

## Orbital Occupancy Order in $V_2O_3$ : Resonant X-Ray Scattering Results

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Resonant x-ray scattering experiments at the vanadium  $K$  edge demonstrate the existence of orbital ordering in  $V_2O_3$ . Bragg peaks due to the long-range order of  $3d$  orbitals occupancy are observed when the photon energy is tuned to the threshold of the vanadium  $3d$  bands. The azimuthal dependence of the resonant intensities confirms that the resonance arises from the ordering of the vanadium orbital occupancy. The observed orbital structure accounts for the complex magnetic structure of  $V_2O_3$ . The measured magnetic and orbital responses have the same critical temperature  $T_N$ . [S0031-9007(99)09287-X]

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Twenty years ago, Castellani *et al.* [1] proposed that long-range order in the occupancy of the vanadium  $3d$  orbitals was responsible for the complex magnetic properties of  $V_2O_3$ . Upon doping with Cr and/or under the application of hydrostatic pressure [2,3]  $V_2O_3$  exhibits both insulating and metallic phases with peculiar magnetic correlations [4–6]. It was suggested [1] that the spatial ordering of the occupancy of degenerate electronic orbitals accounts for the anisotropic exchange integrals found in the antiferromagnetic insulator phase (AFI) [5]. Furthermore, fluctuations in the orbital occupancy have been invoked to explain the evolution of the magnetic correlations in various phases of the  $V_2O_3$  system [6]. It appears that orbital occupancy plays a central role in the physics of  $V_2O_3$ , but no direct proof for orbital order could be produced experimentally since the original proposal in the late 1970s.

In this Letter we present resonant x-ray scattering (RXS) experiments at the  $K$  edge of vanadium that demonstrate unambiguously the existence of orbital order in  $V_2O_3$  and provide information on the type of ordering. RXS is sensitive to the occupancy of electronic orbitals because it probes the symmetry of vacant electronic states through resonant multipole electric transitions; the variation of the orbital resonant scattering cross section with the direction of the incident polarization (azimuthal angle  $\Phi$ ) reflects the spatial symmetry of ordered orbitals. Furthermore, RXS may be tuned to probe selectively the electronic shells where orbital order takes place. In the case of  $V_2O_3$ , theoretical calculations [7] have shown that the resonance at the vanadium  $K$  edge provides observable cross sections arising from the order of the  $3d$  vanadium states.

RXS experiments were performed at the ID20 magnetic scattering undulator beam line at the European Synchrotron Radiation Facility [8]. A double crystal, Si(111),

monochromator located between two focusing mirrors defined a narrow energy band around the vanadium  $K$  edge (FWHM 0.8 eV) with a high degree of linear  $\sigma$  polarization. The x-ray beam was diffracted by the sample onto a pyrolytic graphite crystal analyzer [(004) reflection] to separate the  $\sigma$  and  $\pi$  components of the scattered radiation. The sample was mounted with beeswax in a closed cycle refrigerator which could be rotated about the scattering vector to perform azimuthal scans.

In  $V_2O_3$ , the transition from paramagnetic and trigonal (space group  $R\bar{3}c$ ) phase to antiferromagnetic and monoclinic (space group  $I2/a$ ) symmetry is strongly first order and destructive [2,3]. In order to mitigate the consequences of the lattice parameter changes at the phase transition we selected a Cr-doped sample. Another effect of Cr doping is to increase  $T_N$  from 150 K in stoichiometric  $V_2O_3$  to  $\sim 181$  K in our samples. Single crystals of  $(V_{1-x}Cr_x)_2O_3$  with different Cr doping were grown at Purdue University using a skull melting technique [9]. The stoichiometry of the crystals used in this study was determined to be  $x = 2.8\%$  by electron probe microanalysis. The sample shape [cleavage plane perpendicular to (11.0) hexagonal axis] and size ( $1.0 \times 0.8 \times 0.050$  mm<sup>3</sup>) was optimized to ensure that a single monoclinic twin of the AFI phase was present in the sample. The mosaic spread in the disordered and ordered phases was  $0.011(3)^\circ$  and  $0.052(4)^\circ$ , respectively. Below the phase transition, we refined the monoclinic lattice parameters to be  $a = 7.276(2)$  Å,  $b = 5.003(5)$  Å,  $c = 5.539(2)$  Å, and  $\beta = 96.83(5)^\circ$  at  $T = 100$  K, in excellent agreement with published values [3]. In the following, we will adopt the monoclinic Miller indices. Because of the  $I$  centering, the allowed crystal structure Bragg peaks obey the extinction rule (A):  $h + k + l = \text{even}$ . This centering is lost below  $T_N$  [4]; the vanadium sites form ferromagnetic

