Metal-Insulator Transitions of V_2O_3: Magnetic Susceptibility and Nuclear-Magnetic-Resonance Studies

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Magnetic susceptibilities have been measured and ^{51}V nuclear magnetic resonances have been observed in a series of compounds $(V_{1-x}Cr_x)_2O_3$ and $(V_{1-x}Al_x)_2O_3$ $(0 \leq x \leq 0.04)$. The compounds are of interest because of their metal-insulator transition in the composition and temperature (4.2–900 °K) range studied. The paramagnetic insulating phase is found to possess a higher susceptibility than the metallic phase, a more positive ^{51}V nuclear-resonance frequency shift, and a reduced d-spin hyperfine coupling constant. The nuclear-resonance relaxation and linewidth are understood in terms of a metallic state with a high band susceptibility and an insulating state with local paramagnetic moments. Anomalies observed previously in ^{51}V frequency-shift-susceptibility relationships for pure V_2O_3 are shown to result from the gradual supercritical change from metalliclike to insulatinglike behavior of pure V_2O_3. A high degree of covalency in the insulating phase is implied by the frequency shifts of ^{27}Al nuclear resonances also observed in the samples containing Al.

I. INTRODUCTION

Metal-insulator (M-I) transitions in transition metal oxides are sometimes, but not always, accompanied by magnetic ordering. Occurrence of magnetic order or of localized magnetic moments produces energy level shifts and symmetry changes which may result in the conductivity transition. A fundamental question is then whether the magnetic ordering is the cause of the transition to insulating behavior or vice versa.[1] In the present work, we pursue the magnetic behavior in the M-I transitions of the pure transition-metal compound V_2O_3[2,3] and in V_2O_3 containing dilute amounts of Al and Cr.[4] We look for evidence of the occurrence of local magnetic moments, for the spin dynamics of the metallic state, and for magnetic information differentiating the metallic and insulating states. Further, we look for possible precursors of the M-I transition.

The magnetic susceptibility of V_2O_3 through the region of the ~170 °K M-I transition was studied by several investigators,[5–10] who found a reduced susceptibility below the transition temperature. Although the behavior bore some resemblance to an antiferromagnet, it differed from a classical antiferromagnet in that there was a susceptibility discontinuity at the transition and a nonmonotonic temperature dependence above the transition. However, from NMR,[11] Mössbauer effect,[2] and neutron diffraction[13] measurements, it was finally revealed that the low-temperature state was antiferromagnetic. It was also shown that the crystal transformed at the transition to a monoclinic structure.[14]

Anomalies were also found in the metallic state, with a minimum in the high-temperature susceptibility,[6,8–10] an anomalously high paramagnetic Curie-Weiss θ,[10] and a nuclear-resonance frequency shift that did not track the susceptibility.[15] The temperature at which these anomalies occurred corresponded to that where weak electrical resistivity and thermal expansion singularities had previously been found.[16]

The V_2O_3 M-I transition has also been studied as a function of pressure,[17] with the discovery that pressures greater than 26 kbar suppress the insulating state, leaving V_2O_3 metallic to the lowest temperatures. A search for local moments using high-pressure NMR[18] showed that there are apparently no static moments in the metallic phase. A strongly volume-dependent spin susceptiblity and a d-spin ^{51}V nuclear relaxation, some two orders of magnitude faster than in vanadium metal, were also deduced from the NMR measurements.

The source of the antiferromagnetic and M-I transitions of V_2O_3 is unfortunately obscured by the accompanying structural transformation, since the trigonal to monoclinic symmetry change may introduce gaps in the electronic energy spectrum responsible both for the magnetic and electrical phenomena.

An alternative means of studying the M-I transition without the complication of an accompanying structural symmetry change has been offered by V_2O_3 containing Al and Cr.[4] The observation that Al_2O_3 and Cr_2O_3 are insulating, while V_2O_3 (above 170 °K) is metallic, suggested that metallic V_2O_3 would be converted to an insulator by addition of Cr or Al. Structural studies showed a sharp drop in c/a of V_2O_3 on addition of ~1% Al or Cr.[7] Subsequently, it was shown that a transition to insulating behavior occurred at the same time.[4] No magnetic ordering or symmetry change accompanied

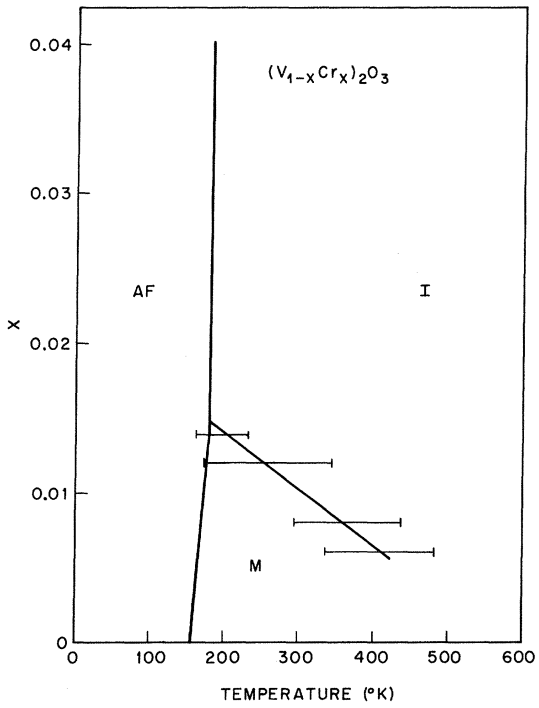

FIG. 1. Phase diagram for $(V_{1-x}Cr_x)_2O_3$ produced from crystallographic data [Ref. 4 and P. D. Dernier (private communication)]. AF denotes antiferromagnetic, I insulator, and M metal. Two-phase regions exist near the M-I transition. The horizontal bars shown the regions where M and I phases are found to coexist.

this transition. Phase diagrams were determined for the metallic (M), paramagnetic insulating (I), and antiferromagnetic insulating (AF) regimes, as functions of temperature, pressure, and composition.[19] The phase diagram determined crystallographically appears in Fig. 1. Susceptibilities were measured for the samples containing Cr,[10,20] and it was found that I-phase material had a larger susceptibility than M-phase material. Because of possible magnetic moments on the Cr sites in these samples, however, it was difficult to partition with certainty the portions of the susceptibility localized at the Cr atoms and those portions ascribable to the V_2O_3 host-matrix susceptibility. In the present work we attempt to solve this problem by studying V_2O_3 doped with Al, where a transition to insulating behavior occurs quite similarly,[21] but where the impurity sites are assuredly nonmagnetic. We shall also apply the study of ^{51}V NMR to give a local measurement of the vanadium-site magnetic response in both Cr-doped and in Al-doped samples. Preliminary results of this work were reported in Ref. 22.

