Reinvestigation of $YTiO_3$ with X-ray Resonance Exchange Scattering

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Introduction

Lately, there has been renewed interest in transition metal oxides, especially titanates and vanadates, since they seem to exhibit unusual orbital ordering phenomena. In contrast to $LaTiO_3$, which does not show any sign of long-range orbital ordering and has been assigned to an orbital liquid state [1], $YTiO_3$ gives rise to an x-ray resonance signal, which has been attributed to an orbitally ordered state [2]. Nevertheless, this resonant signal is not showing any variation in intensity with temperatures up to room temperature. Therefore, one could question whether this resonant signal should be assigned not to orbital ordering but rather to some structural distortions present in the material. According to the new predictions on the arrangement of orbitals in the $YTiO_3$ unit cell by Khaliullin and Okamoto [3], a different azimuthal behavior of the resonant signal is expected as a result of the ordering of these orbitals.

We have therefore reinvestigated the resonant x-ray resonant scattering at the absorption K edge from the (1 0 0) reflection of $YTiO_3$ by taking into account the theoretical predictions proposed in Ref. 3. According to the latter, the azimuthal (ψ) variation of the resonant intensity due to orbital ordering is expected to show a behavior that is different from the behavior observed until now, as shown in Fig. 1

Methods and Materials

$YTiO_3$ crystallizes in Pnma symmetry with the 127K lattice constants of a = 5.690 0.004 Å, b = 7.583 ±0.006 Å and c = 5.318 0.005 Å [4]. It is semiconducting at room temperature and becomes an insulating ferromagnet at 29K.

The experiment was conducted at the sector 6 beamline at the APS. The beamline was tuned to the titanium K edge at 4.966 keV. The sample was mounted in a Displex cryostat and allowed to reach temperatures as low as 6K. The scattered beam was analyzed by a polarization analyzer using a graphite (4 0 0) reflection. The scattering angle at the K-edge energy of Ti therefore was $\theta = 48.1°$, which is close to the optimum scattering angle of $\theta = 45°$. Scattering was analyzed in both $\sigma \rightarrow \sigma'$ and $\sigma \rightarrow \pi'$ geometry. The energy resolution was about 1 eV, which allows the separation of very narrow structures in energy.

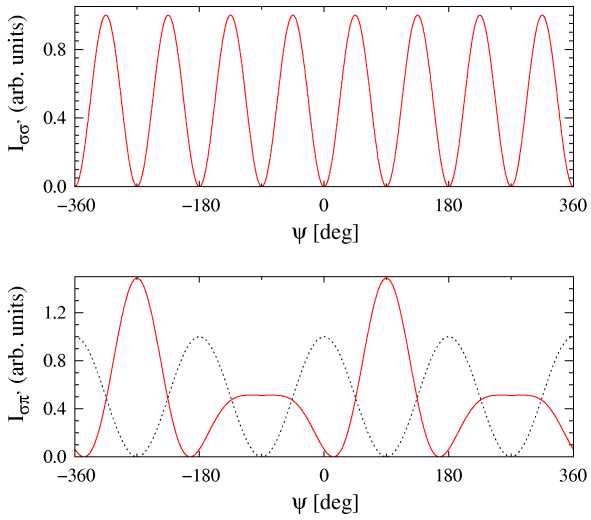

FIG. 1. Theoretical predictions of the variation in intensity of the (1 0 0) reflection due to orbital order as proposed in Ref. 3 (solid line) and Ref. 2 (dashed line) for (top) $\sigma \rightarrow \sigma'$ and (bottom) $\sigma \rightarrow \pi'$ geometry.

Results

First, the scattered intensity in $\sigma \rightarrow \sigma'$ geometry was investigated, where, according to Ref. 2, no resonance signal should be measured. Because of the fact that the graphite analyzer is not scattering exactly at a 90° angle, there is still a relatively large contribution from the $\sigma \rightarrow \pi'$ signal visible. This signal is obstructing possible weak signals we were expecting to see according to Ref. 3. Therefore, the resonance signal in $\sigma \rightarrow \pi'$ geometry was investigated instead. The ψ dependence of the integrated intensity of the resonance signal of the (1 0 0) position is shown in Fig. 2.

Here at $\psi = 90°$, where the other signal is minimum, according to Fig. 1, a contribution due to the orbital arrangement proposed in Ref. 3 should occur. In Fig. 3b) and 3c), the intensity of the resonant signal for $\psi = 0°$ and $\psi = 90°$ is shown as a function of the incident photon energy together with the fluorescence [Fig. 3a)]. From Fig. 3c), it is clearly seen that no signal at all is found for this ψ value.

