example, at 79 °K the percent deviation is nearly 10%. To try to gain insight into the failure of the fit to reproduce the data in this range, we recalculated the fit allowing  $\Theta_R$  to vary throughout the temperature range of the data. It is well known that  $\Theta_D$  as measured by specific heat is usually a function of temperature, and it may be unrealistic to expect one value of  $\Theta_R$  to give a good fit to the resistivity data over the entire range of temperatures. To allow for a variation of  $\Theta_R$  with temperature we fit the same model to a data sample of 35 consecutive points. We changed the sample by discarding the two lowest temperature points and adding two new ones at the upper temperature end, and so forth, until all the data had been used. For each value of  $\Theta_R$  calculated from the data sample we associated the average temperature of that sample. We show the results in Fig. 7.

There are apparently two regimes for  $\Theta_R$ . At temperatures less than 70 °K,  $\Theta_R \cong 450$  °K; and at temperatures greater than 150 °K,  $\Theta_R \cong 800$  °K.

For comparison, Zumsteg and Pearsall<sup>11</sup> have measured the specific heat of  $\text{ReO}_3$  between 1.2 and 4.2 °K and find  $\Theta_D = (460 \pm 10)$  °K. This value is in correspondence with the low-temperature val-

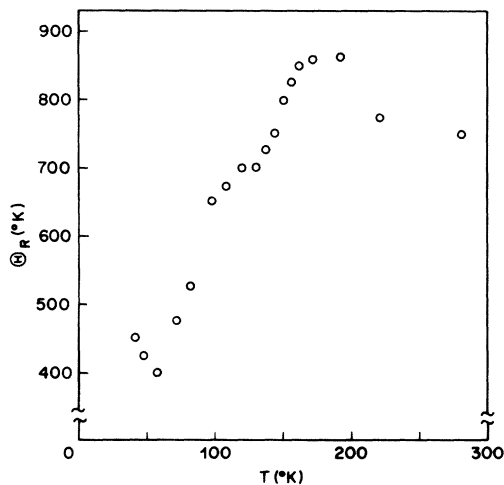


FIG. 7.  $\Theta_R$  as a function of temperature. These points were generated as explained in the text. It shows a low-temperature region where  $\Theta_R \cong 450$  °K and a high-temperature region where  $\Theta_R \cong 800$  °K.

ue found here, and also with the measurements of Vest *et al.*<sup>12</sup> on the closely related compounds  $\text{Na}_x\text{WO}_3$ .

#### IV. DISCUSSION AND CONCLUSIONS

The behavior of the electrical transport properties of  $\text{ReO}_3$  is metallic. The free-electron model with one electron per unit cell gives both the resistivity and Hall effect within 10% of their measured values. This picture of  $\text{ReO}_3$  as a well-behaved metal is also supported by the general features of the band-structure calculation by Mattheiss.<sup>8</sup> Such a conclusion contrasts a commonly held belief that electronic states in the conduction bands of

transition-metal compounds display much of the atomic *d* character of the transition-metal ion. An attempt to fit a model of electron-phonon and electron-electron scattering to the resistivity data failed to reproduce the data within the limits of experimental error. Separation of the scattering into distinct events can be done successfully only if scattering events are relatively rare. That is, the time between collisions must allow the electron distribution to return to equilibrium. In the present case, the fit broke down when the contributions from electron-electron and electron-phonon scattering were of the same magnitude, suggesting that the scattering in this temperature range is more than a simple sum of the individual contributions. That the predominant scattering mechanisms below 70 °K are different from those at 300 °K is illustrated by the variation of  $\Theta_R$  with temperature. Since the low-field Hall coefficient is responsive to changes in electron scattering parameters, the variation of the Hall coefficient with temperature may be related to this behavior of  $\Theta_R$ . The difference between the value of  $\Theta_R$  calculated for all the data ( $\Theta_R = 720$  °K) and  $\Theta_D$  from specific-heat measurements ( $\Theta_D = 460$  °K) is not particularly disturbing. The large variation in values of  $\Theta_R$  required to fit intervals of data, however, suggests that the scattering model is incomplete or incorrect. Changes of this order make it difficult to attach much physical significance to the magnitudes of the various scattering terms. In this context, determining  $\Theta_R$  from the Grüneisen term is not appropriate and the need for a better model is indicated.

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†Present address: Bell Laboratories, Holmdel, N. J. 07733.

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