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Crystal Field Spectrum of Ni^{2+} in Olivine

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Abstract

The absorption spectrum of synthetic $(Mg_{0.9}Ni_{0.1})_2SiO_4$ has been determined at room temperature in the energy range 5000–50,000 cm^{-1}. The observed absorption bands are assigned to crystal field transitions of Ni^{2+} in the two nonequivalent cation sites of olivine. On the basis of the two-site assignment, the calculated values of the spectral parameters Dq and B are:

	Dq	B
$M1$	870 cm^{-1}	900 cm^{-1}
$M2$	768 cm^{-1}	882 cm^{-1}

The *d*-orbital energy levels of Ni^{2+} in the distorted cation polyhedra have been calculated using the point charge method of Wood and Strens (1972). Good agreement between calculated and observed positions of the non-degenerate $^3A_2 \rightarrow {}^3T_2$ transitions result.

Introduction

The magnitudes of the crystal field parameters of transition ions residing in silicate sites have in general been obtained by spectral observation of naturally occurring phases (for example, White and Keester, 1966; Bancroft and Burns, 1967; Burns, 1970a,b). For these, the dominant contributor to their crystal field spectra is the Fe^{2+} ion which, in sites of regular symmetry, exhibits one spin-allowed transition, $^5T_{2g} \rightarrow {}^5E_g$ (octahedral coordination) or $^5E \rightarrow {}^5T_2$ (tetrahedral or eight-fold cubic coordination). In the distorted sites of silicates however, the ground- and excited-state degeneracies are lifted, and up to four bands corresponding to the $T \rightarrow E$ transition may be observed for each site. In such cases absorption spectra provide information on the relationships between site distortion and *d*-orbital splittings.

Spectral measurements also enable the crystal field stabilization energies (CFSE's) of transition ions to be estimated. Considerable use has been made of these energies to interpret partition in natural systems (Curtis, 1964; Burns and Fyfe, 1967; Henderson and Dale, 1969; Wood and Strens, 1971) and to discuss partition between octahedral and tetrahedral sites in spinels (Dunitz and Orgel, 1957).

Although detailed spectra are available for most Fe^{2+} silicates, there is little direct evidence of the magnitudes of *d-d* splittings of other ions in silicate sites; the effects of the site distortion on energy levels are generally assumed to be similar to those observed for Fe^{2+} (Burns, 1970a). Reinen (1968) has determined the absorption spectra of a number of Ni–Mg olivines, but has not attempted to relate the lifting of excited state degeneracies to the observed bands. In an attempt to elucidate the relationships between Ni^{2+} crystal field splittings and site distortion, the absorption spectrum of synthetic $(Mg_{0.9}Ni_{0.1})_2SiO_4$ has been determined at room temperature. The observed band energies are compared with those predicted from point-charge calculations of the *d*-orbital energy levels in the two cation sites of olivine.

Experimental Procedures

A starting composition corresponding to $(Mg_{0.9}Ni_{0.1})_2SiO_4$ was prepared from mixtures of ground silica glass and laboratory grade MgO and NiO. The powdered oxide mixture was intimately ground under acetone and then pressed into pellets. These were fired at 1150°C in air for two periods of three days then one of ten days. Between each firing, the pellets were re-ground and re-pressed and the products were identified by X-ray diffraction. Complete reaction was demonstrated by the presence of single phase olivine. The spectrum was determined at room temperature on a Unicam SP 700 C spectrophotometer fitted with a diffuse reflectance accessory, freshly prepared magnesium oxide being used as a reflectance standard.

Results

Most of the several absorption bands in the spectrum of nickel olivine (Fig. 1) may be provisionally attributed to crystal field transitions of Ni^{2+}. The distortions of the octahedral olivine sites necessitate some caution in assignment of observed bands since they result in the lifting of excited state degeneracies.

