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Single crystal spectra of olivines in the range 40,000-5,000 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 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, polychlortrifluor-ethylene was used as embedding material.

For the olivine (100) plate, containing optical XY, a band at 34,000 cm^{-1} was seen to shift by about -5 cm^{-1}/kbar to the red up to pressures of 100 kbar, and then to increase its shift rate to nearly -20 cm^{-1}/kbar. No strong changes with pressure in absorption intensity between 36,000 and 40,000 cm^{-1} were observed for the (100) plate. Although the 34,000 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 cm^{-1} was seen in the plate. This intensity effect, combined with the movement of the 34,000 cm^{-1} band, leads to the creation of an absorption minimum at about 35,000 cm^{-1}.

For the fayalite (010) and (001) plates, containing the optical YZ and XZ directions respectively, an absorption edge shift of -20 cm^{-1}/kbar ($-24.8 \cdot 10^{-4}$ 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 Fa_{10} spectra, it is likely that these strong effects in fayalite are due to the pressure behavior of the 34,000 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 Fe^{2+} at 7,600 and 9,300 cm^{-1} shifted to the blue with the rates of $+14$ cm^{-1}/kbar and $+16.3$ cm^{-1}/kbar and $+12$ cm^{-1}/kbar and $+12$ cm^{-1}/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 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 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 cm^{-1} in olivines with mantle composition, 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 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

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conjunction with poly-chlortrifluor-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 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× (Zeiss) were used as objective and condenser. The diameter of the measuring area was 40 μm. 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 Fe^{3+} contents are introduced by the substitution

$$3Fe^{2+[6]} = 2Fe^{3+[6]} + \square^{[6]}$$

(Cemič *et al.*, 1980).

Experimental results

High pressure spectra of olivine Fa_{10} and fayalite (Table 1) are shown in Figures 1 and 2 respectively. For the Fa_{10} olivine (001) plate, there is a decrease in absorption intensity near 40,000 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 cm^{-1}. The two effects combine to create a window near 35,000 cm^{-1}.

Table 1. Samples studied*

Sample		Olivine 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_2	40.67(59)		30.01(71)	
	MgO	49.53(22)		0.010(8)	
	FeO	9.33(47)		67.75(72)	
	MnO	0.35(16)		0.68(23)	
	Fe_2O_3	n.d.		1.38(69)	
	Cr_2O_3	0.024(12)		0.038(58)	
	Total	99.90		99.87	
No.of points analyzed		8		10	
Atoms per 4 oxygen atoms	Si	0.996(8)		1.013(4)	
	Mg	1.810(10)	2.011		1.973
	Fe^{2+}	0.194(6)		1.901(33)	
	Fe^{3+}			0.035(17)	
	Mn^{2+}	0.007(4)		0.020 (7)	
	$\square$			0.017 (9)	
Means of orientation for optical spectroscopy		crystal morphology and optics		Laue photographs	
Spectra are taken from plates		(001), t = 33 µm (100), t = 29 µm		(001), t = 24 µm (010), t = 30 µm	

*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 Fe^{3+}/Fe_{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 cm^{-1} is noted at pressures up to 160 kbar. An absorption shoulder near 34,000 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 cm^{-1} is possible.

In fayalite, for both the (010) and the (001) plates, the spectra showed a low energy shift of -20 cm^{-1}/kbar ($-24.8 \cdot 10^{-4}$ 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 Fe^{2+} spin allowed dd bands with pressure. Because the *Z* spectrum gives the strongest absorption in the 12,000 to 5,000 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 cm^{-1} (shifting by -900 cm^{-1}/100 kbar) no significant movements were detected for other weak components at 24,600, 22,000, and 20,000

