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# Critical Behavior of the Mott Transition in Cr-Doped $V_2O_3$

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The metal-insulator (M-I) transition in Cr-doped $V_2O_3$, which has been shown to be a Mott transition, was investigated by following the resistance as a function of pressure at temperatures above 298 °K. This study has shown that the M-I phase boundary terminates at a critical point in the $P$-$T$ plane, in accordance with the earlier prediction. The discontinuous resistance drop at the transition, which is about two orders of magnitude at 298 °K, progressively diminishes with temperature and beyond a certain critical temperature, depending upon the Cr concentration, vanishes altogether. Above the critical temperature only a smooth but somewhat anomalous change in resistance is seen. The critical pressure and temperature for $(V_{1-x}Cr_x)_2O_3$ with $x = 0.0375$, $x = 0.0187$, and $x = 0.0135$ were determined as 12.5 kbar, 390 °K; 5.5 kbar, 433 °K; and 3.5 kbar, 443 °K, respectively. A straight-line extrapolation of these data yields $P_c = -1.5 \times 0.2$ kbar and $T_c = (474 \pm 5)$ °K for pure $V_2O_3$. The high-temperature resistance anomaly in pure $V_2O_3$ near 500–600 °K is due to supercritical behavior. X-ray studies at atmospheric pressure on Cr-doped samples with $x = 0.0137$ to $x = 0.004$ show that the $\Delta V$ associated with the M-I transition decreases with increasing temperature and finally vanishes near about $x = 0.005$. The behavior is exactly analogous to the $\gamma$- to $\alpha$-Ce phase boundary which is known to terminate at a critical point. Indeed the M-I transition in Cr-doped $V_2O_3$ and the $\gamma$- to $\alpha$-Ce transition have many similarities, and these are discussed.

## INTRODUCTION

Recently, it has been shown[1] that a metal-insulator transition occurs in Cr-doped $V_2O_3$, which has the characteristics of a Mott transition. In this transition the conduction electrons localize to form the insulating state and the long-range order of the crystal does not change; the $\alpha$-corundum structure is common to both the insulating (I) and metallic (M) phases,[2] but the volume of the latter is smaller. Elsewhere in this issue,[2] a detailed account of the effects of pressure, temperature, and Cr concentration on the phase transitions encountered in the system $(V_{1-x}Cr_x)_2O_3$ is presented. It is found[1,2] that the M-I transition shifts to higher pressures with increasing Cr concentration and that high pressure is equivalent to decreasing Cr concentration. A phase diagram showing the relationship between the M phase, I phase, and a monoclinic antiferromagentic (AF) insulator phase has been presented as a function of both the Cr concentration as well as pressure (see also Fig. 15 of Ref. 2). Based on an extrapolation of the M-I transition boundary to pure $V_2O_3$ and from the nature of the resistance anomaly observed in pure $V_2O_3$ in the 500–600 °K region,[3] it has been suggested[1] that the M-I phase boundary terminates at a critical point. In this paper we present results of resistance-versus-pressure studies on several Cr-doped $V_2O_3$ samples and show that the M-I phase boundary does terminate at a critical point in the pressure-temperature plane, in accordance with the earlier prediction.[1] Results of x-ray diffraction studies on several of these samples at different temperatures are presented which are consistent with the termination of the Mott transition at a solid-solid critical point.

## I. EXPERIMENTAL RESULTS

Single crystals of Cr-doped $V_2O_3$ were grown by a new flux technique.[2] For resistivity measurements, samples were contacted with four leads placed approximately at the corners of a square. In some experiments these were pressure contacts, but in most cases four chromium-gold dots were evaporated onto the sample surface and leads were soldered on to the gold dot using tin. Two adjacent leads served for current while the opposite two measured the voltage. A stabilized dc source provided constant current through the sample, and the voltage drop was continuously recorded as a function of pressure at fixed temperatures. Hydrostatic pressure was generated in a piston-cylinder device, using the Teflon cell technique.[4] The pressure cell had an internal Nichrome heating coil immersed in the pressure medium which was usually isoamyl alcohol. In a few experiments Teflon was used as a pressure medium, in which case a graphite sleeve surrounding the Teflon served as the internal heater. A chromel-alumel thermocouple placed near the sample recorded the temperature.

