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Temperature-dependent EXAFS study of ferro-orbital ordered FeV_2O_4

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The orbital degree of freedom has attracted interest in the condensed-matter physics because of adding of new functional functionalities. Couplings between orbital and spin degrees of freedom in transition metal (TM) oxides exhibit a wide variety of interesting physical phenomena studied in strongly correlated electron systems. The orbital degeneracy of t_{2g} or e_g orbitals, split by the crystal field in TM oxides, gives rise to the orbital ordering phenomena in perovskite-type Fe or V oxides accompanied by Jahn-Teller distortion. Spinel-type FeV_2O_4 is a candidate to study orbital ordering since orbital magnetic moments of Fe^{2+} (d^6) are strongly affected by the Jahn-Teller distortion in the Fe sites, which brings the ferro orbital ordering in V sites through the spin-orbit interaction. An unresolved issue related to orbital ordering of spinel-type vanadium oxides is the relationship between the orbital magnetic moments in vanadium sites and orbital ordering [1]. In case of FeV_2O_4, the V orbital states consist of complex wave functions of degenerated *yz* and *zx* states, which expect the ferro-orbital ordering with the large orbital moments of almost 1 μ_B. On the other hand, in the case of MnV_2O_4, real wave functions in the V sites which are described as d_{yz} and d_{zx} are ordered alternatively, resulting in an antiferro orbital ordering with quenching orbital moments [2]. Therefore, the investigation of orbital moments in V sites enables to discuss the types of orbital ordering.

In this study, we aim to investigate the element-specific electronic and structural properties of FeV_2O_4 by temperature-dependent XAFS and EXAFS across the orbital-ordered temperature. We examined the relationship between orbital magnetic moments and orbital ordering. We found that the finite orbital magnetic moments in V sites contribute to the orbital ordering type through the mixing of real and complex wave functions accompanied by the distortion of Fe sites.

Spinel-type FeV_2O_4 was synthesized by a solid-state reaction method in the polycrystalline form. Then, single crystals were grown from the polycrystalline samples using the floating-zone method. The magnetic ordering temperature of single-crystalline bulk FeV_2O_4 was estimated to be 110 K under applying 500 Oe. Fe *K*-edge XAFS and V *K*-edge XAFS were performed at BL-12C, Photon Factory, High-Energy Accelerator Organization (KEK), Japan. Temperature-dependent spectra were measured by the transmission geometry. Photon energies for XAFS measurements were calibrated using Fe and V foil as references. Transmitted x-rays were detected in an ionization chamber filled with a mixture of N_2 and Ar gases. The sample used for XAFS measurements was diluted with BN powder formed into pellets. The sample was cooled by the conventional helium cryostat method from room temperature to 15 K.

Figure 1 shows the Fe and V *K*-edge XAFS at room temperature and 20 K. The *K*-edge XAFS probes the bulk information compared with the *L*-edge one. Spectral line shapes indicate that Fe^{2+} with the additional components of Fe^{3+} and single V^{3+} states. Small pre-edge structures originating from 1*s* to 3*d* transitions appear for both absorption edges, which reflects the environments generated by ligand fields around Fe ions. Furthermore, spectral line shapes almost remain unchanged depending on temperature. This suggests that the electronic states are not modulated through the spin and orbital ordering transitions. Therefore, we can confirm that the phase transitions depending on temperature do not affect directly the changes in valence electronic states. On the other hand, EXAFS profile clearly exhibits the peak shift of first nearest neighbor site. The distance becomes large at low temperature, which is the opposite tendency with a thermal vibration effect. It probes the trigonal distortion of atomic sites across the orbital ordering [3].

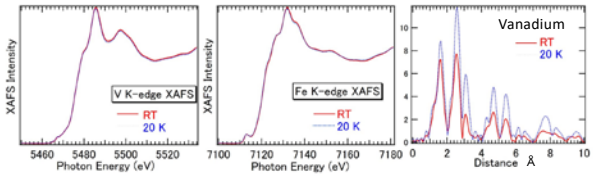

Fig. 1. Temperature-dependent XAFS spectra of FeV_2O_4 for (a) V and (b) Fe *K*-edges. (c) EXAFS of V site.

References

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