

Crystal field spectrum of synthetic clinoferrosilite

NANCY L. ROSS and JOHN R. SOWERBY

Department of Geological Sciences, University College London, London WC1E 6BT, U.K.

Abstract—The optical and near-infrared absorption spectrum of synthetic clinoferrosilite, FeSiO_3 , was measured from 4,000 to 20,000 cm^{-1} at ambient conditions and at high pressure. Polarised and unpolarised spectra obtained from single crystals at ambient conditions display four absorption bands: (a) a very strong absorption band between 11,000–11,300 cm^{-1} that is attributed to Fe^{2+} in the M2 site (${}^3\text{A}_1 \rightarrow {}^5\text{A}_1$); (b) a strong peak near 10,100 cm^{-1} assigned to Fe^{2+} in M1 (${}^3\text{B}_{2g} \rightarrow {}^5\text{A}_{1g}$); (c) a weaker band near 8,200 cm^{-1} attributed to Fe^{2+} in M1 (${}^5\text{B}_{2g} \rightarrow {}^5\text{B}_{1g}$), and (d) a peak at 5,100 cm^{-1} due to Fe^{2+} in M2 (${}^3\text{A}_1 \rightarrow {}^5\text{B}_1$). The latter two bands are not observed in the spectra obtained from polycrystalline samples of clinoferrosilite. The estimated crystal-field splitting parameter (Δ_0) and crystal-field stabilisation energy (CFSE) of Fe^{2+} in the octahedral sites are: (i) M1: $\Delta_0 \approx 8,640$ cm^{-1} and CFSE $\approx 3,956$ cm^{-1} ; and (ii) M2: $\Delta_0 \approx 7,325$ cm^{-1} and CFSE $\approx 3,830$ cm^{-1} .

High-pressure spectra were collected between 0 and 5 GPa from a polycrystalline sample of clinoferrosilite. Between 0 and 1.85 GPa, the absorption bands near 11,000 cm^{-1} and 10,300 cm^{-1} increase at rates of 104 $\text{cm}^{-1}/\text{GPa}$ and 121 $\text{cm}^{-1}/\text{GPa}$, respectively. At 1.85 GPa, the absorption bands show a discontinuity corresponding to the transition from the structure with $\text{P}2_1/c$ symmetry to a high-density structure with $\text{C}2/c$ symmetry. Above the transition, the peak near 11,000 cm^{-1} increases to higher energy at a rate of 163 $\text{cm}^{-1}/\text{GPa}$, and the band near 10,300 cm^{-1} increases to higher energy at a rate of approximately 149 $\text{cm}^{-1}/\text{GPa}$. The transition is fully reversible and displays no detectable hysteresis.

INTRODUCTION

PYROXENES WITH composition $(\text{Mg,Fe})\text{SiO}_3$ are important constituents of the Earth's upper mantle (e.g., RINGWOOD, 1975). Until recently, the stable structure of $(\text{Mg,Fe})\text{SiO}_3$ pyroxene throughout the Earth's mantle has always been considered to be an orthopyroxene. However, high-pressure single-crystal X-ray diffraction experiments on low-clinoenstatite (ANGEL *et al.*, 1992) and clinoferrosilite (HUGH-JONES *et al.*, 1994), which both have $\text{P}2_1/c$ symmetry, combined with phase equilibria data for MgSiO_3 (PACALO and GASPARIK, 1990; KANZAKI, 1991) and FeSiO_3 (LINDSLEY, 1965; AKIMOTO *et al.*, 1965) have confirmed the stability of a high-pressure clinopyroxene phase with $\text{C}2/c$ symmetry (Fig. 1).

Orthoenstatite of composition MgSiO_3 transforms to this high-pressure clinoenstatite structure at pressures corresponding to a depth of 200–300 km within the Earth's upper mantle. ANGEL *et al.* (1992), for example, found that the transition from low-clinoenstatite to the high-density $\text{C}2/c$ structure occurs at approximately 8 GPa at room temperature, and that the $\text{C}2/c$ phase persists with release of pressure to approximately 5 GPa where it back-transforms to the $\text{P}2_1/c$ structure. The addition of iron in the structure has a dramatic effect on the $\text{P}2_1/c \rightleftharpoons \text{C}2/c$ transition. The transition pressure is lowered and little hysteresis is observed. In FeSiO_3 , HUGH-JONES *et al.* (1994) have bracketed the tran-

sition between 1.48 and 1.75 GPa at room temperature (Fig. 1).

