Absorption Spectra of Co(II) Ions Doped in Magnesium Thallium Sulphate Hexahydrate

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The optical obsorption spectrum of Co(II) ions doped in magnesium thallium sulphate hexahydrate is studied at room and liquid nitrogen temperatures. The crystal exhibits characteristic absorption of the Co(II) ion in the visible and near infrared. The observed bands are assigned to transitions from the ground state $^4T_{1g}(F)$ to various excited quartet and doublet levels of the Co(II) ion in octahedral symmetry. The splitting of one of the bands at liquid nitrogen temperature is explained to be due to spin-orbit splitting. All band positions have been fitted by the parameters B, C, Dq and ξ.

1. Introduction

Co(II) ions occur with a variety of coordination numbers and coordination geometries and are able to bind many different ligands. Because of this, the optical absorption spectrum of high spin cobalt(II) has been extensively studied [1–8]. Recently, Srivastava and Pandey [9] and Srivastava et al. [10] studied the low symmetry effects in the optical absorption spectra of Co(II) ions doped in Tutton-salt single crystals. The optical absorption spectra of divalent cobalt ions doped in magnesium thallium sulphate hexahydrate (MTSH) is studied in the present investigation.

MTSH belongs to the monoclinic system with space group $P2_{1/a}$ [11, 12] and contains two Mg atoms per unit cell. The two Mg atoms are on equivalent sites. In the lattice, the Mg(II) ion is octahedrally surrounded by six water molecules.

Jain et al. [13, 14] 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. This is confirmed by optical absorption studies of Ni(II) ions in MTSH [15].

2. Experimental

The crystals were grown at room temperature from an aqueous solution of MTSH to which a few mol% of cobalt sulphate were added. The crystals were clear and pink in colour. The crystal was mounted such that its optic axis is oriented parallel to the incident beam. 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 spectra in the visible and near infrared regions observed at room temperature are shown in Figs. 1 (a) and (b), respectively. There is one band in the near infrared at 7800 cm^{-1} and two in the visible at 19995 cm^{-1} and 21270 cm^{-1}. Among these three bands, the band at 19995 cm^{-1} is the most intense one.

On cooling the crystal to liquid nitrogen temperature (cf. Fig. 2), in addition to the bands observed at room temperature, three weak bands are observed in the visible region at 14490, 15690 and 29275 cm^{-1}. Further the band at 21270 cm^{-1} splits into two components with maxima at 21325 and 21770 cm^{-1}. Also the bands observed at room temperature at 7800 and 19995 cm^{-1} are shifted to 8050 and 20620 cm^{-1}, respectively.

The spectum observed at liquid nitrogen temperature is very similar to that of other hydrated cobalt salts, indicating that the Co(II) ion in the crystal is coordinated with water molecules.

Co(II) ion has seven d electrons. This configuration gives rise to ^4F, ^4P and several other doublet states. According to Hund's rule, the ground state in the free ion is ^4F. The sevenfold orbitally degenerate ground

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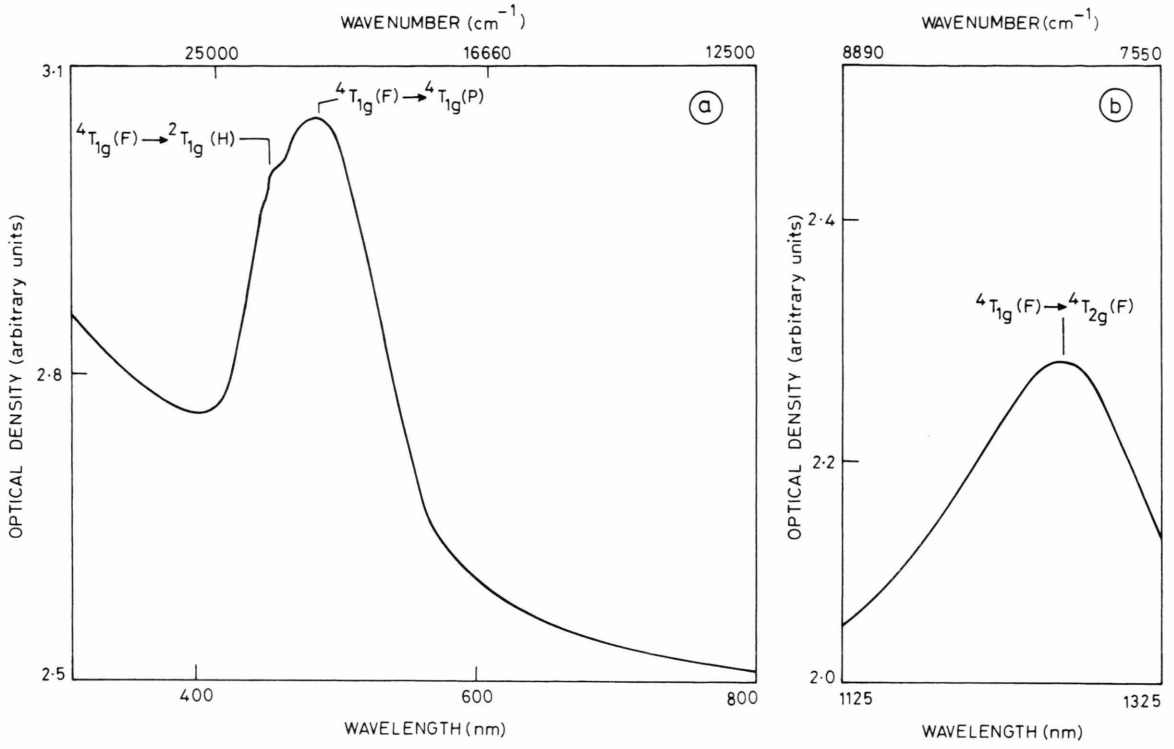

