Spin Order in FeCr$_2$O$_4$ Observed by Mössbauer Spectroscopy

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Abstract

$^{57}$Fe Mössbauer spectroscopy has been conducted on a single crystal FeCr$_2$O$_4$, in order to examine Fe$^{2+}$ spin order. By adding a slight compression along the cubic [001] axis during cooling through the transition temperatures, single domain states of tetragonal and orthorhombic phases were attained. In the ferrimagnetic phase below 65 K, the spins are in the $c$-plain of the orthorhombic phase and directed at about 45º from the $a$-axis. With decreasing temperature, the spins tend to rotate toward the $a$-axis. Below 35 K in the spiral magnetic phase, the spins are directed in two directions in the $c$-plane; one is directed at about 60º from the $a$-axis, while the other is directed along the $a$-axis. This indicates that more complicated spin order than a simple cone conical structure is realized.

Keywords: FeCr$_2$O$_4$, single domain crystal, Jahn-Teller effect, ferrimagnet, spiral magnet, $^{57}$Fe Mössbauer spectroscopy

1 Introduction

Investigation on spinel oxides containing Fe$^{2+}$ ions on the A-site, such as FeV$_2$O$_4$ (Takei, et al., 2007; Katsufuji, et al., 2008), FeCr$_2$O$_4$ (Ohtani, et al., 2010; Sagayama, et al., 2011), and Fe$_2$TiO$_4$ (Yamanaka, et al., 2009; Nakamura and Fuwa, 2014), have been revived due to the recent discovery of orbital ordering or multiferroic properties. The iron chromite spinel FeCr$_2$O$_4$ belongs to this family. The room temperature structure is cubic (space group $Fd-3m$) with the lattice constant of $a = 8.378$ Å and the oxygen parameter of $u = 0.3861$ (Shirane, et al. 1964). The A-site (tetrahedral site) is occupied by Fe$^{2+}$ ion (3d$^6$ configuration), whereas the B-site (octahedral site) is occupied by Cr$^{3+}$ ion (3d$^3$ configuration). The high spin Fe$^{2+}$ ion on the tetrahedral site is a Jahn-Teller active ion and induces cubic-tetragonal phase transition at 135 K. With further decreasing temperature, successive phase transition to orthorhombic phase occurs at 70 K due to the spin or orbital ordering. The space group of
the tetragonal phase is \( I4_1/amd \) with the lattice constants of \( c/\sqrt{2}a < 1 \) (Tsuda, et al., 2010). Although the space group of the orthorhombic phase has not been reported, the lattice constants were determined as \( a > b > c \) (Ohtani, et al., 2010). Accordingly rich magnetic phases appear in the orthorhombic phase. Neutron powder diffraction revealed a ferrimagnetic order below around 70 K, followed by a spiral magnetic order below 35 K (Shirane, et al. 1964). In the ferrimagnetic phase, the magnetic moments align along the cubic [110] axis, but the net magnetic moment is approximately 1 \( \mu_B/\text{f.u.} \), only half of the expected value of 2 \( \mu_B/\text{f.u.} \) from Néel model. On the other hand, in the spiral magnetic phase, a triple cone conical structure with the propagation vector along the cubic [110] axis seems to be probable, as observed in a similar compound MnCr\(_2\)O\(_4\) (Hastings and Corliss, 1962). But neutron powder diffraction analysis failed to index some magnetic peaks, which indicates necessity of certain modification (Shirane, et al. 1964). Mössbauer spectroscopic studies of this compound were also conducted by using powder specimens in the early stage of the investigation (Hartmann-Boutron and Imbert, 1968; Tanaka, et al., 1966; Kose and Iida, 1984). In the magnetically ordered state, the direction of hyperfine field (or magnetic moment) of Fe\(^{2+}\) ion is always perpendicular to the principal axis of the electric field gradient (EFG), \( z \)-axis. Below 40 K, the hyperfine field increases abruptly, and the spectrum decomposes into two subspectra with the angles of 0 and 45º from the \( x \)-axis of EFG. The analysis, however, could not refer to the magnetic structure, because of the lack in the information on the low temperature crystal structure at that period. The resolution of the spectrum was not high enough to determine exactly the direction of the magnetic moment, neither.

In this research, we have applied \(^{57}\)Fe Mössbauer spectroscopy by using a single crystal FeCr\(_2\)O\(_4\) in order to investigate the magnetic structure in detail. In the ferrimagnetic phase, we observed the same spin order as reported previously, whereas in the spiral magnetic phase, we found more complicated spin order than a simple cone conical structure.