Some of the anomalies in undoped V_2O_3 mentioned above can be associated with a gradual return from metal to insulator with increasing temperature in the 500 °K range. In fact, detailed studies of the phase diagram[19] showed that while at Cr concentrations greater than ~0.5% there is a first-order phase transition to the high-temperature paramagnetic I state, at lower Cr content there is only a gradual change, characteristic of supercritical behavior, toward an I state. Thus, instead of undoped V_2O_3 returning abruptly to I-state behavior, the change is gradual. Above 500 °K, however, the resistivity, susceptibility, and lattice constants of V_2O_3 asymptotically approach those of the I-phase (Cr-doped) materials which underwent first-order phase transitions. We have extended NMR measurements to temperatures as high as 900 °K in order to traverse more completely the supercritical regime and to obtain microscopic evidence of the accompanying change in electronic structure.

At the outset, we wish also to recall the other vanadium oxides in which M-I transitions have been reported. An earlier M-I transition reported in VO was apparently caused by impurities of V_2O_3 in the sample.[3] NMR studies[23] showed the ^{51}V resonance to be observable down to low temperatures, proving that the majority of vanadium sites have no static magnetic moments. Vanadium "monoxide" exists over a wide range of composition, however, and oxygen-rich samples were found to have higher, Curie-like susceptibilities and higher semiconductorlike resistivities than oxygen-poor samples.[24] The NMR linewidth and frequency-shift behavior were interpreted in terms of the appearance of several percent of vanadium local moments, which apparently order at low temperatures in samples which are $\gtrsim 20\%$ oxygen rich.

The role of magnetism in the 350 °K M-I transition of VO_2 is not yet clearly defined. Although NMR measurements at[25] 77 and[18] 4.2 °K show that no magnetic long-range ordering occurs, and although the susceptibility shows little temperature dependence[26] and NMR frequency shifts show essentially no temperature dependence down to He temperature,[18] there is a possibility of the existence of localized moments bound in singlet pairs. Arguments have been given that such pairing may exist between moments on adjacent crystallographically paired vanadium ions in the distorted rutile structure.[27]

M-I transitions and accompanying susceptibility discontinuities[28] have also been observed in V_5O_9, V_6O_{11}, V_4O_7, and V_6O_{13}, but no evidence of magnetic ordering has been found for these systems.

II. EXPERIMENTAL

The previously reported susceptibility measurements on samples of V_2O_3 containing up to 4% Cr $[(V_{0.96}Cr_{0.04})_2O_3]$ were made on single crystals prepared by a flux technique.[4] Since trace

amounts of VN remained in these samples, giving rise to VN ^{51}V nuclear-resonance lines, it was necessary, instead, to perform the nuclear-resonance measurements on ceramic powder samples which contained no nitride. The preparation of such ceramic samples was described earlier.[21] The compounds containing aluminum were also prepared by the reported ceramic powder technique by reacting V_2O_3 and Al_2O_3. For nuclear-resonance measurements, in order to achieve rf field penetration, the ceramic compacts were pulverized sufficiently with an agate mortar and pestle to allow passage through a 200-mesh screen.

Susceptibility measurements were made by a force technique in an inhomogeneous magnetic field using a Cahn microbalance.[10] At temperatures above 300 °K, the samples were sealed in quartz tubes under argon.

NMR measurements in the temperature range up to 500 °K were made with a commercial cw crossed-coil induction apparatus operating at 16 MHz. Variable temperatures were achieved with a blowing N_2 gas temperature controller, with an accuracy of ± 5 °K being obtained. An Al-free rf probe was used in order to avoid the interference of ^{27}Al probe signals with the desired ^{51}V sample resonances, which lay in the same frequency range. Resonance frequency shifts were measured relative to ^{51}V NMR in a $NaVO_3$ solution, with 0.01% accuracy for V_2O_3 and 0.03% accuracy in doped samples. In the temperature range from 300 to 1000 °K, NMR was also observed using pulsed techniques. ^{51}V free-induction decay signals were detected coherently from samples sealed under vacuum in quartz vials. Frequency shifts were measured to 0.02% accuracy. The high-temperature apparatus is described elsewhere.[29]

III. SUSCEPTIBILITY RESULTS

The magnetic susceptibilities reported earlier[10] for single crystals of V_2O_3 and for $(V_{0.99}Cr_{0.01})_2O_3$ and $(V_{0.96}Cr_{0.04})_2O_3$ are shown in the upper half of Fig. 2. In the bottom half of Fig. 2 are shown the magnetic susceptibilities of ceramic $(V_{0.99}Al_{0.01})_2O_3$ and $(V_{0.97}Al_{0.03})_2O_3$. X-ray powder patterns of the samples[21] containing Al, as well as electrical resistivity measurements, have shown that a very similar phase diagram to that of Cr (Fig. 1) prevails for $(V_{1-x}Al_x)_2O_3$. Thus, the $(V_{0.99}Al_{0.01})_2O_3$ is insulating and monoclinic at low temperatures, becomes metallic trigonal corundum at 180 °K, and then transforms to insulating trigonal corundum with decreased c/a ratio and increased volume between 275–425 °K.