Fig. 1. Absorption spectrum of Co(II) ions in magnesium thallium sulphate hexahydrate at 300 K. (a) Visible region. (b) Near infrared region.

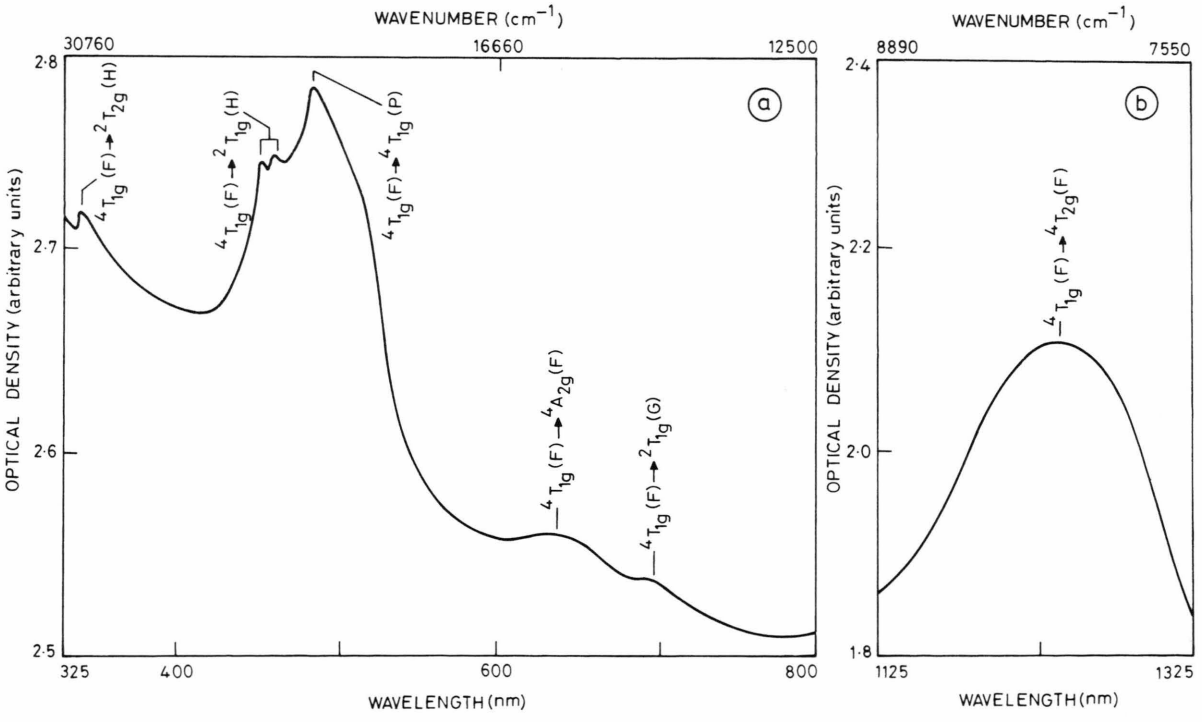

Fig. 2. Absorption spectrum of Co(II) ions in magnesium thallium sulphate hexahydrate at 77 K. (a) Visible region. (b) Near infrared region.

state splits n a cubic field of anions into two orbitally degenerate triplets, $^4T_{1g}(F)$ and $^4T_{2g}(F)$, and the orbital singlet $^4A_{2g}(F)$. Of these, $^4T_{1g}(F)$ is the ground state. The upper ^4P does not split but transforms as $^4T_{1g}(P)$. The two intense bands are assigned to the spin-allowed quartet to quartet transitions. The band at 7800 cm^{-1} is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition, while the band at 19995 cm^{-1} is assigned to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The positions of these bands at liquid nitrogen temperature are 8050 and 20620 cm^{-1}, respectively. The band observed at 300 K at 21270 cm^{-1} is assigned to the transition $^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$.

