

Optical absorption spectrum of Ni²⁺ ion doped in synthetic lecontite

S V J LAKSHMAN and T V KRISHNA RAO

Department of Physics, Sri Venkateswara University, Tirupati 517 502, India

MS received 6 August 1982

Abstract. The optical absorption spectrum of Ni²⁺ ion doped in lecontite (sodium ammonium sulphate dihydrate) single crystal has been studied at room and liquid air temperatures. All the bands could be assigned assuming O_h symmetry for the Ni²⁺ ion in the crystal. The splitting of ${}^3T_{1g}(F)$ band at liquid air temperature has been attributed to spin-orbit interaction. The crystal field and spin-orbit parameters derived are $Dq = 1000 \text{ cm}^{-1}$; $B = 740 \text{ cm}^{-1}$; $C/B = 4.27$ and $\zeta = 600 \text{ cm}^{-1}$. All the bands observed show a blue shift when the crystal was cooled to liquid air temperature.

Keywords. Optical absorption spectrum; lecontite; spin-orbit interaction; crystal field; Racah parameters.

1. Introduction

The optical absorption spectrum of Ni²⁺ ion doped in several host lattices has been extensively studied (Piper and Koentge 1960; Pryce *et al* 1964; Solomon and Ballhausen 1975; Datta and Debabala 1976; Lakshman and Janardhanam 1978; and Lakshmana Rao and Purandar 1981). The present investigation reports the optical absorption spectrum of Ni²⁺ ion doped in sodium ammonium sulphate dihydrate, $\text{NaNH}_4\text{SO}_4 \cdot 2\text{H}_2\text{O}$ single crystal. This synthetic crystal is identical with natural lecontite as reported by Faust and Bloss (1963). The crystal structure of synthetic lecontite has been determined by Corazza *et al* (1967). The unit cell is orthorhombic with $a = 8.216$, $b = 12.854$ and $c = 6.232 \text{ \AA}$ and space group $P 2_1 2_1 2_1$. The structure shows chains of Na octahedra sharing one face with each other (Na–Na distance is 3.15 \AA). The SO_4 tetrahedron is regular. The NH_4^+ ion coordinates seven oxygen atoms forming an irregular polyhedron.

2. Experimental

Single crystals of sodium ammonium sulphate dihydrate doped with Ni²⁺ were grown by slow evaporation of equimolar solution of sodium sulphate and ammonium sulphate to which nickel sulphate (1 mole % by wt) was added as an impurity. The crystals were clear, transparent and green in colour. A crystal of 2.5 mm thickness was found suitable in the present work.

The optical absorption spectrum was recorded on a Hilger medium quartz spectrograph both at room and liquid air temperatures in the wavelength region λ 300 to

900 nm on ORWO NP 27 film and Kodak IN plates. Wavelengths of the band maxima and oscillator strengths of the bands were calculated from their microphotometric profiles taken on a moll recording microphotometer.

3. Theory

The Ni^{2+} ion has the electron configuration $3d^8$. In the presence of a strong octahedral crystal field, the electronic states of Ni^{2+} ion arising from the ground and excited electronic configurations are as follows:

Ground	$t_{2g}^6 e_g^2$:	${}^3A_{2g}$,	${}^1A_{1g}$,	1E_g .	
First excited	$t_{2g}^5 e_g^3$:	${}^3T_{1g}$,	${}^3T_{2g}$,	${}^1T_{1g}$,	${}^1T_{2g}$.
Second excited	$t_{2g}^4 e_g^4$:	${}^3T_{1g}$,	${}^1A_{1g}$,	1E_g ,	${}^1T_{2g}$.

The ground state is ${}^3A_{2g}$ for all the strengths of the crystal field being the lowest according to Hund's rule.