A fit to a Curie-Weiss plus constant-term temperature dependence was made for the Cr-doped samples.[10] In the I phase, p_{eff} lay between 2.3 and 3.0 μ_B, and θ between 320 and 380 °K, in the composition range from $(V_{0.99}Cr_{0.01})_2O_3$ to $(V_{0.80}Cr_{0.20})_2O_3$. The Al-doped sample susceptibilities are similar to the Cr-doped results, but lie slightly higher, and in the 1%-Al sample show a more gradual transition from M-state to I-state susceptibility behavior. The susceptibility of the Al-doped samples is slightly greater than that of the corresponding Cr-doped materials, and the transition between M-phase and I-phase behavior is also more gradual for the Al-doped than for the Cr-doped samples. Unfortunately, Al-doped samples also show a more appreciable low-temperature Curie term in the AF phase, somewhat similar to that seen in V_2O_3 samples containing excess oxygen.[21] Because of the unknown magnitude of this term above the AF transition, no attempt was made to analytically fit the Al-doped sample susceptibilites.

In the Cr-doped materials it was not possible to distinguish between the increase of χ due to the host material and increases due to possible localized magnetization on the Cr sites as the material switched from metal to insulator. It is now seen that a comparable (actually slightly larger) increase is occurring on passing to the I phase by addition of Al. Since Al would not be expected to have a

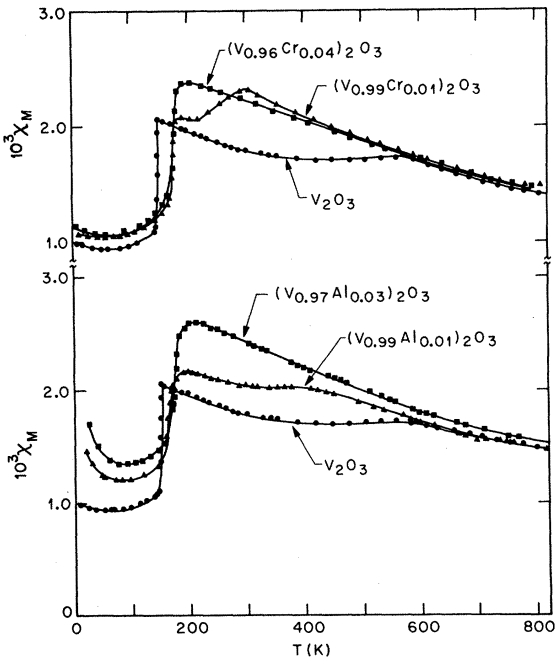

FIG. 2. Magnetic susceptibility vs temperature for V_2O_3 and for Cr- and Al-containing V_2O_3. The V_2O_3 and samples containing Cr were single crystals with susceptibility parallel to the pseudohexagonal c axis being shown. (No anisotropy of the susceptibility was observed for $T > 180$ °K.) The samples containing Al were ceramic powder aggregates.

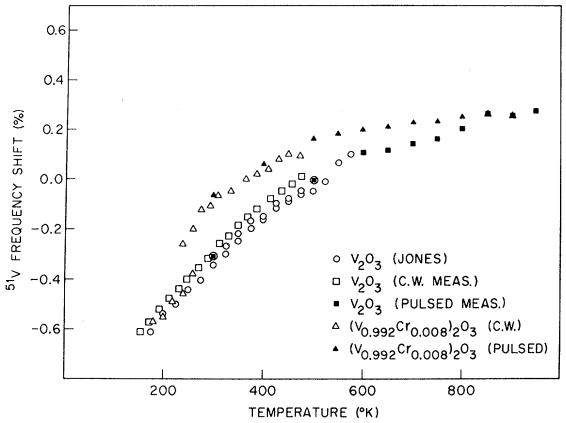

FIG. 3. ^{51}V frequency shifts vs temperature for V_2O_3 and $(V_{0.992}Cr_{0.008})_2O_3$. The three sets of data shown for V_2O_3 were made with three different samples while both the cw and pulsed measurements were made on the same $(V_{0.992}Cr_{0.008})_2O_3$ sample. The upper curve is associated in the text with I phase and the lower curve with M phase. Above 800 °K V_2O_3 has become I-like.

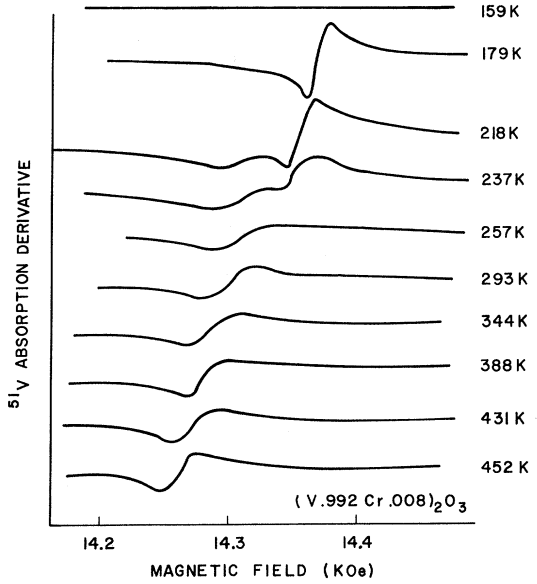

FIG. 5. ^{51}V NMR absorption derivatives for $(V_{0.992}Cr_{0.008})_2O_3$ as a function of magnetic field at a frequency of 16 MHz. Recorded noise is not reproduced in these tracings. The absence of any signal at 159 °K is caused by antiferromagnetism. Two absorption lines are observed simultaneously at 218 and 237 °K, apparently from coexisting M-phase and I-phase regions of the samples.

localized magnetic moment, it is now clear that the host V_2O_3 susceptibility is raised by transition to the I state. The spatial distribution of magnetization is not yet determined, however.