A weak and broad hump observed at 77 K is assigned to the second spin-allowed transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$. Generally, the spin allowed band should be strong and intense. But the observed spin-allowed band at 15690 cm^{-1} is found to be weak, because the transition to the $^4A_{2g}(F)$ level involves a two electron jump [16], and hence its intensity is normally very weak. The remaining bands in the spectrum are identified with the spin-forbidden quartet to doublet transitions.

Using the Tanabe-Sugano energy level diagram, the bands observed at 14490 and 29275 cm^{-1} are assigned to $^4T_{1g}(F) \rightarrow {}^2T_{1g}(G)$ and $^4T_{1g}(F) \rightarrow {}^2T_{2g}(H)$ transitions, respectively.

4. Discussions

Koide [16] and Bose [17] extensively studied the optical absorption spectra and magnetic properties of cobalt salts and found that the effect due to the spin-orbit interaction is greater than the effect due to the lowering of symmetry. In many cases, spin-orbit splitting is observed for $^4T_{1g}(P)$ and $^2T_{1g}(H)$ bands. In the present work we observed splitting at liquid nitrogen temperature for the $^2T_{1g}(H)$ band only. Narayana et al. [18] also did not observe any splitting for the $^4T_{1g}(P)$ band at 78 K. The splitting for the $^4T_{1g}(P)$ band may be observed at still lower temperatures. The observed splitting at liquid nitrogen temperature of the $^2T_{1g}(H)$ band is attributed to spin-orbit effects. The cubic field energy matrices are formed by adding to the elements of the spin-orbit matrices. $\Gamma_6(9 \times 9)$, $\Gamma_7(9 \times 9)$ and $\Gamma_8(21 \times 21)$ to the appropriate cubicfield elements of Tanabe and Sugano. The resulting energy matrices are solved for different B, C, Dq and ξ values. The best fit of the observed bands could be obtained for $Dq = 890\ cm^{-1}$, $B = 840\ cm^{-1}$, $C = 3200\ cm^{-1}$, and $\xi = 500\ cm^{-1}$.

The energy level diagram for the Co(II) ion in an octahedral crystal field with spin-orbit interaction is shown in Figure 3. The observed and calculated band positions along with the oscillator strengths at room and liquid nitrogen temperature are presented in Table 1.

Table 1. The observed and calculated energies and oscillator strengths of the bands of Co(II) ions in magnesium thallium sulphate hexahydrate single crystal. $Dq = 890\ cm^{-1}$, $B = 840\ cm^{-1}$, $C = 3200\ cm^{-1}$, $\xi = 500\ cm^{-1}$.

Transition from $^4T_{1g}(F)$	Wavenumbers cm^{-1}			Oscillator strengths ($\times 10^{-4}$)	
	Γ_6 calculated	observed 77 K	observed 300 K	300 K	77 K
$^4T_{2g}(F)$	Γ_6 8285 Γ_8 8325 Γ_8 8430 Γ_7 8608	8050	7800	2.5	2.1
$^2T_{1g}(G)$	Γ_8 14383 Γ_6 14885	14490			
$^4A_{2g}(F)$	Γ_8 15015 Γ_8 18555	15690			
$^4T_{1g}(P)$	Γ_7 19665 Γ_8 19680 Γ_6 20440	20620	19995	6.4	4.2
$^2T_{1g}(H)$	Γ_6 21500 Γ_8 21560	21325 21770	21270		
$^2T_{2g}(H)$	Γ_7 29130 Γ_8 29265	29275			

Table 2. Energy parameters in cm^{-1} for the Co(II) ion in various crystals.

