

MAO-HK 72-1422

quire changes in the dynamo models of the earth's magnetic field.

INTERPRETATION OF THE PRESSURE EFFECT
ON THE OPTICAL ABSORPTION BANDS OF
NATURAL FAYALITE TO 20 kb*

H. K. Mao and Peter M. Bell

Major absorption bands in olivine have been assigned to known electronic transitions in iron caused by photon absorption (Mao and Bell, *Year Book* 70). Many small intensity bands are observed, however, whose interpretation, much less assignment, is obscure. The ambiguities arise because the weak bands are difficult to distinguish in the background produced by other, more intense absorption, also caused by iron. Recently, high-resolution procedures have eliminated most of the ambiguities, and it is now possible to accurately measure small bands (Bell and Mao, this report).

The low-intensity bands in olivine could be caused by a number of processes other than those that cause the major bands. Most such processes can be eliminated from consideration in explaining bands that occur in all iron-bearing olivines, regardless of the mode of origin of the olivines. The bands either are caused by crystal-field effects and are sensitive to site symmetry or are charge-transfer bands and therefore are insensitive to symmetry. The shift of minor bands as a function of pressure can be used as an aid to classifying them. At present, a fully rational theoretical analysis is not possible, but even an empirical understanding of the low-intensity bands would be useful, especially when there is supporting chemical data. For example, the ability to distinguish minor bands in olivine may significantly aid in the interpretation of divalent and trivalent iron to deduce the state of oxidation (Bell and Mao, this report).

* Work supported in part by National Science Foundation grant GA 22707.

As discussed in a previous report (Bell and Mao, *Year Book* 68), the Hund rule of maximum spin multiplicity describes the ground state in a weak or zero field, and the Laporte rule forbids $d-d$ transitions. Under some conditions, however, overlap of orbital wave functions occurs, causing transitions that are normally forbidden by the selection rules. Spin-forbidden transitions do not cause intense absorption, but they behave much like spin-allowed bands, in contrast to charge-transfer bands.

It is thought that pressure causes a blue shift (higher energy) of crystal-field bands and a red shift (lower energy) of charge-transfer bands (Shankland, 1966; Zahner and Drickamer, 1961; Mao and Bell, *Year Book* 70; Mao and Bell, 1972b). This generality can be violated when t_{2g} and e_g are further split into several levels for a site of low symmetry. Pressure distorts the site, thus causing a change in the pattern of splitting. Therefore, the energy differences between some of the levels may decrease, although the average Δ_0 increases. Other exceptions may exist as well.

Figure 101 shows high-pressure polarized spectra of several low-intensity peaks of a single crystal of natural fayalite (Inyo County, California, Mao and Bell, elsewhere in this report; for a typical olivine absorption spectrum, see Bell and Mao, this report).

The pressure shift of the crystal-field bands caused by Fe^{2+} in the M1 octahedral site can be seen to be toward higher energy (Fig. 101A). Fig. 101 A, B shows the red pressure shifts of two weak bands that are at present not assigned. The preliminary interpretation is that these bands are caused by charge transfer transition in Fe^{3+} .

Most reported absorption spectra for olivine contain the bands shown in Fig. 101 (Burns, 1970). The olivine structure cannot accommodate much Fe^{3+} (less than 1 wt %; Bragg and Brown, 1926) in comparison with Fe^{2+} . It is conceivable

