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# High-pressure Mössbauer study of synthetic clinoferrosilite, $FeSiO_3$

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**Abstract**—Mössbauer spectra were recorded of a polycrystalline sample of clinoferrosilite ($FeSiO_3$) with $P2_1/c$ space group that was synthesised at 8 GPa and 1150°C using a multianvil press. In situ experiments were performed at 293 K using a diamond anvil cell at pressures up to 3.8 GPa. The transition to the C2/c structure was observed between 1.33 and 1.74 GPa, and is characterised by a large increase in quadrupole splitting ($\Delta E_Q$) for the M1 site, and a small decrease in $\Delta E_Q$ for the M2 site. The centre shift ($\delta$) data for the M1 site show no change within experimental error through the transition, while $\delta$ increases slightly for the M2 site. The values of $\partial\delta_o/\partial P$ ($\delta_o$ = isomer shift) were determined by correcting centre shift data for the pressure dependence of the second-order Doppler shift. For the $P2_1/c$ structure $\partial\delta_0/\partial P = -6(4) \times 10^{-3}$ and $+8(4) \times 10^{-3}$ mm $s^{-1}$ $GPa^{-1}$, and for the C2/c structure $\partial\delta_o/\partial P = +1(3) \times 10^{-3}$ and $+1(3) \times 10^{-3}$ mm $s^{-1}$ $GPa^{-1}$ for the M1 and M2 sites, respectively. The positive slopes imply a contribution to the electron density from changes in electron orbital occupation. For the $P2_1/c$ structure $\partial\Delta E_Q/\partial P = +6.3(9) \times 10^{-2}$ and $+4.0(9) \times 10^{-2}$ mm $s^{-1}$ $GPa^{-1}$, and for the C2/c structure $\partial\Delta E_Q/\partial P = +6(6) \times 10^{-3}$ and $+3.6(6) \times 10^{-2}$ mm $s^{-1}$ $GPa^{-1}$ for the M1 and M2 sites, respectively. The results are used to deduce the relative changes in the splitting of the $Fe^{2+}$ ground state ($^5T_{2g}$) as a function of pressure.

## INTRODUCTION

PYROXENES CONSTITUTE a significant proportion of the Earth's upper mantle. Recent experiments have established that a high-pressure phase with space group C2/c has a large stability region at high P,T for the endmember phases $MgSiO_3$ (ANGEL *et al.*, 1992) and $FeSiO_3$ (HUGH-JONES *et al.*, 1994). The transition from the low pressure form with space group $P2_1/c$ to the C2/c modification can be observed at room temperature and high pressures and is reversible. *In situ* single crystal X-ray diffraction experiments on $FeSiO_3$ by HUGH-JONES *et al.* (1994) have shown that the transition involves a 3% decrease in unit cell volume with considerable structural rearrangement of the tetrahedral chains. The two sites occupied by $Fe^{2+}$, M1 and M2, behave differently through the transition: the size and distortion of the M2 site changes significantly, while the M1 site remains relatively unaltered. Recent optical absorption spectra measurements of $FeSiO_3$ at high pressure provide information on the crystal-field parameters of the two polymorphs (ROSS and SOWERBY, 1996). Complementary data can be obtained from $^{57}Fe$ Mössbauer spectroscopy, which is highly sensitive to changes in the electronic environment of the iron atoms. There are relatively few studies of the effects of pressure on the hyperfine parameters of silicate minerals, and the system $FeSiO_3$ provides an excellent opportunity to combine results from structural and electronic studies with Mössbauer data to characterise the effect of pressure on the $P2_1/c$ and C2/c structural modifications, and the changes that occur through the phase transition.

## EXPERIMENTAL DETAILS

### *Preparation of clinoferrosilite*

Clinoferrosilite was synthesised from a starting mixture of Fe powder, $Fe_2O_3$ and $SiO_2$, with a net enrichment in $^{57}Fe$ of 21%, roughly ten times the natural abundance. A mixture of the starting material was loaded into a Ag capsule and run at 8 GPa and 1150°C for 20 h using a multianvil press at the Bayerisches Geoinstitut. The run product was checked by X-ray powder diffraction for crystalline impurities and by Mössbauer spectroscopy for iron-containing impurities. Nearly all diffraction peaks corresponded to published reflections for $P2_1/c$ clinoferrosilite, with only a few extremely weak peaks (<5% relative intensity) that could not be identified. The room temperature Mössbauer spectrum contains two doublets, which are assigned to $Fe^{2+}$ in the M1 and M2 sites. The two doublets account for at least 99% of spectrum absorption, with the possibility of a small impurity corresponding to less than 1% of the total area. Addition of absorption corresponding to the impurity changed the hyperfine parameters of the M1 and M2 doublets by less than 0.002 mm/s; therefore the effect of the impurity is neglected in subsequent data analysis.