In Fig. 1 the resistance-versus-pressure isotherms are reproduced for a Cr-doped sample of $V_2O_3$ containing 3.75-at.% Cr. The isotherms clearly demonstrate that the magnitude of the abrupt resistance decrease accompanying the transition strikingly diminishes as the termperature is in-

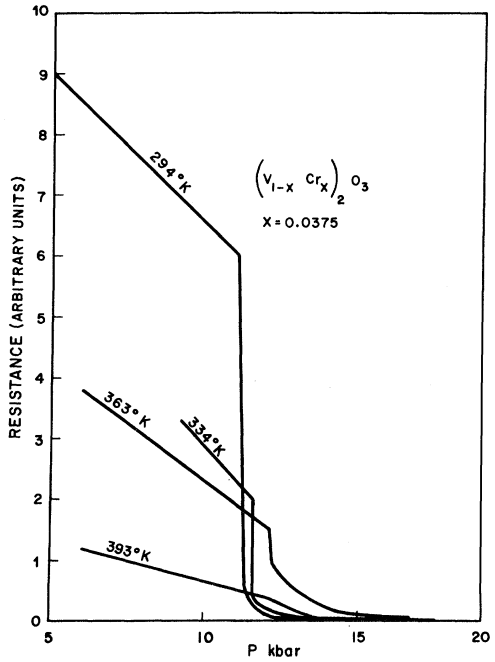


FIG. 1. Resistance-pressure isotherms for Cr-doped $V_2O_3$.

creased. At room temperature the abrupt resistance drop associated with the transition is about two orders of magnitude. In the 393 °K isotherm no abrupt change in resistance can be noticed; only a small anomaly is observed. Isotherms recorded at closer temperature intervals show that the discontinuous resistance decrease vanishes at about 390 °K for this sample. In Fig. 2 the phase diagram for $V_2O_3$ containing 3.75-at.% Cr is shown. In this the AF to M and AF to I phase boundaries are from Fig. 12 of Ref. 2. Data points above 300 °K for the M-I boundary are from present measurements and were obtained on increasing pressure. There is a hysteresis associated with the transition, but this was not studied. The boundary is terminated at the point where the discontinuous resistance drop goes to zero, and in the present case the critical pressure and temperature thus obtained are 12.5 ± 0.5 kbar and (390 ± 5) °K.

Pressure-temperature runs were also made on $V_2O_3$ samples containing 1.87- and 1.35-at.% Cr. With decreasing Cr content the critical temperature for the Mott transition progressively shifts to higher temperature while the critical pressure decreases. Table I summarizes the critical temperature and critical pressure for all the samples studied and Fig. 3 shows their M-I transition boundaries. From the observed variation of $P_c$ and $T_c$ with concentration, a linear extrapolation to pure $V_2O_3$ gives a critical point of $P_c = -1.5 \pm 0.2$ kbar and $T_c = (474 \pm 5)$ °K (see Fig. 3, point $x$). The critical point for pure $V_2O_3$ thus lies in the negative pressure region, as does the M-I boundary which is indicated by the dotted and dashed line in Fig. 3. This boundary has been drawn parallel to the experimentally determined M-I boundaries shown in the same figure. When extrapolated to zero pressure, the M-I phase boundary for pure $V_2O_3$ intersects the temperature axis precisely in the region where the high-temperature resistance anomaly occurs in pure $V_2O_3$ (see Fig. 4), showing that the anomaly is due to supercritical behavior of the Mott transition.