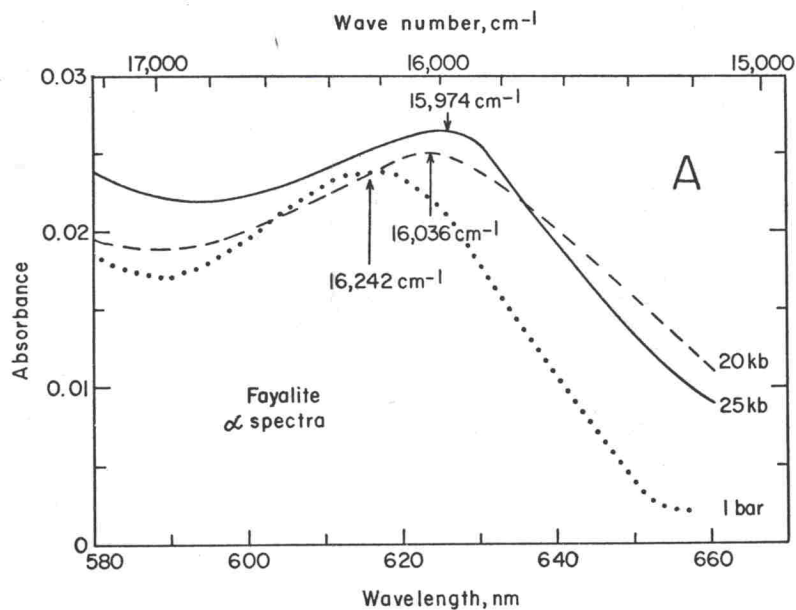
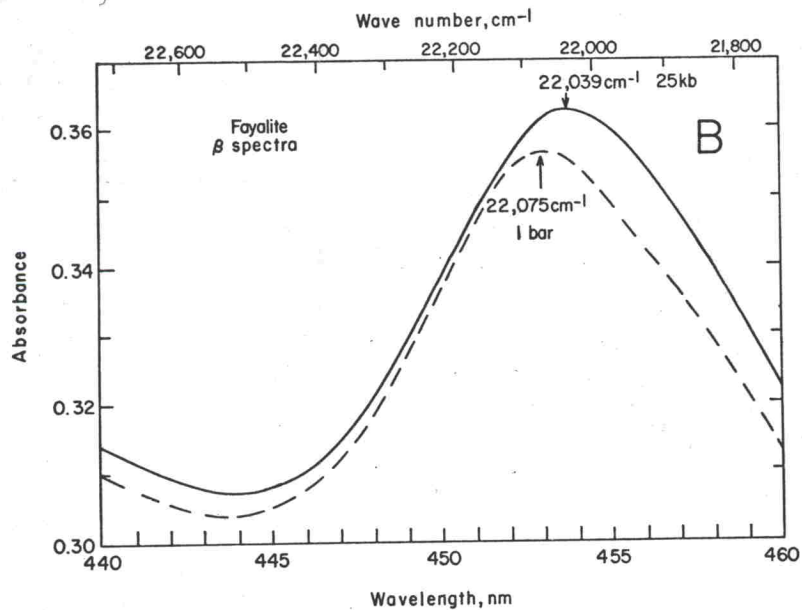
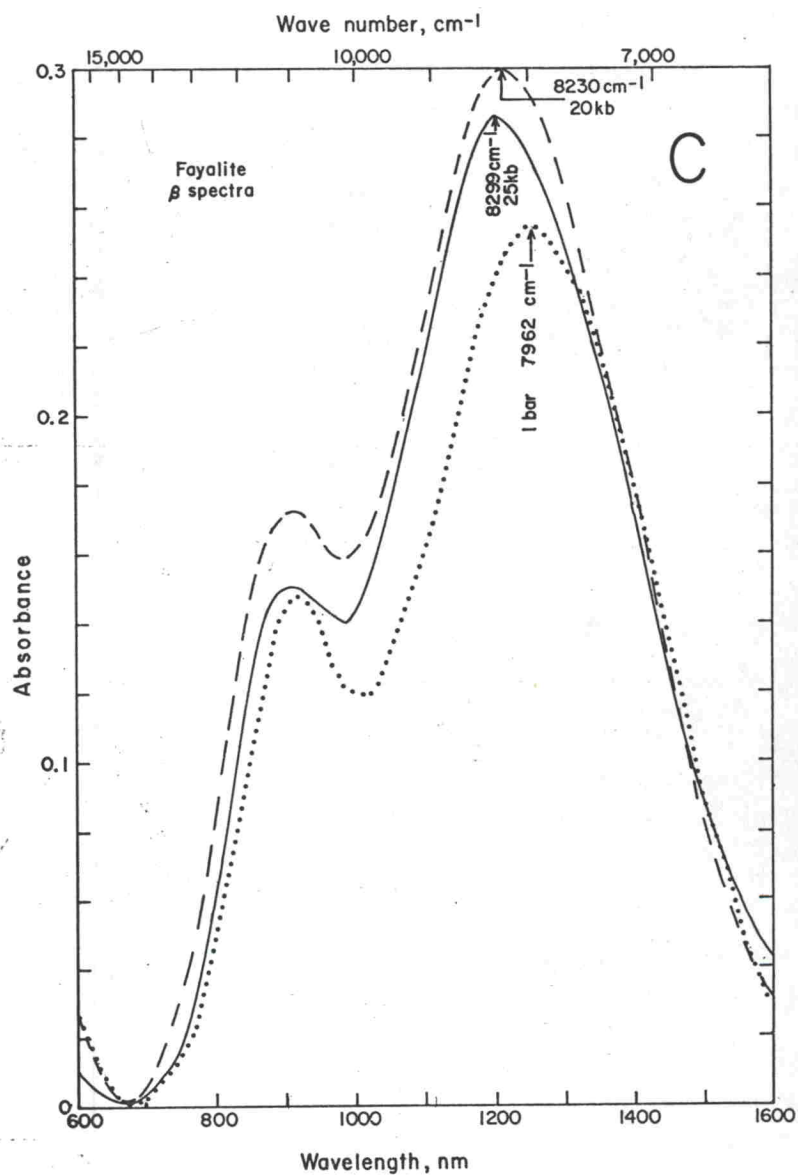


