Optical absorption spectrum of Ni²⁺ doped in ammonium zinc sulphate

S V J LAKSHMAN AND K JANARDHANAM

Spectroscopic Laboratories, Department of Physics, Sri Venkateswara University, College of Sciences, Tirupati 517 502

Abstract. The optical absorption spectrum of Ni²⁺ ion doped in ammonium zinc sulphate has been studied at room and liquid air temperatures. From the nature and the positions of the bands a successful interpretation of all the bands could be made assuming O_h symmetry for the Ni²⁺ ion in the crystal. The fine splitting of the $^3T_1{}^1$ band at liquid air temperature has been successfully interpreted to be due to spin-orbit interaction. The crystal field and spin-orbit parameters derived are $Dq = 1000$ cm⁻¹ ; $B = 750$ cm⁻¹; $C = 3.45B$ and $\xi = 600$ cm⁻¹.

1. Introduction

Lakshman and Reddy (1974) studied the optical absorption spectrum of Ni²⁺ ion doped in ammonium aluminium sulphate single crystal and reported O_h symmetry for the ion in the alum. In the present work, the optical absorption spectrum of Ni²⁺ ion doped in ammonium zinc sulphate has been reported for the first time.

2. Experimental

Single crystals of ammonium zinc sulphate doped with Ni²⁺ were grown in the laboratory at 10 cm pressure by slow evaporation of saturated solution of ammonium zinc sulphate to which was added 1 mole % by weight of nickel sulphate as an impurity. Ammonium zinc sulphate was prepared in the laboratory as detailed by Vogel (1968). A crystal of thickness 0·2 cm was found suitable in the present work.

The absorption spectrum of the crystal was recorded at room and liquid air temperatures on a Hilger medium quartz spectrograph. Spectra were recorded both for polarised and unpolarised beams of incident radiation. Spectra were recorded in about 30–60 min on Kodak IN, Ilford Astra, R-20 and Zenith 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 electronic states of Ni²⁺ in a strong octahedral field arising from the ground and

excited electronic configurations are as follows (the subscript g is omitted for convenience).

Ground $t_2{}^6 \, e^2 : {}^3A_2, \, {}^1A_1{}^1, \, {}^1E^1$

First excited $t_2{}^5 \, e^3 : {}^3T_1{}^1, \, {}^3T_2, \, {}^1T_1, \, {}^1T_2{}^1$

Second excited $t_2{}^4 \, e^4 : {}^3T_2{}^1, \, {}^1A_1{}^2, \, {}^1E^2, \, {}^1T_2{}^2$

According to Hund's rule, ${}^3A_2$ lies lowest and forms the ground state of the ion.

The energy expressions for all the states in the absence of spin-orbit interaction were given in the form of matrices by Tanabe and Sugano (1954). Lakshman and Lakshmana Rao (1972) had presented these matrices in a linear form.

In the presence of spin-orbit interaction, the energy levels are designated as Γ_1, Γ_2, Γ_3, Γ_4 and Γ_5. The energy matrices for these spin-orbit levels were presented by Liehr and Ballhausen (1959) in terms of F_2, F_4, Dq and λ, and in terms of B, C, Dq and ξ by Lakshman and Reddy (1974).

4. Results

Four absorption bands have been observed at room temperature—one in the near infrared at 11919 cm^{-1}, two in the visible at 15545 cm^{-1} and 20436 cm^{-1} and one in the near ultraviolet at 25967 cm^{-1}.

On cooling the crystal to liquid air temperature, the band at 25967 cm^{-1} is shifted to 26171 cm^{-1}. The band at 15545 cm^{-1} exhibited splitting into five components at 15684, 15823, 16216, 16394 and 16718 cm^{-1}. Further two additional bands have been observed at 18813 cm^{-1} and 19348 cm^{-1}.

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

The wavelengths, wave numbers and assignments of the bands at room and liquid air temperatures are given in table 1.

Table 1. Wavelength (λ), wave number (ν) and assignments for the bands of Ni^{2+} in ammonium zinc sulphate.