TABLE I. Critical pressure and temperature of $V_2O_3$ and Cr-doped $V_2O_3$.

| Composition $(V_{1-x}Cr_x)_2O_3$ | $P_c$ (kbar) | $T_c$ (°K) |
|---|---|---|
| $x = 0.0135$ | 3.5 | 443 |
| $x = 0.0187$ | 5.5 | 433 |
| $x = 0.0375$ [a] | 12.5 | 390 |
| $x = 0 (V_2O_3)$ | − 1.5 [b] | 474 [b] |

[a] In Ref. 2, $x = 0.0375$ is rounded off to $x = 0.04$.

[b] These values were obtained by extrapolation (see Fig. 3).

## II. X-RAY STUDIES

The published[1] composition-versus-temperature diagram (see also Fig. 15 of Ref. 2) shows that at atmospheric pressure, decreasing Cr concentration shifts the M-I transition progressively to higher and higher temperature. Also Fig. 3 indicates that

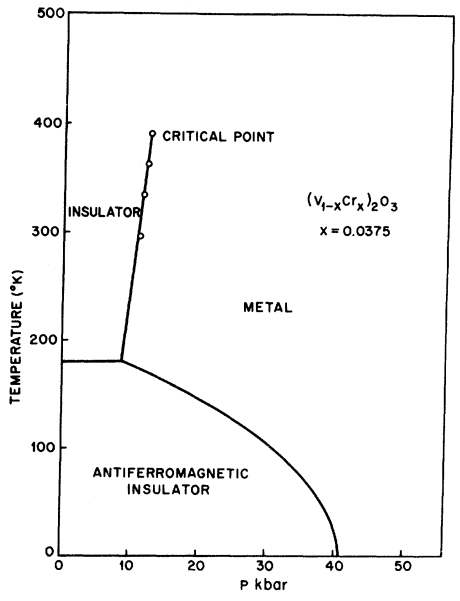


FIG. 2. Phase diagram of Cr-doped $V_2O_3$ containing 3.75-at.% Cr. The I and M phases have the corundum structure and the AF insulator is monoclinic.

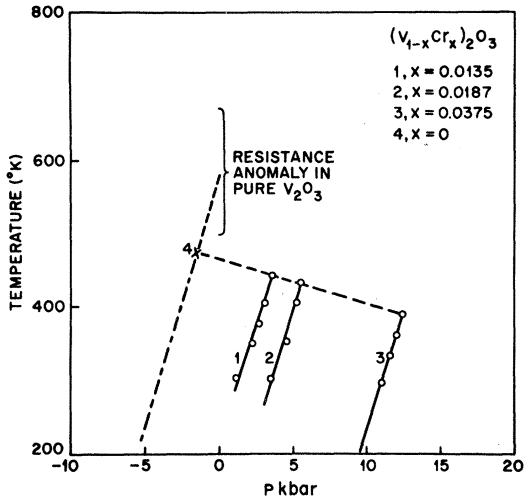


FIG. 3. M-I phase boundaries of three Cr-doped $V_2O_3$ samples (solid line). The dotted line in the negative pressure region (experimentally unrealizable) is for pure $V_2O_3$ and has been drawn parallel to the solid lines. The critical point ($x$) for $V_2O_3$ (obtained by extrapolation) has $P_c = -1.5$ kbar and $T_c = 474$ °K. The extrapolated dashed line beyond the critical point intersects the temperature axis in the region where the high-temperature resistance anomaly in $V_2O_3$ is observed.

