($T=78°$K):

$$D=-20.6 \text{ kMc/sec}, \quad E=+5.22 \text{ kMc/sec}.$$

The signs are determined by comparing intensities at 2°K and at 4°K. From the tetragonal eigenfunctions, for which m is a good quantum number, our functions are transformed by the matrix[6]

$$\begin{array}{ccc} \pm\frac{5}{2} & \pm\frac{1}{2} & \mp\frac{3}{2} \end{array}$$
$$\begin{bmatrix} 0.990 & -0.134 & 0.035 \\ 0.113 & 0.917 & 0.387 \\ -0.087 & -0.378 & 0.921 \end{bmatrix}$$

The fact that the linear Zeeman effect for H along the three magnetic axes as predicted from these functions agrees with our observations (for $g=2.0$) means that the fourth-order terms in the spin are small within the accuracy of our measurements.

[6] For an explicit description of the evaluation of a spin Hamiltonian, see T. O. Woodruff and W. Känzig, J. Phys. and Chem. Solids **5**, 268 (1958).

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Electrical Conduction in Crystals and Ceramics of WO_3†

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The specific resistivities of crystals and ceramics of WO_3 have been measured from room temperature to 1000°C, and the sign and order of magnitude of the Hall coefficient have been examined near room temperature. From the results for single crystals, it was found that WO_3 behaves like an impurity semiconductor having a saturation region below 740°C and becoming intrinsic above 910°C. The specific resistivity *versus* temperature curve had a distinct anomaly at 740°C suggesting an alteration in the electronic structure at this temperature. Below 740°C, the specific resistivity of ceramic samples showed a remarkable hysteresis phenomenon, probably arising from a cracking of crystallites on heating. The sign of the Hall coefficient was positive at room temperature and its magnitude gave reasonable values for the number and mobility of the carriers. Nonohmic and rectifying characteristics were observed by means of an oscilloscope.

I. INTRODUCTION

ALTHOUGH WO_3 has attracted much notice from the viewpoint of ferroelectricity and antiferroelectricity, the measurement of the dielectric constant and the observation of D-E hysteresis loops are difficult because of its semiconductive property. On the other hand, only a few measurements of electrical conduction have been reported.[1–3] No measurements of electrical conduction in single crystals have been made. In this investigation, the specific resistivities of single crystals and ceramics were measured from room temperature to 1000°C, and the sign and order of magnitude of the Hall coefficient were examined near room temperature.

II. EXPERIMENTAL PROCEDURE

Electrical measurements were performed by the dc method using five probes.[4,5] Silver and platinum alloy-paste electrodes were found to be undesirable owing to their reactive properties with WO_3 at high temperatures and finally, as reported in a previous paper,[3] platinum electrodes pressed on the sample by springs were again used. A sample holder and furnace were devised in flat forms suitable for insertion between the poles of a magnet. Lavite was used as the heat-resistive material.

In Fig. 1 the sample holder is shown, composed of a main part A and a lid B. Two platinum plates C as

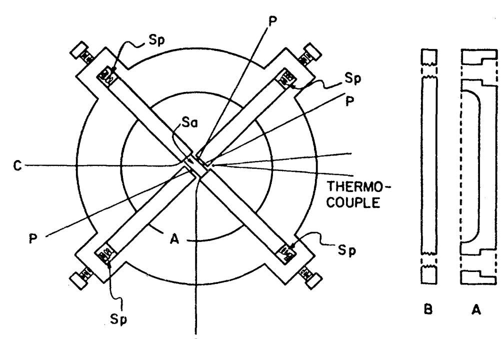

FIG. 1. Sample holder. A: main part; B: lid; Sa: sample; Sp: springs; C: current electrodes; P: potential probes.

