Spin correlations in metallic and insulating phases of V$_2$O$_3$ and its derivatives are investigated using magnetic neutron scattering. Metallic samples have incommensurate spin correlations varying little with hole doping. Paramagnetic insulating samples have spin correlations only among near neighbors. The transition from either of these phases into the low temperature insulating antiferromagnetic phase is accompanied by an abrupt change of dynamic magnetic short range order. Our results support the idea that the transition into the antiferromagnetic insulator is also an orbital ordering transition.

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Orbital order and disorder have been popular ingredients for explanations of many curious phenomena in solids, most notably the transition metal oxides [1,2]. In spite of large interest among condensed matter physicists, the evidence for nontrivial, in the sense of not simply being due to conventional spin-orbit coupling, orbital fluctuations and order is generally quite indirect. We have been able to make progress by taking advantage of a very sensitive measure of electronic orbitals, namely the exchange interactions linking the spins on neighboring atoms, which are determined by integrals over outer electron wave functions. In particular, we report the discovery of a dramatic switching of magnetic exchange interactions on moving between the high and low temperature insulating phases of the classic transition metal oxide V$_2$O$_3$. The switching is most naturally explained in terms of an orbital ordering transition. In addition, we find that the high temperature spin fluctuations in metallic V$_2$O$_3$ are insensitive to hole doping, showing little evolution on going from a stochiometric sample with an insulating antiferromagnetic ground state to a sample which remains metallic down to the lowest temperatures and displays a low moment spin density wave (SDW). Furthermore, the magnetic fluctuations in the paramagnetic metal are similar to those in the paramagnetic insulator, which suggest that orbital fluctuations play an important role in the metal as well as in the insulator.

Figure 1 shows the phase diagram of V$_2$O$_3$ as a function of temperature and two kinds of doping. Vanadium deficiency drives the material metallic by populating the 3d band with holes, while Cr$^{3+}$ (3d$^3$) substitution for V$^{3+}$ (3d$^2$) stabilizes an insulating state [3]. Three single crystal samples studied in this work, and indicated by color bars on the figure, cover all four phases of V$_2$O$_3$. The samples were grown using a skull melter and in the stoichiometric and vanadium deficient samples, oxygen content was controlled to within $\delta y = 0.003$ by annealing sliced crystals for two weeks at 1400 °C in a suitably chosen CO-CO$_2$ atmosphere [4]. The sensitivity of our experiment was increased by mutually aligning several crystals so that the total mass reached $\sim 15$ g for V$_{1.973}$O$_3$, 8 g for V$_2$O$_3$ (Néel temperature $T_N = 170$ K) and 6.4 g in the case of (V$_{0.97}$Cr$_{0.03}$)$_2$O$_3$ ($T_N = 180$ K).

The neutron scattering experiments were carried out on thermal neutron triple axis spectrometers at NIST and

![ Phase Diagram of V$_2$O$_3$ ](image)

FIG. 1(color). Phase diagram of V$_2$O$_3$ [3]. PI denotes the paramagnetic insulating phase; PM, the paramagnetic metallic phase; AFI, the antiferromagnetic insulating phase; and SDW, the metallic spin-density-wave phase. The PM-PI phase boundary terminates at a critical point. The color bars mark the samples and the temperature ranges explored in this work. Inset: spin and orbital orders in the AFI phase [2,5]. The two degenerate (in the single ion limit) vanadium orbitals are represented by red and blue, respectively. A-D label four kinds of near-neighbor pairs.
A graphite filter was used to remove high-order neutrons. After correcting for the $h\omega$-dependent efficiency of the spectrometer, the magnetic neutron scattering intensity was normalized to inelastic scattering from transverse acoustic phonons to yield absolute measurements of the dynamic spin correlation function,

$$S(Q,\omega) = \frac{1}{2} \sum_{\alpha/\beta} (\delta_{\alpha/\beta} - \tilde{Q}_\alpha \tilde{Q}_\beta) |F(Q)|^2 \left(\frac{g \mu_B^2}{2\pi N\hbar}\right)$$

$$\times \int dt e^{i\omega t} \sum_{RR'} e^{-iQ \cdot (R-R')} \langle S_\alpha^\beta(t) S_R^\beta(0) \rangle.$$  \hspace{1cm} (1)

Wave vector $Q$ will be indexed in the hexagonal reciprocal lattice with $a^* = 4\pi/\sqrt{3}a = 1.47(1)$ Å$^{-1}$ and $c^* = 2\pi/c = 0.448(1)$ Å$^{-1}$ in the metallic phases, $a^* = 1.46(1)$ Å$^{-1}$ and $c^* = 0.449(2)$ Å$^{-1}$ in the AFI phase, and $a^* = 1.45(1)$ Å$^{-1}$ and $c^* = 0.451(2)$ Å$^{-1}$ in the PI phase.

