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 χ_d yields Curie-Weiss behavior for χ_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

groups.[5-7] In the present investigation, we studied the behavior of the susceptibility of the different phases established by McWhan and Remeika.[4] We extended the susceptibility measurements to 1000 °K in order to define the behavior of the susceptibility well above the broad high-temperature anomaly from the insulating to metallic state which has been observed in the resistivity[8,9] and x-ray investigations.[4] Considerable disagreement exists between the NMR data of Jones[10] and the magnetic susceptibility in this region, since Jones did not observe any high-temperature anomaly in the NMR frequency shift.

McWhan, Rice, and Remeika[2-4] studied the effect of pressure on the electrical properties and crystal structure of pure and Cr-doped V_2O_3. To a first approximation, increasing pressure and decreasing Cr concentration make the system more metallic. First-order metal-insulator transitions, without a change in the long-range order, have been found as a function of both Cr concentration and pressure.[2-4] Jayaraman et al.[11] showed that this metal-insulator phase boundary terminates at a line of critical points. For $x \geq 0.04$, the compounds showed insulating characteristics at all temperatures. McWhan, Rice, and Remeika[2-4] defined for $0 \leq x \leq 0.12$ a phase diagram with clearly defined phases: metallic (M), insulating (I), and antiferromagnetic insulating (AF).

V_2O_3 and Cr_2O_3 form a completely miscible system. They show different magnetic structures. According to Moon,[1] V_2O_3 is antiferromagnetic and has the moments aligned ferromagnetically along a direction which makes an angle of 71° to the c axis of the hexagonal cell and lies in a plane perpendicular to the a vector of the hexagonal cell. The planes are stacked antiferromagnetically along the a vector. The magnetic moments are aligned antiferromagnetically along the c axis in Cr_2O_3.[12] Our measurements covered the whole system from pure V_2O_3 to pure Cr_2O_3. This was necessary in order to see how the different contributions to the magnetic susceptibility change as a function of composition. We also wanted to observe the changes in the susceptibility due to the change of the magnetic structures in going from V_2O_3 to Cr_2O_3. The results of our measurements will be discussed on the basis of crystallographic and electrical properties of these materials.

I. EXPERIMENTAL PROCEDURES AND RESULTS

Measurements on samples with $0 \leq x \leq 0.04$ were performed on single crystals. Their preparation has been described elsewhere.[4] For $0.04 < x < 1.00$, ceramic samples, and for Cr_2O_3, a powder sample, were measured.

The magnetic susceptibility measurements were made by the Faraday method, utilizing a Cahn balance. For measurements above room temperature the materials were sealed in quartz crucibles under reduced argon pressure. Special attention was given to the reproducibility of the data at elevated temperatures. Data points were taken for increasing and decreasing temperatures to check that no chemical decomposition of the samples had occurred. The corrections due to the quartz containers were determined separately and taken into account.

Figure 1 shows the molar magnetic susceptibility as a function of temperature of 12 different compositions. Table I lists the compositions corresponding to each of the curves shown in this figure. For the $(V_{1-x}Cr_x)_2O_3$ samples, where $0 \leq x \leq 0.04$, the low-temperature data were taken as a function of decreasing temperature with the magnetic field aligned perpendicular to the c axis. In contrast to Carr and Foner,[5] we observed a smaller anisotropy in the susceptibility, especially in the metallic region, for different orientations of the crystals in the applied field. Our results are shown in Fig. 2(a). A hysteresis of about 12 °K occurs at the metal-to-insulator transition (M to AF). The low-temperature transition T_N, which coincides with the metal-to-insulator transition (M to AF) and associated crystallographic distortion, is shifted to higher temperatures with increasing Cr content. In addition, the susceptibility also shows anomalies in the high-temperature region $(T > T_N)$. For pure V_2O_3, a shallow relative maximum occurs between 400 and 550 °K (see also Fig. 4). This maximum moves to lower temperature and becomes more pronounced with increasing Cr content. Sample No. 2 $(x = 0.008)$ shows a well-defined phase transition at 250 °K in addition to the one at 175 °K, as shown in Fig. 1 and enlarged in Fig. 2(b). This coincides with the first-order transition found by x-ray diffraction and resistivity measurements on crystals with similar Cr

TABLE I. Compositions of $(V_{1-x}Cr_x)_2O_3$ materials corresponding to the susceptibility data shown on Fig. 1.