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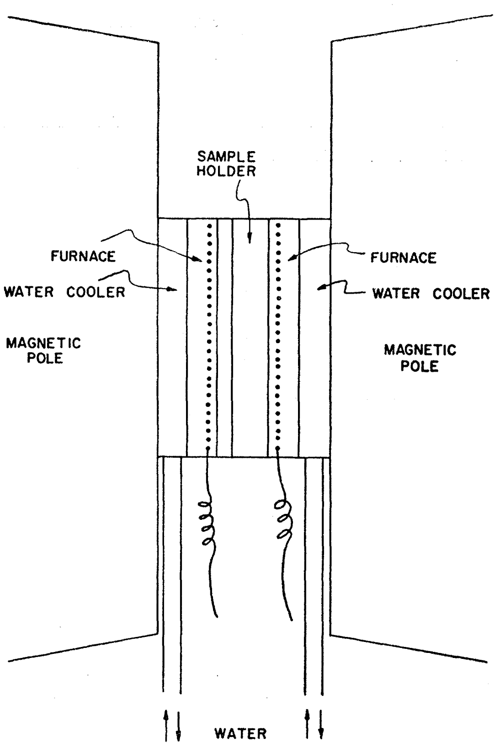


FIG. 2. The sample holder with the furnaces and the water coolers between the magnetic poles.

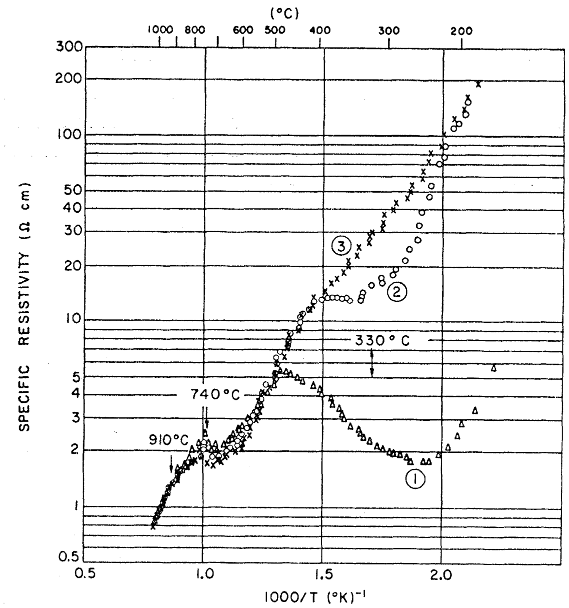


FIG. 4. Specific resistivity of a ceramic sample *vs* temperature. Numbers attached to each curve show the order of measurement.

current electrodes and three platinum knife-edges P as potential probes were pressed onto the sample Sa by four springs Sp kept near room temperature. As shown in Fig. 2, the sample holder, held on each side by a plate furnace having spiral windings and by a spirally wound copper pipe for water-cooling, was fixed in place between the poles of the magnet.

A 12-inch electromagnet (Varian) was used, in which a magnetic field of 10 000 gauss was produced inside a two-inch pole gap by a magnet current of 1.05 amp. A constant current of either 10 ma or 1 ma flowed through the sample from a meter calibrator (Kay Laboratory, Model M 10A-10). The potential difference was measured by a potentiometer (Leeds Northrup K-3 Universal Type, sensitivity 0.1 μv).

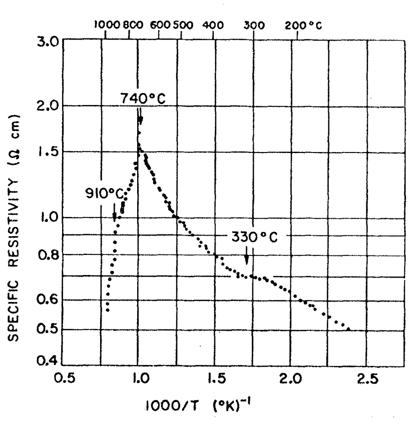


FIG. 3. Specific resistivity of a crystal *vs* temperature.

