

X-RAY RESONANT SCATTERING AND ORBITAL ORDER IN V_2O_3

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X-ray resonant scattering has provided unambiguous evidence for the appearance of orbital order in V_2O_3 confirming the hypothesis made twenty years ago [1] to explain the complex behavior of this material. Our results demonstrate that the resonant x-ray methods can be exploited to extract information on the electronic orbital degrees of freedom in solids.

In 3d transition metal compounds, the unscreened 3d electrons take part in the chemical bonding and contribute to the electronic and magnetic properties. This leads to a delicate interplay between the magnetic interactions and the chemical bond configurations. In particular, the electronic spin and orbital degeneracies can induce very intricate associations of electronic and magnetic states. If it is relatively easy to obtain immediate evidence for spin or charge ordering through the usual scattering techniques or local probes, the direct observation of orbital order is hindered by the lack of sensitivity of the standard scattering methods.

Resonant x-ray scattering (RXS) is a technique which is used to label chemical species and electronic shells. When the incident photons have an energy close to an absorption edge of a constituent of the material, scattering arising from this particular species is enhanced. Resonant scattering arises from coherent processes determined by the local point symmetry. Two well-known examples are Templeton scattering (TS) and magnetic resonant scattering (MRXS). In the case of MRXS, it is the onset of a local magnetic moment that breaks the symmetry, whereas low point symmetry of a site in a crystal gives rise to TS.

The lowering of symmetry can be brought about by the ordering of electronic orbitals. When electronic configurations are degenerate, the crystal may restructure by removing the degeneracy of the orbital occupancy in order to minimize its total free energy. On the one hand, this leads to lattice distortions (cooperative Jahn-Teller effect) which can be observed by usual scattering methods; on the other hand, the uneven occupation of equivalent electronic orbitals opens new channels for resonant scattering [2,3] even in the absence of lattice distortions.

We have used the RXS method to bring to light the onset of long range orbital order in V_2O_3 . This material exhibits a rich phase diagram [4], involving metallic and insulating phases with different magnetic states. Twenty years ago, the long range order of the 3d

orbital occupancy was invoked to account for the complex magnetic structure [1] and excitation spectrum but so far there has been no direct evidence for such a new periodicity in V_2O_3 crystals.

Encouraged by theoretical predictions, we have undertaken a search for the onset of orbital order in V_2O_3 . This compound exhibits a para-antiferromagnetic transition which is strongly first-order and destructive. In order to mitigate these effects, we have selected a Cr-doped sample whose shape and dimensions (1.0 x 0.8 x 0.05 mm³) were optimized to ensure that the single crystal would survive through the phase transition. The RXS experiments were performed at the ID20 Magnetic Scattering undulator beamline at the ESRF around the vanadium K-edge at 5.476 keV.