An examination of the Tanabe-Sugano diagram for Ni^{2+} in an octahedral environment (see, for example, Cotton, 1963, p. 211) shows that up to eight transitions are possible in the energy range of interest, three spin-allowed ($\Delta s = 0$) and five spin-forbidden ($\Delta s \neq 0$). Spin-allowed bands are usually much more intense than spin-forbidden bands, so one would predict three intense and five weak bands if Ni^{2+} occupied only one type of cation site. In this case, however, six of the seven observed bands are moderately intense and, in addition, assignment in accordance with a single Ni^{2+} spectrum gives a poor fit to the calculated spectral parameters *Dq*, *B*, and *C*. The two crystallographically nonequivalent sites of olivine are sufficiently dissimilar to produce separable components of the $^5T_{2g} \rightarrow {}^5E_g$ absorption band of Fe^{2+} (Burns 1970b) and of the $^3A_2 \rightarrow {}^3T_2$ band of Ni^{2+} in Mg–Ni olivines (Reinen, 1968). The six intense bands have therefore been assigned in groups of two, each pair arising from the same spin-allowed transition in the two cation sites. Knowledge of the positions of the spin-allowed bands enables calculation of *Dq* and *B* for the two olivine sites from the equations for the band energies:

$$^3A_2 \rightarrow {}^3T_2 = 10Dq = \nu_1$$

$$^3A_2 \rightarrow {}^3T_1(\mathrm{F}) = 15Dq + 7.5B - 6B(1+\mu)^{1/2} = \nu_2$$

$$^3A_2 \rightarrow {}^3T_1(\mathrm{P}) = 15Dq + 7.5B + 6B(1+\mu)^{1/2} = \nu_3$$

$$\text{where } \mu = [(10Dq - 9B)/12B]^2$$

In this case *Dq* and *B* are of similar magnitude and μ is thus of the order of 0.01 and may be neglected. B for Ni^{2+} in each of the two sites may therefore be calculated from $\nu_3 - \nu_2 = 12B$.

Reinen (1968) showed that the lower-energy components of the absorption bands in Mg–Ni olivines are due to Ni^{2+} in the *M*2 (C_s symmetry) site. Following this assignment the low energy component of each of the three bands has been attributed to *M*2 and values of *Dq* and *B* are calculated to be:

$$M1 \quad Dq = 870\ \mathrm{cm}^{-1} \quad B = 900\ \mathrm{cm}^{-1}$$

$$M2 \quad Dq = 768\ \mathrm{cm}^{-1} \quad B = 882\ \mathrm{cm}^{-1}$$

Agreement between predicted and observed band positions (Table 1) is good for the two higher-energy spin-allowed bands of *M*2. The greater spread between calculated and observed transition energies for *M*1 may be attributed to the non-degeneracy of the Ni^{2+} excited states, since each 'band' represents three overlapping bands of similar energy.

The energies of the spin-forbidden $^3A_2 \rightarrow {}^1A_1$ transitions are given by:

$$^3A_2 \rightarrow {}^1A_1 = 16B + 4C - 108B^2/10Dq$$

where *C* (the Racah *C* parameter), normally in the range of 4.5–4.7*B* for Ni^{2+}, was taken to be 4.65*B* approximately. The energy of the weak band agrees well with the calculated transition energy for *M*2, with the corresponding band in *M*1 covered by the spin-allowed $^3A_2 \rightarrow {}^3T_1$(F) bands.

The Racah *B* parameters for the two sites correspond closely to the values of 890 cm^{-1} for Ni^{2+} in MgO (Pappalardo *et al*, 1961), 881 cm^{-1} in CaNiSi$_2$O$_6$, and 1039 cm^{-1} in Ni$_{0.05}$Mg$_{0.95}$SiO$_3$ (White *et al*, 1971). The *B* parameter gives a rough measure of the degree of covalent bonding between metal and ligands. In all five oxygen-coordinated sites, *B* is close to that of the free ion (1041 cm^{-1}), implying a high degree of ionic character of the metal-oxygen bond.

