Determination of the electric field gradient tensor of Fe$^{3+}$ in the M1 site of aegirine by single crystal Mössbauer spectroscopy

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The electric field gradient (EFG) tensor of the $^{57}$Fe Mössbauer nucleus is a basic physical property that is important in Mössbauer spectra measurements of a single crystal because the EFG provides a constraint on the intensity of quadrupole splitting peaks. To reveal the EFG tensor of Fe$^{3+}$ in the octahedral M1 site of clinopyroxene, Mössbauer spectra of six crystallographically oriented single crystal of aegirine in thin sections were measured. The asymmetric parameter ($\eta$) of the EFG tensor of aegirine was almost equal to 1. The principal axes of the EFG tensor of aegirine were almost oriented along the $b \times c$, $b$, and $c$ axes, and the $V_{xx}$ component of the EFG was along the $b$ axis. To compare the experimental results with theoretical EFGs, three EFG tensors due to ligand oxygen ions were calculated based on atomic positions determined by X-ray structural analysis. The calculated EFG tensors were not necessarily consistent with the experimentally determined EFG tensors. This indicates that experimental determination of EFG is necessary for single crystal Mössbauer measurements because the calculated EFG may be inaccurate.

Keywords: Mössbauer spectroscopy, Electric field gradient (EFG) tensor, Aegirine

INTRODUCTION

Mössbauer spectroscopy is an excellent method for the analysis of the oxidation state and intracrystalline distribution of transition elements in inorganic solid materials and of the magnetic structure of crystals (e.g., Bancroft, 1973). $^{57}$Fe Mössbauer spectroscopy has been used widely for the analysis of Fe and magnetic structure in Fe-bearing minerals and for the characterization of Fe-O bonding (e.g., Bancroft et al., 1967, 1968; Bancroft, 1973; Akasaka and Shinno, 1992; McCammon, 1995).

Commonly, a few tens of mg of powdered mineral is used as a Mössbauer sample. Thus, despite the usefulness of the conventional method, it is not useful for the Mössbauer analysis of small areas in crystals or mineral grains. To overcome the disadvantage of spatial resolution of the powder method, McCammon et al. (1991) developed a Mössbauer milliprobe with a spatial resolution of approximately 500 µm. Recently, multicapillary X-ray (MCX) lenses, which are used to focus X-rays by total reflection on the inner surfaces of capillaries, have been developed and employed in Mössbauer microspectroscopy experiments (Yoshida et al., 2009), enabling the measurement of Mössbauer spectra from any local area in a crystal or mineral. In the future, Mössbauer microspectroscopy will be widely used to measure the spectra of individual grains in thin section.

In Mössbauer spectra of powder samples showing quadrupole splitting, two strongly overlapping doublets are commonly fitted by constraining the peak widths and intensities of the component peaks in a doublet to be equal (Bancroft et al., 1968; and others), although some minerals such as babingtonite (Akasaka et al., 2013) and siderite (Gol’Danskii et al., 1968) show an asymmetry of quadrupole splitting components in their Mössbauer spectra. However, in single crystal Mössbauer spectra obtained from thin sections, the intensities of the component peaks of a quadrupole doublet are asymmetric and vary depending on the angle between the direction of incident $\gamma$-rays and the crystallographic orientation of the thin section. In this study, the intensity of the quadrupole doublet is conventionally represented as a ratio of the area % of the higher Doppler velocity component peak against the sum of the area of the doublet: $I^h = \frac{\text{Area}^h}{\text{Area}^h + \text{Area}^l}$, where $I^h$ is the conventional intensity of...
the doublet and $A_{red}^b$ and $A_{red}^d$ are the areas of the higher and lower Doppler velocity component peaks, respectively. Least squares fitting of such closely overlapping doublet peaks does not reduce to a unique solution but gives several possible results, depending on the starting values. This is a disadvantage of Mössbauer spectroscopic analysis of minerals in thin section. In fitting the component peaks of an asymmetric doublet, the estimated intensity of the component peaks of the doublet can facilitate obtaining a unique solution. The component peak intensities of a $^{57}$Fe Mössbauer doublet are related to an electronic field gradient (EFG) tensor of the site containing Fe$^{2+}$ and Fe$^{3+}$ (Zimmermann, 1975, 1983). Thus, EFG determination is important in single crystal Mössbauer measurements of minerals in thin section. In principle, the EFG tensor can be calculated based on the crystal structure because the EFG tensor components result from ligand and valence electron contributions and are the second partial derivatives of the potential of a point charge of an electron at the Mössbauer nucleus. However, as shown in this study, the EFG tensors and the asymmetric parameter $\eta$ calculated from the crystal structure show considerable variation, depending on small differences in atomic position suggested by X-ray diffraction analysis. Thus, the EFG calculated from crystal structure analysis may not be reliable for predicting the correct EFG and the intensity of a quadrupole doublet. Experimental determination of EFG is required for single crystal Mössbauer measurements.

Zimmermann (1975, 1983) introduced an experimental determination method of the EFG tensor from the Mössbauer spectrum of a single crystal and proposed a formulation of the EFG tensor from the intensities of the component peaks of an asymmetric Mössbauer doublet of a monoclinic crystal as an example. In clinopyroxene, Fe$^{2+}$ in the octahedral $M1$ site, Fe$^{2+}$ in the $8h$-coordinated $M2$ site, and Fe$^{3+}$ in the $M1$ site are possible. Fe$^{2+}$ ions occupying $M1$ and $M2$ sites yield two closely overlapped doublets (Dyar et al., 2013). As three doublets overlap in the Mössbauer spectrum of pyroxene, it is important to reveal the EFG of all doublets to analyze the Mössbauer spectrum of a pyroxene crystal in thin section. Tennant et al. (2000) applied Zimmermann’s method to single crystal Mössbauer spectra of hedenbergite and revealed the EFG tensor of Fe$^{2+}$ at the $M1$ site of clinopyroxene. However, the EFG tensors due to Fe$^{2+}$ in $M2$ and Fe$^{3+}$ in $M1$ of clinopyroxene remain unknown.