Electronic absorption spectra provide information about the role of transition metals such as iron in mineral structures not obtainable through other methods (e.g., BURNS, 1993). Although many optical and near-infrared absorption spectra of natural and synthetic orthoferrosilites have been reported (WHITE and KEESTER, 1966; BANCROFT and BURNS, 1967; MAO and BELL, 1971; RUNCIMAN *et al.*, 1973; GOLDMAN and ROSSMAN, 1976, 1977; and 1979; LANGER and ABU-EID, 1977; ROSSMAN, 1980 and 1988; STEFFEN *et al.*, 1988; BURNS, 1993), none have been described for clinoferrosilite. We report here the first electronic absorption spectra of clinoferrosilite and compare it with spectra of natural and synthetic orthoferrosilites. In addition, spectra collected *in situ* at high pressure are described and the effect of the $\text{P}2_1/c \rightleftharpoons \text{C}2/c$ transition on the crystal field spectrum of FeSiO_3 .

EXPERIMENTAL METHOD

Clinoferrosilite was synthesised at 8 GPa and 1200°C in a multianvil press at the Bayerisches Geoinstitut. Further details of the sample assembly and experimental run are described in WOODLAND and O' NEILL (1993) and HUGH-JONES *et al.* (1994). Compositional analyses using energy-dispersive X-ray analysis with a Phillips CM20 FEG transmission electron microscope at the Bayerisches Geoinstitut indicated that the sample was pure endmember FeSiO_3 and contained no impurities. Mössbauer experiments performed by C. McCammon on the clinofer-

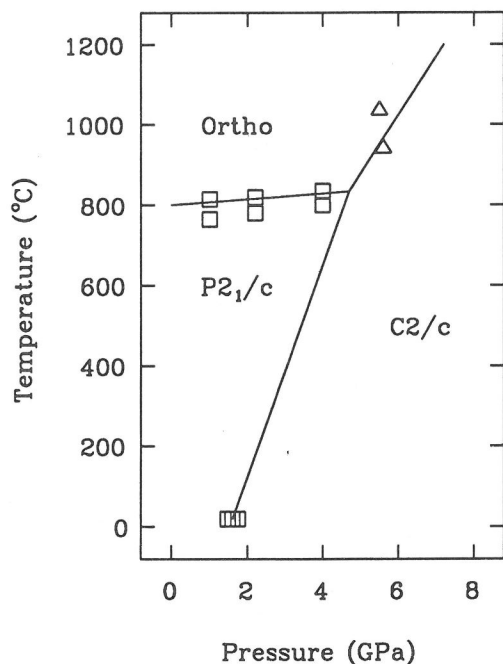


FIG. 1. Phase diagram of FeSiO₃ as postulated by HUGH-JONES *et al.* (1994) with their reversal of P2₁/c = C2/c at 298K (squares). Also shown are results from LINDSLEY's (1965) reversals (squares), and AKIMOTO *et al.*'s (1965) data (triangles).

rosilite crystals displayed no peaks that could be attributed to Fe³⁺, implying that the concentration of Fe³⁺ in the sample was less than 0.8% (HUGH-JONES *et al.*, 1994).

Optical and near-infrared absorption spectra were collected at room pressure from single crystals of clinofersilite in the range from 4,000 to 20,000 cm⁻¹ using a Bruker IFS HR high-resolution FTIR spectrometer equipped with a Bruker IR microscope at the Bayerisches Geoinstitut. Typically, two hundred scans with 4 cm⁻¹ resolution were accumulated between 4,000 to 10,000 cm⁻¹ with a CaF₂ beamsplitter, tungsten source and MCT detector. Between 9,000 and 15,000 cm⁻¹, two hundred scans were collected with 8 cm⁻¹ resolution using CaF₂ and quartz beamsplitters, tungsten source and Si diode detector, and, in the region from 12,500 to 20,000 cm⁻¹, a quartz beamsplitter, xenon arc source and Si diode detector were used. Spectra were merged and baseline-corrected to produce the final spectrum. Unpolarised spectra collected on different crystals in different orientations yielded similar spectra. Polarised spectra were collected from the (100) face of a doubly-polished euhedral single crystal with dimensions of 100 × 80 × 30 μm using a 60 μm diameter beam.

Spectra were collected between 0 and 5 GPa from a polycrystalline sample of clinofersilite at University College London using a Bruker IFS88 FTIR spectrometer. A thin film of powdered sample was loaded into a Diacell Products lever-arm diamond anvil cell (DAC) with a 4:1 mixture of methanol-ethanol as the pressure-transmitting medium. A small ruby chip was also included in the cell for pressure determination by measuring the shift of R₁

fluorescence peak with pressure (MAO *et al.*, 1986). For each spectrum, five hundred scans with 4 cm⁻¹ resolution were accumulated in the spectral ranges 4000 to 9000 cm⁻¹ (CaF₂ beamsplitter, tungsten source, MCT detector), and from 9000 to 20,000 cm⁻¹ (quartz beamsplitter, tungsten source, Si diode detector).