We begin by surveying the spin fluctuations in three of the phases of $V_2O_3$: the metallic antiferromagnet (SDW), the metallic paramagnet (PM), and the insulating paramagnet (PI) (Fig. 1). Other workers have successfully surveyed spin waves in the fourth phase, the insulating antiferromagnet (AFI) [6]. Figures 2(a) and 2(b) show contour maps of the dynamic spin correlation function $S(Q,\omega)$ in metallic antiferromagnetic $V(1.97)O_3$ at 1.4 K and in paramagnetic, but still metallic $V_2O_3$ at 200 K. In both cases we observe ridges, with bandwidths exceeding 18 meV and centered near $Q = (1,0,0.3)$ and (1,0,2.3), wave vectors which characterize the magnetic order in the hole-doped material (e.g., $V_{1.97}O_3$) [7]. As is appropriate, given the higher temperature for frame (b) than frame (a), the ridges are sharper for frame (a). On moving to the PI phase [Fig. 2(c)] at nearly the same temperature, however, there is further broadening. Indeed, the data are now best described as a single broad ridge along the $h\omega$ axis centered at $Q = (1,0,0.8)$. From the half-width-at-half-maximum of constant energy cuts through this ridge [see Fig. 3(d) and Ref. [8]], we estimate spin correlation lengths $\xi_c = 1.5$ Å and $\xi_\alpha = 2.0$ Å along the $c$ axis and in the basal plane, respectively.

One of the most remarkable features of the metal-insulator transition in $V_2O_3$ is that the antiferromagnetic order (see inset of Fig. 1) which develops in the insulator is different from the SDW which occurs in vanadium deficient samples [7,9]. Specifically, as may also be seen in the inset of Fig. 1, vanadium atoms in $V_2O_3$ have three nearest neighbors within a puckered honeycomb plane. In the SDW phase each spin is approximately antiparallel to all of its three in-plane neighbors, whereas in the AFI the threefold symmetry is broken with one nearest neighbor parallel, the two others antiparallel. The two types of local spin arrangements are conveniently labeled (10$\ell$)-type and (0.5,0.5,0$\ell$)-type, respectively, according to which line in reciprocal space contains the magnetic Bragg peaks of the corresponding long range ordered structure. In the following we show that irrespective of whether we consider static or dynamic properties, (0.5,0.5,0$\ell$)-type

FIG. 2(color). Contour maps of $S(Q,\omega)$ for $Q$ along the (10$\ell$) direction in (a) $V(1.97)O_3$ at 1.4 K, (b) $V_2O_3$ at 200 K, and (c) $(V_{0.97}Cr_{0.03})O_3$ at 205 K. Intensity is indicated by the color bars in units of $\mu_B^2$/meV per unit cell, which contains 6 formula units. The $Q$ range covers a Brillouin zone, with nuclear Bragg points (10$\ell$) and (10$\ell$) at the ends. Resolutions in both $Q$ and $\omega$ are narrower than the widths of features by at least a factor 2 [9,8] [see, e.g., Figs. 3(b) and 3(d)].

FIG. 3(color). Constant $h\omega = 9$ meV scans along (10$\ell$) and constant $h\omega = 12$ meV scans along (0.5,0.5,$\ell$) for $V_{2-x}O_3$ [(a) and (b)] and $(V_{0.97}Cr_{0.03})O_3$ [(c) and (d)] inside (open symbols) and outside (filled symbols) the AFI phase. (10$\ell$) scans look similar over explored $h\omega$ range (see Fig. 2). The horizontal bars indicate the FWHM of the projection of the resolution function on the scan direction. Peaks in (a) and (c) are resolution limited. We use $E_T = 13.7$ meV. Collimations are 60’-40’-40’-80’, 60’-40’-80’-80’, and 60’-40’-40’-60’ at NIST for (a), (b), (c), and (d), respectively; (c) shows data from ORNL with 50’-40’-40’-70’.
correlations exist only in the AFI phase while \((1, 0, \ell)\) -type correlations exist only outside this phase.

