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Effect of High Pressure on the Electronic Properties of VO_2*

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Samples of VO_2 were prepared at 50 kbar and 800°C in a belt apparatus. The products were then annealed in evacuated silica tubes at 800°C for 1 week. The X-ray diffraction patterns of these samples, before and after annealing, were compared with polycrystalline and ground single crystals of VO_2. In addition, the resistivity above and below 67°C was measured. The effect of high pressure on the metal–semiconducting transition is discussed in terms of the relative positions of the $t_{\parallel}$ and π^* bands.
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Introduction

Vanadium (IV) oxide, VO_2, is known to undergo a semiconductor-to-metal transition at 340 K (*1*) which is accompanied by a crystallographic change from monoclinic (*2, 3*) to tetragonal symmetry (*4*). The semiconductor–metal transition observed for VO_2 has resulted in detailed studies on this compound (*5–7*). Below 340 K, VO_2 has been reported to show a distorted rutile-type structure with monoclinic symmetry ($P2_1/C$). The metal atoms are located within the strings of VO_6 octahedra occurring as doublets, as in the MoO_2 structure type. Heckingbottom and Linnett (*3*) have indicated that there is little evidence for direct metal–metal bonding along these chains.

However, Goodenough (*5*) has proposed and Rogers (*8*) has utilized a band model in which the *d*-electrons of t_{2g} symmetry are delocalized by strong metal–metal interactions ($t_{\parallel}$ band) and strong covalent mixing with oxygen p_{π} orbitals (π^* band). Above the transition temperature these bands overlap and are each partially filled giving rise to metallic conductivity. The compound is tetragonal ($P4_2/mnm$) and all the V–V distances are equal (2.87 Å). Below the transition temperature, the formation of V–V pairs along the tetragonal *c*-axis and consequent doubling of the crystallographic unit cell (*9*) splits the $t_{\parallel}$ band in two. The resulting lower band becomes filled and lies below the bottom of the π^* band (arising from covalent mixing) which becomes empty (*5*). Hence semiconducting behavior is observed. The splitting of the bands proposed by Goodenough is shown in Fig. 1.

In this study, the effect of pressure on the crystallographic transformation and electronic properties of VO_2 will be determined.

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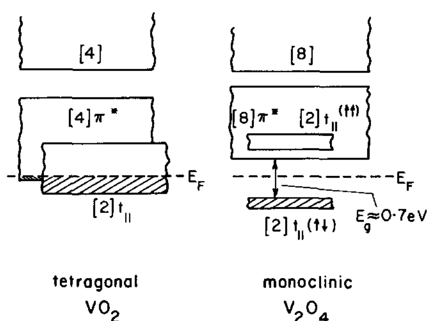

FIG. 1. Electron Energy diagram. Band structure of VO_2 as proposed by Goodenough (*5*).

Any observed changes will be correlated with the width of the π^* band as well as the degree of splitting of the remaining $t_{\|}$ band.

Experimental Section

Preparation

All vanadium compounds were prepared from reagent grade ammonium metavanadate which was purified by recrystallization as described by Brauer (*10*). The purified ammonium metavanadate was heated in a covered platinum crucible for 4 days at 450°C to yield pure V_2O_5.

The V_2O_5 was reduced to V_2O_3 in an Ar/H_2 (85 : 15) atmosphere at 1000°C. Polycrystalline VO_2 was obtained by reacting an equimolar mixture of V_2O_5 and V_2O_3 in an evacuated silica tube at 800°C for 72 hr. After cooling, the tube was shaken for 1 hr and reheated to 800°C for 24 hr.

Single crystals of VO_2 were prepared by chemical vapor transport using tellurium(IV) chloride as the transport agent. A concentration of 2.0 mg/cm^3 of tellurium(IV) chloride was used. The temperature of the charge zone was 1000°C and the growth zone was maintained at 900°C. Crystal growth was allowed to proceed for 1 week. All products were then removed from the transport tube and washed immediately with dilute hydrochloric acid; the crystals were then washed with distilled water and dried.

Samples of polycrystalline VO_2 powder were heated in Pyrex capsules in a belt apparatus of the type described by Hall (*11*) at 50 kbar and 800°C for 1 hr. Some of these high-pressure samples were annealed in evacuated silica tubes at 800°C for periods up to 2 weeks.

X-Ray Analysis

Powder diffraction patterns were obtained with a Norelco diffractometer using monochromatic high-intensity Cu$K\alpha_1$ radiation (λ = 1.5405 Å). Fast scans of 1° 2θ/min were taken to determine the phases present in each sample. Lattice parameters were determined from slow scans of 1/4° 2θ/min with a chart speed of 30 in./hr. The parameters were refined by a least-square fit of the data from high-angle reflections ($2\theta > 50°$) corrected relative to an internal Pt standard. Slow-scanned peaks were digitized on an H.P.7225A plotter and were integrated by the Gaussian method to determine their areas from which the relative intensities of the various reflections were obtained.