RESULTS AND DISCUSSION

Single crystal spectra at room pressure

The merged, unpolarised spectrum from the doubly-polished single crystal of clinofersilite is shown in Fig. 2. The spectrum is dominated by a strong absorption band near 10,500 cm⁻¹ with a shoulder at approximately 8,000 cm⁻¹ and a moderately intense band near 5,000 cm⁻¹. In order to investigate the fine structure of the crystal field, peaks with Gaussian components were fit to the spectra. A minimum of four peaks is required to obtain a reasonable fit to the spectrum. The refined peak positions are 10,926 cm⁻¹, 10,026 cm⁻¹, 8,166 cm⁻¹, and 5,081 cm⁻¹ with widths of 2,366 cm⁻¹, 1,006 cm⁻¹, 1,445 cm⁻¹, and 1,149 cm⁻¹, respectively (Fig. 2). No evidence for any charge-transfer bands was observed in any of the spectra collected which is consistent with the lack of evidence for any Fe³⁺ from the Mössbauer spectra.

The observed absorption bands of clinofersilite correspond well with spin-allowed Fe²⁺ bands observed in the electronic of natural and synthetic orthoferrosilites (MAO and BELL, 1971; GOLDMAN and ROSSMAN, 1977 and 1979; LANGER and ABUEID, 1977; ROSSMAN, 1980 and 1988; STEFFEN *et al.*, 1988; BURNS, 1993). The crystal field spectra arise from electronic transitions among the partially-filled d orbitals of the Fe²⁺ cations occupying six-coordinated sites in the orthopyroxene structure. The orthopyroxene structure contains single-chains of corner-sharing [SiO₄] tetrahedra running parallel to the c-axis which are cross-linked by cations located in sites designated as M1 and M2. Although the M1 site has site symmetry C₁, it is only slightly distorted from octahedral symmetry and is usually approximated with O_h symmetry. STEFFEN *et al.* (1988), however, have shown that the M1 octahedron is better approximated with D_{4h} symmetry because of the observed quadrupole splitting in the Mössbauer spectra of orthoferrosilite. The M2 site also has site symmetry C₁, but it is much more distorted than the M1 site. It is generally agreed that the effective symmetry of the M2 site is C_{2v} (*e.g.*, ROSSMAN, 1988).

In order to aid in the band assignments, polarised spectra from the (100) face of the doubly-polished single crystal of clinofersilite were collected parallel and perpendicular to its c-axis (Fig. 3). The

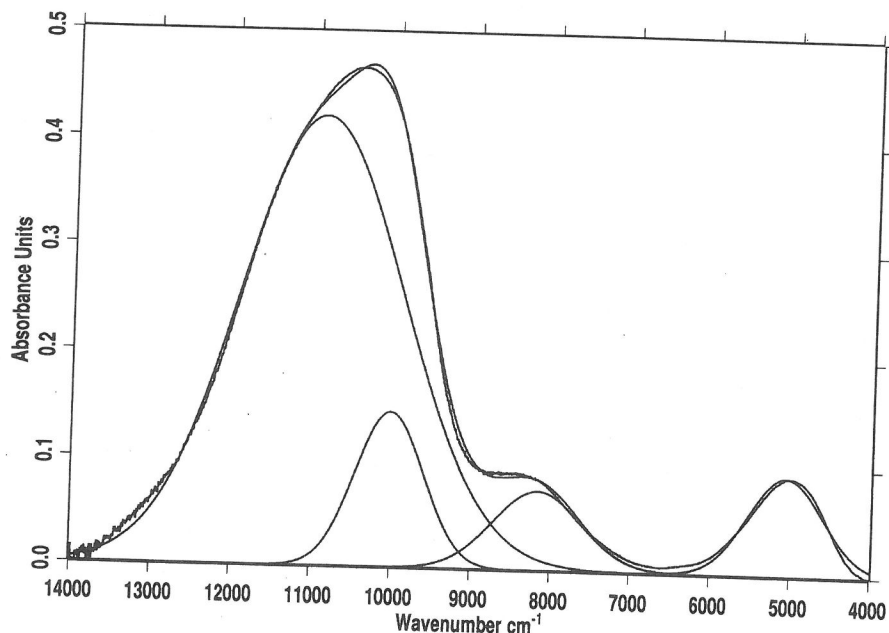


FIG. 2. Unpolarised optical and near infrared absorption spectrum from the (100) face of a doubly-polished ($30\ \mu\text{m}$ thick) single-crystal of clinoferrosilite after subtraction of an almost linear background. Deconvolution into four Gaussian components and the resulting simulated profile are also shown.

