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We wish to thank Mr. James Moore for his help in taking and analyzing these data.

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[2] The perovskite-structure type, with the general formula *AB*O_3, has a cubic unit cell with the *A* atom located at the corners, the *B* atom at the center, and the O atoms at the face centers of the cube. In the nonstoichiometric bronzes (the best-known member of this class is the sodium-tungsten bronze Na_xWO_3), the *A* position is only partially (and in general randomly) occupied, while the *B* site is filled by a transition metal. In the related cubic compound ReO_3, the *A* position is empty and the *B* position is occupied by Re.

[3] Efforts to prepare crystals of Na_xWO_3 having resistivity ratios sufficiently high to allow observations of the de Haas–van Alphen effect were unsuccessful. Resistivity ratios ≤16 were obtained on crystals prepared both by melt fusion and hydrothermal techniques.

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[9] X-ray diffractometer powder patterns were taken on $Na_{0.93}MoO_3$ at room temperature and at 4.2°K. No deviations from crystallographic cubic symmetry were observed at 4.2°K.

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MOTT TRANSITION IN Cr-DOPED V_2O_3

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A first-order metal-insulator transition at room temperature has been found in Cr-doped V_2O_3 as a function of both Cr concentration and pressure. This is shown to be a Mott transition in which the conduction electrons localize to form the insulator. A generalized phase diagram relating the metallic, insulating, and antiferromagnetic insulating phases is presented.

A sharp metal-insulator transition has been found in Cr-doped V_2O_3 as a function of both Cr concentration and pressure at room temperature. There is no change in the long-range order at the transition and, from a study of the entropy and susceptibility, it is inferred that the insulating phase has local moments. We conclude that this is an example of a transition in which the conduction electrons localize to form an insulator as predicted on theoretical grounds by Mott in 1949.[1,2] It is postulated that the metal-insulator (M-I) phase boundary terminates at higher temperatures at a critical point. At lower temperatures the local moments order to form an antiferromagnetic (AF) state.[3-5] In pure V_2O_3 we identify the high-temperature anomaly[6] as a continuous M-I transition above the critical point, and the sharp discontinuity in electrical resistivity at low temperatures with the M-AF transition.[7]

Striking anomalies occur in the c/a ratio of the lattice parameters of the corundum structure as a function of the transition metal (see inset in Fig. 1).[8] From a study of single-crystal samples in the system $(V_{1-x}Cr_x)_2O_3$ we find that a sharp drop in c/a and a volume expansion of 1% occurs at $x=0.009$. At room temperature pure V_2O_3 is a poor metal (resistivity ~10^{-3} Ω cm), and an addition of a few percent Cr raises the resistivity several orders of magnitude.[9] Below we report extensive measurements made on single-crystal rhombohedral prisms of $(V_{1-x}Cr_x)_2O_3$ with $x=0$, 0.01, 0.02, 0.04, and 0.10, which were prepared by a new technique.

The results of some of our x-ray diffraction measurements as a function of temperature are shown in Fig. 1. For $T \gtrsim 600$°K, V_2O_3 and the 4%-Cr-doped sample have similar c/a ratios. The ratio in the Cr-doped sample increases smoothly down to the Néel temperature, whereas in V_2O_3 there is an anomaly in c/a at high temperature corresponding to that found in the resistivity. A refinement of the crystal structures of V_2O_3 and $(V_{0.96}Cr_{0.04})_2O_3$ at room temperature shows that the overall volume and all nearest-neighbor vanadium-vanadium distances are larger in the Cr-doped sample.[10] On cooling V_2O_3 through the M-AF transition we find that both a axes expand while c contracts, whereas the opposite occurs in the Cr-doped sample. (The gen-

