High-pressure $^{57}$Fe $\gamma$ resonance and compressibility of Ca(Fe,Mg)Si$_2$O$_6$ clinopyroxenes

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ABSTRACT

Three synthetic samples of the hedenbergite-diopside join Ca(Fe$_{1-x}$Mg$_x$)Si$_2$O$_6$ ($x = 1$, $x = 0.80$, and $x = 0.60$) were studied between ambient conditions and 10 GPa (293 K) by use of $^{57}$Fe $\gamma$ resonance (Mössbauer effect) with a clamp-technique pressure cell. The isomer shift $\delta$ and quadrupole splitting $\Delta E_0$ of Fe$^{2+}$ at the M1 position decrease with increasing pressure. They exhibit a discontinuity between 3.8 and 4.3 GPa in all three samples, indicating a reversible phase transition of first order. An approximately linear relationship between $\delta$ and $\Delta E_0$ was observed. The value of $\delta$ at constant pressure is independent of Fe/Mg ratio, whereas $\Delta E_0$ decreases with decreasing Fe/Mg ratio. The $\partial \delta / \partial \ln V$ and $\partial \Delta E_0 / \partial \ln V$ values were derived.

The axial and volume compressibilities of two samples ($x = 1$ and $x = 0.60$) were determined from the unit-cell parameters measured by powder X-ray diffraction between ambient pressure and 10 GPa using a diamond-anvil cell. The axial compressibility ratio $\beta_3/\beta_1/\beta_2$ of hedenbergite is 0.65(4):1.00(6):0.79(6). Isothermal bulk moduli for Hd and H$_{0}$D$_{10}$ were determined by fitting a Birch-Murnaghan equation of state to the pressure-volume data, assuming $K'_0 = 4$. They are 119(2) and 82.7(1) GPa, respectively. An inverse relationship of the unit-cell parameters between pressure and temperature was observed. Pressure change in $\delta$ below 4 GPa results mainly from changes in Fe$^{2+}$ valence orbitals. The change in $\Delta E_0$ is due to changes in the three lowest 3d orbitals of Fe$^{2+}$ coupled with changes in octahedral geometry. For the changes in $\delta$ and $\Delta E_0$ above 4 GPa, changes in overlap between Fe$^{2+}$ and ligand orbitals are important.

The decrease in $\Delta E_0$ with decreasing Fe/Mg ratio at constant pressure results mainly from the change in geometry of the M1 octahedra occupied by Fe$^{2+}$. The relatively invariable $\delta$ in the three samples at constant pressure suggests that the bond distances of the Fe$^{2+}$ octahedra are distinct from those of the Mg$^{2+}$ octahedra.

INTRODUCTION

Pyroxenes with compositions near Ca(Fe,Mg)Si$_2$O$_6$ have drawn attention over more than half a century mainly because of their important role in the Earth’s lower crust and upper mantle. The end-members diopside CaMgSi$_2$O$_6$ and hedenbergite CaFeSi$_2$O$_6$ have been the subject of many experimental studies. Whereas the crystal structures and physical properties of the Ca(Fe,Mg)Si$_2$O$_6$ system are well known at ambient conditions, there are comparatively few crystallographic data obtained simultaneously at high temperatures and high pressures that correspond to the conditions of the lower crust or upper mantle. However, experimental studies carried out either at high temperature or high pressure have been reported on isothermal compression (Vaidya et al., 1973), thermal expansion (Cameron et al., 1973), elasticity (Levien et al., 1979; Kandelin and Weidner, 1988), temperature or pressure effects on the crystal structure (Cameron et al., 1973; Levien and Prewitt, 1981), phase transformations at high pressure or high temperature (Kim et al., 1989; Tamai and Yagi, 1989), and so forth.

Although some compositions of the system Ca(Fe,Mg)Si$_2$O$_6$ have been examined extensively at high temperatures, data from high-pressure experiments are more limited. Important problems concerning the nature of atomic bonding at high pressure, its initiating role in phase transitions, and its effect on some of the physical properties are still open to question. Progress in this direction requires more accurate data on details of the atomic bond as a function of temperature and pressure within the temperature-pressure stability field of pyroxene.

High-pressure $^{57}$Fe $\gamma$ resonance (Mössbauer effect) may provide detailed information on the pressure-dependent behavior of Fe at its crystallographic site, its bonding to the adjacent ligands, polyhedral distortion, etc. Since such measurements probe directly the properties of the crystallographic site in question, they are sensitive to electronic properties at the site and to subtle local changes depending on pressure or temperature. They may be complementary to structural refinements by diffraction techniques.

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The Mössbauer effect of $^{57}$Fe at high pressure has been hampered in the past for three reasons: (1) the high-pressure technique adapted (Stanek et al., 1986a) was limited to a pressure range that was low compared with the rather small compressibility of the relevant mineral, (2) pressure calibration was not continuous over the entire range of pressure applied, and (3) the absorber was thick compared with the resolution required and consequently the resonant absorption curves were deformed (Burns et al., 1972; Huggins et al., 1974). To overcome these difficulties, new techniques were employed in the present study.

The aims of the present work on the Ca(Fe,Mg)Si$_2$O$_6$ system were, first, to observe the effect of pressure on the electronic structure of Fe$^{2+}$; second, to correlate the $^{57}$Fe hyperfine data with those of the unit cell at high pressure; and third, to study the dependence of the Fe$^{2+}$ electronic structure on chemical composition at high pressures.

**Experimental**

**Samples**

Clinopyroxene samples with compositions along the hedenbergite-diopside join with Fe/(Fe + Mg) ratios according to H$_d$, H$_{d0.2}$D$_{i0.8}$, and H$_{d0.4}$D$_{i0.6}$ were synthesized hydrothermally at 600 °C and 0.1 GPa H$_2$O vapor pressure over a period of 7 d. Ferrous oxalate (natural abundance of $^{57}$Fe) was used for the synthesis. The products were examined with X-ray diffraction as well as $^{57}$Fe γ resonance at ambient conditions. No foreign phases were detected. The experimental products were finely ground for the $^{57}$Fe experiments. The samples H$_d$ and H$_{d0.4}$D$_{i0.6}$ were also studied using powder X-ray diffraction at high pressure for determination of the linear and volume compressibilities (Zhang et al., 1989).