Tanabe-Sugano (1954) gave the energy expressions for all the states in the absence of spin-orbit interaction in the form of matrices. Lakshman and Lakshman Rao (1972) presented these matrices in a linear form. The energy levels are designated as Γ_1 , Γ_2 , Γ_3 , Γ_4 and Γ_5 in the presence of spin-orbit interaction. Liehr and Ballhausen (1959) presented these energy matrices in terms of Condon-Shortley parameters F_2 and F_4 while Lakshman and Lakshmana Rao (1979) expressed the energy matrices in terms of Racah parameters B and C .

4. Results and analysis

The observed spectrum is characteristic of Ni^{2+} in octahedral symmetry. At room temperature four bands have been observed at 12015, 15670, 19600 and 25120 cm^{-1} . On cooling the crystal to liquid air temperature, the band at 15670 cm^{-1} showed splitting into three components with maxima at 15830, 16150 and 16290 cm^{-1} . The other three bands shifted towards blue with maxima at 12160, 19800 and 25635 cm^{-1} .

The medium quartz spectrograms of these bands at room and liquid air temperatures are shown in figure 1.

The ground state electronic configuration of Ni^{2+} ion in octahedral symmetry is ${}^3A_{2g}(F)$. According to the energy level scheme, three spin-allowed strong bands should be observed, which arise due to transitions from the ground state to the excited states ${}^3T_{2g}(F)$, ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ arranged in the increasing order of energy. From the nature and position of the bands at 15670 and 25120 cm^{-1} they could be attributed to ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ levels. The ${}^3T_{2g}(F)$ band could not be observed in the present work. The ${}^3T_{1g}(F)$ band exhibited splitting at 80°K. This type of splitting in ${}^3T_{1g}(F)$ band has been reported in literature by several investigators (Piper and Koentge 1960; Pryce *et al* 1964; Solomon and Ballhausen 1975; Datta and Debabala 1976; Lakshman and Janardhanam 1978; Lakshmana Rao and Purandar 1981). This characteristic splitting of the band further supports the assignment.

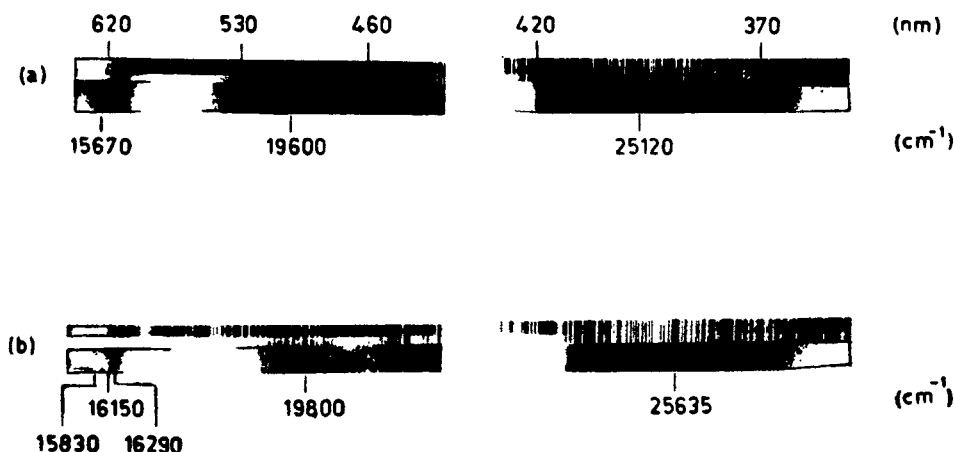


Figure 1. Medium quartz spectrograms (λ 650 to 300 nm) a. At room temperature (300°K). b. At liquid air temperature (80°K)

Table 1. Assignments of the bands with their wavelengths (λ) and wavenumbers (ν) at room and liquid air temperatures.

Transition from ${}^3A_{2g}(F)$	Band position			
	300°K		80°K	
	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$
${}^1E_g(D)$	832	12015	822	12160
${}^3T_{1g}(F)$	638	15670	632	15830
			619	16150
			614	16290
${}^1A_{1g}(G)$	510	19600	505	19800
${}^3T_{1g}(P)$	398	25120	390	25635

According to the theory, some spin-forbidden triplet-singlet bands could also appear and the intensity of such bands would be low. The bands at 12015 and 19600 cm^{-1} could be assigned to ${}^1E_g(D)$ and ${}^1A_{1g}(G)$ states from Tanabe-Sugano diagram and other calculations. They exhibited blue shift on cooling the crystal to liquid air temperature in accordance with the positive slopes of their energy levels, thus confirming the assignments.