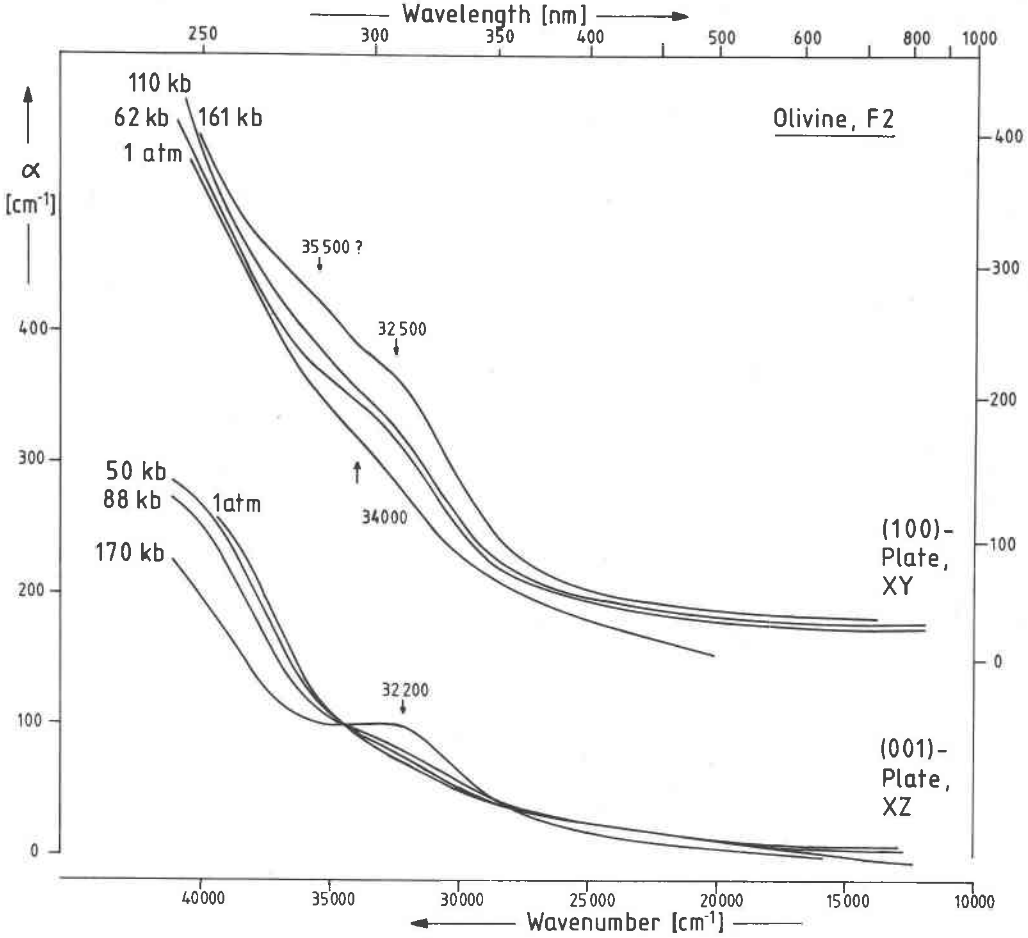

Fig. 1. Unpolarized high pressure spectra of oriented crystal sections of Fa_{10} olivine (Table 1) taken at room temperature. In the (001) section, note the presence of a window at 35,000 cm^{-1} at pressures above 90 kbar.

cm^{-1} (Fig. 2). These low intensity bands presumably result from spin-forbidden transitions of Fe^{2+}. Figure 2 shows further that with increasing pressure a band near 5,500 cm^{-1}, with a relatively small half width of ~700 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 μm to approx. 50 μm) 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 cm^{-1} band (lying further from the edge) than for the 9,300 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

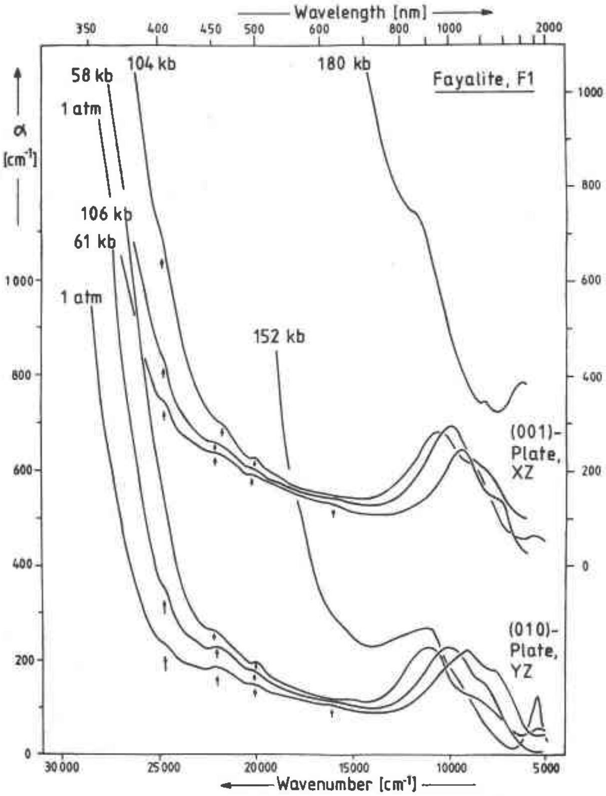

Fig. 2. Unpolarized high pressure spectra of oriented crystal sections of fayalite (Table 1) taken at room temperature. The edge is defined as the wave-number position at which the linear absorption coefficient, $\alpha = \log (I_0/I)/d$, is 800 cm^{-1} (*i.e.*, a thin section of 30 μm thickness has 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 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 Fa_{10} olivine show a prominent shoulder ($Y > X \gg Z$) at 34,000 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 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 cm^{-1} band. The "window effect" in the XZ spectra is a combination of the red shift of the 34,000 cm^{-1} band and either a blue shift of a 39,500 cm^{-1} shoulder ($Z > X > Y$), found by Runciman *et al.* (1973), or a decrease in its intensity.