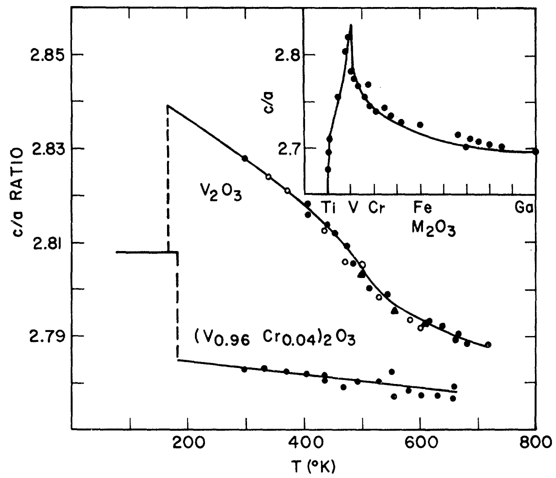

FIG. 1. c/a ratio versus temperature for V_2O_3 and $(V_{0.96}Cr_{0.04})_2O_3$. Figure shows broad anomaly at 500-600°K in V_2O_3 and transition of both oxides to monoclinic-antiferromagnetic phase at low temperature (pseudo c/a ratio is shown). For pure V_2O_3 the different symbols show the reproductibility of the high-temperature anomaly on heating (solid circles, first cycle; solid triangles, second cycle) and cooling (open circles). Below 298°K the results of a continuous monitoring of the lattice parameters are indicated by solid lines. Above 298°K the data were collected at fixed temperatures. Inset: c/a ratio versus transition metal for corundum structure. Sharp drop in c/a occurs at ≈1% Cr in V_2O_3.

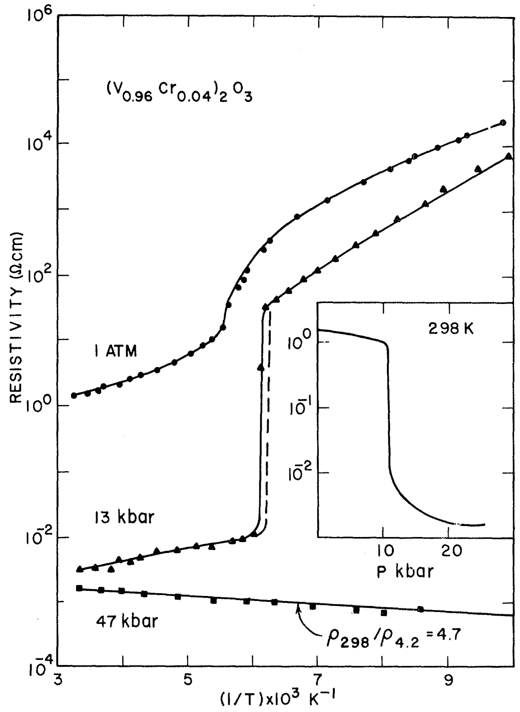

FIG. 2. Resistivity versus reciprocal temperature at different pressures for $(V_{0.96}Cr_{0.04})_2O_3$. Inset shows I-M transition at room temperature as a function of pressure. Below 10 kbar the AF → I transition occurs on warming (solid circles). Above 10 kbar the AF → M transition occurs (solid triangles). Above 40 kbar the sample is metallic from 4.2 to 298°K (solid squares).

erally quoted model for the crystallographic distortion in the AF phase in which vanadium atoms pair in the basal plane[6,11] appears to be based on a misinterpretation of the data of Warekois.[12]) The structure of the AF phase is monoclinic,[12] and a pseudohexagonal c/a ratio is shown in Fig. 1. Our lattice parameters for the reduced monoclinic cell are $a=7.255\pm0.003$, $b=5.002\pm0.002$, $c=5.548\pm0.002$ Å, and $\beta=96.75\pm0.02°$; possible space groups are $I2/a$, $I2$, and Ia. This crystallographic distortion does not double the volume of the primitive unit cell and appears to be magnetostrictive in origin because the volume change at the corundum to monoclinic transition in the Cr-doped sample is very small.

The resistivity at 298°K of the 4%-Cr sample as a function of pressure is shown in the inset of Fig. 2. An I-M transition occurs at ≈10 kbar. The resistivity as a function of temperature at pressures below and above the 10-kbar transition is shown in Fig. 2. Below 10-kbar there is an I → AF transition on cooling. At pressures above 10 kbar a M → AF transition occurs. From our earlier work on pure V_2O_3 it is known that the AF phase can be suppressed completely by the application of pressure.[13] For the Cr-doped sample the critical pressure was found to be ≈40 kbar in contrast to ≈25 kbar for V_2O_3, and the resistivity of the Cr sample at 47 kbar is shown in Fig. 2.

