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An approach to specify the spin configuration in the RFe_2O_4 (R=Y, Ho, Er, Tm, Yb, and Lu) family: ^{57}Fe Mössbauer study on a single crystal $LuFe_2O_4$

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Abstract

Polarized ^{57}Fe Mössbauer spectroscopy was applied to a stoichiometric single crystal $LuFe_2O_4$ in order to determine the spin configuration of Fe ions. The compound is one of the RFe_2O_4 (R=Y, Ho, Er, Tm, Yb, and Lu) family, which show some characteristics of a two-dimensional antiferromagnet on a triangular lattice. The antiferromagnet is composed of positive and negative ferrimagnetic domains. It was concluded that among three types of Fe^{3+} ions, two of them contribute to the minority spins and the rest to the majority spin in a domain. All Fe^{2+} ions contribute to the majority spins. The spin configuration is consistent with that suggested by the previous investigations.

Keywords: $LuFe_2O_4$; Polarized ^{57}Fe Mössbauer spectroscopy; Two-dimensional antiferromagnet on a triangular lattice; Spin configuration

1. Introduction

A family of oxides RFe_2O_4 (R=Y, Ho, Er, Tm, Yb, and Lu) is known to show some characteristics of a two-dimensional antiferromagnet on a triangular lattice. The compounds have rhombohedral structures with the space group $R\bar{3}m$. The crystal structure is shown in Fig. 1, as a hexagonal cell for convenience (a=3.438 Å and c=25.25 Å for R=Lu) [1]. It is composed of the alternate stacking of the hexagonal $Fe_2O_{2.5}$ layer (W-layer) and the hexagonal $RO_{1.5}$ layer (U-layer) along the c-axis. This crystallographic arrangement leads to the two-dimensional behaviour in their electrical and magnetic properties. For R=Y, which has the largest ionic radius in this family, the Fe spins and charges order three-dimensionally at low temperatures. The two-dimensionality is more notable for R ions with small radii, especially for R=Lu.

Equal numbers of Fe^{2+} and Fe^{3+} ions occupy the crystallographically equivalent sites in the W-layer, which leads to the semiconductive conduction due to the electron hopping. The R ions are paramagnetic down to 4.2 K, whereas the spins of Fe ions order below around 240 K [1,2]. The magnetic easy axis is the c-axis. Many investigations such as high-field magnetization measurements [1,2], ^{57}Fe Mössbauer spectroscopy [3,4], neutron diffraction [5], and dielectric measurements [6] have been conducted so far. The magnetic ordering is strongly related to the charge ordering. Especially, Mössbauer spectroscopy with an applied magnetic field revealed the ferrimagnetic domain structure. Detailed studies concerning the Fe^{3+} spectra proved the existence of three kinds of Fe^{3+} ions in a domain. Two of them contribute to the minority spins and the rest to the majority spin [3]. In order to account for the net magnetic moment, 2.8 μ_B/f.u. at 4.2 K, all the Fe^{2+} ions should contribute to the majority spins. From these results, Siratori et al. proposed a model of two-dimensional spin-charge orderings of Fe ions [7]. This assumption, however, has not been yet confirmed directly, though the Fe^{2+} spectra could be separated from the total spectra [4].

In this paper, we deal with the Mössbauer spectra of a stoichiometric single crystal $LuFe_2O_4$. By means of the polarized Mössbauer technique, we could determine the

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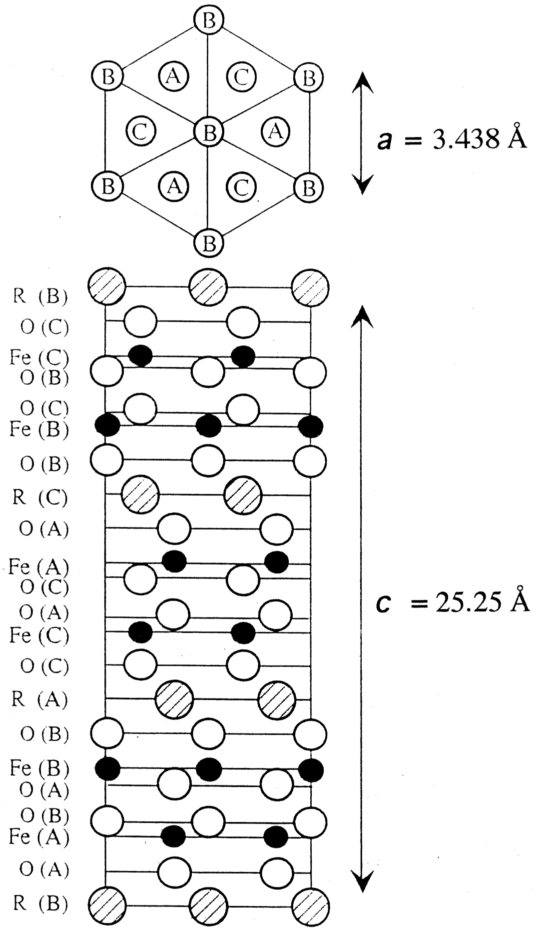