(0, 1, 0) planes [4] with a  $1.2\mu_B$  magnetic moment tilted away from the trigonal axis by  $71^\circ$  [4,10]. The resulting magnetic structure (Fig. 1) is such that magnetic Bragg peaks ( $h, k, l$ ) satisfy a different extinction rule (B):  $k - l = \text{odd}$  and  $h = \text{even}$ .

Below  $T_N = 181$  K, we have observed two different sets of Bragg reflections, with resolution-limited  $Q$  width, that are forbidden according to extinction rule (A). The first set of reflections satisfies the extinction rule (B): These Bragg peaks are magnetic in origin as confirmed by polarization analysis. The variation of the intensity of one of these magnetic Bragg peaks with photon energy is displayed in Fig. 2 (central panel). Two resonances can be observed at energies around the  $K$  edge (5.476 keV as deduced from the fluorescence signal; Fig. 2, top panel) with two distinct polarization dependences on top of a nonresonant signal. The broad high-energy resonance (between 5.47 and 5.49 keV) appears only in the rotated  $\sigma$ - $\pi$  channel for all observed magnetic reflections. Therefore, we assign this resonance to the dipolar transitions [11] from the  $1s$  core level to the  $4p$  bands. The second magnetic resonance that occurs at the prepeak energy in the fluorescence curve contributes to both polarization channels; consequently, it contains contributions from quadrupolar transitions to the strongly spin-polarized  $3d$  states. In the nonresonant regime, the polarization analysis of the observed magnetic scattering intensities has provided a determination of the contribution from the orbital momentum  $\langle L \rangle$  to the total magnetization  $\langle L \rangle + 2\langle S \rangle$  [12,13]. We have found  $\langle L \rangle / 2\langle S \rangle \approx -0.3$  [10]. Combining this

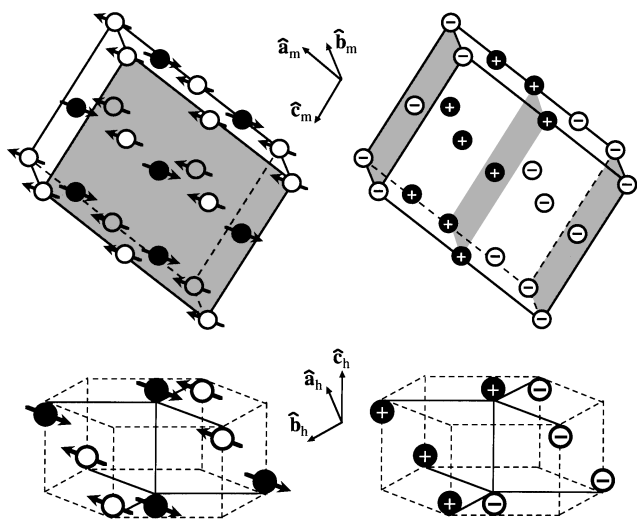


FIG. 1. Antiferromagnetic (left-hand-side diagrams) and orbital (right-hand-side diagrams) structures of  $V_2O_3$ . In phase V atoms are located in shaded planes. The arrows show the magnetic moments direction, whereas the  $+/-$  signs denote the occupation of even/odd combinations of V  $3d$  orbitals. The upper figures show the arrangements in the  $12/a$  monoclinic unit cell. The lower figures describe the same arrangements of a cluster of eight V atoms with a bound V-V pair along the hexagonal  $c$  axis.

result with the value  $1.2\mu_B$  for the ordered moment [4,10] leads to  $2\langle S \rangle \approx 1.7$  and  $\langle L \rangle \approx -0.5$  in the AFI phase. The large value obtained for the averaged spin moment is compatible with a  $S = 1$  spin state for the  $3d^2$  configuration of  $V^{2+}$  [14]. It should be noted that the same absolute value with the opposite sign for orbital contribution to the Van Vleck susceptibility has been measured in the paramagnetic phase [15].

