

Weak Ferromagnetic Ordering in Brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ and its Effect on Electric Field Gradients

Mössbauer spectroscopy analysis showed that the magnetic moment is slightly canted against the a -axis for $\text{Ca}_2\text{Fe}_2\text{O}_5$ (CFO). The Dzyaloshinskii–Moriya (DM) interaction possibly causes canted magnetic ordering. The electric field gradient (EFG) refined from Mössbauer spectroscopy at 287 K is larger than that at 750 K, which is higher than T_N . This suggests that the EFG remarkably changes below T_N . A possible reason for the change in EFG is local electric polarization induced by the DM interaction. As a result, strong correlations among magnetic ordering and electrical properties appear in CFO.

Brownmillerite $\text{Ca}_2\text{Fe}_2\text{O}_5$ (CFO) is orthorhombic ($Pnma$) at room temperature [1-3]. The Fe ions are surrounded in the octahedral or tetrahedral oxygen coordination (FeO_4 or FeO_6). In this report, we define Tetra as FeO_4 and Octa as FeO_6 . With increasing temperature, CFO undergoes a phase transition from $Pnma$ to $Icmm$ at 963 K [2]. CFO is antiferromagnetic below $T_N \sim 730$ K [1, 2, 4-6]. Although many studies have already been reported, the following issues remained unclear.

(1) The magnetic structure in CFO: Some studies reported that CFO was pure antiferromagnetic, whereas other studies stated that it was weakly ferromagnetic. Other works reported that its weak ferromagnetic behavior came from the secondary iron oxide phase [7]. In order to solve the issue, this study investigated the field cooling effects on magnetization in CFO. In addition, we performed combinational analysis of the crystal structure and ^{57}Fe Mössbauer spectroscopy.

(2) Correlation between magnetic and electrical properties: A recent study reported that CFO shows magnetoresistance (MR) of $\sim 12\%$ at room temperature [8]. Magnetoresistance means a strong correlation between electrical and magnetic properties. We investigated whether an anomaly of electrical conductivity is present near T_N . Based on the results of the temperature dependence of the electrical conductivity, crystal structure,

and Mössbauer parameters, this study investigated the correlation between magnetic ordering and electrical properties.

Figure 1 shows the Mössbauer spectra investigated at 287 and 750 K. Two different spectra of magnetically ordered phases were observed at 287 K. The two different spectra correspond to two different Mössbauer parameters, coming from the Tetra and Octa. At 750 K, the spectra changed from magnetically ordered phases to doublets, because of the magnetic transition. We investigated the magnetic structure based on the Mössbauer spectra obtained at 287 K. For a precise analysis, first, we evaluated the principal axes of the electric field gradient (EFG). The EFG tensor for each Fe site can be calculated based on the crystal structure. The crystal structure of CFO was investigated by synchrotron radiation X-ray powder diffraction (SXRPD) at room temperature at BL-4B2. Based on the EFG principal axes, other Mössbauer parameters were appropriately refined [9].

Figure 2 illustrates a scheme of the magnetic structures at 287 K from the refinement. The magnetic moments for each Fe site are canted against the crystallographic axes. This cant causes a net spontaneous magnetic moment along the c -direction. We also confirmed that spontaneous magnetization appeared below T_N , after the field cooling treatment. If the spontaneous

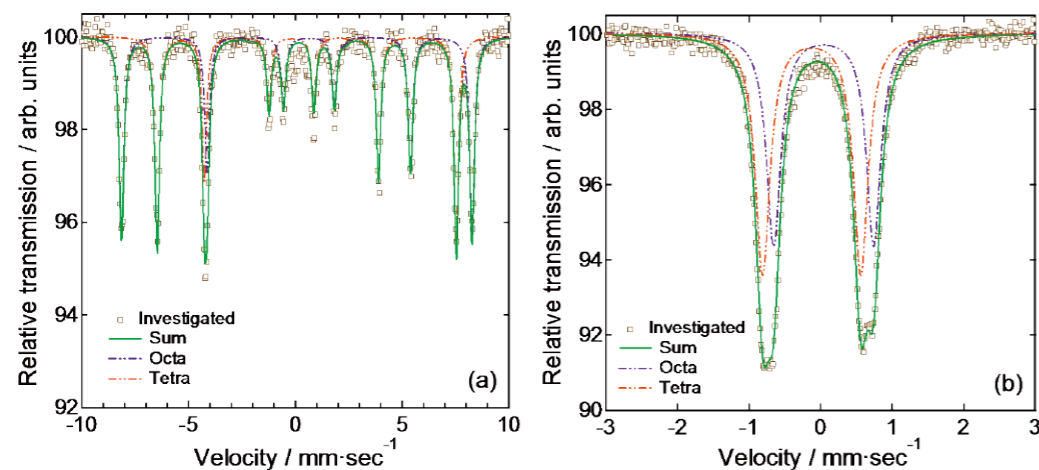


Figure 1: Mössbauer spectra investigated at (a) 287 K and (b) 750 K. The open squares indicate the investigated spectra. The solid or dashed lines are obtained by refinement.