for a certain critical Cr concentration, the critical point for the M-I transition boundary should lie exactly at zero applied pressure. These facts suggest that the $\Delta V$ associated with the transition can be followed as a function of temperature over a wide range of temperatures by choosing samples with varying Cr concentration and studying them at atmospheric pressure using standard x-ray diffraction techniques. We have studied several samples of Cr-doped $V_2O_3$ and in Table II these are listed. All the samples were crushed single-crystal material except the one with $x = 0.004$, which was a ceramic sample. The powdered sample was mounted on a copper disc which in turn was fitted on to the sample holder of a Phillips Norelco diffractometer. The temperature was varied by blowing cold or warm nitrogen on the sample. With this arrangement the sample could be heated to a maximum temperature of about 440 °K. For higher temperatures, the powdered sample was placed directly on a flat piece of Pt strip attached to the holder and heated by passing current through the Pt. A chromel-alumel thermocouple placed in intimate contact with the copper disc or the Pt strip monitored the temperature. Cu $K\alpha$ radiation was used and the (214) and (300) (hexagonal indices) peaks of the insulator and metal phases were scanned at different temperatures.

In the diffractometer trace, reflections from both the M and I phases appear over a broad temperature interval. In Fig. 5 the line profiles associated with the (300) reflections are reproduced. The pairs of (300) reflections are clearly resolved and well separated at higher Cr concentrations. Proceeding to samples with less Cr, the separation between the M and I (300) peaks narrows, while the background between the pairs gradually fills. For the sample with $x = 0.006$, the (214) reflections are no longer resolved at 403 °K and the (300) pair are only partially resolved. At 438 °K both pairs are unresolved, although a shoulder on the (300) insulator peak can still be observed for this sample. Figure 6 illustrates the effect of temperature on the (300) peak associated with the M phase for the sample with $x = 0.006$. At higher temperatures the peak associated with the M phase moves to smaller $2\theta$, while at the same time the I phase appears and grows in intensity. At 473 °K the M peak has almost merged with the I peak and at 503 °K only the I peak is seen. Figure 6 illustrates the fact that the metal phase exhibits a much larger thermal expansion relative to the I phase. A similar effect is shown in Fig. 4 of Ref. 2 for pure $V_2O_3$ and the 3.75% Cr-doped $V_2O_3$ sample. In the case of the sample with $x = 0.004$ no separate peaks for the M and I phases are seen at any temperature. The (300) metal peak moves continuously with temperature to lower angle $2\theta$, indicating absence of any phase separation. In Fig. 7 the lattice constant $a$ is plotted against temperature for two

TABLE II. Percent volume change for various Cr-doped $V_2O_3$ at the M-I transition.

| Composition $(V_{1-x}Cr_x)_2O_3$ | M-I Transition (°K) | $\Delta V/V_I$ (%) |
|---|---|---|
| $x = 0.0137$ | 206 | 1.26 |
| $x = 0.0118$ | 248 | 1.12 |
| $x = 0.0079$ | 357 | 0.85 |
| $x = 0.006$ | 420 | 0.56 |
| $x = 0.004$ | No discontinuous transition | |

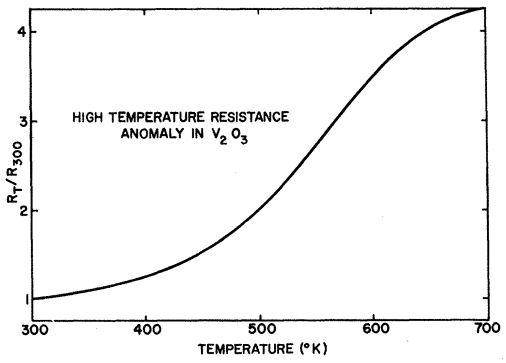


FIG. 4. High-temperature anomaly in pure $V_2O_3$, from the data of Feinlieb and Paul (Ref. 3).

samples. For the sample with $x = 0.006$, since a separate I peak starts to appear at about 370 °K, a jump in the lattice constant is shown, while for the sample with $x = 0.004$, $a$ varies smoothly but somewhat anomalously in the 450–525 °K range. This suggests that for the sample with $x = 0.006$, the temperature at which the M-I boundary is intersected at atmospheric pressure is just below the critical temperature, while for the sample with $x = 0.004$ this temperature is just above the critical temperature.