### *High-pressure Mössbauer measurements*

Mössbauer data were collected at high pressure using a modified Merrill-Bassett diamond anvil cell (DAC) (HAZEN and FINGER, 1982) mounted with 0.125 carat diamonds with culet diameters of 1.0 mm. A 250 $\mu$m thick $Ta_{90}W_{10}$ gasket (pre-indented to 150 $\mu$m) with a 500 $\mu$m diameter hole provided collimation for the gamma radiation. Powdered clinoferrosilite was compressed between two glass slides and loaded as a thin plate into the DAC to ensure uniform absorber distribution. A 4:1 methanol:ethanol liquid was added as a pressure medium along with small ruby grains (~10 $\mu$m diameter) for pressure calibration. The DAC was mounted in a custom cryostat with the base of the bottom diamond at a distance of approximately 1 mm from the radioactive source. Further description of the apparatus is given in McCammon (1992). Mössbauer spectra were collected at each pressure over time periods ranging from 2 to 4 days. Experiments were made during several cycles of increasing and decreasing pressure; the numerical sequence of the measurements is given in Table 1.

Mössbauer spectra were recorded in transmission mode on a constant acceleration Mössbauer spectrometer with a nominal 50 mCi $^{57}$Co source in a 6 $\mu$m Rh matrix (room pressure) and a nominal 20 mCi high specific activity source (2 Ci/cm$^2$) in a 12 $\mu$m Rh matrix (high pressure). The velocity scale was calibrated relative to 25 $\mu$m $\alpha$-Fe foil using the positions certified for National Bureau of Standards standard reference material no. 1541. Room temperature line widths for the outer lines of $\alpha$-Fe were 0.28 mm/s for the conventional source and 0.42 mm/s for the high specific activity source. The density of iron in the room pressure absorber was 5 mg Fe/cm$^2$, and in the high-pressure experiments the density was estimated to correspond to 10 mg of natural Fe/cm$^2$. Mössbauer spectra were fit using the commercially available fitting program NORMOS written by R. A. Brand (distributed by Wissenschaftliche Electronik GmbH, Germany).

Table 1. Mössbauer parameters of clinoferrosilite at room temperature.

| | M1 | | M2 | | |
|---|---|---|---|---|---|
| P GPa | $\delta^{\alpha}$ mm s$^{-1}$ | $\Delta E_Q$ mm s$^{-1}$ | $\delta^{\alpha}$ mm s$^{-1}$ | $\Delta E_Q$ mm s$^{-1}$ | N[b] |
| clinoferrosilite in air | | | | | |
| 0.00 | 1.174 | 2.609 | 1.124 | 1.959 | |
| | ±0.005 | ±0.005 | ±0.005 | ±0.005 | |
| clinoferrosilite in cell[c] | | | | | |
| *$P2_1/c$ phase* | | | | | |
| 0.00 | 1.177 | 2.638 | 1.126 | 1.933 | 3 |
| 0.31 | 1.181 | 2.650 | 1.129 | 1.958 | 8 |
| 0.59 | 1.171 | 2.672 | 1.128 | 1.953 | 4 |
| 1.00 | 1.170 | 2.700 | 1.137 | 1.987 | 11 |
| 1.14 | 1.170 | 2.700 | 1.130 | 1.985 | 9 |
| 1.33 | 1.169 | 2.722 | 1.133 | 1.983 | 14 |
| *mixed phase* | | | | | |
| 1.40 | 1.169 | 2.800 | 1.143 | 1.915 | 13 |
| 1.54 | 1.168 | 2.829 | 1.146 | 1.907 | 12 |
| *C2/c phase* | | | | | |
| 1.74 | 1.166 | 2.925 | 1.145 | 1.937 | 7 |
| 1.95 | 1.172 | 2.908 | 1.158 | 1.933 | 10 |
| 2.02 | 1.165 | 2.919 | 1.145 | 1.946 | 2 |
| 2.24 | 1.149 | 2.909 | 1.154 | 1.945 | 5 |
| 2.90 | 1.159 | 2.928 | 1.150 | 1.985 | 1 |
| 3.84 | 1.166 | 2.928 | 1.147 | 2.005 | 6 |
| 0.0[d] | 1.165 | 2.904 | 1.152 | 1.870 | |
| | ±0.007 | ±0.014 | ±0.007 | ±0.014 | |
| orthoferrosilite in air (DOWTY and LINDSLEY, 1973) | | | | | |
| 0.00 | 1.182 | 2.490 | 1.130 | 1.906 | |
| | ±0.003 | ±0.005 | ±0.002 | ±0.004 | |

[a] relative to α-Fe
[b] numerical sequence of experiment
[c] estimated standard errors for high-pressure determinations of δ and $\Delta E_Q$ are 0.005 and 0.01 mm s$^{-1}$, respectively
[d] extrapolated from high-pressure data

The Mössbauer spectrum of clinoferrosilite recorded in air at atmospheric pressure is illustrated in Fig. 1a, and was fitted to two Lorentzian lines using the conventional constraint of equal component linewidths. The areas of component doublets are not exactly 1:1 because of slight preferred orientation due to the method used for sample preparation.