To probe dynamic correlations corresponding to the two structures, we performed constant-energy scans along each of these two directions in reciprocal space. The results are shown in Fig. 3 where the right and left columns probe \((10\ell)\) -type and \((0.5, 0.5, \ell)\) -type correlations, respectively. Filled symbols correspond to high temperature probe each of these two directions in reciprocal space. The re-
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correlations exist only outside this phase.

Coincident with the transition to the AFI phase (vertical dashed lines) is an abrupt switch between the two types of dynamic spin correlations. A remarkable similarity exists between the transitions to the AFI phase from the paramagnetic metal \((V_{2}O_{3}, \text{ left column})\) and from the paramagnetic insulator \((V_{1.94}Cr_{0.06}O_{3}, \text{ right column})\), which suggests a common mechanism which is independent of whether or not a Fermi surface, associated with metallic behavior, exists in the high temperature phase.

Our discoveries find no comprehensive explanation within a one-band Hubbard model [10]. The most serious difficulty is the abrupt switch of the magnetic wave vector which occurs at the transition to the AFI. In addition the insulating paramagnet is characterized by magnetic correlations which are shorter ranged than those of the paramagnetic metal. Like many single-band Hubbard calculations, the doped copper oxides which eventually become high temperature superconductors display none of these anomalous features.

The most obvious potential cause for the anomalous short range correlations in the PI phase is that conventional exchange interactions between spins lead to a frustrated Heisenberg model which is unable to develop long range order at \(T \sim J/k_{B}\). Solid state chemistry, however, speaks against this possibility because only \(A\) and \(B\) types of nearest neighbors (see Fig. 1) have appreciable exchange interactions in \(V_{2}O_{3}\) [2] and a Heisenberg model with only these interactions is not frustrated [11].

A more likely explanation of our data is based on work of Castellani et al. who established how covalent bonding between doubly degenerate 3d orbitals control the sign and magnitude of spin-spin interactions in \(V_{2}O_{3}\) [2]. The basic idea is that the magnetically active electron on a single vanadium ion can exist in one of two degenerate orbitals. Even so, the exchange integrals, which determine the coupling between spins on neighboring ions, depend strongly on which orbitals are occupied. Indeed, when orbitals on neighboring ions are orthogonal, the resulting spin coupling is ferromagnetic, while if they are not, the coupling tends to be antiferromagnetic. The net Hamiltonian for insulating \(V_{2}O_{3}\) then involves orbital as well as spin degrees of freedom at each site, where the spin-orbit coupling is not a bilinear coupling on a single site, as in conventional magnets, but actually involves the relative spin and orbital occupancies on neighboring sites [2]. Castellani et al. examined many possible orbital configurations for \(V_{2}O_{3}\) and concluded that the most likely is that represented by the colors used to locate the V ions in Fig. 1. Here the magnetic unit cell is doubled in the basal planes because the orbital ordering doubles the unit cell also. On warming through \(T_{N}\), we are left with disorder in both spin and orbital occupancies. The magnetic short range order in the paramagnetic phase then depends on whether we are looking at frequencies (a) large or (b) small compared to the relaxation rate \(\Gamma_{\text{orb}}\) characterizing the orbital fluctuations. When (a) \(\omega \gg \Gamma_{\text{orb}}\) the interactions with the neighbors will be similar to those below

