Absorption Spectrum of Ni(II) Ions Doped in Magnesium Thallium Sulphate Hexahydrate

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The optical absorption spectrum of Ni(II) ions doped in magnesium thallium sulphate hexahydrate has been studied at room- and liquid nitrogen-temperature. The crystal shows characteristic absorption of Ni(II) ion in the visible and near infrared region. The observed bands are assigned as transitions from the ground state $^3A_{2g}(F)$ to various excited triplet and singlet levels of the Ni(II) ion in octahedral symmetry. The splitting in one of the bands at liquid nitrogen temperature has been explained to be due to spin-orbit splitting. All the observed band positions have been fitted with the parameters B, C, Dq, and ξ.

1. Introduction

Tutton salts are excellent hosts for optical and paramagnetic resonance studies. The optical absorption spectra of Ni(II) ion in various environments have been studied in [1–9]. In the present investigation we report on the optical absorption spectra of divalent nickel ions doped in magnesium thallium sulphate hexahydrate (MTSH). This Tutton salt belongs to the monoclinic system with space group $P2_{1/a}$ [10, 11] and contains two Mg atoms per unit cell. In the lattice, the Mg(II) ion is surrounded by six water molecules forming approximately octahedral symmetry.

Jain et al. [12, 13] studied the EPR spectra of certain first group transition metal ions doped in MTSH and reported that the divalent first group transition metal ion substitutes Mg(II) in the MTSH lattice.

2. Experimental

The crystals were grown at room temperature from an aqueous solution of MTSH to which a few mol% of nickel sulphate were added. The crystals grown were clear and green in colour. The unpolarized spectra were recorded at room- and liquid nitrogen-temperature on a Hitachi 3400 UV-VIS-NIR spectrophotometer.

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3. Results and Analysis

The optical absorption spectrum in the visible and near infrared regions observed at room temperature is shown in Figs. 1 a and b, respectively. Five bands have been observed at room temperature, one in the near infrared at 9090 cm^{-1}; three in the visible at 13 985 cm^{-1}, 15 195 cm^{-1} (and 15 385 cm^{-1}) and 22 220 cm^{-1}, and one in the near ultra-violet at 25 640 cm^{-1}. Among these five bands, the band in the near ultra-violet is the most intense one.

On cooling the crystal to liquid nitrogen temperture, changes in the intensity and band positions are observed. At 77 K, the band at 15 195 cm^{-1} splits into three components with maxima at 15 150 cm^{-1}, 15 505 cm^{-1} and 16 130 cm^{-1}, while the bands at 9090 cm^{-1}, 13 985 cm^{-1}, 22 220 cm^{-1} and 25 640 cm^{-1} are shifted to 9435 cm^{-1}, 14 045 cm^{-1}, 22 885 cm^{-1} and 26 110 cm^{-1}, respectively. The spectra observed at liquid nitrogen temperature are shown in Figs. 2 a and b. They are very similar to those of the other hydrated nickel salts [8, 14, 15], indicating that the nickel ion is coordinated with water molecules in the crystal. From the nature and position of the bands, they have been attributed to Ni(II) ion in octahedral symmetry. The ground state electronic configuration of the Ni(II) ion in octahedral symmetry is $^3A_{2g}(F)$. According to the energy level scheme, three spin allowed bands would be observed which arise due to the transitions from the ground state to the excited states $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ arranged in the

