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The Polarized Spectra of Iron in Silicates: Olivine. A Discussion of Neglected Contributions from Fe^{2+} Ions in M(1) Sites

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Introduction

The olivine structure contains two six-coordinated sites, identified as the centrosymmetric *M*(1) and non-centrosymmetric *M*(2) sites. In the forsterite-fayalite series, Mg^{2+} and Fe^{2+} ions are essentially randomly distributed between the two sites, so that contributions from Fe^{2+} ions in both the *M*(1) and *M*(2) positions might be expected to be seen in the crystal field spectra of Mg-Fe olivines. Numerous published spectra of olivines show the characteristic polarization dependence of the near infrared spectra around one μm, leading to the γ ($E \parallel a$) spectrum being more intense than the α ($E \parallel b$) and β ($E \parallel c$) spectra. In a study of eleven Mg-Fe olivines, Burns (1970) demonstrated that each polarized spectrum could be resolved into three component bands, the relative intensities of which remain approximately constant for a given polarization across the forsterite-fayalite series (Burns, 1970, Fig. 4). Moreover, the peak maxima in the spectral profiles and the resolved spectra show compositional variations, and shift linearly to lower energies with increasing Fe_2SiO_4 content. Burns (1970) assigned absorption bands occurring around 11700 cm^{-1} (band I), and 9000 cm^{-1} (band III) in a forsterite Fa_{12}, for example, to Fe^{2+} ions in the *M*(1) sites, and the more polarization-dependent band at 9540 cm^{-1} (band II) to Fe^{2+} ions in *M*(2) sites.

Recently, Runciman, Sengupta, and Gourley (1973) re-interpreted the near infrared spectra of forsterite in terms of transitions in Fe^{2+} ions in the non-centrosymmetric *M*(2) sites, and rejected any possible contributions to the spectra from Fe^{2+} ions in the *M*(1) sites on the grounds that "transition probabilities are usually an order of magnitude smaller for centrosymmetric sites." Although they again assigned the band at 9540 cm^{-1} to Fe^{2+} ions in *M*(2) sites, Runciman, Sengupta, and Gourley (1973, p. 455) concluded that: "Thus, it appears that there is no simple explanation for the prominent shoulders in the olivine spectra." These "prominent shoulders" are, in fact, absorption bands with distinct maxima in other polarized spectra of olivines, and component bands I, II, and III may be resolved at similar energies in all three polarized spectra of each olivine (Burns, 1970, Figs. 2 and 4; this paper, Figs. 1 and 2).

The purpose of the present note is to draw attention to published data and to reiterate the evidence not considered by Runciman, Sengupta, and Gourley (1973), which shows that Fe^{2+} ions in the *M*(1) sites produce the crystal field bands around 11700 cm^{-1} and 9000 cm^{-1} in absorption spectra of olivines.

Evidence for Spectral Contributions from Fe^{2+} Ions in M(1) Sites

At least five arguments may be presented to show that Fe^{2+} ions in the *M*(1) sites contribute to the near infrared spectra of olivines. These are based on: (a) trends in the spectra of Fe-Mn olivines; (b) the spectrum of iron monticellite; (c) site occupancies in Mg-Fe olivines and consistency of absorption spectra; (d) compositional variations of peak maxima; and (e) extinction coefficient data.

(a) *Trends in the Spectra of Fe-Mn Olivines*

Site occupancy data for several manganiferous olivines from different sources, including X-ray structure refinements (Brown *et al*, 1970), E.S.R. measurements (Chatelain and Weeks, 1970; Michoulier, Gaite, and Maffeo, 1969), and infrared spectroscopy (Huggins, 1973) indicate that the larger Mn^{2+} ions favor the larger *M*(2) sites of the olivine structure. As a result, the *M*(1) sites are enriched in Fe^{2+} ions as manganese content increases along the fayalite-tephroite series. These changes in cation distribution are portrayed in the crystal field spectra of Fe-Mn olivines. Burns (1970, Fig. 7) demonstrated that the intense band II at 9300 cm^{-1} in the γ spectrum of fayalite assigned to Fe^{2+} ions in *M*(2) positions *decreases* in intensity relative to bands I and III in manganiferous olivines. There is therefore a direct correlation between the emergence of spectral bands