Figure 1b shows the spectrum of the same sample mounted in the diamond anvil cell. Increased source linewidth and the relatively high effective thickness of the absorber cause broader linewidths and non-Lorentzian lineshapes; therefore all high-pressure spectra were fit using the Voigt lineshape. As well as the conventional constraints of equal component Lorentzian linewidths and Gaussian standard deviations, the following additional constraints were applied to high-pressure spectra of the $P2_1/c$ phase: the Lorentzian linewidth, Gaussian standard deviation and spectrum area of the M1 doublet were constrained to be equal to the corresponding parameters of the M2 doublet. Such constraints were justified on the basis of fits to the spectrum of the absorber recorded in air, where the lines are well resolved (Fig. 1a). Application of these constraints during the fitting process to the spectrum recorded in air changed the hyperfine parameters by less than 0.0005 mm/s compared to an unconstrained fit. Component areas were allowed to vary in the high-pressure spectra to account for slight preferred orientation effects. The similar component area ratios for all spectra are consistent with the similar method of sample preparation, where crystallites were pressed at right angles to the plane of the absorber in both cases, either by the sample holder (sample in air) or by a glass slide (diamond anvil cell sample).

Mössbauer spectra from the C2/c phase are well resolved (Fig. 1c) and robust hyperfine parameters could be determined using only the conventional constraints of equal component Lorentzian linewidths and Gaussian standard deviations.

## RESULTS AND DISCUSSION

The hyperfine parameters determined for clinoferrosilite are listed in Table 1. By analogy with orthoferrosilite, the doublet with large quadrupole splitting is assigned to the M1 site and the doublet with small quadrupole splitting to the M2 site. The Mössbauer parameters of orthoferrosilite (Dowty and Lindsley, 1973) are given in Table 1 for comparison. X-ray diffraction experiments have shown that the transition $P2_1/c \rightarrow C2/c$ occurs between

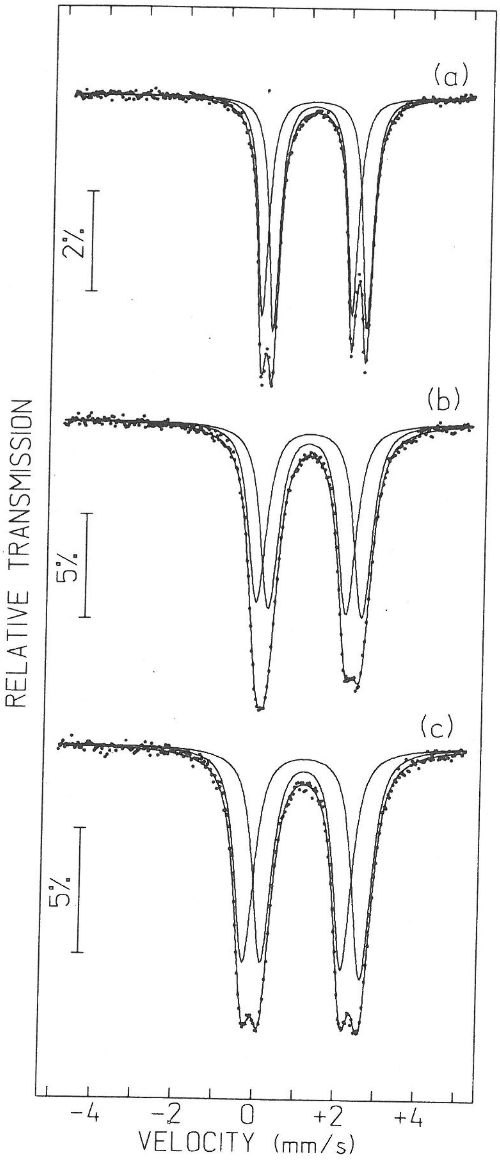

FIG 1. Room temperature Mössbauer spectra of clinoferrosilite (a) in air, and in a diamond anvil cell at (b) 0.1 MPa and (b) 3.84 GPa. The velocity scales are relative to Fe in Rh (−0.114 mm/s relative to $\alpha$-Fe).