IV. NMR RESULTS

The ^{51}V nuclear resonance of V_2O_3 as observed initially by Jones[11] and then by Jesser and Silhouette[9] had a temperature-dependent frequency shift in the temperature range 175–550 °K. The dependence of the shift in Jones's work (although not in the Jesser-Silhouette work) was a monotonic Curie-Weiss behavior over the entire range. Below 175 °K the resonance disappeared, and this was correctly ascribed to the onset of antiferromagnet order. The linewidths were observed to be independent of temperature and magnetic field, and no evidence was found for quadrupolar structure of the line, admissible because of the noncubic symmetry of the vanadium sites. The frequency shifts in V_2O_3 observed with the present samples are slightly more positive than those of Jones and considerably more positive than those of Jesser and Silhouette above 300 °K. As mentioned above, pulsed measurements of the higher-temperature-region frequency shifts were also made. Attempts to observe ^{51}V nuclear-spin echoes were not successful, apparently because of a rapid spin-spin relaxation rate T_2^{-1}. This rate was evidently of the same order of magnitude as the linewidth or rate of dephasing, T_2^{*-1}. The frequency shifts as obtained from plots of the free-induction decay amplitude as a function of swept dc magnetic field are also presented in Fig. 3.

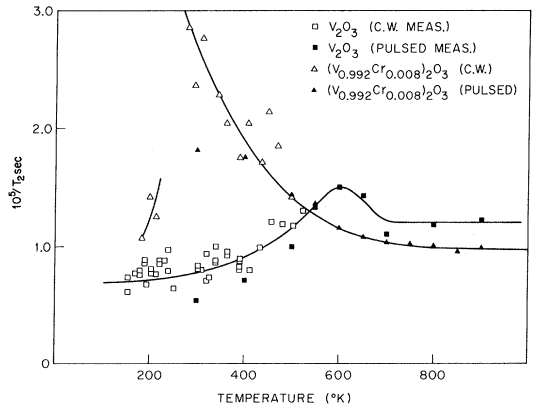

FIG. 4. Reciprocal free-induction-decay lifetime $1/T_2^*$ for ^{51}V nuclear resonance in V_2O_3 and $(V_{0.992}Cr_{0.008})_2O_3$. The values of $1/T_2^*$ shown for the cw measurements were taken from the peak-to-peak separation of the nuclear absorption derivative spectra using the relationship expected for a Lorentzian line shape: $1/T_2^* = \sqrt{3}\,\pi\Delta\nu_{pp}$. The generally higher values of $1/T_2^*$ obtained in the cw measurements apparently result from an inadequacy of the Lorentzian description of the line shape. The linewidth maxima occur in the region intermediate between M- and I-like behavior for V_2O_3 and near the M-I phase transition for $(V_{0.992}Cr_{0.008})_2O_3$.

Linewidths of the ^{51}V NMR obtained by the cw technique and the free-induction decay rate T_2^{*-1} are

shown in Fig. 4. In making the plot, a Lorentzian correspondence was made between the peak-to-peak cw absorption derivative widths and T_2^{*-1} ($T_2^{*-1} = \sqrt{3}\pi\Delta\nu$). The low-temperature cw linewidth of 12 G agrees with that of Jesser and Silhouette,[9] but is narrower than the 16 G of Jones.[11] It is seen that the linewidth passes through a maximum in the 600 °K range. It is also seen that in the range below 500 °K there is a slight temperature dependence of the width. It is interesting that the peak, clearly observable with the pulsed measurements, occurs in the region of the supercritical transformation from M-like to I-like characteristics.

Also shown in Figs. 3 and 4 are the frequency shifts and linewidths for a sample containing 0.8% Cr [$(V_{0.992}Cr_{0.008})_2O_3$]. Here the sample passed through the first-order M-I phase transition as temperature decreased, with the apparent temperature for the center of the transition ~250 °K, somewhat lower than observed by x rays in crushed single-crystal material. A discontinuity in Knight shift is observed at the M-I transition with coexistence of two resonance lines. (Figure 5 shows a series of resonance line shapes observed in this sample.) The resonance lines with the lower frequency shift are associated with M-phase regions, and those with higher frequency (more positive) with I-phase regions. It is interesting to note that at high temperature the frequency shifts of V_2O_3 and the I-phase $(V_{0.992}Cr_{0.008})_2O_3$ become nearly equal. A peak in the linewidth is observed in the transition region. The discreteness of the two lines and their simultaneous existence proves immediately the discreteness of the M and I phases in the doped sample. In contrast, the single line with unreduced

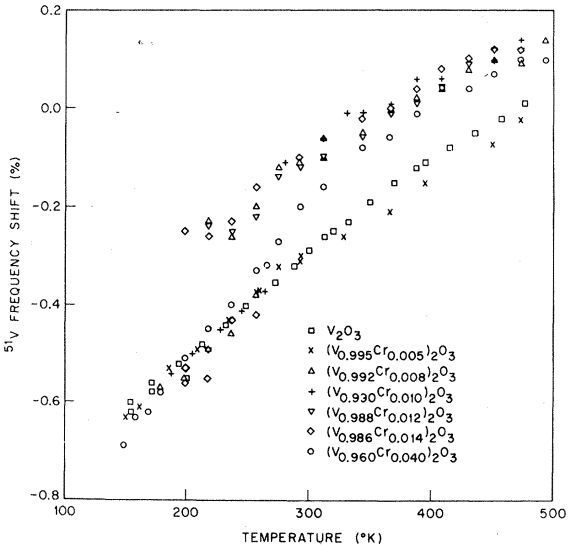

FIG. 6. ^{51}V NMR frequency shifts vs temperature for V_2O_3 and for Cr-doped V_2O_3 based on cw measurements.

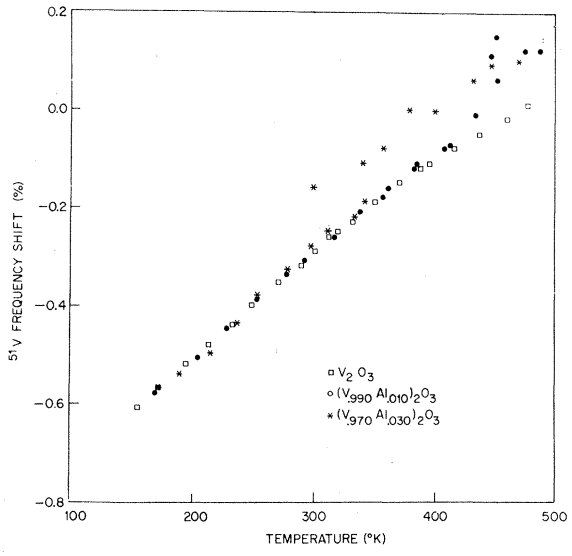

FIG. 7. ^{51}V NMR frequency shifts vs temperature for Al-doped V_2O_3 based on cw measurements.

intensity observed in V_2O_3 showed that only one phase exists there. The peak in the linewidth of the Cr-doped materials may at least partially be explained in terms of the simultaneous occurrence of the two resonance lines, but that in the pure V_2O_3 may also involve fluctuation phenomena.