**Mössbauer effect of $^{57}$Fe at high pressures**

The high-pressure $^{57}$Fe resonance experiment was carried out by use of the clamp technique. The pressure cell consists of two symmetric Bridgman-type Bi,C anvils (Moser et al., 1980). Each anvil was bound and supported by two rings made of hardened Cu$_{0.98}$Be$_{0.02}$ (CuBe). The assembly as shown in Figure 1 was placed in a CuBe clamp. Pressure was established by a hydraulic press and maintained by tightening the clamp, which was removed subsequently from the press for the $^{57}$Fe experiment. The sample was contained in the pyrophyllite gasket. An external steel ring outside the pyrophyllite gasket kept variation of the sample area to a minimum. Paraffin (melting point 45–50 °C) was used as the pressure-transmitting medium.

The relatively large sample volume (about 3.5 mm$^3$) of the high-pressure cell makes it possible to place manometers of metallic Pb and Bi into the cell (cf. Fig. 1). This permits continuous, in situ calibration of the pressure by measuring the electrical resistance of Pb and observing the abrupt change of Bi electrical resistance at the three phase-transition points 2.55, 2.69, and 7.3 GPa (Eiling and Schilling, 1981). Simultaneous use of the two pressure calibrants enabled continuous determination of pressure between 0 and 13 GPa. The error of the pressure determination was estimated to be ±0.1–0.5 GPa, yielding a larger error at higher pressure. An estimate of the pressure gradient was also possible from the observation of the sharpness of the Bi phase transitions. The observed pressure gradients depended on the absolute value of pressure. In our experiments, they were 2–3% at 2.55 GPa and 5–7% at 7.3 GPa.
One of the advantages of using B₃C anvils is the relatively large area of the anvil face available for resonant absorption (0.13 cm²). This allows the use of thin absorbers. Absorber thickness in Fe was about 5 mg/cm² (0.11 mg ⁵⁷Fe/cm² based on natural concentration). It was not necessary to use samples enriched in ⁵⁷Fe for this study.

The ⁵⁷Fe spectra at high pressures were recorded using a transmission setup as shown in Figure 2. We used ⁵⁷Co/Rh point sources of 10–25 mCi. The ratio R/d was about 0.21, the line broadening resulting from the "cosine smearing effect" (Spijkerman et al., 1965) being reasonably small. Here R is the radius of detector window and d, the distance between source and detector.

Two mirror-symmetrical spectra were recorded simultaneously in a 1024 channel analyzer using constant acceleration. The total number of counts for a spectrum was about 10⁶ per channel. The spectra were fitted after folding to 512 channels. The point of zero velocity was obtained by the least-squares method in the folding procedure. Recording a spectrum generally required 4–7 d depending on the strength of the source. Source and absorber were held at 293 K over the period of experiment. In view of the rather small pressure-induced changes in the ⁵⁷Fe hyperfine parameters of the Ca(Fe,Mg)Si₂O₆ system, we attempted to attain identical conditions with respect to such factors as geometry, counting rate, γ-ray scattering, and Doppler velocity control for the recording of each spectrum.

In general, B₃C used for the anvils contains small traces of Fe, which yield a rather complex ⁵⁷Fe spectrum with paramagnetic, superparamagnetic, and magnetic components arising from chemically not-well-defined Fe-containing particles. This ⁵⁷Fe spectrum was the same at ambient pressure and at 10 GPa. The intensity of the strongest line in this spectrum was about 2%. Since it is important to keep the absorbers reasonably thin, it was necessary to determine this superimposed background spectrum for each pair of anvils by a precursor experiment without pyroxene absorber using the same total count number as for the sample spectrum. The pyroxene spectra were corrected by deduction of the (raw) background spectrum from the sample spectrum using a least-squares fitting procedure. The resulting resonant absorption of the pyroxene lines was 3–4%. The background correction because of Fe contamination of the anvils produced by far the largest contribution to the total error of the determined hyperfine parameters.

The intensities and widths of the two lines of the observed ⁵⁷Fe doublet at ambient conditions were equal.
within less than 1%. No systematic asymmetry in intensity or width could be found in the high-pressure spectra. For this reason the $^{57}$Fe hyperfine parameters were determined by fitting the spectra through direct solution of the Hamiltonian for the nuclear quadrupole interaction based on one experimental line width, neglecting possible effects of texture or anisotropic vibrational displacement of $^{57}$Fe.

### RESULTS

The $^{57}$Fe spectrum of paramagnetic clinopyroxenes along the join CaFe$_2$Si$_2$O$_6$-CaMgSi$_2$O$_6$ at 293 K consists of a single doublet, which is assigned to Fe$^{2+}$ at the octahedrally coordinated M1 sites. This holds for all the spectra between ambient pressure and 10 GPa. The doublet was well resolved over the entire range of pressures studied. The fitted parameters were background counting rate (assumed to be independent of Doppler velocity), center position, splitting, intensity, and line width of the doublet. Two typical spectra recorded at ambient pressure and 10 GPa are shown in Figure 3. The $^{57}$Fe hyperfine parameters obtained from the fits are listed in Tables 1, 2, and 3.

#### Experimental error of the $^{57}$Fe hyperfine parameters

An estimate of the total experimental error is important in view of the rather small pressure-induced changes in the hyperfine data and the relatively long recording time of a high-pressure spectrum. The statistical error of the fit was considered using $\chi^2$ as criterion for the deviations between the counting data and the fitted Lorentzians. Determination of the total error including all systematic contributions is, however, much more involved. The following procedure has been adopted in this study. A spectrum of a metallic Fe absorber was taken before and after each high-pressure spectrum of the studied sample. The difference between the hyperfine parameters of the experimental spectrum using the two sets of calibration data should to some extent account for the experimental error resulting from the instability of the electronic system, mechanical driving device, etc. A time-dependent test of the systematic error was also undertaken by fitting the total error of position and splitting of the doublet was smaller than 0.01 mm/s.

