PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980 J. PHYS. SOC. JAPAN **49** (1980) SUPPL. A p. 869–872

K0.3MOO3: A NEW ONE DIMENSIONAL CONDUCTOR WITH A PEIERLS TRANSITION

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The optical reflectivity of the blue bronze K₀ $_{MOO_3}$ has been measured on single crystals for photon energies between 0.03 eV and 12 eV using polarized light at temperatures from 10 K to 300 K. It is shown that this compound is a one dimensional metal at 300 K and the metal-semiconductor transition at 180 K is due to a Peierls transition, leading to a gap of about 0.15 eV.

I. Introduction

The blue bronze K₀ MOO₆ is well known for its semiconductor-metal transition at 180° K³[1]. The 300 K crystal structure is side centered monoclinic with the space group C2/m, where corner sharing MOO₆ octahedra form infinite sheets, separated by K ions [1]. Single crystals of this layer type material cleave parallel to the



Fig.(1) Polarized reflectivity of $K_{0.3}$ MoO₃ at 100 K and 300 K

monoclinic b axis and to the [102] direction. The layers are constructed by clusters of 10 distorted MoO octahedra sharing edges and the unit cell contains 2 clusters or 20 formula units. There are three independent Mo sites, Mo(1), Mo(2) and Mo(3). The high temperature metallic conductivity is due to the K ions which donate electrons to the Mo d-states. Only recently the anisotropy of the electrical conductivity in the cleavage plane has been measured, amounting to about one order of magnitude parallel or perpendicular to the b direction above and below 180 K [2]. In the semiconducting, low temperature phase the blue bronze is diamagnetic [3].

II. Experimental Results

The optical reflectivity of single crystals of $K_0^{3}MOO_3$ has been measured for light incident on the cleavage plane, polarized parallel or perpendicular to the b-axis.

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The spectral range was between photon energies of 0.03 eV and 12 eV and the temperature between 10 K and 300 K. The polarized reflectivity at 100 K and 300 K (there is no significant temperature dependence below about 150 K) is shown in Fig.(1) and in the infrared (IR) with an expanded scale in Fig.(2). For photon energies larger than about 2.0 eV there is practically no polarization dependence, but it is obvious that below about 1 eV drastic changes occur. Thus for the polarization (P) // b the material resembles a metal at 300 K, but for P | b it is a semiconductor with an absorption edge near 0.5 eV and many sharp lines for photon energies less than about 0.12 eV. At low temperatures the semiconductor spectrum only sharpens up, but hardly changes qualitatively, whereas the metallic spectrum exhibits a decrease of the reflectivity below about 0.2 eV and two sharp peaks emerge near 0.07 eV. At 300 K the polarized reflectivity spectrum has been extended to photon energies as low as about 1 meV $(10 \text{ cm}^{-1})[4]$ where the reflectivity for P // b has risen to practically 100% and for P \perp b a few more sharp lines are encountered.

The spectra have been analyzed in terms of the dielectric functions ε_1 and ε_2 by means of the Kramers-Kronig relation with suitable standard extrapolations for $\omega \rightarrow 0$ and $\omega \rightarrow \infty$. In Fig.(3) such a spectrum is shown for the real and imaginary part of the dielectric function at 150 K for P // the b-axis in the IR region.

III. Discussion

At 300 K and for P // b the dielectric functions ε_1 and ε_2 tend to very large values (-500 and +600, respectively), confirming the metallic conductivity // to the b axis. ε_1 intersects the abscissa at 1.35 eV which yields the plasma frequency ω' , screened by interband transitions. Either by using a decoupling procedure as described in Ref.[5]



Fig.(2) Polarized IR reflectivity of $K_{0.3}^{MOO}$ at 100 K and 300 K

involving the Kramers-Kronig transformation, or by using a fit with the Drude theory in the far IR, one obtains the unscreened, free carrier plasma frequency ω_p =2.7 eV. Now $\omega_p^2 = 4\pi e^2 N/m^*$, from which one obtains the effective carrier concentration N* = Nm/m* =5.4 \cdot 10^{21} cm^3 The unit cell has $1.2 \cdot 10^{-21} cm^3$ [1], containing 20 formula units, which yields 1 m/m* charges /K ion. The damping factor of the plasmons is Γ = 0.51 eV from which one derives an optical mobility μ = $e/m^*\Gamma$ = 2.3 cm²/Vsec, using m* = m.