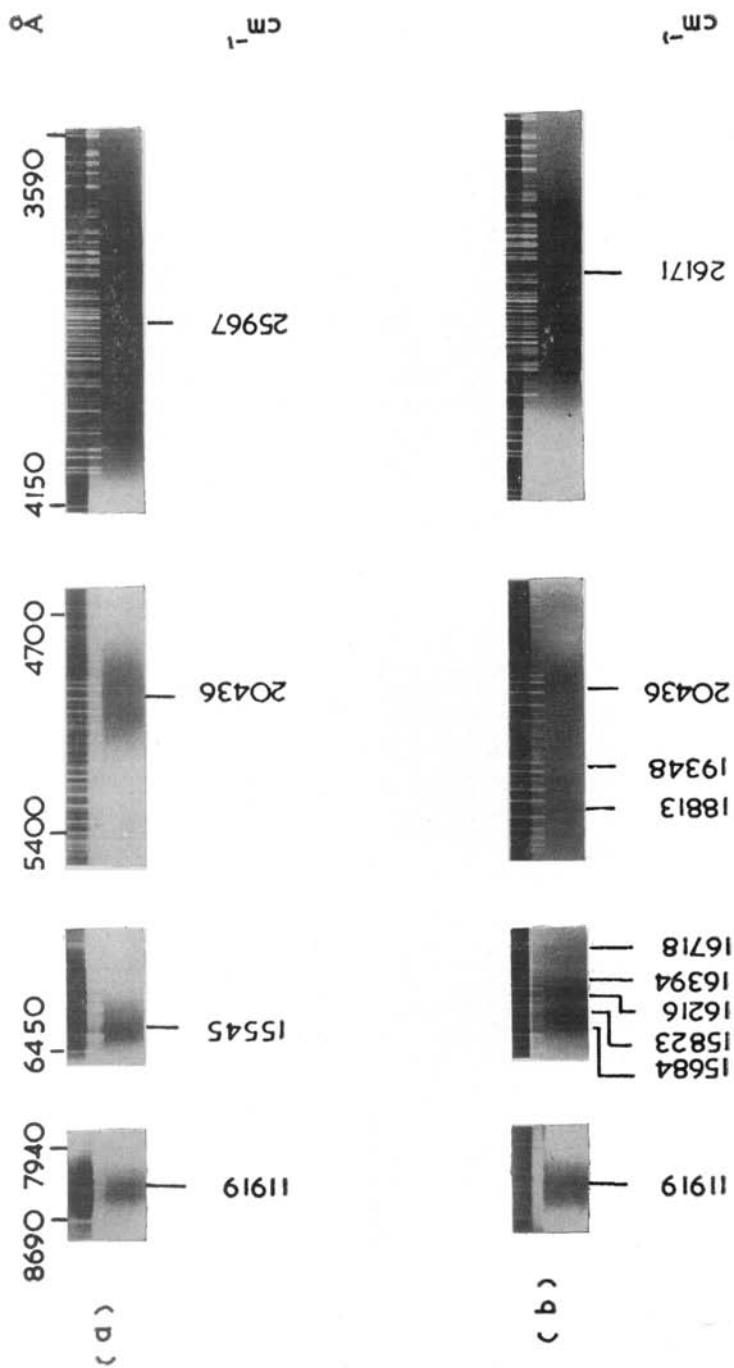| Transition from ${}^3A_2$ | Band Positions | | | |
| | 300°K | | 80°K | |
	λ (Å)	ν (cm^{-1})	λ (Å)	ν (cm^{-1})
${}^3T_2$	8388	11919	8388	11919
${}^3T_1{}^1$	6431	15545	—	—
(a)	—	—	6374	15684
(b)	—	—	6318	15823
(c)	—	—	6165	16216
(d)	—	—	6098	16394
(e)	—	—	5980	16718
	—	—	5314	18813
	—	—	5167	19348
${}^1T_2$	4892	20436	4892	20436
${}^3T_1{}^2$	3850	25967	3820	26171

Figure 1. Medium quartz spectrogram of Ni²⁺ in ammonium zinc sulphate (a) At 300°K (b) At 80°K

