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CRITICAL PRESSURE FOR THE METAL-SEMICONDUCTOR TRANSITION IN V_2O_3

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The metal-semiconductor transition in V_2O_3 is found to be suppressed above 26 kbar which corresponds to a volume compression of 0.9%. The temperature and volume dependence of the resistivity of the metallic phase is consistent with semimetallic behavior and a pressure-dependent band overlap. We propose that the metal-semiconductor transition in V_2O_3 may be driven by the Coulomb attraction between electrons and holes and may be an example of an excitonic phase change.

V_2O_3 belongs to the small class of materials which undergo a metal-semiconductor transition with decreasing temperature at room pressure.[1,2] By applying pressure in excess of 26 kbar we have suppressed the low-temperature insulating phase and have studied the resistivity of the metallic phase down to 2°K. We find that both the temperature and volume dependence of the resistivity are very different from that of ordinary metals and may be explained if we assume a semimetallic state for V_2O_3 with an overlap varying as a function of pressure. These results do not support the current theoretical models[2] for the metal-semiconductor transition and lead us to propose that the metal-semiconductor transition in V_2O_3 may be an excitonic phase change.

The experiments were done in a high-pressure cryostat using a girdle die with AgCl as the pressure-transmitting medium.[3,4] The pressure calibration at room temperature was relative to the 25.4-kbar transition in a Bi wire mounted in the die, and it was assumed that at constant applied load the pressure was independent of temperature. The samples were single crystals grown by flame fusion.[5] The transition temperature of the large crystals at 1 atm was $T_0 = 176$ and 164 K on warming and cooling, respectively. However, T_0 in another sample composed of smaller chips (sample 2) was $T_0 = 119$ and 95 K. X-ray Guinier powder patterns showed that both samples had the α-corundum structure with $a = 4.948 \pm 0.002$ Å and $c = 13.97 \pm 0.01$ Å. This supports the suggestion that earlier reports of $T_0 \approx 100$ K in samples of vanadium oxide may be attributable to nonstoichiometric or impure V_2O_3.[2]

The results of T_0 vs P are shown in Fig. 1 and ρ vs T at $P > P_c$ in Fig. 2. The results were normalized to the absolute resistivities determined at 1 atm of 540 ± 100 $\mu\Omega$ cm (sample 1) and 325 ± 60 $\mu\Omega$ cm (sample 2). As the pressure was quasihydrostatic, the validity of the results was demonstrated by their reproducibility and insensitivity to the orientation of the crystals in the pressure cell.[6] Also, the pressure and temperature coefficients are in reasonable agreement with those determined under true hydrostatic pressure: $d\ln\rho/dT = +0.0018 \pm 0.0001$ K^{-1} (sample 1), $+0.0012 \pm 0.002$ (sample 2), and $+0.0023$ (hydrostatic)[7]; $d\ln\rho/dP = -0.010 \pm 0.002$ kbar^{-1} (sample 1), -0.005 ± 0.001 (sample 2), -0.005 and -0.006 (hydrostatic – ρ_{33} and ρ_{11}, respectively).[7] These coefficients refer to $T = 298$ K and $P \approx 25$ kbar except for the hydrostatic temperature coefficient, where $P = 1$ atm. Repeated cycling through the transition does lead to some sample deterioration as T_0 determined at 1 atm after the pressure experiment is ≈10 K lower (Fig. 1).

The Clausius-Clapeyron equation relates the pressure dependence of a first-order transition to the entropy and volume changes at the transi-

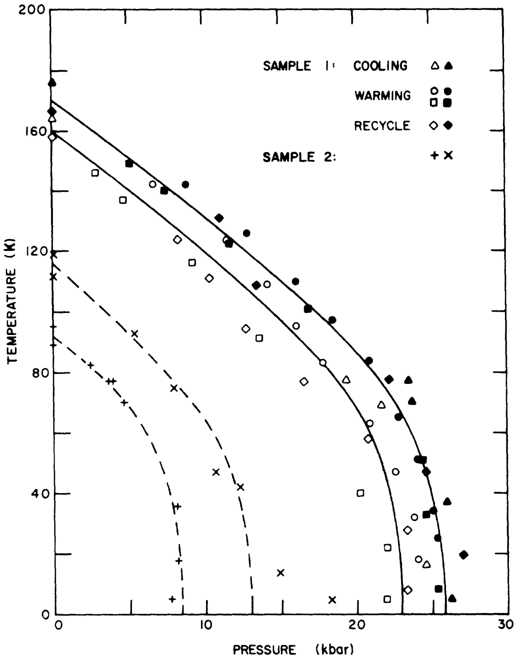

FIG. 1. Metal-semiconductor transition temperature versus pressure for V_2O_3. The solid lines are smooth curves drawn through the data using the initial slope given in J. Feinlieb and W. Paul, Phys. Rev. 155, 841 (1967); I. G. Austin, Phil. Mag. 7, 961 (1962). Only the general trend is given for sample 2 as insufficient material was available. The closed and open symbols refer to increasing and decreasing temperature (pressure), respectively.