polarised spectrum collected parallel to the c -axis is approximately 50% weaker than the one collected perpendicular to the c -axis. Three peaks with Gaussian components were fit to the spectrum collected parallel to the c -axis as shown in Fig. 3a. The refined peak positions are $10,290\ \text{cm}^{-1}$, $8,200\ \text{cm}^{-1}$ and $5,050\ \text{cm}^{-1}$. This spectrum is similar to the γ spectrum of natural and synthetic orthoferrosilites. MAO and BELL (1971), for example, observed bands at $10,549\ \text{cm}^{-1}$, $8,333\ \text{cm}^{-1}$, and $4,878\ \text{cm}^{-1}$ in the γ spectrum of a synthetic crystal of pure endmember orthoferrosilite. BURNS (1993) reported bands in the γ spectra of two orthopyroxenes, enstatite $\text{Fs}_{14.5}$ and ferrosilite $\text{Fs}_{86.4}$, at approximately $11,000\ \text{cm}^{-1}$, $8,500\ \text{cm}^{-1}$ and $5,300\ \text{cm}^{-1}$ with the absorption band at $8,500\ \text{cm}^{-1}$ becoming more prominent in the Fe^{2+} -rich sample. The spectrum of clinoferrosilite collected perpendicular to the c -axis was also deconvoluted into three Gaussian components shown in Fig. 3b. The spectrum is dominated by an intense absorption band at $11,310\ \text{cm}^{-1}$ with less intense bands at $10,080\ \text{cm}^{-1}$ and $5,140\ \text{cm}^{-1}$. MAO and BELL (1971) measured a combined α and β spectrum that has features similar to this spectrum. The $\alpha + \beta$ spectrum is much stronger than the γ spectrum and is dominated by an intense absorption band at $10,627\ \text{cm}^{-1}$

and a less intense band at $4,878\ \text{cm}^{-1}$. In the polarised spectra of natural ferrosilites (e.g., BURNS 1993), the α spectrum is dominated by an intense band at approximately $10,700\ \text{cm}^{-1}$ and the β spectrum generally contains moderately intense bands near $11,000\ \text{cm}^{-1}$ and $5,000\ \text{cm}^{-1}$.

The strong correspondence between the electronic spectra of clinoferrosilite and orthoferrosilite is due to their similar structures. The γ spectrum of clinoferrosilite resembles that of orthoferrosilite because the chains of SiO_4 tetrahedra cross-linked by strips of edge-sharing M1 and M2 octahedra run parallel to the c -axis in both structures (e.g., CAMERON and PAPIKE, 1980). In addition, the average bond distances and distortions in the M1 and M2 sites of the two structures are almost identical (Table 1). The average Fe—O bond lengths for the M1 and M2 sites in clinoferrosilite are $2.137\ \text{\AA}$ and $2.224\ \text{\AA}$, respectively, compared with $2.135\ \text{\AA}$ and $2.228\ \text{\AA}$ in orthoferrosilite, respectively (BURNHAM, 1966; SUENO *et al.*, 1976). The M1 sites in both structures are close to regular octahedra and have similar quadratic elongation (QE) parameters (Table 1). The M2 sites are much more distorted with QE values of 1.0641 for clinoferrosilite and 1.0706 for orthoferrosilite (BURNHAM, 1966; SUENO *et al.*, 1976).

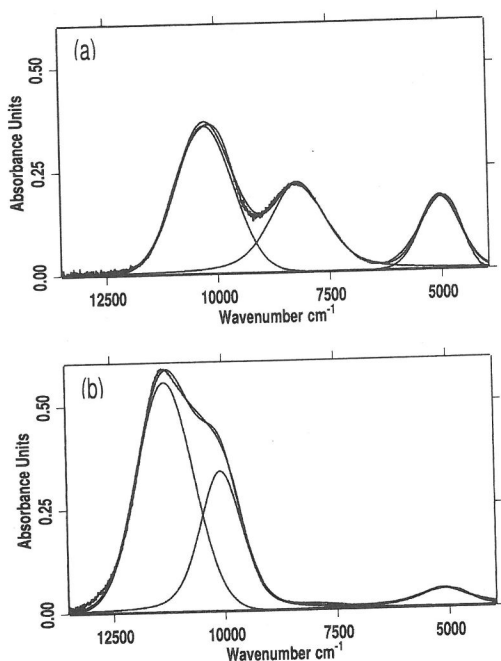


FIG. 3. Polarised optical and near infrared absorption spectra of the same crystal in Fig. 2 collected (a) parallel to the *c*-axis and (b) perpendicular to the *c*-axis. Deconvolution of both spectra into three Gaussian components and the resulting simulated profile are also shown.