1.48 and 1.75 GPa (HUGH-JONES *et al.*, 1994), and measurements using optical absorption spectroscopy have found the transition to occur between 1.61 to 1.85 GPa (ROSS and SOWERBY, 1996). Our observation of the transition between 1.33 and 1.74 GPa (Fig. 2) is in good agreement with these previous observations. In the Mössbauer data there is a region between 1.44 and 1.74 GPa with apparently intermediate values of the hyperfine parameters. Since the transition is first order with a 3% decrease in volume (HUGH-JONES *et al.*, 1994), the intermediate values represent a mixture of the $P2_1/c$ and $C2/c$ phases rather than an intermediate structure. The hysteresis might be due in part to microstructure in the sample caused by excessive cycling through the transition (the spectra with intermediate hyperfine parameters were recorded on the sixth cycle; see Table 1). HUGH-JONES (1995) has noted significant broadening of X-ray diffraction peaks after several cycles through the transition, which could arise from strain within the lattice. Such strain could broaden the pressure interval over which the transition occurred. The presence of strain does not affect the hyperfine parameters, however; results from the final spectrum recorded (1.33 GPa) are fully consistent with all other data from the $P2_1/c$ phase.

### *Effect of pressure on the centre shift*

The centre shift ($\delta$) is composed of the isomer shift ($\delta_o$) plus the second-order Doppler shift ($\delta_{SOD}$). The centre shift and isomer shift are often taken to

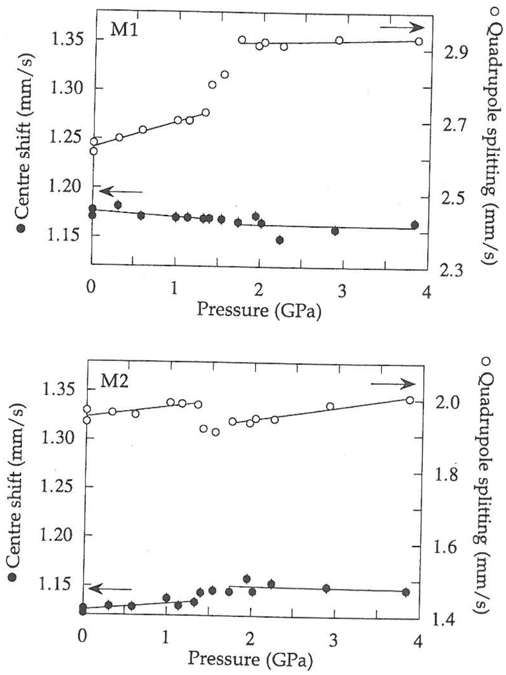

FIG. 2. Variation of hyperfine parameters for the M1 and M2 sites in clinoferrosilite as a function of pressure. Solid lines indicate linear least-square fits to the data corresponding to the $P2_1/c$ and $C2/c$ phases. Arrows indicate the relevant axis for the data.

be equal, since $\delta_{SOD}$ is similar for most materials and is relatively small. However both $\delta_o$ and $\delta_{SOD}$ are pressure dependent, so the pressure dependence of $\delta$ at constant temperature is approximated by

$$\partial\delta/\partial P = \partial\delta_o/\partial P + \partial\delta_{SOD}/\partial P. \qquad (1)$$

We can estimate the volume dependence of $\delta_{SOD}$ following the method of WILLIAMSON (1978):

$$\frac{\partial\delta_{SOD}}{\partial \ln V} = \gamma\frac{9k\Theta}{16mc}F(T/\Theta) \qquad (2)$$

where $\gamma$ is the lattice Grüneisen parameter, $\Theta$ is the Debye temperature, m is the mass of the Mössbauer isotope, T is the temperature, k is the Boltzmann constant, c is the speed of light, and the function F is given by:

$$F(T/\Theta) = 1 + \frac{8}{e^{T/\Theta}-1} - 24\left(\frac{T}{\Theta}\right)^{4}\int_0^{T/\Theta}\frac{x^3}{e^x-1}\,dx. \qquad (3)$$

The Grüneisen parameter can be calculated from the thermal expansion, volume, bulk modulus and heat capacity data according to $\gamma = \alpha V K_T/C_V$. Since thermodynamic data are not available for clinoferrosilite, we used the Grüneisen parameter ($\gamma = 2.3$) calculated from enstatite data taken from AHRENS (1995). Using the value $\Theta = 719$ K for enstatite (KIEFFER, 1985), we calculated $(\partial\,\delta_{SOD}/\partial \ln V)$ to be 0.25 mm/s, which is comparable to the values 0.15–0.57 mm/s determined by ZHANG and HAFNER (1992) for hedenbergite. The pressure dependence of $\delta_{SOD}$ can be calculated using the elastic data reported by HUGH-JONES (1995) for the $P2_1/c$ phase of clinoferrosilite ($K_T = 100 \pm 4$ GPa for $K_T'$ fixed at 4.3) and is reported in Table 2. The C2/c phase of clinoferrosilite is less compressible than the $P2_1/c$ phase ($K_T = 114 \pm 7$ GPa for $K_T'$ fixed at 4.3; HUGH-JONES, 1995) and if we assume a 10% increase in $\Theta$, this results in an increase of only 5% in the value of $\partial\delta_{SOD}/\partial P$. The uncertainties for the calculated quantities in Table 2 were estimated by propagating the likely uncertainties in the input data through the calculation.