Fig. 1. Crystal structure of RFe_2O_4. A, B, and C correspond to the atomic positions in a hexagonal layer. The lattice constants are for R=Lu.

spin configuration of Fe^{3+} and Fe^{2+} ions. Our results are consistent with the spin configurations suggested by the previous investigations.

2. Experiment

A stoichiometric single crystal $LuFe_2O_4$ was made by the floating zone melting method in an atmosphere of controlled oxygen pressure. The specimen used for the Mössbauer measurements was a *c*-plane platelet with about 80 mm thickness and 8×5 mm area. The specimen was cooled once from above the Curie temperature (240 K) down to 2 K with an applied magnetic field of 40 kOe, parallel to the *c*-axis. Thus only positive ferrimagnetic domains are formed.

The Mössbauer spectra were taken at 2 K by a transmission method with an incident γ ray parallel to the *c*-axis. In this case, the absorption due to $\Delta m_I=0$ transitions, so-called 2- and 5-lines, should not be observed. Here m_I represents the nuclear magnetic quantum number. ^{57}Co-in-Rh was used as the γ ray source. The Doppler velocity scale was calibrated by a metallic Fe at room temperature. In order to determine the direction of the hyperfine field, or the spins, a magnetic field (H_{ex}) of 40 kOe was applied parallel to the *c*-axis during measurement. In this experiment, we applied the same magnetic field to the source, too. We call this technique the 'polarized Mössbauer method', which provides definite information on the spin direction. That is, when the energy level of the source undergoes Zeeman splitting due to an applied magnetic field, the emitted γ rays have four different energies corresponding to each $\Delta m_I=\pm1$ transitions. The polarized γ ray is absorbed to the sample selectively according to Δm_I change. The resultant spectrum is schematically illustrated in Fig. 2 (a) and (b) for positive and negative hyperfine field (H_{hf}), respectively. Hyperfine fields parallel and antiparallel to the direction of H_{ex} are defined as positive and negative signs, respectively. Note that the coupling constant between a 3d magnetic moment and its hyperfine field is negative for a 3d transition metal. Each absorption line is composed of a set of a stronger and a weaker lines, of which intensity ratio is 3:1. The shift δ is equal to $0.58H_{ex}$. We have to concentrate mainly on the shifts of the 3- and 4-line positions to determine the sign of H_{hf}, or the direction of the spins. The spectra without

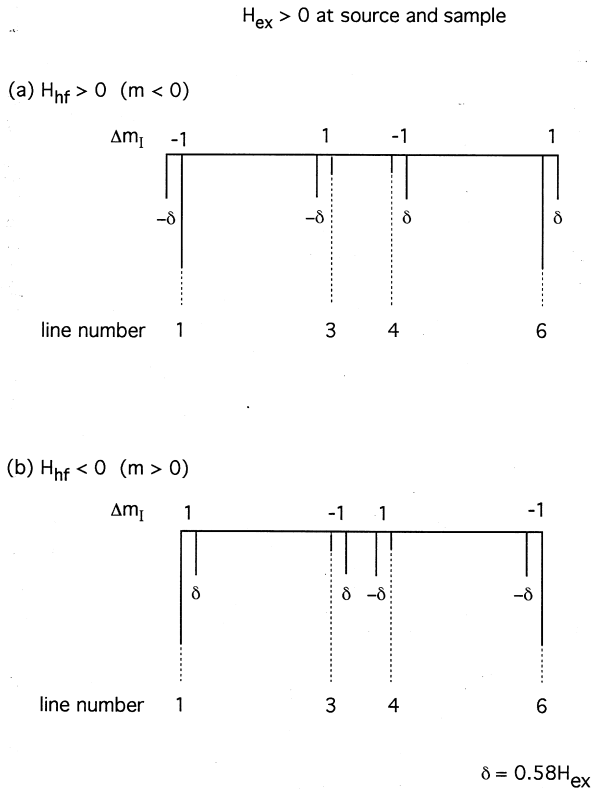

Fig. 2. Schematic polarized Mössbauer spectrum for (a) positive and (b) negative hyperfine fields. In this case, the magnetic field H_{ex}, parallel to the γ ray propagation, is applied both to a sample and a source. The broken lines indicate the line positions for the $\Delta m_I=\pm1$ transition without magnetic field (conventional spectrum). The shift δ is equal to $0.58H_{ex}$.

applied magnetic field, by a conventional method, was also taken at 2 K for comparison.

