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Observed and calculated energy spectra of Bragg-forbidden reflections in YVO_3.

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Abstract. Resonant x-ray scattering measurements have been performed at the (011) Bragg forbidden reflection of YVO_3 at the vanadium K-edge. Data were taken above and below the orbital, magnetic and structural transition occurring at 77 K. Energy spectra calculated by the FDMNES code are shown to be in excellent agreement with our experimental data, conclusively showing the signal to originate from anisotropic tensor of susceptibility scattering; *ie.* solely due to distortions of the lattice and hence the crystal field. We thus resolve the ambiguous origin of the resonant energy spectra in the literature.

1. Introduction

The RVO$_3$ series, where R=rare earth or yttrium, forms a set of materials in which magnetic and orbital order, and the associated structural distortions are closely coupled, giving rise to a rich phase diagram[1]. From the desire to understand this complexity, stems a large amount of research involved in unravelling the microscopic mechanisms responsible for the interactions observed. Resonant x-ray scattering (RXS) provides a probe of long range electronic order; however when x-rays are tuned to transition metal K-edges, 1s→4p, the origin of the diffraction signal can be quite ambiguous. We are not directly sensitive to the underlying electronic order in the 3d states, and only sensitive to a modulation of the 4p states. Bragg forbidden reflections at these edges can therefore result from a Coulomb interaction of the 4p states with underlying 3d orbital order, spin polarisation from magnetic order of the 3d states, anisotropic tensor of susceptibility scattering (ATS)[2] or simply a lowering of the crystal symmetry. In this study we unravel the origin of Bragg forbidden reflections in YVO_3 by *ab-initio* calculations of RXS energy spectra.

On cooling below T_{OO} = 200 K, YVO_3 undergoes a transition from its room temperature orthorhombic structure ($Pbnm$) to a monoclinic structure. By tracking optically active phonons through the structural phase transition, A. A. Tsvetkov *et al* [3] determined the monoclinic phase to have $Pb11$ symmetry; allowing dimerization of the vanadium ions along the c-axis. However, knowledge of the atomic positions is essential for the calculations performed in this

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work, and only structural refinements assuming $P2_1/b$ symmetry have been published[4, 5]. We are therefore forced to adopt this higher symmetry in our calculations of the monoclinic phase. This transition is accompanied by the onset of G-type orbital order, as predicted by generalized gradient approximation (GGA) calculations[6]. $T_N = 116$ K marks the onset of C-type antiferromagnetic order. Interestingly, at $T_{OO2/N2} = 77$ K, YVO_3 undergoes a further transition whereby the orbital order switches to C-type and the magnetic order to G-type. Furthermore, the crystal structure returns to the *Pbnm* symmetry, shown in figure 1. This transition is specific to the R = Lu, Yb, Er, Y and Dy members of the RVO_3 series.

Energy resonances of the (100) and (011) Bragg forbidden reflections have been observed by Noguchi *et al* [7] at the vanadium K-edge in YVO_3, in both the low temperature and intermediate phases. In their study the forbidden reflections were explained as superlattice orbital order reflections, with differences in energy spectra evident above and below $T_{OO2/N2}$ being due to the change in orbital order from G-type to C-type. *Ab-initio* calculations based upon the local-density approximation (LDA) by Takahashi *et al* [8] showed, on the contrary, that such forbidden reflections, and associated energy spectra, can be explained simply in terms of lattice distortions; *ie.* ATS reflections. However, the spectra calculated by Takahashi are not in good agreement with experimental data, particularly in reproducing the differences either side of $T_{OO2/N2}$. In this work we have remeasured the energy spectra of the (011) Bragg forbidden reflection above and below $T_{OO2/N2}$ and performed our own *ab-initio* calculations by employing the FDMNES code[9]. By doing so we have conclusively shown that the vanadium K-edge resonances originate solely from lattice distortions.

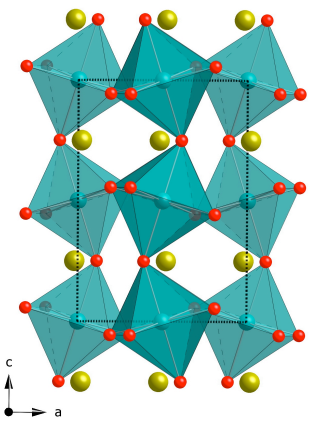

Figure 1. The low temperature *Pbnm* crystallographic structure of YVO_3. Vanadium ions and their octahedral oxygen coordinations are shown in blue, yttrium ions in yellow and oxygen in red. Note the distorted orientation of the octahedra from the true perovskite structure homotype.