The pressure dependence of the centre shifts ($\partial\delta/\partial P$) were determined from the experimental data using linear regression, and the results are listed in Table 2. It is evident that while $\partial\delta_{SOD}/\partial P$ can be ignored to a first approximation in calculating $\partial\delta_o/\partial P$ for the $P2_1/c$ phase, it cannot be ignored for the C2/c phase. For consistency we used equation (1) to calculate $\partial\delta_o/\partial P$ for all phases.

The isomer shift ($\delta_o$) is directly proportional to the difference in s electron density at the nucleus between the source and the absorber, where the constant of proportionality is negative for $^{57}$Fe. Two effects have been suggested for changing the s electron density at the nucleus with pressure: (1)

Table 2. Pressure dependence of δ and $\Delta E_Q$ for clinoferrosilite.

| | phase | site | $P2_1/c$ | C2/c | ref |
|---|---|---|---|---|---|
| $\partial\delta/\partial P$ mm $s^{-1}$ $GPa^{-1}$ | cfs | M1 | $-8(4) \times 10^{-3}$ | $-7(28) \times 10^{-4}$ | 1 |
| | cfs | M2 | $6(4) \times 10^{-3}$ | $-1(3) \times 10^{-3}$ | 1 |
| | Hd | M1 | | $-8 \times 10^{-3}$ | 2 |
| $\partial\delta_{SOD}/\partial P^*$ mm $s^{-1}$ $GPa^{-1}$ | cfs | | $-2(1) \times 10^{-3}$ | $-2(1) \times 10^{-3}$ | 1 |
| | Hd | | | $-1 \times 10^{-3}$ | 2 |
| $\partial\delta_o/\partial P^*$ mm $s^{-1}$ $GPa^{-1}$ | cfs | M1 | $-6(4) \times 10^{-3}$ | $1(3) \times 10^{-3}$ | 1 |
| | cfs | M2 | $8(4) \times 10^{-3}$ | $1(3) \times 10^{-3}$ | 1 |
| | Hd | M1 | | $-7 \times 10^{-3}$ | 2 |
| $\partial\Delta E_Q/\partial P$ mm $s^{-1}$ $GPa^{-1}$ | cfs | M1 | $6.3(9) \times 10^{-2}$ | $6(6) \times 10^{-3}$ | 1 |
| | cfs | M2 | $4.0(9) \times 10^{-2}$ | $3.6(6) \times 10^{-2}$ | 1 |
| | Hd | M1 | | $-3 \times 10^{-2}$ | 2 |

*calculated
cfs: clinoferrosilite; Hd: hedenbergite
numbers in parentheses represent the standard deviation of the last digit
References: [1]this work; [2]ZHANG and HAFNER (1992)

changes in orbital occupation; and (2) distortion of the wavefunctions—either compression of the s electrons or spreading out of the 3d electrons (increase in covalency) (DRICKAMER *et al.*, 1969). The second factor, an increase in covalency, causes an increase in s electron density and hence a decrease in $\delta_o$. The first factor includes transfer of electrons between the iron 3d and 4s levels, between different iron 3d levels, and between iron orbitals and orbitals of the co-ordinating anions. It can either increase or decrease $\delta_o$ depending on the nature and direction of transfer. The similarity of pressure coefficients for ionic compounds despite a variety of ligands suggests that metal—ligand transfer plays a minor role for these compounds (WILLIAMSON, 1978).

For the $P2_1/c$ phase, $\partial\delta_o/\partial P$ is negative for the M1 site while it is positive for the M2 site (Table 2). This cannot be attributed to differential compression of the sites: excluding changes in orbital occupation, the effect of polyhedral compression is to decrease $\delta_o$, and differential compression would change the magnitude of the decrease, but not the sign. One possibility is electron transfer from 4s to 3d iron orbitals as a function of pressure at the M2 site, which would decrease s electron density and hence increase $\delta_o$. Such a bonding change might be expected to accompany changes in the distortion of the coordination octahedron with pressure. As discussed by HUGH-JONES *et al.* (1994), increasing pressure tends to rotate the tetrahedral chains in the $P2_1/c$ structure to maintain stability, hence changing the configuration of the M2 site. It should be emphasised, however, that the overall change in $\delta_o$ with pressure for the M2 site is small, implying only minor changes in the configuration.