In order to construct a three-dimensional pressure-temperature-composition phase diagram the P-T diagrams for $(V_{0.96}Cr_{0.04})_2O_3$ and V_2O_3[13] were determined from resistivity measurements. These were combined with a T-composition diagram at 1 atm determined from x-ray and resistivity measurements. The resulting diagram consisted of three surfaces, intersecting at a line. These surfaces separated the metallic, insulating, and antiferromagnetic-insulating regions. The M-I surface intersects pure V_2O_3 at 1 atm at the temperature where the anomalous changes in both the resistivity and the c/a ratio occur. In contrast, at room temperature the M-I surface represents a first-order transition with a sharp drop in resistivity and change in volume. Therefore, it is postulated that the M-I surface terminates at a critical line. The high-temperature anomaly in pure V_2O_3 would then reflect supercritical behavior above this critical line. The M-I boundary for a given composition would terminate at a critical point similar to that observed in Ce metal.[14] There appears to be a similarity between doping with Cr and negative pressure, and this leads us to approximate the three-dimensional phase diagram by a two-dimensional generalized diagram for the present range of composition. The pressure was scaled to the composition using the difference in the critical pressures for V_2O_3 and the 4% Cr sample and the resulting phase diagram is shown in Fig. 3.[15] The addition of Ti to V_2O_3 is reported to stabilize the metallic phase as suggested by Fig. 3.[9]

The entropy changes associated with each of the transitions can be calculated from the Clausius-Clapeyron equation, $\Delta S = \Delta V/(dT/dP)$, using the measured volume changes and the experimental slopes of the phase boundaries. For the I → M transition at 298°K, $\Delta V = -0.39$ cm^3/mole V_2O_3 and $dT/dP \approx 40$°K/kbar which gives $\Delta S = -0.2$ cal/°K mole. For the AF → M transition in V_2O_3, $\Delta V = -0.41$ cm^3/mole and $dT_N/dP = -3.78$°K/kbar[6] which gives $\Delta S = 2.6$ cal/°K mole. For the AF → I transition in the Cr-doped sample, ΔV (0.05 cm^3/mole) and dT_N/dP (0 ± 1°K/kbar) are very small and therefore ΔS was calculated from the conservation of entropy around the triple point. This gives $\Delta S = 2.8$ and $dT_N/dP = +0.4$ which is consistent with the measured value. Fully localized V ions would contribute a somewhat larger entropy of $S \sim 2k \ln 3 \sim 4.4$ cal/°K/mole.

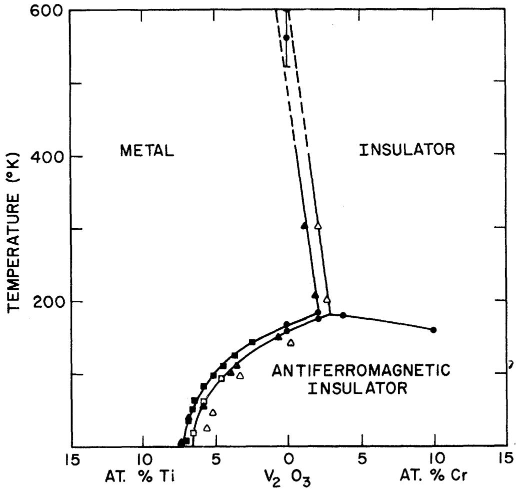

FIG. 3. Generalized phase diagram of transition temperature versus both pressure and at.% Cr and Ti in V_2O_3: Closed circles are from mixed oxides at 1 atm; solid and open squares are V_2O_3 on increasing and decreasing pressure, respectively; solid and open triangles are $(V_{0.96}Cr_{0.04})_2O_3$ on increasing and decreasing pressure. There are large experimental uncertainties (±2 kbar) in the pressure calibration below 10 kbar and therefore in the M-I phase boundary.