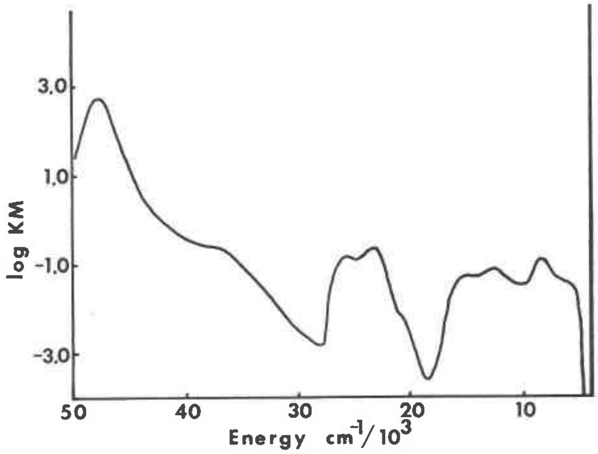

FIG. 1. Reflectance spectrum of (Mg$_{0.9}$Ni$_{0.1}$)$_2$SiO$_4$ in the energy range 5000–5000 cm^{-1}. The ordinate log$_{10}$KM, is the logarithm of the Kubelka-Munck function of the reflectance obtained from:

$$\mathrm{KM} = (1 - r_x)^2/2r_x$$

r_x is the proportion of the incident radiation reflected.

TABLE 1. Calculated and Observed Band Energies of Ni^{2+} in $(Mg_{0.9}Ni_{0.1})_2SiO_4$ in cm^{-1}

Site 1			Site 2	
Calculated*	Observed	Assignment	Observed	Calculated**
8700	8400	$^3A_2 \rightarrow {}^3T_2$	6600	7680
14400	14700	$^3A_2 \rightarrow {}^3T_1(F)$	12800	12800
21220	21300	$^3A_2 \rightarrow {}^1A_1$	--	15800
25300	25500	$^3A_2 \rightarrow {}^3T_1(P)$	23400	23400

*$Dq = 870\ cm^{-1}$ $B = 900\ cm^{-1}$

**$Dq = 768\ cm^{-1}$ $B = 882\ cm^{-1}$

The low-energy (5000–11000 cm^{-1}) bands (Fig. 2) correspond to the non-degenerate $^3A_2 \rightarrow {}^3T_2$ transition of Ni^{2+}. Inspection of the composite band suggests the presence of three intense components at about 5900, 7250, and 8500 cm^{-1} with the possibility of a weak high-energy band at about 9500 cm^{-1}. In order to estimate the energies of these bands more accurately, a Dupont 310 curve resolver was used to generate a four band spectrum. A reasonably good fit could be obtained provided a fifth band of low intensity was inserted at about 6300 cm^{-1}. This last band is of dubious significance (even though it does fit one of the calculated transitions, see below), but it seems probable that the four main components are significant. No other combination of band positions and intensities gives a reasonable fit to the spectrum.

The observed bands may be assigned to the two olivine sites using crystal field calculations of the type described by Wood and Strens (1972). The calculations use a point-charge model of the metal-oxygen interactions with the *d*-orbital energies being obtained from equations derived by Ballhausen (1954). It has been found that the energy of a *d*-orbital, relative to the baricenter, may be calculated from:

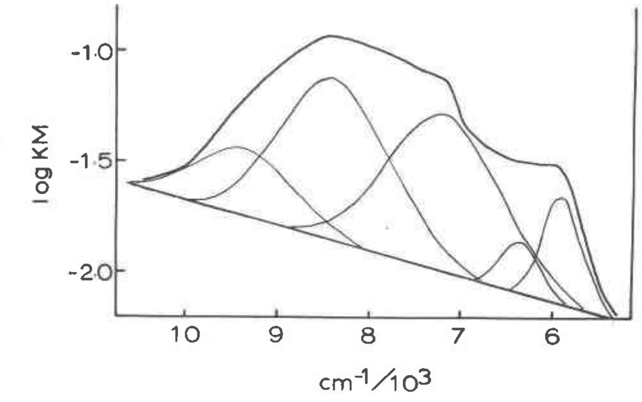

FIG. 2. Low-energy bands in the $(Mg_{0.9}Ni_{0.1})_2SiO_4$ spectrum with a five-band fit obtained using a Dupont 310 Curve resolver. Band shapes were assumed to be gaussian.

