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The Preparation and Characterization of $CdVO_3$ Prepared at Ambient and High Pressure

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The solid state reaction of VO_2 and CdO yielded a phase of unknown structure, which transforms to $CdVO_3$(I) after treatment under 60–65 kbar pressure at 1200°C. The high-pressure product was characterized by crystallographic, electrical and magnetic properties. $CdVO_3$(I) is an orthorhombic perovskite-type compound and a metallic conductor, exhibiting Pauli paramagnetic behavior. In contrast, the ambient pressure phase displays Curie–Weiss magnetic behavior above 77°K.

Introduction

An ambient pressure cadmium vanadium oxide of composition $CdVO_3$ has been prepared *via* solid state reaction of CdO and VO_2 by Reuter and Müller (*1*). Earlier, Galy and Bouloux (*2*) reported a phase slightly deficient in cadmium, $Cd_{0.95}VO_3$, with essentially the same X-ray powder pattern. They obtained this phase by reacting $Cd(VO_3)_2$, containing pentavalent vanadium, with cadmium metal.

We wish to report the preparation, crystallographic and magnetic properties of $CdVO_3$(I), prepared under high pressure, and also the magnetic properties obtained for the ambient-pressure phase.

Experimental

Reactants

Vanadium dioxide, VO_2, was prepared by the solid state reaction of V_2O_5 and V_2O_3 at 1000°C in an evacuated, fused-silica tube for 24 hr. High purity cadmium oxide was obtained from Spex Industries, Inc. The reactants were mixed in an agate mortar, pressed into a pellet, and heated *in vacuo* in a sealed fused-silica ampoule at 750°C for 15 hr, followed by heating at 800°C for 24 hr.

Samples of the ambient pressure product were heated at 60–65 kbar in a tetrahedral anvil (*3*) to 1200°C for 2 hr, followed by quenching. A blue-black microcrystalline product was obtained.

Apparatus and Measurements

The X-ray data on the high pressure product were obtained with a deWolff–Guinier camera using $CuK\alpha_1$ radiation and an internal KCl standard ($a = 6.2931$ Å). The magnetic data were obtained for both the ambient and high-pressure materials on a Faraday balance utilizing a Cahn microbalance. The low-temperature system was standardized with $HgCo(CNS)_4$ as the calibrant. The high-temperature system was calibrated with Gd_2O_3. The observed susceptibilities were corrected for the diamagnetism of the ions according to values listed in Selwood (*4*).

Crude measurements of electrical resistivity were carried out on powder compacts of the materials prepared at ambient and high pressure with a Heathkit vacuum tube voltmeter.

Thermogravimetric analyses were carried out in O_2/Ar gas mixtures on a du Pont 990 Thermal Analyzer. The products were heated from room temperature to approximately

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800°C, at which temperature oxidation and further weight increase had ceased. The products of the oxidations were examined by powder diffraction methods.

Results and Discussion

$CdVO_3$

Ambient-pressure syntheses in evacuated fused-silica tubes using equimolar mixtures of the oxides yielded a sintered, dark-brown, crystalline product. The X-ray powder pattern was nearly identical to those previously reported (*1*, *2*). Attempts to index the pattern were unsuccessful.

Crystal growth experiments were conducted in an effort to obtain single crystals of the ambient-pressure material suitable for subsequent examination by X-ray diffraction. Flux growth was attempted using $CdCl_2$ as the flux in a platinum vessel. The evacuated fused-silica tube, which contained the platinum vessel and the melt was slow-cooled, and the resulting material treated with hot distilled water to dissolve the flux. Ternary oxides of tetravalent vanadium were not obtained.

Vapor phase transport experiments using small amounts of I_2 or NH_4Cl were also conducted in evacuated fused silica ampoules heated in a temperature gradient. These experiments also failed to yield crystals of the ambient-pressure material.

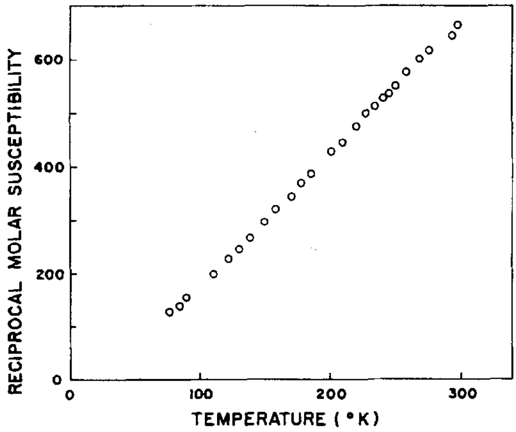

FIG. 1. Reciprocal molar susceptibility versus temperature (°K) for the ambient-pressure form of $CdVO_3$.