The assignments of the bands with their wavelengths and wavenumbers at room and liquid air temperatures are presented in table 1.

The energy expressions of Lakshman and Lakshmana Rao (1972) have been solved for different values of Dq/B and C . It has been found that the best fit for the observed bands at 300 °K could be obtained for $C/B=4.27$. The crystal parameters derived are $B=740 \text{ cm}^{-1}$ and $Dq=990 \text{ cm}^{-1}$. The band maxima positions calculated with these parameters along with the observed band positions and their oscillator strengths at room temperature are presented in table 2.

5. Discussion

The nature of the splitting observed at liquid air temperature for the ${}^3T_{1g}(F)$ band appears to be due to spin-orbit effect. The ${}^3T_{1g}(F)$ level splits into three ($\Gamma_3 + \Gamma_5$,

Table 2. Observed and calculated energies, assignments and oscillator strengths for the bands of Ni²⁺ in sodium ammonium sulphate dihydrate at room temperature.

Transition from ³ A _{2g} (F)	Band positions (cm ⁻¹)		Oscillator strengths f × 10 ⁶
	Observed	Calculated	
¹ E _g (D)	12015	11925	3.0
³ T _{1g} (F)	15670	15675	5.0
¹ A _{1g} (G)	19600	20010	1.2
³ T _{3g} (P)	25120	25125	6.7

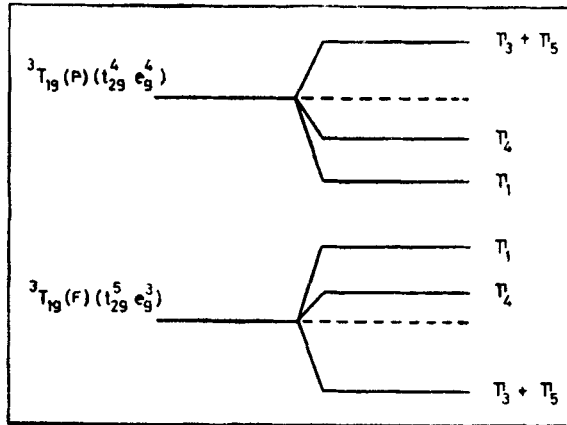


Figure 2. First order spin-orbit splitting for ³T_{1g} (P) and ³T_{1g} (F)

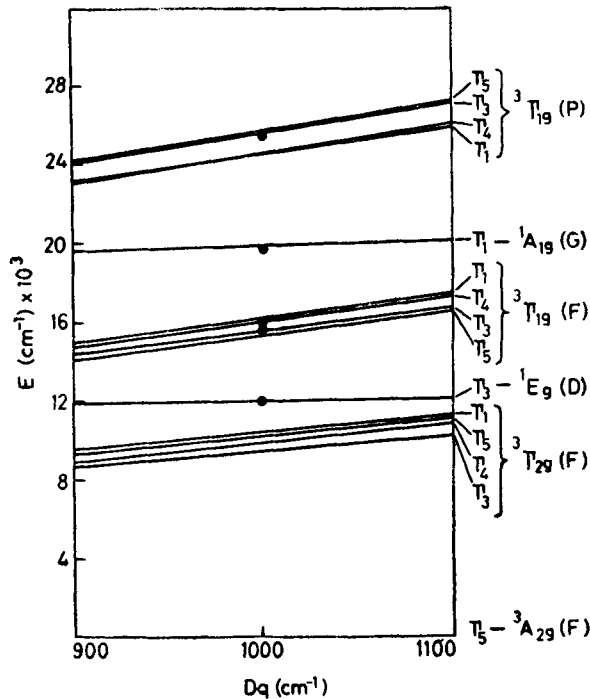


Figure 3. Energy level diagram.