In the present study, Zimmermann’s method was applied to analyze single crystal $^{57}$Fe Mössbauer spectra of an aegirine crystal in oriented thin sections to determine the EFG tensor of Fe$^{2+}$ at the $M1$ site of $C2/c$ clinopyroxene. This was done to advance the method of estimating the intensity of each component peak of any asymmetric doublet in single crystal Mössbauer spectra measured for minerals in thin section. The experimentally determined EFG tensor and $\eta$ were compared with the EFGs and $\eta$s calculated from the crystal structure of aegirine reported by Clark et al. (1969) and Redhammer et al. (2000).

**EXPERIMENTAL**

**Oriented thin sections of aegirine single crystal**

A single crystal of aegirine from Mt. Malosa, Malawi, was used for this study. Energy dispersive X-ray spectroscopy (EDS) analysis (Na$_2$O, 14.39; Fe$_2$O$_3$, 32.00; SiO$_2$, 55.20; Al$_2$O$_3$, 0.90 wt%) indicated that the chemical formula was almost an ideal aegirine composition of Na$_{1.03}$(Fe$_{0.89}$Al$_{0.04}$)Si$_{2.04}$O$_6$. The lattice constants of aegirine, determined by Clark et al. (1969), are $a = 9.658$ Å, $b = 8.795$ Å, $c = 5.294$ Å, $\beta = 107.44^\circ$.

To analyze the EFG tensor by Zimmermann’s method, a rectangular coordinate system ($X$, $Y$, $Z$) must be defined. In this study, a rectangular coordinate system was defined as $X \parallel a \times b$, $Y \parallel a$, $Z \parallel b$, forming a right-handed system, as shown in Figure 1, where $a$, $b$, and $c$ are real lattice vectors and $a \times b$ is the vector product of $a$ and $b$, the direction of which is perpendicular to $a$ and $b$ and parallel to the $c^*$ axis on the X-ray photograph, where $a^*$, $b^*$, and $c^*$ are the reciprocal lattice vectors of aegirine. Six crystallographically oriented thin sections of aegirine were analyzed to determine the EFG tensor.

![Figure 1. Relationship between monoclinic and rectangular coordinates and γ-ray direction.](image-url)

**Figure 1.** Relationship between monoclinic and rectangular coordinates and $\gamma$-ray direction. $a$, $b$, $c$, $a^*$, $b^*$, $c^*$ - vector of monoclinic system of aegirine; $X$, $Y$, $Z$ - rectangular coordinate set for analysis of EFG. $\theta$ and $\phi$ are the angles between the incident $\gamma$-ray with respect to the $X$, $Y$, and $Z$ axes. $\beta$ is the angle between the $c$ and $a$ axes.
sections were prepared by confirming their orientations using an X-ray precession camera. The arrangement of a thin section, the goniometer, and the rotation stage is shown in Figure 2a. The angular precision of the crystallographic axes determined by the X-ray precession camera was within 1°. Thin sections #1 and #2 were normal to the \( b / b^* \) axis and parallel to the (110) cleavage plane, respectively, and were mounted on an Al plate with holes with a diameter of 1 mm. Thin section #3 was normal to \( b \times c / a^* \) axis. It was mounted on a goniometer and adjusted so that the \( b \) axis was brought into alignment with the dial axis with the horizontal direction of the goniometer (Fig. 2a). Figure 2b shows an X-ray precession photograph of thin section #3 mounted on the goniometer head, where the polar and azimuthal angles of \( \gamma \)-ray with \( XYZ \) are \( \theta = 90^\circ \) and \( \phi = 90^\circ \), that is, the dial axis (horizontal in the photograph) matches the \( b \) axis of the aegirine crystal. Other \( \gamma \)-ray directions with \( \theta = 90^\circ \) and \( \phi = 74, 24, 123, \) and \( 45^\circ \) for thin section #3 were set by rotating the thin section around the dial axis (\( b \) axis of the aegirine crystal). Thin sections #4 and #5 were normal to the \( b \) axis and were mounted on the goniometer so that the \( a \times b / c^* \) and \( a \) axes could be aligned along the dial axis, respectively. The \( \gamma \)-ray directions with \( \theta = 45^\circ \) and \( \phi = 270 \) and \( 90^\circ \) were obtained by rotating thin section #4 along the dial axis (\( a \times b \)). For thin section #5, the \( \gamma \)-ray directions with \( \theta = 45^\circ \) and \( \phi = 180 \) and \( 0^\circ \) were set by rotating the thin section. Thin section #6 was normal to \( a \times b \). The polar angles, \( \theta \) and \( \phi \), of \( \gamma \)-ray directions with respect to \( X, Y, \) and \( Z \) axes, designated by circled number symbols \( 1 \)–\( 12 \), and the sample thicknesses for the oriented thin sections #1–#6 are summarized in Table 1. Twelve incident \( \gamma \)-ray directions are plotted against the \( X(a \times b), Y(a), \) and \( Z(b) \) axes in Figure 3.