#### Pressure-dependent line broadening

Substantial line broadening was observed with increasing pressure. In the case of hedenbergite the widths $\Gamma$ of

### Table 1. Values of $^{57}$Fe hyperfine parameters at M1 in $\text{Hd}_2$ between 0 and 10 GPa (293 K)

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\delta^*$ (mm/s)</th>
<th>$\Delta E_0$ (mm/s)</th>
<th>$\Gamma^{**}$ (mm/s)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.191(1)</td>
<td>2.253(2)</td>
<td>0.304(3)</td>
<td>0.85</td>
</tr>
<tr>
<td>0.8</td>
<td>1.189(1)</td>
<td>2.233(2)</td>
<td>0.294(4)</td>
<td>0.57</td>
</tr>
<tr>
<td>1.5</td>
<td>1.179(1)</td>
<td>2.172(1)</td>
<td>0.313(4)</td>
<td>0.70</td>
</tr>
<tr>
<td>1.9</td>
<td>1.175(1)</td>
<td>2.182(2)</td>
<td>0.328(3)</td>
<td>1.16</td>
</tr>
<tr>
<td>2.6</td>
<td>1.172(1)</td>
<td>2.165(2)</td>
<td>0.303(3)</td>
<td>0.71</td>
</tr>
<tr>
<td>3.2</td>
<td>1.160(1)</td>
<td>2.131(2)</td>
<td>0.360(3)</td>
<td>0.74</td>
</tr>
<tr>
<td>4.4</td>
<td>1.145(2)</td>
<td>2.026(3)</td>
<td>0.386(5)</td>
<td>2.53</td>
</tr>
<tr>
<td>5.7</td>
<td>1.142(2)</td>
<td>1.993(3)</td>
<td>0.440(5)</td>
<td>0.83</td>
</tr>
<tr>
<td>7.9</td>
<td>1.131(1)</td>
<td>1.922(2)</td>
<td>0.418(4)</td>
<td>1.28</td>
</tr>
<tr>
<td>9.2</td>
<td>1.129(1)</td>
<td>1.886(3)</td>
<td>0.460(5)</td>
<td>1.73</td>
</tr>
<tr>
<td>9.9</td>
<td>1.121(1)</td>
<td>1.894(3)</td>
<td>0.460(5)</td>
<td>1.73</td>
</tr>
</tbody>
</table>

Note: Standard deviations are given in parentheses. Experiments at 7.9, 9.2, 3.2, 0.0 GPa were consecutively carried out after experiments 10 and 12, with rising pressure. These two points were not given in Figure 5.

### Table 2. Values of $^{57}$Fe hyperfine parameters at M1 in $\text{Hd}_{30}\text{Di}_{70}$ between 0 and 7 GPa (293 K)

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\delta^*$ (mm/s)</th>
<th>$\Delta E_0$ (mm/s)</th>
<th>$\Gamma^{**}$ (mm/s)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.191(1)</td>
<td>2.205(2)</td>
<td>0.293(3)</td>
<td>0.62</td>
</tr>
<tr>
<td>1.0</td>
<td>4.0</td>
<td>2.113(1)</td>
<td>2.118(3)</td>
<td>0.345(4)</td>
</tr>
<tr>
<td>1.4</td>
<td>4.2</td>
<td>2.169(2)</td>
<td>2.109(3)</td>
<td>0.343(4)</td>
</tr>
<tr>
<td>4.0</td>
<td>6.0</td>
<td>2.149(2)</td>
<td>2.030(3)</td>
<td>0.378(5)</td>
</tr>
<tr>
<td>5.7</td>
<td>7.2</td>
<td>2.142(2)</td>
<td>1.979(4)</td>
<td>0.405(6)</td>
</tr>
<tr>
<td>6.1</td>
<td>5.1</td>
<td>2.154(2)</td>
<td>2.030(3)</td>
<td>0.364(6)</td>
</tr>
<tr>
<td>7.8</td>
<td>4.4</td>
<td>2.155(1)</td>
<td>2.032(3)</td>
<td>0.303(4)</td>
</tr>
<tr>
<td>8.4</td>
<td>4.1</td>
<td>2.161(1)</td>
<td>2.070(3)</td>
<td>0.342(4)</td>
</tr>
<tr>
<td>10.0</td>
<td>3.4</td>
<td>1.164(1)</td>
<td>2.103(3)</td>
<td>0.333(4)</td>
</tr>
<tr>
<td>12.0</td>
<td>2.4</td>
<td>1.170(1)</td>
<td>2.129(3)</td>
<td>0.324(3)</td>
</tr>
<tr>
<td>12.1</td>
<td>2.0</td>
<td>1.181(1)</td>
<td>2.161(2)</td>
<td>0.315(3)</td>
</tr>
<tr>
<td>13.0</td>
<td>3.4</td>
<td>1.192(1)</td>
<td>2.179(3)</td>
<td>0.319(4)</td>
</tr>
</tbody>
</table>

Note: Standard deviations are given in parentheses.

### Table 3. Values of $^{57}$Fe hyperfine parameters at M1 in $\text{Hd}_{30}\text{Di}_{70}$ between 0 and 8 GPa (293 K)

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>$\delta^*$ (mm/s)</th>
<th>$\Delta E_0$ (mm/s)</th>
<th>$\Gamma^{**}$ (mm/s)</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.191(2)</td>
<td>2.106(4)</td>
<td>0.339(7)</td>
<td>0.57</td>
</tr>
<tr>
<td>0.9</td>
<td>1.182(2)</td>
<td>2.067(4)</td>
<td>0.339(7)</td>
<td>0.57</td>
</tr>
<tr>
<td>2.3</td>
<td>1.173(2)</td>
<td>2.050(4)</td>
<td>0.348(7)</td>
<td>0.57</td>
</tr>
<tr>
<td>3.6</td>
<td>1.182(2)</td>
<td>2.038(4)</td>
<td>0.351(7)</td>
<td>0.57</td>
</tr>
<tr>
<td>3.9</td>
<td>1.161(3)</td>
<td>1.962(7)</td>
<td>0.371(11)</td>
<td>0.57</td>
</tr>
<tr>
<td>4.6</td>
<td>1.162(3)</td>
<td>1.933(6)</td>
<td>0.392(8)</td>
<td>0.57</td>
</tr>
<tr>
<td>5.2</td>
<td>1.152(3)</td>
<td>1.910(6)</td>
<td>0.395(11)</td>
<td>0.57</td>
</tr>
<tr>
<td>5.8</td>
<td>1.150(3)</td>
<td>1.906(5)</td>
<td>0.406(9)</td>
<td>0.57</td>
</tr>
<tr>
<td>6.4</td>
<td>1.149(3)</td>
<td>1.895(5)</td>
<td>0.413(9)</td>
<td>0.57</td>
</tr>
<tr>
<td>6.7</td>
<td>1.148(3)</td>
<td>1.886(6)</td>
<td>0.417(10)</td>
<td>0.57</td>
</tr>
<tr>
<td>7.9</td>
<td>1.135(3)</td>
<td>1.827(6)</td>
<td>0.428(10)</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Note: Standard deviations are given in parentheses. Spectra at 2.3, 3.6, 5.2, 6.4, 7.8 GPa were taken in the rising pressure experiment and 6.7, 5.8, 5.6, 4.6, 3.9, 0.9, 0.0 GPa in the releasing pressure experiment.

