Orbital ordered states in $RVO_3 (R=\text{Y, Tb})$ studied by a resonant x-ray scattering

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Abstract. The orbital ordered states of $V^{3+}$ in $RVO_3 (R=\text{Y, Tb})$ have been investigated by a resonant x-ray scattering (RXS) technique. The RXS signals at (0 1 1) were measured near the $V$ $K$-edge energy in the $G$-type orbital ordered ($G$-OO) phase. We found two kinds of the RXS signals, which reflect the orbital state and the local crystal symmetry. The former signal disappears in the orbital disordered phase, while the latter still survives. Moreover, the signals have different azimuthal angle dependence. Using the dependence of the RXS signal reflecting the orbital state, we evaluated the orbital ordered structure in the $G$-OO phase. Consequently, we succeeded in determining the $G$-type orbital arrangement of $V$ orbitals by the RXS technique.

1. Introduction

Perovskite-type transition metal oxides, $RMO_3 (R$: rare earth, $M$: transition metal) and the doped compounds have shown intriguing physical properties such as high $T_C$ superconductivity, colossal magnetoresistance effects, magnetoelectric effects, and so on. The strong coupling among charge, spin, orbital of the 3$d$ electrons and lattice degrees of freedom causes these phenomena. In particular the orbital ordering and the related phenomena have attracted much attention [1]. In order to observe the orbital states, the resonant x-ray scattering (RXS) is a useful technique and made clear many orbital ordered structures [2-9].

In $RVO_3 (R$: rare earth or Y), the two valence electrons of $V^{3+}$ ions occupy the triply degenerated $t_{2g}$ orbitals. As a result, $RVO_3$ shows various physical properties coupled with the orbital and spin states [10]. Two types of orbital orderings were reported in $RVO_3$ systems [7,11-13]. One is $C$-type orbital ordering ($C$-OO) with the antiferro-type arrangement of $d_{1x}^1 d_{1y}^1$ and $d_{2y}^1 d_{2x}^1$ in the $ab$-plane and the ferro-type arrangement along the $c$-axis. The other is $G$-type orbital ordering ($G$-OO) with the antiferro-type arrangement in all three directions. The crystal lattice of the $C$-OO and the orbital disordered (OD) phases is an orthorhombic structure with the space group $Pbnm$, while the $G$-OO phase has a monoclinic structure with the space group $P2_1/b$ [11-13]. The orbital states were studied by the structural analysis of x-ray and neutron scattering experiments [11-13]. In TbVO$_3$, the orbital ground state is the $G$-OO state which is transformed to the OD state at $T_{OO1} = 192$ K. In YVO$_3$ with a relatively small $R$-ionic radius,
on the other hand, the ground state becomes the C-OО state; the G-OО phase still survives in 
the intermediate temperature region (77 K < T < 200 K). The orbital orderings in YVO₃ were 
also investigated by the RXS technique [7]. The orbital ordered structures were estimated by the 
azimuthal angle dependence of the RXS signal at (0 1 1), which corresponds to the propagation 
vector for G-OО and is the forbidden reflection in the space group Pbnm (OD, C-OО) and 
P2₁/b (G-OО). However, the difference between the C-OО and the G-OО phases was not clear. 
As discussed in the Ti system [5,6], the RXS intensity reflects not only the orbital ordering but 
also the local crystal symmetry. Hence we must note the origin of these RXS components to 
determine the orbital ordered structure. In this study, we have investigated the RXS in TbVO₃ 
and YVO₃. The RXS was precisely measured in the G-OО and the OD phases to detect the 
RXS component reflecting the orbital state.

