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MAGNETIC SUSCEPTIBILITY AND NUCLEAR RESONANCE STUDIES OF METAL-INSULATOR TRANSITION OF $(V_{1-x}Cr_x)_2O_3$ AND $(V_{1-x}Al_x)_2O_3$

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Résumé. — L'addition de Cr ou de Al dans V_2O_3 provoque le passage d'une phase métallique à une phase isolante paramagnétique. Nous rapportons les comportements de la susceptibilité magnétique et de la résonance magnétique nucléaire qui résultent de cette transition. Les mesures de susceptibilité entre 4 °K et 905 °K montrent une augmentation finie de $\sim 0,5 \times 10^{-3}$ (e. u. m./mole) au passage dans l'état isolant paramagnétique. Le déplacement de Knight du ^{51}V augmente de $\sim 0,1$ % dans la phase isolante. Les résultats fournissent une preuve microscopique d'une modification du premier ordre dans la structure électronique des électrons d, lors de la transition métal-isolant.

Abstract. — Addition of Cr or Al to V_2O_3 produces a transition from a metallic phase to a paramagnetic insulating phase. We report the magnetic susceptibility and nuclear magnetic resonance behavior which results from this transition. Susceptibility measurements from 4 °K to 950 °K showed a discrete increase of $\sim 0.5 \times 10^{-3}$ (e. m. u./mole) on passing to the paramagnetic insulating state. The ^{51}V Knight shift increased by ~ 0.1 % in the insulating phase. The results constitute microscopic evidence of a first order change in the electronic structure of the d electrons in the metal-to-insulator transition.

V_2O_3 doped with Cr^{1+} or Al^{2+} shows a very interesting phase diagram. The diagram includes insulating antiferromagnetic (AF), insulating paramagnetic (I), and metallic paramagnetic (M) phases. The diagram for small concentrations of Cr is shown in the inset of figure 1. A similar diagram exists for Al additions. The

X-ray data [1], sample lengths [6], electrical resistivity [2], [6], [7] and magnetic susceptibility data [5], [8], [9] all exhibit anomalies at the high temperature transition. However, Jones [4] and Arnold and Mires [5] have observed that the nuclear magnetic resonance of ^{51}V in pure V_2O_3 does not reproduce the susceptibility anomaly. In this paper we report magnetic susceptibility and Knight shift measurements on pure, Al, and Cr-doped V_2O_3 in order to study the properties of the different phases and the changes involved with the phase transition both below and above the critical point.

Figure 1 shows our magnetic susceptibility data as a function of temperature between 4.2 °K and 800 °K. The data of the Cr-doped samples have been reported and discussed in detail [9]. The magnetic susceptibility reflects all three phases. At low temperatures a discontinuous change in the susceptibility occurs. For $0 \leq x < 0.03$ it corresponds to the transition from the insulating antiferromagnetic phase (AF) to the metallic paramagnetic phase (M) and for $x < 0.03$ to the transition from the insulating antiferromagnetic state (AF) to the insulating paramagnetic state (I). At high temperature the magnetic susceptibility in the metallic phase shows an increase with increasing temperature towards the values of the insulating samples. This increase represents the high temperature metal-insulator transition which is a gradual one for V_2O_3 and which is smeared out for the doped samples due to inhomogeneities in the Cr- or Al-distribution.

Jones [10] observed the nuclear magnetic resonance of ^{51}V in pure V_2O_3 at temperatures above the AF transition temperature. The nuclear resonance frequency shift was temperature dependent, varying from -0.6 % to 0.0 % and was represented from $175^\circ K < T < 300^\circ K$ as

$$\frac{\Delta H}{H} = \alpha\chi_{VV} + \beta\chi_{spin}(T).$$

In light of the increases in susceptibility now observed

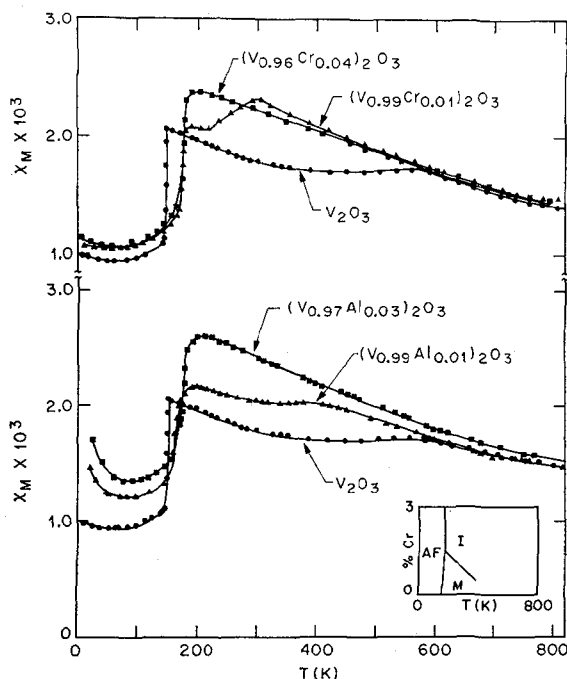


FIG. 1. — Magnetic susceptibility (e. m. u. per mole) of pure V_2O_3 and a) Cr-doped V_2O_3 , b) Al-doped V_2O_3

phase boundary of the high temperature metal-insulator (M to I) transition is terminated by a critical point [3] and pure V_2O_3 therefore shows a gradual supercritical transition from the metallic (M) to the insulating phase (I) as well as the well-known lower temperature AF to M transition.

on conversion from M-phase to I-phase by addition of Cr and Al, we have undertaken a nuclear magnetic resonance study of those systems. We observed ^{51}V NMR in V_2O_3 samples containing 0.5 %, 0.6 %, 0.8 %, 1.0 %, 1.2 %, 1.4 % and 4.0 % Cr and 0.5 %, 1.0 % and 3.0 % Al, thus spanning the M-I phase boundary. The resonances were observed by conventional nuclear absorption derivative observations with swept magnetic fields at a frequency of 16 MHz. An rf probe containing no aluminum was used. Similar NMR measurements on these same systems have been made independently by M. Rubinstein [11] with qualitatively similar results.

