Local and dynamic Jahn-Teller distortion in ulvöspinel Fe$_2$TiO$_4$

Shin Nakamura · Akio Fuwa

Abstract ^{57}Fe Mössbauer spectroscopic study on ulvöspinel Fe$_2$TiO$_4$ has been conducted in a wide temperature range from 16 K to 500 K. The paramagnetic spectra are composed of several high spin Fe^{2+} doublets even at 500 K, which is rather strange because the point symmetry of the A-site is completely cubic ($-43m$). We explain the electric field gradient (EFG) at A-site by the local arrangement of Fe^{2+} and Ti^{4+} on the B-site. The spectra were successfully analyzed by four-subspectra model, which is based on the B-site arrangement. The model also fits rather well to the magnetically ordered spectra. Thus the temperature variations of the hyperfine parameters were obtained. The Néel temperature (T_N) is estimated to be about 125 K. The quadrupole coupling constants $e^2qQ/2$ of A-site subspectra show little change around cubic-tetragonal transition temperature ($T_t = 163$ K), but rapidly increase below T_N. From the temperature variation of line width, we found local and dynamic Jahn-Teller distortions around A-site Fe^{2+} ions in the cubic phase.

Keywords Fe$_2$TiO$_4$ · Spinel structure · Antiferromagnet · Local and dynamic Jahn-Teller distortion · ^{57}Fe Mössbauer spectroscopy · Motional narrowing effect

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1 Introduction

Investigation on spinel oxides containing Fe^{2+} ions on the A-site (tetrahedral site), such as $FeCr_2O_4$ and FeV_2O_4, has been revived due to the recent discovery of orbital ordering or multiferroic properties [1–4]. The high spin Fe^{2+} ion on the tetrahedral site is a Jahn-Teller active ion and induces cubic-tetragonal phase transition at low temperature. With further decreasing temperature, successive phase transition to orthorhombic phase occurs due to the spin or orbital ordering. Accordingly rich magnetic phases appear such as ferrimagnetism, spiral magnetism, or non-collinear magnetism.

The ulvöspinel Fe_2TiO_4 also belongs to this family. The room temperature structure is cubic (*Fd-3m*) with the lattice constants of $a = 8.5469$ Å and $u = 0.3861$ [5]. The crystal structure is shown in Fig. 1a. The A-site is occupied by Fe^{2+} ion, whereas the B-site does equally by Fe^{2+} and Ti^{4+} ions. No charge ordering on the B-site was found. The cubic-tetragonal transition takes place at $T_t = 163$ K [5]. The low temperature tetragonal structure ($I4_1/amd$) is shown in Fig. 1b. The lattice constants are $a = 6.0129$ Å and $b = 8.5237$ Å at 123 K, slightly elongated along the *c*-axis ($c/a\sqrt{2} = 1.0024$). Neutron diffraction study indicates that the magnetic structure is a Néel type antiferromagnet with weak ferromagnetic moment [6]. Néel temperature (T_N) is about 130 K and the magnetic easy axis is *c*-axis [7]. The Mössbauer spectroscopic studies on this compound have not been conducted so much, presumably because of its complicated spectrum [7–9]. The paramagnetic spectrum consists of broad doublets and cannot be easily separated into two sub-spectra assigned to A- and B-sites Fe^{2+} ions. Vanleerberghe and Vandenberghe [9] reported an excellent analysis on the paramagnetic spectra, where they applied external magnetic field in order to separate A- and B-site subspectra and assumed distributions of quadrupole splitting. But no feature related to the Jahn-Teller effect was found. On the other hand for the magnetically ordered spectrum, the analysis could not be achieved due to further complicated spectra [7].

Here in this research, we have measured ^{57}Fe Mössbauer spectra of Fe_2TiO_4 in a wide temperature range from 16 K to 500 K. The spectra were successfully analyzed by four-subspectra model, which is based on the local arrangement of the B-site ions. We discuss possible origin of electric field gradient at the A-site, and also the local and dynamic Jahn-Teller distortions around A-site Fe^{2+} ions in the cubic phase.