Samples with a number of other Cr dopings were observed in the temperature range to 500 °K, and their frequency shifts vs temperature are shown in Fig. 6. It is observed in all cases that the frequency shifts in the I phase are more positive than in M-phase material at the same temperatures. As the Cr content is increased, the transitions from M to I are observed to occur at lower temperatures in accordance with the slope of the M-I phase boundary of Fig. 1. In the more concentrated samples containing Cr, the metallic phase is completely suppressed.

Measurements of the NMR of the same system of compounds have been reported by Rubinstein[30] with similar results. There are several details, however, in which the present measurements differ. The temperature region of coexistence of the M-phase and I-phase NMR lines is found to be smaller in the present work. Presumably the narrower range of transition is a result of more homogeneous composition of our samples. The extra lines due to ^{27}Al NMR of the probe body are not seen in the present work because of our use of an Al-free probe. Absorption-mode, rather than dispersion-mode, measurements were used here, permitting more accurate linewidth measurements. The I-phase frequency shifts at low temperatures in the higher-concentration Cr samples lie below those

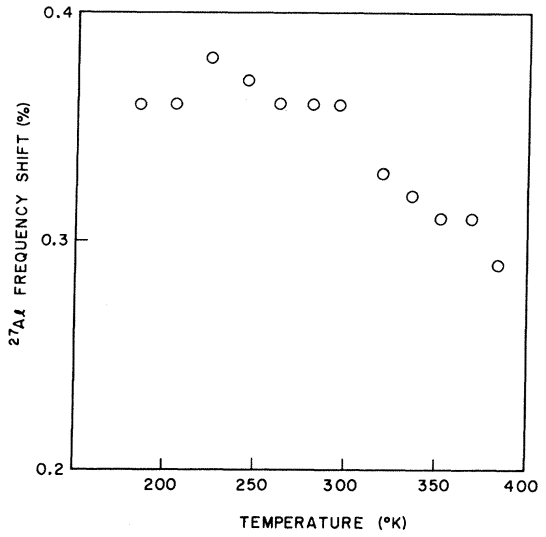

FIG. 8. ^{27}Al NMR frequency shift vs temperature for $(V_{0.96}Al_{0.04})_2O_3$.

shifts of the Rubinstein work, although the reason for this behavior is not yet clarified. Finally, susceptibilities were also measured for a number of our samples.

The ^{51}V nuclear resonances were also observed in materials containing Al. Previous measurements had shown that these compounds possessed a similar phase diagram to the Cr-doped V_2O_3, with quantities of order 1% Al producing a transition to a paramagnetic I phase.[21] As before, no nuclear resonance was observable in the AF phase. The ^{51}V frequency shift vs temperature behavior of samples containing 1 and 3% Al is shown in Fig. 7. Again, a resonance line with more positive frequency shift appears in the I phase. In addition to the ^{51}V lines, it was also possible to observe ^{27}Al nuclear resonance in these samples, and the frequency shifts vs temperature for the Al^{27} resonances is seen in Fig. 8. The magnitude of these shifts is nearly twice that observed for Al metal and is noticeably temperature dependent. Unfortunately, the ^{27}Al resonance could only be observed in the I state, due to the accidental fact that in the M-phase the stronger ^{51}V response shifted to the same position as the ^{27}Al and obscured the weaker ^{27}Al NMR line.

V. DISCUSSION

The observation of different susceptibilities and of separate nuclear-resonance responses from metal and insulating phases of our samples establishes that the two phases are distinct on a microscopic scale. But the ^{51}V frequency shift on transition to the insulating phase was initially surprising. An increase in the spin paramagnetism, coupled to the nuclei by a negative d-spin core-polarization hyperfine coupling constant, would have been expected to lead to a more negative frequency shift in the I phase. In fact, however, the reverse was observed. We shall argue that this implies that the hyperfine coupling constant, as well as the susceptibility, is changed in the M-I transition.

Figure 9 shows a plot of frequency shift vs susceptibility for four samples: V_2O_3, $(V_{0.992}Cr_{0.008})_2O_3$, $(V_{0.96}Cr_{0.04})_2O_3$, and $(V_{0.97}Al_{0.03})_2O_3$. The susceptibility $\chi(T)$ and frequency shift $K(T)$ can be considered to consist of spin and orbital contributions[31]:

$$\chi(T) = \chi_{\rm orb} + \chi_{\rm spin}(T) + \chi_{\rm dia} ,$$

$$K(T) = K_{\rm orb} + [H^{\rm hf}_{\rm spin}(T)/A\mu_B]\chi_{\rm spin}(T) + K_{\rm dia} .$$

$\chi_{\rm orb}$ is the Van Vleck paramagnetic susceptibility, which should be substantially temperature independent. $\chi_{\rm spin}(T)$ is the spin paramagnetic susceptibility associated with the 3d electrons, to which we attribute the temperature dependence of the susceptibility. We expect 4s electrons to contribute negligibly to the susceptibility. The diamagnetic terms are also negligible. $K_{\rm orb}$ will be positive, and is given by $2\langle r^{-3}\rangle\chi_{\rm orb}/A$, while $H^{\rm hf}_{\rm spin}$ is the hyperfine field (per Bohr magneton) of the 3d-spin magnetization, arising predominantly from core-polarization effects. $\chi(T)$, $\chi_{\rm orb}$, and $\chi_{\rm spin}$ are susceptibilities per mole of V_2O_3, i.e., per 6.02×10^{23} V_2O_3 units, and A is Avogadro's number. Jones observed a linear relationship between $K(T)$ and $\chi(T)$ in V_2O_3 as the temperature varied in the range from 175 to 300 °K. Using a calculated value of $H^{\rm hf}_{\rm orb} = +395$ kOe/μ_B, the determined $K_{\rm orb} = +1.52\%$, $\chi_{\rm orb} \simeq 0.4\times10^{-3}$ emu/mole, and $H^{\rm hf}_{\rm spin} = -140$ kOe/μ_B. However, when the susceptibility was measured at higher temperatures,[8-10] it was found to