There is no observed change in $\delta_o$ for the M1 site between the $P2_1/c$ and $C2/c$ phases, which is consistent with single crystal structure refinements which show negligible change in the M1 site bond lengths and distortion through the transition (HUGH-JONES *et al.*, 1994). The slight increase in $\delta_o$ for the M2 site through the transition to the $C2/c$ phase implies a decrease in s electron density. This suggests that the increase in s electron density which accompanies the shorter Fe—O bond distances in the $C2/c$ phase (HUGH-JONES *et al.*, 1994) must be offset by a greater decrease in s electron density caused by changes in orbital occupation.

For the $C2/c$ phase, both M1 and M2 sites show similar behaviour: no change in $\delta_o$ with pressure in this pressure range within experimental error (Table 2). HUGH-JONES (1995) has shown that compression of the M1 and M2 octahedra occurs in this pressure range, so decreasing bond distances must be offset by slight changes in orbital occupation that are similar for both sites.

Finally, we note that $\partial\delta_o/\partial P$ for the M1 site in hedenbergite is identical within experimental error to that observed for the M1 site in the $P2_1/c$ phase of clinoferrosilite. This suggests a similar compression of the M1 octahedra in both structures.

### *Effect of pressure on the quadrupole splitting*

The change in quadrupole splitting ($\Delta E_Q$) during the transition from the $P2_1/c$ to the $C2/c$ phase is significantly higher for the M1 site compared to the M2 site (Fig. 2). Yet high-pressure structure refinements by HUGH-JONES *et al.* (1994) show that the M1 octahedron in the $C2/c$ phase at high pressure is similar to the M1 octahedron in the $P2_1/c$ phase at room pressure. DOWTY and LINDSLEY (1973) used the model of INGALLS (1964) to account for differences in $\Delta E_Q$ between the M1 and M2 sites in clinopyroxenes. The same model can be used to account for the above discrepancy, and to explain qualitatively the changes in $\Delta E_Q$ in clinoferrosilite with pressure.

In the model of INGALLS (1964) $\Delta E_Q$ for $Fe^{2+}$ in octahedral coordination is expressed in terms of a reduction function F:

$$\Delta E_Q = C\,\alpha^2\,F(\Delta_1, \Delta_2, \lambda_o, \alpha^2, T) \qquad (4)$$

where C is a constant ($= 2/7e^2\,Q\,(1 - R_o)\,\langle r^{-3}\rangle_o$), $\Delta_1$ and $\Delta_2$ are the ground state splittings of the crystal field levels, $\alpha^2$ is a covalency factor which decreases with increasing covalency, $\lambda_o$ is the spin-orbit coupling constant for the free ion and T is the temperature. The reduction function, F, has two contributions, one from the valence electrons (valence term) and one from the influence of the crystal lattice (lattice term). The values of $\Delta_1$ and $\Delta_2$ are related to the distortion of the coordination octahedron from cubic symmetry. The valence term is highly temperature dependant and increases with increasing distortion, eventually reaching a maximum value. The lattice term, which is largely independent of temperature, also increases with increasing distortion, but is of opposite sign. The reduction function F therefore increases initially with increasing distortion to a maximum value, but then decreases with further increase in distortion as the contribution from the lattice term becomes greater.

We have calculated the reduction function according to the INGALLS (1964) model for the M1 and M2 sites of $P2_1/c$ clinoferrosilite. Since crystal field parameters are not available for this phase, we used values for orthopyroxene determined by

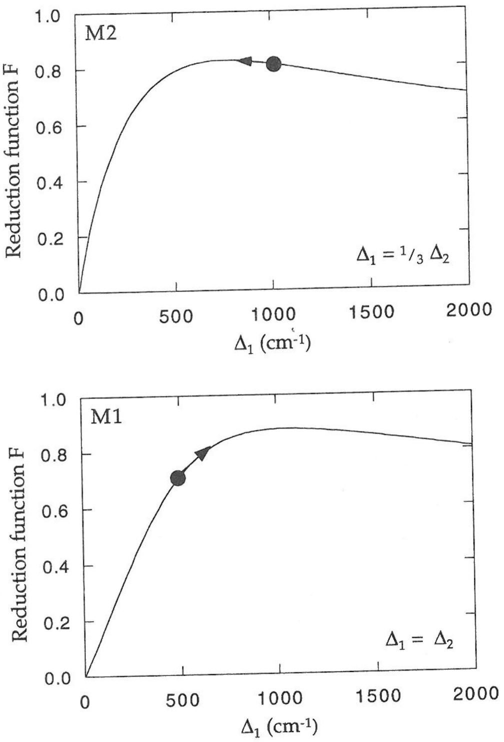

FIG. 3. Calculated curves for the reduction function as a function of ground-state splitting ($\Delta_1$ and $\Delta_2$) for the M1 and M2 sites in P2$_1$/c clinoferrosilite according the the model of INGALLS (1964). The solid circles indicate the approximate position corresponding to the site at ambient pressure, and the arrows indicate the direction of movement during compression.