Material	Susceptibility curve	Nature of sample
V_2O_3	1	Single crystal
$(V_{0.99}Cr_{0.01})_2O_3$	3	Single crystal
$(V_{0.992}Cr_{0.008})_2O_3$	2	Single crystal
$(V_{0.981}Cr_{0.019})_2O_3$	4	Single crystal
$(V_{0.96}Cr_{0.04})_2O_3$	5	Single crystal
$(V_{0.88}Cr_{0.12})_2O_3$	6	Ceramic
$(V_{0.85}Cr_{0.15})_2O_3$	7	Ceramic
$(V_{0.80}Cr_{0.20})_2O_3$	8	Ceramic
$(V_{0.75}Cr_{0.25})_2O_3$	9	Ceramic
$(V_{0.70}Cr_{0.30})_2O_3$	10	Ceramic
Cr_2O_3	11	Powder
$(V_{0.4}Cr_{0.6})_2O_3$	12	Ceramic
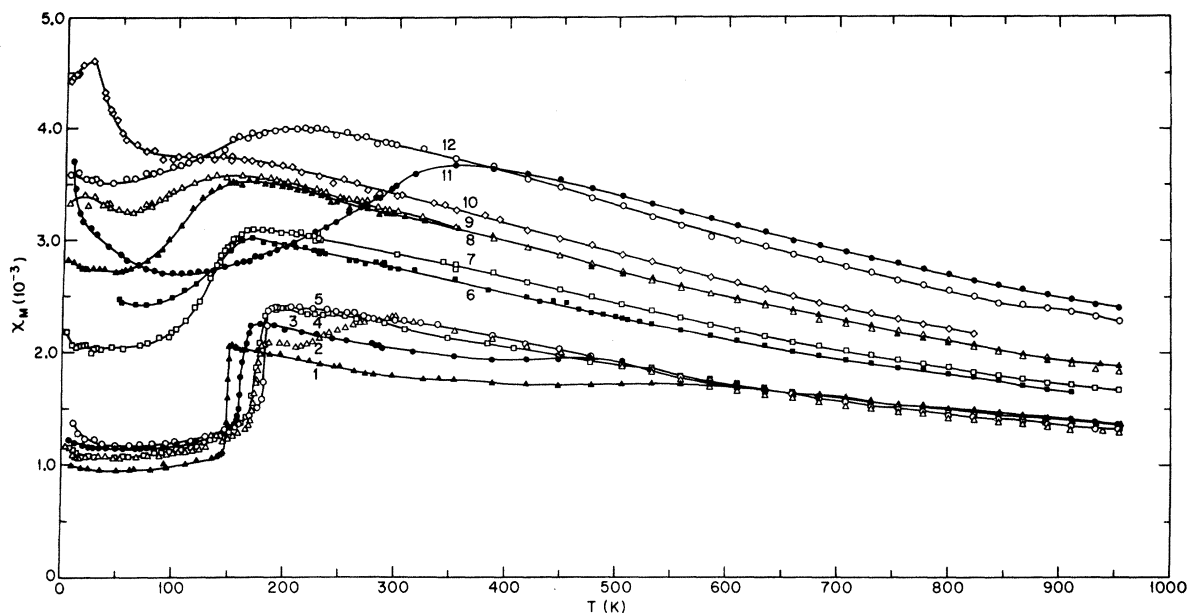
FIG. 1. Molar magnetic susceptibility as a function of temperature. The compositions are given in Table I.