5. Analysis

From the nature and observed band positions, analysis is made with the assumption that the bands belong to Ni^{2+} ion in O_h symmetry. The three bands at 11919 cm^{-1}, 15545 cm^{-1} and 25967 cm^{-1} were found to be in the order of increasing intensity as their energies. As we can expect only three spin allowed transitions $^3A_2 \rightarrow {}^3T_2$, $^3A_2 \rightarrow {}^3T_1{}^1$ and $^3A_2 \rightarrow {}^3T_1{}^2$ for Ni^{2+} ion in O_h symmetry in the order of increasing energy, we attributed the above three bands to these three transitions respectively. The most intense band at 25967 cm^{-1} exhibited a violet shift to 26171 cm^{-1} when the crystal was cooled to liquid air temperature. This is in accordance with the theory since the energy level ($^3T_1{}^2$) corresponding to this band has a positive slope in the Tanabe-Sugano (1954) energy level diagram. No such shift could be observed for the next intense $^3T_1{}^1$ band as it exhibited splitting at 80° K. Using Tanabe-Sugano diagram for d^8 configuration, the weak band at 20436 cm^{-1} is assigned $^3A_2 \rightarrow {}^1T_2$ transition.

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 could be obtained for $C = 3\cdot45\,B$. The crystal parameters derived are $B = 750$ cm^{-1} and $Dq = 1000$ cm^{-1}.

The band maxima positions calculated with these parameters along with the observed band positions and their oscillator strengths are presented in table 2.

6. Discussion

The nature of the splitting observed at liquid air temperature for the $^3T_1{}^1$ band at 15545 cm^{-1} appears to be that due to spin-orbit effect. The $^3T_1$ band splits into three ($\Gamma_3 + \Gamma_5$, Γ_4 and Γ_1) and four (Γ_5, Γ_3, Γ_4 and Γ_1) component levels respectively in the first order and second order configurational interactions. The first order spin-orbit splitting for $^3T_1{}^1$ and $^3T_1{}^2$ arising from $t_2{}^5\,e^3$ and $t_2{}^4\,e^4$ electron configurations are shown in figure 2.

Using the free ion spin-orbit coupling parameter of $\xi = 600$ cm^{-1}, the calculated separation between the components of $^3T_1{}^1$ state would be of the order of 280 cm^{-1}. Since the observed splittings of (15823—15684) 139 cm^{-1}, (16216—15823) 393 cm^{-1} and (16394—16216) 178 cm^{-1} are of the order of spin-orbit splitting expected for Ni^{2+} ion in the crystal, the energy matrices inclusive of spin-orbit effect are diagonalised on IBM 370/155 computer for different values of ξ with $B = 750$ cm^{-1}, $C = 3\cdot45\,B$ and

Table 2. Observed and calculated energies, assignments and the oscillator strengths for the bands of Ni²⁺ in ammonium zinc sulphate
$B = 750$ cm^{-1} $C = 3\cdot45\,B$ $Dq = 1000$ cm^{-1}.

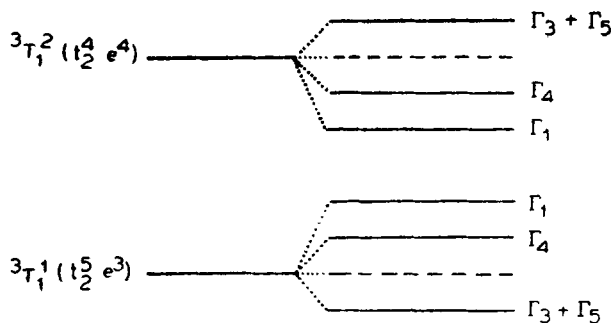| Transition from $^3A_2$	Band positions (cm^{-1})		Oscillator strengths
	Observed at 300°K	Calculated	
$^3T_2$	11919	10000	$2\cdot22 \times 10^{-6}$
$^3T_1{}^1$	15545	15840	$2\cdot30 \times 10^{-5}$
$^1T_2$	20436	20580	$2\cdot10 \times 10^{-6}$
$^3T_1{}^2$	25967	25409	$2\cdot71 \times 10^{-4}$