Full width at half intensity.
the lines increased from 0.30 mm/s at ambient pressure to 0.46 mm/s at 10 GPa (51%). For \( \text{Hd}_{60}\text{Di}_{20} \) and \( \text{Hd}_{60}\text{Di}_{40} \) the broadenings were 38 and 26%, respectively. The increasing line width with increasing pressure was due in part to a pressure gradient over the sample area, which produces a distribution of \( \Delta E_0 \) across the sample area. The \( \Delta \Delta E_0/\Delta P \) values determined from Tables 1, 2, and 3 are collected in Table 4.

### Pressure dependence of the center shift \( \delta \)

The center shift \( \delta \), i.e., the shift of the geometrical center of the \( ^{57}\text{Fe} \) doublet, may be written as

\[
\delta(T, P) = \delta_0(P) + \delta_\text{SOD}(T, P)
\]

where \( \delta_0 \) is the chemical or isomer shift at 0 K, \( \delta_\text{SOD}(T, P) \) is the second-order Doppler (SOD) shift; the value of \( \delta_\text{SOD} \) of \( ^{57}\text{Fe}^{2+} \) in octahedrally coordinated sites of chain silicates at ambient conditions is about \( \delta_\text{SOD} = -0.23 \text{ mm/s (e.g., Lin et al., in preparation)}. \) In this study it is considered to be independent of the Fe/Mg ratio. It should be noted that \( \delta \) in the present paper is referred to pyroxene at 293 K, whereas in previous studies it has been often referred to pyroxene at 78 K.

The pressure derivative of the \( \delta \) at constant temperature, \( (\partial \delta/\partial P)_T \), consists mainly of two contributions:

\[
(\partial \delta/\partial P)_T = \partial \delta_0/\partial P + (\partial \delta_\text{SOD}/\partial P)_T.
\]

By adopting the Debye model, \( \partial \delta_\text{SOD}/\partial P \) can be estimated from the Grüneisen parameter \( \gamma \) and the Debye temperature \( \theta_D \) (Williamson, 1978), taking into account that

\[
\partial \delta_\text{SOD}/\partial \ln V = \gamma (9k\theta_D/16Mc) F(T/\theta_D).
\]

In Equation 3 \( V \) is the volume of the unit cell, \( k \) is the Boltzmann constant, \( M \) is the mass of the resonant nucleus, and \( c \) is the velocity of light. The Grüneisen parameter \( \gamma = \alpha V/\beta C_V \) may be obtained approximately by calculating the volume expansivity at constant pressure \( \alpha \), the volume compressibility at constant temperature \( \beta \) using the high-temperature (Cameron et al., 1973) and high-pressure (Zhang et al., 1989) data of hedenbergite, and the heat capacity at constant volume \( C_V \), which was approximated by \( C_p \) calculated for diopside using the relationship of Krupka et al. (1985).

The \( F \) value in Equation 3 may be formulated as

\[
F(T/\theta_D) = 1 + 8/(e^{T/\theta_D} - 1) - 24(T/\theta_D)^4,
\]

In Equation 4 \( x = h\nu/kT \), where \( h \) is the Planck’s constant and \( \nu \) is the frequency of harmonic oscillators; \( \theta_D \) was taken from Kieffer (1985) for diopside.

The \( \partial \delta_\text{SOD}/\partial \ln V \) values calculated in this way are listed in Table 4. They show that the volume dependence of \( \delta_\text{SOD} \) is about 1 order of magnitude smaller than that of \( \delta \). \( \delta_\text{SOD} \) should, therefore, not be neglected generally. For our simplified discussion in this paper, the pressure dependence of \( \delta_\text{SOD} \) will be ignored. The \( \delta_\text{SOD} \) is considered to be independent of pressure and Fe/Mg ratio of the sample, \( \delta \) being interpreted in terms of \( \delta_0 \).

### Discontinuity of \( \delta \) and \( \Delta E_0 \) between 3.8 and 4.3 GPa

Generally, \( \delta \) and \( \Delta E_0 \) of \( ^{57}\text{Fe} \) at M1 in Ca(Fe,Mg)Si,O\(_6\) clinopyroxenes decrease with increasing pressure between ambient pressure and 10 GPa as shown in Figures 4 and 5. The reductions of \( \delta \) for \( \text{Hd}, \text{Hd}_{60}\text{Di}_{20}, \) and \( \text{Hd}_{60}\text{Di}_{40} \) are 0.08, 0.05, and 0.06 mm/s, and those of \( \Delta E_0 \) are 0.36 (15.9%), 0.23 (12.7%), and 0.28 mm/s (16.5%), respectively. This study demonstrates the existence of abrupt changes between 3.8 and 4.3 GPa in \( \delta \) and \( \Delta E_0 \). This is particularly pronounced for \( \Delta E_0 \), where a reduction of 0.07–0.10 mm/s (about 4%) occurs. For \( \delta \), the change between 3.8 and 4.3 GPa is small (about 0.015 mm/s at 4.3 GPa for hedenbergite). If Mg is substituted for Fe in hedenbergite, the discontinuity occurs at a somewhat lower pressure. In the cases of \( \text{Hd}_{60}\text{Di}_{20} \) and \( \text{Hd}_{60}\text{Di}_{40} \), however, the precision of \( \delta \) and \( \Delta E_0 \) determination is somewhat reduced because of a nonstatistical distribution of \( ^{57}\text{Fe}^{2+} \) and \( ^{57}\text{Mg}^{2+} \) over the M1 sites, producing some line broadening.

