

OPTICAL ABSORPTION SPECTRUM OF Ni²⁺ IN GARNIERITE: A DISCUSSION

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ABSTRACT

The absorption spectrum of a mineral-oil mull of a specimen of garnierite (nickeloan chrysotile) from New Caledonia shows three principal absorption envelopes having maxima at 9,100, 15,200 and 26,300 cm⁻¹, respectively. By using an appropriate energy-level diagram for a d⁸ ion in an octahedral crystal-field, it is established that the observed features are due to six-coordinate Ni²⁺ in garnierite, as expected. This correlation demonstrates that recently published work stating that Ni²⁺ has tetrahedral site-symmetry in garnierite is erroneous.

From a linear plot of crystal-field splitting-parameters vs. average M-O bond distance of a number of Ni²⁺-bearing materials, it is estimated that the average Ni²⁺-O distance in garnierite is 2.01 ± 0.015 Å.

INTRODUCTION

Recently, Lakshman & Reddy (1973) stated that the site-symmetry of Ni²⁺ in garnierite is tetrahedral, their evidence being obtained from optical absorption spectra. This finding, however, is in conflict with previous spectral work by the present author (Faye 1971), and with structural and thermodynamic expectations for Ni²⁺ in silicate minerals. Therefore, it is considered worthwhile to show, unequivocally, that Ni²⁺ in garnierite has sixfold coordination, and to indicate the probable reasons for the erroneous conclusions of Lakshman & Reddy. In addition, it will be shown how the average Ni-O bond distance for Ni²⁺ in garnierite and in mineral carbonates can be estimated to within ± 0.015 Å from crystal-field spectra.

EXPERIMENTAL DETAILS

Absorption spectra of a garnierite specimen from New Caledonia were measured at room temperature with a Cary 14H spectrophotometer using a mull technique (Faye 1971). Although x-ray diffraction patterns indicated that the specimen was mainly nickeloan chrysotile with a minor amount of lizardite, the term "garnierite" is used in this note for convenience. [See Faust (1966) for an account of the nomenclature of hydrous nickel-magnesium silicates.]

Chemical analysis of the garnierite gave the following weight percentages: Ni 39.0, Fe 0.2, Mg 2.4; Mn was not detected.

Mull spectra of NiSO₄·7H₂O, NiSO₄·6H₂O and stoichiometric NiO were also measured and data pertaining to these materials are presented in Table 1.

DESCRIPTION OF GARNIERITE SPECTRUM

The optical absorption spectrum of a mineral-oil mull of garnierite is shown in Figure 1. There are three absorption envelopes whose principal components are designated as γ₁, γ₂ and γ₃, and whose energies are 9,100, 15,200 and 26,300 cm⁻¹, respectively. Minor absorption envelopes are also observed at ~7,200 cm⁻¹ and between 4,000 and 4,500 cm⁻¹. Because of their sharpness (half-width ~150 cm⁻¹) they are clearly vibrational in origin, and are not part of the electronic absorption spectrum of garnierite. Note that these minor features will be compared later with bands at 4,098 and 4,348 cm⁻¹ in the garnierite spectrum of Lakshman & Reddy.

TABLE 1. BOND DISTANCES AND SPECTRAL DATA FOR Ni²⁺-BEARING MATERIALS

Material	Average M _{oct} -O Bond Distance	Reference	Crystal Field Splitting Parameter, "Δ ₁₀ "	Source of Spectral Data
Spinel (35 mole % Ni ²⁺)	1.91 Å	Sakurai <i>et al.</i> (1969)	10,150 cm ⁻¹	Sakurai <i>et al.</i> (1969)
Al ₂ O ₃ (Ni ²⁺ = 0.1-0.3%)	1.92	Newnham & DeHaan (1969)	9,925	Minomura & Drickamer (1961)
NiSO ₄ ·7H ₂ O	2.03	Beevers & Schwartz (1935)	8,800	This work
NiSO ₄ ·6H ₂ O	2.06	Shannon & Prewitt (1969)	8,660	This work
CaNiSi ₂ O ₆	2.08	White <i>et al.</i> (1971)	8,400	White <i>et al.</i> (1971)
NiO	2.08	Shannon & Prewitt (1969)	8,550	This work
MgO(Ni ²⁺)	2.11	White <i>et al.</i> (1971)	8,600	Low (1958)
CaO(Ni ²⁺)	2.41	Wyckoff (1948)	5,650	Ishigame & Sakurai (1968)