Figure 2. (a) Arrangement for setting oriented thin sections on the Mössbauer spectrometer. \( \gamma \), \( \gamma \)-ray source; Pb, Pb pinhole; C, oriented thin section; Si, Si-PIN detector; G, goniometer head; R, rotation stage. (b) X-ray precession photograph of thin section #3 set at \( \theta = 90^\circ \) and \( \phi = 90^\circ \), where the \( \gamma \)-rays propagate along the direction normal to the X-ray photograph (the \( \gamma \)-rays are parallel to the \( a \) axis in the Mössbauer measurement).

Mössbauer spectroscopic measurements

Mössbauer spectroscopic measurements were conducted in transmission mode on a constant acceleration spectrometer with a Si-PIN semiconductor detector (XR–100CR, AMPTEK, Inc.) and a multichannel analyzer with 1024 channels. The \( \gamma \)-ray source was 1.85 GBq \( ^{57}\text{Co} \) in Rh with a diameter of 4 mm. An \( ^{57}\text{Fe} \)-enriched iron foil was used as the velocity calibrant. Figure 2 shows the setup of the \( \gamma \)-ray source, Pb pinhole (PH), Si-PIN detector head, and an oriented thin section (C) on the goniometer head (G) fixed on a rotation stage (R). The two symmetric spectra were folded, and the Doppler velocity range was set to \( \pm 5 \) mm/s.

RESULTS AND DISCUSSION

\( ^{57}\text{Fe} \) Mössbauer spectra of aegirine single crystals in oriented thin sections

Figure 4 shows representative Mössbauer spectra of oriented single crystal aegirine with \( \gamma \)-rays parallel to \( Z(b^*) \) (\( \gamma \)-ray direction \( 1 \) in Table 1), \( a^* \) (\( \gamma \)-ray direction \( 3 \)), \( X(c^*) \) (\( \gamma \)-ray direction \( 12 \)), and \( YZ \) (\( \gamma \)-ray direction \( 13 \)), respectively. The dots in Figure 4 are raw data represented by transmittance. Transmittance is given as (Count at each Doppler velocity)/(Baseline count) \( \times 100 \). All Mössbauer spectra consist of a doublet with asymmetric component peaks. Because absorptions of all twelve peaks were intense, absorption peaks of the raw spectra may be modified from the Lorenzian function. To obtain true intensity and area of absorption peaks, thickness corrections of the raw spectra were performed by the transmission integral method with the MossWinn program (MossWinn, 2018). The effective thickness (\( t \)), which is necessary for the thickness correction, was calculated using following formula:

\[
t = d \rho \frac{w N_A a}{100} \sigma_0 f \tag{1}
\]

where \( d \) is the sample thickness in cm, \( \rho \) is the density of aegirine (3.5 g/cm\(^3\)), \( w \) is the weight percent of Fe, \( N_A \) is Avogadro’s constant, \( A \) is the atomic weight of Fe, \( a \) is the fractional abundance of \( ^{57}\text{Fe} \) (0.022), \( \sigma_0 \) is the resonant cross-section of Mössbauer nuclei (206.4 \( \times 10^{-20} \)), and \( f \) is the source recoilless fraction, which is 0.874 for aegirine according to Grave and Alboom (1991). Absorption area corrected by the transmission integral method can be regarded as area of thin sample. Table 1 shows sample thickness (\( d \)), effective thickness (\( t \)), areas of higher and lower Doppler velocity component peaks and in-
Table 1: Mössbauer dataset to determine the macroscopic intensity and local EFG tensors of Fe\(^{3+}\) in M1 site of aegirine

<table>
<thead>
<tr>
<th>Oriented thin section</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )-ray direction</td>
<td>( \theta (^\circ) )</td>
<td>0</td>
<td>43.7</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>( \phi (^\circ) )</td>
<td>90</td>
<td>74</td>
<td>24</td>
<td>123</td>
<td>90</td>
<td>45</td>
</tr>
<tr>
<td>Sample thickness (( d ) (( \mu m) ))</td>
<td>154</td>
<td>40</td>
<td>88</td>
<td>88(134)</td>
<td>88(137)</td>
<td>88(92)</td>
</tr>
<tr>
<td>Effective thickness (( t ))</td>
<td>5.57</td>
<td>1.45</td>
<td>3.18</td>
<td>4.85</td>
<td>4.96</td>
<td>3.33</td>
</tr>
</tbody>
</table>

\( \gamma \)-ray direction, indicated in stereograph in Figure 3; thickness, sample thickness and (calculated thickness due to inclination of thin section around dial axis); crystal orientation, relation between \( \gamma \)-ray and crystallographic orientations; \( \theta \) and \( \phi \), polar and azimuthal angles of \( \gamma \)-ray against XYZ; \( Area^h(\%) \) and \( Area^l(\%) \), area of transmittance (\( \% \)) of lower and higher velocities; \( I^h \), intensity; IS, QS, \( \Gamma \) are isomer shift, quadrupole split, line width in mm/s.