Figure 2a shows the ^{51}V frequency shift as a function of temperature between 175 °K and 500 °K for pure V_2O_3 , for $(\text{V}_{0.992}\text{Cr}_{0.008})_2\text{O}_3$ and for the I-phase compounds $(\text{V}_{0.96}\text{Cr}_{0.04})_2\text{O}_3$ and $(\text{V}_{0.97}\text{Al}_{0.03})_2\text{O}_3$. The frequency shift of the I-phase samples is displaced positively by $\sim +0.1$ %. In intermediate concentra-

tions (e. g., 0.8 % Cr and 1.0 % Al), a discontinuous change in the frequency shift occurs with two lines being visible at several temperatures near the M-I transition. The observation of discrete lines confirms that the M and I phases are distinct. In figure 2b are plotted the frequency shifts vs. susceptibility for V_2O_3 and for the 3 % Al and 4 % Cr (I) samples.

The most striking feature of these results is that the frequency shifts of the I-phase (doped) samples are quite differently related to the susceptibility than are the frequency shifts of pure V_2O_3 . In terms of the above expression for the frequency shift, this constitutes direct microscopic evidence for a first order change in the electronic structure of the d electrons of V_2O_3 on transition from M to I phase [13]. Specifically, the I phase points lie higher on the $\Delta H/H$ vs. χ plots than the line through the M phase points. This requires changes in other factors than $\chi_{\text{spin}}(T)$ and thus requires a first order change in the electronic d states. A reduced core polarization hyperfine coupling constant or a changed Van Vleck paramagnetism is necessary for the I phase.

A second striking feature of the result is the deviations from straight line behavior for the $\Delta H/H$ vs. χ points of each sample. For V_2O_3 , the deviation occurs at high temperatures (low χ) and is just the anomaly of Jones and Arnold and Mires, which is now seen to result from a gradual supercritical transition at higher temperature toward I phase d electron structure. For the I-phase samples, on the other hand, the points which deviate from linear behavior are low temperature points which lie below the straight line fit. This behavior is believed to result from the appearance of minority, undetected M phase at low temperature.

In conclusion, we have shown that conversion of metallic V_2O_3 to the paramagnetic insulating phase by addition of aluminum results in a qualitatively similar increase in susceptibility to that which occurs on addition of chromium. The susceptibility increases must be ascribed to change in the V_2O_3 matrix susceptibility upon phase transition. The observation of discrete M-phase and I-phase ^{51}V nuclear resonance lines establishes the distinctness of the two phases in the doped material. The different shift-susceptibility relations for the two phases is evidence of a first order change in the d band electronic structure. The single NMR response in pure V_2O_3 , on the other hand, confirms the gradual supercritical change from M to I behavior in that case.

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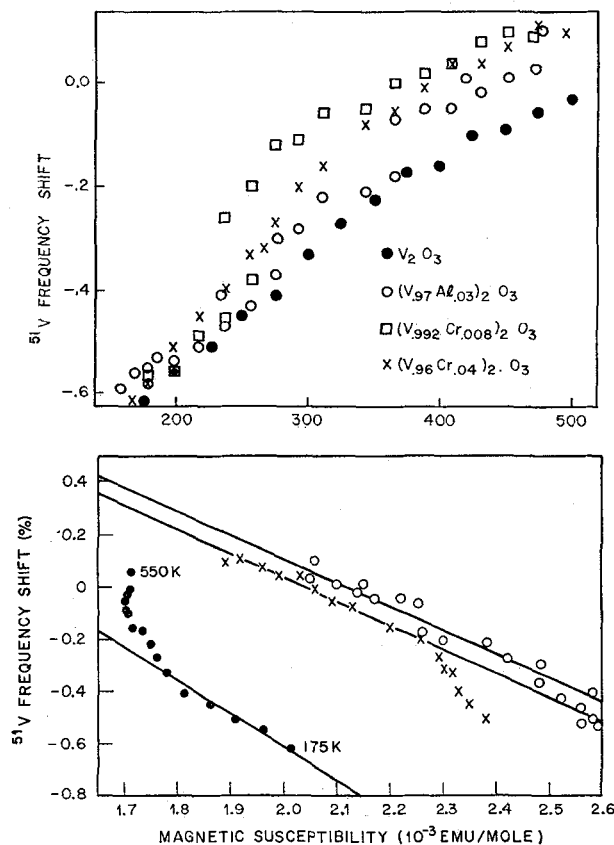


FIG. 2. — ^{51}V nuclear magnetic resonance frequency shifts of pure and doped V_2O_3 a) vs. temperature, b) vs. magnetic susceptibility with temperature an implicit variable. The shifts are relative to a NaVO_3 reference solution. Closed circles: V_2O_3 , open circles: $(\text{V}_{0.97}\text{Al}_{0.03})_2\text{O}_3$, open squares, $(\text{V}_{0.992}\text{Cr}_{0.008})_2\text{O}_3$, crosses: $(\text{V}_{0.96}\text{Cr}_{0.04})_2\text{O}_3$.

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