Single crystals, high-pressure VO_2 samples, and annealed high-pressure preparations of VO_2 were also X-rayed with CrK_α radiation (λ = 2.2896 Å) using a Gandolfi camera. The patterns obtained were compared with those from the ground samples in order to confirm that no change occurred as a result of the grinding process.

Density and Electrical Measurements

The density of a high-pressure VO_2 sample was determined using the hydrostatic technique described by Adams (*12*). A Mettler H54 analytical balance was employed and the density fluid, perfluoro (1-methyldecalin), was calibrated with a high-purity silicon crystal (ρ = 2.328 g/cm^3 at 22°C).

The resistances of single crystals and high-pressure VO_2 samples were measured

using a two-probe method from room temperature to 70°C. Contacts were made by attaching copper wire to the samples with Electrodag, a colloidally dispersed graphite, and allowed to dry overnight.

The ohmic behavior of all the samples was established by measuring their current–voltage characteristics. Four probe van der Pauw resistivity measurements were made at room temperature to provide sample-to-sample normalization.

Results and Discussion

In VO_2, the *d*-electrons of t_{2g} symmetry are delocalized by strong overlap of vanadium t_{2g} orbitals with oxygen p_π orbitals. Above the transition temperature of 67°C, these bands overlap and are each only partially filled. Below the transition temperature, the formation of V–V pairs along the *c*-axis causes a doubling of the crystallographic unit cell (*9*) and a splitting of the $t_\parallel$ band in two, as shown in Fig. 1. The lower $t_\parallel$ band becomes filled, which lowers the Fermi energy below the bottom of the remaining π^* bands. Consequently, these bands formed by covalent mixing become empty. It can be seen from Fig. 1 that the gap from the top of the filled $t_\parallel$ band to the bottom of the π^* band is 0.7 eV (*5*), which gives rise to the semiconducting behavior of VO_2 below 67°C.

The X-ray diffraction patterns for polycrystalline and ground single crystal samples of VO_2, crystallizing with monoclinic symmetry, correspond to that reported by Andersson (space group $P2_1/C$) (*2*). Upon heating these samples above the transition temperature of 67°C, the additional peaks, associated with the monoclinic distortion, disappear and the resulting pattern can be indexed on the basis of a tetragonal unit cell (space group $P4_2/mnm$, a = 4.558(2) c = 2.866(2)). The 2θ values and the relative intensities of ground single crystals of VO_2, polycrystalline VO_2 powder heated in a belt apparatus at 50 kbar and 800°C, and high-pressure VO_2 disks annealed in evacuated silica tubes at 800°C for 1 week are plotted in Fig. 2. It can be seen that all of the diffraction peaks have the same 2θ values and are identical to the values reported by Andersson (*2*). Hence, it can be seen that all three samples of VO_2 show a distorted rutile-type structure with monoclinic symmetry.

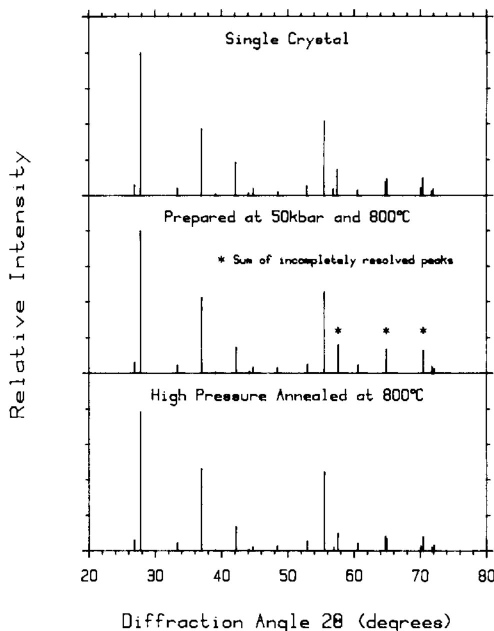

FIG. 2. Comparison of the room-temperature X-ray diffraction patterns for ground VO_2 single crystals, VO_2 prepared at 50 kbar and 800°C, and high-pressure VO_2 annealed at 800°C for 1 week. The patterns are all similar when allowance is made for the broadening of the peaks for the as-prepared high-pressure sample.