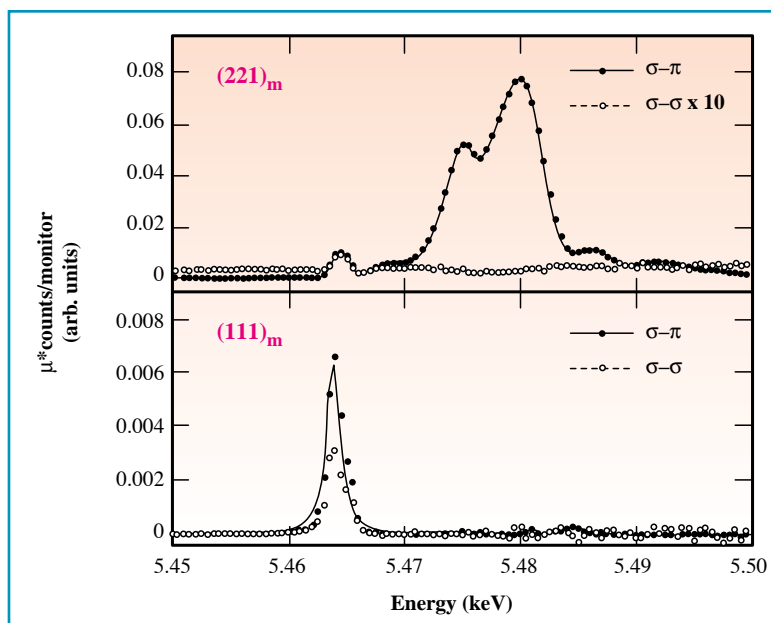
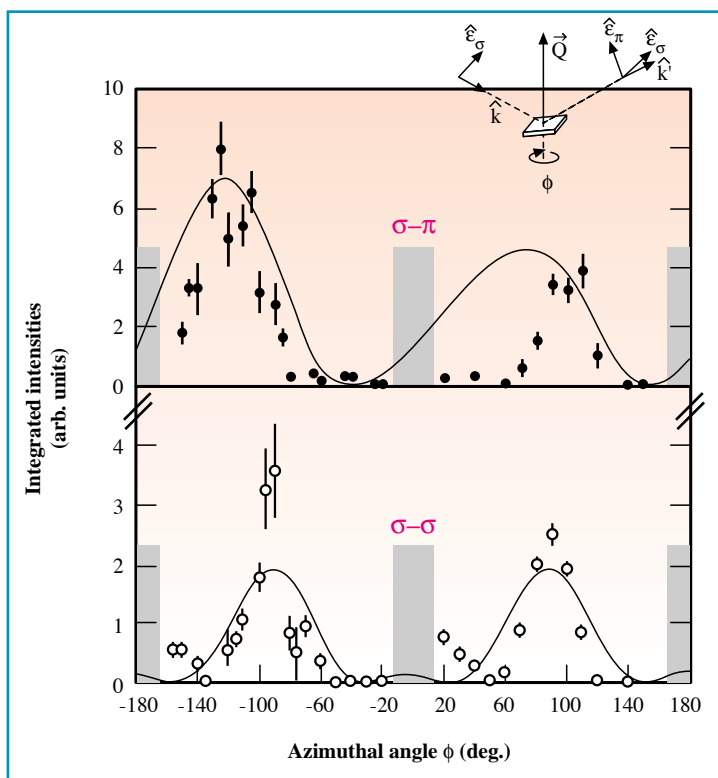


Fig. 1: Energy dependence of the (221)_m magnetic reflection (top panel) and the (111)_m orbital peak (bottom panel) at $T = 100$ K for the two polarization channels $\sigma\text{-}\sigma$ and $\sigma\text{-}\pi$.



Polarized integrated intensities of the (111) orbital reflection measured at different azimuthal angles for a photon energy of 5.464 keV. The shaded areas indicate zones that were inaccessible due to the sample mount.

Below the Néel temperature $T_N = 181$ K, two new and distinct sets of Bragg reflections can be observed. The first set of reflections corresponds to the antiferromagnetic order: their position in reciprocal space coincides with the magnetic propagation wavevector and the polarization analysis of the scattered intensities confirms their magnetic character. The variation of the intensity of one of these reflections with photon energy is displayed in Figure 1 (top panel). Two resonances can be observed at energies above and below the vanadium K-edge on top of the non-resonant magnetic scattering. The second set of reflections can be detected only at the low energy resonance (5.464 keV) over a narrow energy window of 1.6 eV (Figure 1 lower panel). These new Bragg peaks are associated with the long range order of orbital ordering in V_2O_3 for two reasons: i) the energy and polarization dependence denotes the vanadium d-electrons as the origin of the scattering, ii) the azimuthal dependence (Figure 2) of the resonant intensity follows predictions by Fabrizio *et al.* [2]. Furthermore, the observed propagation wavevector was suggested by Castellani [1] to account for the magnetic couplings in V_2O_3 . We have also monitored the temperature dependence of the magnetic and orbital responses in the Cr-doped V_2O_3 sample: the two order parameters

follow similar temperature dependences below $T_N = 181$ K as determined from susceptibility measurements. Such behavior illustrates the intimate coupling between orbital order and magnetic order in V_2O_3 . Our experimental observation of long range ordering in the occupancy of 3d orbitals in V_2O_3 confirms predictions made twenty years ago and underlines the central role of orbital occupancy in electronic properties of solids.

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