2. Experiment

A single crystal sample of YVO_3 with dimensions approximately 5 x 5 x 5 mm was grown by the floating zone technique[10] at the University of Oxford. A face with (011) scattering vector surface normal was cut and polished with diamond paste down to a roughness of 1 μm. Resonant x-ray scattering (RXS) measurements were performed at beamlines BM28[11] and ID20[12] at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. In both experiments the sample was mounted on a copper puck and secured within a closed cycle ^{4}He cryostat giving sample temperatures down to 5 K. Measurements were made in the rotated polarization channel $\sigma - \pi$' in order to maximize the signal to noise ratio and minimize contamination from higher harmonic Bragg reflections. This was done using a graphite polarization analyzer crystal, scattering from the (004) reflection. A leak-through between σ' and π' channels of less than 0.5 % was calculated. Energy spectra were measured by scanning the incident beam energy through the vanadium K-edge, whilst maintaining a constant wavevector at the forbidden (011)

Bragg reflection. Contamination by multiple scattering was evident, so the measurement was performed at a number of azimuth angles to selectively exclude multiple scattering from the energy spectra. The fluorescence spectrum was measured by scanning the x-ray energy with $\theta - 2\theta$ angles far from any diffraction condition.

3. Results and Discussion

The FDMNES code[9] was used to calculate the energy spectra. This code is based upon the monoelectronic approach using multiple scattering theory, and has been shown to reproduce K-edge RXS energy spectra successfully[13, 14].

The main input parameter for the calculation is the crystal structure. Structural parameters of YVO_3 have been determined in a number of articles [4, 5, 15]. For all calculations in this work we chose the most recent structure determination by Reehuis *et al* [5], using a cluster radius of 6.6 Å, containing 115 atoms. The Fermi level was determined by analysis of the calculated density of states based upon the crystal structure, and was found to be 4.8 eV below the vanadium K-edge binding energy of 5.465 keV. In the final stage of the calculation a convolution with an arctangent function was performed to simulate a broadening dependent upon the widths of the ground and excited states. Surprisingly it was found that this broadening had to be constant and fixed to the core level width to give the best agreement with the experimental data. This suggests that the sum of the initial and excited state widths is rather unphysically small. This is not currently understood by the authors. All calculated spectra have been corrected to include the calculated self-absorption. No charge, magnetic or orbital long range order was invoked in the calculation, thus the model simply represents the structural distortions of YVO_3 and hence the crystal field.

First we calculated the XANES absorption spectra and compared it to the experimental fluorescence spectra, effectively providing a measure of the sample absorption. By doing so we were able to find the necessary shift in energy to calibrate the calculation with respect to the experimental data. The inset in figure 2a shows the fluorescence spectrum (black circles) measured through the vanadium K-edge. The FDMNES calculation is overlaid, shown by the red line. The calculation clearly reproduces the features of the fluorescent spectra, providing a successful initial test of the calculation.