$$E = 0.6(\sum_{xyz} \Delta(C_1(B_2/B_4 + C_2)$$

where the summation extends over the three cartesian axes, and is, for each axis, obtained from summations over all the ligands. For example,

$$\Delta_x = \sum_i \Delta^i \cos^2 \theta_x{}^i$$

$\theta_x{}^i$ is the angle between the *i*th metal-oxygen vector and the *x* axis of the site and Δ^i is the value of Δ for the *i*th oxygen atom.

Since the constants C_1, C_2, *etc* are known, the requisite data are the B_2/B_4 ratio of radial integrals, an accurate determination of the structure, and Δ at known metal-oxygen distance. In accordance with the point charge model, Δ is assumed to vary as the inverse fifth power of the metal-oxygen distance.

Good agreement between predicted and observed transition energies of Fe^{2+} in orthopyroxene has been obtained by assuming $B_2 = 2.0\ B_4$ (Wood and Strens, 1972), and since this is a reasonable approximation for most first-row transition elements (Basolo and Pearson, 1967) it has been retained for the Ni^{2+} calculations described below. Structural data were taken from the work of Birle *et al* (1968).

The cation positions occupied by Mg^{2+} in forsterite (Fig. 3) have point symmetry C_i ($M1$) and C_s ($M2$). However, as pointed out by Burns (1970b), the two sites closely approximate the higher symmetry groups D_{4h} and C_{3v}. Among directions within the $M2$ site that are sufficiently pseudotriad to permit their selection as the electronic *z* axis are (1) the direction [100] as suggested by Burns (1970), and (2) a direction defined by projecting the bisector of the angle $O_3 - M_2 - O_1$ (Fig. 3) onto (001). This second direction lies at a 5° angle above the $+b$-axis. Calculations gave the closest fit to the Ni^{2+} and Fe^{2+} spectrum of forsterites if electronic *z* was aligned parallel to this second direction; for example, in the case of Fe^{2+} the intense band observed at 9500 cm^{-1}, Burns (1970) has calculated energy of 8828 cm^{-1} with the first assignment and 9517 cm^{-1} with the second. Thus electronic *z* was aligned parallel to the second direction with *x* assigned to [001] and *y* at about 5° to [100] within plane (001). Note, however, that Runciman *et al* (1973) have interpreted the polarized spectra of Fe^{2+} ions in olivine *M*2 sites on the basis of C_{2v} symmetry. Their calculations yield band energies of 9540 cm^{-1} and 9100 cm^{-1} of correct polarization dependence. By analogy with Burns (1970b), the z axis of the *M*1 site was taken to be the pseudotetrad along direction $O_3 - M1 - O_3$ with x and y in the plane perpendicular to z being along the vectors $O_2 - M1 - O_2$ and $O_1 - M1 - O_1$ respectively.

The standard value of Δ for Ni in MgO (*M*–O bond length 2.10 Å) is about 8100 cm^{-1} (Pappalardo *et al*, 1961); the value adopted here is slightly lower, 8000 cm^{-1} at an *M*–O distance of 2.10 Å. Since the $^3A_2 \rightarrow {}^3T_2$ transition has an energy of $10Dq$ (Δ_o) in undistorted octahedra, the relative energies of the five 3*d* orbitals are directly related to the observed transition energies, *i.e.*, an $xy \rightarrow z^2$ transition has an energy corresponding to the energy difference between the two orbitals.