EFG tensor due to Fe\(^{3+}\) in the M1 site of aegirine

Assuming that a Mössbauer nucleus and a point charge \( q \) are located at \( (0, 0, 0) \) and \( (x, y, z) \) positions in rectangular coordinates \( X, Y, \) and \( Z \), EFG components \( V^h_{ij} \) due to the point charge are calculated by the following equation:

\[
V^h_{ij} = -q \left( 3x_ix_j - r^2 \delta_{ij} \right) / r^5 \tag{2}
\]

where \( i, j = 1-3 \), \( x_1 = x, x_2 = y, x_3 = z \), \( r = (x^2 + y^2 + z^2)^{1/2} \) is the distance between the Mössbauer nucleus and the point charge (Travis, 1971). If the number of point charge is \( N \), the EFG components \( V^h_{ij} \) are calculated by the following equation:

\[
V^h_{ij} = -\sum_{k=1}^{N} q_k \left( 3x_{ik}x_{jk} - r^2 \delta_{ij} \right) / r_k^5 \tag{3}
\]

Aegirine belongs to space group \( C2/c \), and the number of formula units per unit cell (\( Z \)) is 4. The symmetry indicates 4 equivalent M1 local sites for Fe\(^{3+}\) ions in a unit cell. The M1 sites of the clinopyroxene structure occupy special positions on a diad axis along the \( b \) axis (Cameron and Papke 1980); therefore, \( \text{MIO}_6 \) octahedra...
have a diad axis along the Z axis. Assuming an M\textsubscript{1} site at (0, 0, 0) and a charge at (x, y, z), the identical charge is located at \( \bar{x}/2, \bar{y}/2, z \) from equation (2), \( V'(2)_{ij} \)'s due to \( \bar{x}/2, \bar{y}/2, z \) are related to \( V'(1)_{ij} \)'s due to (x, y, z) as

\[
V'(2)_{xx} = V'(1)_{xx}, \quad V'(2)_{yy} = V'(1)_{yy}, \quad V'(2)_{zz} = V'(1)_{zz},
\]

\[
V'(2)_{xy} = V'(1)_{xy}, \quad V'(2)_{yz} = V'(1)_{xz}, \quad V'(2)_{zx} = V'(1)_{yz}.
\]

Thus, a local EFG tensor \( V'(1) \) of the M\textsubscript{1} site has no xz and yz components and is given as

\[
V'(1) = \begin{pmatrix}
V_{xx} & V_{xy} & 0 \\
V_{yx} & V_{yy} & 0 \\
0 & 0 & V_{zz}
\end{pmatrix}
\]

where “Ⅰ” means local. The EFG components \( V'^{(2)}_{ij} \) of the other M\textsubscript{1} octahedra, which are generated by the mirror symmetry perpendicular to the b(c) axis, are obtained by replacing \( z \) for \( -\bar{z} \) as follows:

\[
V'^{(2)}_{xx} = V'^{(1)}_{xx}, \quad V'^{(2)}_{yy} = V'^{(1)}_{yy}, \quad V'^{(2)}_{zz} = V'^{(1)}_{zz},
\]

\[
V'^{(2)}_{xy} = V'^{(1)}_{xy}, \quad V'^{(2)}_{yz} = V'^{(1)}_{xz}, \quad V'^{(2)}_{zx} = V'^{(1)}_{yz}.
\]

In the same way, the EFG components \( V'^{(4)}_{ij} \) at (\( \bar{x}, \bar{y}, \bar{z} \)) are represented as

\[
V'^{(4)}_{xx} = V'^{(1)}_{xx}, \quad V'^{(4)}_{yy} = V'^{(1)}_{yy}, \quad V'^{(4)}_{zz} = V'^{(1)}_{zz},
\]

\[
V'^{(4)}_{xy} = V'^{(1)}_{xy}, \quad V'^{(4)}_{yz} = V'^{(1)}_{xz}, \quad V'^{(4)}_{zx} = V'^{(1)}_{yz}.
\]

Thus, EFG tensor \( V \) of the M\textsubscript{1} site obtained by summing \( V'^{(1)}_{ij} - V'^{(4)}_{ij} \) is given as

\[
V = \begin{pmatrix}
V_{xx} & V_{xy} & 0 \\
V_{yx} & V_{yy} & 0 \\
0 & 0 & V_{zz}
\end{pmatrix}
\]

where \( V_{xx} + V_{yy} + V_{zz} = 0 \).

Experimental determination of EFG tensor due to Fe\textsuperscript{3+} in the M\textsubscript{1} site of aegirine

By applying the method of Zimmermann (1975, 1983), the intensities of the doublets, \( I_h \), and EFG tensors due to Fe\textsuperscript{3+} in the M\textsubscript{1} site in aegirine were determined by the following procedure. According to Zimmermann (1983), the EFG tensor \( V \) and intensity tensor \( I \) are related by the following equation:

\[
I_{ij} = \frac{1}{2} \delta_{ij} \frac{eQ}{8|\Delta E_Q|} V_{ij},
\]

where \( \delta_{ij} = 0 \) if \( i \neq j \), and \( \delta_{ii} = 1 \) if \( i = j \), the positive and negative terms apply to higher and lower energy, respectively, \( e \) is the positive elementary charge, \( Q \) is the nuclear quadrupole moment, \( \Delta E_Q \) is quadrupole splitting, and \( V_{xx} + V_{yy} + V_{zz} = 0 \). From equation (9), the traceless intensity tensor \( T \) is derived as \( T_{ij} = I_{ij} - (1/2) \delta_{ij} \) for the higher energy peak (Zimmermann, 1983). \( T \) is given as follows:

\[
T_{ij} = \frac{eQ}{8|\Delta E_Q|} V_{ij},
\]

which indicates that the EFG tensor is proportional to the traceless intensity tensor \( T \). From equations (8) and (9), the intensity tensor \( I \) is given as follows:

\[
I = \begin{pmatrix}
I_{xx} & I_{xy} & 0 \\
I_{yx} & I_{yy} & 0 \\
0 & 0 & I_{zz}
\end{pmatrix}
\]

where \( I_{xx} + I_{yy} + I_{zz} = 3/2 \).