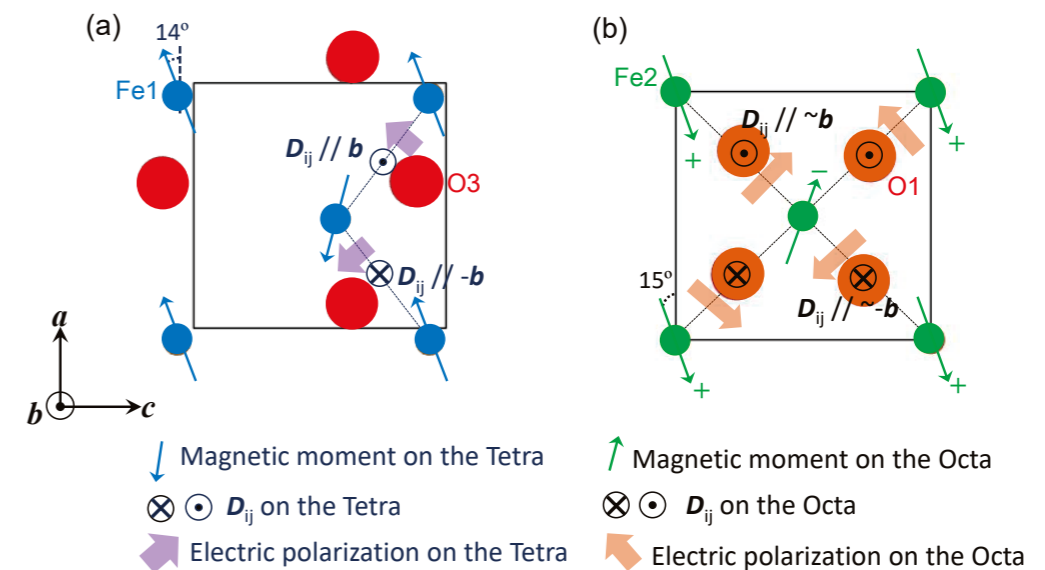


Figure 2: Scheme of the magnetic structures at 287 K on (a) the (0 4 0) and (b) the (0 0 0) plane, estimated from the refined Mössbauer parameters. The magnetic moments on Fe1 (Tetra) are canted against the a -axis on the a - c plane. The magnetic moments on Fe2 (Octa) are slightly canted against the a - c plane as well as the a -axis. The notation “+” indicates that the moments are canted to the $+b$ -direction against the a - c plane. The notation “-” is the opposite direction. The local electric polarizations are directed along $\langle 101 \rangle$ for the Tetra, and along approximately $\langle 101 \rangle$ for the Octa.

magnetization is due to other iron oxides, the critical temperature at which spontaneous polarization appears would be different from the T_N of CFO. Thus, the spontaneous magnetization is not due to contamination, but to the canted magnetic moments in CFO itself.

The value of $e^2qQ/2$ evaluated from the Mössbauer spectroscopies showed a remarkable difference between 287 K and 750 K. This difference of $e^2qQ/2$ is unusual for other iron oxides. In general, $e^2qQ/2$ is independent of temperature as long as no structural phase transition appears. We suppose that the difference is caused by the local electric polarizations induced by the Dzyaloshinskii–Moriya (DM) interaction. As indicated in eq. (1), the Dzyaloshinskii vector \mathbf{D}_{ij} depends on a unit vector \mathbf{r}_{ij} along the line connecting magnetic moments and an O^{2-} displacement \mathbf{d} from the connecting line [10]:

$$\mathbf{D}_{ij} = \mathbf{d} \times \mathbf{r}_{ij} \quad (1)$$

The presence of \mathbf{D}_{ij} encourages the displacement of O^{2-} ions. This displacement may result in a local electric polarization perpendicular to the line connecting magnetic ions. In the case of CFO, local electric polarizations \mathbf{P} are induced along the $[101]$ directions for the Tetra and approximately the $[101]$ directions for the Octa, as illustrated in Fig. 2. The local electric polarization \mathbf{P} is a possible reason for the remarkable difference in EFG ($e^2qQ/2$). The Arrhenius plots of total electrical conductivity show a kink around $T_N \sim 730$ K, suggesting that the EFG modulated by the DM interaction affects the hole conductivity. When a part of the weak ferromagnetic domains aligns with the applied magnetic field, the EFG also changes, and thus contributes to

electrical conductivity. This is a possible reason for the MR observed in a recent study [8].

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