Structural and Magnetic Properties in Spinel Type Fe$_{1-x}$Zn$_x$V$_2$O$_4$

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Abstract. Structural and magnetic properties in spinel type Fe$_{1-x}$Zn$_x$V$_2$O$_4$ have been investigated for $x \leq 0.4$. Successive structural transitions of cubic-to-tetragonal ($c < a$), tetragonal-to-orthorhombic and orthorhombic-to-tetragonal ($c > a$) are observed for $x \leq 0.2$. On the other hand, the only cubic-to-tetragonal ($c > a$) structural transition is observed for $0.3 \leq x \leq 0.4$. The result of the magnetic measurements indicates that the ferrimagnetic transition is observed for $x \leq 0.4$ and the transition temperature is close to the tetragonal-to-orthorhombic transition temperature for $x \leq 0.2$, and the cubic-to-tetragonal transition one for $0.3 \leq x \leq 0.4$. These results are discussed in terms of Jahn-Teller distortions of FeO$_4$ tetrahedron and VO$_6$ octahedron, and spin-orbital interaction at Fe$^{2+}$ ion.

1. Introduction

The orbital degrees of freedom in 3d transition metal compounds play important roles in appearance of their various physical properties. In particular, spinel vanadium oxides AV$_2$O$_4$ (A = Mg$^{2+}$, Zn$^{2+}$, Mn$^{2+}$, etc.), in which V$^{3+}$ ion at the octahedral site (B-site) has two 3d electrons in the triply degenerate $t_{2g}$ states, have received considerable attention in the last decade because of their peculiar orbital and magnetic ordering [1-4]. Among such spinel vanadium oxides, FeV$_2$O$_4$ is a unique compound in which both Fe$^{2+}$ and V$^{3+}$ ions have orbital degrees of freedom; Fe$^{2+}$ ion at the tetrahedral site (A-site) has three 3d electrons in the doubly degenerate $e$ states. Recently, structural and magnetic properties of the spinel FeV$_2$O$_4$ were reported [4]. This compound exhibits successive structural transitions from cubic to compressed tetragonal with the lattice constants of $c < a$ at $T_{s1} \sim 140$ K, from tetragonal to orthorhombic accompanied by a ferrimagnetic transition at $T_{s2} \sim 110$ K, and from orthorhombic to elongated tetragonal with $c > a$ at $T_{s3} \sim 60$ K with decreasing temperature for polycrystalline samples. The structural transition at $T_{s1}$ is due to the cooperative Jahn-Teller distortion of FeO$_4$ tetrahedron, which is caused by the orbital degree of freedom of the $e$ orbital electrons in Fe$^{2+}$ ion. For the structural transitions below $T_{s2}$, it was suggested that the possible scenario is the competition and cooperation of Fe$^{2+}$ and V$^{3+}$ orbitals, however, the origin is not completely understood. In this study, we investigate the effect of substitution of Zn$^{2+}$ for Fe$^{2+}$ at A-site in FeV$_2$O$_4$, i.e., the structural and magnetic properties of Fe$_{1-x}$Zn$_x$V$_2$O$_4$. Because Zn$^{2+}$ has neither orbital degree of freedom nor spin, the substitution of Zn$^{2+}$ for Fe$^{2+}$ induces voids in terms of orbital degree of freedom and spin at A-site. This substitution may reduce the effect of the cooperative Jahn-Teller distortion of FeO$_4$ tetrahedron, and it is therefore expected to clarify roles of the $e$ orbital electrons in Fe$^{2+}$ at A-site and $t_{2g}$ ones in V$^{3+}$ at B-site for the successive structural transition in FeV$_2$O$_4$. 

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2. Experimental
Polycrystalline samples of Fe$_{1-x}$Zn$_x$V$_2$O$_4$ with $x = 0.1$, 0.2, 0.3 and 0.4 were prepared by a solid state reaction. The stoichiometric amounts of high purity powders of Fe, Fe$_2$O$_3$, ZnO and V$_2$O$_3$ were mixed and pressed into pellets and heated at the temperatures between 1273 K and 1373 K in sealed quartz tubes. The samples were identified as single phases with a cubic spinel structure at room temperature by conventional powder diffraction measurement. Temperature dependences of magnetization were measured by SQUID magnetometer. High-resolution X-ray powder diffraction experiments using synchrotron radiation were performed at a beamline of BL-6C at the Photon Factory, KEK in Japan. The wavelength of incident beam used was 1.198 Å. A flat Si(111) crystal analyzer was used in order to obtain the high angular resolution. The temperature dependences of the peak profiles of 111, 400 and 440 reflections of the cubic spinel structure were measured.