FIG. 2. (a) Magnetic susceptibility $\chi_{\parallel}$ and $\chi_{\perp}$ below room temperature of pure V_2O_3. (b) Magnetic susceptibility versus temperature of samples 1, 2, and 5 (see Table I for sample identification).

concentration. The transition temperatures, taken as the midpoint of the transition regions, are reproduced as a function of Cr content in Fig. 3.
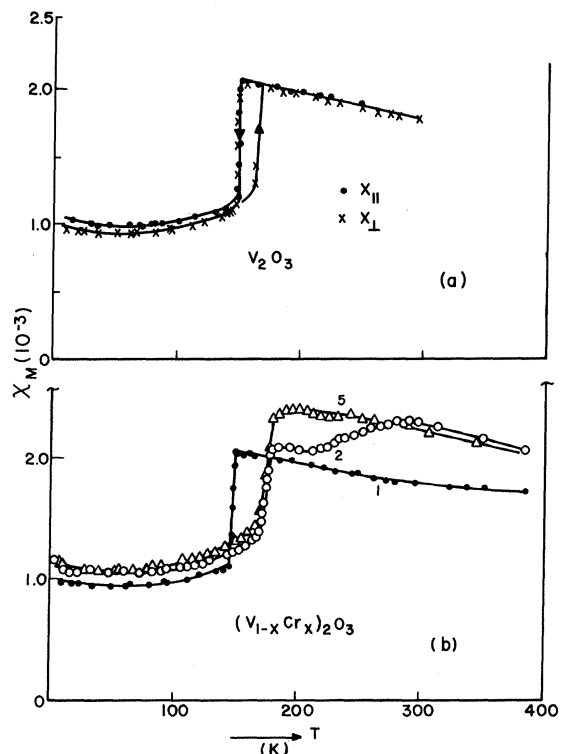
They depend very strongly on composition and, therefore, small inhomogeneities in the Cr distribution in the V_2O_3 lattice can cause a broadening of the observed transition. We will discuss later in this paper in more detail the reasons for the broad character of the high-temperature transitions of pure V_2O_3 and $(V_{1-x}Cr_x)_2O_3$ (M to I).

For the $(V_{1-x}Cr_x)_2O_3$ samples in which $0.04 < x \leq 1.0$, the following features of our results are of interest. All compositions show a Curie-Weiss-like behavior at high temperature. With decreasing temperature, the susceptibility either flattens out or shows a maximum. These maxima or the point where the curves flatten out (see curve 10, for example) are identified as Néel temperatures T_N and are reproduced in the phase diagram shown in Fig. 3. Actually, the T_N temperatures were taken from plots of the inverse susceptibility with temperature as will be shown later.

The magnetic susceptibility of $(V_{0.70}Cr_{0.30})_2O_3$ (No. 10) flattens out at 160 °K, stays almost constant down to 70 °K, increases strongly below 70 °K, and shows a maximum at 23 °K. A similar behavior, but much less pronounced, was observed for sample $(V_{0.75}Cr_{0.25})_2O_3$ (No. 9). The temperatures corresponding to the point at which the susceptibility increases from the flat portion and the maximum in susceptibility are reproduced together with the Néel temperature (end of the Curie-Weiss behavior) in Fig. 3.

Powdered Cr_2O_3 shows a maximum in the susceptibility near 310 °K, which agrees well with the reported Néel temperature for the crystalline material.[12,13] The unusual behavior of the susceptibil-
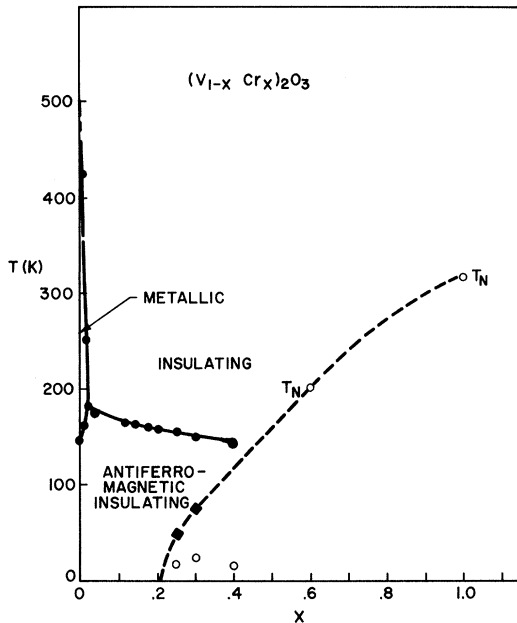
FIG. 3. Phase diagram of $(V_{1-x}Cr_x)_2O_3$ as deduced from magnetic susceptibility data shown in Fig. 1: closed circles, transition points (or midpoint of transition regions); open circles, maxima in the susceptibility as a function of temperature; and closed squares, temperature where the susceptibility starts to increase again with decreasing temperatures.

ity below T_N (= 308 °K) is due to particle reorientation effects within the loose powder and is of no physical significance.