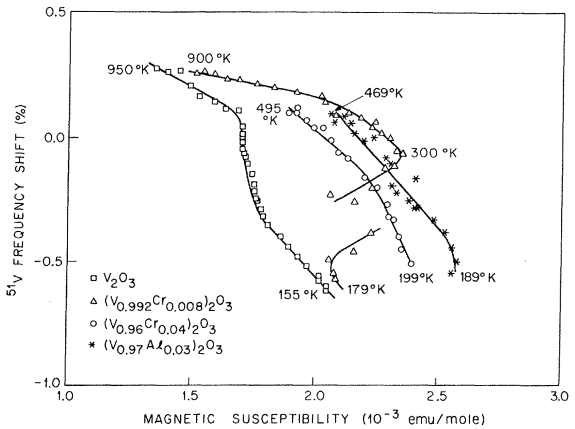

FIG. 9. Plot of ^{51}V NMR frequency shifts vs susceptibility with temperature an implicit parameter. The susceptibility values vs temperature are shown in Fig. 2.

stop decreasing and to pass a weak maximum, whereas $K(T)$ continued to become monotonically more positive. This resulted in the nonlinearity of the points seen in Fig. 9. When I-phase materials were examined, it was found that their frequency shifts and susceptibilities were related still differently. For $(V_{0.97}Al_{0.03})_2O_3$ and $(V_{0.96}Cr_{0.04})_2O_3$, the points lie higher. For unchanged χ_{orb} this implies that the hyperfine coupling constant H^{hf}_{spin} is *smaller* in the I-phase than in the M-phase. For the I-phase we estimate $H^{hf}_{spin} \sim -100$ kOe/μ_B, which produces the more positive I-phase frequency shifts. This compares with $H^{hf} = -133$ kOe/μ_B for V^{3+} in Al_2O_3 as determined by EPR.[32] Because of scatter in the data points and residual uncertainties in the magnetic susceptibility, however, an accurate determination of H^{hf}_{spin} in the I state is not possible. The smaller hyperfine coupling also resolves the anomalous dependence of K upon χ observed in pure V_2O_3. The high-temperature increase in K is caused by the gradual change toward the I state as V_2O_3 is heated, which produces an attendant decrease in the hyperfine coupling constant. Existence of two hyperfine coupling constants in V_2O_3 was recently proposed by Goodenough who associated the two constants with two bands.[33] At the highest temperatures, the points for V_2O_3 nearly coincide with the ones for $(V_{0.992}Cr_{0.008})_2O_3$, confirming that the supercritical transformation of V_2O_3 to I behavior is essentially complete by ~800 °K. The deviation from a linear K-χ relationship in the 0.8% Cr-doped and in the 4.0% Cr-doped sample in the low-temperature range suggests a possible tendency toward some metallic characteristics in these temperature ranges in the samples containing Cr.

A possibility which we have not treated here, but which would also produce a more positive frequency shift in the I phase, is an increase in Van Vleck temperature-independent orbital paramagnetism on transition to the I state. We feel that this is unlikely to have occurred, however, since the K-χ plot points at high temperatures in I-phase material extrapolate to a *lower* Van Vleck paramagnetism than in the M phase. Furthermore, the fit to the I-state bulk susceptibility also yields a *lower* temperature-independent term.

The $3d$-spin hyperfine coupling constant is dependent on several factors which are sensitive to the phase of the sample. These are the degree of covalency (increasing covalency would reduce the coupling constant), the radius of the $3d$ wave functions, the possible presence of $4s$ electrons in the M phase,[34] and the presence of unquenched components of orbital angular momentum. Since the total hyperfine coupling constant contains canceling positive and negative contributions, changes in any of these factors could produce a difference in coupling constant of the observed magntiude between the two phases.

We next look for differences in the relaxation processes in the M and I phases. These processes should be quite sensitive to the degree of moment localization of the phases. In the M phase there are no static magnetic moments, while the I-phase material apparently does have such moments. The evidence for the local moments is primarily the observed susceptibility, which for the I phase is well described by a Curie-Weiss behavior.[10] The effective I-phase magneton numbers of 2.3–3.0 μ_B are close in magnitude to the trivalent free-ion value, while the observed Weiss temperatures of 320–380 °K are only moderately higher than the value of 290 °K obtained for the Néel temperature by extrapolation of the AF-phase data above the AF-M transition.[13] The deduced M-phase Weiss temperature of 600 °K, on the other hand, reflects a lower and less temperature-dependent susceptibility. It suggests that the M-phase susceptibility should be described from a narrow-band temperature-dependent Pauli-paramagnetism point of view, rather than a Curie-Weiss local moment approach. This point of view was confirmed by the high-pressure low-temperature NMR of V_2O_3 which showed that there are no localized magnetic moments in M-phase V_2O_3. Under these conditions a Korringa-like nuclear spin-lattice relaxation rate with $1/T_1$ proportional to T would be expected from the $3d$ bands of the M state. The expected relaxation can be written as[35]

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{core polarization}} + \left(\frac{1}{T_1}\right)_{\text{orb}} + \left(\frac{1}{T_1}\right)_{s} + \left(\frac{1}{T_1}\right)_{\text{dipolar}} .$$