Sample \( \text{Hd}_{60}\text{Di}_{20} \) was studied in detail for hysteresis behavior. For this, experiments were carried out consecutively from ambient pressure to 7.2 GPa and back to ambient pressure. A hysteresis was observed between 1.9 and 7.2 GPa. An additional spectrum was taken at ambient pressure after releasing pressure (point 13 in Fig. 5) and another one after increasing pressure to 1.9 GPa (point 12 in Fig. 5) for a second time as part of the same series. This procedure yielded consistently reproducible hyperfine parameters (cf. Fig. 5). The onset of the abrupt change may be estimated to be between 4.0 and 4.2 GPa.

### Compressibilities in the system Ca(Fe,Mg)Si,O\(_6\)

For an interpretation of the \( \partial \delta/\partial P \) and \( \partial \Delta E_0/\partial P \), information on the compression of the local volume around the position of the resonantly absorbing nucleus is needed over the pressure range studied. Unfortunately, the pressure dependence of the atomic positions between ambient pressure and 10 GPa is not well known for crystal structures of the system Ca(Fe,Mg)Si,O\(_6\). The unit-cell volumes between ambient pressure and 10 GPa were determined for \( \text{Hd} \) and \( \text{Hd}_{60}\text{Di}_{40} \) by Zhang et al. (1989) from the polycrystalline samples used in this study.

### Table 4: Pressure and volume dependence of \( \delta, \delta_\text{SOD}, \Delta E_0, \) and \( \Gamma \) of hedenbergite

<table>
<thead>
<tr>
<th>Range of ( P ) (GPa)</th>
<th>( \delta/\delta P ) (mm/s GPa)</th>
<th>( \delta/\delta \ln V ) (mm/s)</th>
<th>( \gamma )</th>
<th>( \delta_\text{SOD}/\delta \ln V ) (mm/s)</th>
<th>( \delta_{\text{SOD}} ) (mm/s)</th>
<th>( \Delta \Delta E_0/\delta P ) (mm/s)</th>
<th>( \partial T/\partial P ) (mm/s GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4–4.2</td>
<td>(-8 \times 10^{-5})</td>
<td>1.03</td>
<td>1.50</td>
<td>0.15</td>
<td>(5 \times 10^{-4})</td>
<td>-0.029</td>
<td>0.014</td>
</tr>
<tr>
<td>4.4–9.9</td>
<td>(-4 \times 10^{-3})</td>
<td>2.23</td>
<td>5.81</td>
<td>0.57</td>
<td>(6 \times 10^{-2})</td>
<td>-0.015</td>
<td>0.007</td>
</tr>
</tbody>
</table>

For an interpretation of the \( \partial \delta/\partial P \) and \( \partial \Delta E_0/\partial P \), information on the compression of the local volume around the position of the resonantly absorbing nucleus is needed over the pressure range studied. Unfortunately, the pressure dependence of the atomic positions between ambient pressure and 10 GPa is not well known for crystal structures of the system Ca(Fe,Mg)Si,O\(_6\). The unit-cell volumes between ambient pressure and 10 GPa were determined for \( \text{Hd} \) and \( \text{Hd}_{60}\text{Di}_{40} \) by Zhang et al. (1989) from the polycrystalline samples used in this study. Single-crystal data on the compression of the M1 polyhedron in...
diopside between ambient pressure and 5 GPa were reported by Levien and Prewitt (1981).

Hedenbergite and HdsDi40 exhibit anisotropic compression, b being the most compressible direction. In hedenbergite the compression along a is clearly smaller than along c, whereas in HdsDi40 it is apparently about the same in those directions. The experimental errors of the HdsDi40 data were, however, larger than those of hedenbergite. The compressibilities $\beta_a$, $\beta_b$, and $\beta_c$ for the system Ca(Fe,Mg)Si2O6 are listed in Table 5.

The unit-cell volume of hedenbergite decreases between ambient pressure and 5 GPa by 3.3%. The bulk moduli $K_0$ were calculated from a least-squares fit of the pressure-volume data using a Birch-Murnaghan equation of state. For this, ($\partial K_0/\partial P)_T = 4$ was assumed. $K_0$ of hedenbergite is in agreement with the previous determination of Kandelin and Weidner (1988) from Brillouin spectroscopy. The $K_0$ values obtained for several compositions of the system Ca(Fe,Mg)Si2O6 are presented in Table 6. They do not reveal any dependence on the Fe/Mg ratio within the experimental error.
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Table 5. Axial and volume compressibilities of clinopyroxenes Ca(Fe,Mg)Si_2O_6

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\beta_a) (x10^1 GPa)</th>
<th>(\beta_b) (x10^1 GPa)</th>
<th>(\beta_c) (x10^1 GPa)</th>
<th>(\beta_v) (x10^1 GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HaD_C_40</td>
<td>2.22(8)</td>
<td>3.3(1)</td>
<td>2.6(1)</td>
<td>7.6(7)</td>
</tr>
<tr>
<td>H_aD_C_40</td>
<td>1.94(2)</td>
<td>3.1(2)</td>
<td>2.1(1)</td>
<td>6.0(2)</td>
</tr>
<tr>
<td>D_H</td>
<td>2.59(3)</td>
<td>3.27(4)</td>
<td>2.59(3)</td>
<td>7.85(1)</td>
</tr>
</tbody>
</table>

Note: \(\beta_a, \beta_b, \beta_c\) are the axial compressibilities, \(\beta_v\) is the volume compressibility; errors calculated using error propagation procedure.

Table 6. Bulk moduli (Mbar) of clinopyroxenes

<table>
<thead>
<tr>
<th>Sample</th>
<th>(K'_v)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HaD_C_40</td>
<td>1.19(2)</td>
<td>this work</td>
</tr>
<tr>
<td>HaD_C_40</td>
<td>0.82(1)</td>
<td>this work</td>
</tr>
<tr>
<td>Hedenbergite</td>
<td>0.71(2)</td>
<td>a</td>
</tr>
<tr>
<td>Fassaite</td>
<td>1.20</td>
<td>b</td>
</tr>
<tr>
<td>Diopside</td>
<td>0.99(1)</td>
<td>c</td>
</tr>
<tr>
<td>Diopside</td>
<td>1.14(6)</td>
<td>d</td>
</tr>
<tr>
<td>Diopside</td>
<td>1.22(2)</td>
<td>e</td>
</tr>
</tbody>
</table>

* Fitted by use of a Birch-Murnaghan equation of state assuming \(K'_v = 4.0\).
** Fitted to data \(\geq 3.7\) GPa.
† Fitted to data \(\geq 3.1\) GPa.

