

Note

Electrical Resistivity of Hexagonal Tungsten Bronzes

The electrical resistivities of single crystals of hexagonal Rb_xWO_3 ($x = 0.26, 0.33$) and $\text{Tl}_{0.33}\text{WO}_3$ have been measured from 4.2 to 300 K both perpendicular and parallel to the c -axis. No anomalies in the resistivities are observed. There is, however, considerable anisotropy with the resistivity in the basal plane being about twice the resistivity perpendicular to the basal plane. The thallium bronze sample shows a superconducting transition in the resistivity at 1.58 K.

No low-temperature resistivity data on hexagonal Tl_xWO_3 seem to have been reported, and data on Rb_xWO_3 exhibit anomalies according to some investigators (1, 2). Early work on the tungsten bronzes (3) showed that selection of homogeneous samples and proper annealing were necessary if one was to obtain reliable and reproducible electrical data. In many cases apparent anomalies vanish in the tungsten bronzes if the samples are selected to be homogeneous and annealed. In this note we present resistivity data on several samples taken after careful attention to homogeneity and annealing procedures.

Single crystals of Rb_xWO_3 and Tl_xWO_3 were prepared by fused salt electrolysis in an electrolytic cell developed by Shanks (4). Rectangular samples having dimensions 1.1 to 2.0 mm² in cross section and 3 to 5 mm long were cut with a diamond saw from large single crystals so that each sample was either parallel or perpendicular to the c -axis. Sample homogeneity was determined by the procedure suggested by Ellerbeck *et al.* (3). Samples were then annealed in a vacuum furnace at 700°C and 10⁻⁶ Torr for 24 hr. The sample homogeneity of each crystal was rechecked and the sample with the best homogeneity for each concentration and for each orientation was selected for measurement of resistivity as a function of tempera-

ture. The average deviation after annealing was usually less than 2%. The values of x were determined by neutron activation analysis.

The electrical resistivities of $\text{Rb}_{0.26}\text{WO}_3$, $\text{Rb}_{0.33}\text{WO}_3$, and $\text{Tl}_{0.33}\text{WO}_3$ were measured as functions of temperature both parallel and perpendicular to the c -axis. Figures 1, 2, and 3 show the temperature and orientation dependence. The electrical resistivities vary with temperature from 4 to 300 K much like those of a normal metal, but the resistivities show considerable anisotropy; resistivities perpendicular to the c -axis are approximately twice the resistivities parallel to the

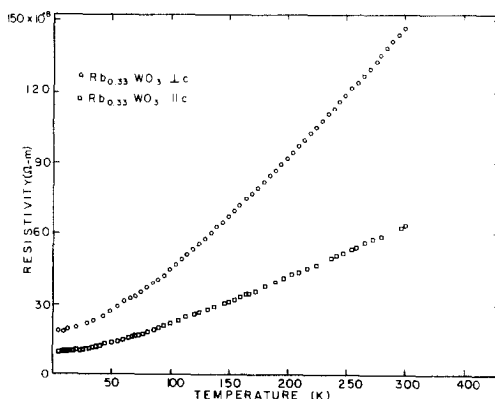


FIG. 1. Electrical resistivity of $\text{Rb}_{0.33}\text{WO}_3$ as a function of temperature parallel and perpendicular to the c -axis.

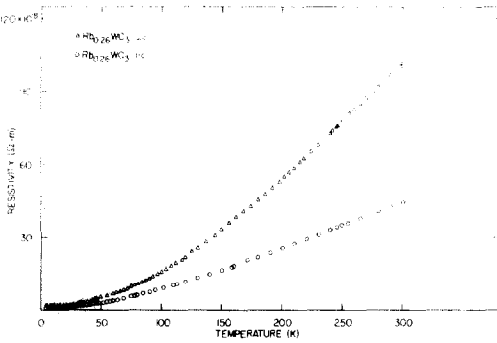


FIG. 2. Electrical resistivity of $\text{Rb}_{0.26}\text{WO}_3$ as a function of temperature parallel and perpendicular to the c -axis.

c -axis. This anisotropy is probably caused by distortion of the WO_6 octahedron in the basal plane. The data show no anomalies in the resistivities as functions of temperature.