Given the similarity between the crystal field spectra clinoferrosilite spectra and orthoferrosilite, tentative band assignments for the Fe^{2+} crystal field spectra of clinoferrosilite can be made using the band assignments of orthoferrosilite as a guide. Figure 4 shows schematic 3d orbital energy level diagrams for Fe^{2+} ions in the M1 and M2 sites of clinoferrosilite constructed following BURNS' (1993) and STEFFEN *et al.*'s (1988) analyses of or-

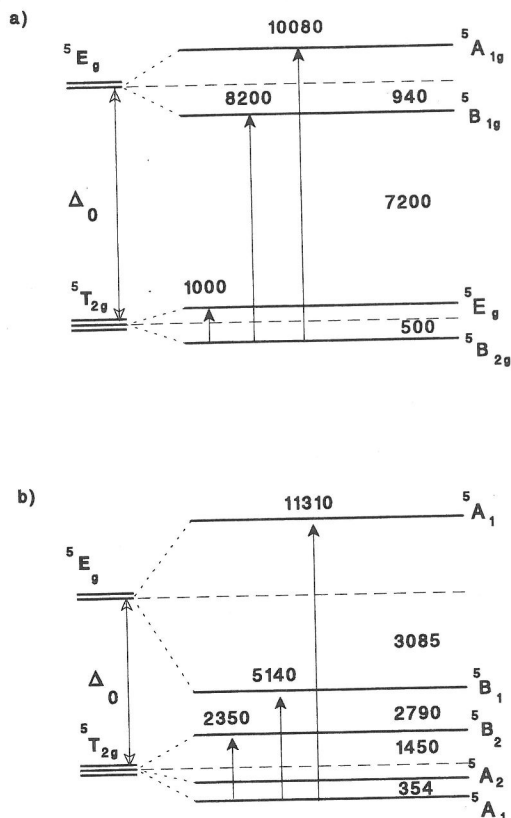


FIG. 4. Schematic 3d orbital energy level diagrams for Fe^{2+} ions in clinoferrosilite on (a) M1 site and (b) M2 site. Observed transitions in clinoferrosilite (Fig. 3) are indicated.

thoferrosilite. We assign the strong $11,310\text{ cm}^{-1}$ band (Fig. 3b) to ${}^5\text{A}_1 \rightarrow {}^5\text{A}_1$ (Fe^{2+} in M2) and the less intense band at $10,080\text{ cm}^{-1}$ (Fig. 3a) to ${}^5\text{B}_{2g} \rightarrow {}^5\text{A}_{1g}$ (Fe^{2+} in M1) in agreement with MAO

Table 1. Crystal chemical data determined at room pressure for clinoferrosilite and orthoferrosilite and data for high-density clinoferrosilite determined at 1.87 GPa

COMPOUND:	Clinoferrosilite	Orthoferrosilite	High-density Clinoferrosilite
Space Group:	$P2_1/c$	Pbca	$C2/c$
M1 Site:			
$\langle \text{Fe-O} \rangle$ (Å)	2.137	2.135	2.14
QE^1	1.0091	1.0087	1.0083
M2 Site:			
$\langle \text{Fe-O} \rangle$ (Å)	2.224	2.228	2.18
QE^1	1.0641	1.0706	1.0182
REFERENCES:	BURNHAM (1966)	SUENO <i>et al.</i> (1976)	HUGH-JONES <i>et al.</i> (1994)

¹ QE is the quadratic elongation parameter as defined by ROBINSON *et al.* (1971).

and BELL (1971) and STEFFEN *et al.* (1988). The band at 5,140 cm⁻¹ (Fig. 3b) is assigned to the ⁵A₁ → ⁵B₁ transition of Fe²⁺ in M2 octahedra, and the band at 8,200 cm⁻¹ (Fig. 3a) is attributed to the ⁵B_{2g} → ⁵B_{1g} transition of Fe²⁺ in M1 octahedra. In order to estimate the crystal field splitting parameter (Δ₀) and crystal field stabilisation energy (CFSE) for Fe²⁺ in the M1 and M2 sites, the splitting of the lower level t_{2g} orbitals is needed. Since the splittings of the lower t_{2g} orbitals for the M1 and M2 sites are unknown, we follow BURNS' (1993) approximation. For the M1 site, a small value of 500 cm⁻¹ is assumed since the M1 coordination polyhedron is not significantly distorted from octahedral symmetry. For the M2 site, lower-level splittings of 2,350 cm⁻¹ and 354 cm⁻¹ determined for enstatite (GOLDMAN and ROSSMAN, 1977 and 1979; ROSSMAN, 1988) are assumed and applied to clinoferrosilite. Values of Δ₀ and CFSE for Fe²⁺ in the two sites are therefore estimated to be:

$$\text{M1 site: } \Delta_0 = 8640 \text{ cm}^{-1};$$

$$\text{CFSE} = 0.4\Delta_0 + 500 = 3956 \text{ cm}^{-1}$$

$$\text{M2 site: } \Delta_0 = 7325 \text{ cm}^{-1};$$

$$\text{CFSE} = 0.4\Delta_0 + 900 = 3830 \text{ cm}^{-1}$$

These values are compared with natural and synthetic orthoferrosilites in Table 2. Both Δ₀ and CFSE of Fe²⁺ in the M1 site of clinoferrosilite are less than those of orthoferrosilite whereas Δ₀ and CFSE of Fe²⁺ in the M2 site are greater. Thus our approximations suggest that the difference in CFSE between the M1 and M2 sites in clinoferrosilite is less than those found in orthoferrosilites. These results also suggest that the splitting of the e_g orbitals of the M1 and M2 sites in clinoferrosilite, 1,880 cm⁻¹ and 6,170 cm⁻¹, respectively, differ from those observed in orthoferrosilites which typically have splittings of 2,200 cm⁻¹ and 5,800 cm⁻¹, respectively (MAO and BELL, 1971; BURNS, 1993).