The second set of reflections can be observed only at the low-energy resonance (5.464 keV) over a narrow energy window of 1.6 eV at different  $Q$  vectors. The new reflections satisfy the extinction rule  $k - l = \text{even}$  and  $h = \text{odd}$ . Scattered intensities are observed in  $\sigma$ - $\sigma$

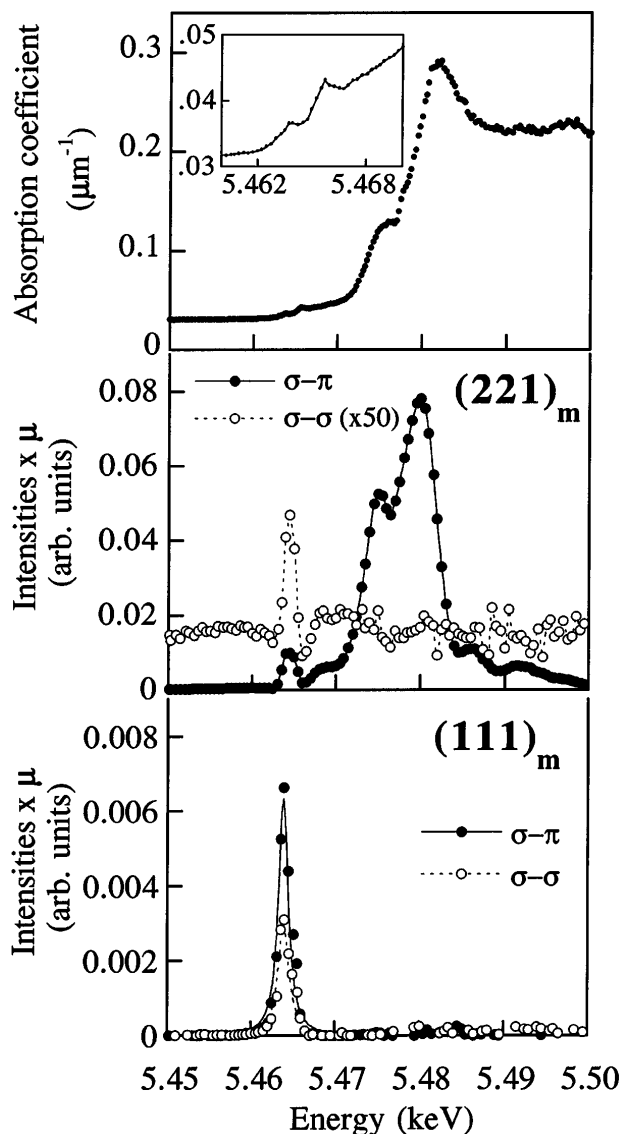


FIG. 2. Energy dependence of the (221) magnetic reflection (middle panel) and the (111) orbital peak (bottom panel) at  $T = 100$  K. The two polarization channels  $\sigma$ - $\sigma$  and  $\sigma$ - $\pi$  are shown. The absorption coefficient (top panel) has been obtained from fluorescence data. The inset shows details of the spectrum near the  $3d$  threshold.

and  $\sigma$ - $\pi$  polarization channels (Fig. 2, lower panel) and are consistent with structure factors based on vanadium sites in phase in the (1,0,0) plane. For this reason we characterize these peaks by the propagation vector  $Q_O = (1,0,0)$ . We associate these extra Bragg peaks with the long-range order of orbital occupancy in  $V_2O_3$  for the following reasons: (i) The observed propagation wave vector is one of the solutions suggested by Castellani [1] to account for the complex magnetic structure of  $V_2O_3$ ; (ii) the energy dependence points to the  $d$  orbital ordering of vanadium orbitals only as the origin of the scattering; and (iii) the azimuthal dependence (Fig. 3) of the resonant intensity is reminiscent of the predictions for the orbital peaks by Fabrizio *et al.* [7].