II. ANALYSIS OF EXPERIMENTAL RESULTS

Jones[10] and Arnold and Mires[7] found that for V_2O_3, within the temperature range of 160–400 °K, the total susceptibility $\chi_{(T)}$ can be represented by

$$\chi_{(T)} = \chi_{VV} + \chi_{d(T)}, \tag{1}$$

with

$$\chi_{d(T)} = C/(T-\theta_p). \tag{2}$$

χ_{VV} and $\chi_{d(T)}$ are the temperature-independent Van Vleck and the d-spin terms in the susceptibility, respectively. For the metallic phase (M), Jones[10] and Arnold and Mires[7] found $\chi_{VV} = 0.42 \times 10^{-3}$ (emu/mole), $C = 0.68$ (emu/mole °K), and $\theta_p = -600$ °K.

Figure 4 shows our data, corrected for the Van Vleck susceptibility

$$\chi_{VV} = 0.21 \times 10^{-3} \text{ (emu/mole)}$$

plotted reciprocally as a function of temperature over the temperature range 160–1000 °K. Only for this specific value of χ_{VV} was Curie-Weiss behavior obtained for χ_d in the high-temperature region (I). The data points fit well on a line with a paramagnetic Curie temperature of −600 °K and a slope corres-

ponding to 2.69 μ_B per V ion. The data points in the metallic phase (M) fit within experimental errors a line calculated from the parameters (θ_p = −600 °K, p = 2.37μ_B per V ion) reported by Jones[10] and Arnold and Mires.[7] The high-temperature anomaly, which appeared only as a shallow relative maximum in the susceptibility-versus-temperature plot, is now clearly visible. Our results demonstrate, in agreement with Jesser and Silhoutte,[5] very clearly the existence of a Curie-Weiss law at elevated temperatures, which was only roughly indicated by the work of Arnold and Mires.[7]

Susceptibility measurements by Foner[14] on Cr_2O_3 single crystals show a nonvanishing susceptibility $\chi_{||} = 0.22 \times 10^{-3}$ (cgs/mole) at zero temperature. Silverstein and Jacobs[15] interpreted this result in terms of a Van Vleck susceptibility. We used this value to evaluate our high-temperature data on Cr_2O_3 according to Eqs. (1) and (2). On this basis the paramagnetic Curie point is θ_p = −520 °K and the effective Bohr magneton number per Cr ion $p = 3.6\mu_B$. This should be compared to the spin-only value of $3.87\mu_B$ for the free trivalent Cr ion. These values are reproduced in Figs. 5 and 6. Foex and Graff[16] found, without correcting their result for the Van Vleck susceptibility, a Curie constant corresponding to $3.87\mu_B$ per Cr ion. Since the Van Vleck susceptibilities of pure V_2O_3 and Cr_2O_3 are almost identical, we used the same value for all our materials, namely, the one for pure V_2O_3.

Our data was evaluated according to Eqs. (1) and (2). The Néel temperatures shown in Fig. 3 correspond to the sharp break obtained on plots of the inverse of the susceptibility χ_d as a function of tem-
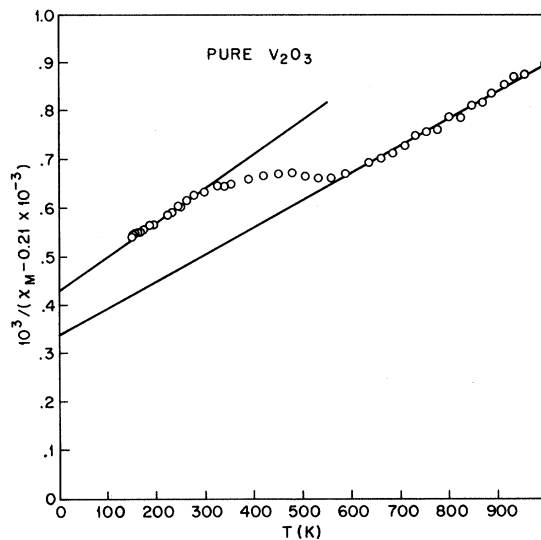