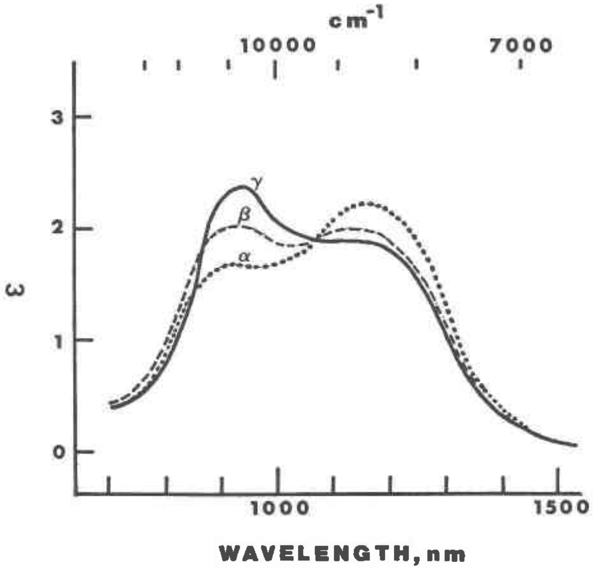

FIG. 1. The polarized near-infrared spectra for α, β, and γ of an iron monticellite. The kirschsteinite contains 69.4 mole percent $CaFeSiO_4$.

I and III and the Fe^{2+} enrichment in *M*(1) sites of Fe-Mn olivines. This suggests that Fe^{2+} ions in olivine *M*(1) sites contribute to the crystal field spectra in the near infrared region.

(b) *Spectra of Iron Monticellite*

In the crystal structure of monticellite Ca(Mg, Fe) SiO_4, calcium completely fills the *M*(2) positions, so that Mg^{2+} and Fe^{2+} ions can occur only in the olivine *M*(1) site (Onken, 1965). Any features in the absorption spectra of monticellite are therefore directly attributable to Fe^{2+} ions in the *M*(1) sites.

The polarized spectra of an iron-rich monticellite (kirschsteinite) containing 69.4 mole percent $CaFeSiO_4$ are shown in Figure 1. Each spectrum consists of two broad bands centered at about 10900 cm^{-1} and 8700 cm^{-1} (Burns, 1965), having molar extinction coefficients, ε, of approximately 2 $l.mole^{-1}$ cm^{-1}. There is is a conspicuous absence of an absorption band around 9300 cm^{-1} attributable to Fe^{2+} ions in *M*(2) sites, particularly in the γ spectrum. The positions of the bands at 10900 cm^{-1} and 8700 cm^{-1} correspond closely to those of bands I and III measured in the spectra of Fe-Mn and Mg-Fe olivines (Fig. 2). The one-site occupancy of Fe^{2+} ions in the monticellite structure provides another reason for assigning bands I and III in absorption spectra of olivines to Fe^{2+} ions in *M*(1) positions.

(c) *Site Occupancies in Mg-Fe Olivines and Consistency of Absorption Spectra*

Recent measurements of Mg-Fe olivines by a variety of techniques, including X-ray structure refinements (Birle *et al*, 1968; Finger, 1970, 1971; Brown, 1971; Wenk and Raymond, 1971, 1973), the Mössbauer effect (Bush, Hafner, and Virgo, 1970; Duncan and Johnston, 1973), vibrational spectra (Burns and Huggins, 1972; Huggins, 1973), and electronic absorption spectroscopy (Burns, 1970)—all demonstrate that cation ordering is minor or absent in several olivines of different compositions from a