In view of the high d-state susceptibility, the s term may be neglected,[9] and the dipolar term is also expected to be negligible in comparison to the first two terms. In the absence of exchange enhancement of the susceptibility, we expect the spin and orbital terms in the M phase to be

$$\frac{1}{T_1} = \frac{4\pi kT}{\hbar}\left(\frac{\gamma_n}{\gamma e}\right)^2 (K_{spin})^2 q + \frac{4\pi kT}{\hbar}\left(\frac{\gamma_n}{\gamma e}\right)^2 (K_{spin})^2 \left(\frac{H^{hf}_{orb}}{H^{hf}_{spin}}\right)^2 p$$

where q and p are reduction factors between 0 and 1 which may be anisotropic and which can be calculated only when the symmetries and orbital degeneracies of the Fermi-surface electrons are specified.[35] If the susceptibility becomes so greatly enhanced that the relative enhancement varies appreciably between different wave-vector components of the susceptibility, then further changes in the expression for $1/T_1$ occur. At 300 °K, with $K_{spin} = -1.8\%$ and[11]

$$\frac{H_{\text{orb}}^{\text{hf}}}{H_{\text{spin}}^{\text{hf}}} = \frac{395\ \text{kOe}}{-140\ \text{kOe}},$$

the above expression gives $1/T_1T = 81.2q + 647p$. An experimental rate $1/T_1T \lesssim 50\ \text{sec}^{-1}\,^{\circ}\text{K}^{-1}$ was deduced from the 4.2 °K high-pressure observations. The experimentally observed rate lies near the low end of the allowable range and gives some indication that p is small, requiring a low orbital degeneracy at the Fermi energy. This spin-lattice rate is also expected to produce an apparent dynamic spin-spin dephasing rate T_2^{-1} of the observed transition. In fact, the observed 300 and 400 °K T_2^{*-1} are nearly an order of magnitude faster than the predicted rate. This difference may arise partly from the uncertainties of the 4.2 °K T_1 measurements, partly from static sources of T_2^{*-1}, and partly from uncertainties in our knowledge of the quadrupolar structure of the line. [In a quadrupole-broadened spectrum of a nuclear spin I, the T_2 equilibration of the center of the spectrum will occur up to a factor $(I+\frac{1}{2})^2$ faster than the T_1 equilibration of the entire spectrum.]

The existence of localized moments in the I-phase, inferred from the Curie-Weiss susceptibility, should also produce relaxation of the nuclear resonance. Since the I phase is paramagnetic, the moments will fluctuate in time, giving rise to fluctuating hyperfine fields, and thus nuclear relaxation. Spins S, coupled to ^{51}V nuclei by a hyperfine coupling interaction $A\vec{I}\cdot\vec{S}$ and fluctuating at a frequency ω_{ex}, will produce relaxation rates[36,37]

$$\frac{1}{T_1} = \frac{1}{T_2} = (\sqrt{2\pi})\left(\frac{A}{\hbar}\right)^2 \frac{S(S+1)}{3\omega_{ex}}.$$

Taking $A/\hbar = 1.4\times10^9\ \text{sec}^{-1}$, $S=1$,

$$\omega_{ex} = 3kT_c/2\hbar[ZS(S+1)]^{1/2} = 1.1\times10^{13}\ \text{sec}^{-1},$$

$T_c = 290$ °K, and $Z=6$, we calculate

$$1/T_1 = 1/T_2 = 3\times10^5\ \text{sec}^{-1}.$$

This is close to the observed relaxation rate in confirmation of the essential features of the local moment model for the I state, i.e., a well-developed local moment with reduced hyperfine interaction in the I phase. The detailed agreement may be a bit fortuitous, however, since itinerancy limitation of the electronic-spin-state lifetimes might decrease the calculated rate, while quadrupole broadening might increase the rate expected for the central portion of the line. The observed T_2^{*-1} may also be somewhat greater than T_2^{-1} if there are inhomogeneous broadening components of the dephasing rate T_2^{*-1}. On balance, however, the observed rates accord well with those expected from paramagnetic local moments.

At the transition between M and I phases, there are two ways in which we might expect linewidth and relaxation to be affected. Very near the solid-solid critical point one should observe critical broadening from critical fluctuations of the susceptibility and hyperfine field. We suspect that in actual fact, stoichiometry inhomogeneities smear the critical point sufficiently to obscure such critical fluctuations. The inhomogeneities lead in turn, however, to a second source of linewidth. This arises from the fact that the two phases will coexist in different regions of the sample near the transition temperature. The nuclear resonance then consists of superimposed responses from the two phases with a resultant broadening. In pure V_2O_3, where the chemical homogeneity is higher, the possibility exists that passage through the supercritical region leads to narrowed, more highly correlated bands, and a faster T_2. Above the supercritical region, exchange interactions among the local moments produce a narrowing. Experiments (e.g., echo, rather than free-induction decay) which would distinguish T_2 from T_2^* would have been useful in this regard, but were unfortunately not practicable because of the rapid T_2 process and the short times which were involved.

Some comment should also be made on the consistency between the present measurements and the earlier pressure-dependence measurements[18] on V_2O_3. Pressure converted the material containing Cr from I to M phase while addition of Cr converted V_2O_3 from M to I phase. The equivalence factor was -3.6 kbar/(% Cr).[17] The ^{51}V frequency shifts in pure V_2O_3 were strongly pressure sensitive with $dK/dp = (+0.009\pm0.005)\%$/kbar. The pressure, producing the same M-I transition temperature change as 0.8% Cr, would then lead to a +0.03% frequency shift (always remaining in the M state). This frequency shift is only on the limits of observability and thus is consistent with the observed lack of any systematic *composition* dependence of the ^{51}V frequency shift in the M state.

