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OPTICAL ABSORPTION SPECTRUM OF Ni^{2+} IN GARNIERITE — DISCUSSION

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Faye (1971) studied the mull spectrum of garnierite at room temperature and reported three bands. He assigned them to transitions $^3A_2 \rightarrow {}^3T_2(F)$, $^3A_2 \rightarrow {}^3T_1(F)$ and $^3A_2 \rightarrow {}^3T_1(P)$ respectively without mentioning the ion responsible for these bands and its site symmetry. Lakshman & Reddy (1973) studied the optical absorption spectrum of garnierite both at room and liquid-air temperatures. The oscillator strengths of the bands were calculated as detailed by Stout (1959). From the observed features, the absorption bands were attributed to an ion of Ni^{2+} in tetrahedral symmetry.

Faye (1974) repeated the same experiment at room temperature and concluded that the Ni^{2+} ion in garnierite has octahedral site-symmetry.

The bands of Ni^{2+} in garnierite observed by Lakshman & Reddy (1973) as well as those observed by Faye (1974) are presented in Table 1, along with their respective assignments.

Lakshman & Reddy (1973) stated clearly in the introduction part of their paper that Faye observed three bands at approximately λ 11000Å, 6500Å and 4000Å and assigned them to the transitions mentioned above. In our work (1973), the absorption beyond 4000Å looked like edge absorption and the beginning and ending of the band could not be located with certainty both at room and liquid-air temperatures. If the symmetry is really octahedral, the band, if any, beyond 4000Å should have exhibited its contours on cooling the crystal to liquid-air temperature. As the present authors did not observe these features, they made the analysis with the rest of the bands.

The band reported by Faye (1974) at 26300 cm^{-1} (which the present authors did not observe) in all probability may be a charge-transfer band or a band of another impurity ion. Faye assigned a $^3A_2(F) \rightarrow {}^3T_1(P)$ transition to this band. If the band belongs to a $^3T_1(P)$ excited state, it should exhibit spin-orbit splitting. Faye can prove or disprove his interpretation by studying the optical spectrum of garnierite at liquid-hydrogen or liquid-helium temperatures.

Lakshman & Reddy in fact observed (at 90° K) spin-orbit splitting in the band at about 15000 cm^{-1}, confirming the $^3T_1{}^1 \rightarrow {}^3T_2{}^2$ transition assigned by them.

Faye is of the opinion that since the bands around 4000 cm^{-1} have half-widths of about 250 cm^{-1}, they should be vibrational in nature. However, sharpness is not the sole criterion for identifying the vibrational origin of the bands. The ligand-field bands are sharp (half-width could be 100 cm^{-1}) if the number of t_2 electrons is the same in both the excited and ground states (Tanabe 1960; Ballhausen 1962). Bands are also sharp if they belong to the spin-orbit components of the main band. The two peaks at 4098 cm^{-1} and 4348 cm^{-1} shown in Figure 1 are seen clearly as components of a main band around 4200 cm^{-1} whose intensity is comparable with that of the band at 9346 cm^{-1}.

In Figure 1, vibronic bands of H_2O are shown at 7410 cm^{-1}, 5920 cm^{-1} and 5290 cm^{-1}; if the band around 9000 cm^{-1} is electronic in origin, that at 4200 cm^{-1} should also be electronic in origin.

Multiplet T_1 and T_2 bands exhibit spin-orbit splittings. The magntiude of the splitting observed in the band around 4200 cm^{-1}, namely (4348-4098) 250 cm^{-1}, is of the value expected for $^3T_2$ of Ni^{2+} and therefore suggests correct

TABLE 1. BAND MAXIMA POSITIONS AND ASSIGNMENTS FOR Ni^{2+} IN GARNIERITE

Lakshman & Reddy (1973)		Faye (1974)	
Observed at 90°K	Transition	Observed at 300°K	Transition
4098* cm^{-1}	$({}^3T_1^1) \rightarrow \gamma_4({}^3T_2)$	~4000 cm^{-1}	vibrational bands (?)
4348*	$\rightarrow \gamma_5({}^3T_2)$	~4500	
9346*	$\rightarrow \gamma_5({}^3A_2)$	9100	$^3A_2(F) \rightarrow {}^3T_2(F)$
13602	$\rightarrow \gamma_3({}^1E)$	13000	$\rightarrow {}^1E(D)$
15823	$\rightarrow \gamma_5({}^3T_1^2)$	15200	$\rightarrow {}^3T_1(F)$
16385	$\rightarrow \gamma_3({}^3T_1^2)$		
20168	$\rightarrow \gamma_5({}^1T_2)$	23500	$\rightarrow {}^1A_1(G)$
			$\rightarrow {}^1T_2(D)$
		26300	$\rightarrow {}^3T_1(P)$

* Data at 300°K

For γ, read Γ

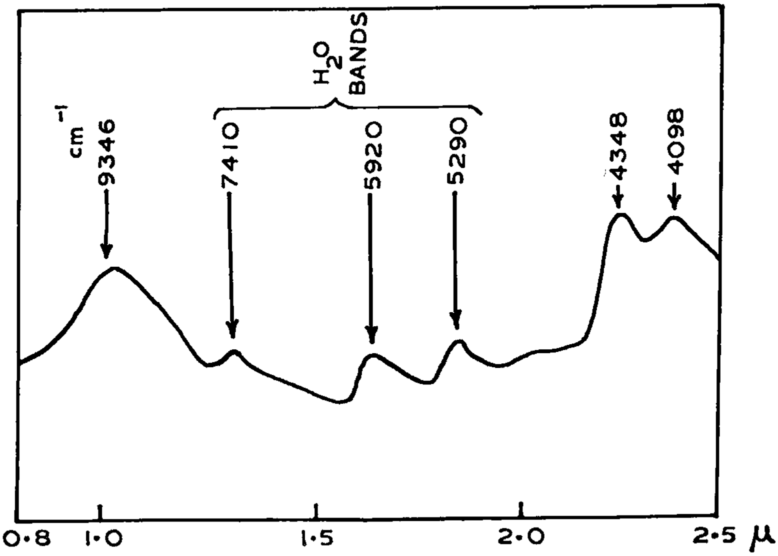

FIG. 1. Trace of the spectrophotometric record in the near-infrared region for the bands of Ni^{2+} in garnierite G I at 300°K.

assignment to spin-orbit levels of the excited $^3T_2$ state. If Faye's assignment of $^3T_2$ to the band around 9000 cm^{-1} is correct, the band should have exhibited splitting at liquid-air temperature. As no such splitting has been observed, the present authors attributed the $^3A_2$ state to this band.

Using the band around 26300 cm^{-1}, but omitting the bands around 4200 cm^{-1}, Faye interpreted the bands of garnierite as those of Ni^{2+} in *Oh* symmetry.

It may be concluded that the symmetry of the Ni^{2+} ion in garnierite can be confirmed only if the spectrum is studied at low temperatures.

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