

## Single crystal spectra of olivines in the range 40,000-5,000 $\text{cm}^{-1}$ at pressures up to 200 kbar

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### Abstract

Room temperature, unpolarized high pressure spectra of oriented sections (100) and (001) of olivine  $\text{Fa}_{10}$  and (010) and (001) of synthetic fayalite have been measured up to 200 kbar in a diamond anvil cell. To produce low pressure broadening of the calibrating ruby  $R_1$  line, polychlorotrifluoro-ethylene was used as embedding material.

For the olivine (100) plate, containing optical  $XY$ , a band at  $34,000 \text{ cm}^{-1}$  was seen to shift by about  $-5 \text{ cm}^{-1}/\text{kbar}$  to the red up to pressures of 100 kbar, and then to increase its shift rate to nearly  $-20 \text{ cm}^{-1}/\text{kbar}$ . No strong changes with pressure in absorption intensity between  $36,000$  and  $40,000 \text{ cm}^{-1}$  were observed for the (100) plate. Although the  $34,000 \text{ cm}^{-1}$  band is less prominent in the (001) plate, containing optical  $XZ$ , its pressure behavior was found to be similar to that of the (100) plate. With increasing pressure, particularly above 100 kbar, a loss of intensity near  $40,000 \text{ cm}^{-1}$  was seen in the plate. This intensity effect, combined with the movement of the  $34,000 \text{ cm}^{-1}$  band, leads to the creation of an absorption minimum at about  $35,000 \text{ cm}^{-1}$ .

For the fayalite (010) and (001) plates, containing the optical  $YZ$  and  $XZ$  directions respectively, an absorption edge shift of  $-20 \text{ cm}^{-1}/\text{kbar}$  ( $-24.8 \cdot 10^{-4} \text{ eV/kbar}$ ) up to pressures of approximately 100 kbar was observed. In agreement with Mao and Bell (1972), above this pressure the rate of movement of the edge was observed to dramatically increase, such that both plates became opaque at about 180 kbars. On the basis of the observations made for the olivine  $\text{Fa}_{10}$  spectra, it is likely that these strong effects in fayalite are due to the pressure behavior of the  $34,000 \text{ cm}^{-1}$  band, which, due to its very high intensity, is not directly accessible in the iron end member.

In the (010) and (001) sections of fayalite, spin-allowed dd bands of the  $\text{Fe}^{2+}$  at  $7,600$  and  $9,300 \text{ cm}^{-1}$  shifted to the blue with the rates of  $+14 \text{ cm}^{-1}/\text{kbar}$  and  $+16.3 \text{ cm}^{-1}/\text{kbar}$  and  $+12 \text{ cm}^{-1}/\text{kbar}$  and  $+12 \text{ cm}^{-1}/\text{kbar}$  respectively.

### Introduction

Earlier spectral studies of olivines in the pressure range up to about 50 kbar include those of Runcorn (1956), Balchan and Drickamer (1959), Pitt and Tozer (1970), Mao and Bell (1971), Shankland et al. (1974), and Abu-Eid (1976). For olivines with about 10 mole % fayalite end member, these studies revealed a red shift of an absorption edge and red and blue shifts for the spin allowed  $\text{Fe}^{2+}$  dd transitions. With the advent of optical techniques for pressures up to 300 kbar, Mao and Bell (1972) showed a spectacular red shift of an edge at pressures greater than 100 kbar on measuring powder spectra of fayalite.

In most of these experiments the influence of the crystal orientation was largely neglected and most

studies presented spectra only for energies below  $25,000 \text{ cm}^{-1}$ . Further, Smith and Langer (1982) found that, depending on the crystal orientation, there are difficulties in defining an uv-absorption edge below  $40,000 \text{ cm}^{-1}$  in olivines with mantle composition,  $\text{Fa}_{10}$ . In this paper, we extend our earlier work and are concerned with spectra of single crystal slices of olivine and fayalite in the spectral range  $40,000$  to  $5,000 \text{ cm}^{-1}$  and at nearly hydrostatic pressures up to 200 kbar.

### Experimental methods and samples studied

Room temperature high pressure spectra were measured using a type II diamond anvil optical cell, which has been fully described by Smith and Langer (1982). The gasket technique was employed in

conjunction with poly-chlorotrifluor-ethylene as embedding material. At pressures above 100 kbar, this material gives lower band half widths of the ruby  $R_1$  line than those found with other embedding materials (Smith and Langer, 1982). Pressures were calibrated by the ruby  $R_1$  line shift, which was measured in a Laser Raman spectrometer arrangement (Langer *et al.*, 1979). The data of Piermarini *et al.* (1975) and Mao and Bell (1976) were used to calibrate the pressures.