Turning to the ^{27}Al NMR, we note that some information on the covalent distribution of spin in the I phase of $(V_{1-x}Al_x)_2O_3$ may be obtained from the ^{27}Al frequency shifts. Whereas the Al-metal shift of ^{27}Al is +0.16%, the shift in $(V_{0.96}Al_{0.04})_2O_3$ varied from +0.29 to +0.38%. Under the assumption that the ^{27}Al hyperfine coupling constant to unpaired Al electrons is the same in the V_2O_3 host as in Al metal, we may calculate that the magnetization per Al atom localized on the Al atom is $\langle\mu\rangle_{Al} \sim 0.04\langle\mu\rangle_V$, where $\langle\mu\rangle_V$ is the magnetization per vanadium atom. (This is based on[38] $\chi^{\text{Pauli}} = 17\times10^{-6}$ emu/mole for Al metal.) If, in fact, the ^{27}Al hyperfine coupling constant is smaller (p-like), the magnetization per Al atom in V_2O_3 must be still greater. A measure of the covalency implied by this Al moment mea-

surement is obtained by comparison with the supertransferred hyperfine interaction observed at ^{27}Al nuclei in Al_2O_3 doped with 3*d* transition elements. Data for V^{3+} doping does not exist, but in Fe^{3+}, a supertransferred hyperfine coupling constant $a_{^{27}Al\text{-}Fe^{3+}} = 3.3 \times 10^6$ sec^{-1} was obtained by ENDOR.[39] An Al impurity in V_2O_3 is surrounded by one nearest- and three next-nearest-neighbor vanadium atoms. If the coupling of the ^{27}Al to these four neighbors were additive and equal, a coupling constant $a_{^{27}Al\text{-}V^{3+}} = 11.8 \times 10^6$ sec^{-1} would produce the observed ^{27}Al frequency shifts. This is nearly four times the ENDOR value observed for ^{27}Al-Fe^{3+} coupling. Together with the value for the local polarization at the Al site, it indicates that the covalency in V_2O_3 is indeed of an unusually large magnitude. Since the I-state material is near the instability of carrier formation, it is presumably a poor insulator with rather broadened bands and appreciable transfer integrals, all of which may result from enhanced covalency. A more complete characterization of the covalency awaits study of the transferred hyperfine interaction at the oxygen sites.

Finally, some comment may be made on the magnitude of the saturation sublattice magnetic moments observed in the antiferromagnetic state by neutron diffraction.[13] Whereas the spin moment expected for $S=1$ with quenched orbital angular momentum is 2 μ_B per V^{3+} ion, the observed value is only 1.2 μ_B. Several mechanisms could produce this V^{3+} ion moment reduction. A filled covalent bonding band with no spontaneous magnetic moment and a localized band with 1 μ_B per V^{3+} ion could be formed from the two available 3*d* electrons. This would reduce the moment to 1 μ_B per vanadium ion from the magnetized band and a small induced moment from the nonmagnetized band.[33] Alternatively, the reduction could be produced by formation of singlet spin-pair states by one electron per ion,[27] the remaining electron again contributing 1 μ_B per ion. However, it is also possible that the moment reduction is the result of itinerant antiferromagnetism or of covalency with a cancellation of covalently transferred magnetic moment occurring on either V^{3+} or O^{2-} sites. The requirement in order to explain the *entire* V^{3+} moment reduction by cancellation on the O^{2-} sites is the covalent transfer of (2.0–1.2) μ_B of magnetization from each V^{3+} site and the resultant occurrence simultaneously of $\frac{1}{3}$(2.0–1.2) μ_B of up and down magnetization on each O^{2-} site. Some indication of the actual covalent transfer to the O^{2-} might be obtained from study of the paramagnetic state. At temperatures above the Néel temperature, the time-average field-induced spin polarizations will be parallel on all vanadium sites, and the average covalently transferred spin polarizations on the oxygen sites will be additive. The average O^{2-} site polarization will then be exactly $\frac{2}{3}$ of the spin polarization transferred away from the vanadium site. Thus, a 40% transfer of the V^{3+} spin polarization (required for reduction of the AF moment from 2 to 1.2 μ_B) would require an O^{2-} site susceptibility of 0.27 times the total observed paramagnetic state susceptibility. This may be compared with our local Al-site susceptibility of 0.04 times the total susceptibility. An alternate explanation of the reduced moments would involve unquenched components of orbital angular momentum. This is difficult to calculate without knowledge of the energy levels of V^{3+}, which in turn are difficult to obtain because of changes in the energy levels introduced by magnetic ordering and the monoclinic distortion. The *g* value in the ground-state spin triplet ($g_{\parallel} = 1.915$) of V^{3+} in[32] Al_2O_3 is insufficiently small to produce the observed small saturation moment, however, and it seems quite possible that a significant portion of the reduction is caused by covalent spin transfer.

VI. CONCLUSIONS

The I phase which is gradually attained with increasing temperature in V_2O_3 and which is abruptly reached on Al or Cr additions is distinct in several ways. In addition to the lattice constant and resistivity differences from the M phase, it is now found to be characterized by higher susceptiblity of the host and to have a reduced ^{51}V *d*-spin hyperfine coupling constant. The most consistent explanation of our results comes from a nonmagnetized band description of the metal and a localized moment picture of the insulator. The metallic bands have a high susceptibility (~10 times that of V metal) while there is a high degree of covalency in the I state. Anomalous nuclear-resonance frequency-shift behavior observed in earlier work on pure V_2O_3 is shown to be a result of the gradual change to I-state behavior in high-temperature V_2O_3.

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Elastic Constants of Copper-Rich Alloys with Gold †

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The elastic constants of Cu-(0.23 at.%)Au, Cu-(2.8 at.%)Au, and Cu-(10.0 at.%)Au have been experimentally measured over the temperature range 300–4.2 °K. The elastic constants at 0 °K have been fitted with the Neighbors-Smith model for shear elastic constants of dilute monovalent-metal alloys.

INTRODUCTION

Cohesion in a metal crystal is especially complicated by the influence of the electron sea. As a result, the elastic constants of metal single crystals are difficult to relate to atomic theory, except for a few special cases. Fuchs,[1] for instance, has proposed a theory of elastic constants for monovalent metals which gives rather good agreement with experimental data for the alkali metals and the noble metals.[2,3] This model deals with shear strains, which do not affect the atomic volume of the Wigner-Seitz cell surrounding each metal ion. As a result the shear elastic constants $c' = \frac{1}{2}(c_{11} - c_{12})$ and c_{44}