This suggests that the distortion of the M2 site is greater in clinoferrosilite than orthoferrosilite and the M1 site is less distorted although the site distortions determined from X-ray structure refinements are virtually identical (Table 1). X-ray refinements, however, obtain an average of all the M1 and M2 octahedra whereas absorption spectroscopy sees more local detail of the octahedral sites.

Polycrystalline spectra at high pressure

Representative spectra collected from a polycrystalline sample in the diamond anvil cell are shown in Fig. 5. At 0.34 GPa (Fig. 5a), the spectrum contains a single, broad absorption feature at approximately 10,500 cm⁻¹ which corresponds to the strong absorption band observed at approximately the same position in the unpolarised single crystal spectrum (Fig. 2). Two peaks with Gaussian components were fit to the spectrum yielding refined positions of 10,876 cm⁻¹ and 10,245 cm⁻¹ and widths of 1,584 cm⁻¹ and 1,193 cm⁻¹, respectively. These compare well with the peak positions at 10,837 cm⁻¹ (width 1,523 cm⁻¹) and 10,110 cm⁻¹ (width 1,144 cm⁻¹) obtained from a polycrystalline spectrum at 0 GPa outside the DAC. Based on the discussion above, the peak at approximately 11,000 cm⁻¹ is most likely due to the ⁵A₁ → ⁵A₁ transition of Fe²⁺ in M2, and the peak near 10,300 cm⁻¹ can be attributed to the ⁵B_{2g} → ⁵A_{1g} transition of Fe²⁺ in M1. Refined peak positions for the other pressures are given in Table 3.

Figure 6 shows the shift of the peaks between 0 and 5 GPa. In general, both peaks show a shift to higher energy with increasing pressure. However, the shift of the peaks with pressure is not linear, but displays a discontinuity at approximately 1.85 GPa. In a high-pressure single-crystal X-ray diffraction study, HUGH-JONES *et al.* (1994) observed a reversible transition in FeSiO₃ between 1.48 and 1.75 GPa at room temperature from a structure with

Table 2. Comparison of Δ₀ and CFSE for clinoferrosilite (P2₁/c) with a synthetic orthoferrosilite (MAO and BELL 1971) and natural orthoferrosilite (BURNS 1993) calculated using the splittings of the lower level t_{2g} orbitals for the M1 and M2 sites described in the text

COMPOUND:	Synthetic FeSiO ₃ : Clinoferrosilite	Synthetic FeSiO ₃ : Orthoferrosilite	Natural FeSiO ₃ : Orthoferrosilite
M1 site:			
Δ ₀	8640 cm ⁻¹	8941 cm ⁻¹	9150 cm ⁻¹
CFSE	3956 cm ⁻¹	4076 cm ⁻¹	4160 cm ⁻¹
M2 site:			
Δ ₀	7325 cm ⁻¹	6852 cm ⁻¹	6900 cm ⁻¹
CFSE	3830 cm ⁻¹	3641 cm ⁻¹	3660 cm ⁻¹

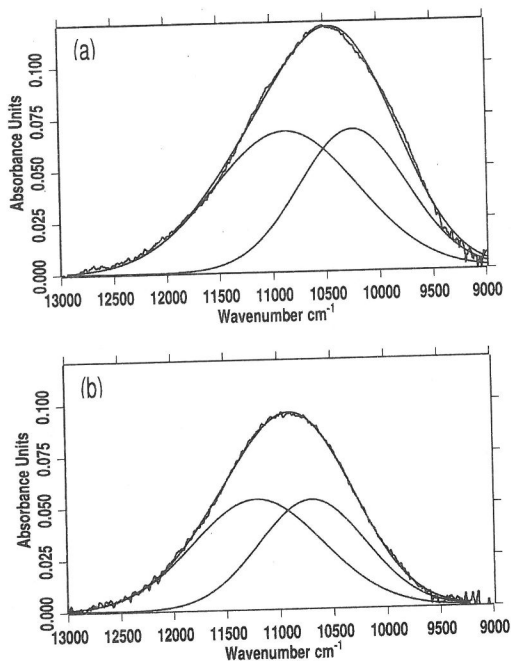


FIG. 5. Electronic absorption spectrum of polycrystalline FeSiO_3 clinoferrosilite collected at (a) 0.34 GPa and (b) 2.28 GPa after subtraction of a linear background. The two Gaussian components of both spectra and the resulting simulated profile are also shown.