FIG. 4. Inverse susceptibility of $\chi_{d(T)}$ as a function of temperature of pure V_2O_3.
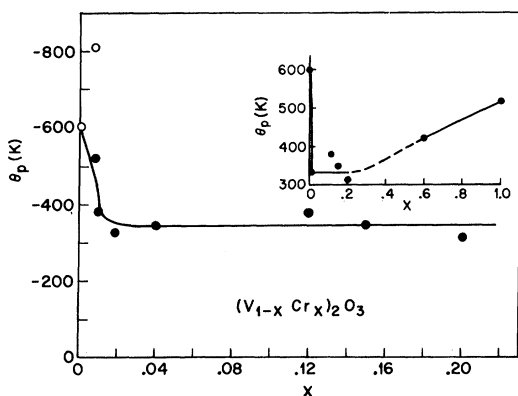
FIG. 5. Extrapolated paramagnetic Curie temperatures as a function of Cr content. Closed circles correspond to the insulating high-temperature phase and open circles to the metallic phase.

perature. The transition temperatures (for the broad high-temperature transitions) were taken at the midpoints of the anomalies, as pointed out earlier. The paramagnetic Curie temperature θ_p and the effective Bohr magneton numbers are given in Figs. 5 and 6, except for the samples No. 9 and 10. In these two samples the chosen Van Vleck susceptibility did not result in Curie-Weiss behavior for χ_d, i. e. , the data did not yield a straight line when the reciprocal of χ_d was plotted as a function of temperature. These are the same compositions that showed the marked increase in the susceptibility at temperatures below the Néel temperature.

III. DISCUSSION

The information derived from the susceptibility measurements presented above is summarized in Figs. 3, 5, and 6. The results shown in Fig. 3 are in good agreement with those obtained by means of electrical resistivity and x-ray diffraction measurements. [2-4] They reflect all three phases M, I, and AF. The properties of the materials in each of the three regions are markedly different and are labeled in Fig. 3 as metallic, insulating, and antiferromagnetic. McWhan, Rice, and Remeika[2-4] suggested that the metal-to-insulator transition (M to I) is a Mott transition from band to localized behavior of the d electrons. The magnetic susceptibility in each region will be discussed below in the light of this interpretation.

The susceptibility shows little anisotropy in the low-temperature insulating phase of pure V_2O_3, and this was one of the reasons V_2O_3 was not regarded as ordering antiferromagnetically. According to Moon,[1] the antiferromagnetic axis lies in a plane parallel to the c axis (in the hexagonal cell) and perpendicular to one of the a axes and makes

an angle of about 71° to the c axis in this plane. On the basis of this special direction and the fact that measurements of the susceptibility were performed only perpendicular or parallel to the basal plane, one can understand the small observed anisotropy. By computing and averaging the projections of $\chi_{\parallel}$ to the v axis and the basal plane, one calculates an anisotropy of less than 20% at low temperature.

According to Moon,[1] the sublattice magnetization does not depend strongly on temperature in the insulating state (AF). This, together with the facts that the value of the susceptibility is small compared to the value above the transition and its weak temperature dependence, indicates that the extrapolated second-order Néel temperature would be higher than the transition temperature (M to AF). Moon[17] estimated a temperature at which the sublattice magnetization goes to zero on the basis of its temperature dependence in the AF phase. The extrapolated second-order Néel temperature is 290°K.

The broad nature of the high-temperature anomaly (see Fig. 3) has to be attributed to the fact that it occurs above the critical point which terminates the metal-insulator phase boundary found for the Cr-doped samples. [11] The broadness of this transition has a physical reason in contrast to the others (samples 2, 3, and 4) which are due to inhomogeneities in the Cr distribution. It is a continuous transition from the metallic to the insulating corundum phase. The observed effective Bohr magneton numbers for the two phases are $2.37\mu_B$ and $2.69\mu_B$, respectively. Both values are lower than the spin-only value for the free V^{+3} ion $(2.83\mu_B)$ with the high-temperature value closer to it.