In Fig. 8 the $\Delta V$ of transition obtained from the x-ray data is plotted against temperature. The data show that the $\Delta V$ of transition decreases progressively with temperature first and drops somewhat precipitously near the critical region. This is precisely the behavior expected of a phase transition approaching the critical point. (According to classical theory, close to the critical point $\Delta V$ should be proportional to $t^{1/2}$, where $t = T_c - T$. This square-root behavior would lead to an infinite slope at $T = T_c$ in Fig. 8. Although the present data

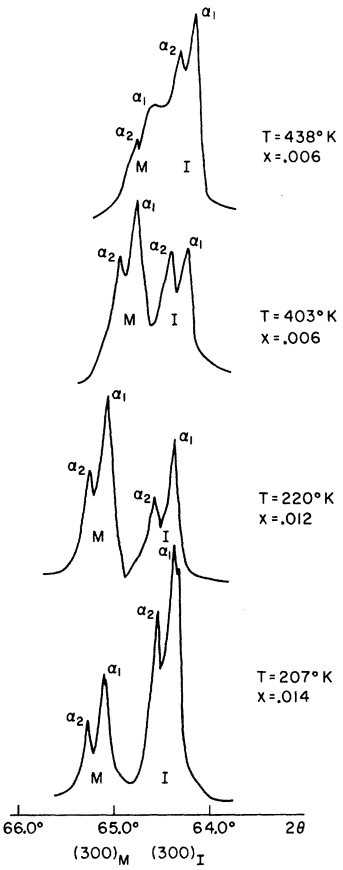


FIG. 5. X-ray powder diffraction line profiles of the (300) reflections from the metal (M) and insulator (I) phases of Cr-doped $V_2O_3$. The twin peaks are from Cu $K\alpha_1$ and Cu $K\alpha_2$ radiation.

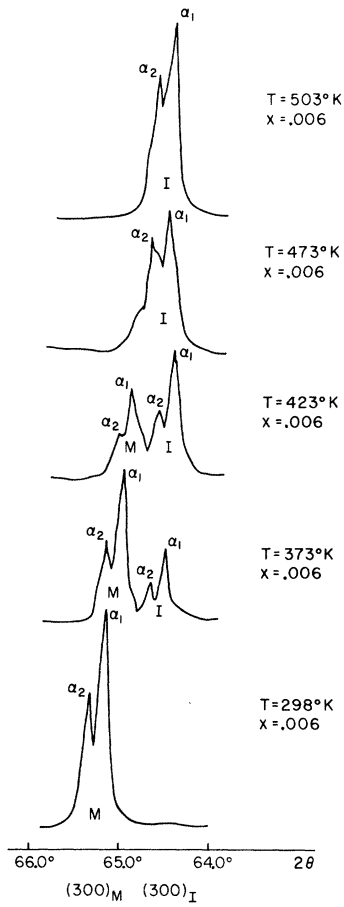


FIG. 6. X-ray powder diffraction line profiles for the (300) reflection from a 0.6% Cr-doped $V_2O_3$. The (M) peak shifts more rapidly to smaller $2\theta$ with temperature compared to the (I) peak.

are not adequate to determine unequivocally the true behavior, the dotted line as drawn is not inconsistent with the experimental points.) The last datum point in Fig. 8 was calculated from Fig. 3 and was experimentally confirmed.

Both the resistance and x-ray data thus clearly demonstrate that no phase separation takes place above a certain critical temperature; only a smooth and continuous variation of properties is observed. The experimental results strongly support the critical termination of the M-I phase boundary.