The intensity of a fitted doublet \( I \), given by calculation of \( \text{Area}_x(Area_y + Area_z) \), depends on the direction of the incident \( \gamma \)-rays used for the measurement of the experimental determination of EFG tensor due to Fe\textsuperscript{3+} in the M\textsubscript{1} site of aegirine.
Mössbauer spectrum, that is, the $\theta$ and $\phi$ angles with respect to the $X$, $Y$, and $Z$ axes, and it is represented by the following equation (Zimmermann, 1983):

$$I^h(\theta, \phi) = \begin{pmatrix} e_x & e_y & e_z \end{pmatrix} \begin{pmatrix} e_x \\ e_y \\ e_z \end{pmatrix}$$  (12),

where $e_x$, $e_y$, and $e_z$ are functions of angles $\theta$ and $\phi$ with respect to $X$, $Y$, and $Z$: $e_x = \sin \theta \cos \phi$, $e_y = \sin \theta \sin \phi$, and $e_z = \cos \theta$. From equation (12), an observation equation for least-squares fitting (LSQ) is given as

$$I_{XX} + (\sin^2 \theta \cos^2 \phi - \cos^2 \theta)I_{YY} + 2(\sin^2 \theta \cos \phi \sin \phi)I_{XY} = I_i(\theta, \phi) - \frac{3}{2}\cos^2 \theta$$  (13),

where $i$ is the number of measurements 1–12 and $\theta_i$ and $\phi_i$ are the angles of $\gamma$-ray of the $i$-th measurement. By employing equation (13) for $I^h(\theta, \phi)$ with the $\theta$, $\phi$, and $I^h = A_{red}(A_{red} + A_{red'})$ listed in Table 1 in LSQ calculations, we obtained the most probable values of $I_{XX}$, $I_{YY}$, $I_{ZZ}$, and $I_{XY}$ ($= I_{YX}$), which are given as follows:

$$I_{XX} = 0.666(5), I_{YY} = 0.331(5), I_{ZZ} = 0.503(10)$$

and $I_{XY} = I_{YX} = -0.144(5)$.

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**Figure 4.** Mössbauer spectra of oriented aegirine with $\gamma$-rays parallel to (a) $b$, (b) $a$, (c) $a \times b$, and (d) $YZ$. 

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Thus, the intensity tensor is given as equation (14).

\[ I = \begin{pmatrix} 0.666(5) & -0.144(5) & 0 \\ -0.144(5) & 0.331(5) & 0 \\ 0 & 0 & 0.503(10) \end{pmatrix} \] (14).

The intensity of the doublet due to Fe\(^{3+}\) in the M\(_1\) site of an aegirine single crystal can be calculated from equations (12) and (14).

From \( T_{ij} = I_{ij} - (1/2) \delta_{ij} \), the traceless intensity tensor \( T' \) is given as

\[ T' = \begin{pmatrix} 0.166 & -0.144 & 0 \\ -0.144 & -0.169 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \] (15).

According to Zimmermann (1983), components of \( T \) must be scaled as

\[ T = \begin{pmatrix} 0.163 & -0.141 & 0 \\ -0.141 & -0.166 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \] (19).

Table 2. Atomic positions of an Fe\(^{3+}\)O\(_6\) octahedron from #ae100/F3d aegirine of Redhammer et al. (2000) and calculated EFG tensor

<table>
<thead>
<tr>
<th>Atom</th>
<th>( (x, y, z)_{\text{mono}} )</th>
<th>( (x, y, z)_{\text{rect}} )</th>
<th>( (X', Y', Z')_{\text{rect}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1(Fe)</td>
<td>0.0000</td>
<td>0.8985</td>
<td>0.2500</td>
</tr>
<tr>
<td>O1(A11)</td>
<td>0.1118</td>
<td>1.0772</td>
<td>0.1378</td>
</tr>
<tr>
<td>O1(A12)</td>
<td>-0.1118</td>
<td>1.0772</td>
<td>0.3622</td>
</tr>
<tr>
<td>O1(A13)</td>
<td>-0.1118</td>
<td>0.9228</td>
<td>-0.1378</td>
</tr>
<tr>
<td>O1(A14)</td>
<td>0.1118</td>
<td>0.9228</td>
<td>0.6378</td>
</tr>
<tr>
<td>O2(A15)</td>
<td>-0.1401</td>
<td>0.7540</td>
<td>0.3026</td>
</tr>
<tr>
<td>O2(A16)</td>
<td>0.1401</td>
<td>0.7540</td>
<td>0.1974</td>
</tr>
</tbody>
</table>

\( T'_{XX} \) \( T'_{YY} \) \( T'_{ZZ} \) \( T'_{XY} \) \( T'_{XZ} \) \( T'_{YZ} \)

\[ \begin{array}{cccc}
T'_{XX} & T'_{YY} & T'_{ZZ} & T'_{XY} \\
-0.0533 & 0.1480 & -0.0668 & 0.222 \\
0.0806 & -0.0888 & -0.0368 & 0.211 \\
0.0806 & 0.0088 & 0.0368 & -0.0373 \\
0.0420 & -0.2011 & 0.2011 & 0.000 \\
0.0420 & 0.0088 & 0.0368 & 0.000 \\
0.0296 & 0.0000 & 0.0000 & 0.000 \\
\end{array} \]

\( I'_{\Delta} = 16 \left( T_{\Delta}^{\Delta} + \frac{1}{3} (T_{XX} - T_{YY})^2 \right) + \frac{4}{3} (T_{XZ} + T_{YZ})^2 \) (16).

By applying \( T' \) components to equation (16), \( I'_{\Delta} \) is calculated as

\[ I'_{\Delta} = 16 \left( T'_{\Delta}^{\Delta} + \frac{1}{3} (T'_{XX} - T'_{YY})^2 \right) + \frac{4}{3} (T'_{XZ} + T'_{YZ})^2 \] (17).