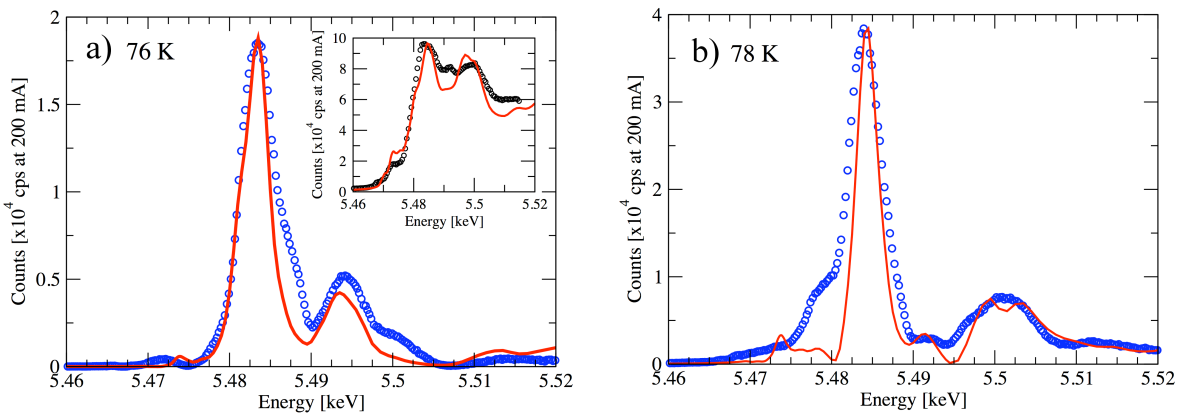

Figure 2. Energy spectra measured at the (011) Bragg forbidden reflection, through the vanadium K-edge, at a) 76 K, below the low temperature transition, and at b) 78 K, above the low temperature transition. Data points are shown in blue (circles) and the FDMNES calculation in red (line). The inset shows the fluorescence spectrum (black points) with the absorption calculation superimposed (red line).

Figures 2a (main panel) and 2b show the resonant energy spectra (blue circles) measured at the (011) Bragg forbidden position, below and above $T_{OO2/N2}$, respectively. We observed significant differences in the energy spectra either side of the transition above 5.49 keV. This compares well with the energy spectra measured by Noguchi *et al* [7]. In both cases the spectrum is well reproduced by our calculation (red line) except for the pre-edge shoulder in the 78 K spectra. It is interesting to note that, if one constrains the crystal symmetry to *Pbnm* both below and above the transition, the calculation yields identical spectra. The differences observed at higher energies are only reproduced by lowering the symmetry to monoclinic in the higher temperature phase.

4. Conclusions

We have remeasured energy spectra of the (011) Bragg forbidden reflection, above and below the low temperature transition of YVO_3, and the results are consistent with those measured by Noguchi *et al* . *Ab-initio* calculations performed using the FDMNES code predict both the fluorescence and the RXS energy spectra to a good level of agreement. Importantly, our calculations predict changes in the energy spectra either side of the 77 K transition where the calculations by Takahashi [8] do not. We have therefore conclusively shown that the main features of the RXS signal measured here can be fully explained solely by structural distortions (ATS), and that changes in the (011) energy spectra result from changes in the crystal structure.

Acknowledgments

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References

[1] Miyasaka S, Okimoto Y, Iwama M and Tokura Y 2003 *Phys. Rev.* B **68** 100406(R)
[2] Dmitrienko V E 1983 *Acta Cryst.* **A 39** 29-35
[3] Tsvetkov A A, Mena F P van Loosedrecht P H M, van der Marel D, Ren Y, Nugroho A A, Menovsky A A, Elfimov I S and Sawatzky G A 2004 *Phys. Rev.* B **69** 075110
[4] Blake G R, Palstra T T M, Ren Y, Nugroho A A and Menovsky A A 2002 *Phys. Rev.* B **65** 174112
[5] Reehuis M, Ulrich C, Pattison P, Ouladdiaf B, Rheinstadter M C, Ohl M, Regnault L P, Miyasaka M, Tokura Y and Keimer B 2006 *Phys. Rev.* B **73** 094440
[6] Sawada H, Hamada N, Terakura K and Asada T 1996 *Phys. Rev.* B **53** 12742
[7] Noguchi M, Nakazawa A, Oka S, Arima T, Wakabayashi Y, Nakao H and Murakami Y 2000 *Phys. Rev.* B **62** R9271
[8] Takahashi M and Igarashi J 2002 *Phys. Rev.* B **65** 205114
[9] Joly Y 2001 *Phys. Rev.* B **63** 125120
[10] Prabhakaran D and Boothroyd A T 2005 *Frontiers in Magnetic Materials*, ed A Narlikar (Berlin: Springer-Verlag) p 97-115
[11] Brown S D *et al* 2001 *J. Sync. Rad.* **8** 1172
[12] Paolasini L *et al* 2007 *J. Sync. Rad.* **14** 301
[13] Di Matteo S, Chatterji T, Joly Y, Stunault A, Paixao J A, Suryanarayanan R, Dhalenne G and Revcolevschi A 2003 *Phys. Rev.* B **68** 024414
[14] Nazarenko E, Lorenzo J E, Joly Y, Hodeau J L, Mannix D and Marin C 2006 *Phys. Rev. Lett.* **97** 056403
[15] Kawano H, Yoshizawa H and Ueda Y 1994 *J. Phys. Soc. Jpn.* **63** 2857-2861