Orbital Order and Structural Phase Transitions in Vanadium Spinel FeV$_2$O$_4$

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Orbital degrees of freedom plays an important role in condensed matter physics because it is strongly related with phase transitions and induces the fascinating physical properties. A spinel oxide FeV$_2$O$_4$ is one of the peculiar examples because this compound has double orbital degrees of freedom at both Fe$^{2+}$ and V$^{3+}$ ions. Furthermore, this material represents exotic physical properties [1,2], i.e.; multiferroic, large magnetostriction, and successive structural transitions with decreasing temperature: cubic - tetragonal (c < a: tetraHT, 138K) - orthorhombic (orthoHT, 108 K) - tetragonal (c > a: tetraLT, 68 K). However, the origin of structural transitions and physical properties is controversial until now. In order to clarify the origin, we have performed synchrotron x-ray diffraction experiments at low temperatures at beamline BL02B2 (for the powder samples) in SPring-8 and BL-4C (for the single crystal) of the Photon Factory, KEK. Furthermore, we have carried out the magnetization and the specific heat measurements using polycrystalline samples and single crystal of FeV$_2$O$_4$. We have firstly found another orthorhombic phase (orthoLT) below 30 K in the polycrystalline sample of FeV$_2$O$_4$, shown in figure 1. The Rietveld analysis was performed, and the overall qualities of fittings were fairly good. In order to investigate the details of the orbital state of Fe$^{2+}$ and V$^{3+}$ in FeV$_2$O$_4$, we have performed the normal mode analysis, which is based on static displacements of the tetrahedron of FeO$_4$ and octahedron of VO$_6$. In the orthoLT phase, we found the orbital order of Fe$^{2+}$ ions, which is mixture of 3z$^2$-r$^2$ and y$^2$-z$^2$ orbitals, without change of orbital order of V$^{3+}$ ions. This result indicates that the origin of the orthoLT phase is derived from the competition between cooperative Jahn-Teller effect and relativistic spin-orbit coupling of Fe$^{2+}$ ions. We also discuss the origins of the other phase transitions considering the orbital state of V$^{3+}$ and Fe$^{2+}$ ions, and then the orbital dilution effect, where the structural and magnetic properties are investigated by using powder samples substituted for Fe$^{2+}$ and V$^{3+}$ ions by other ions (Mn$^{2+}$ and Fe$^{3+}$) with no orbital degrees of freedom.


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