2C/2004G194

Ti 2p soft x-ray emission spectroscopy of Ti$_2$O$_3$

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Introduction

Ti$_2$O$_3$ exhibits a gradual metal (high-temperature phase) - insulator (low-temperature phase) transition (MIT) around 450 K. The Ti $3d$ levels in Ti$_2$O$_3$ split into the t_{2g} and e_g^σ levels. Due to the trigonally distorted crystal field, the t_{2g} level further splits into the e_g^π and a_{1g} levels. Tanaka has proposed a new MIT model taking into account the many-body effect and predicted that the Ti $3d$ configuration of the Ti ion pair along c-axis changes from $(a_{1g}\uparrow, a_{1g}\downarrow)$ in the insulating phase to $(a_{1g}\uparrow, e_g^\pi\uparrow)$ in the metallic phase [1]. Recently, we have detected the $3d$ configuration change due to MIT by means of polarization-dependent Ti $2p$-$3d$ absorption spectroscopy [2]. In this study, we have measured Ti $3d$-$2p$ soft x-ray emission spectra (SXES) for Ti$_2$O$_3$ in order to derive the Ti $3d$ level splitting using the observed peak due to d-d* excitation.

Experimental

The Ti $3d$-$2p$ SXES experiments were carried out at BL-2C using a Rowland-type SXES spectrometer with depolarized configuration. Samples used for the present experiments were single crystal and the SXES spectra were measured with $E//c$ and $E\perp c$ conditions, where E denotes a polarization vector of incidence light. Note that the Ti ion pair is parallel to the c-axis.

Results and discussion

As is well known, the Ti $3d$-$2p$ SXES spectra strongly depend on the excitation energy around the Ti $2p$-$3d$ absorption region because both the Raman and fluorescence components contribute to the spectra. As an example, the SXES spectra measured with $E//c$ and $E\perp c$ conditions at room temperature (insulating phase) are shown in Fig. 1 as a function of the Raman shift. The excitation energy is just between the $2p_{3/2}$-$3d$ and $2p_{1/2}$-$3d$ absorption regions (see Fig. 1 of Ref. 2). The spectra exhibit two Raman peaks at 1.3 and 3.3 eV and two fluorescence structure at 5-20 eV, judging from the excitation energy dependence. The Raman peaks at 1.3 and 3.3 eV are attributed to the a_{1g}-e_g^π and a_{1g}-e_g^σ excitations, respectively. Elastic scattering peak is not observed because the elastic scattering is forbidden.

Except for the whole intensity, we recognize the clear E–dependence in the Raman peak at 3.3 eV. This peak is clearly observed in the $E//c$ spectrum while is strongly suppressed in the $E\perp c$ spectrum. Such a behaviour of the
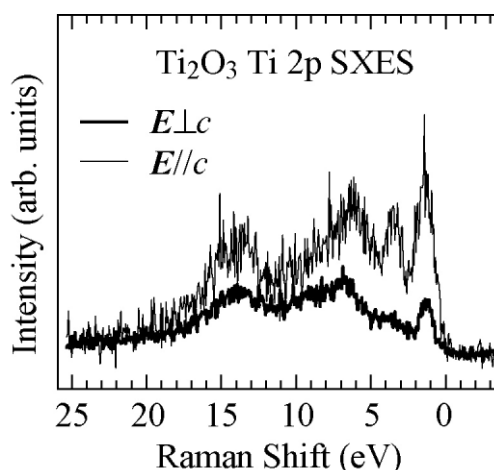

Fig. 1. SXES spectra of Ti$_2$O$_3$ at room temperature measured between the $2p_{3/2}$-$3d$ and $2p_{1/2}$-$3d$ absorption regions.

a_{1g}-e_g^σ-derived peak is qualitatively reproduced by the multiplet calculation in regard to the relative intensities of the two Raman peaks, which supports the attributions of the Raman peaks. These experimentally-derived level splitting energies are well reproduced by the DV-Xα calculation [3]. If we assume that the Ti $3d$ configuration changes simply from the $(a_{1g}\uparrow, e_g^\pi\uparrow)$ to $(a_{1g}\uparrow, e_g^\pi\uparrow)$ at the MIT temperature, $\Delta E(a_{1g}$- $e_g^\pi)$~1.3 eV leads to $J \sim \Delta E/3 \sim 0.4$ eV.

We have also SXES experiments at 520 K (metallic phase) and found that the elastic peak is observed only for the $E//c$ spectra. This result is considered to reflect the Ti $3d$ configuration change due to MIT.

References

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