$P2_1/c$ symmetry to one with $C2/c$ symmetry. This corresponds well with the results shown in Fig. 6. The slightly higher transition pressure observed in this study may be due to obtaining spectra from a polycrystalline sample rather than a single crystal. A representative spectrum of the high-density $C2/c$ phase collected at 2.28 GPa is shown in Fig. 5b.

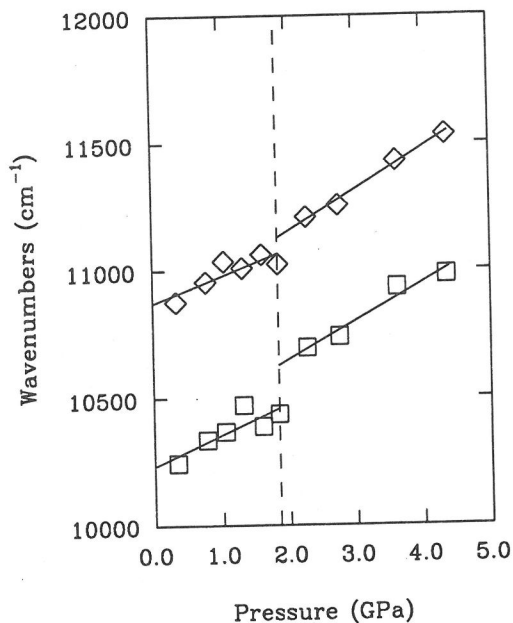


FIG. 6. Shift of the crystal-field bands of a polycrystalline sample of clinoferrosilite with pressure.

HUGH-JONES *et al.* (1994) determined that the transition is first-order in character accompanied by a 3% decrease in volume of the unit cell. The change in symmetry is related to the rotation of the chains of silicate tetrahedra. The low-pressure $P2_1/c$ structure consists of two distinct chains of tetrahedra, the A chain which is S-rotated and more extended than the B chain which is O-rotated and considerably kinked (BURNHAM, 1966). The edge sharing of the tetrahedra and the M2 site, resulting

Table 3. Optical absorption bands of clinoferrosilite as a function of pressure obtained by fitting two Gaussian components to the spectra. Peak #1 is attributed to the ${}^3B_{2g} \rightarrow {}^5A_{1g}$ transition of Fe^{2+} in M1 and Peak #2 is assigned to the ${}^5A_1 \rightarrow {}^5A_1$ transition of Fe^{2+} in M2. All peak positions and widths are given in cm^{-1} .

Pressure (GPa)	Peak #1		Peak #2	
	Position	Width	Position	Width
0.34	10,245	1,193	10,876	1,584
0.78	10,335	890	10,954	1,170
1.05	10,367	975	11,034	1,188
1.32	10,472	915	11,008	1,298
1.61	10,388	1,010	11,060	1,194
1.85	10,436	890	11,023	1,148
2.28	10,696	1,175	11,208	1,429
2.76	10,739	945	11,255	1,358
3.62	10,932	979	11,429	1,249
4.36	10,980	910	11,531	930

from the S-rotation of the A chain, makes the M2 site extremely distorted. At the transition pressure, the A chain rotates through a straight chain configuration, becoming O-rotated and geometrically equivalent to the B chain above the transition pressure (HUGH-JONES *et al.*, 1994). In the high-pressure C2/c structure, the tetrahedra of the A chain no longer share edges with the M2 sites and therefore the M2 octahedra are significantly smaller and less distorted than in the P2₁/c structure. The QE parameter of the M2 site changes from 1.0641 in the P2₁/c structure to 1.0182 in the C2/c structure, and the M1 site shows a slight decrease from 1.0091 to 1.0083 (Table 1). Corresponding changes are observed in the high pressure electronic spectra. Between 0 and 1.85 GPa, the peak near 11,000 cm⁻¹ attributed to the ⁵A₁ → ⁵A₁ transition of Fe²⁺ in M2, increases at a rate of 104 cm⁻¹/GPa. Above 1.85 GPa, however, the band increases at a rate of approximately 163 cm⁻¹/GPa (Fig. 6). The peak near 10,200 cm⁻¹ associated with ⁵B_{2g} → ⁵A_{1g} transition of Fe²⁺ in M1 also shows a change across the transition. Between 0 and 1.85 GPa, this band shifts to higher energy at a rate of approximately 121 cm⁻¹/GPa, and above the transition pressure, the band increases a greater rate of approximately 149 cm⁻¹/GPa. Both bands show a distinct break at 1.85 GPa (Fig. 6).