Co(II) ion in	Dq	B	C	ξ	Reference
CoF_2	715	971	–	–	[21]
Zinc Thallium sulphate hexahydrate	910	900	4.2 B	500	[7]
Magnesium Thallium sulphate hexahydrate	890	840	3.8 B	500	Present work
Zinc Potassium Sulphate hexahydrate	882	771	3.87 B	–	[10]
$CoCl_2$	630	880	4.4 B	420	[19]
$CoBr_2$	640	760	4.4 B	420	[19]
CdI_2	520	680	4.0 B	–	[20]

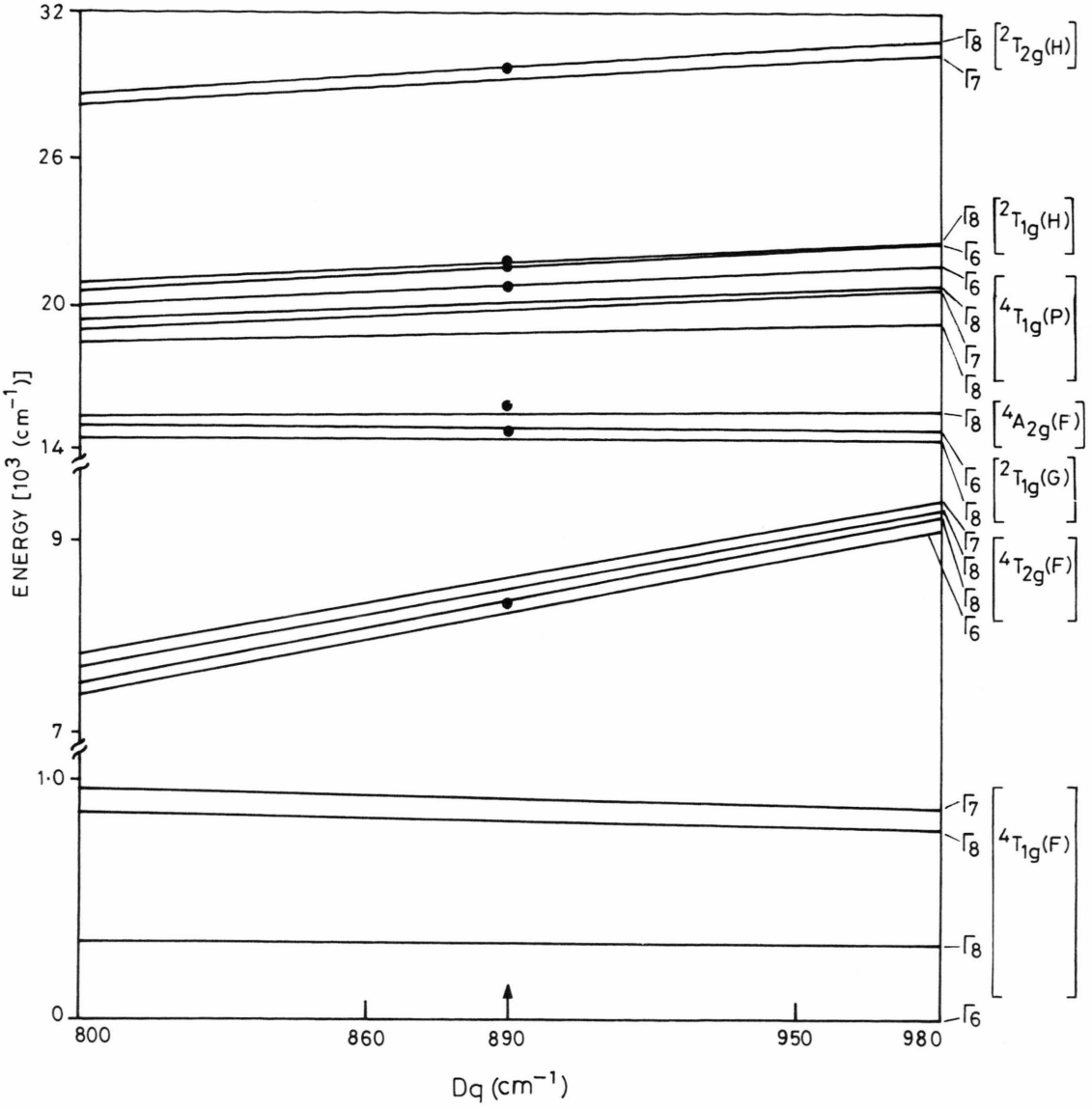

Fig. 3. Energy level diagram of Co(II) ions in magnesium thallium sulphate hexahydrate in octahedral symmetry, plotted as a function of crystalfield parameter Dq with $B = 840\ cm^{-1}$, $C = 3200\ cm^{-1}$ and $\xi = 500\ cm^{-1}$. The solid circles show the experimental values at 77 K.

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

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

This sequence was also found by Hennel [22], and confirms that in the present work, the Co(II) ions are surrounded by H_2O molecules. As compared with other compounds of the Co(II) ion, considering spectrochemical series, the value of Dq obtained in the present work is reasonable.