At 300 K and for P \perp b the reflectivity even at 1 meV photon energy is only about 70%, thus $\omega_p << 0.03 \text{ eV}$, indicating that in the semiconducting direction the carrier concentration is 4 to 5 orders of magnitude less than in the metallic direction (a much larger anisotropy than obtained in conductivity studies [2]). Thus K_{0.3}MoO₃ can be truely termed a one-dimensional conductor.

In order to assign the optical transitions to the electronic structure we start from an electronic level scheme proposed by Dickens and Neild [6]. Since the Mo-Mo distance in this compound is too large to form a 4d-band via direct overlap, a covalent model is more appropriate and overlap is mediated through the oxygen ions. In the left hand side of Fig.(4) the levels of one Mo and three oxygen are shown where the numbers in brackets signify the number of levels. In an ${\rm MoO}_{\rm 6}$ octahedron the 5p, 5s and ${\rm 4de}_{\rm q}$ orbitals of the Mo mix with 6 sp hybrid orbitals of the O to give 6 bonding σ and 6 antibonding σ^* molecular orbitals. The Mo $4dt_{2g}$ orbitals combine with 3 0 per octahedron to form bonding π and antibonding π^* bands. 3 0 p π orbitals per octahedron form non-bonding levels. The bonding σ , π and the nonbonding $p\pi$ oxygen levels are occupied and form together the valence band. The σ^* and the π^* levels form the conduction band. The density of states is sketched for crystallographic directions // and \perp to the b-axis at temperatures above and below the phase transition at 180 K. Where we have to assume the density of states independent of the direction in the crystal a three dimensional form « \sqrt{E} has been assumed, otherwise a one dimensional form $\propto 1/\sqrt{E}$. X-ray fine structure analysis has revealed [7] that the three different Mo sites are partially occupied to various degrees, the sum of the electrons being equal to 1 electron per K ion, which thus has donated its electron to the conduction band, the empty K level not being identified in the spectrum. Looking now at the 300 K metallic b direction we expect two pronounced transitions, mainly from the π and $p\pi$ valence states to empty π^* and σ^* (mostly de character) which we assign to peaks at 3.7 eV and 4.5 eV in Fig. (1). These transitions can also be found in pure MoO, [6]. Further we expect at about 0.8 eV a transition from the occupied part of the π^* band to the empty σ^* band, and indeed we find a shoulder at this energy in Fig.(1) (much more pronounced in the not shown ε spectrum). The free carriers in the π^* band produce the plasma edge of the reflectivity at about 1.5 eV and the metallic character in the b direction. Perpendicular to b, in the [102] direction, we have to assume the π^* states as localized, since the collective plasma oscillation is absent. The three different Mo sites will have three levels separated in energy, occupied levels below $E_{\rm p}$ and



Fig.(3) Dielectric functions for P // b at 150 K in the IR

empty above. These levels may have a fine structure which will be discussed below. Again we expect transitions from the valence band to the empty localized states above E_F at the same energies as for the metallic direction, the localized nature of the final states not becoming obvious since we start from a broad band. We will have a strong transition at about 0.8 eV (see Fig.(1)) terminating at a σ^* band, since the localized nature of the initial π^* states is not visible. Finally we must have transitions from occupied, localized π^* levels to empty π^* levels in the IR (Fig.(2)). Here the highest energy triplet at 0.12 eV would correspond to transitions from the lowest π^* state

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Fig.(4) Energy level scheme of $K_{0,3}MOO_3$

to the three empty π^* states and a further triplet at 0.08 eV can be discerned at low temperature. Excited states of these localized levels corresponding to a hydrogen sequence $(1/n^2)-1$ have been identified at 0.0434 eV (n=2), 0.0521 eV (n=3), 0.0552 eV (n=4) and 0.0564 eV (n=5), see Fig.(2).

A one dimensional metal must undergo a Peierls transition at some temperature, accompanied by a, possibly small, lattice distortion. Due to a pairing of atoms (charge density wave) a gap will form and at low temperatures the material will be a semiconductor. On the right hand side of Fig.(4) this gap is shown, separating two π^* subbands. The fact that we have a full-and an empty subband is indicated by the absence of sharp lines in Fig.(3) at 150 K, by a drop in ε_{2} at about

0.15 eV, indicating the Peierls gap, and the appearance of phonon lines at 0.064 eV and 0.072 eV. Two TO phonons are indeed expected for the C2/m structure.

In conclusion the optical measurements have shown for the first time that $K_{0,3}MOO_3$ is a one dimensional conductor at room temperature. We identify the semiconductor-metal transition at 180 K with a Peierls transition, creating a gap of about 0.15 eV in the π^* band.

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