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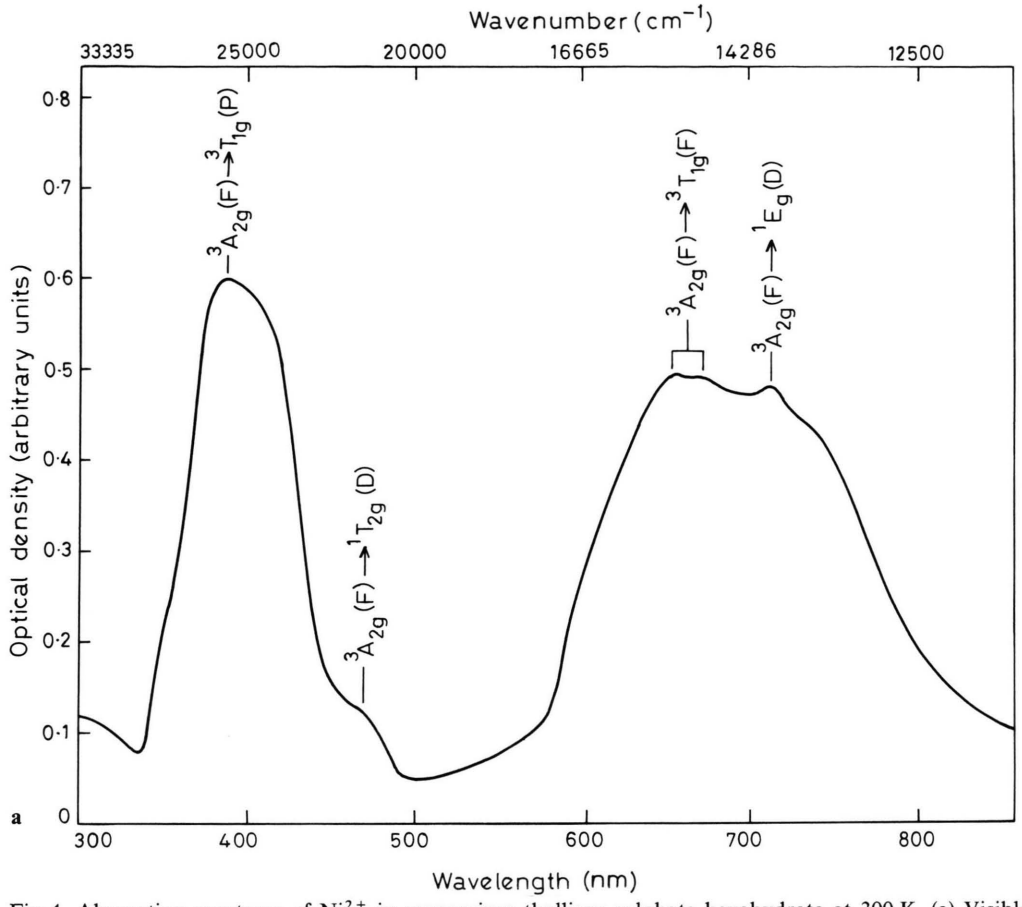
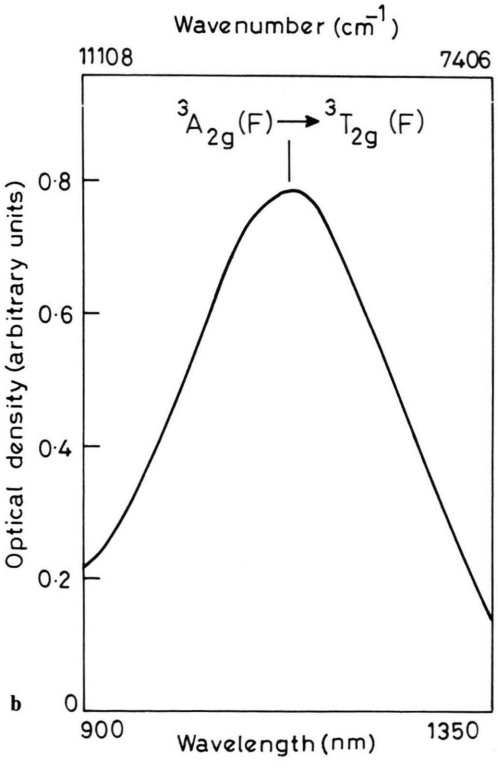