![Schematic view of the experimental setup of the specimen.](image)

**Fig.1** Schematic view of the experimental setup of the specimen.

## 2 Experiments

A single crystal specimen of FeCr\(_2\)O\(_4\) was prepared by a floating zone (FZ) method in a controlled oxygen pressure (\( P_{O_2} = 10^{-10} \) atm). As-grown specimen was heat treated at 1473 K in \( P_{O_2} = 10^{-10} \) atm for 7 days. X ray diffraction measurement (Cu \( K_\alpha \)) confirmed the cubic spinel structure with the lattice constant of approximately 8.375 Å at room temperature. An elliptic (100) platelet with about 5 mm x 3 mm x 30 \( \mu \)m size was used as an absorber. In order to obtain a single domain state in the low temperature phases, a slight compression along the cubic [001] axis was added by attaching epoxy resin on its both edges. The schematic view of the experimental setup of the specimen is shown in Fig.
1. Mössbauer spectroscopy was conducted in conventional transmission geometry by using $^{57}$Co-in-Rh (25mCi) as γ ray source. The Doppler velocity scale was calibrated using an Fe metal foil at room temperature. The incident γ ray direction was parallel to the [100] axis within the accuracy ±5º. The measurements were conducted at the temperatures of 4.2, 17, 30, 35, 40, 50, 60, 62, 70, 79, 100, 120, 130, 140, 150, 160, 180, 200, 250, and 291 K. The magnetically ordered spectra were analyzed precisely by using a mixed magnetic and quadrupole Hamiltonian. Lorentzian line shapes were assumed for the analysis.

3 Results and Discussion

The paramagnetic spectra at several temperatures are shown in Fig. 2. The room temperature spectrum consists of a singlet reflecting the cubic symmetry (site symmetry $-43m$). The isomer shift is 0.937 mm/s, indicative of high spin Fe$^{2+}$ state. With decreasing temperature, the spectrum splits into an asymmetric doublet even in the cubic region. The quadrupole splitting $Q_S$ increases gradually with decreasing temperature. The absorption intensity ratio of the doublet, $I_2/I_1$, is about 2.2 between 150 and 250 K. In the case of tetragonal symmetry where the asymmetry parameter $\eta$ is 0, the intensity ratio is given by

![Fig.2 Paramagnetic spectrum of single crystal FeCr$_2$O$_4$ at various temperatures.](image1)

![Fig.3 Magnetically ordered spectrum of single crystal FeCr$_2$O$_4$ at various temperatures.](image2)
\[
\frac{I(\pm \frac{3}{2})}{I(\pm \frac{1}{2})} = \frac{1 + \cos^2 \theta_\gamma}{\frac{2}{3} + \sin^2 \theta_\gamma} .
\]

Here \(\theta_\gamma\) denotes angle between the incident \(\gamma\) ray direction and the EFG z-axis (c-axis in tetragonal symmetry). When the cubic [001] axis is successfully transformed into the tetragonal c-axis, \(\theta_\gamma\) is 90° and \(I_2/I_1\) should be 0.6 (for \(QS > 0\)) or 1.67 (for \(QS < 0\)). The observed value of 2.2 is far from these values. This indicates that the cubic symmetry is broken only locally. In addition, the absorption line width increases from 0.346 mm/s at 250 K to 0.488 mm/s at 140 K, which is unusual in the sense of the lattice vibration. These features in the cubic phase are due to the local and dynamical Jahn-Teller effect (Nakamura and Fuwa, 2014; Tanaka, et al., 1966). The intensity ratio \(I_2/I_1\) suddenly decreases below 150 K, just above the transition temperature, and reaches the constant value of \(I_2/I_1 \sim 1.67(10)\) in the tetragonal phase below 135 K [see Fig.4]. This assures that the single domain tetragonal phase is attained with the c-axis transformed from the cubic [001] axis. The sign of the quadrupole splitting is minus.