Table 7. Volume coefficients of \(\delta\) and \(\Delta E_0\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>(\delta) (GPa)</th>
<th>(\Delta E_0) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HaD_C_40</td>
<td>0.0-4.2</td>
<td>0.64(4) : 1.00(6) : 0.79(6)</td>
</tr>
<tr>
<td>H_aD_C_40</td>
<td>4.4-9.9</td>
<td>0.61(1) : 1.0(1) : 0.7(1)</td>
</tr>
<tr>
<td>Diopside</td>
<td>3.9-7.9</td>
<td>0.96 : 1.00(4) : 0.793(2)</td>
</tr>
</tbody>
</table>

Note: \(\delta\) calculated from the lattice constants of Zhang et al. (1989).

Discussion

The hyperfine parameters \(\delta\) and \(\Delta E_0\) are sensitive probes of the pressure-dependent electronic structure at the Fe\(^{2+}\) sites in the crystal. In the following sections the relationships between \(\delta, \Delta E_0\), compression, and Fe/Mg ratio in Ca(Fe,Mg)Si_2O_6 pyroxenes are discussed.

Pressure dependence of \(\delta\)

The value of \(\delta\) (neglecting \(\delta_{soo}\)) is proportional to the electronic charge density \(\rho(0)\) at the resonantly absorbing nucleus. For \(^{57}\)Fe, \(\delta\) decreases with increasing \(\rho(0)\): \(\delta = \alpha \rho(0)\), where \(\alpha\) is a nuclear constant with a negative sign for \(^{57}\)Fe. In general (Güitlich et al., 1978), \(\rho(0)\) may be considered as

\[ \rho(0) = \rho_{\text{free ions}}(0) + \rho_{\text{ov}}(0) + \rho_{\text{valence}}(0). \]

In the case of high-spin Fe\(^{2+}\), \(\rho_{\text{free ions}}(0)\) is the 1s, 2s, 3s contribution of the free Fe\(^{2+}\) core, \(\rho_{\text{ov}}(0)\) is the overlap contribution \(\rho_{\text{ov}}(0) = \rho_{\text{ov}}(0) - \rho_{\text{free ions}}(0)\), where \(\rho_{\text{ov}}(0)\) is the contribution of the 1s, 2s, 3s orbitals of the effective Fe\(^{2+}\) core, and \(\rho_{\text{valence}}(0)\) is the contribution from the 3d, 4s, 4p valence orbitals of Fe\(^{2+}\) and 2s, 2p orbitals of O\(^2-\). The two terms \(\rho_{\text{ov}}(0)\) and \(\rho_{\text{valence}}(0)\) are expected to be dependent on compression. It should be noted that an effect of pressure on \(\delta\) is possible only by change in bond distances and bond angles around the position of the resonantly absorbing nucleus. It is, therefore, necessary to interpret \(\delta / \delta P\) in terms of compression.

It is known that for pressures smaller than 5.3 GPa, the compression of the unit-cell volume \(V\) in diopside is primarily due to the compression of the M1 and M2 polyhedral volumes \(V_{M1}\) and \(V_{M2}\) (Levien and Prewitt, 1981). It is proposed that this is also valid for hedenbergite since the relative reduction in \(V\) is similar for diopside and hedenbergite in that range of pressures (Zhang et al., 1989). Consequently, \(\delta / \delta \ln V\) and \(\delta / \delta \ln V_{M1}\) in hedenbergite may be regarded as similar. Values of \(\delta / \delta \ln V\) for hedenbergite and \(\Delta E_0\) calculated from data of Tables 1 and 3 and lattice parameters obtained by Zhang et al. (1989) are listed in Table 7.

Experimental high-pressure studies of \(^{57}\)Fe resonance in FeF_3 and molecular orbital calculations of \(\rho(0)\) (Reschke et al., 1977, and references cited therein) showed that \(\rho_{\text{ov}}(0)\) increases with increasing pressure, whereas \(\rho_{\text{valence}}(0)\) decreases. The observed net decrease of \(\delta\) was, therefore, ascribed to a predominant contribution of \(\rho_{\text{ov}}(0)\), i.e., increased overlap between the s orbitals of the Fe\(^{2+}\) core and the valence orbitals of the ligands. The decrease of \(\rho_{\text{valence}}(0)\) results from a decrease of Fe\(^{2+}\) 4s population coupled with an increase of Fe\(^{2+}\) 3d population. The crystal structure of FeF_3 is of the rutile type, Fe\(^{2+}\) being octahedrally coordinated. The volume compression of the FeF_6 octahedra in FeF_3 is 4.10\% between ambient pressure and 4 GPa. The electronic state of Fe\(^{2+}\) at M sites as well as the degree of covalent Fe\(^{2+}\)-ligand participation in chain silicates may be expected to be comparable to those of FeF_3.

The linear relationship between \(\delta\) and \(V\) as well as the comparatively small magnitude of \(\delta / \delta \ln V\) in hedenbergite between ambient pressure and 4.2 GPa suggest that the observed net increase in \(\rho(0)\) results mainly from the compression of the valence orbitals due to bond shortening, without changing \(\rho_{\text{ov}}(0)\) significantly. At pressures >4.2 GPa, however, \(\delta / \delta \ln V\) is greater than in the lower range of pressures. This implies that additional fac-
tors are important. The increase of $\delta \phi / \delta P \ln V$ at pressures $>4.2$ GPa cannot be attributed to a concomitantly higher compressibility, since the compressibility decreases at higher pressure. There must be excess change in $\rho_{\alpha}(0)$ that additionally contributes to $\rho(0)$ at pressures $>4.2$ GPa. This is just what was found in FeF$_3$ (Reschke et al., 1977).