In the Ni^{2+} ground state, all three of the lower-lying energy levels have two electrons and a transition to the non-degenerate excited states can arise from any of them. There are thus six possible transitions from each site, all of which may be observed in an unpolarized spectrum. Band assignment is facilitated, however, by the low symmetry of the *M*2 site. Absorption bands due to cations in this non-centrosymmetric site should be much more intense than those of the centrosymmetric *M*1 position. Ferrous ions in the latter site contribute only weak low- and high-energy (8000–9200 and 1100–11800 cm^{-1}) bands to the spectra of ferromagnesian olivines (Burns, 1970b).

The band at about 8500 cm^{-1} agrees well with the predicted xy, $xz \rightarrow z^2$ transition in *M*2, and there are three possible components of the 7250 cm^{-1} band which may arise in *M*2—$yz \rightarrow z^2$, $xy \rightarrow x^2 - y^2$ and $xz \rightarrow x^2 - y^2$. All of these are within 250 cm^{-1} of the observed transition energy. The 5900 cm^{-1} band can be assigned to the $yx \rightarrow x^2 - y^2$ transition (5916 predicted) of Ni^{2+} in *M*2. The probable contributors from the *M*1 site are the weak high-energy band which has its maximum at about 9350 cm^{-1} and the low-energy 6300 cm^{-1} band.

TABLE 2. Calculated and Observed Ni^{2+} Energy Levels in Olivine Sites (cm^{-1})

M 1				M 2		
Orbital	Calculated Energy*	Predicted Transitions	Observed	Predicted Transitions	Calculated Energy*	Orbital
$x^2 - y^2$	5684	9261	9350		5277	z^2
z^2	3881	9023	8500	8741	3702	$x^2 - y^2$
xy	-2650	8334		8579	-2214	yz
yz	-3339	7458	7250	7491	-3302	xz
xz	-3577	7220		7166	-3464	xy
		6531	6300	7004		
			5900	5916		
Δ_o = 800 cm^{-1} Ro = 2.10 Å B2/B4 = 2.0				Δ_o = 800 cm^{-1} Ro = 2.10 Å B2/B4 = 2.0		

*Energies given relative to the baricenter.

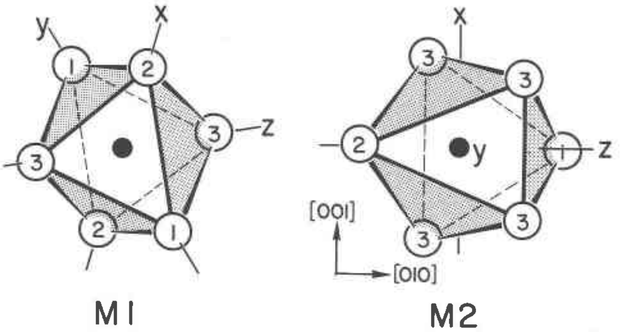

FIG. 3. Pseudo-octahedral sites occupied by Mg^{2+} in forsterite (from Birle *et al*, 1968). Numbered positions are those of the oxygen atoms. **x, y, z** refer to electronic axes used in the crystal field calculations.

Conclusions

The environments of transition ions in the *M*1 and *M*2 sites of olivine are sufficiently dissimilar for separate components of absorption bands to be distinguished for each site. By fitting of spectral parameters to the band energies it has been shown that ions in the more distorted *M*2 site have lower values of Racah *B* parameter and *Dq* than those in *M*1. Calculations of *d*-orbital energy levels agree well with observed band positions and demonstrate that Ni^{2+} bands arising in *M*2 are considerably more intense that those of *M*1. Similar effects have been noted by Burns (1970b) in Fe^{2+}-bearing olivines.

A summation over the five energy levels of Ni^{2+} enables calculation of CFSE's in the two olivine sites. Calculated values are 27.3 kcals per gram atom in *M*1 and 25.7 kcals in *M*2, rather lower than the corresponding value for spinels (Dunitz and Orgel, 1957) of 29.2 kcals per gram atom.

Acknowledgments

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