For the range 40,000 to 5,000  $\text{cm}^{-1}$ , spectra were scanned in an automated single beam microscope spectrometer (Langer and Frentrup, 1979) operating in a wavenumber step scanning procedure. UV transparent ultrafluars  $10\times$  (Zeiss) were used as objective and condenser. The diameter of the measuring area was 40  $\mu\text{m}$ . The single beam method overcomes the difficulty of base line problems brought about by the use of two diamond cells in double beam microspectrometers, since with the single beam the light path through the whole instrument including the diamonds is identical for the I and  $I_0$  measurements.

It is pointed out that, due to pressure induced birefringence of the diamond windows above certain pressures, the plane of polarization of the measuring radiation cannot be controlled with respect to the optical directions of the crystal under study (Smith and Langer, 1982). In the present paper, since polarized spectra at pressures above about 30 kbars could not be measured, unpolarized spectra of oriented crystal sections are reported.

Table 1 summarizes sources, chemical compositions, sizes and orientations of the single crystal slices studied. The crystallochemical formula for the fayalite sample was calculated on the assumption that the  $\text{Fe}^{3+}$  contents are introduced by the substitution



(Cemič *et al.*, 1980).

### Experimental results

High pressure spectra of olivine  $\text{Fa}_{10}$  and fayalite (Table 1) are shown in Figures 1 and 2 respectively. For the  $\text{Fa}_{10}$  olivine (001) plate, there is a decrease in absorption intensity near 40,000  $\text{cm}^{-1}$  with increasing pressures up to 90 kbar. Above 90 kbar, this effect becomes more prominent, occurring simultaneously with an increase in absorption near 32,200  $\text{cm}^{-1}$ . The two effects combine to create a window near 35,000  $\text{cm}^{-1}$ .

Table 1. Samples studied\*

Sample	Olivine $\text{Fa}_{10}$ F2	Fayalite F1
Source	large, idiomorphic crystal of gem quality from Seberget/Egypt	plate of a synthetically grown fayalite single crystal
Analyzed composition (wt.%)	SiO <sub>2</sub> 40.67 (59) MgO 49.53 (22) FeO 9.33 (47) MnO 0.35 (16) Fe <sub>2</sub> O <sub>3</sub> n.d. Cr <sub>2</sub> O <sub>3</sub> 0.024 (12)	30.01 (71) 0.010 (8) 67.75 (72) 0.68 (23) 1.38 (69) 0.038 (58)
Total	99.90	99.87
No. of points analyzed	8	10
Atoms per 4 oxygen atoms	Si 0.996 (8) Mg 1.810 (10) Fe <sup>2+</sup> 0.194 (6) Fe <sup>3+</sup> 2.011 Mn <sup>2+</sup> 0.007 (4) □	1.013 (4) 1.901 (33) 0.035 (17) 0.020 (7) 0.017 (9)
Means of orientation for optical spectroscopy	crystal morphology and optics	Laue photographs
Spectra are taken from plates	(001), t = 33 $\mu\text{m}$ (100), t = 29 $\mu\text{m}$	(001), t = 24 $\mu\text{m}$ (010), t = 30 $\mu\text{m}$

\*Analyses are mean values from a number of point analyses by a Cameca Camebax. The standard deviation of the last decimal point is given in brackets. The  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  ratio in fayalite was determined from Mössbauer spectra. n.d. = not determined. Thicknesses of samples, t, were directly measured with the microscope.

In the corresponding spectra of the (100) plate, no strong decrease in absorption near 40,000  $\text{cm}^{-1}$  is noted at pressures up to 160 kbar. An absorption shoulder near 34,000  $\text{cm}^{-1}$  was observed to increase in intensity with pressure and to move to lower energies. Although it is not certain, an additional band arising with pressure near 35,500  $\text{cm}^{-1}$  is possible.