Below 65 K, the magnetically ordered spectrum is observed as shown in Fig. 3. We consider that the cubic [100], [010], and [001] axes shown in Fig. 1 are successfully transformed into the orthorhombic \(a\), \(b\), and \(c\)-axes, respectively. All the spectra can be analyzed well regarding that the incident \(\gamma\) ray direction is parallel to the \(a\)-axis, and thus the single domain orthorhombic phase is supposed to be attained. The spectrum consists of only one component down to 40 K, which corresponds to the collinear ferrimagnetic order. Below 35 K, however, the spectrum consists of distinct two subspectra, \(S_1\) and \(S_2\). Since there is no report that two crystallographic sites exit in the orthorhombic phase, we regard that the two subspectra originate from the two different directions of the spins. The intensity ratio of the two subspectra is almost 1:1.

The resultant Mössbauer parameters, \(I_2/I_1\), isomer shift (\(IS\)), quadrupole coupling constant (\(e^2qQ/2\)), absorption line width (\(W\)), hyperfine filed (\(H_{hf}\)), and Euler angle between the hyperfine field and the principal axis of EFG (only \(\eta\) is shown), are shown in Figs. 4 – 9, respectively. The Euler angle \(\theta\) is almost 90° below 65 K. The temperature variation of \(IS\) is normal for the high spin Fe\(^{2+}\). In the paramagnetic region, \(e^2qQ/2\) is obtained from the relation

\[
QS = \frac{e^2qQ}{2} \left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}}
\]

with \(\eta = 0\) for the cubic and tetragonal symmetry. A slight change in \(e^2qQ/2\) may be seen around 70 K but no drastic change is observed around 35 K, indicating that the electronic state or orbital state does not change so much through these temperatures. The line width \(W\) shows peaks around the transition temperatures, reflecting structural (135 K) or magnetic (70 and 35 K) fluctuations. An increase in \(W\) of \(S_2\) below 35 K seems to be a result of distribution of the spin direction. It is noted that \(H_{hf}\) of \(S_1\) increases rapidly below 35 K, as reported in the previous work (Hartmann-Boutron and Imbert, 1968). The difference of \(H_{hf}\) between \(S_1\) and \(S_2\) is about 5.5 T. The contribution to the hyperfine field of Fe\(^{2+}\) is expressed as

\[
H_{hf} = H_c + H_{orb} + H_{dip} ,
\]

where \(H_c\), \(H_{orb}\), and \(H_{dip}\) denote Fermi contact, orbital, and magnetic dipolar terms, respectively (Okiji and Kanamori, 1964). The first term \(H_c\) is related to the electron spin and gives major contribution. The latter two terms are related to orbital or valence electron state, and have opposite sign to \(H_c\), which is the origin of small \(H_{hf}\) value in Fe\(^{2+}\) compounds. If the orbital momentum \(L\) decreases, \(H_{orb}\)
decreases and as a result, $H_{hf}$ will increase. But as we see in Fig. 6, notable change in $e^2qQ/2$ is not detected around 35 K, which means the orbital state does not change through this temperature. The magnetic dipolar field $H_{dip}$ is related to the quadrupole interaction and the thermal average of the spin $<S>$ and expressed as

$$H_{dip} = 1.5(e^2qQ/2)<S>.$$  

Equation (4) gives $H_{dip} \sim 9$ T in our case. Since $H_{dip}$ is anisotropic and has the same angular dependence as the quadrupole interaction, this can produce a difference in $H_{hf}$. The Euler angle $\theta$, however, is almost 90° for both $S_1$ and $S_2$. This means that the angular dependence of $H_{dip}$ cannot explain the difference of about 5.5 T. Therefore we refer to a recent neutron diffraction analysis on the similar compound MnCr$_2$O$_4$. The analysis reveals a fluctuating transverse spin component in the ferrimagnetic phase and a freezing of the transverse component in the spiral magnetic phase (Tomiyasu, et al., 2004). The rapid increase of $H_{hf}$ seems to be consistent with this scheme. This feature may be also responsible for a slight increase of the magnetization below around 35 K (Ohtani, et al., 2010). On the other hand, $H_{hf}$ of $S_2$ grows rather smoothly from the ferrimagnetic region into the
spiral magnetic region. This may imply that a similar magnetic order remains partially in the spiral magnetic phase. The fluctuating transverse spin component may still arrive in $S_2$.

