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Structural phase transitions in spinel compound $(Fe_{1-x}Co_x)V_2O_4$

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1 Introduction

Spinel vanadium oxides AV_2O_4, in which A^{2+} and V^{3+} ions are located at the tetrahedral (A-site) and octahedral (B-site) sites, have received considerable attention in the last decade because of their peculiar physical properties. Among such vanadium spinels, when the A site occupies magnetic ions (e.g., A = Fe^{2+}, Mn^{2+}), it is known to show orbital ordering accompanied by the lattice distortion as well as ferrimagnetic ordering. In particular, FeV_2O_4 is a unique compound in which both Fe^{2+} and V^{3+} ions have orbital degrees of freedom. FeV_2O_4 exhibits successive phase transitions from cubic to tetragonal ($c < a$: tetraHT) due to $3z^2 - r^2$ orbital ordering (OO) of Fe^{2+} ions at 140 K, from tetraLT to orthorhombic (ortho) accompanied by ferrimagnetic transition at 110 K, and from ortho to tetragonal ($c > a$: tetraLT) accompanied by OO of V^{3+} ions at 60 K[1,2]. On the other hand, CoV_2O_4, in which Co^{2+} does not have orbital degrees of freedom, shows ferrimagnetic transition at ~145 K and another phase transition at ~60 K, which may be due to the OO of V^{3+} ions. However, the detailed crystal structure at low temperatures of CoV_2O_4 has not been reported. In the present study, we examined the substitution effect of Co^{2+} for Fe^{2+} at A-site in FeV_2O_4 and the detail of the crystal structure of CoV_2O_4 at low temperatures.

2 Experiment

The polycrystalline samples of $(Fe_{1-x}Co_x)V_2O_4$ were prepared by a solid state reaction in an evacuated silica tube. Temperature dependences of the powder diffraction patterns were measured using a Debye-Scherrer camera installed at a beamline of BL-8B station. The high-angular resolution powder diffraction experiments were performed for CoV_2O_4 down to 80 K using a diffractometer with multiple detector system at a beamline BL-4B$_2$ station in order to examine the existence of the structural transition.

3 Results and Discussion

Figure 1 shows the temperature dependences of lattice constants estimated by the Le Bail analysis using the whole pattern data obtained by the BL-8B beamline. For x = 0.1, the successive structural transitions of cubit-to-tetraHT, tetraHT-to-ortho, and ortho-to-tetraLT occur at ~110 K, ~100 K and ~80 K, respectively as shown in Fig. 1(a). These phase transitions are similar to those observed in FeV_2O_4 though the transition temperatures are slightly different. On the other hand, the only structural transition of cubic-to-tetraLT is observed at ~100 K for x = 0.2 and 0.3, and at ~80 K for x = 0.5, as shown in Fig. 1(b-d). Our magnetic measurements show that the ferrimagnetic transition temperatures are close to the structural transition ones of tetraHT-to-ortho for x = 0.1 and cubic-to-tetraLT for x = 0.2 and 0.3. Even for x = 0.5, structural transition still occurs, however, the transition temperature (~90 K) is lower than that of ferrimagnetic transition temperature (~125 K). Similar phase transitions are observed in the $(Fe_{1-x}Zn_x)V_2O_4$ system[3], however, the transition temperatures of cubic-to-tetraLT rapidly decrease with increasing x, and the transition disappears for x = 0.5. This difference suggests that the magnetic moments at A-site play an important role to stabilize the tetraLT phase, which is consistent with that the tetraLT phase is stabilized by a spin-orbit coupling of Fe^{2+} ions.

On the other hand, the high-resolution x-ray diffraction experiments for CoV_2O_4 indicate that the peak splitting due to the lattice distortion was not observed within its resolution down to 80 K. The diffractions measurements below 80 K and the detailed structural analysis of the $(Fe_{1-x}Co_x)V_2O_4$ system are now in progress.

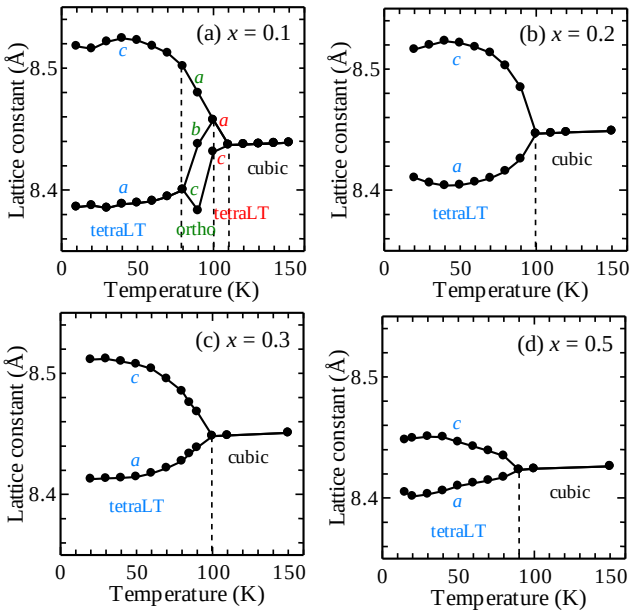

Fig. 1: Temperature dependences of lattice constants of $(Fe_{1-x}Co_x)V_2O_4$ for (a) x = 0.1, (b) x = 0.2, (c) x = 0.3 and (d) x = 0.5.

References

[1] T. Katsufuji *et al.*, *J. Phys. Soc. Jpn.* **77**, 114711 (2008).
[2] Y. Nii *et al.*, *Phys. Rev.* B **85**, 125142 (2012).
[3] H. Ishibashi and Y. Kitadai, *J. Phys. Conf. Ser.* **391**, 012095 (2012).

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