Thermogravimetric analyses of the ambient-pressure material conducted in O_2/Ar gas mixtures showed an average weight increase consistent with the empirical formula $CdVO_{2.99}$. Identical analyses carried out on the high-pressure material gave the empirical formula $CdVO_{2.96}$. The cadmium:vanadium ratio was assumed to be one. The oxidation product obtained from both materials was the pentavalent vanadium compound $Cd_2V_2O_7$.

The magnetic data collected from 77°K to 297°K for the ambient-pressure material are plotted in Fig. 1, as reciprocal molar susceptibility versus temperature. A least-squares program was used to determine the best straight line plot of the data, which are in good agreement with Curie–Weiss behavior with a Weiss constant of $\theta = 28°K$ and an effective magnetic moment, $\mu_{eff} = 1.80\ \mu_B$. A powder compact of the pure product displayed insulating electrical behavior at several temperatures between 77°K and ca. 500°K (of the order 10^6 ohm).

Previous investigators have not reported physical properties for the ambient-pressure materials obtained. The ambient-pressure product reported in this work shows reasonable magnetic behavior for a V^{4+} (d^1 electron configuration) compound with limited cooperative effects. The spin-only moment for one unpaired *d* electron is 1.73 μ_B, and magnetic moments up to 1.78 μ_B have been observed for V^{4+} in several coordination compounds (*5*).

$CdVO_3(I)$

The microcrystalline material prepared at high pressure gave powder diffraction data which were suitably indexed on an orthorhombic (perovskite-type) basis. The cell parameters were refined using a least-squares computer technique, giving: $a = 5.265(1)$, $b = 7.529(2)$, $c = 5.336(2)$ Å and $V = 211.53$ Å^3. The indexed powder data are given in Table I. The magnetic data from 77°K to 626°K suggest Pauli paramagnetic behavior. A temperature-independent molar susceptibility value of approximately 550×10^{-6} cgs units was observed between 200°K and 626°K. An increase in susceptibility below 200°K was observed due to slight traces of a paramagnetic impurity. There was little appreciable

TABLE I

X-RAY DIFFRACTION DATA FOR ORTHORHOMBIC $CdVO_3$(I)

$h\,k\,l$	I	d_{obsd}	d_{calcd}
1 0 1	25	3.753	3.748
1 1 1	15	3.346	3.355
0 0 2	25	2.666	2.668
1 2 1	100	2.653	2.656
2 0 0	35	2.630	2.632
0 1 2	10	2.513	2.515
2 0 1	5	2.360	2.361
1 3 0	10	2.264	2.266
2 1 1	10	2.252	2.253
0 2 2	60	2.177	2.177
2 2 0	60	2.158	2.157
1 3 1	10	2.085	2.085
1 2 2	5	2.011	2.012
2 2 1	5	2.002	2.000
0 4 0	20	1.882	1.882
2 0 2	60	1.873	1.874
0 3 2	15	1.828	1.828
2 1 2	20	1.820	1.818
2 3 1	2	1.720	1.720
1 4 1	15	1.683	1.682
3 0 1	10	1.668	1.667
1 1 3	15	1.645	1.644
1 2 3	50	1.539	1.538
2 4 0	20	1.532	1.531
3 2 1	50	1.525	1.524
1 3 3	15	1.401	1.399
0 0 4	5	1.336	1.334
2 4 2	15	1.330	1.328
4 0 0	8	1.316	1.316

variation of the molar susceptibility with magnetic field strength.

The electrical resistivity of a dense compact obtained from the high-pressure experiment indicates metallic behavior. The measured resistance of the pellet was approximately 1 ohm as the sample was warmed from 77°K to ca. 500°K. Metallic conductivity and Pauli paramagnetic behavior are consistent with a delocalized electron system. $CaVO_3$ has been shown to display similar physical properties (*6*), and also has the orthorhombic perovskite structure. Ca^{2+} and Cd^{2+} have similar ionic radii in oxides, as determined by Shannon and Prewitt (1.35 and 1.31 Å, respectively) (*7*). However, $CaVO_3$ can be prepared at high temperature without the application of pressure (*8*). In contrast, $CdVO_3$ decomposes at elevated temperatures (*1*, *2*) and $CdVO_3$(I) undergoes an exothermic transformation to the ambient-pressure material at 630°C, as evidenced by DTA and powder diffraction patterns of the polycrystalline product.

Conclusions

High pressure has been used to convert an ambient-pressure cadmium vanadium oxide of unknown structure to the orthorhombic perovskite-type, $CdVO_3$(I). Like $CaVO_3$ and $SrVO_3$, the new phase displays Pauli paramagnetic behavior and metallic conductivity, consistent with a delocalized, metallic model proposed by Goodenough for perovskite-type compounds having a d^1 electron system.

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