3. Results and discussion
Figure 1(a) shows the temperature dependence of peak profiles of 400 reflection corresponding to the cubic spinel structure for $x = 0.1$. The 400 peak of the cubic structure is split into two peaks at ~110 K and three peaks at ~90 K, and then these are merged into two peaks again at ~60 K with decreasing temperature. This result indicates that the successive structural transitions from cubic to tetragonal
\( c < a \), tetragonal \( c < a \) to orthorhombic and from orthorhombic to tetragonal \( c > a \) occur, which are similar to those observed in FeV\(_2\)O\(_4\) though the transition temperatures are different. Hereafter, we call the compressed tetragonal \( c < a \) and the elongated tetragonal \( c > a \) phases to ‘tetragonal I’ and ‘tetragonal II’, respectively. The temperature dependence of the lattice constants estimated from the peak position of the Bragg reflections and the magnetization for \( x = 0.1 \) are shown in figure 1(b). The structural transition temperatures from cubic to tetragonal I, from tetragonal I to orthorhombic and from orthorhombic to tetragonal II for \( x = 0.1 \) are \( T_{s1} \approx 120 \text{ K}, T_{s2} \approx 100 \text{ K} \) and \( T_{s3} \approx 70 \text{ K} \), respectively. The diffraction pattern below \(~ 30 \text{ K}\) indicates peak broadening as shown in figure 1(a). This is probably due to the tetragonal-to-orthorhombic transition observed in the single crystal of FeV\(_2\)O\(_4\) [4], however, we regard this phase as tetragonal in here because of the difficulties of the peak decomposition. The magnetization indicates the sharp increase corresponding to the ferrimagnetic transition at \( T_N \approx 100 \text{ K} \), which is close to \( T_{s2} \).

Figure 2 shows the temperature dependence of peak profiles of 400 reflection, lattice constants and magnetization for \( x = 0.3 \). A single structural transition from cubic to tetragonal II is observed at \( T_{s3} \approx T_{s2} \approx 60 \text{ K} \), and both tetragonal I and orthorhombic phases are absent. The magnetization indicates the ferrimagnetic transition at \( T_N \approx 55 \text{ K} \).

The phase diagram of Fe\(_{1-x}\)Zn\(_x\)V\(_2\)O\(_4\) for \( x \leq 0.4 \) is summarized in figure 3. The cubic-to-tetragonal I structural transition temperature \( T_{s1} \) decreases with increasing \( x \) for \( x \leq 0.2 \) and the tetragonal I phase disappears for \( x \geq 0.3 \). The ferrimagnetic transition temperature \( T_N \) also decreases with decreasing temperature for \( x \leq 0.4 \). Furthermore, it is found that \( T_N \) is close to the tetragonal I-to-orthorhombic structural transition temperature \( T_{s2} \) for \( x \leq 0.2 \) and the cubic-to-tetragonal II one \( T_{s3} \) \(( = T_{s2} \) for \( 0.3 \leq x \leq 0.4 \), which suggests a strong correlation between structure and magnetism.

Here we discuss the origin of the phase diagram on the assumption that the lattice distortion is corresponding to the distortion of FeO\(_4\) tetrahedron and VO\(_6\) octahedron. In FeV\(_2\)O\(_4\), the tetragonal I phase is caused by the cooperative Jahn-Teller distortion of FeO\(_4\) octahedron, which is compressed along \( c \)-axis because two of three \( e \) orbital electrons in Fe\(^{2+}\) ion occupy \( 3z^2 − r^2 \) orbital with lower energy [4, 5]. The substitution of Zn\(^{2+}\) for Fe\(^{2+}\) which induces voids in terms of orbital degree of freedom may reduce the cooperative Jahn-Teller distortion, and consequently \( T_{s1} \) decreases with decreasing temperature and the tetragonal I phase is suppressed for \( x \geq 0.3 \).