As noted above, the 34,000 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 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

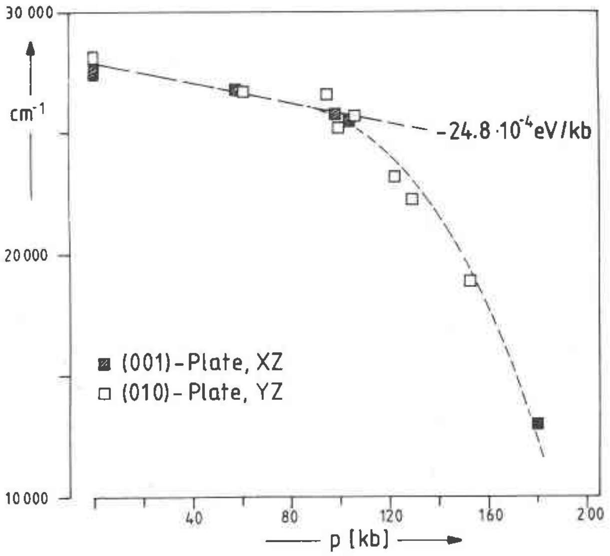

Fig. 3. Red shift of the absorption edge in fayalite crystal sections (definition of edge *cf.* Fig. 2).

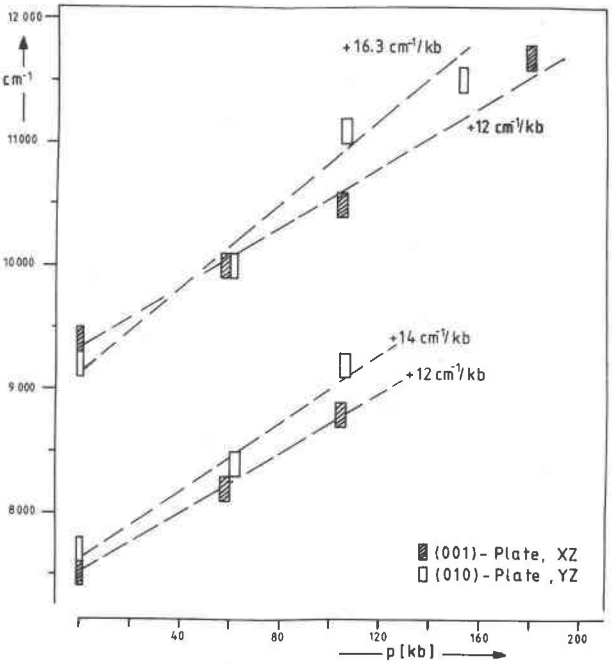

Fig. 4. Blue shifts of spin-allowed Fe^{2+} dd transitions in fayalite.

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

The high energies of the 39,500 and 34,000 cm^{-1} components make it likely that these bands originate from O–Fe ligand to metal charge transfer transitions in either $(Fe^{2+}O_6)^{10-}$ or $(Fe^{3+}O_6)^{9-}$ 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 cm^{-1} are connected with O–Fe^{2+} or O–Fe^{3+} CT transitions by tempering both fayalite and Fa_{10} olivine samples at reducing and oxidizing oxygen fugacities (QFI and QFM buffer, 800°C/21 d and 850°C/5 d respectively) proved inconclusive since no changes in the spectra were observed.

Tossel (1976) reported that Fe^{2+} ligand to metal transitions $\varepsilon_{1t_{1g\downarrow}} \rightarrow \varepsilon_{2t_{2g\downarrow}}$ and $\varepsilon_{2t_{2g\downarrow}} \rightarrow \varepsilon_{2t_{2g\uparrow}}$ first increase and then decrease in energy with decreasing Fe^{2+}–O distance, while the Fe^{3+} ligand to metal transition $\varepsilon_{2t_{2g\downarrow}} \rightarrow \varepsilon_{2t_{2g\uparrow}}$ 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 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 kbar and that no pressure broadening of the Fe^{2+} bands was observed.

For forsterite, Hazen (1976) found that with increasing pressure up to 50 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 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 Δ_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 Fe^{2+} (M2) spin allowed band at 9,300 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 kbar, the major splitting occurs between the t_{2g} levels (just as at 1 atm), then the large movement of the 9,300 cm^{-1} band (2,300 cm^{-1} over 170 kbars) would indicate a splitting of ≥5,000 cm^{-1} between the levels. One might then expect to observe a new band at energies ≥5,000 cm^{-1} and, apart from the questionable absorption at 5,500 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 Δ_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 Fe^{2+} in M(2) is likely to increase at a faster rate with pressure than that of Fe^{2+} in M(1), which was found to change by about 100 cm^{-1} over a range of 40 kbar (Abu-Eid, 1976). Therefore, it could be that the 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_{O_2} (Nover and Will, 1981) conditions under which olivines have formed in nature.

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