3. Results and discussion

The Mössbauer spectrum of the single crystal $LuFe_2O_4$ at 2 K without applied magnetic field is shown in Fig. 3. Although the measurements were conducted until the absorption counts summed up to 10^6 counts, well defined spectra could not be obtained. This is essentially due to the presence of Lu ions which has a large mass absorption. As reported by M. Tanaka et al., Fe^{3+} spectra are decomposed into three subspectra, termed C-, P-, and M-spectra, with equal absorption intensities [3]. It has been proposed that the former two correspond to the minority spins and the latter to the majority spins. The hyperfine fields H_{hf} are 491.0 (±2), 480.3 (±2) and 454.7 (±2) kOe, respectively, and the quadrupole shifts ε_q are 0.02 (±0.02), 0.20 (±0.02), and −0.13 (±0.02) mm/s, respectively. The isomer shifts *IS* are assumed to be the same, 0.42 (±0.02) mm/s. These parameters are in good agreement with those at 4.2 K [4]. The solid curve in Fig. 3 represents the full Fe^{3+} spectrum and the resultant Fe^{2+} spectrum is shown in Fig. 4. It is seen that the Fe^{2+} spectrum is also composed of presumably three subspectra. It is, however, very difficult to decompose, so here we treat them as one, for convenience. The Mössbauer parameters are roughly estimated to be $H_{hf}\approx275$ kOe, $IS\approx1.0$ mm/s, and $\varepsilon_q\approx-0.65$ mm/s.

The polarized Mössbauer spectrum at 2 K is shown in Fig. 5. In comparison with Fig. 3, it is seen that

1. the separation between 3- and 4-line groups of Fe^{3+} spectra becomes larger,
2. the intensity of the 3-line group of Fe^{3+} spectra becomes smeared, and
3. the absorption at the 4-line groups of Fe^{3+} spectra, where 3- and 4-line groups of Fe^{2+} spectra are superposed, becomes stronger and sharper.

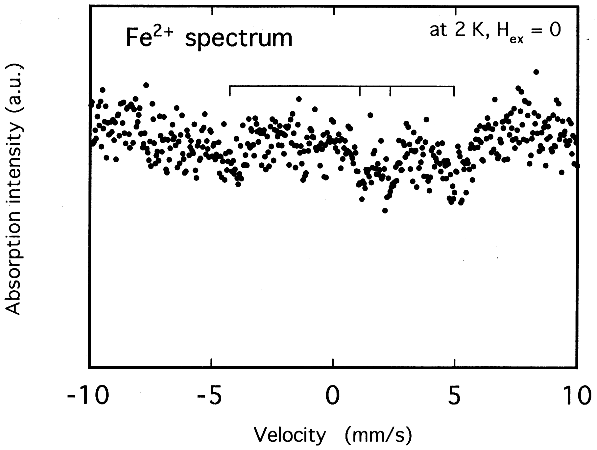

Fig. 4. Fe^{2+} spectrum at 2 K without the applied magnetic field.

The positions of 1- and 6-line groups of Fe^{3+} and Fe^{2+} spectra remain unchanged, although their shapes become slightly broader due to the presence of weaker absorption lines nearby (see Fig. 2). Here we concentrate on the stronger absorption lines only. The observation (1) indicates that most of the 3- and 4-line groups of Fe^{3+} spectra move outward [corresponding to Fig. 2 (a)]. The observation (2) indicates that there exists some portion of the 3-line of Fe^{3+} which moves inward [corresponding to Fig. 2 (b)]. And the observation (3) indicates that the 3- and 4-line groups of Fe^{2+} spectra get so close each other and overlap to the 4-line group of Fe^{3+} spectra. Taking into account the shifts δ (=23.2 kOe), the stronger line positions of each subspectra are indicated by the assignments in Fig. 5. The full Fe^{3+} spectrum is indicated by the solid curve in the figure and the resultant Fe^{2+} spectrum is