LIN *et al.* (1993) and VAN ALBOOM *et al.* (1993). Assuming the M1 site to have tetragonal distortion ($\Delta_1 = \Delta_2$), and the M2 site to have rhombic distortion (assuming $\Delta_1 = \frac{1}{3}\Delta_2$, which approximates the situation for orthopyroxene), we calculated the reduction functions illustrated in Fig. 3. The curves should not be regarded as a quantitative determination of the quadrupole splitting, being based on an approximate model with a number of simplifying assumptions, but rather as a qualitative guide to factors that influence the quadrupole splitting.

Using the values for ground-state splitting for orthopyroxene of $\Delta_1 = \Delta_2 = 500$ cm$^{-1}$ for the M1 site and $\Delta_1 \approx \frac{1}{3}\Delta_2 = 1000$ cm$^{-1}$ for the M2 site (LIN *et al.*, 1993; VAN ALBOOM *et al.*, 1993), the approximate position of clinoferrosilite on the reduction function curves can be located (indicated by solid circles on Fig. 3). As postulated by DOWTY and LINDSLEY (1973) based on values of $\Delta E_Q$ for M1 and M2 sites, we see that the two sites indeed fall on opposite sides of the reduction function maximum.

The increase in $\Delta E_Q$ for the M1 site implies an increase in distortion with pressure. The increase is likely to be small since $\partial\delta_o/\partial P$ is also small (see above), but the steep slope in that region of the reduction curve produces a relatively large increase in $\Delta E_Q$ with small distortion increase for the M1 site. In contrast, the position of the M2 site on the reduction function curve implies that increasing pressure produces a decrease in $\Delta_1$. This is consistent with $\partial\delta_o/\partial P$ results above which also suggest a change in distortion as well as compression of the M2 site in the P2$_1$/c phase with increasing pressure.

There is a large change in $\Delta E_Q$ for the M1 site between the P2$_1$/c and C2/c phases of clinoferrosilite. This is surprising considering the results of structure refinements that show negligible change in bond lengths and site distortion of the M1 site between the two polymorphs (HUGH-JONES *et al.*, 1994). But $\Delta E_Q$ is sensitive not only to the nearest neighbour coordination shell, but also to the next-nearest neighbour shell, which includes the iron atoms in M2 sites (the M1 and M2 octahedra share common edges). It is therefore likely that the significant change in M2 site geometry in the C2/c phase compared to the P2$_1$/c phase is reflected in $\Delta E_Q$ for the M1 site. The decrease in $\Delta E_Q$ for the M2 site between the P2$_1$/c and C2/c phases would appear to suggest an increase in $\Delta_1$ according to Fig. 3a, but we know from single crystal structure refinements that the distortion of the M2 site is lower in the C2/c structure than in the P2$_1$/c structure (HUGH-JONES *et al.*, 1994). One possibility is that the change in $\Delta_1$ is so large that the value for the P2$_1$/c phase moves to the left side of the reduction function maximum in Fig. 3a, where $\Delta E_Q$ decreases with decreasing $\Delta_1$. Another explanation, which is probably more likely, is that the change in bonding of the M2 site is so large between the P2$_1$/c and C2/c structures that Fig. 3a cannot be used for both phases. This is consistent with structure refinements that show that the P2$_1$/c → C2/c transition involves breaking of one of the M2—O bonds in the P2$_1$/c structure and reconstruction at a different location in the C2/c structure (ANGEL *et al.*, 1992; HUGH-JONES *et al.*, 1994).

For the C2/c phase, $\Delta E_Q$ increases with increasing pressure for both the M1 and M2 sites, where the slope for the M2 site is significantly greater than the slope for the M1 site (Fig. 2 and Table 2). Since $\partial\Delta E_Q/\partial P$ for the M2 site in the C2/c structure is identical within experimental error to the value for the P2$_1$/c structure (Table 2), this would suggest a similar change in $\Delta_1$ for the M2 site in both structures as a function of pressure.

The hedenbergite structure provides an interesting comparison for the clinoferrosilite data. In hedenbergite Ca occupies the M2 site, which is eight-coordinated and very distorted compared to the M2 sites in both clinoferrosilite polymorphs. The signs of $\partial\Delta E_Q/\partial P$ are opposite for the M1 site in the hedenbergite structure compared to the M1 site in the $P2_1/c$ phase (Table 2). According to the INGALLS (1964) model and Fig. 3a, this would imply that the distortion of the M1 site in hedenbergite decreases with increasing pressure. ZHANG and HAFNER (1992) reached the same conclusion based on a similar analysis. The values of $\partial\delta_c/\partial P$ are identical for the two phases, implying that compression of the octahedra with pressure is similar (see above). One explanation for the opposite slopes might be the effect of next-nearest neighbours (i.e. the different M2 sites) on $\partial\Delta E_Q/\partial P$.