The structural transition accompanied by the ferrimagnetic transition similar to that observed in the spinel-type Fe\(_{1-x}\)Mn\(_x\)Cr\(_2\)O\(_4\) system, in which the \( e \) orbital electron in Fe\(^{2+}\) ion at A-site is dominant to their phase transitions [5]. It was proposed that the magnetic ordering stabilizes the orbital with the shape of \( x^2 − y^2 \) type by the second term of spin-orbit coupling. For example, when the magnetization direction is parallel to \( x \) axis, \( y^2 − z^2 \) orbital becomes stable, in consequence FeO\(_4\) octahedron elongates along \( a \)-axis. In the present case, the lattice constant \( a \) and the

![Figure 3](image_url)
magnetization simultaneously increase with decreasing temperature for the orthorhombic phase as shown in figure 1(b). Therefore it is suggested that the magnetization direction is parallel to \( a \)-axis, which is consistent with the results of X-ray diffraction and stain experiments using single crystals of FeV\(_2\)O\(_4\) in an applied magnetic field [4]. Just below \( T_{c2} \), \( 3z^2 - r^2 \) electron is still dominant and FeO\(_4\) tetrahedron is compressed along \( c \)-axis, however, increase in the magnetization with decreasing temperature makes \( y^2 - z^2 \) electron stabilized by spin-orbit coupling, which gives rise to the elongation of FeO\(_4\) tetrahedron along \( a \)-axis. From the above consideration, it is suggested that the orthorhombic distortion is due to the competition of the \( 3z^2 - r^2 \) and \( y^2 - z^2 \) orbital electrons at A-site. On the other hand, the reason why the orthorhombic phase is absent for 0.3 \( \leq x \leq 0.4 \) is as follows: the long-range ordering of \( 3z^2 - r^2 \) electron is suppressed, and thus the ferrimagnetic transition stabilizes only \( x^2 - y^2 \) orbital, inducing the tetragonal II phase.

The structure of the ground state of the present system is different from that of Fe\(_{1-}\)Mn\(_{x}\)Cr\(_2\)O\(_4\) for small \( x \) region, i.e., Fe\(_{1-}\)Mn\(_{x}\)Cr\(_2\)O\(_4\) remains orthorhombic [5] though Fe\(_{1-}\)Zn\(_{x}\)V\(_2\)O\(_4\) becomes elongated tetragonal. It is noted that Cr\(^{3+}\) ion at B-site in Fe\(_{1-}\)Mn\(_{x}\)Cr\(_2\)O\(_4\) does not have orbital degree of freedom. This suggests that the orbital state of V\(^{3+}\) at octahedral site plays important role to stabilize the tetragonal II phase appearing in Fe\(_{1-}\)Zn\(_{x}\)V\(_2\)O\(_4\). If the VO\(_6\) octahedron is elongated along \( c \)-axis, energy level of \( t_{2g} \) orbital splits into two; doubly degenerate \( zx \) and \( yz \) orbitals with lower energy and \( xy \) orbital with higher energy. V\(^{3+}\) ion in Fe\(_{1-}\)Zn\(_{x}\)V\(_2\)O\(_4\) has two \( t_{2g} \) electrons, and thus elongated VO\(_6\) octahedron becomes stable by occupying the electrons in the \( zx \) and \( yz \) orbitals. However, the structural analysis indicated that VO\(_6\) is compressed for the elongated tetragonal phase [4], which is inconsistent with the present results. The further studies are necessary to understand the role of \( t_{2g} \) electron V\(^{3+}\) for the tetragonal II phase.

4. Summary

We have investigated the structural and magnetic properties of Fe\(_{1-}\)Zn\(_{x}\)V\(_2\)O\(_4\) system. Successive structural transitions of cubic-to-tetragonal (\( c < a \)), tetragonal-to-orthorhombic accompanied by ferrimagnetic transition and orthorhombic-to-tetragonal (\( c > a \)) are observed for \( x \leq 0.2 \). On the other hand, the only cubic-to-tetragonal (\( c > a \)) structural transition accompanied by ferrimagnetic transition is observed for 0.3 \( \leq x \leq 0.4 \). The ferrimagnetic transition induces the \( x^2 - y^2 \) type orbital in Fe\(^{3+}\) ion at A-site due to the spin-orbit coupling, causing the orthorhombic phase for \( x \leq 0.2 \) and tetragonal (\( c > a \)) one for 0.3 \( \leq x \leq 0.4 \). Further, \( t_{2g} \) electrons in V\(^{3+}\) ion at B-site may also play an important role to stabilize the tetragonal (\( c > a \)) phase.

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