If we assume the concentration of free electrons n to be equal to the concentration of Rb (or Tl) atoms, the mobilities of the electrons μ can be found from the equation $\mu = 1/nep$ and the results compared with the mobilities obtained by Sienko and Morehouse (5). The agreement as shown in Fig. 4 is excellent. In both investigations, however, the temperature dependence of the mobility is more nearly $T^{-3/2}$ rather than T^{-1} probably because the measurements were made

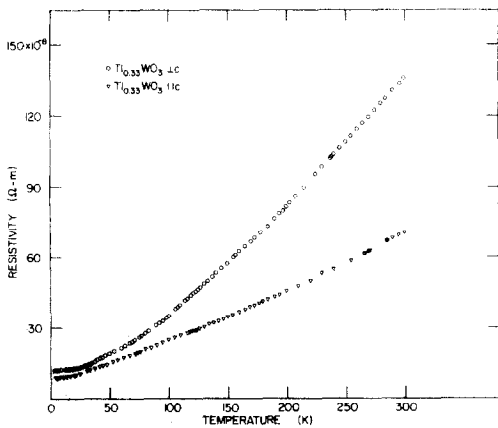


FIG. 3. Electrical resistivity of $\text{Tl}_{0.33}\text{WO}_3$ as a function of temperature parallel and perpendicular to the c -axis.

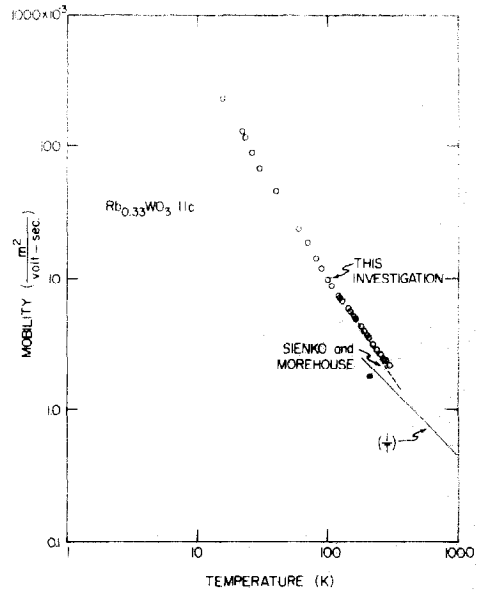


FIG. 4. Electronic mobility of $\text{Rb}_{0.33}\text{WO}_3$ parallel to the c -axis versus temperature compared to the values found by Sienko and Morehouse (5).

at temperatures below the Debye temperature which is about 400 K.

Figure 5 shows the resistivity of $\text{Tl}_{0.33}\text{WO}_3$ from 1.4 to 4.6 K. There is a superconducting transition temperature at 1.58 K in reasonable agreement with the value of 1.5 K found from heat capacity measurement by Bevolo *et al.* (6).

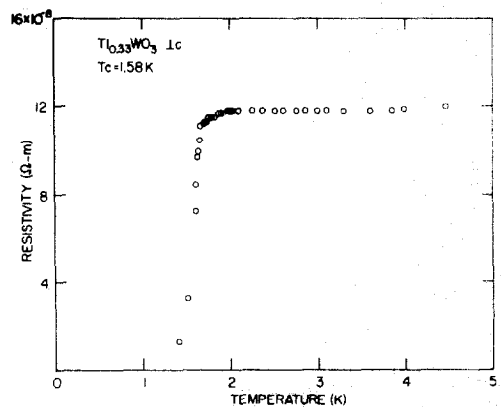


FIG. 5. Resistivity of $\text{Tl}_{0.33}\text{WO}_3$ perpendicular to the c -axis as a function of temperature from 1.4 to 4.6 K. There is a superconducting transition temperature at 1.58 K.

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