Electrical Properties of Niobium Tetrachloride*

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The electrical conductivity of niobium tetrachloride increases sharply by a factor of 10^4-10^5 on heating to 533°K, but the temperature dependence remains typical for a semiconductor.

Nonmetal-to-metal and nonmetal-to-nonmetal transitions occur as the temperature is increased in a number of sulfides and oxides, particularly those to the left-hand side of the periodic table.[1] We report here the first observation of such a transition in a metal halide.

The structure of niobium tetrachloride at room temperature is composed of octahedrally coordinated niobium atoms, each $NbCl_6$ octahedron sharing opposite edges with two similar octahedra to form infinite strings parallel to the *b* axis of the monoclinic unit cell. However, the metal atoms are displaced from their octahedron centers so that the niobium-niobium distances are alternately short and long (3.06 and 3.76 Å) because of direct bonding between pairs of niobium atoms.[2] Similar structures are observed for the tetrachlorides of tantalum, molybdenum (α isomer), and tungsten.[3]

Alternatively, the structure can be considered to be derived from that of VO_2 or NbO_2 by removal of all the metal atoms from every second layer of octahedral sites formed by the close packing of anions. This reduction in cation-to-anion ratio leads to a simpler structure in which only the above one-dimensional edge sharing of octahedra need be considered. This is in contrast to the three-dimensional corner sharing plus edge sharing of octahedra present in VO_2 and NbO_2, in which the infinite strings are linked together by the corner sharing of octahedra.

Single crystals of niobium tetrachloride were prepared as described elsewhere.[4] The electrical conductivity along the *b* axis of the monoclinic cell was measured by dc methods using a four-probe technique.

The electrical conductivity as a function of temperature is shown in Fig. 1. The two sets of points represent values obtained from two different crystals. At 533°K the conductivity increases sharply by a factor of 10^4-10^5, but the temperature dependence remains typical for a semiconductor. The crystals decompose at about 600°K.

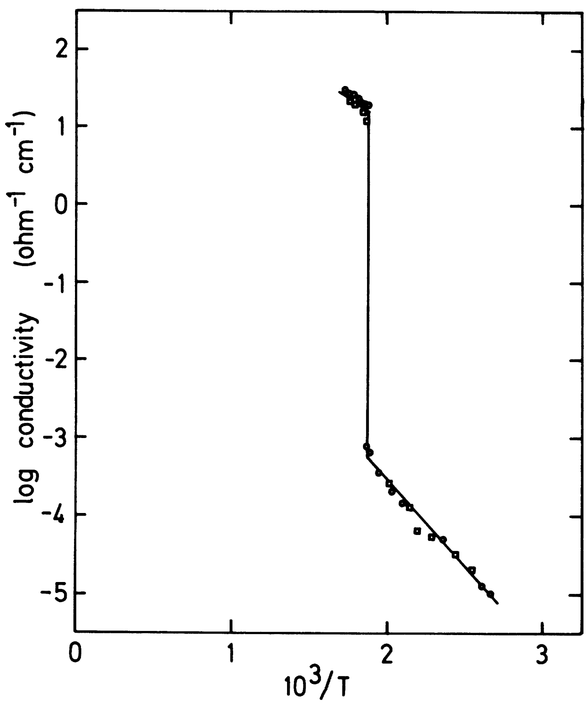

FIG. 1. Electrical conductivity of $NbCl_4$ as a function of temperature.

A similar transition is known for NbO_2, and is associated with a breaking of the bonds between the pairs of metal atoms.[5]

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