By scaling \( T'_{ij} \) using equation (16) as

\[ T_i = \sqrt{1/I_{\Delta}} T'_i \] (18).

According to Redhammer et al. (2000), the principal axes of the EFG tensor are given with respect to aegirine monoclinic axes.

Thus, the intensity tensor is given as equation (14).

\[ I = \begin{pmatrix} 0.666(5) & -0.144(5) & 0 \\ -0.144(5) & 0.331(5) & 0 \\ 0 & 0 & 0.503(10) \end{pmatrix} \] (14).

The intensity of the doublet due to Fe\(^{3+}\) in the M\(_1\) site of an aegirine single crystal can be calculated from equations (12) and (14).

From \( T_{ij} = I_{ij} - (1/2) \delta_{ij} \), the traceless intensity tensor \( T' \) is given as

\[ T' = \begin{pmatrix} 0.166 & -0.144 & 0 \\ -0.144 & -0.169 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \] (15).

According to Zimmermann (1983), components of \( T \) must be scaled as

\[ T = \begin{pmatrix} 0.163 & -0.141 & 0 \\ -0.141 & -0.166 & 0 \\ 0 & 0 & 0.003 \end{pmatrix} \] (19).
Diagonalization of $T$ using the Euler angles matrix $U$,

$$U = \begin{pmatrix} \cos 69.6^\circ & -\sin 69.6^\circ & 0 \\ \sin 69.6^\circ & \cos 69.6^\circ & 0 \\ 0 & 0 & \cos 0^\circ \end{pmatrix}$$

(20)

gives the diagonalized traceless intensity tensor $T$:

$$T = U^\dagger T U$$

(21)

$T$ in italic font is the traceless intensity tensor before diagonalization of the matrix, and $T$ in normal font is that of the diagonalized matrix. The components $V_{XX}$, $V_{YY}$, and $V_{ZZ}$ of the diagonalized EFG tensor $V$ are proportional to those in $T$ (eq. 21), whereas these should be rearranged as $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}|$ (Travis, 1971) with non-italic fonts. The component 0.003(10) is clearly the minimum absolute value, and the $X$ axis of the EFG tensor is the $Z(b)$ axis. The absolute value of the negative component $-0.218(5)$ is slightly larger than that of the positive component 0.215(5). Therefore, in this study, the $-0.218(5)$ component is proposed to correspond to $V_{ZZ}$ and the 0.215(5) component is proposed to correspond to $V_{YY}$. The Euler angles in the Euler angles matrix $U$ indicate that the principal axes of EFG $(X \ Y \ Z)$ are oriented along the solid lines and $b$ axis in Figure 3. The EFG principal axis $V_{XX}$ is along the $b$ axis, and the $V_{YY}$ and $V_{ZZ}$ axes are almost along the $c$ and $b \times c$ axes, respectively (Fig. 3). The asymmetry parameter $\eta$ is determined as $\eta = (T_{XX} - T_{YY})/T_{ZZ} = 0.97(5)$, which is 1 within standard deviation. Tennant et al. (2000) determined the EFG tensor for hedenbergite $\text{CaFe}_{0.54}\text{Mg}_{0.46}\text{Si}_2\text{O}_6$, in which Fe$^{2+}$ ions occupy the M1 site of the clinoxyroxene structure, using an oriented single crystal by Zimmermann’s formulation. They obtained three components $[0.003, -0.218(4), 0.215(4)]$ as those of the traceless intensity tensor. The three components in equation (21) of this study are almost the same as the values reported by Tennant et al. (2000). They indicated that large-magnitude principal values $[-0.218(4), 0.215(4)]$ lie along the $c$ and $b$ axes and that a small-magnitude principal axis lies along the $a^*$ axis. The principal axes of hedenbergite are shown in Figure 3 as dotted lines. Although the principal axes are almost concordant with those of aegirine, $V_{XX}$ is the $b$ axis in aegirine and the $a^*$ axis in hedenbergite.

By applying the experimentally determined parameters of $T_{XX} = 0.003(10)$, $T_{YY} = 0.215(5)$, and $T_{ZZ} = -0.218(5)$, where the $T'$ components are arranged as $|T_{XX}| \leq |T_{YY}| \leq |T_{ZZ}|$, and the asymmetry parameter $\eta = 0.97(5)$, $QS(\Delta EQ)$ is expressed as follows:

$$\Delta E_Q = \frac{1}{2} e Q V_{XX} \sqrt{1 + \frac{1}{3} \eta^2}$$

(22)

Using a $QS$ of 1 mm/s = $4.80 \times 10^{-8}$ eV, $\Delta E_Q = 0.299$ mm/s (this study), and $Q = 0.16 \times 10^{-28}$ barn (Dufek et al., 1995), the EFGs are $V_{XX} = 2.05(4) \times 10^{19}$, $V_{YY} = 1.54(2) \times 10^{21}$, and $V_{ZZ} = -1.56(2) \times 10^{21}$ C/m$^3$.