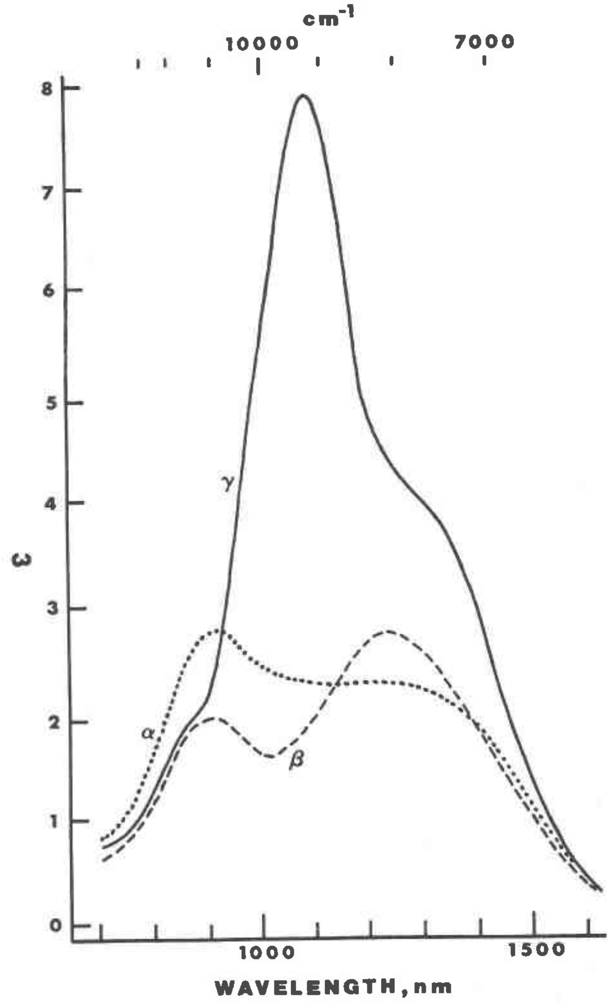

FIG. 2. The polarized near-infrared spectra of a fayalite. The specimen contains 97.9 mole percent Fe_2SiO_4. Note that the α and β spectra have spectral profiles and intensities similar to those in the polarized spectra of iron monticellite (Fig. 1) assigned to Fe^{2+} ions in olivine *M*(1) sites.

variety of terrestrial and lunar rocks. If Fe^{2+} ions in *M*(2) and *M*(1) each contribute to absorption spectra, then spectral profiles might be expected to be similar for all Mg-Fe olivines, both lunar and terrestrial, of different compositions across the forsterite-fayalite series. Such similarities are indeed apparent in the numerous published spectra of olivines of diverse compositions occurring in lunar rocks (Bell and Mao, 1972 a, b; Mao and Bell, 1971; Burns, Huggins, and Abu-Eid, 1972; Burns *et al*, 1973) and in terrestrial rocks (Farrell and Newnham, 1965; White and Keester, 1966; Grum-Grzhimailo, Boksha, and Varina, 1969; Burns, 1970; Gaffney, 1972; Runciman, Sengupta, and Gourley, 1973). These close resemblances imply that the crystal field spectra have identical origins in all of the olivines measured by different mineral spectroscopists. The spectra of iron monticellite and Fe-Mn olivines demonstrate that bands I and III are not associated with Fe^{2+} ions in the *M*(2) sites. Since there is also a constant distribution of Fe^{2+} ions in the *M*(1) and *M*(2) sites of Mg-Fe olivines, the simplest explanation for the uniform olivine spectra is to assign band II to Fe^{2+} ions in *M*(2) sites, and bands I and III to Fe^{2+} ions in *M*(1) sites.

(d) *Compositional Variations of Peak Maxima for Mg-Fe Olivines*

The polarized spectral measurements by Burns (1970) of the eleven Mg-Fe olivines spanning 8.4 to 97.9 mole percent Fe_2SiO_4 demonstrate that all peak maxima, including those in individual spectral profiles and their component bands I, II, and III, move to longer wavelengths with increasing iron contents of the olivine. These compositional variations form the basis of an olivine composition determinative curve (Burns, 1970, Fig. 3), to which the recent data of Runciman, Sengupta, and Gourley (1973) conform well. The shifts of absorption maxima may be explained by the expansion of the unit cell as larger Fe^{2+} ions replace smaller Mg^{2+} ions in the olivine structure. Increased metal-oxygen distances in the coordination sites lead to the well-known decrease of crystal field splittings, and shifts of absorption bands to lower energies. Since bands I and III do not arise from Fe^{2+} ions in *M*(2) sites, the simplest explanation for the compositional variation of bands I and III is that they represent crystal field transitions within Fe^{2+} ions in *M*(1) sites, the energies of which are influenced by changes in the *M*(1)–oxygen distances.

(e) *Extinction Coefficient Data*

In discrediting bands I and III in the olivine spectra as contributions from Fe^{2+} ions in *M*(1) sites, Runciman, Sengupta, and Gourley (1973) based their arguments on intensity correlations predicted for centrosymmetric [*e.g.*, olivine *M*(1)] versus non-centrosymmetric [*e.g.*, olivine *M*(2)] sites. It is pertinent therefore to examine published data on molar extinction coefficients measured for Fe^{2+} ions in olivines and other ferromagnesian silicates.

In the polarized spectra of olivines, extinction coefficients for band maxima in the spectral profiles of the three individual polarized spectra range from $\epsilon = 7\text{–}8$ $\text{l.mole}^{-1}\ \text{cm}^{-1}$ for the γ spectra to $\epsilon = 2\text{–}3$ $\text{l.mole}^{-1}\ \text{cm}^{-1}$ in the α and β spectra (Fig. 2). The latter intensities are comparable to those measured for all three polarized spectra of iron-monticellite (Fig. 1). When the γ spectra of Mg-Fe olivines are resolved into the three component bands (Burns, 1970, Fig. 4), individual molar extinction coefficients have the approximate values: band I, $\epsilon = 2$; band II, $\epsilon = 6$; band III, $\epsilon = 3$. Furthermore, the bands conform with the Beer-Lambert Law because the molar extinction coefficients remain approximately constant across the forsterite-fayalite series. Thus, band II attributed to Fe^{2+} ions in olivine *M*(2) sites (Burns, 1970; Runciman, Sengupta, and Gourley, 1973) is no more than 2 or 3 times more intense than bands I and III assigned by Burns (1970) to Fe^{2+} ions in *M*(1) positions. These data suggest that there is a fallacy in the fundamental assumption of Runciman, Sengupta, and Gourley (1973, p. 452) that "transition probabilities are usually an order of magnitude smaller for centrosymmetric sites."