Our measurements establish the existence of a first-order M-I transition with no change in long-range order. Such a transition cannot be explained in terms of the Adler-Brooks model which requires a change in long-range order to obtain an insulating phase.[16] A model involving a band uncrossing with the low-temperature phase as an "excitonic" phase[13] is not compatible with a larger entropy in the I phase. On the other hand, the large entropy and the large susceptibility of the I phase suggest the existence of local moments which cannot be described in Bloch-Wilson band theory. The transition has all the qualitative features expected for a Mott transition, i.e., a sharp M-I transition as a function of density. In the I phase the Coulomb interaction causes a localization of the electrons, giving rise to local moments and a Mott-Hubbard correlation gap. In the low-temperature phase the local moments have ordered antiferromagnetically. This ordering gives an additional reduction in free energy of the insulating phase relative to the metal, and can cause the sequence of phases, insulator → metal → antiferromagnetic insulator, to occur as the temperature is lowered, at certain pressures and compositions.

The change in resistivity at the M-I phase boundary is only a factor of 150. This suggests that both the metallic phase and the insulating phases are greatly modified by the impending transition and, in fact, the properties of the metallic phase of pure V_2O_3 are highly anomalous. V_2O_3 has an even number of electrons per unit cell and a p-type Hall coefficient corresponding to 0.6 carriers per vanadium, suggesting semimetallic behavior.[17-19] The volume dependence of the resistivity is 10 times that found in a typical transition metal, while the T^2 term observed in the resistivity for $T \lesssim 50$°K at $P \gtrsim 26$ kbar was 10^3 larger than in transition metals.[13] Finally, the large entropy change at the AF → M transition implies an enhanced specific heat at low temperatures in the metallic phase. Starting from a band model on the metallic side one would expect to have large spin fluctuations as the Mott transition is approached. Various authors have shown that both an enhanced specific heat and a T^2 term in the resistivity can arise from spin fluctuations in nearly ferromagnetic systems (paramagnons).[20] Mott has proposed a model for the metallic state starting from a localized picture.[2] In this model the metallic phase is composed of a degenerate gas of n- and p-type small polarons. The M-I transition occurs when the Mott-Hubbard correlation gap exceeds twice the polaron binding energy.

It is clear that further theoretical and experimental work is needed to elucidate the detailed nature of the transition. A complete report of the results will be published elsewhere.

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[15] The coordinates of the triple point and the actual size of the hysteresis are subject to large errors because our pressure calibration is relative to the fixed point at 25.4 kbar in Bi. Also the pressure is only quasihydrostatic and differences of a few tenths of a kilobar were observed in the M-I transition pressure in crystals with different orientations of the crystallographic axes with respect to the axis of applied load. Details of the experimental methods can be found in D. B. McWhan, T. M. Rice, and P. H. Schmidt, Phys. Rev. 177, 1063 (1969).

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INTERFERENCE OF LIGHT- AND HEAVY-HOLE CONTRIBUTIONS TO THE ELECTROREFLECTANCE SPECTRUM OF GERMANIUM*

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We have observed as many as 11 half oscillations in electroreflectance spectra of germanium at the direct edge ($\Gamma_8^+ \to \Gamma_7^-$) at room temperature. In addition, near the experimental sixth half oscillation where the light- and heavy-hole contributions are of opposite signs, we observe destructive interference which greatly modifies the signal line shape in that region. The experimental results also demonstrate that neither thermal broadening nor field inhomogeneity need be a problem in electroreflectance measurements.

The electroreflectance technique has been fruitful in identifying energies at which critical points occur[1-4] but has been disappointing in its inability to specify uniquely the symmetry point in k space from whence the signal is obtained. Several improvements to the basic technique have been developed lately in an effort to overcome this problem. For instance, Hamakawa et al.[5] developed a method for modulating from flat band. More recently, Koeppen and Handler[6] showed that the variation of the electric field in the space-charge region, which was found important in near-in-