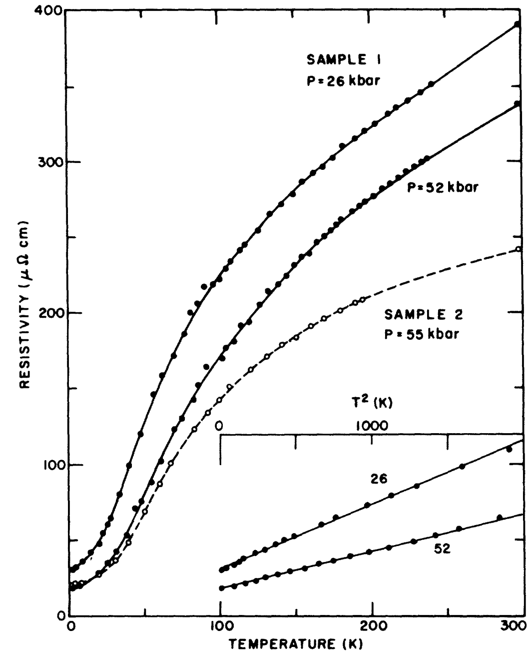

FIG. 2. Resistivity versus temperature in the metallic phase of V_2O_3 above the critical pressure. The inset shows the T^2 dependence of the resistivity at low temperatures.

tion: $dT_0/dP=\Delta V/\Delta S$. It would be desirable to determine the variation of ΔS and ΔV separately along the phase boundary. However, even at 1 atm there are uncertainties in the determination of ΔV, and values ranging from 0.6[8,9] to 3.5%[10] have been reported in the literature, whereas a value of 2.3% is obtained from the direct measurement of $\Delta S=4.08$ eu[11] and $dT_0/dP=-3.78$ K/kbar.[7] Further, in the metallic phase the a and c lattice parameters change oppositely under pressure and may cause ΔV to change substantially under pressure.[12] If we assume that ΔV is constant, then the pressure dependence of the transition temperature can be fit by taking combinations of lattice and electronic terms in ΔS. All of these fits however predict that at 1 atm the extrapolated specific heat of the insulating phase should lie considerably below the metallic specific heat contrary to the data of Anderson[11] and Cook.[13] In view of these uncertainties it would be premature to attempt a detailed fit to the transition temperature curve at present. We can say, however, that the data are consistent with the transition remaining first order down to 0 K and with $\Delta S\to 0$ as $T\to 0$ K. The critical pressure is 25.8 ± 1.0 kbar and 23.0 ± 1.0 kbar for increasing and decreasing pressure corresponding to a volume compression of ≈0.9%.[14]

The resistivity of the metallic phase as a function of temperature is shown in Fig. 2. The temperature dependence of the resistivity is markedly different from a usual metal. At low temperatures the resistance rises quadratically with temperature and the inset in Fig. 2 shows a plot of ρ vs T^2 for $T\lesssim 45°\text{K}$. Writing $\rho-\rho_0=BT^2$ we find very large values for the coefficient B. In sample 1, $B=0.042$ μΩ cm K^{-2} at $P=26$ kbar and $B=0.025$ μΩ cm K^2 at $P=52$ kbar. These values are ~10^3 times the typical values of B for the transition metals but comparable with that found in α-Mn ($B=0.14$ μΩ cm K^{-2}).[15] At higher temperatures the resistance rises much more slowly. This suggests that there is strong electron-electron (or electron-hole) scattering and an effective degeneracy temperature of approximately 100 K. The room-temperature resistance is strongly volume dependent with $d\ln\rho/d\ln V=42$ and 20 at $P=1$ atm and 25 kbar, respectively, along the a axis,[7] and this is much larger than the typical value for transition metals of

≈3. Finally, the magnitude of the resistivity is much higher than in transition metals.

The behavior of the resistivity bears a striking resemblance to that observed in Sr and Yb under pressure.[4] In Sr, resistivity measurements on the purest sample indicate that the band overlap shrinks but never actually goes through zero. For pressures in the range 30-40 kbar, the temperature dependence of the resistivity is similar with a large T^2 term at low temperatures which saturates around 100°K. The magnitude of the resistivity is similar and the volume dependence is anomalously large but opposite in sign from V_2O_3 (Sr, $d\ln\rho/d\ln V = -10$ at 30 kbar). The resistivity of Yb is similar for pressures in the neighborhood of 9 kbar.