On cooling the crystal, the bands are shifted towards higher energies. This could be attributed to the thermal depopulation of lower vibronic states, partly due to the contraction of the lattice. At 77 K, a decrease in intensity of the $^4T_{2g}(F)$ and $^4T_{1g}(P)$ band is

noticed. This decrease is characteristic of a vibronic intensity mechanism and is expected for the d–d transition of an octahedral transition metal complex.

EPR studies of Mn(II) doped Tutton salts have shown that the cubic crystalfield parameter b_4° is greater for Mn(II):$ZnTl_2(SO_4)_2 \cdot 6H_2O$ ($b_4^\circ = 3.7$ gauss) [23] than for Mn(II):$MgTl_2(SO_4)_2 \cdot 6H_2O$ ($b_4^\circ = 2.7$ gauss) [23]. This apparently contradicts the results of optical absorption studies which show that the value of the crystalfield parameter Dq is slightly higher for Co(II):$ZnTl_2(SO_4)_2 \cdot 6H_2O$ [$Dq = 910\ cm^{-1}$] [7] than for Co(II):$MgTl_2(SO_4)_2 \cdot 6H_2O$ [$Dq = 890\ cm^{-1}$] [present work]. This contradiction can, however, be understood if one realizes that the Dq parameter in optical absorption shows directly the effect of the crystalfield on the ground and excited states, whereas the b_4° parameter in EPR exhibits the effect of the field the electronic ground state, the splitting being via the spin-orbit interaction for S state ions like Mn(II).

The interelectronic repulsion parameter B for a free Co(II) ion is $1120\ cm^{-1}$. In the present work we obtained a B value equal to $840\ cm^{-1}$, and this shows that the bonding is moderately covalent in the complex. The ionic radius of the Co(II) ion is 0.72 Å, and that of the Mg(II) ion is 0.66 Å, and it is reasonable to assume that the Co(II) ions, substitute the Mg(II) ions. From the observed optical absorption spectra we conclude that Co(II) ions substitute Mg(II) ions, and the site symmetry is distorted octahedral.

[1] O. G. Holmes and D. S. McClure, J. Chem. Phys. **26,** 1686 (1957).
[2] R. Pappalardo, Phil. Mag. **4,** 219 (1959).
[3] N. S. Hush and R. J. M. Hobbs, Progress in Inorganic Chemistry, Interscience, New York 1968, p. 259.
[4] J. Ferguson, Progress in Inorganic Chemistry, Interscience, New York 1970, p. 159.
[5] J. P. Srivastava, J. Phys. Chem. Solids **32,** 279 (1971).
[6] L. Banci, A. Bencini, C. Benelli, D. Gatteschi, and C. Zanchini, Structure and Bonding, Springer, Berlin 1982, p. 38.
[7] J. Lakshmana Rao, M. Ramachandra Reddy, and S. V. J. Lakshman, Physica (b) **153,** 191 (1988).
[8] P. S. S. Prasad and S. Radha Krishna, Phys. stat. sol. (b) **164,** 213 (1991).
[9] K. M. K. Srivastava and S. D. Pandey, Phys. Rev. (B) **42(6),** 3719 (1990).
[10] K. M. K. Srivastava, A. K. Mishra, and S. D. Pandey, Solid State Communications **79,** 539 (1991).
[11] R. W. G. Wyckoff, Crystal Structure, Vol. 3, Interscience, New York 1931.
[12] H. Montgomery and E. C. Lingafelter, Acta Cryst. **20,** 728 (1966).
[13] V. K. Jain, Z. Naturforsch. **32a,** 1364 (1977).
[14] V. K. Jain, V. S. Yadav, and Jitender Singh, Solid State Commun. **64,** 929 (1987).
[15] A. Venkata Subbaiah, J. Lakshmana Rao, R. Murali Krishna, and S. V. J. Lakshman, Z. Naturforsch. **47a,** 813 (1992).
[16] S. Koide, Phil. Mag. **4,** 243 (1959).
[17] A. Bose, Indian J. Phys. **22,** 276 (1948).
[18] P. A. Narayana, A. Mehra, and Putcha Venkateswarlu, Canadian J. Phys. **46,** 325 (1968).
[19] J. Ferguson, D. L. Wood, and K. Knox, J. Chem. Phys. **39,** 881 (1963).
[20] P. R. Boudewijn, A. Meetsma, and C. Haas, Physica **106,** 165 (1981).
[21] L. J. Zimring and J. W. Stout, J. Chem. Phys. **51,** 4197 (1968).
[22] A. M. Hennel, J. Phys, C, Solid State Physics **11,** L389 (1978).
[23] S. K. Misra and M. Kahrizi, Congr. AMPERE Magn. Reson. Relat. Phenom. Proc. 22nd, 222 (1981).