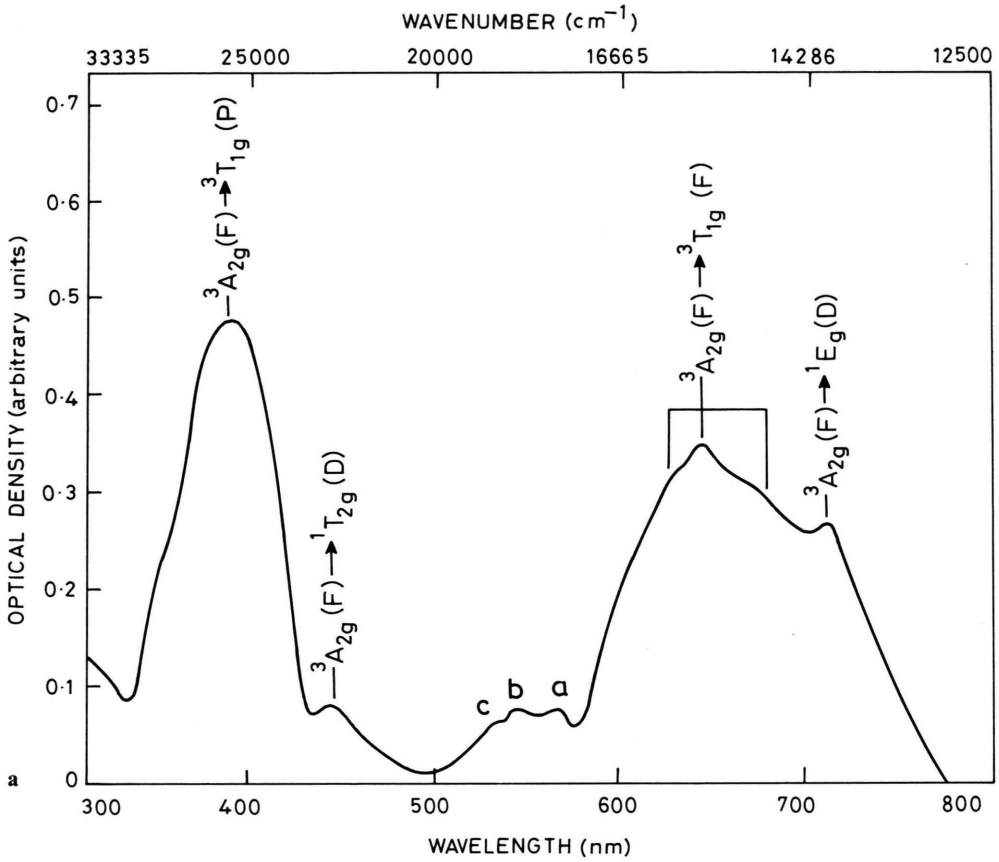
Fig. 1. Absorption spectrum of Ni^{2+} in magnesium thallium sulphate hexahydrate at 300 K. (a) Visible region. (b) Near infrared region.



order of increasing energy. The intense bands observed at 9090 cm^{-1} and 25 640 cm^{-1} have ben attributed to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively.

Most of the nickel complexes show a double peaked absorption at room temperature [8, 9, 15, 16]. Indeed, also in the present work a double peaked band located at 15 195 cm^{-1} and 15 385 cm^{-1} is observed which is attributed to the $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ transition. The three spin-allowed bands are expected to show a blue shift at low temperature, as their corresponding states $^3T_{2g}(F)$, $^3T_{1g}(F)$ and $^3T_{1g}(P)$ have positive slopes in the Tanabe-Sugano energy level diagram [17] given for d^8 configuration. Thus the observed blue shifts of the $^3T_{2g}(F)$ and $^3T_{1g}(P)$ bands at low temperature are in accordance with the theory. No such observation could be made for the $^3T_{1g}(F)$ band as it has been found to split at liquid nitrogn temperature. Such splittings of the $^3T_{1g}(F)$ band have been reported by several authors [7–9]. This characteristic splitting of the band further supports the assignment.

Lever [16] noted that $^3T_{1g}(F)$ appears as well defined double peaked band if Dq/B is near unity. The calculated Dq/B ratio at room temperature in the



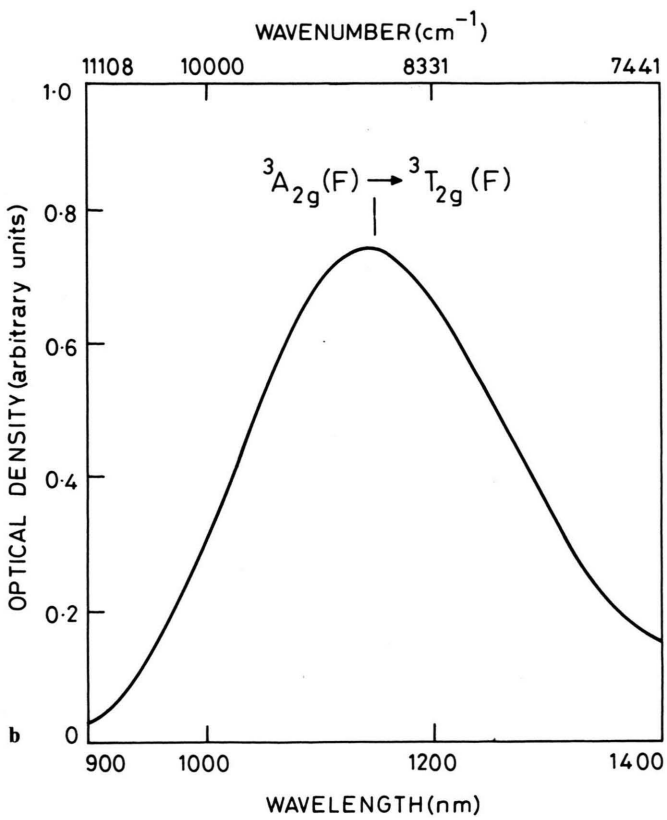


Fig. 2. Absorption spectrum of Ni^{2+} in magnesium thallium sulphate hexahydrate at 77 K. (a) Visible region. (b) Near infrared region.