**Calculation of EFG due to ligand oxygens nearest neighbors to Fe$^{3+}$ in the M1 site of aegirine**

EFG tensor components result from ligand and valence electron contributions around the Mössbauer nucleus. Fe$^{3+}$ in aegirine occupies the M1 site. Additionally, the M1O$_6$ octahedron in aegirine is slightly distorted from the regular octahedron to monoclinic symmetry (Redhammer et al., 2006). Fe$^{3+}$ ions have five 3$d$ valence electrons in the outer shell. According to crystal field theory, the energy levels of the 3$d$ orbitals $(3d_{x^2}, 3d_{y^2}, 3d_{z^2}, 3d_{xy}, 3d_{xz}$, and $3d_{yz})$ of Fe in a regular M1O$_6$ octahedron split into two levels in the distorted octahedron: $e_g$ and $t_{2g}$. The $e_g$ level is due to $3d_{x^2}$ and $3d_{y^2}$ orbitals, which point toward ligand oxygen ions. The $t_{2g}$ level is due to $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, which have lobes projecting between ligand oxygen ions. In the M1O$_6$ octahedron with mono-
clinic distortion, further subtle splittings occur in the $e_g$ and $t_{2g}$ levels. Five electrons of Fe$^{3+}$ in octahedral sites in minerals are generally in a high spin configuration, in which the five electrons occupy all 3$d$ orbitals. As equivalent occupation of the five 3$d$ orbitals gives a spherical electron charge around the nucleus, the contributions of these five electrons to the EFG can be ignored as a first approximation. In this section, the EFG due to ligand contributions is calculated from the nearest–neighboring six oxygens coordinating Fe$^{3+}$ in aegirine using equations (2) and (3) as a first approximation.

Redhammer et al. (2000) refined the atomic positions in synthetic hedenbergite–aegirine solid solutions using the X-ray Rietveld method. In this study, $T$ components and $\eta$ of Fe$^{3+}$ due to ligands coordinating Fe$^{3+}$ in the synthetic aegirines (#ae100/F3d, #ae100/F2f, and #lae100/12) studied by Redhammer et al. (2000) were calculated using the atomic positions in #ae100/F3d and #lae100/12 aegirines and the cell parameters of #ae100/F2f and #lae100/12 aegirines, as described below.

An atomic position $(x, y, z)_{\text{mono}}$ in a monoclinic unit cell (lattice constants $a$, $b$, $c$, $\beta$) is converted to rectangular coordinates $(x, y, z)_{\text{rec}}$, where $x$ // $a$, $y$ // $b$ and $z$ // $c$ = $a \times b$ as

$$
(x, y, z) = \left( ax + cz \cos \beta, by, cz \sin \beta \right)
$$

In aegirine, Fe$^{3+}$ and O occupy special 4$e$ and general 8$f$ Wyckoff positions, respectively. From aegirine’s symmetry and the atomic positions of #ae100/F3d aegirine indicated by Redhammer et al. (2000), the atomic coordinates of Fe$^{3+}$O$_6$ octahedron near (0, 0, 0) positions in the unit cell are represented as $(x, y, z)_{\text{mono}}$ in Table 2. The monoclinic coordinates $(x, y, z)_{\text{mono}}$ are then converted into $(X', Y', Z')_{\text{rec}}$ by equation (23). The positions $(x, y, z)_{\text{rec}}$ are arranged into the $(X', Y', Z')_{\text{rec}}$ of this study as $(X'//Z, Y'//X, Z'//Y)$. The rectangular coordinates of the six oxygens that resulted from moving Fe$^{3+}$ to (0, 0, 0) are shown as $(X, Y, Z)_{\text{rec}}$ in Table 2. As $q$ is set to $q = -1$, because all the ligands are oxygen anions, the EFG components before scaling and diagonalizing the $T$ tensor; $T_{XX} - T_{ZZ}$, $T$ components after diagonalizing the $T$ tensor; $\eta$, asymmetric parameter [$= (T_{XX} - T_{YY})/T_{ZZ}$]; cell parameters, $a = 9.6549$, $b = 8.7947$, $c = 5.2938$, $\beta = 107.394$ (#lae100/12)
By scaling the $T'_{ij}$ components of equation (24) by (16), $T$ is given as

$$T = \begin{pmatrix} 0.0040 & -0.0296 & 0 \\ -0.0296 & -0.0055 & 0 \\ 0 & 0 & 0.0015 \end{pmatrix}$$

(25).

Table 3. (Continued)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$X(a \cdot b)$</th>
<th>$Y(a)$</th>
<th>$Z(b)$</th>
<th>$r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M'1(Fe)$</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>O1(A1)1</td>
<td>-0.5688</td>
<td>1.2798</td>
<td>1.5699</td>
<td>2.1038</td>
</tr>
<tr>
<td>O1(A1)2</td>
<td>0.5688</td>
<td>-1.2798</td>
<td>1.5699</td>
<td>2.1038</td>
</tr>
<tr>
<td>O1(A1)3</td>
<td>-1.9571</td>
<td>-0.4885</td>
<td>0.2120</td>
<td>2.0283</td>
</tr>
<tr>
<td>O1(A1)4</td>
<td>1.9571</td>
<td>0.4885</td>
<td>0.2120</td>
<td>2.0283</td>
</tr>
<tr>
<td>O2(A1)5</td>
<td>0.2475</td>
<td>-1.4428</td>
<td>-1.2638</td>
<td>1.9339</td>
</tr>
<tr>
<td>O2(A1)6</td>
<td>-0.2475</td>
<td>1.4428</td>
<td>-1.2638</td>
<td>1.9339</td>
</tr>
</tbody>
</table>

$\eta = 0.161$

Diagonalization of $T$ using the Euler angles matrix $U$,

$$U = \begin{pmatrix} \cos 49.6^\circ & -\sin 49.6^\circ & 0 \\ \sin 49.6^\circ & \cos 49.6^\circ & 0 \\ 0 & 0 & \cos 0^\circ \end{pmatrix}$$

(26).

gives the diagonalized traceless intensity tensor $T$ (Tables 2 and 4):

$$T = U^{-1}T U = \begin{pmatrix} -0.222 & 0 & 0 \\ 0 & 0.211 & 0 \\ 0 & 0 & 0.011 \end{pmatrix}$$

(27).