The resistance versus temperature data for the three samples are plotted in Fig. 3. The transition of about a factor of four at 67.3° observed for VO_2 single crystals was accompanied by a large hysteresis. Kimizuka *et al.* (*13*) and Goodenough (*5*) have pointed out that the transition in stoichiometric VO_2 shows greater hysteresis and less amplitude than for oxygen-rich materials. This transition is not present in the

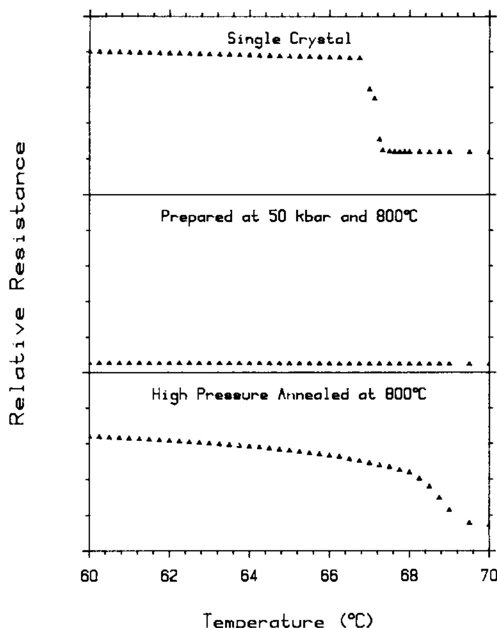

FIG. 3. Comparison of the variation of relative resistance with temperature for a VO_2 single crystal, VO_2 prepared at 50 kbar and 800°C, and high-pressure VO_2 annealed at 800°C for 1 week. The single crystal undergoes a sharp metal–semiconductor transition at 67.3°C, whereas the as-prepared high-pressure sample remains metallic. After many recyclings, the room-temperature resistance of the single crystal is approximately four times that of the metallic state. However, the metal–semiconductor transition is partially restored by annealing the high-pressure sample at 800°C for 1 week.

high-pressure sample; however, annealing the high-pressure sample of VO_2 for 1 week resulted in the reappearance of the semiconductor–metal transition. Densities were determined for both the high-pressure and annealed samples. Values of greater than 99% of the theoretical density were obtained and hence the failure to observe the electronic transition in high-pressure samples cannot be attributed to grain boundaries.

Although the semiconductor–metal transition was not observed for the high-pressure sample of VO_2, the crystallographic change from monoclinic to tetragonal symmetry did occur. It appears that the high-pressure treatment does not prevent the formation of V–V pairs along the tetragonal c-axis and resultant doubling of the crystallographic unit cell. Consequently, the $t_{\|}$ band is still split in two, but the lower band must now either lie within or overlap the bottom of the π^* band (see Fig. 1), presumably because of lattice distortion; then, metallic behavior of the sample could be anticipated. It can be seen from Fig. 3 that the resistance versus temperature plot for the high-pressure sample approaches metallic behavior. Annealing of the sample at 800°C for 1 week appears to reduce the lattice distortion sufficiently so that the metal–semiconductor transition is again observed. It can be concluded that high pressure can affect the relative position of the filled lower $t_{\|}$ band with respect to the empty π^* band. The Fermi level can thus be raised from below the bottom of the π^* band to within the π^* band. Hence, near-metallic behavior for the monoclinic phase prepared at high pressures is observed.

Acknowledgments

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References

1. F. J. MORIN, *Phys. Rev. Lett.* **3**, 34 (1959).
2. G. ANDERSSON, *Acta Chem. Scand.* **8**, 1599 (1954).
3. R. HECKINGBOTTOM AND J. V. LINNETT, *Nature (London)* **194**, 678 (1962).
4. S. WESTMAN, *Acta Chem. Scand.* **15**, 217 (1961).
5. J. B. GOODENOUGH, *Bull. Chem. Soc. Fr.* **4**, 1200 (1965).
6. P. F. BONGERS, *Solid State Commun.* **3**, 275 (1965).

7. L. LADD AND W. PAUL, *Solid State Commun.* **7,** 425 (1969).
8. D. B. ROGERS, R. D. SHANNON, A. W. SLEIGHT, AND J. L. GILLSON, *Inorg. Chem.* **8,** 841 (1969).
9. G. Z. HÄGG, *Phys. Chem. B* **29,** 192 (1935).
10. G. BRAUER, *Handb. Prep. Inorg. Chem.* **2,** 1272 (1965).
11. H. T. HALL, *Rev. Sci. Instrum.* **31,** 25 (1960).
12. R. A. ADAMS, Ph.D. thesis, Brown University (1973).
13. N. KIMIZUKA, M. ISHII, I. KAWADA, M. SAEKI, AND M. NAKAHIRA, *J. Solid State Chem.* **9,** 69 (1974).