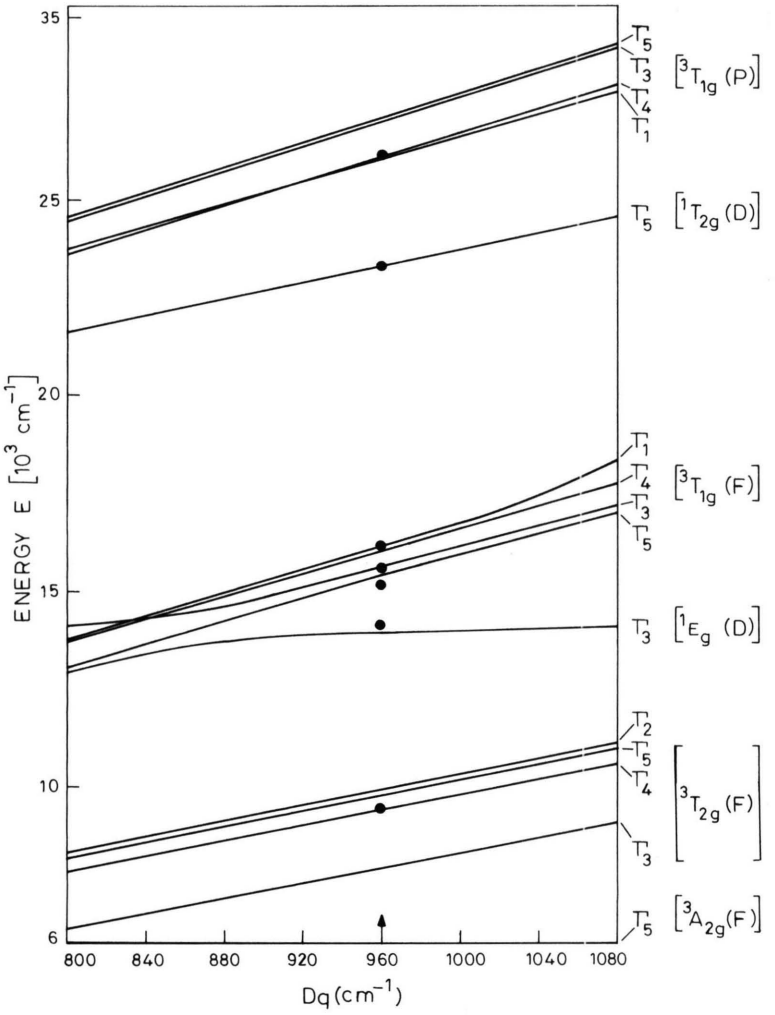


Fig. 3. Energy level diagram of Ni^{2+} in magnesium thallium sulphate hexahydrate in cubic envirnoment plotted as a function of the crystal field parameter Dq with $B=900\ cm^{-1}$, $C=3660\ cm^{-1}$, and $\xi=600\ cm^{-1}$. The solid circles show the experimental values at 77 K.

Table 1. The observed and calculated energies and assignments for the bands of Ni^{2+} in magnesium thallium sulphate hexahydrate ($B=900\ cm^{-1}$, $Dq=960\ cm^{-1}$, $C=3660\ cm^{-1}$ and $\xi=6000\ cm^{-1}$).

Transition assignment $^3A_{2g}(F)$	Spin-orbit designation	Band position (cm^{-1})		
		Room temperature (observed)	Liquid nitrogen temperature (observed)	Calculated
$^3T_{2g}(F)$	$\begin{bmatrix}\Gamma_3\\ \Gamma_4\\ \Gamma_5\\ \Gamma_2\end{bmatrix}$	9 090	9 435	7 955 9 421 9 775 9 900
$^1E_g(D)$	$[\Gamma_3]$	13 985	14 045	13 970
$^3T_{1g}(F)$	$\begin{bmatrix}\Gamma_5\\ \Gamma_3\\ \Gamma_4\\ \Gamma_1\end{bmatrix}$	15 195 15 385	15 150 15 505 16 130	15 373 15 592 16 032 16 139
	a		17 790	
	b		18 580	
	c		19 005	
$^1T_{2g}(D)$	$[\Gamma_5]$	22 220	22 885	23 295
$^3T_{1g}(P)$	$\begin{bmatrix}\Gamma_1\\ \Gamma_4\\ \Gamma_3\\ \Gamma_5\end{bmatrix}$	25 640	26 110	25 967 26 150 26 961 27 047

present work is also unity. This also justifies the assignment of the double peaked band to the transition from $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$.