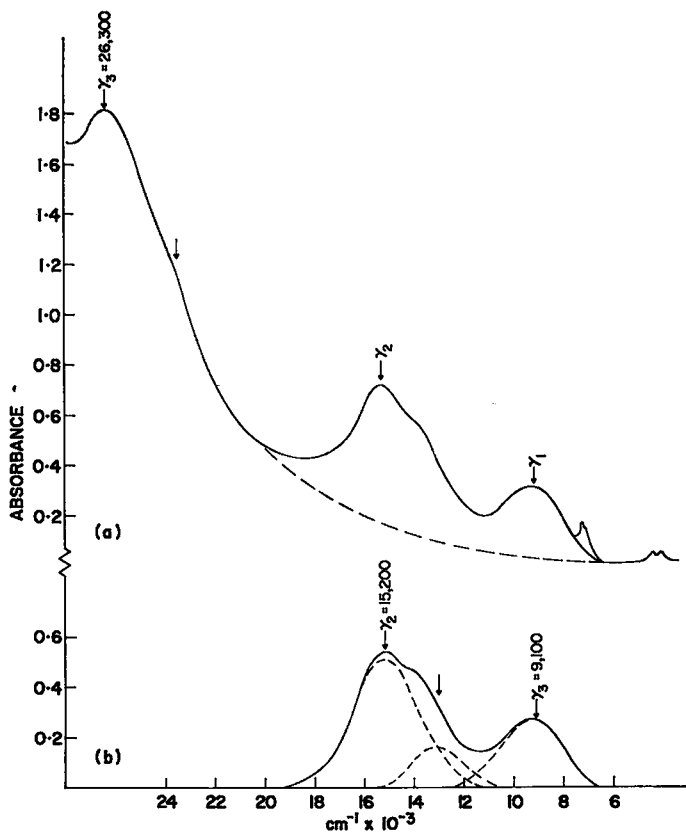


FIG. 1 (a) Mull spectrum of garnierite from New Caledonia, thickness ~ 0.01 cm.
 (b) — Resolution of γ_1 and γ_2 absorption envelopes after subtraction of the background indicated by dashes in (a).

DISCUSSION

On the basis of ionic radii (Whittaker & Munstus 1970) and charge alone, it is to be expected that Ni^{2+} (0.77\AA) would readily substitute for six-coordinate Mg^{2+} (0.80\AA) in hydrous nickel-magnesium silicates. Indeed, the Ni^{2+} — Mg^{2+} diadochy is well-established for this and other classes of silicate minerals (Deer, Howie & Zussman 1962; Faust 1966; Burns 1970). Consequently, we desire to show that the absorption spectrum of garnierite, (Fig. 1) is also consistent for Ni^{2+} in a site of pseudo-octahedral symmetry.

In an octahedral crystal field, Ni^{2+} , a d^8 ion, gives rise to three spin-allowed electronic transitions, ${}^3A_2(F) \rightarrow {}^3T_2(F)$, ${}^3A_2(F) \rightarrow {}^3T_1(F)$ and ${}^3A_2(F) \rightarrow {}^3T_1(P)$, whose energies depend upon the strength of the crystal field, as shown in the energy-level diagram in Figure 2. Absorption bands due to these transitions have been ob-

served in the spectra of many materials in which Ni^{2+} is octahedrally coordinated to oxygen atoms; therefore, it is reasonable to begin with the assumption that the bands marked γ_1 , γ_2 and γ_3 in the garnierite spectrum (Fig. 1) correlate with these transitions.

From the spectrum of a d^8 ion with octahedral site-symmetry, it is known (see Fig. 2) that γ_1 gives the value of the crystal-field-splitting parameter (which we symbolize here as Δ_{v1} to account for distortions from pure O_h symmetry). Also, the Racah B -parameter can be calculated from

$$\gamma_3 + \gamma_2 - 3\gamma_1 = 15B \quad (\text{Lever 1968}).$$

For the garnierite spectrum $B = 947\text{ cm}^{-1}$, which is close to the value of 928 cm^{-1} that Berkes (1968) used to calculate the energy-levels in Figure 2. Using the observed γ_1 -values of $9,100\text{ cm}^{-1}$ for Δ_{v1} , it can be seen that there is excellent agreement between the energies of the observed band-maxima and those taken from

Figure 2. Moreover, there is also excellent correspondence between the minor features at $13,000\text{ cm}^{-1}$ and $\approx 23,500\text{ cm}^{-1}$ in the garnierite spectrum and the spin-forbidden transitions ${}^3A_2(F) \rightarrow {}^1E(D)$ and ${}^3A_2 \rightarrow [{}^1A_1(G); {}^1T_2(D)]$, respectively. It can be concluded with certainty, therefore, that the absorption spectrum of garnierite, as expected, is due to Ni^{2+} replacing Mg^{2+} in six-coordinate sites in nickeloan chrysole.