## III. DISCUSSION

The only other example of a solid-solid phase boundary which is known to terminate at a critical point is the $\gamma$- to $\alpha$-Ce phase boundary in cerium metal.[5] Both volume studies[6] and $\Delta S$ measurements[7] on this transition indicated a critical termination of the phase boundary. A study of the resistivity variation with pressure[5] at different temperatures showed that the abrupt resistance decrease asso-

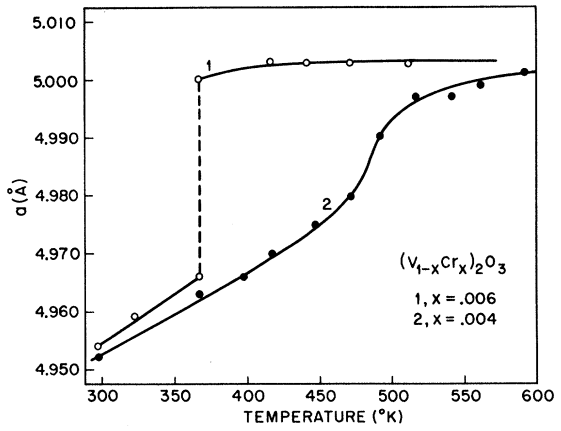


FIG. 7. Change in the lattice constant ($a$) for two Cr-doped $V_2O_3$ samples as a function of temperature. The sample with $x = 0.006$ exhibits a discontinuous jump. Sample with $x = 0.004$ shows a continuous and smooth but somewhat anomalous variation. The former is characteristic of suberitical and the latter of supercritical behavior.

ciated with the transition progressively diminished with temperature and disappeared altogether near 18 kbar and 550 °K. Above this temperature only a somewhat anomalous but smooth decrease in resistance with pressure could be seen. Thus, the resistivity behavior[5] of the $\gamma$- to $\alpha$-Ce transition was quite analogous to the $P$-$V$ isotherms of a vapor-liquid system, above and below the critical temperature, and lent strong evidence for the termination of the phase boundary at a critical point. The resistance-pressure isotherms of the M-I transition in Cr-doped $V_2O_3$ exhibit essentially the same characteristics as those observed in Ce and are therefore consistent with the termination of this phase boundary at a critical point.

It is of interest to compare the transition in Ce and Cr-doped $V_2O_3$, since they have many common features. In both, the transition is electronic in origin and involves no change in the lattice symmetry; fcc in the case of Ce,[8,9] corundum in the case of $(V_{1-x}Cr_x)_2O_3$. In Ce, it is the $4f$ electron that is delocalized[10] in the transition as a result of the crossing of the $5d$ conduction band[11] and the $4f$ level, whereas in Cr-doped $V_2O_3$ the $3d$ electrons are delocalized, forming essentially a $3d$ conduction band.

In Ce as well as in Cr-doped $V_2O_3$ the phases in which the electron is localized occur as the high-temperature phases and the $dT/dP$ of the phase boundaries are positive.[2,5] This signifies that both $\gamma$-Ce and the I phase of Cr-doped $V_2O_3$ have a higher entropy relative to $\alpha$-Ce and the M phase of Cr-doped $V_2O_3$, respectively. This rather peculiar behavior owes its origin to the magnetic characteristics of the respective phases. The localization of the $3d$ electrons on the V in the insulating phase of Cr-doped $V_2O_3$ gives rise to local moments and, hence, the phase is paramagnetic,[12] whereas the M phase has no such moments.[13] Rice and McWhan[14] have pointed out that the presence of disordered spins in the paramagnetic I phase would result in a higher entropy for this phase relative to the M phase which does not have any spin disorder contribution to the entropy. Kaplan and Bari[15] have also considered this problem theoretically, obtaining a similar result. Although at very high temperatures the M phase could have a higher entropy, the above situation should prevail at sufficiently low temperatures. Similar arguments would hold for the case of Ce: $\gamma$-Ce is paramagnetic and, hence, the spin disorder contribution enhances the entropy of this phase relative to $\alpha$-Ce which, like the M phase of $V_2O_3$, has lost its magnetic $4f$ electron and hence has no local moment.