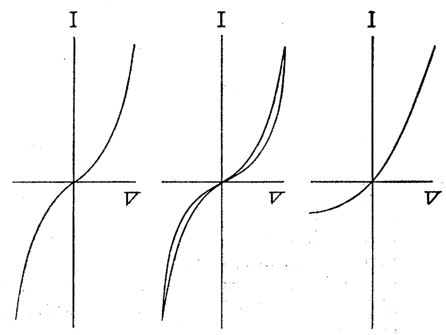
III. RESULTS OF MEASUREMENTS

Although the domain structure of the sample crystals must have been rather complicated due to the unavoidable use of pressed platinum electrodes, the a axis seems to have been nearly aligned in the direction of the current. The pressed platinum electrodes were relatively stable, but had considerably high contact resistance with the sample. An aging effect and a nonohmic property of WO_3, in addition to the high contact resistance between the electrodes and the sample, made measurements of the small Hall voltages inaccurate. For example, at room temperature, $\rho=1.7\times10^{-1}$ ohm cm (specific resistivity) and $R=+6.2$ cm^3/coul (Hall coefficient) were obtained for one crystal (length 4.0×10^{-1} cm, interval between probes on one side 1.6×10^{-1} cm, breadth 7.99×10^{-2} cm, thickness in the direction of magnetic field 6.90×10^{-2} cm; current 10 ma). The positive sign of R agreed with the sign of the thermoelectric power.[3] Using the above values of ρ and R, we find for the number of carriers $n=1/Re=10^{18}/\text{cm}^3$ and for the Hall mobility $\mu=R/\rho=36$ cm^2/sec volt. Such relatively large and low values of n and μ do not seem unreasonable for WO_3. The value of R seemed to decrease slightly with increasing temperature.

The temperature dependence of the specific resistivity of a crystal, measured for a current density of 1 ma/0.794 mm^2, is shown in Fig. 3. This characteristic curve was reproducible in repeated measurements on the same crystal, and the same result was also obtained for different crystals. Figure 3 shows that WO_3 is a typical impurity semiconductor and becomes intrinsic above 910°C, the activation energy being about 1.3 ev. The temperature region below 740°C is a saturation region and the sharp peak at 740°C suggests that the electronic structure must be altered in the phase transition at this temperature.

Figure 4 shows the temperature dependence of the specific resistivity of a ceramic sample for a current density of 1 ma/6.67 mm^2. Numbers attached to each curve show the order of measurement. As is seen in the figure, a hysteresis effect is noticeable for the ceramic sample below 740°C; that is, the specific resistivity increased in each measurement and became nearly stable after the third run. Such a remarkable hysteresis phenomenon could be due to a cracking of crystallites on each heating. If so, the value of the activation energy calculated from the slope of a curve like Curve 3 would not have any important meaning, and it might, therefore, have been accidental that the value of 2.2 ev obtained from the slope of log ρ *versus* $1/T$ near 550°C coincided with the value obtained for the optical absorption edge, as reported in a previous paper.[3] Above 910°C, the same curve was obtained for repeated resistivity measurements on the same ceramic sample, as well as for each measurement on different ceramic samples; and this curve for ceramic samples agreed very well with the curve for single crystals above 910°C. Hence the resistivity curve above 910°C must be intrinsic to WO_3 and independent of the impurity concentration.

The absolute values of the specific resistivity obtained in the present measurements were twenty or thirty times larger than the absolute values of the specific resistivity previously reported.[3] This difference is considered to be due partly to the inaccuracy in the measurement of dimensions of the small sample previously used, and partly to the difference between methods of measurement, the constant voltage method having been used in the previous research.



(a) (b)

FIG. 5. Nonlinear and rectifying characteristics. (a) Symmetrical electrodes. (b) Asymmetrical electrodes.

When a current-voltage characteristic was observed by an oscilloscope for single crystals and ceramic samples, nonlinear and rectifying characteristics were obtained as shown qualitatively in Fig. 5.

IV. CONCLUSIONS

The true electrical conduction in WO_3 can be found only by measurements on single crystals. In order to determine the anisotropy of the specific resistivity of a crystal, it is necessary to obtain an electrode which imposes no mechanical stress upon the crystal. An electrode which is stable and has low contact resistance should be devised in order to measure the Hall voltage more accurately and as a function of temperature.