The energy dependence shown in Fig. 3b) for $\psi = 0°$ shows five clearly distinct peaks in and above the absorption edge as well as a pre-edge peak at a photon energy of 4972 eV.

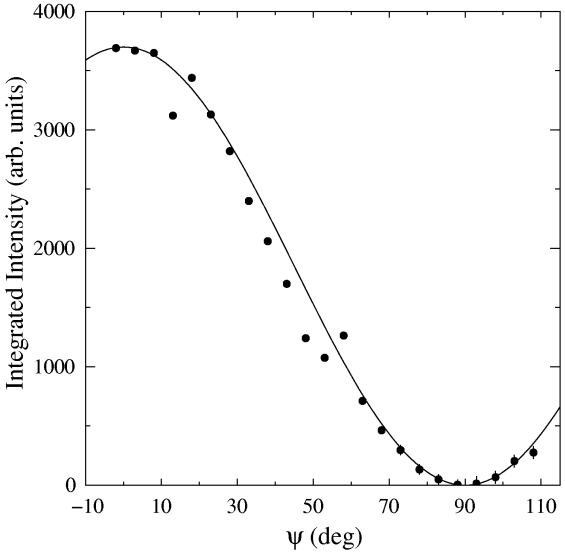

FIG. 2. Dependence of the integrated intensity at E = 4.9944 keV on the azimuthal angle ψ in $\sigma \rightarrow \pi$ geometry. The solid line shows a fit of the $\cos^2\psi$ law to the experimental data.

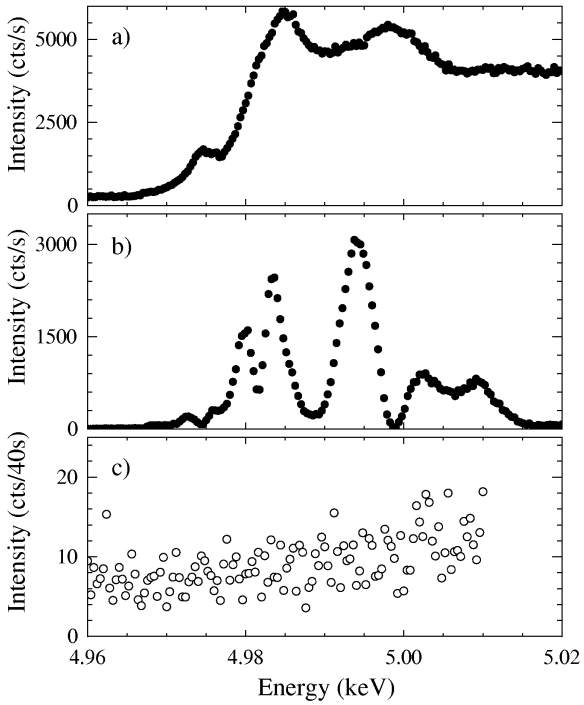

FIG. 3. Energy dependency of a) the fluorescence and energy dependencies of the resonant signal at the (1 0 0) position for b) $\psi = 0°$ and c) $\psi = 90°$ in $\sigma \rightarrow \pi'$ geometry.

Discussion

The energy dependence of the resonant signal of the (1 0 0) reflection in Fig. 3b) shows several clearly separated peaks, which could be resolved much better than they were in the data presented by Nakao et al. [2] because of the superior energy resolution at the APS. We could show that down to a level of three orders of magnitude below the observed signal at a $\psi = 90°$, there is no additional signal, which could correspond to an orbital ordering predicted in Ref. 3. On the other hand, for $LaMnO_2$, Benedetti et al. [5] could show that the resonance signal at the Mn K edge is directly related to the orthorhombicity of the lattice. Therefore, the resonant signal observed in $YTiO_3$ can be understood by band structure calculations and is sensitive to fine details in the lattice distortions but does not probe directly the orbital order of the 3d states. Nevertheless, such probing should generally be possible at edges, where a transition directly into the 3d band is involved.

Acknowledgments

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References

[1] G. Khaliullin and S. Okamoto, Phys. Rev. Lett. **89**, 167201 (2002).
[2] H. Nakao et al., Phys. Rev. B **66**, 184419 (2002).
[3] G. Khaliullin and S. Okamoto (submitted, 2003).
[4] J.R. Hester et al., Acta Crystallogr. B **53**, 739 (1997).
[5] P. Benedetti et al., Phys. Rev. B **63**, 060408 (2001).