In fayalite, for both the (010) and the (001) plates, the spectra showed a low energy shift of  $-20 \text{ cm}^{-1}/\text{kbar}$  ( $-24.8 \cdot 10^{-4} \text{ eV/kbar}$ ) at pressures up to 100 kbar (Fig. 3). At higher pressures, the edge invaded the visible range resulting in the samples becoming dark brown to opaque (Figs. 2 and 3). Figure 4 shows the dependence of the energy of the fayalite  $\text{Fe}^{2+}$  spin allowed dd bands with pressure. Because the Z spectrum gives the strongest absorption in the 12,000 to 5,000  $\text{cm}^{-1}$  range (Burns 1970 a, b), only small differences in pressure gradients of the component bands are observed for the YZ and XZ plates (Fig. 4). With the exception of the weak band at about 16,100  $\text{cm}^{-1}$  (shifting by  $-900 \text{ cm}^{-1}/100 \text{ kbar}$ ) no significant movements were detected for other weak components at 24,600, 22,000, and 20,000

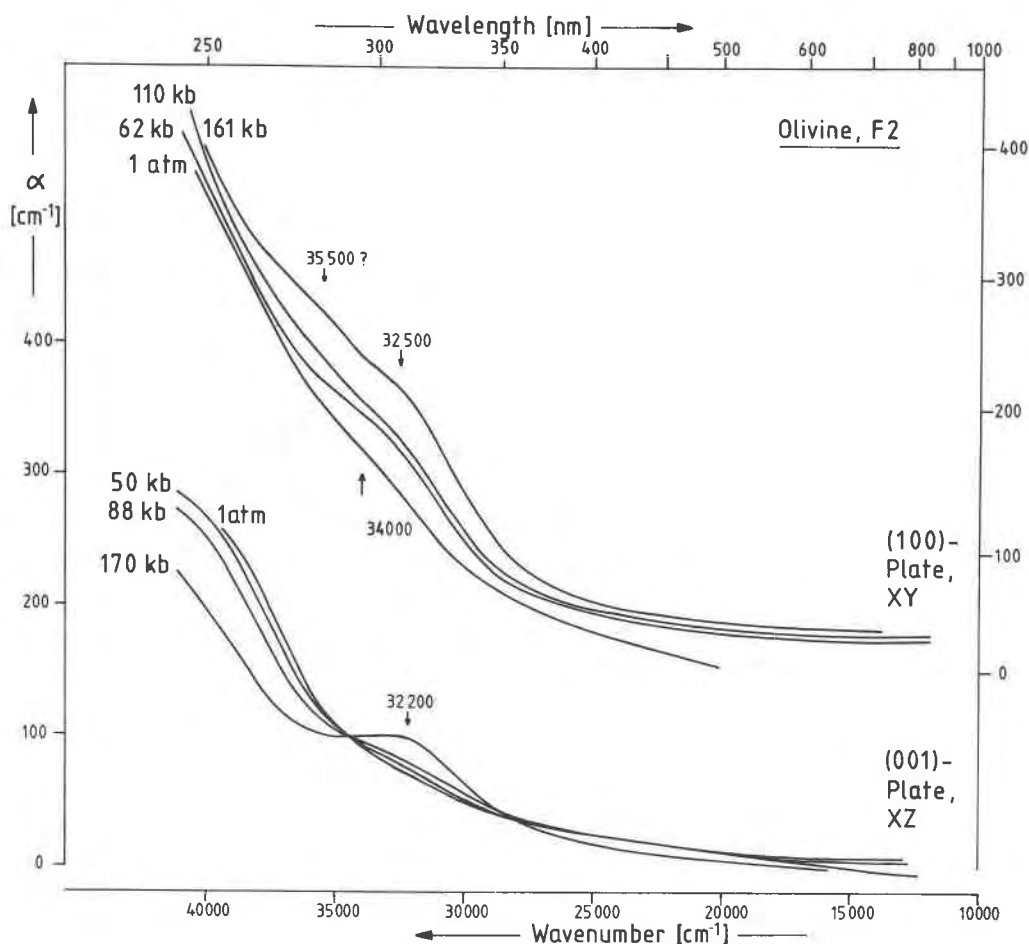


Fig. 1. Unpolarized high pressure spectra of oriented crystal sections of  $Fa_{10}$  olivine (Table 1) taken at room temperature. In the (001) section, note the presence of a window at  $35,000\text{ cm}^{-1}$  at pressures above 90 kbar.

$\text{cm}^{-1}$  (Fig. 2). These low intensity bands presumably result from spin-forbidden transitions of  $\text{Fe}^{2+}$ . Figure 2 shows further that with increasing pressure a band near  $5,500\text{ cm}^{-1}$ , with a relatively small half width of  $\sim 700\text{ cm}^{-1}$ , arises and shifts slightly to higher energies. The origin of this band is unknown and it is not ruled out that the band could be an artefact of experimental procedure, although no obvious error in measurement could be detected.