Let us discuss briefly the energy line shape and the azimuthal dependence of orbital resonant diffraction peaks at  $Q_O$ . The resonance of the orbital intensities is very sharp (1.6 eV FWHM); after deconvolution with the instrument energy resolution, we can extract a broadening  $\Gamma = 1.4$  eV due to the  $3d$  band and core-hole lifetime, in agreement with published values [16]. It is worth noting the following two points: (i) The resonance takes place at the sharp  $3d$  threshold, indicating that the resonance arises from  $d$  orbital occupation [17]; and (ii) no signal is observed away from the resonance, suggesting that charge displacements induced by the orbital order are vanishingly small. The dependence of the (1,1,1) orbital peak on the azimuthal angle  $\Phi$  gives further evidence for orbital order as shown in Fig. 3. The two intensities, in the  $\sigma$ - $\sigma$  and  $\sigma$ - $\pi$  polarization channels, have different periodicities in  $\Phi$ , which is to be contrasted with what is expected for mag-

netic peaks. The intensity of the  $\sigma$ - $\pi$  channel presents two well defined maxima, while the  $\sigma$ - $\sigma$  intensity shows four extrema. The overall observed  $\Phi$  dependence is similar to the theoretical calculations for orbital order peaks [7]. Finally, we have measured the temperature dependence of the magnetic and orbital response in our Cr-doped  $V_2O_3$  sample. Both responses take finite values below the same ordering temperature defined as  $T_N = 181$  K from susceptibility measurements. This simultaneity demonstrates an intimate coupling between orbital and magnetic order in the insulating phase of  $V_2O_3$ .

The observed intensities of the new Bragg peaks at  $Q_O$  shows that the plane waves for the orbital order are [100] monoclinic planes. (Note that the magnetic structure consists of ferromagnetic [010] planes that are coupled antiferromagnetically.) The resulting orbital order structure is shown in Fig. 1. It consists of alternating orbital occupancy for pairs along the  $c$  axis of the hexagonal structure while the arrangement in the basal plane is the same as the magnetic order; this is the model labeled as RO(2)-RS in Castellani's paper [1]. The energy dependence of the observed resonant peaks at  $Q_O$  yields a clue about their origin: Only the states near the  $3d$  threshold energy contribute to the scattering. It would be tempting to assign the resonance to quadrupolar transitions. However, in  $V_2O_3$  the vanadium sites lack inversion symmetry, which allows hybridization of vanadium  $4p$  and  $3d$  states; therefore, dipole transitions from the  $1s$  level are sensitive to the orbital occupancy of  $3d$  states. Since at this periodicity  $Q_O$  no signal is observed at the  $4p$  threshold energy (above the  $K$  edge), we infer that the vanadium  $4p$  levels occupancy is not ordered according to  $Q_O$ ; because these levels are sensitive to local distortions through hybridization with the neighboring oxygen  $2p$  electrons, we also conclude that the charge displacements accompanying the orbital ordering are extremely small. The absence of non-resonant signal confirms this conclusion. Parallel studies on manganite materials [18,19] have shown that the *non-magnetic* resonant scattering extends over a broad energy range at the  $4p$  threshold of the Mn  $K$  edge, indicating possible contributions from charge displacements to the scattering. In  $V_2O_3$ , the two V electrons in the  $3d^2$  configuration occupy the  $t_{2g}$  orbitals which, due to the trigonal crystal field, split into a singlet  $a_{1g}$  and an orbital doublet  $e_g^\pi$  [7,14]. The  $a_{1g}$  orbital points toward the nearest neighbor V site and forms a strong covalent bond along the hexagonal  $c$  axis. There remains some controversy about the nature of the empty orbital state: It is either a pure  $e_g^\pi$  state [1,7,19] or an admixture  $e_g^\pi$ - $a_{1g}$  [14]. Our interpretation is based on the assumption that only one V  $d$  electron is accommodated in a double degenerate orbital state with some  $p$  character. The orbital order parameter is given by the difference in occupation of odd and even combinations of these degenerate orbitals. The  $p$ - $d$  hybridization and the larger dipole matrix elements are such that the dipole transitions account for most of the