Fig. 101. High-pressure polarized optical spectra of three absorption bands in fayalite. (A) 15,000-17,000 cm^{-1} , (B) 21,800-22,600 cm^{-1} , (C) 6000-15,000 cm^{-1} .





that the sites available for Fe^{3+} are usually filled regardless of the amount of Fe^{2+} present. The interpretation was first suggested in part by Shankland (1966) on the basis of observations of the bands in forsterite before and after treatment with hydrogen gas. The band energies are not inconsistent with values calculated for charge-transfer transitions in Fe^{3+} (Tanabe and Sugano, 1954) and are similar to those measured for Fe^{3+} in MgO (G. A. Slack, communication in Shankland, 1966).

If the interpretation of these minor absorption bands in olivine is valid, it provides a powerful tool for estimating the lower limit of oxidation in olivine-bearing rocks. The fact that these bands occur in lunar olivine (Mao and Bell, 1972b) suggests that Fe^{3+} occurs on the moon.

CRYSTAL-FIELD STABILIZATION OF THE OLIVINE-SPINEL TRANSITION*

H. K. Mao and P. M. Bell

The olivine-spinel transition is thought to be of major importance in the earth's mantle, and much effort has been made to characterize the transition. Syono, Tokonami, and Matsui (1971), using traditional arguments based on ionic radius ratios, have calculated that the pressure of the transition of fayalite to spinel (both Fe_2SiO_4) occurs at 150 kb, 1000°C. They noted the large discrepancy between their calculated value and the experimentally determined value of 50 kb, 1000°C (Akimoto, Komada, and Kushiro, 1967) and pointed to the inadequacy of the theory.

It is known that the geochemical control and partitioning of iron are governed by crystal-field effects rather than by the traditional rules of electronegativity (Curtis, 1964). Syono, Tokonami, and Matsui (1971) concluded that the same effects could influence the olivine-spinel

transition and could, in part, explain their failure to predict the pressure. The present study is a direct measurement of the crystal-field energy in spinel and its relation to the transition pressure.

The crystal-field spectrum of synthetic spinel (Fe_2SiO_4) was measured with a newly developed, high-resolution technique (Bell and Mao, this report). Figure 102 shows a plot of the spectrum. A strong absorption band centered at 11,100 cm^{-1} is caused by Fe^{2+} in the octahedral site. Comparison of this value with crystal-field parameters for Fe^{2+} in octahedral sites in olivine (M1 and M2) gives the relative stabilization of the structures. The excess or difference in crystal-field stabilization energy (CFSE) is given by

$$\text{CFSE}_{\text{spinel}} - \text{CFSE}_{\text{olivine}} = (2/5) [2\Delta_{\text{spinel}} - (\Delta_{\text{olivine(M1)}} + \Delta_{\text{olivine(M2)}})], \quad (1)$$

where Δ is the crystal-field splitting parameter.

Using the wave-number value from Fig. 102 for spinel and the values of Burns (1970) for olivine,

$$\begin{aligned} \text{CFSE}_{\text{spinel}} - \text{CFSE}_{\text{olivine}} &= \\ 2084 \text{ cm}^{-1} \text{ per molecule} &= \\ 249.3 \text{ kb cm}^3/\text{mole}. & \quad (2) \end{aligned}$$

At constant temperature, the relationship between the true pressure of the transition—the pressure of the transition calculated without considering the crystal-field effect—and the excess crystal-field stabilization energy is given by

$$\begin{aligned} \text{CFSE}_{\text{spinel}} - \text{CFSE}_{\text{olivine}} &= \\ = \int_{P_t}^{P_t + \Delta P} \Delta V dP, & \quad (3) \end{aligned}$$

where P_t is the true pressure of the transition; $P_t + \Delta P$ is the pressure of the transition calculated by Syono, Tokonami, and Matsui (1971); ΔV is $V(\text{olivine}) - V(\text{spinel})$; V is the specific volume.

The ΔV term is corrected for thermal expansion to approximately 1000°C (1%

* Work supported in part by National Science Foundation grant GA 22707.

From:

Carnegie Institution of Washington
Geophysical Laboratory
~~20~~ 2801 UPTON STREET, N.W.
Washington, D.C. 20008