Further effects observed in our olivine and fayalite samples under pressure and after release of pressure are of interest:

#### Fayalite F1

(1) At pressures near 100 kbar, the crystal slices were observed to increase in the two longer dimensions. This increase implied that the crystalline material had started to creep. This deformation is

anisotropic. We noted, however, that after the run, the gasket thickness, although significantly reduced (from  $270\text{ }\mu\text{m}$  to approx.  $50\text{ }\mu\text{m}$ ) was larger than the sample thickness.

(2) The effect of pressure on the optical transmittance of fayalite was not found to be entirely reversible, with samples remaining light brown in color weeks after pressure release. The spectra showed an edge extending into the visible. The affect of pressure on the spin allowed bands appeared to be reversible, the reversibility being clearer for the  $7,600\text{ cm}^{-1}$  band (lying further from the edge) than for the  $9,300\text{ cm}^{-1}$  absorption.

(3) The sample after release of pressure was full of cracks and fissures. Due to light scattering, these fissures may be partially or wholly accountable for the above noted light brown color of the sample. The other possibility is that an irreversible phase

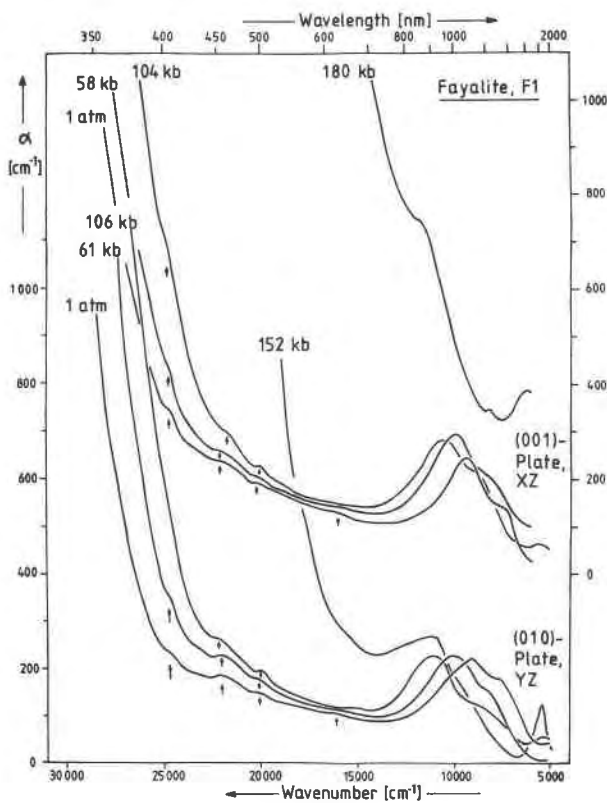


Fig. 2. Unpolarized high pressure spectra of oriented crystal sections of fayalite (Table 1) taken at room temperature. The edge is defined as the wave-number position at which the linear absorption coefficient,  $\alpha = \log(I_0/I)/d$ , is  $800 \text{ cm}^{-1}$  (i.e., a thin section of  $30 \mu\text{m}$  thickness has transmittance 0.4%).

transition occurred in the fayalite although no first order effects were found by Mao and Bell (1972). However, from our recent high pressure work on garnets, it seems likely that the light brown color noted for the fayalite sample after release of pressure was due to light scattering through cracks and fissures and not due to a phase transition.

#### Olivine F2

(1) Repeated measurements of spectra at 1 atm. and high pressures led to good reproducibility of movement of the  $34,000 \text{ cm}^{-1}$  band but showed variations in its intensity. That band intensity versus pressure dependencies could only be qualitatively and not quantitatively assessed may be due to pressure being slightly non-hydrostatic, implying slightly different thicknesses of samples at the same pressure in different runs, or simply that the transmittance of the diamond windows (difficult to keep entirely free from foreign matter) was variable from

run to run leading to different degrees of scattering. It seems likely that small intensity/pressure dependencies could be difficult to assess with diamond anvil techniques.

#### Discussion

Room temperature 1 atm. polarized spectra of  $\text{Fa}_{10}$  olivine show a prominent shoulder ( $Y > X \gg Z$ ) at  $34,000 \text{ cm}^{-1}$  (Runciman *et al.*, 1973; Smith and Langer, 1982). This shoulder increases strongly in intensity with increasing fayalite content of olivine solid solution (Smith and Langer, 1981).