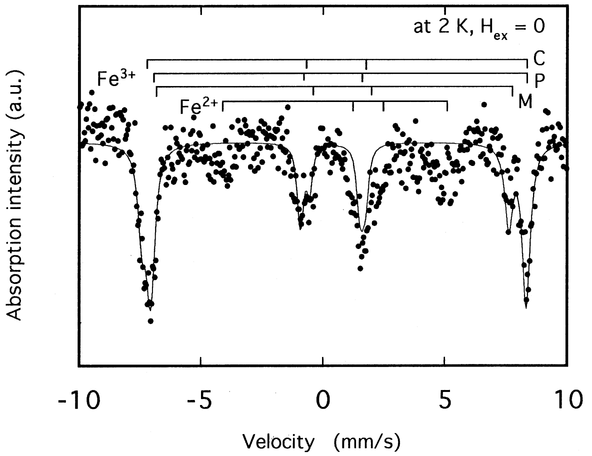

Fig. 3. Mössbauer spectrum of the single crystal $LuFe_2O_4$ at 2 K without the applied magnetic field. The solid curve indicates the full Fe^{3+} spectrum.

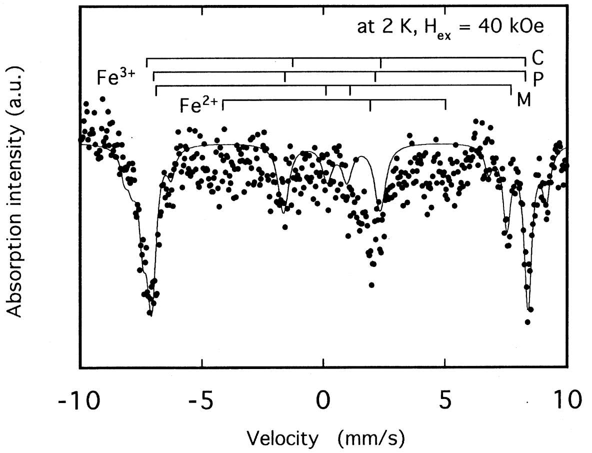

Fig. 5. Polarized Mössbauer spectrum of the single crystal $LuFe_2O_4$ at 2 K with applied magnetic field of 40 kOe. Only the stronger absorption lines are assigned. The solid curve indicates the full Fe^{3+} spectrum.

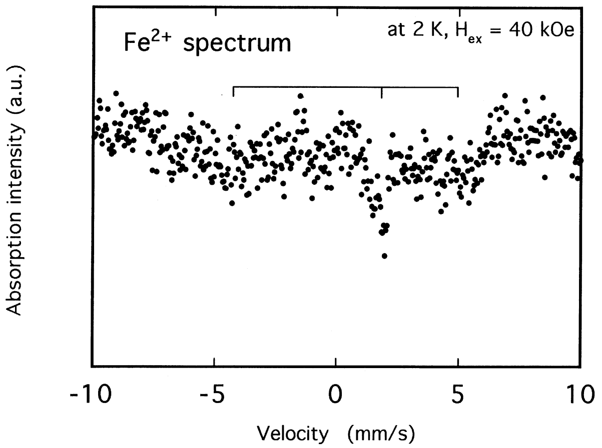

Fig. 6. Polarized Fe^{2+} spectrum at 2 K with applied magnetic field of 40 kOe. Only the stronger absorption lines are assigned.

shown in Fig. 6. Comparing with Fig. 4, it is clear that 3- and 4-line groups of Fe^{2+} spectra get close each other and its H_{hf} is negative [corresponding to Fig. 2 (b)].

Thus we can determine that the sign of the hyperfine fields against H_{ex} is positive for C and P-spectra of Fe^{3+}, while it is negative for M-spectrum of Fe^{3+} and all Fe^{2+} spectra groups. The positive hyperfine field corresponds to the minority spins and the negative one to the majority spins. The resultant spin configuration is indicated in Table 1. This configuration is consistent with that suggested by the previous Mössbauer investigations.

In conclusion, we could determine the spin configuration of Fe^{3+} and Fe^{2+} in $LuFe_2O_4$ by the polarized Mössbauer effect, which is consistent with that suggested by our previous works. More detailed analysis of the spectra is required to determine the precise Mössbauer parameters of Fe^{2+} ions.

Table 1
The spin configuration of Fe ions on ferrimagnetic sublattice for RFe_2O_4

Ion	Majority spin	Minority spin
Fe^{2+}	↑ ↑ ↑	
Fe^{3+}	↑ (M)	↓ (C) ↓ (P)

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