From the $T$ tensor (27), the asymmetry parameter $\eta$ at the Fe$^{3+}$ position in the aegirine of $#1ae100/F3d$ is 0.902. Therefore, the calculated $T$ components in equation (27) and the asymmetry parameter $\eta$ in (27) are consistent with the experimentally determined $T$ represented by equation (21) and the $\eta [0.97(5)]$ of this study. However, the asymmetry parameter $\eta$ calculated from atomic positions in the aegirine of $#1ae100/12$ is 0.161 (Tables 3 and 4), which is not consistent with the experimentally determined parameter. As shown in Tables 3 and 4, the $T$ calculated using structural data of the $#1ae100/12$ aegirine,

$$T = \begin{pmatrix} 0.249 & 0 & 0 \\ 0 & -0.144 & 0 \\ 0 & 0 & -0.104 \end{pmatrix}$$

(28).

is also not consistent with the experimentally determined ones in the present study. Furthermore, the $T$ and the asymmetry parameter $\eta$ of aegirine calculated using the lattice constants and atomic positions of aegirine refined by Clark et al. (1969) are

$$T = \begin{pmatrix} 0.250 & 0 & 0 \\ 0 & -0.120 & 0 \\ 0 & 0 & -0.130 \end{pmatrix}$$

(29).

and $\eta = 0.041$ (Table 4; details of the calculation are omitted), which are also not consistent with the experimentally determined ones. This value is also not consistent with the experimentally determined one in the present study. Table 4 shows three examples of calculated $T$ components and $\eta$ due to ligand oxygen nearest neighbors to Fe$^{3+}$ in the $M1$ site of aegirine.

As described above, the $T$ and $\eta$ calculated using the atomic positions of Fe$^{3+}$ and O$^{2-}$ and the unit cell parameters of aegirine determined by X-ray diffraction methods are not necessarily in agreement with the experimental values; thus, experimental determination of EFG is nec-

Table 4. Calculated $T$ components and $\eta$ due to ligand oxygen nearest neighbors to Fe$^{3+}$ in the M1 site of aegirine

<table>
<thead>
<tr>
<th>Source of aegirine</th>
<th>$T_{XX}$</th>
<th>$T_{YY}$</th>
<th>$T_{ZZ}$</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>The $#1ae100/F3d$ aegirine by Redhammer et al. (2000)</td>
<td>-0.222</td>
<td>0.211</td>
<td>0.011</td>
<td>0.902</td>
</tr>
<tr>
<td>The $#1ae100/12$ aegirine by Redhammer et al. (2000)</td>
<td>0.249</td>
<td>-0.144</td>
<td>-0.104</td>
<td>0.161</td>
</tr>
<tr>
<td>Natural aegirine by Clark et al. (1969)</td>
<td>0.250</td>
<td>-0.120</td>
<td>-0.130</td>
<td>0.041</td>
</tr>
</tbody>
</table>
The twelve $^{57}$Fe Mössbauer spectra of crystallographically oriented single crystal thin sections of aegirine, measured with different γ-ray directions, consisted of a doublet consisting of asymmetric component peaks. The isomer shift, quadrupole splitting, and line width were 0.399, 0.294–0.306, and 0.170–0.215 mm/s, respectively, which are attributable to Fe$^{3+}$ at the octahedral $M_1$ site. By LSQ calculation of the observation equations constructed using the data of the polar and azimuthal angles of incident γ-ray with $X$,$Y$,$Z$, θ and φ, and $Area_b$ ($Area_b + Area_\delta$) values of the doublets given from the measured Mössbauer spectra, the most probable values of $I_{XX}$, $I_{YY}$, $I_{ZZ}$, and $I_{XY} = I_{XZ} = I_{YZ}$ are $I_{XX} = 0.666(5)$, $I_{YY} = 0.331(5)$, $I_{ZZ} = 0.503(10)$, and $I_{XY} = I_{XZ} = I_{YZ} = -0.144(5)$. By applying the method of Zimmermann (1975, 1983), the three components of the traceless intensity tensor of the doublet due to Fe$^{3+}$ in the $M_1$ site of aegirine and the asymmetric parameter in our study were determined experimentally as $-0.218(5)$, $0.215(5)$, $0.003(10)$, and $\eta = 0.97(5)$. The EFGs were finally determined to be $V_{XX} = 2.05(4) \times 10^{19}$, $V_{YY} = 1.54(2) \times 10^{21}$, and $V_{ZZ} = -1.56(2) \times 10^{21}$ C/m$^3$. EFG tensors due to ligand oxygens calculated based on the atomic positions are not necessarily consistent with the experimentally determined EFG. Thus, EFGs calculated from the structural data obtained by X-ray structural analysis may not be reliable for predicting actual EFG, and experimental determination of EFG is necessary for single crystal Mössbauer spectral analysis.

ACKNOWLEDGMENTS

We thank Dr. Masahide Akasaka for critical and valuable comments that improved the manuscript. We also thank Dr. Hiroki Okudera for handling and checking the manuscript. This research was conducted at the Institute for Integrated Radiation and Nuclear Science, Kyoto University, within the Visiting Researcher Program, and was supported by a Kakenhi Grant-in-Aid (No. JP24540519) from the Japan Society for the Promotion of Science (JSPS).

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Manuscript received January 9, 2019
Manuscript accepted May 7, 2019
Manuscript handled by Hiroki Okudera