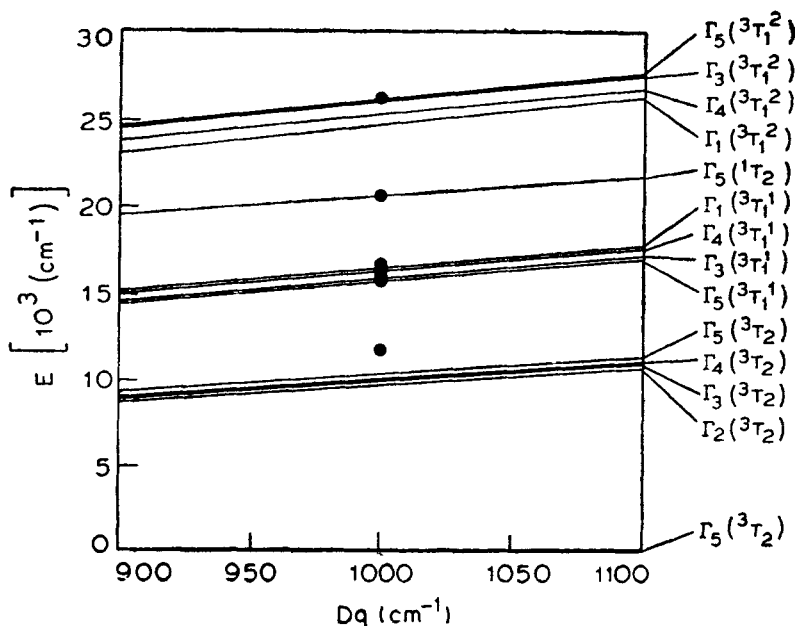**Figure 2.** First order spin-orbit splitting for $^3T_1{}^1$ and $^3T_1{}^2$.

Figure 3. Energy level diagram of Ni^{2+} in ammonium zinc sulphate in cubic environment plotted as a function of the crystal field parameter Dq, with $B = 750$ cm^{-1}, $C = 3.45$ B and $\xi = 600$ cm^{-1}. The solid circles show the experimental values at $80°K$

$Dq = 1000$ cm^{-1} and also with different values of Dq with $B = 750$ cm^{-1}, $C = 3.45$ B and $\xi = 600$ cm^{-1}. The best fit is obtained at $\xi = 600$ cm^{-1}, $Dq = 1000$ cm^{-1}, $B = 750$ cm^{-1} and $C = 3.45$ B. The corresponding energy level diagram (E vs Dq) is shown in figure 3. The band energy values read from this graph are presented along with the observed band maxima positions and their oscillator strengths in table 3.

7. Vibrational frequencies of ions

The nature of the band at 16718 cm^{-1} appears not to be a component of the split band at 15545 cm^{-1}. The wave number separations between this band at 16718 cm^{-1}

Table 3. Observed and calculated energies, assignments and the oscillator strengths for the bands of Ni^{2+} in ammonium zinc sulphate

$B = 750 \text{ cm}^{-1}$ $C = 3·45B$ $Dq = 1000 \text{ cm}^{-1}$ $\xi = 600 \text{ cm}^{-1}$.

Transition from $^3A_2$	Band positions (cm^{-1})		Oscillator strengths
	Calculated*	Observed at 80° K	
$^3T_2$	9769 ⎫		
$^3T_2$	9894 ⎪	11919	2·27 × 10⁻⁶
$^3T_2$	9896 ⎬		
$^3T_2$	10283 ⎭		
$^3T_1^1$	15557	15684 ⎫	1·20 × 10⁻⁵
$^3T_1^1$	15648	15823 ⎬	
$^3T_1^1$	16193	16216 ⎫	5·25 × 10⁻⁶
$^3T_1^1$	16322	16394 ⎬	
$^1T_2$	20654	20436	2·42 × 10⁻⁶
$^3T_1^2$	24599 ⎫		
$^3T_1^2$	25269 ⎪	26171	1·83 × 10⁻⁴
$^3T_1^2$	25925 ⎬		
$^3T_1^2$	25972 ⎭		

*Values taken from figure 3.