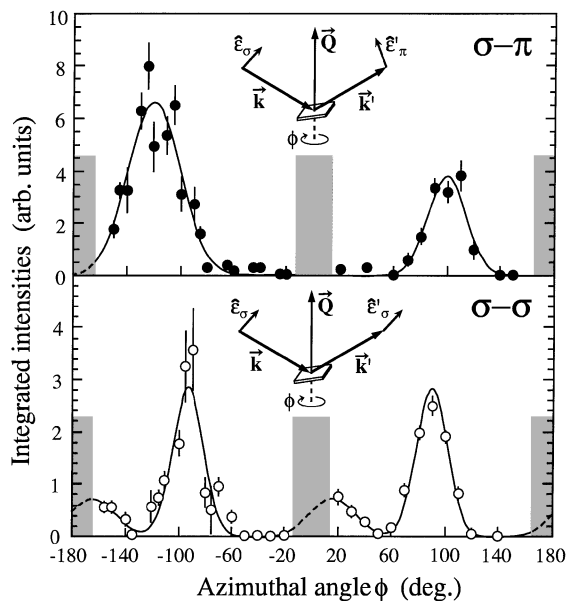


FIG. 3. Polarized integrated intensity of the (111) orbital reflection measured at different azimuthal angle  $\Phi$  of rotation of the [111] plane about the (111) direction for a photon energy of 5.464 keV. The shaded areas indicate zones that were blind due to the sample mount. Lines are guides for the eyes.

total resonant scattering amplitude due to orbital ordering in  $V_2O_3$  [7]. It should be noted that the orbital dipole scattering operator takes a more complicated form than the equivalent one for magnetic scattering, which, in particular, excludes  $\sigma$ - $\sigma$  scattering. Indeed, we have found resonant *orbital* scattering in both polarization channels. Furthermore, the azimuthal dependence (Fig. 3), which reflects the local symmetry and bonding configuration, is consistent with the predictions based on dipole transitions only [7]. We have obtained estimates for the orbital scattering amplitude by scaling orbital intensities to nonresonant magnetic intensities [10]. Using the  $\langle S \rangle$  and  $\langle L \rangle$  values above, the calculated nonresonant magnetic scattering amplitude ( $1.3 \times 10^{-3} r_0$  per vanadium atom) leads to a resonant *orbital* scattering amplitude around  $(1-2) \times 10^{-2} r_0$  per vanadium atom, much weaker than the predicted value for the most favorable case [7]. It should be noted that the *magnetic* resonant amplitudes are of the same order of magnitude ( $2.2 \times 10^{-2} r_0$  and  $1.7 \times 10^{-2} r_0$  for the dipolar resonance amplitude and the low-energy resonant amplitude, respectively). The *magnetic* resonances also point to *p-d* hybridization of the *3d* orbitals. The broad magnetic resonance (10 eV wide which is consistent with the width of *4p* bands) above the edge appears only in the  $\sigma$ - $\pi$  channel as expected for a dipole resonance to the *4p* orbitals that are weakly spin polarized. However, at the *magnetic* resonance below the *K* edge, which usually is attributed to quadrupole transitions to pure *3d* orbitals, the resonant intensity is predominantly in the  $\sigma$ - $\pi$  channel, giving less  $\sigma$ - $\sigma$  scattering than anticipated for quadrupolar transitions. Probably, this resonance involves also virtual dipolar transitions.

In conclusion, we have observed the long-range ordering of the *3d* orbitals occupancy in antiferromagnetic insulating  $V_2O_3$  and confirmed the validity of the one of the proposed orbital structures [1]. Long after the first prediction was made, our results demonstrate that the orbital degrees of freedom are essential ingredients to the physics of  $V_2O_3$ . We have also confirmed that the x-ray resonant scattering associated with the orbital order contains dipolar contributions due to the partial *p* character of the degenerate orbitals. These results offer an example of the intricate interplay between orbital degeneracy and magnetism [20,21] as well as an illustration of an experimental tool to study orbital order. Further work on the theoretical and the experimental fronts is needed to include the full symmetry of the vanadium degenerate orbital states; such studies would be needed to extract an estimate of the orbital order parameter.

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