As Lakshman & Reddy correctly stated, there are few examples of tetrahedrally-coordinated Ni^{2+} , especially in silicates. No doubt this reflects the preference of Ni^{2+} in oxo-structures for octahedral over tetrahedral coordination by $\approx 21\text{ kcal/mole}$ (Burns 1970). Despite this and the structural matters discussed earlier, Lakshman & Reddy presumed that Ni^{2+} has tetrahedral site-symmetry in garnierite. Their premise was apparently based on restricted spectral measurements, between $4,000$ and $22,000\text{ cm}^{-1}$, which showed features at $4,100$ - $4,300$, $\sim 9,300$ and $15,800$ - $16,400\text{ cm}^{-1}$. These were ascribed to the three spin-allowed transitions expected for Ni^{2+} in a tetrahedral crystal-field, namely ${}^3T_1(F) \rightarrow {}^3T_2(F)$, ${}^3T_1 \rightarrow {}^3A_2(F)$ and ${}^3T_1 \rightarrow {}^3T_1(P)$.

Considering band energies alone, this assignment agrees only approximately with the corresponding values of $\sim 3,000$, $\sim 7,000$ and $\sim 15,000\text{ cm}^{-1}$, obtained from an appropriate energy-level diagram (Berkes 1968) and the spectral parameters of Lakshman & Reddy for Δ_{v1} ($4,220\text{ cm}^{-1}$) and B (810 cm^{-1}). However, the assignment scheme can be dismissed because it does not take into account the existence of the prominent γ_3 -band at $26,300\text{ cm}^{-1}$ in the garnierite spectrum (Fig. 1). Although Lakshman & Reddy ignored this band, they were aware of the garnierite spectrum published by Faye (1971), which clearly showed the feature at $26,300\text{ cm}^{-1}$.

Another reason for rejecting the interpretation of Lakshman & Reddy concerns the narrow (half-width $\sim 250\text{ cm}^{-1}$) features at $4,098$ and $4,348\text{ cm}^{-1}$, which they assigned to components of the ${}^3T_1(F) \rightarrow {}^3T_2(F)$ electronic transition. Such narrow bands are probably vibrational in nature and similar to the sharp, minor features in the infrared portion of Figure 1; those at $\sim 7,200\text{ cm}^{-1}$ are thought to be due to the first overtone of the hydroxyl stretching-frequency (Burns 1970).

It is worth noting also that the intensity (oscillator strength) of $d-d$ transitions for tetrahedrally-coordinated ions is expected to be significantly greater than that for those in octahedral coordination. Clearly, this could not pertain to the weak narrow infrared bands in Figure 1 or

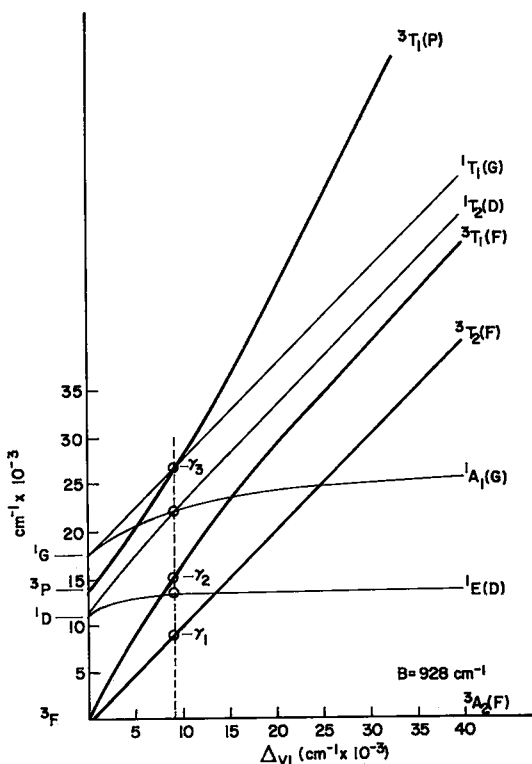


FIG. 2. Energy-level diagram for a d^8 ion in an octahedral crystal field (after Berkes 1968). The open circles give the energy of the observed bands or shoulders in the garnierite spectrum.

to corresponding bands in the spectrum of Lakshman & Reddy. For the latter, Lakshman & Reddy calculated oscillator strengths of $\sim 1 \times 10^{-5}$ from a mull spectrum without indicating how they measured the mull thickness, the concentration of Ni^{2+} in the mull, or the molar extinction coefficients for the bands.