![FIG. 4(color). Temperature variations of the neutron scattering intensity from \((10\ell)\) -type and \((0.5, 0.5, \ell)\) -type magnetic fluctuations in pure \(V_{2}O_{3}\) [(a) and (b)] and from the paramagnetic insulator \((V_{1.94}Cr_{0.06}O_{3}, \text{ right column})\), which suggests a common mechanism which is independent of whether or not a Fermi surface, associated with metallic behavior, exists in the high temperature phase. Our discoveries find no comprehensive explanation within a one-band Hubbard model [10]. The most serious difficulty is the abrupt switch of the magnetic wave vector which occurs at the transition to the AFI. In addition the insulating paramagnet is characterized by magnetic correlations which are shorter ranged than those of the paramagnetic metal. Like many single-band Hubbard calculations, the doped copper oxides which eventually become high temperature superconductors display none of these anomalous features. The most obvious potential cause for the anomalous short range correlations in the PI phase is that conventional exchange interactions between spins lead to a frustrated Heisenberg model which is unable to develop long range order at \(T \sim J/k_{B}\). Solid state chemistry, however, speaks against this possibility because only \(A\) and \(B\) types of nearest neighbors (see Fig. 1) have appreciable exchange interactions in \(V_{2}O_{3}\) [2] and a Heisenberg model with only these interactions is not frustrated [11]. A more likely explanation of our data is based on work of Castellani et al. who established how covalent bonding between doubly degenerate 3d orbitals control the sign and magnitude of spin-spin interactions in \(V_{2}O_{3}\) [2]. The basic idea is that the magnetically active electron on a single vanadium ion can exist in one of two degenerate orbitals. Even so, the exchange integrals, which determine the coupling between spins on neighboring ions, depend strongly on which orbitals are occupied. Indeed, when orbitals on neighboring ions are orthogonal, the resulting spin coupling is ferromagnetic, while if they are not, the coupling tends to be antiferromagnetic. The net Hamiltonian for insulating \(V_{2}O_{3}\) then involves orbital as well as spin degrees of freedom at each site, where the spin-orbit coupling is not a bilinear coupling on a single site, as in conventional magnets, but actually involves the relative spin and orbital occupancies on neighboring sites [2]. Castellani et al. examined many possible orbital configurations for \(V_{2}O_{3}\) and concluded that the most likely is that represented by the colors used to locate the V ions in Fig. 1. Here the magnetic unit cell is doubled in the basal planes because the orbital ordering doubles the unit cell also. On warming through \(T_{N}\), we are left with disorder in both spin and orbital occupancies. The magnetic short range order in the paramagnetic phase then depends on whether we are looking at frequencies (a) large or (b) small compared to the relaxation rate \(\Gamma_{\text{orb}}\) characterizing the orbital fluctuations. When (a) \(\omega \gg \Gamma_{\text{orb}}\) the interactions with the neighbors will be similar to those below...
$T_N$, and we expect to see heavily damped renditions of the spin waves seen below $T_N$. On the other hand, if (b) $\omega \ll \Gamma_{\text{orb}}$, one can average over the orbital degrees of freedom and obtain an effective spin Hamiltonian where all couplings are antiferromagnetic.

We now consider whether limit (a) or (b) is more appropriate for our $(V_{0.97}Cr_{0.03})_2O_3$ sample. Obviously, because we see no remnants of the low-temperature spin waves, description (a) cannot apply. We can check whether (b) applies, especially in the detailed sense of its prediction that all interactions are antiferromagnetic, by rewriting the observed structure factor $S(Q, \omega)$ as the Fourier transform of the two-spin correlation function in real space and then checking the signs of the near-neighbor correlations. A remarkably good fit ($\chi^2 = 1.5$) to the experimental $S(Q, \omega)$ [12] is obtained when we truncate the series to include correlations among only four types of spin pairs (see inset of Fig. 1). More specifically, we find that $\langle S_0 \cdot S_{[1/3,2/3,3/2]} \rangle^B = -0.19(8)$, $\langle S_0 \cdot S_{[2/3,1/3,1/6]} \rangle^C = 0.18(8)$, and $\langle S_0 \cdot S_{[2/3,1/3,1/6]} \rangle^D = -0.09(3)$, where $\delta = 0.026$ and we normalized so that $\langle S_0 \cdot S_0 \rangle = 1$. The curve through the 205 K data in Fig. 3(d) was calculated using this model. Thus measurable correlations are not all antiferromagnetic and we do not have a state (b) with $\langle S_0 \cdot S_0 \rangle = 1$. The orbital ordering breaks translational symmetry and is the orbital analog of antiferromagnetism. This is to be contrasted with the celebrated orbital order in the cubic uranium pnictides [14], which while it leads to spectacular anisotropies, does not break translation symmetry and indeed can be traced to single-ion spin-orbit coupling. Finally, our data represent strong evidence for the long-standing notion that orbital, charge, and spin degrees of freedom need to be considered on an equal footing near the metal-insulator transition in generic transition metal oxides.

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[12] C. Broholm et al., J. Appl. Phys. 79, 5023 (1996). Included in the fits were scans from (1,0,0) to (1,0,10), from (001) to (201), and from (005) to (205).