2 Experiments

Single phase Fe_2TiO_4 is stable only in a limited thermodynamic condition with respect to temperature and oxygen partial pressure [10]. Reagent grade (99.9 %) a-Fe_2O_3 and TiO_2 powders were used as starting materials. These powders were mixed, pressed into a rod (about 8 mm diameter and 50 mm length), and fired at 1573 K in controlled oxygen atmosphere of $P_{O2} = 5 \times 10^{-12}$ atm for 12 hrs. The rod was used as a seed to fabricate a single crystal by floating zone melting (FZ) method at about 1823 K in $P_{O2} = 10^{-8}$ atm. The crystal growth rate was 10 mm/hr. The Cu K_α X-ray diffraction proved the specimen to have a single phase cubic spinel structure with a lattice constant of 8.534(10) Å at room temperature. The powdered

Fig. 1 Crystal structure of Fe$_2$TiO$_4$ in **a** high temperature cubic phase and **b** low temperature tetragonal phase

(a)

(b)
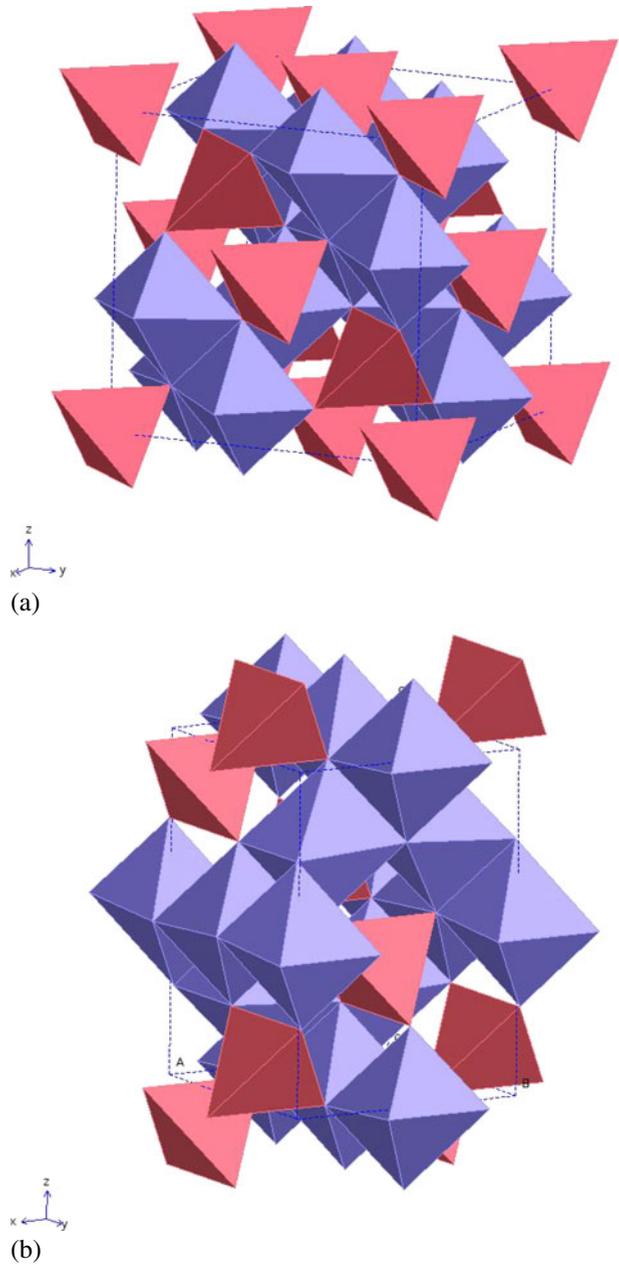
specimen was used as an absorber. The ^{57}Fe Mössbauer spectroscopy was conducted in conventional transmission geometry by using ^{57}Co-in-Rh (25 mCi) as the γ ray source. The spectra were measured in the temperature range from 16 K to 500 K. The high temperature spectra were measured in a vacuum furnace (10^{-2}Torr). Above

