Vanadium spinel oxides AV₂O₄ have attracted much attention for recent years because they show the peculiar physical properties which are caused by competition and cooperation of spin, orbital and lattice degrees of freedom. Among such compounds, FeV₂O₄ is a unique compound showing successive phase transitions: cubic to tetragonal (c < a) at ~140 K, from tetragonal to orthorhombic accompanied by ferrimagnetic transition at ~110 K and from orthorhombic to tetragonal (c > a) at ~70 K with decreasing temperature. It is suggested that these phase transitions originate from the orbital degrees of freedom of both Fe²⁺ ions at A-site (tetrahedral site) and V³⁺ ones at B-site (octahedral site), however, the origin remains controversial. In the present study, we investigate the substitution effect of Fe²⁺ with Co²⁺ having no orbital degrees of freedom to clarify the role of the orbital degree of Fe²⁺ at the A-site. We carried out magnetization and specific heat measurements and synchrotron powder diffraction experiments by the Debye-Scherrer camera at the beamline BL-8B at Photon Factory in KEK. For x ≤ 0.1, the successive structural transitions similar to that observed in FeV₂O₄ occur although the transition temperature of cubic-to-tetraLT transition rapidly decreases with increasing x. For 0.2 ≤ x ≤ 0.6, the only structural transition from cubic to tetragonal (c < a) was observed, however, the transition temperatures were somewhat different from the ferrimagnetic transition ones. On the other hand, for x ≥ 0.7, the crystal structure remains cubic down to 10 K similar to that of CoV₂O₄. These structural properties are discussed in terms of the orbital states of Fe²⁺ ions obtained by the normal mode analysis, and they are compared with the results of the specific heat and magnetization measurements.


Keywords: spinel oxide, orbital ordering, x-ray powder diffraction