Adler and Brooks[16] have proposed a model for a metal-semiconductor transition driven by a crystalline distortion. This model, which is a band generalization of the Jahn-Teller effect, has been applied in the limit of narrow half-filled bands to the transition in V_2O_3 by Adler, Feinleib, Brooks, and Paul.[17] In this limit, the energy gained by the distortion is linear in the strain so that the crystal will always be distorted at 0 K independent of the strength of electron-electron interaction and the electronic entropy of the metallic state is constant. In the wide-band limit the energy gained by the distortion is quadratic in the strain so the crystal may or may not distort at 0 K, and there will be a critical bandwidth for a distortion to occur. Since a volume change of less than 0.9% is sufficient to suppress the distortion at 0 K, it would appear that in the crystalline distortion model the bandwidth of V_2O_3 must be very close to the critical value. A major prediction of the Adler and Brooks model[16] in the narrow-band limit is that the ratio of the energy gap in the insulating phase to the transition temperature E_{g_0}/kT_0 should be constant under the application of an external variable such as pressure. The results of the resistivity and optical measurements at low pressures of Feinlieb and Paul[7] appear to confirm this. There are however large uncertainties in the optical determination of the gap. It is clear that if the transition remains first order as $T_0 \to 0$, as indeed appears to be the case, the ratio E_{g_0}/kT_0 will diverge to infinity as $T_0 \to 0$. This ratio therefore must vary very rapidly as a function of lattice parameter. Finally their model does not predict the anomalous resistivity which we have observed in the metallic phase.

Mott has proposed a model for the vanadium oxides in which the metallic state is composed of a gas of n- and p-type small polarons.[18] The polaron coupling constant is large and the binding energy of a polaron is more than half the Mott-Hubbard correlation energy gap from the Coulomb interactions. At low temperatures the polarons will form a degenerate gas with a weak Coulomb interaction. In this model electron-hole scattering dominates in the resistivity, and this is in agreement with the observed T^2 term in the resitivity. However, in Mott's model one might expect magnetic ordering due to Mott-Hubbard correlations or possibly superconductivity because of the large electron-phonon interaction. No anomalies, which would accompany such phase transitions, were observed in the resistivity of the metallic phase down to ≈2°K. It is not clear if this model can account for the large volume dependence of the resistivity.

An alternative model which we should like to propose is a two (or more) band model[19] with a fairly small overlap in the metallic phase. A symmetry analysis of the band structure of metallic V_2O_3 along the c axis[20] is consistent with this model. At high pressure the overlap will be large enough to stabilize the metallic phase, and the resistance will be dominated by electron-hole scattering due to the Coulomb and electron-phonon interactions. As the pressure drops, the overlap decreases, and the transition to the insulating phase will be driven by the Coulomb attraction between electrons and holes. This transition would be an example of the excitonic phase transition discussed by a number of authors.[21] In the presence of strong electron-phonon coupling the excitonic phase will be characterized by a lattice distortion[21] as is observed. We have no explanation for the very weak antiferromagnetism which is also seen in the insulating phase. In V_2O_3 the energy gaps which open up in the insulating phase are not small perturbations on the electronic structure, and the transition must be a strong-coupling version of the excitonic transition. This is consistent with the observation of a large first-order transition rather than a second-order transition.[22]

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SUBMILLIMETER CYCLOTRON RESONANCE IN TELLURIUM

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We report cyclotron resonance measurements in high-purity tellurium at submillimeter wavelength confirming that the isoenergetic surfaces involved at low magnetic fields are ellipsoids grouped by pairs symmetrical with respect to the Brillouin-zone corners. We explain the violent perturbation of the Landau levels at high magnetic field by assuming the ellipsoids to coalesce into dumb-bell surfaces, as for the Shubnikov–de Haas effect.

A recent band-structure calculation[1] for tellurium predicts near the corner M of the Brillouin zone a valence band of the shape depicted in Fig. 1(a). Near the maximum of the valence band the isoenergetic surfaces are ellipsoids, of revolution around the trigonal axis c, centered in N and N' symmetrical with respect to M [surfaces S_{E_1} in Fig. 1(b)]. When the energy increases up to E_S these ellipsoids coalesce into a "dumb-bell" shaped surface (surface S_{E_2}). Such a model, with the assumption of a constant quadratic dependence of E with $k \perp c$, allowed the interpretation of Shubnikov–de Haas results.[2,3] Previous cyclotron resonance experiments at magnetic fields lower than ours[4-6] showed ellipsoidal isoenergetic surfaces

$$E(k) = \hbar^2\left[\frac{k_x^2 + k_y^2}{2m_1} + \frac{k_z^2}{2m_3}\right],$$

with

$$m_1 = (0.119 \pm 0.006)m_0, \quad m_3 = (0.25 \pm 0.01)m_0$$

(Ref. 4);

$$m_1 = (0.109 \pm 0.003)m_0, \quad m_3 = (0.264 \pm 0.008)m_0$$

(Ref. 5).

Our experiment has been realized with high-