A very interesting point is the discrepancy between the temperature dependence of the Knight shift and the susceptibility through the high-tem-
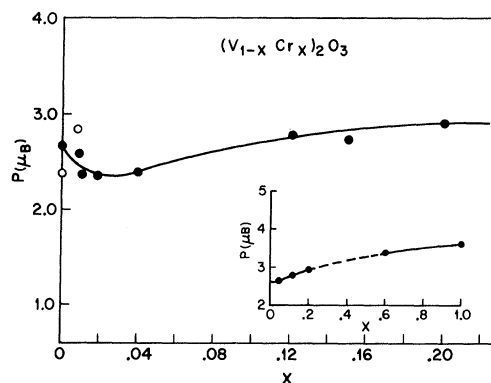

FIG. 6. Effective moment per transition metal ion in $(V_{1-x}Cr_x)_2O_3$ as a function of Cr content. Closed circles correspond to the insulating phase and open circles to the metallic phase.

perature anomaly. The susceptibility parameters of the metallic phase agree well with the NMR frequency-shift results. The absence of the high-temperature anomaly in the NMR data can, therefore, only be related to a change in the d-spin hyperfine coupling.[18] The large magnetic susceptibility and its strong temperature dependence of pure metallic V_2O_3 (M phase) stimulated Gossard et al.[19] to perform Knight-shift measurements under pressure at 4.2°K. These authors found that pure metallic V_2O_3 does not order magnetically at 4.2 °K. They conclude, therefore, that metallic V_2O_3 does not exhibit a localized moment. The observed temperature dependence of the susceptibility must be related to strongly interacting but still intinerant electrons. Such effects are expected to occur in the vicinity of a Mott transition.[3]

Samples 2 and 3 show a sharp insulator-to-metal transition (I to M) as a function of decreasing temperature from 600 °K within the same crystal structure when examined via resistivity measurements. The results for sample No. 2 (Figs. 1 and 2) demonstrate very nicely how the susceptibility changes from the value of the insulating high-temperature phase (I) to that of pure metallic V_2O_3 (phase M). McWhan et al.[2-4] identified this transition as a Mott transition. The magnetic susceptibility reflects these transitions also. The relative high value of the susceptibility and part of its temperature dependence in the metallic phase of sample No. 3 is partly due to the fact that about 20% of the sample remained in the insulating phase. The open circles in Figs. 5 and 6 represent the parameters for this intermediate metallic phase, evaluated by means of Eqs. (1) and (2). The parameters probably are not significant for sample No. 3 owing to the incomplete phase transition.

The phase diagram reproduced in Fig. 3 has been constructed with the information deduced from our susceptibility data. For $x < 0.12$, it agrees well with the diagram McWhan and Remeika[4] obtained from their x-ray and resistivity results. As shown in Fig. 1, for $0.2 < x < 0.5$, we observed a second increase in susceptibility below 100 °K. The dashed line represents the boundary where the increase occurs. For $x = 0.3$, preliminary x-ray measurements[20] as a function of decreasing temperature are consistent with structural changes at temperatures of 150 and 80°K. On the basis of neutron diffraction studies below 80 °K, Moon[17] reported, as a preliminary result, the observation of a weak peak related to the Cr_2O_3 magnetic structure. These facts led

us to extend the dashed line through the Néel temperature of $(V_{0.4}Cr_{0.6})_2O_3$ and pure Cr_2O_3 as a possible magnetic phase boundary. The increase in magnetic susceptibility for $0.2 < x < 0.5$ at low temperature is, therefore, related to the change from the V_2O_3 to the Cr_2O_3 magnetic structure. Within this region a complicated magnetic structure (e.g., spiral) which changes as a function of temperature may exist as has been suggested for the Cr_2O_3-Fe_2O_3 system.[21] In V_2O_3 the moments are aligned ferromagnetically along the antiferromagnetic axis; in Cr_2O_3 antiferromagnetically. This portion of the phase diagram is under further investigation and more details will be reported later. For $x = 0.6$ (No. 12) we observe the expected increase of the Néel temperature T_N towards Cr_2O_3.