2. Experiments
High-quality single crystals of RVO₃ (R=Y,Tb) were grown by a floating-zone method [14]. The 
lattice constants of TbVO₃ are a=5.321 Å, b=5.605 Å and c=7.611 Å at room temperature. The 
(0 1 1) surface was cut and polished with fine polishing paper and alumina powder. The RXS 
experiments were carried out using a four-circle diffractometer equipped with a closed cycle He 
cryostat at synchrotron x-ray beamlines 4C and 3A at Photon Factory, KEK. The incident x-ray 
was monochromatized by double Si(1 1 1) crystals, giving an energy resolution about 2 eV, and 
focused by a bent cylindrical mirror. Polarization analysis of the scattered beam was performed 
using a PG(0 0 4) analyzer crystal, which gives a scattering angle of 84.8°. The resonating signal was 
clearly observed around 5.482 keV both at 20 K and 220 K. To avoid contamination due to multiple scattering, the energy dependence was measured at several 
azimuthal angles. The resonating signal was clearly observed around 5.482 keV both at 20 K 
and at 220 K. The peak width of the spectrum at 20 K is broader than that at 220 K. Here we 
considered that the new RXS component emerges in the G-OО phase. In fact, the spectrum at 
20 K was nicely fitted with two RXS components as shown in Fig. 1 (b). The RXS component 
at 5.478 keV seems to be the order parameter of the G-OО; that is denoted by the shaded region. 
On the other hand, the RXS component at 5.482 keV mainly reflects the local crystal symmetry 
of the space group Pbnm. The temperature dependence of the (0 1 1) intensity was measured 
at 5.479 keV as shown in Fig. 2. The intensity markedly increases below the G-OО–OD phase 
transition temperature (TOO₁). The (0 1 1) intensity at 5.479 keV remains even above TOO₁, 
because there is the skirt of the RXS signal at 5.482 keV. Thus the new RXS component near 
5.478 keV behaves like the order parameter of the G-OО phase.

An important feature of resonant scattering is the azimuthal angle dependence, which reflects 
the local anisotropy around the absorbed ion, i.e. orbital state. We therefore measured the 
azimuthal angle dependence of the RXS intensity of the σ-π' scattering at 5.477 keV in the G-
OО phase (20 K), which mainly reflects the new RXS component. The dependence at 5.482 keV
was also observed in the OD phase (220 K) for comparison. At each azimuthal angle, \( \theta \)-2\( \theta \) scans were performed. The resulting peak intensities at (0 1 1) were normalized by that of the fundamental peak of (0 2 2) to correct for any variations due to a sample shape. We found that the azimuthal angle dependence at 5.477 keV [Fig. 3 (a)] is different from that at 5.482 keV [Fig. 3 (b)]. The azimuthal angle dependence was calculated using the G-OO model as shown by solid line in Fig. 3 (a). This model calculation is in good agreement with the experimental result. Consequently, we could elucidate that the ground state in TbVO\(_3\) has the G-type orbital ordered structure.

The G-OO phase in YVO\(_3\) was also studied by the RXS technique. The energy dependence of the \( \sigma-\pi' \) scattering intensity was measured at (0 1 1), and the new RXS component was found near 5.478 keV in the G-OO phase. In YVO\(_3\), we could also determine the G-type orbital ordered structure based on the azimuthal angle dependence.

4. Conclusion
The orbital ordered states of V 3\( d \) in RVO\(_3\) (R=Y, Tb) have been studied by the resonant x-ray scattering near the V K-edge energy. We noted the RXS signal at (0 1 1) in the G-OO phase, and found two kinds of RXS signals; those reflect the orbital state and the local crystal symmetry. The former signal actually disappears above \( T_{OO1} \), while the latter still survives in the OD phase. Based on the azimuthal angle dependence of the RXS signal reflecting the orbital state, we succeeded in determining the orbital ordered structure of the G-OO phase in RVO\(_3\).

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Figure 1. (a) Fluorescence of TbVO$_3$ at $\sigma//a$ configuration. (b) Energy dependence of the $\sigma-\pi'$ scattering intensity at the (0 1 1) reflection. The RXS spectrum was fitted using two gauss functions. The fitted function is drawn by a solid line. The two gauss functions are also drawn by a dotted line and a shaded region.

Figure 2. The $\sigma-\pi'$ scattering intensity of (0 1 1) reflection at 5.479 keV as a function of temperature. The intensity of (0 1 1) is normalized by that of the (0 2 2) fundamental peak.

Figure 3. Azimuthal angle dependence of the RXS intensity at (0 1 1) reflection measured (a) at $E = 5.477$ keV in the $G$-OO phase ($T = 20$ K) and (b) at $E = 5.482$ keV in the OD phase ($T = 220$ K). The azimuthal angle $\Psi$ is defined as $\Psi = 0$ at $\sigma//a$. A solid line is the model calculation for the $G$-OO.