Fig. 2 Paramagnetic spectra of Fe_2TiO_4 at several temperatures
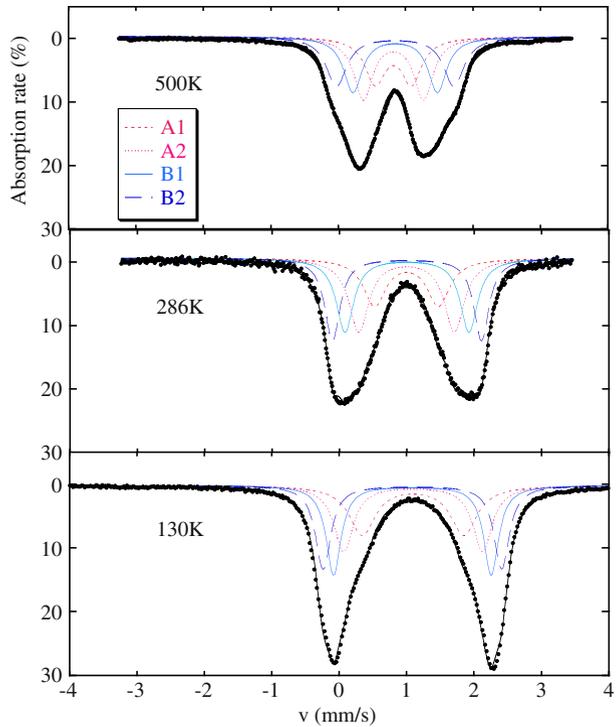
550 K, the specimen oxidized. The Doppler velocity was calibrated by using Fe metal foil at room temperature. Lorentzian line shapes were assumed for the spectra analysis.

3 Results and discussions

In Fig. 2, the paramagnetic spectra at several temperatures are shown. The spectra are composed of several high spin Fe^{2+} doublets even at 500 K. This is not easily comprehensible, because the point symmetry of the A-site is completely cubic ($-43m$) and therefore the A-site spectrum should be a singlet. The presence of electric field gradients (EFG) at A-site in such high temperature range cannot be explained by Jahn-Teller effect. The same feature is observed in hercynite $FeAl_2O_4$ [11–13], where the incomplete normality of the cation distribution (about 15 % of inversion) causes the non-cubic surroundings of A-site. In contrast, the EFG at A-site of Fe_2TiO_4 originates possibly from a random arrangement of Fe^{2+} and Ti^{4+} on the B-site. In order to verify this feature, we here examine the quadrupole splitting. The electric field gradient sensed by ^{57}Fe nucleus, q, is expressed as

$$q = q_{lat} + q_{val},$$

where the former and the latter terms represent lattice and valence electron contributions, respectively. For Fe^{2+} ion, the major contribution is q_{val}, which is difficult

Table 1 Calculated $e^2 q_{lat} Q/2$ and evaluation of q_{val} for several B-site arrangements

B-site arrangement	$e^2 q_{lat} Q/2(A)$	$q_{val}(A)$	$e^2 q_{lat} Q/2(B)$	$q_{val}(B)$
(0) complete random	0	0	+0.09 (mm/s)	negative, small
(1) 1/8 partial order	−0.14 (mm/s)	positive, small	+0.17 (mm/s)	negative, small
(2) 1/4 partial order	−0.27 (mm/s)	positive, large	+0.19 (mm/s)	negative, large