Figures 5 and 6 show the susceptibility parameters deduced from our experimental results in the insulating paramagnetic phase (I) by use of Eqs. (1) and (2). Since the properties on each side of the Mott transition (M to I) are affected by the impending transition, both the metallic (M) and the insulating phase (I) should exhibit fluctuations towards the other state.[2-4] The large magnetic susceptibility and its strong temperature dependence in the metallic phase (M) may be evidence of strong spin fluctuations as the electrons become more and more localized approaching the Mott transition. The increase of θ_p and p of the insulating phase (I) as x goes to 0 indicates the incipient breakdown of the insulating state. Within the dashed region it was not possible to find a Curie-Weiss law for a broad region of Van Vleck susceptibility values. The changes in the magnetic properties and the associated changes in the crystallographic structure at low temperature suggest that the magnetic exchange interactions for these materials depend on temperature.

The magnetic susceptibility data reported in this paper are consistent with the picture developed for pure and Cr-doped V_2O_3 by McWhan, Rice, and Remeika[2-4] on the basis of resistivity and x-ray investigations at atmospheric and at elevated pressures, but a basic understanding of the phenomena is still lacking.

ACKNOWLEDGMENTS

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High-Pressure Nuclear Resonance Study of the Metal-Insulator Transition of V₂O₃

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^{51}V nuclear magnetic resonance (NMR) has been observed in metallic V_2O_3 at pressures up to 65 kbar at 4.2 °K. Pressures greater than 26 kbar suppress the metal-to-antiferromagnetic insulator transition, leaving V_2O_3 a metal at 4.2 °K. ^{51}V NMR shows that the metallic phase, unlike the insulating phase, does not order magnetically down to 4.2 °K. The measurements are the highest-pressure resonance measurements which have been reported in the He temperature range. Knight shifts and relaxation times were measured, the Knight shift having an anomalously strong dependence on volume. The relaxation time allows an upper limit of 10^{-13} sec to be placed on the spin fluctuation lifetime of the d electrons.

INTRODUCTION

V_2O_3 is one of the few materials which are known to exhibit a temperature-induced insulator-metal transition.[1] The low-temperature insulating phase is antiferromagnetic,[2] but the magnetic character of the metallic phase is not clear. Recently it has been found that the addition of 1% Cr_2O_3 to V_2O_3 results in a first-order transition with no change in long-range order from metallic (M) to insulating (I) properties at room temperature.[3] Pure V_2O_3 must then be considered as part of a more general phase diagram consisting of surfaces for a metal-paramagnetic insulator (M-I) transition and for a metal-antiferromagnetic insulator transition (M-AF) as a function of temperature, pressure, and composition. For $x \gtrsim 0.02$ in $(V_{1-x}Cr_x)_2O_3$, there is a purely magnetic (AF→I) transition as a function of temperature. The M-I transition has been interpreted as a Mott transition.[4] In order to elucidate the mechanism of this transition a more complete characterization of the magnetic properties of the metallic phase is necessary.

At 1 atm it is not possible to study the metallic phase at very low temperatures because of the M-AF transition, but at pressures in excess of ≈26 kbar the AF phase of V_2O_3 is suppressed.[5] If there were local moments in the metallic phase they should order magnetically at low temperatures. Studies of the electrical resistivity as a function of temperature at pressures above 26 kbar did not reveal any anomalies which could be associated with magnetic ordering.[5] These are only indirect measurements of the magnetic character of metallic V_2O_3, so it was decided to study the ^{51}V nuclear magnetic resonance (NMR) at high pressure and low temperature. These measurements detect the very sizable (~10^5 Oe/μ_B) hyperfine fields resulting from magnetic ordering and thus provide a direct and critical test of the magnetic character. In addition, it is possible with this technique to measure the effect of the imaginary parts of the electronic susceptibility on nuclear relaxation.

In the present paper, the techniques necessary to do nuclear magnetic measurements at 4.2 °K and pressures in excess of 26 kbar are described. Evi-