In order to discuss the Fe$^{2+}$ spin order in the orthorhombic phase, we calculate the EFG axes on the basis of the crystal structure. The EFG tensor at the Fe site can be calculated using

$$V_{pq} = \sum_i \frac{\partial^2}{\partial p \partial q} V^{(i)}.$$  (5)

Here, $(p, q)$ denote $(x, y, z)$, and $V^{(i)}$ denotes the electric potential by the $i$-element. Unfortunately the crystal structure parameters of the orthorhombic phase have not been reported. In a family compound FeV$_2$O$_4$, a similar successive phase transition was observed. The cubic – tetragonal transition takes place at 140 K, followed by the tetragonal ($I_4/amd$) – orthorhombic ($Fddd$) transition at 110 K, and finally the orthorhombic ($Fddd$) – tetragonal ($I_4/amd$) transition at 65 K (Katsufuji, et al., 2008; Nii, et al., 2012). The structure parameters were precisely determined for these phases. Therefore we assume that the orthorhombic phase of FeCr$_2$O$_4$ is also in the same space group $Fddd$. By applying a point charge model for $V^{(i)}$, the summation over a lattice (within a 100 Å sphere) gives each $V_{pq}$ component. The diagonalization of the tensor yields the principal axes (eigenvectors). The calculated result is shown in Figs. 10. The z and y-axes coincide with the crystallographic c and a-axes, respectively, while the x-axis is directed in $-b$ direction. Thus we can deduce the spin direction with respect to the crystallographic axes from the Euler angle $(\theta, \varphi)$.

The Euler angle $\theta$ is approximately 90º below 65 K, which means that the spins are almost in the $c$-plain. In the ferrimagnetic phase just below 65 K, the spins are directed around $(\theta, \varphi) \sim (90\degree, 45\degree)$, i.e., the cubic [1-10] direction. The spin order in the ferrimagnetic phases is shown in Fig. 10 (a). This is consistent with the collinear ferrimagnetic structure determined by neutron diffraction analysis. With decreasing temperature, however, $\varphi$ increase and reaches 90º, i.e. $a$-direction (or cubic [100]), at 40 K. The $a$-axis is the longest axis in the orthorhombic structure. This feature is unexpected from the pronounced collinear ferrimagnetic structure. We consider that this may be a precursor phenomenon to the spiral magnetic structure below 35 K. In the spiral magnetic phase, the spins are directed in two directions. That of $S_1$ is in $(\theta, \varphi) \sim (90\degree, 30\degree)$, whereas that of $S_2$ is in $(\theta, \varphi) \sim (90\degree, 90\degree)$. That is, both spins are still almost in the $c$-plain, and one is directed about 60º from the $a$-axis, while the other is
directed along the $a$-axis. The spin direction of $S_2$ is almost identical to that of the ferrimagnetic order at 40 K. $H_{hf}$ of $S_2$ also grows smoothly from that of the ferrimagnetic phase [see Fig. 8]. The obtained spin order in the spiral magnetic phases is shown in Fig. 10 (b). Note that the absorption line width of $S_2$ is 0.529 mm/s at 4.2 K, extremely broader than that of $S_1$ (0.295 mm/s) [see Fig. 7], which is suggestive of a distribution in the direction of $S_2$ spins. This spin configuration does not coincide with a simple cone conical structure along the cubic [110] direction, indicating that a more complicated spin order is possibly realized. This feature, however, may be related to the neutron diffraction analysis that some magnetic Bragg peaks cannot be indexed by a simple cone conical structure.

4 Summary

In order to investigate the Fe$^{2+}$ spin order in FeCr$_2$O$_4$, we have conducted $^{57}$Fe Mössbauer spectroscopy by using the single crystal. By adding a slight compression along the cubic [001] axis during cooling the specimen through the transition temperatures, a single domain state was successfully obtained in the tetragonal phase and also in the orthorhombic phase. In the ferrimagnetic phase below 65 K, the spins are directed around the cubic [10-1] direction (approximately 45º from orthorhombic $a$-axis), which is consistent with the collinear ferrimagnetic structure determined by neutron diffraction analysis. With decreasing temperature, however, the spins tend to rotate toward the cubic [100] axis (orthorhombic $a$-axis). In the spiral magnetic phase, the spins are directed in two directions in the orthorhombic $c$-plane; one is directed at about 60º from the $a$-axis, while the other is directed along the $a$-axis. This spin configuration does not coincide with a simple cone conical structure along the cubic [110] direction, which is suggestive of more complicated spin order. Although Mössbauer spectroscopy can detect the direction of Fe$^{2+}$ spins, their periodicity and the information on the Cr$^{3+}$ spins cannot be obtained. We hope that further investigation by neutron diffraction will be conducted on the spiral magnetic structure.

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