According to the theory, some spin-forbidden triplet-to-singlet transitions may appear with low intensity. The bands observed at 13 985 cm^{-1} and 22 220 cm^{-1} are assigned to $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ and $^3A_{2g}(F) \rightarrow {}^1T_{2g}(D)$ transitions, respectively. On cooling the crystal to liquid nitrogen temperature, the $^1T_{2g}(D)$ band exhibited a blue shift as its energy level has a positive slope in the Tanabe-Sugano energy level diagram.

4. Discussion

One important and interesting feature in optical studies is the splitting of some of the bands at low temperatures. The reason for this splitting may be spin-orbit interaction or lowering of symmetry or superposition of certain vibrational modes of radicals or ligands. If the bands are split due to the lowering of symmetry, the other orbital doublet and triplet states are also expected to split into various components. This is not observed in the present work. The intensity of the splitting of the bands observed due to simultaneous electronic and vibrational transition is very weak [1]. In the present work, the average intensity of the split bands is not weak. So the nature of the splitting observed at liquid nitrogen temperature for the $^3T_{2g}(F)$ band appears to be due to the spin-orbit effect. Therefore ligand field calculations were carried out in terms of the octahedral field combined with spin-orbit coupling by which the $^3T_{1g}(F)$ level splits into the four components Γ_5, Γ_3, Γ_4 and Γ_1. The energy matrices including the spin-orbit effect have been diagonalised and the best fit of the experimental values at 77 K is obtained for $B = 900\ cm^{-1}$, $C = 3660\ cm^{-1}$, $Dq = 960\ cm^{-1}$ and $\xi = 600\ cm^{-1}$. The corresponding energy level diagram (E versus Dq) is shown in Figure 3. The observed and calculated band maxima positions along with their assignments are presented in Table 1.

When the crystal is cooled from room temperature to liquid nitrogen temperature, all the bands showed a decrease in intensity, which is characteristic of the vibronic intensity mechanism and is expected for the d–d transitions of an octahedral transition metal ion complex. Similar observations were reported by McPherson and Devaney [18] and Lakshman and Rao [6] in their absorption studies of Ni(II) complexes.

Table 2. Energy parameters for the Ni^{2+} ion in various crystals.

Ni^{2+} ion in	Dq	B	C	ξ	Ref.
NiF_2	745	965	4173	–	[20]
TMSH	960	900	3660	600	present work
$NiCl_2$	692	819	3185	820	[21]
$NiBr_2$	680	765	2975	780	[21]
NiI_2	740	–	–	–	[22]

The interelectronic repulsion parameter B for free Ni(II) ion is 1080 cm^{-1} [19]. In the present work, B equaled 900 cm^{-1} at 77 K, and this suggests that ionic bonding is predominant in the complex.

It is well known that the electric dipole transitions that are assumed to give rise to optical absorption spectra in the visible region in the case of first group transition metal ions are in general vibronic in nature, that is they are assisted to odd vibrational modes of the ligand nuclei. Therefore, in addition to ligand field bands some bands belonging to vibrational frequencies of free radicals are often observed [14, 15].

In the present work, three bands are observed at 17 790, 18 580 and 19 005 cm^{-1}. These bands are associated with the $^3T_{1g}(F)$ band. Taking the energy difference between the $^3T_{1g}(F)$ band (15 505 cm^{-1}, the average of thre split components is taken) and the bands marked *a*, *b*, and *c*, we have

$$17\,790 - 15\,505 = 2285\ cm^{-1},$$
$$18\,580 - 15\,505 = 3075\ cm^{-1},$$
$$19\,005 - 15\,505 = 3500\ cm^{-1}.$$

These bands are attributed to the frequencies of the H_2O stretching vibrations.

The energy parameters obtained in the present work are presented in Table 2 along with the energy parameters reported for Ni(II) ion in various crystals. From the table it is clear that the B value decreases in the following order:

$$F^- < H_2O < Cl^- < Br^-.$$

This confirms that in the present work the Ni(II) ions are surrounded by H_2O molecules. As compared with other compounds of the Ni(II) ion, considering spectrochemical series, the value of Dq obtained in the present work is also reasonable.

The ionic radius of the Ni(II) ion is 0.69 Å and of the Mg(II) ion is 0.68 Å, and also it is reasonable to assume that Ni(II) ions substitute for Mg(II) ions. From the observed optical absorption spectra it is concluded that Ni(II) ions substitute Mg(II) ions and the site symmetry is distorted octahedral.

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