The lack of generality of this assumption is further demonstrated by published intensity data for other Fe^{2+} compounds and minerals summarized in Table 1. These data demonstrate the variability of molar extinction coefficients for Fe^{2+}, not only for polarization-dependent bands within one mineral, but also for centrosymmetric and non-centrosymmetric sites between different minerals. An important feature emerging from the data summarized in Table 1 is the low molar extinction coefficient for the olivine *M*(2) site compared to other non-centrosymmetric sites. This discrepancy points to a flaw in the arguments presented by Runciman, Sengupta, and Gourley (1973). Therefore, the criterion used by Runciman, Sengupta, and Gourley (1973) to discredit Fe^{2+} *M*(1) site contributions to olivine spectra lacks gen-

TABLE 1. Extinction Coefficients for Fe^{2+} in Selected Minerals

Compound or Mineral	Coordination Symmetry	Absorption Band (cm⁻¹)	ε (ℓ.mole⁻¹ cm⁻¹)	Reference
$Fe(H_2O)_6^{2+}$	centrosymmetric octahedral	10,000	1.7	Cotton and Meyers (1960)
almandine	non-centrosymmetric 8-coordinated	4,000-8,000	0.5-1.11	White and Moore (1972)
gillespite	centrosymmetric square-planar	20,000	10($E \parallel c$) 2.5($E \perp c$)	Burns, Clark, & Stone (1966)
staurolite	non-centrosymmetric tetrahedral	5,000-7,000	13	Burns and Fyfe (1967)
enstatite	non-centrosymmetric *M*(2) site, pseudo-C_{2v}	11,000	25(α) 5(β) 3(γ)	Burns (1969)
cummingtonite	non-centrosymmetric *M*(4) site, C_{2v}	10,500	300(β) 100(α) 25(γ)	Burns (1969)
olivine	non-centrosymmetric *M*(2), 6-coordinate	9,540	6(γ)	Burns (1969, 1970; this work)
olivine	centrosymmetric *M*(1), 6-coordinate	11,700 9,000	2(γ) 3(γ)	*ibid, idem*

erality, and needs to be applied with caution when assessing mineral spectra.

Concluding Remarks

Runciman, Sengupta, and Gourley (1973) assigned one absorption band (band II) in the near infrared spectra of olivines on the basis of a model which assumed that the environment around the Fe^{2+} ions in the *M*(2) sites—symmetry: C_s or *m*—approximated the symmetry C_{2v} or *mm*2. The degree of success of this model for olivine may be assessed from the data in Table 1, which illustrate the anomalously low extinction coefficients for Fe^{2+} ions in the non-centrosymmetric olivine *M*(2) sites. Runciman, Sengupta, and Gourley (1973) could offer no explanation for bands I and III consistently found in all Fe^{2+} olivine spectra, but instead chose to reject the possibility that Fe^{2+} ions in *M*(1) sites contribute to the spectra. They thus ignored, without explanation, the corroborative evidence cited by Burns (1970), which is repeated in this note, for assigning bands I and III in olivine spectra to Fe^{2+} ions in *M*(1) sites. As a result, the case presented by Runciman, Sengupta, and Gourley (1973) lacks conviction.

The arguments of Runciman, Sengupta, and Gourley (1973) hinge on a "rule of thumb" principle in spectroscopy that transition probabilities are an order of magnitude lower for ions in centrosymmetric sites. While such a criterion may be valid for isolated coordination polyhedra in transition metal complexes, deviations from it might be expected for ions in multisite mineral structures containing edge-shared coordination polyhedra, where interactions with next-nearest neighbors occur. The data summarized in Table 1 again illustrate the limitations of the spectral transition probability criterion for ions in centrosymmetric versus non-centrosymmetric sites in mineral structures.

Until the problems raised in the present note have been explained adequately, the interpretation of the absorption spectra of olivines offered by Runciman, Sengupta, and Gourley (1973) is unsatisfactory. At the present time, available evidence strongly suggests that Fe^{2+} ions in centrosymmetric *M*(1) sites contribute to the near infrared spectra of olivines.

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