The pressure dependence of $\delta$ at the M1 site in hedenbergite may also be compared with that of metallic Fe. The $\delta \phi / \delta P$ coefficient of Fe (ground state 3d$^6$4s$^2$) is $-7.46$ to $-9.08 \times 10^{-3}$ mm/s GPa. The value $\delta \phi / \delta P = -8 \times 10^{-3}$ mm/s GPa (Table 4) for hedenbergite between ambient pressure and 4.2 GPa is similar to that of Fe. Williamson (1978) pointed out that the $\delta \phi / \delta P$ in metallic and ionic compounds are generally comparable. The decrease in $\delta$ for Fe was interpreted by Williamson (1978) mainly in terms of compression of the 4s orbital.

**Pressure dependence of $\Delta E_0$**

The $^{57}$Fe quadrupole splitting $\Delta E_0$ is determined by the maximum value $V_{zz}$ of the second derivative $V_{ii}$ ($i = X, Y, Z$) and the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$. Here $V$ is the electrostatic potential at the nuclear site. The contribution of $\eta$ to $\Delta E_0$ is minor (maximum 15% for $\eta = 1$). The value of $\eta$ for M1 in hedenbergite at 4.2 K is small (Coey and Ghose, 1985). At temperatures near 293 K, however, $\eta$ is large (Stanek et al., 1986b). At any rate, the contribution of the change in $\eta$ to $\Delta E_0$ is neglected here.

In the case of high-spin Fe$^{2+}$ in predominantly ionic compounds, $V_{zz}$ can be separated into three additive terms (Gütlich et al., 1978): (1) the valence contribution $V_{2zz}$, which results from the unbalanced population of 3d orbitals, (2) the lattice contribution $V_{2zz}$, which originates from the noncubic distribution of ligand charges and the more distant ions around the Fe$^{2+}$ site, and (3) $V_{2zz}$, which accounts for the overlap between Fe$^{2+}$ and ligand orbitals. It is often difficult to arrive at conclusions from variation of $\Delta E_0$ alone about the individual changes in these three components of $V_{zz}$. In principle $V_{2zz}$ provides the predominant contribution to $V_{zz}$ and determines the sign. $V_{2zz}$ is minor and of opposite sign. The sign of $V_{2zz}$ is also opposite to that of $V_{2zz}$.

If it is assumed that the M1 octahedra in hedenbergite remain geometrically similar with increasing pressure, $V_{2zz}$ is expected to increase simply because of bond shortening due to compression. This increase from ambient pressure to 5.3 GPa is calculated to be about 5% for the M1 octahedron using the data for diopside of Levien and Prewitt (1981).

The effect of deviation of the M1 octahedron from cubic symmetry on $\Delta E_0$ may be estimated considering crystal-field splitting (Ingalls, 1964). For the case of quasi-axial symmetry ($\eta = 0$), $\Delta E_0$ can be expressed in terms of a reduction function $F$ as

$$\Delta E_0 = C \alpha^2 F(\Delta, \alpha^2 \lambda_0, T).$$

In Equation 6 $C$ is a constant, $\Delta$ is the energy separation between the 3d$_{1/2,3/2}$ energy levels of Fe$^{3+}$, $\alpha^2$ is the isotropic covalency factor, $\lambda_0$ is the spin orbit coupling constant of the free Fe$^{3+}$ ion, and $T$ is the temperature.

First, the behavior of $\Delta E_0$ at pressures below 4.2 GPa is considered. A study of the temperature dependence of $\Delta E_0$ (Lin et al., in preparation) at M1 in orthopyroxene between 7 and 293 K yielded $\Delta = 480$ cm$^{-1}$ and $\alpha^2 = 0.72$, assuming an effective axial crystal field. Using the same procedure, $\Delta = 515$ cm$^{-1}$ and $\alpha^2 = 0.61$ was obtained for M1 in hedenbergite (Zhang, unpublished data). From the characteristics of $F$ it is clear that for hedenbergite an increase of $\Delta$ is associated with an increase of $F$. This is shown in Figure 6. The increase of $\Delta$ should be interpreted as an increase of the pseudoaxial distortion. The observed decrease of $\Delta E_0$ with increasing pressure implies, therefore, that the pseudoaxial distortion of M1 becomes smaller. Similar observations on the relationship between polyhedral distortion at the Fe$^{2+}$ position and pressure have also been made for FeF$_3$ (Champion et al., 1967; Drickamer et al., 1969). Comparable crystallographic results were reported for a fassaitic clinopyroxene, where it was found that the compressibility of the shortest bond in the M1 octahedron is small and that of the longest bond is large (Hazen and Finger, 1977).

On the other hand, Levien and Prewitt (1981) apparently
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Fig. 7. Unit-cell parameters of hedenbergite at high pressures and high temperatures vs. volume ratio $V/V_0$. The data show inverse behavior of unit-cell parameters at high temperatures and pressures. Units of the ordinate are in Ångströms for $a$, $b$, and $c$ and in degrees for $\beta$.

found no change in the polyhedral geometry of the M1 in diopside up to 5.3 GPa.

It is not clear yet which factors contribute to $V_{zz}$ at pressures higher than 4.2 GPa, where the overlap of the orbitals between Fe and O is greater. Similar to the behavior of $\delta/\partial V$, $\partial \delta/\partial \ln V$ in $V_{zz}$ is substantially higher above 4.2 GPa compared with that at lower pressures (Table 7). This may be accounted for by enhanced covalent participation coupled with distinct polyhedral distortion at pressures above 4.2 GPa.

Inverse effect of $P$ and $T$ on the unit-cell parameters

The comparison of the high-pressure data of Zhang et al. (1989) with the high-temperature data of Cameron et al. (1973) shows an inverse relationship of the effects of pressure and temperature on all unit-cell parameters of hedenbergite. This is illustrated in Figure 7. Levien and Prewitt (1981) also showed this to be the case for diopside. An inverse relationship also exists for the ratios $a/b$ and $h/c$ (Fig. 8); $[\partial(a/c)/\partial T]_p$ and $[\partial(a/c)/\partial P]_T$ are both positive. The consequence of this is $\beta_1 < \beta_4$, whereas $\alpha_1 < \alpha_4$.