The high pressure changes in the UV of the  $\text{Fa}_{10}$  olivine  $XY$  and  $XZ$  spectra (Fig. 1) may be easily explained by a red shift and a possible intensity increase of this  $34,000 \text{ cm}^{-1}$  band. The "window effect" in the  $XZ$  spectra is a combination of the red shift of the  $34,000 \text{ cm}^{-1}$  band and either a blue shift of a  $39,500 \text{ cm}^{-1}$  shoulder ( $Z > X > Y$ ), found by Runciman *et al.* (1973), or a decrease in its intensity.

As noted above, the  $34,000 \text{ cm}^{-1}$  band at 1 atm increases strongly in intensity with increasing fayalite content of the olivine solid solution (Smith and Langer, 1981). This results in an absorption edge in pure fayalite. Assuming it is not a coincidence that the strong shift effects in both  $\text{Fa}_{10}$  olivine and fayalite occur at pressures above about 90 kbar, then the dramatic pressure effect on the absorption edge of the fayalite sample (Fig. 3) may simply be

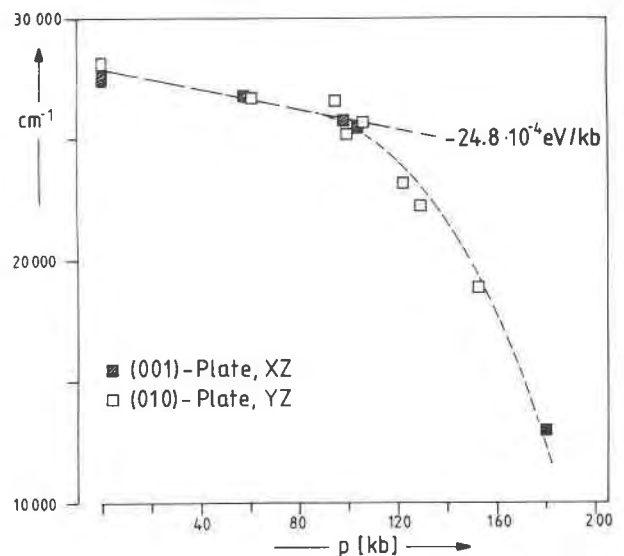


Fig. 3. Red shift of the absorption edge in fayalite crystal sections (definition of edge *cf.* Fig. 2).

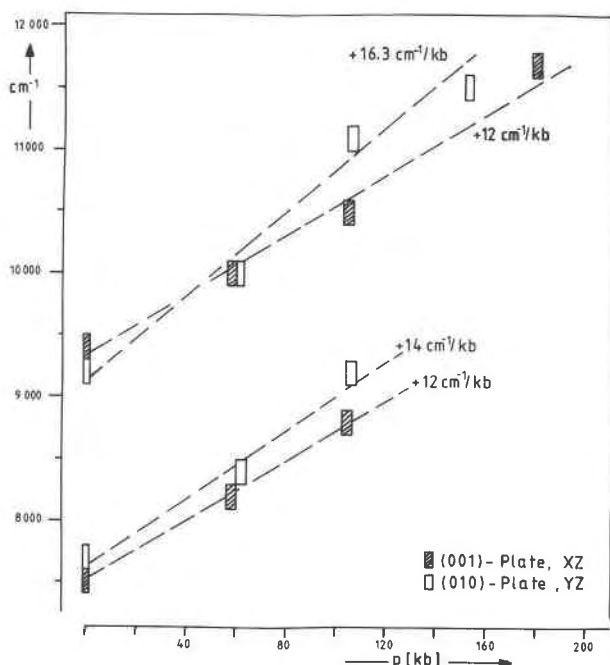


Fig. 4. Blue shifts of spin-allowed  $\text{Fe}^{2+}$  dd transitions in fayalite.

explained by the pressure behavior of the  $34,000\text{ cm}^{-1}$  band.