MAO and BELL (1971) studied the effects of pressure up to approximately 9.0 GPa on a polycrystalline sample of orthoferrosilite. The spectrum is similar to the spectra of the P2₁/c and C2/c polymorphs of FeSiO₃ (Fig. 5) in that it is dominated by a broad, absorption band near 10,700 cm⁻¹. All of these spectra resemble the α spectrum obtained from polarised studies of single crystals and therefore may indicate a preferred orientation of both polymorphs when loaded as polycrystalline aggregates in the diamond anvil cell. MAO and BELL (1971) also performed experiments on single crystals to 2.5 GPa in order to obtain better resolution of the crystal field bands. The absorption band at 10,627 cm⁻¹ corresponding to the ⁵A₁ → ⁵A₁ transition of Fe²⁺ in M2 shifts to higher energy at a rate of approximately 130 cm⁻¹/GPa which is intermediate between what we observed in the P2₁/c structure and the C2/c structure. The absorption band at 10,549 cm⁻¹ attributed to the ⁵B_{2g} → ⁵A_{1g} transition of Fe²⁺ in M1 shifts to higher energy at a rate of approximately 120 cm⁻¹/GPa which again is similar to what we observed in the P2₁/c structure but slightly less than what we observed in the C2/c structure. MAO and BELL (1971) also determined that the bands at 8333 cm⁻¹ (α spectrum) and 4878 cm⁻¹ (β spectrum) shift more rapidly with pressure

at rates of approximately 210 cm⁻¹/GPa and 280 cm⁻¹/GPa. As a result, the crystal field splitting of the e_g orbital group decreases with pressure for both M1 and M2, suggesting less distortion in the octahedral field at high pressure in orthoferrosilite. MAO and BELL (1971) also showed that Δ_o of M1 and M2 increases with pressure.

Single-crystal measurements at high pressure of clinoferrosilite are needed in order to determine the Δ_o and CFSE for the M1 and M2 sites of the high-density C2/c structure. However, we can make some predictions based on the available structural data of the C2/c structure from HUGH-JONES *et al.* (1994). In the C2/c structure at 1.87 GPa, the average Fe—O distance for the M2 site is 2.18 Å with a QE parameter of 1.0182 which compares with an average Fe—O distance of 2.224 Å and a QE of 1.0641 in the P2₁/c structure at ambient conditions (Table 1). Assuming a simple point charge model, Δ_o is proportional to the inverse fifth power of the interatomic metal-oxygen distance (*e.g.*, BURNS, 1993). Therefore Δ_o of the M2 site should increase from the P2₁/c structure to the C2/c structure. Since the average bond length and distortion of the M2 site in the C2/c structure are more similar to the M1 site than observed in either the P2₁/c or orthoferrosilite structures (Table 1), we expect that it will have crystal-field parameters closer to M1 than observed above. In addition, the decrease in the distortion of the M2 site will lead to a decrease in the splitting of the e_g orbitals as detected by MAO and BELL (1971) in their high pressure experiments of orthoferrosilite. A discontinuity should therefore be observed in the shift of the absorption band near 5,100 cm⁻¹ with pressure. In contrast, we predict smaller change in Δ_o and CFSE of the M1 site across the transition since there is little change in the average bond length and distortion of the octahedra between the two polymorphs (Table 1).

CONCLUSIONS

We have obtained the first crystal field spectra of clinoferrosilite from single crystals at ambient conditions and from a polycrystalline sample at high pressure. In general, the spectra are similar to orthoferrosilite with absorption bands near 11,000 cm⁻¹, 10,000 cm⁻¹, 8,200 cm⁻¹, and 5,100 cm⁻¹ that correspond to the spin-allowed transitions of Fe²⁺ on the M1 and M2 sites. Band assignments obtained from comparison of polarised single-crystal spectra of clinoferrosilite with orthoferrosilite suggest, however, that are subtle differences between the two polymorphs: (a) a greater splitting of the e_g orbitals of the M2 site in clinoferrosilite,

and (b) a smaller splitting of the e_g orbitals of the M1 site with smaller values of Δ_0 and CFSE than observed in natural and synthetic orthoferrosilites.

High-pressure spectra collected between 0 and 5 GPa from a polycrystalline sample of clinoferrosilite show a broad absorption band that can be fit with two Gaussian components corresponding to spin-allowed transitions of Fe^{2+} on the M1 and M2 sites. The shift of the peaks with pressure is not linear and displays a discontinuity at approximately 1.85 GPa where the structure transforms from $P2_1/c$ to $C2/c$ symmetry. The transition is reversible with no detectable hysteresis. Work is in progress to obtain more detailed crystal field spectra from single crystals of clinoferrosilite at high pressure. From these, we shall be able to determine Δ_0 and estimate the CFSE of the M1 and M2 sites as a function of pressure. The CFSE may be a contributing factor to why the $P2_1/c \rightleftharpoons C2/c$ transition in $FeSiO_3$ has little hysteresis but the analogous transition in $MgSiO_3$ has a hysteresis of approximately 3 GPa (ANGEL *et al.*, 1992).

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