Table 3. Observed and calculated energies, oscillator strengths and the assignments for the bands of Ni²⁺ in sodium ammonium sulphate dihydrate at liquid air temperature.

$B = 740 \text{ cm}^{-1}$		$C/B = 4.27$	$Dq = 1000 \text{ cm}^{-1}$	$\zeta = 600 \text{ cm}^{-1}$
Transition from ${}^3A_{2g} (F) \Gamma_5$	Band positions (cm ⁻¹)		Oscillator strengths $f \times 10^6$	
	Calculated	Observed		
${}^3T_{2g} (F)$	Γ_3	9645		
	Γ_4	9905		
	Γ_5	10260		
	Γ_2	10385	—	—
${}^1E_g (D)$	Γ_3	12150	12160	2
${}^3T_{1g} (F)$	Γ_5	15525	—	
	Γ_3	15670	15830	
	Γ_4	16175	16150	5
	Γ_1	16370	16290	
${}^1A_{1g} (G)$	Γ_1	20065	19800	2
${}^3T_{1g} (P)$	Γ_1	24605		
	Γ_4	25615	25635	3
	Γ_3	25785		
	Γ_5	25865		

Γ_4 and Γ_1) and four (Γ_5 , Γ_3 , Γ_4 and Γ_1) component levels respectively in the first and second order configurational interactions. The first order spin-orbit splitting for ${}^3T_{1g} (F)$ and ${}^3T_{1g} (P)$ arising from $t_{2g}^5 e_g^3$ and $t_{2g}^4 e_g^4$ electron configurations are shown in figure 2.

With free ion spin-orbit coupling parameter of $\zeta=600 \text{ cm}^{-1}$, the calculated separation between the components of ${}^3T_{1g} (F)$ state would be of the order of 140 and 280 cm^{-1} . Since the observed splittings of 140 cm^{-1} (16290–16150) and 320 cm^{-1} (16150–15830) are of the same order of spin-orbit splitting expected for Ni²⁺ ion in the crystal, the energy matrices inclusive of spin-orbit effect are diagonalised for different values of Dq with $B=740 \text{ cm}^{-1}$, $C/B=4.27$ and $\zeta=600 \text{ cm}^{-1}$. The best fit of the observed bands could be obtained with $Dq=1000 \text{ cm}^{-1}$. The corresponding energy level diagram (E vs Dq) is shown in figure 3. The observed and calculated band maxima positions along with their oscillator strengths are presented in table 3. Attempts to fit the bands for any value other than $\zeta=600 \text{ cm}^{-1}$ were not successful.

Acknowledgements

One of the authors (TVKR) is thankful to the University authorities and to UGC, New Delhi for the award of a fellowship.

References

- Corazza E, Sabelli C and Giuseppetti G 1967 *Acta Crystallogr.* **22** 683
 Datta S K and Debabala D E 1976 *Indian J. Cryogen.* **1** 45
 Faust R J and Bloss F D 1963 *Am. Min.* **48** 180
 Lakshman S V J and Janardhanam K 1978 *Pramana* **11** 697
 Lakshman S V J and Lakshmana Rao J 1972 *Indian J. Pure. Appl. Phys.* **10** 479

Lakshman S V J and Lakshmana Rao J 1979 *Spectrochim. Acta* **A35** 703

Lakshmana Rao J and Purandar K 1981 *Spectrochim. Acta* **A37** 787

Liehr A D and Ballhausen C J 1959 *Ann. Phys. (NY)* **6** 134

Piper T S and Koentge N 1960 *J. Chem. Phys.* **32** 559

Pryce M H L, Agnetta G, Garofano T, Palmavitorelli M B and Palma M V 1964 *Philos. Mag.* **10**
477

Solomon E I and Ballhausen C J 1975 *Mol. Phys.* **29** 279

Tanabe Y and Sugano S 1954 *J. Phys. Soc. Jpn.* **9** 753