### *Comparison of clinoferrosilite with orthoferrosilite*

The Mössbauer parameters of orthoferrosilite (DOWTY and LINDSLEY, 1973) are given in Table 1 for comparison with the $P2_1/c$ and $C2/c$ phases of clinoferrosilite. The centre shifts are nearly identical: differences are close to the experimental error and are too small to interpret with the qualitative models used in this paper. In contrast, there are significant differences in $\Delta E_Q$. The greatest difference is in values for the M1 site, which vary from a maximum of 2.904 mm/s for the $C2/c$ phase (extrapolated to zero pressure) to a minimum of 2.490 mm/s for orthoferrosilite (Table 1). As discussed above, according to the INGALLS (1964) model the value of $\Delta E_Q$ is highly sensitive to the distortion due to the steep slope of the reduction function in that region. Differences in the distortion may reflect variation in next-nearest neighbour coordination (M2 sites) at least as much as they reflect variation in M1 site coordination between structures. Values for $\Delta E_Q$ of M2 sites vary less between the different structures (Table 1), which is consistent with the position of the M2 site on the reduction function plot in the INGALLS (1964) model (Fig. 3b). The nearly identical values for $\Delta E_Q$ corresponding to the M2 site in the $C2/c$ and orthoferrosilite polymorphs is consistent with structure refinements of HUGH-JONES *et al.* (1994) that show identical size and only small differences in distortion for the M2 sites in these two polymorphs.

## CONCLUSIONS

Mössbauer spectra have been recorded of clinoferrosilite as a function of pressure. The relative change in hyperfine parameters has been interpreted in terms of qualitative models that provide insight into changes in the electronic and structural environment of the iron atoms, both as a function of pressure and through the phase transition from the $P2_1/c$ to the $C2/c$ structure.

From the perspective of Mössbauer spectroscopy, the M1 and M2 sites behave quite differently under pressure in the $P2_1/c$ structure. For the M1 site there is only a small change in electronic structure: a slight increase in covalency of the Fe—O bonds and a small increase in the ground-state splitting. The latter is probably due to changes in the next-nearest neighbour environment (i.e. the M2 atoms). For the M2 site the changes are greater: the orbital occupation changes (e.g. transfer of electron density from the iron 4s to 3d orbitals) in addition to a probable increase in covalency of Fe—O bonds, and the ground-state splitting likely decreases. Due to the difficulty of synthesising untwinned single crystals of the $P2_1/c$ phase, single-crystal refinements as a function of pressure are not available. If refinements could be performed, however, one would not expect to observe changes in the M1 site as a function of pressure beyond perhaps a slight shortening of Fe—O bond distances, but changes in the M2 site might be large enough to be observed as a change in site distortion as a function of pressure.

The M1 and M2 sites behave in a more similar manner as a function of pressure in the $C2/c$ structure. In addition to a probable increase in covalency of Fe—O bonds in both sites, there is a slight change in orbital occupation that decreases the s electron density. The ground-state splitting changes for both sites, and the magnitude of the change for the M2 site in the $C2/c$ structure appears to be similar to the change for the M2 site in the $P2_1/c$ structure. Recent refinements of the $C2/c$ phase show that the distortion of the M2 site decreases with increasing pressure to 6.5 GPa (HUGH-JONES, 1995), which is consistent with the above observation.

The M1 and M2 sites behave quite differently through the phase transition from the $P2_1/c$ to the $C2/c$ structure. The M1 site shows no change in covalency or orbital occupation, and a small increase in ground-state splitting; whereas the M2 site undergoes a change in bonding as well as a change in ground-state splitting. These results are consistent with single-crystal refinements of the

$P2_1/c$ phase at room pressure compared to the C2/c phase just above the transition—there is little change in bond lengths or site distortion of the M1 site, but an observable change in the M2 site (HUGH-JONES *et al.*, 1994).

The model used in the present work to interpret relative changes in quadrupole splittings gives a qualitative indication of the trends, but cannot provide quantitative information on observables such as ground-state splittings. Such data would be useful in the interpretation of optical spectra of clinoferrosilite (*e.g.* ROSS and SOWERBY, 1996) and in the prediction of properties such as Fe-Mg partitioning in solid solutions. In view of the large amount of information available on the crystal structure (HUGH-JONES *et al.*, 1994) and electronic structure (ROSS and SOWERBY, 1996), a valuable extension of this work would be a crystal field analysis of the high-pressure spectra similar to the work of LIN *et al.* (1993) or VAN ALBOOM *et al.* (1993), which would provide quantitative data on the detailed electronic structure of these phases.

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