Spectral estimation of average Ni^{2+} -O bond distance

It was stated earlier that the energy of the γ_1 -band, due to the ${}^3A_2(F) \rightarrow {}^3T_2(F)$ transition, gives a direct measure of the strength of the crystal field acting on the Ni^{2+} ion, here symbolized by Δ_{v1} . From Table 1 and Figure 3, it is apparent that a linear relationship exists between Δ_{v1} and the average $M-O$ bond distance for a number of materials containing six-coordinate Ni^{2+} . A similar correlation was established previously for Fe^{3+} -bearing materials (Faye 1972).

On the assumption that the relationship depicted in Figure 3 is applicable to Ni^{2+} in gar-

nerite, which has a Δ_{VI} -value of $9,100 \pm 150$ cm^{-1} , it can be estimated that the average Ni-O distance is $2.01 \pm 0.015 \text{ \AA}$.

It is also of passing interest that mull spectra of NiCO_3 and the Ni-bearing carbonate minerals gaspeite and zaraitite, give Δ_{VI} -values of $8,500 \pm 150$ cm^{-1} . The corresponding Ni-O distance from Figure 3 for these materials is $2.08 \pm 0.015 \text{ \AA}$. Mull spectra of mixtures of garnierite and zaraitite show appropriate intermediate values of Δ_{VI} .

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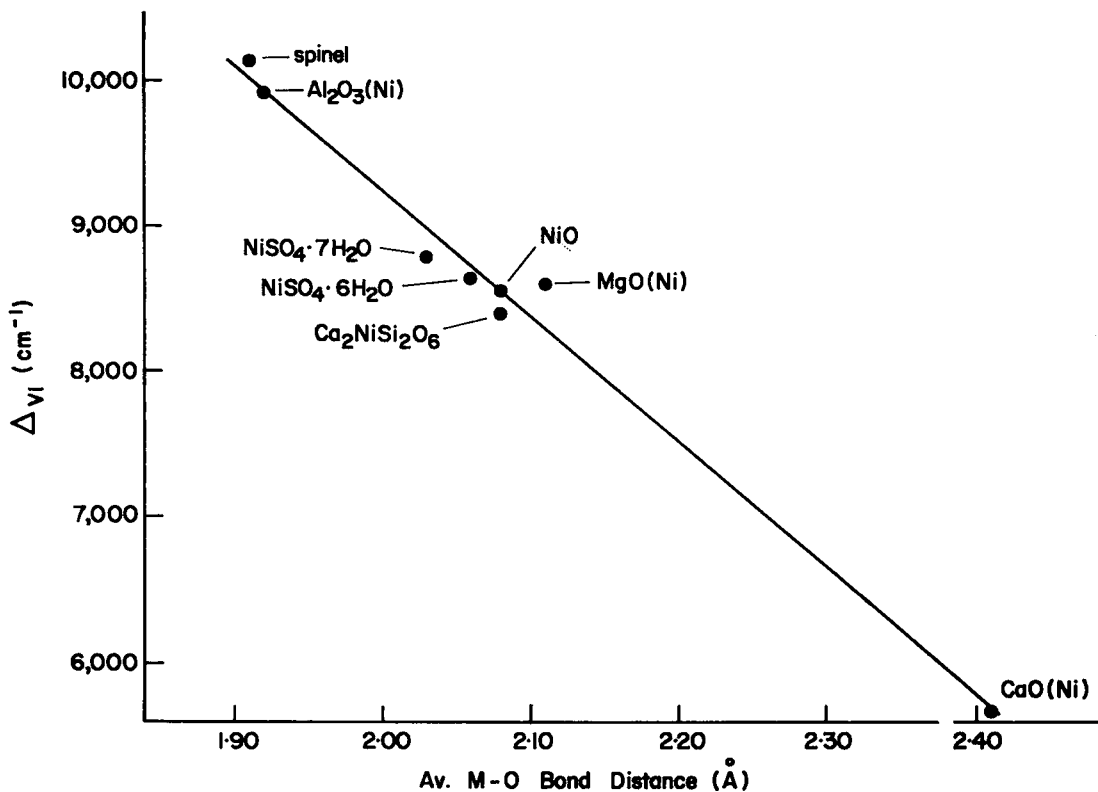


FIG. 3. Plot of the crystal-field-splitting parameter, Δ_{VI} vs. average $M\text{-O}$ bond distance for a number of Ni-bearing materials.

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