Effect of chemical composition at constant pressure

There are two important conclusions from the data of Tables 1, 2, and 3. First, if the $\delta$ and $\Delta E_0$ values are plotted against each other as shown in Figure 9, an approximately linear increase of $\Delta E_0$ with increasing $\delta$ is observed for each of the three chemical compositions studied. Second, $\delta$ plotted against the Fe/Mg ratio at constant pressure is nearly invariable, whereas $\Delta E_0$ systematically decreases with decreasing Fe/Mg ratio. This implies that there is no dependence between $\delta$ and $\Delta E_0$ for the three chemically different samples at any constant pressure. This is also in agreement with the results of Dollase and Gustafson (1982) at ambient pressure.

It is known that the bond distances of the M1 polyhedra in Ca(Fe,Mg)Si$_2$O$_6$ clinopyroxenes decrease with increasing pressure at constant Fe/Mg ratio; they also decrease with decreasing Fe/Mg ratio at ambient pressure. For example, the shortest bond is $d_{Fe-O} = 2.087$ Å and the average bond is $\langle d \rangle_{M1} = 2.130$ Å at M1 in hedenbergite, and $d_{Mg-O} = 2.050$ Å and $\langle d \rangle_{Mg} = 2.077$ Å at M1 in diopside at ambient conditions (Cameron et al., 1973). The relative reduction of 2.5% of $\langle d \rangle$ from hedenbergite to diopside at ambient pressure corresponds to a reduction of 1.7% in diopside from ambient pressure to 5 GPa (Levien and Prewitt, 1981). In view of the pronounced reduction of $\delta$ at high pressure (0.04 mm/s at 4 GPa, cf. Table 1), the invariance of $\delta$ to the substitution of Mg for Fe at constant pressure is remarkable. It implies relatively invariable Fe-O bonds at M1 sites occupied by Fe compared with the corresponding average (Fe,Mg)-O bonds at all M1 sites, at least in the Fe-rich part of the Ca(Fe,Mg)Si$_2$O$_6$ system. In view of the definition of $\delta$ in terms of $p(0)$, especially the shortest Fe-O bond of the FeO$_6$(M1) octahedron seems to be invariable.

The decrease of $\Delta E_0$ with increasing Mg$^{2+}$ substitution is mainly the result of the change in $V_{zz}$, according to Figure 6. It is indicative of a decrease of the pseudoaxial crystal-field splitting $\Delta$ of Fe$^{3+}$ with increasing Mg substitution at M1. The change in the splitting of the 3d$_{xy,zz}$ levels practically does not change the relative s, d electron densities as concluded from the invariance of $\delta$. This is different at high pressures, where both s and d electron densities change with increasing pressure.

Phase transition

It is well established that $\gamma$ resonance may be sensitive to phase transitions since hyperfine parameters such as $\delta$ and $\Delta E_0$ are implicit expressions of the electronic configuration and lattice dynamical effects (Johnson, 1989; Pipkorn et al., 1964; Petrich, 1969). From their electronic nature, $\delta$ and $\Delta E_0$ depend also implicitly on volume and entropy. They provide, therefore, information on the nature of a phase transition (Preston, 1978).

The abrupt discontinuities in $\delta$ and $\Delta E_0$ found between
3.8 and 4.3 GPa are characteristic of a first-order phase transition. The more pronounced discontinuity in $\Delta E_0$ than in $\delta$ indicates that changes in electronic structure due to octahedral distortion play a more important role than simple compression.

The hysteresis in $\Delta E_0$ found in $\text{Hd}_{80}\text{Di}_{20}$ provides additional evidence that the phase transition is thermodynamically of first order. Two coexisting phases, however, could not be resolved in the spectra, probably because of the rather small structural changes, the line broadening due to a pressure gradient over the absorber area, or both. The phase transition is reversible. It could be of the displacive type. Prewitt et al. (1971) reported a thermal hysteresis for the $P2_1/c$-$C2/c$ transition observed in natural pigeonite. This was revealed recently to be a first-order
phase transition by transmission electron microscopy at elevated temperatures (Shimobayashi and Kitamura, 1990).

Examination of high-pressure powder X-ray diffraction data on the same samples showed changes in the pressure derivatives of the cell parameters and small discontinuities at 4 GPa, especially for the c axis (Zhang et al., 1989), the angle $\beta$, and the volume. The volume-pressure data over the entire range of pressures studied, however, cannot be fitted reasonably using a Birch-Murnaghan equation of state. More diffraction data at pressures higher than 5 GPa are needed for further clarification.

### Conclusions

Fe at M1 in clinopyroxenes $\text{Ca(Fe, Mg)}\text{Si}_2\text{O}_6$ is in the high-spin ferrous state between ambient pressure and 10 GPa. Changes in isomer shift $\delta$ and quadrupole splitting $\Delta E_q$ reflect primarily changes in Fe$^{2+}$ electronic structure, whereas lattice dynamical effects such as SOD and change in recoil-free fraction at high pressures are found to be small.

The value of $\delta$ decreases with increasing pressure because of a compression of the valence shell of Fe$^{2+}$. At pressures higher than 4 GPa, additional contributions to $\delta$ are due to overlap between s orbitals of Fe$^{2+}$ and valence orbitals of the ligands. The value of $\Delta E_q$ decreases with increasing pressure mainly because of a change in the distribution of the 3d$^6$ electron over the d$\alpha_l, d\alpha_r, d\alpha_r$ levels related to a change in pseudoaxial distortion. The effect of simple lattice compression on $\Delta E_q$ is small. At pressures higher than 4 GPa, the effects of increased covalent participation in the Fe$^{2+}$-ligand bonds and octahedral distortion on $\Delta E_q$ are relatively enhanced.

Substitution of Mg$^{2+}$ for Fe$^{2+}$ at M1 in the Fe-rich part of the system changes the geometrical configuration of the Fe$^{2+}$ octahedra, the shortest Fe-O bonds, however, remaining nearly invariable. This is indicative of distinct Fe-O and Mg-O bonds at the crystallographically equivalent M1 positions.

The unit cell of hedenbergite shows anisotropic compression: $\beta_1 > \beta_2 > \beta_3$. An inverse behavior of all unit-cell parameters with increasing pressure and increasing temperature is observed.

Discontinuities in the pressure dependence of $\delta$ and $\Delta E_q$ between 3.8 and 4.3 GPa indicate a reversible phase transition of first order.

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