In view of the close similarities between the $\gamma$- to $\alpha$-Ce transition and the M-I transition in Cr-doped $V_2O_3$, it is tempting to regard the former as something akin to a Mott transition. The suggestion of Blandin *et al.*[16] that in cerium a competition by the $d$ electron with the $4f$ electron to screen the nuclear charge would perhaps be responsible for the delocalization of the $4f$ electron is significant in this connection. However, a Mott transition[17] involves localized and itinerant electrons derived from the same electronic state, and in the case of Ce this is clearly not the case. The delocalized $4f$ electron acquires $5d$ character. Further, in Ce both the phases are metallic owing to the presence of conduction electrons derived from the $6s$ and $5d$ states

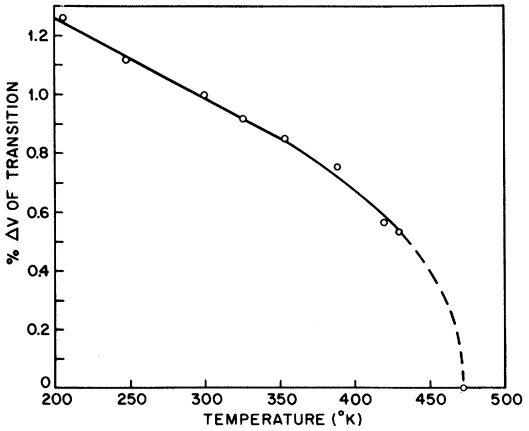


FIG. 8. Percent volume change along the M-I transition boundary obtained from x-ray data at atmospheric pressure, using samples with different Cr concentration. The $\Delta V$ of transition was evaluated at the temperature where the separate (M) and (I) peaks were approximately equal in intensity. Some intermediate data points obtained at other temperatures are also included.

and that Mott's picture[17] applies, in particular, to a M-I transition.

The critical termination of the M-I transition in Cr-doped $V_2O_3$ again emphasizes that for a critical point to exist between two phases there should be no symmetry restriction, a criterion pointed out by Landau.[18] Although resistivity measurements cannot decide whether a sharp second-order transition involving any change in the long-range order exists, we do not believe that any such transition exists above these solid critical points. In fact, we believe that the analogy with vapor-liquid systems exists beyond the critical point.

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# Magnetic Properties of $(V_{1-x}Cr_x)_2O_3$

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The magnetic susceptibility of the $(V_{1-x}Cr_x)_2O_3$ system ($0 \leq x \leq 1$) has been studied over the temperature range 4.2–1000 °K. For $0 \leq x < 0.035$, the susceptibility data clearly indicate both the high-temperature transition from a paramagnetic insulating to a paramagnetic metallic state with decreasing temperature and the sharp low-temperature transition from the paramagnetic metallic phase to the insulating antiferromagnetic phase. Separation of the total susceptibility into a temperature-independent Van Vleck term and a temperature-dependent term $\chi_d$ yields Curie-Weiss behavior for $\chi_d$. As $x$ increases from 0 to 0.035, the extrapolated paramagnetic Curie temperature of the insulating high-temperature phase decreases from 600 to 350 °K and the effective moments from $2.96\mu_B$ to $2.30\mu_B$ per magnetic ion. The change from the $V_2O_3$-type magnetic structure to the $Cr_2O_3$ type occurs in the region $0.21 \leq x \leq 0.45$. The magnetic susceptibility data are consistent with the picture developed for pure and Cr-doped $V_2O_3$ on the basis of resistivity and x-ray investigations at atmospheric and elevated pressures.

## INTRODUCTION

The discovery of the antiferromagnetic properties of $V_2O_3$ in the low-temperature insulating state by Moon[1] and the interesting electrical and structural properties of $(V_{1-x}Cr_x)_2O_3$ with $0 \leq x \leq 0.04$[2–4] led us to investigate the magnetic properties of this system. The magnetic susceptibility of pure $V_2O_3$ has already been measured by different research