Table 4. Comparison of fundamental vibrational frequencies of SO_4^{--} radical with the observed energy differences

Fundamental vibrational frequencies of SO_4^{--} radical cm^{-1}	Observed energy difference cm^{-1}
981 (ν_1)	895
451 (ν_2)	324
1104 (ν_3)	1034
613 (ν_4)	502

and the split components of the 15545 cm^{-1} band are as follows:

$$16718—15684 = 1034 \text{ cm}^{-1},$$
$$16718—15823 = 895 \text{ cm}^{-1},$$
$$16718—16216 = 502 \text{ cm}^{-1},$$
$$16718—16394 = 324 \text{ cm}^{-1}.$$

A comparison of the fundamental vibrational frequencies of SO_4^{--} radical made with these values and shown in table 4 suggests that the band at 16718 cm^{-1} is in all probability the vibrational mode of SO_4^{--} radical.

The extra bands obtained at liquid air temperature at 18813 cm^{-1} and 19348 cm^{-1} also appear from their nature to belong to a vibrational mode of a radical. The energy differences between these two bands and the $^3T_1^1$ band suggest that they might belong to the vibrational mode of NH_4^+ radical. Since the $^3T_1^1$ band exhibits fine

Table 5. Observed near infrared bands, their assignments and calculated energies in Ni^{2+} : $Zn(NH_4)_2 (SO_4)_2 \cdot 6H_2O$

Molecule	Band positions (cm^{-1})		Assignments
	Observed (300°K)	Calculated	
SO_4^{--}	4695	4621	$2\nu_1+\nu_2+2\nu_3$
	5208	5195	$\nu_1+2\nu_2+3\nu_3$
	5436	5440	$2\nu_2+3\nu_3+2\nu_4$
	5781	5808	$\nu_1+2\nu_2+3\nu_3+\nu_4$
NH_4^+	6452	6403	$\nu_1+2\nu_2$
	7246	7224	$\nu_1+3\nu_4$
	9260	9249	$\nu_1+\nu_2+\nu_3+\nu_4$

Calculated from fundamental vibrational frequencies (Herzberg 1962)

SO_4^{--}: $\nu_1 = 981$ cm^{-1}, $\nu_2 = 451$ cm^{-1}, $\nu_3 = 1104$ cm^{-1}, $\nu_4 = 613$ cm^{-1}

NH_4^+: $\nu_1 = 3033$ cm^{-1}, $\nu_2 = 1685$ cm^{-1}, $\nu_3 = 3134$ cm^{-1}, $\nu_4 = 1397$ cm^{-1}

splitting at 80°K, the average of the first two bands (which appear alike) at 15684 and 15823 cm^{-1} is taken as one band (15754 cm^{-1}) and the average of the next two like bands at 16216 and 16394 cm^{-1} as another band (16305 cm^{-1}). The energy difference between the first average band of $^3T_1^1$ at 15754 cm^{-1} and the new band at 18813 cm^{-1} is 3059 cm^{-1}. Similarly the difference between the next average band of $^3T_1^1$ at 16305 cm^{-1} and the new band at 19348 cm^{-1} is 3043 cm^{-1}. Since these two energies namely 3059 and 3043 cm^{-1} are more or less identical to one another, we can conclude that the average band maxima at 15754 cm^{-1} and 16305 cm^{-1} of $^3T_1^1$ correspond to bands at 18813 and 19348 cm^{-1} respectively. The fundamental vibrational frequency ν_1 of NH_4^+ ion is 3033 cm^{-1} (Herzberg 1962) and as the above energy differences are close to this value, we may conclude that the bands at 18813 and 19348 cm^{-1} belong to the vibrational modes of NH_4^+ ion.

It is interesting to note that the near infrared spectrum shows the bands belonging to the ions of SO_4^{--} and NH_4^+. The observed near infrared band maxima positions, their assignments along with the calculated values are given in table 5. This therefore confirms our interpretation of the extra bands.

References

Herzberg G 1962 *Molecular spectra and molecular structure* (New York: Van Nostrand) **2** 167
Lakshman S V J and Lakshmana Rao J 1972 *Indian J. Pure Appl. Phys.* **10** 497
Lakshman S V J and Reddy B C V 1974 (unpublished)
Liehr A D and Ballhausen C J 1959 *Ann. Phys. (New York)* **6** 134
Tanabe Y and Sugano S 1954 *J. Phys. Soc. Jpn.* **9** 753
Vogel A I 1968 *A text book of quantitative inorganic analysis* (London: English Language Book Society and Longmans)