Fig. 3 Magnetically ordered spectra of Fe_2TiO_4 at several temperatures
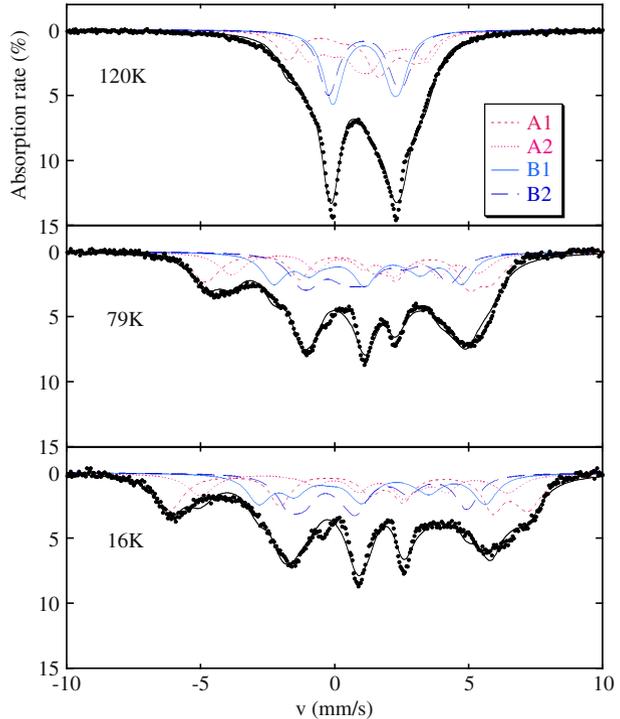
to calculate precisely. However, q_{val} has opposite sign to q_{lat} and has a certain correlation with local structure. Therefore we can evaluate q_{val} by calculating q_{lat} with the equations,

$$V_{pq} = \sum_{i}^{lat} \frac{\partial^2}{\partial p \partial q} V^{(i)}$$

and

$$q_{lat} = (1 - \gamma_\infty) \frac{V_{ZZ}}{e}.$$

Here (p, q) denote (x, y, z) and $V^{(i)}$ denotes electric potential of i-element (point charge model). Taking into account the large difference of ionic radii ($r(Fe^{2+}) = 0.770$ Å and $r(Ti^{4+}) = 0.605$ Å [14]) and Anderson's condition [15], it seems probable that an alternative charge order on the B-site along <110> directions exists locally.

Fig. 4 Temperature dependences of the isomer shifts (*IS*) and the hyperfine fields (H_{hf})
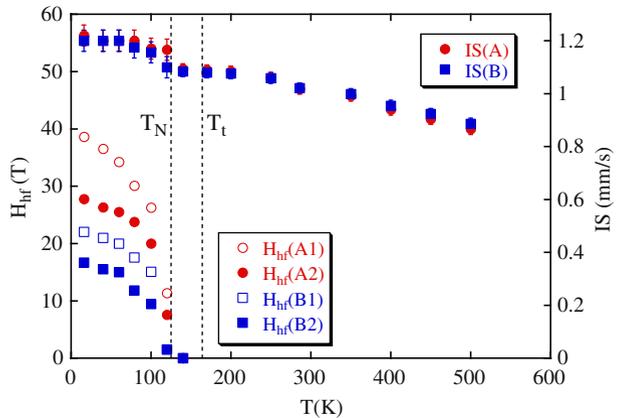
Fig. 5 Temperature dependences of the quadrupole coupling constants ($e^2qQ/2$)
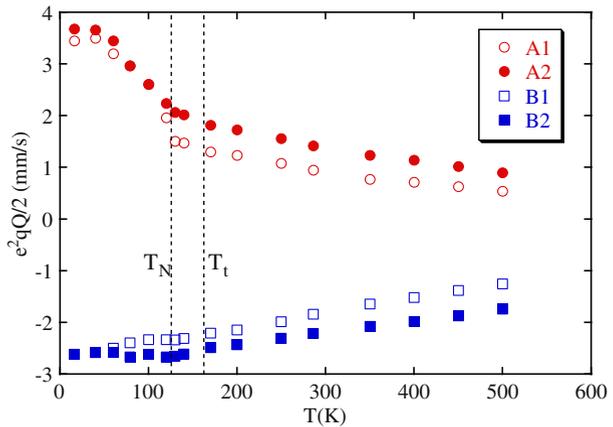
We assume tentatively partially charge ordered arrangements on (1) 1/8 and (2) 1/4 of B-sites in a unit cell. Using $\gamma_\infty = -9.14$ [16] and $Q = 0.187$ barn [17], the quadrupole coupling constants by lattice contribution $e^2q_{lat}Q/2$ are calculated as indicated in Table 1. An extreme case of complete random arrangement (or amalgamation of Fe^{2+} and Ti^{4+}) is also indicated as case (0) for comparison. Expected manner of q_{val} for each case are indicated in Table 1. We see that the local charge order on B-site can generate EFG at the A-site. The arrangements of case (1) and (2) will generate smaller and larger EFG, respectively, for both A- and B-sites. The sign of $e^2qQ/2$ for the A-site is positive, while that for the B-site is negative, which is consistent with the analysis of R. Vanleerberghe and R. E. Vandenberghe [9]. Hereafter, the subspectra originate from the arrangements represented by the case (1) are termed A1 and B1, whereas those by the case (2) are termed A2 and B2, respectively. The four-subspectra model provides good fittings through all temperature range as indicated by the smooth curves in Fig. 2. We assume equal ratio for each subspectrum.