The high energies of the  $39,500$  and  $34,000\text{ cm}^{-1}$  components make it likely that these bands originate from O-Fe ligand to metal charge transfer transitions in either  $(\text{Fe}^{2+}\text{O}_6)^{10-}$  or  $(\text{Fe}^{3+}\text{O}_6)^{9-}$  octahedra or both (Tossel *et al.*, 1973, 1974; Tossel, 1976). That the latter are present in our fayalite sample is evident from the Mössbauer results (Table 1). Attempts to clarify as to whether the bands at  $34,000$  and  $39,500\text{ cm}^{-1}$  are connected with O- $\text{Fe}^{2+}$  or O- $\text{Fe}^{3+}$  CT transitions by tempering both fayalite and  $\text{Fa}_{10}$  olivine samples at reducing and oxidizing oxygen fugacities (QFI and QFM buffer,  $800^\circ\text{C}/21\text{ d}$  and  $850^\circ\text{C}/5\text{ d}$  respectively) proved inconclusive since no changes in the spectra were observed.

Tossel (1976) reported that  $\text{Fe}^{2+}$  ligand to metal transitions  $\epsilon_{1t_{2g\downarrow}} \rightarrow \epsilon_{2t_{2g\downarrow}}$  and  $\epsilon_{2t_{2g\downarrow}} \rightarrow \epsilon_{2t_{2g\uparrow}}$  first increase and then decrease in energy with decreasing  $\text{Fe}^{2+}$ -O distance, while the  $\text{Fe}^{3+}$  ligand to metal transition  $\epsilon_{2t_{2g\downarrow}} \rightarrow \epsilon_{2t_{2g\uparrow}}$  increases in energy with decreasing distance. As to whether these calculations are helpful in the interpretation of observed pressure movements of olivine UV component bands remains to be clarified.

The pressure shifts of the spin-allowed  $\text{Fe}^{2+}$  dd

transitions (Fig. 4) are in accordance with those found at lower pressures by Mao and Bell (1971) and Shankland *et al.* (1974). It should be noted that the gradients in Figure 4 do not change significantly up to pressures around  $150\text{ kbar}$  and that no pressure broadening of the  $\text{Fe}^{2+}$  bands was observed.

For forsterite, Hazen (1976) found that with increasing pressure up to  $50\text{ kbar}$  the mean M(1)-O and M(2)-O distances decrease by approximately  $1.95$  and  $0.75\%$  respectively. However, for fayalite, although the mean M(1)-O distance also decreased ( $-2.33\%$ ) with increasing pressure up to  $42\text{ kbar}$ , the mean M(2)-O distance was observed to increase by approximately  $7.04\%$  (Hazen, 1977).

The fayalite results of Hazen (1977) could present us with a slight problem. If we assume that the increase in the mean M(2)-O distance with pressure results in a decrease of the crystal field parameter  $\Delta_0$ , according to the general relation  $\Delta_0 \propto 1/R^5$ , then to account for the relatively strong blue shift with pressure of the  $\text{Fe}^{2+}$  (M2) spin allowed band at  $9,300\text{ cm}^{-1}$ , we have to assume a strong increase in octahedral distortion with pressure (*cf.* crystal field splitting diagrams of Burns, 1970a, b; and Runciman *et al.*, 1973). Such an increasing distortion should lead to an increasing splitting of either one or both of the  $t_{2g}$  and  $e_g$  levels which would then account for the above blue shift. Assuming that at  $170\text{ kbar}$ , the major splitting occurs between the  $t_{2g}$  levels (just as at  $1\text{ atm}$ ), then the large movement of the  $9,300\text{ cm}^{-1}$  band ( $2,300\text{ cm}^{-1}$  over  $170\text{ kbars}$ ) would indicate a splitting of  $\geq 5,000\text{ cm}^{-1}$  between the levels. One might then expect to observe a new band at energies  $\geq 5,000\text{ cm}^{-1}$  and, apart from the questionable absorption at  $5,500\text{ cm}^{-1}$ , none was observed. However, it is noted that a large splitting of the  $e_g$  levels could explain the absence of the band. The third possibility to interpret this blue shift is an increase in  $\Delta_0$  which does not appear to be compatible with the  $1/R^5$  relation on the basis of Hazen's (1977) results. In the first and third situations, the crystal field stabilization energy of  $\text{Fe}^{2+}$  in M(2) is likely to increase at a faster rate with pressure than that of  $\text{Fe}^{2+}$  in M(1), which was found to change by about  $100\text{ cm}^{-1}$  over a range of  $40\text{ kbar}$  (Abu-Eid, 1976). Therefore, it could be that the  $\text{Fe}^{2+}$  partition between M(1) and M(2) of the olivine structure may depend also on pressure, and not only on temperature and possibly on  $f_{\text{O}_2}$  (Nover and Will, 1981) conditions under which olivines have formed in nature.

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