In Fig. 3, the magnetically ordered spectra at several temperatures are shown. The four-subspectra model fits relatively well even below T_N as indicated by smooth

curves. The signs of $e^2qQ/2$ are still positive and negative for A- and B-sites, respectively. Extremely broad line widths below T_N, 0.8~1.2 mm/s for the outermost, is result of the distribution in hyperfine field and EFG axes due to the B-site ion arrangement, and the formation of crystalline domains though T_t.

The resultant Mössbauer parameters, isomer shift (IS) and hyperfine field (H_{hf}), $e^2qQ/2$, and line width (W) against temperature are shown in Figs. 4, 5 and 6, respectively. The second order Doppler shifts (dIS/dT) are about -7.5×10^{-4} (mm/sK), which is normal for iron oxides (Fig. 4). The T_N is estimated to be about 125 K (Fig. 4). The small H_{hf} and large $e^2qQ/2$ values suggest the presence of the orbital. The $e^2qQ/2$ of A-site subspectra show little change around T_t (Fig. 5), which corresponds to the small tetragonal distortion $\left(c/a\sqrt{2} = 1.0024\right)$. But they rapidly increase below T_N and the values become larger than those for the B-site. This may be suggestive of further phase transition, for example, to orthorhombic one. In Fig. 6, only line widths for the paramagnetic state are indicated, since those for the antiferromagnetic state grow abruptly and scale out. The line widths of B-site subspectra increase with increasing temperature, which is normal in the sense of thermal vibration. On the other hand, those of A-site subspectra decrease with increasing temperature. This is comprehensible as a motional narrowing effect [11] and suggests local and dynamic Jahn-Teller distortions around A-site Fe^{2+} ions. The decrease of W below T_t in the paramagnetic region indicates a stabilization of the tetragonal structure, or a transformation into static Jahn-Teller distortions.

4 Summary

We have measured ^{57}Fe Mössbauer spectra of Fe$_2$TiO$_4$ in a wide temperature range from 16 K to 500 K. The EFG at A-site in the cubic phase is explained by the local arrangement of Fe^{2+} and Ti^{4+} on the B-site. The spectra were successfully analyzed by four-subspectra model, which is based on the arrangement of the B-site ions. Thus the temperature variations of the hyperfine parameters were obtained. The quadrupole coupling constants $e^2qQ/2$ of A-site subspectra show little change around T_t, but

rapidly increase below T_N. The latter may be suggestive of further phase transition, for example, to orthorhombic one. From the temperature variation of line width, we found local and dynamic Jahn-Teller distortions around A-site Fe^{2+} ions in the cubic phase.

We are planning to conduct further Mössbauer investigation by using a single crystal in order to clarify the magnetic structure. We need to prepare the (001) plane disk-shaped specimen and cool it through T_t with squeezing around [001] axis. Thus a single domain state will be attained and precise Mössbauer parameters, including information on the magnetic structure, will be obtained.

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