

Absorption spectrum of Mn^{2+} ions doped in diammonium hexaaquamagnesium(II) sulfate

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Abstract. Optical absorption is a tool to investigate the site symmetry of metal ion and associated distortion in doped single crystals. It provides the energy of different orbital levels of metal ion and separation among them. Mn^{2+} ions in various single crystals and glasses have been the subject of recent investigations [1–3]. We have studied optical absorption spectra of Mn^{2+} doped diammonium hexaaquamagnesium(II) sulfate in order to obtain the energy level ordering using matrices of Tanabe and Sugano [4] and to discuss the associated distortion.

Keywords. Optical absorption; Trees correction; quartet levels; Racah parameters.

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Diammonium hexaaquamagnesium(II) sulfate belongs to Tutton's salt series. Crystal structure of diammonium hexaaquamagnesium(II) sulfate is monoclinic, with the space group $\text{P}2_1/\text{a}$ [5].

The single crystals of diammonium hexaaquamagnesium(II) sulfate doped with Mn^{2+} were grown at room temperature by slow evaporation of an aqueous solution containing stoichiometric quantities of ammonium sulfate and magnesium sulfate, to which 0.01 mol% of MnSO_4 was added. The optical absorption spectrum was recorded in the wavelength range 195–725 nm at room temperature using UNICAM 5625 spectrophotometer.

The spectra recorded in the visible and ultraviolet region are shown in figures 1–4 respectively. Two sharp bands 3 and 5, called ligand field bands, have been observed at 20920 and 27777 cm^{-1} . Ligand field bands are sharp when energy expressions of transitions are independent of D_q , because the number of t_{2g} electrons is the same in both excited and ground states [6]. Thus these two sharp bands are attributed to ${}^6A_{1g}(s) \rightarrow {}^4A_{1g}(G)$, ${}^4E_g(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4E_g(D)$ transitions, respectively as their energy expressions are independent of D_q . The broad band 1 at 15674 cm^{-1} has been assigned to transition ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$. It seems that the two weak bands 2 and 4 appear at 19801 and 24691 cm^{-1} corresponding to transitions

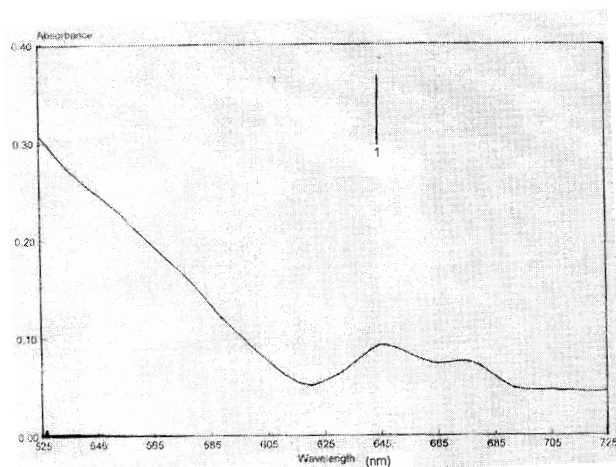


Figure 1. Absorption spectrum of Mn^{2+} in diammonium hexaaquamagnesium(II) sulfate (525–725 nm).

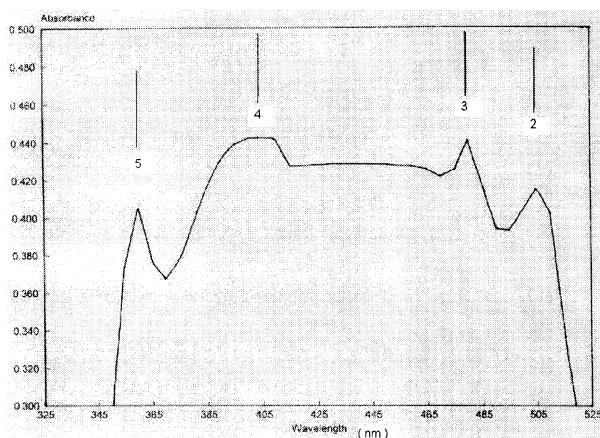


Figure 2. Absorption spectrum of Mn^{2+} in diammonium hexaaquamagnesium(II) sulfate (325–525 nm).

${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$, respectively. The shoulders 6 and 8 at 33222 and 41841 cm^{-1} have been assigned to transitions ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(P)$ and ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(F)$, respectively. A weak band 7 also seems to appear at 37037 cm^{-1} corresponding to ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(F)$ transition.

The value of the crystal field parameter D_q depends on the evaluation of Racah parameters B and C [7]. The Racah parameters B and C are evaluated for the room temperature spectrum using the expressions given by Rao and Purandar [8].

The values of B and C have been used to find a single value of D_q . The energy values for quartet electronic states have been calculated for different values of D_q with $B = 1124\text{ cm}^{-1}$, $C = 1637\text{ cm}^{-1}$ and $\alpha = 76\text{ cm}^{-1}$. A good fit of the

Absorption spectrum of Mn²⁺ ions

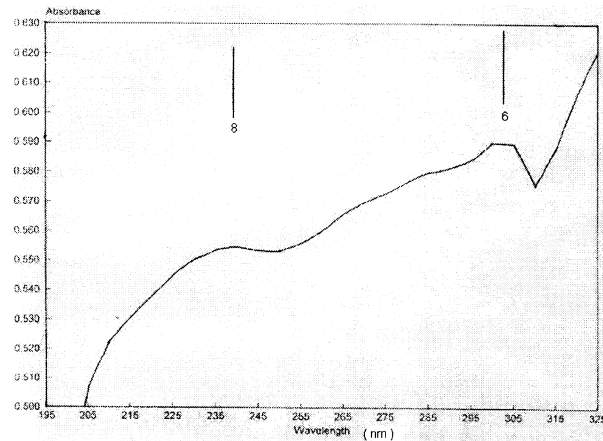


Figure 3. Absorption spectrum of Mn²⁺ in diammonium hexaaquamagnesium(II) sulfate (195–325 nm).

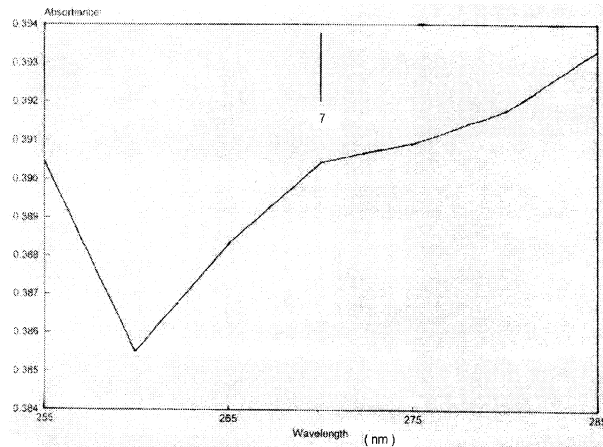


Figure 4. Absorption spectrum of Mn²⁺ in diammonium hexaaquamagnesium(II) sulfate (255–285 nm).

experimentally observed band positions with the calculated ones is obtained for $D_q = 900 \text{ cm}^{-1}$ as shown in figure 5. The observed and calculated energies of the bands along with their assignments are given in table 1. From table 1, we conclude that the assignments made to the different bands are justified.

We have found the first excited level ${}^4T_{1g}(G)$ at 15243 cm^{-1} which is much lower than the value reported by others [8,9]. This suggests a larger value of D_q . The crystal structure of diammonium hexaaquamagnesium(II) sulfate is known to be monoclinic with smaller values of crystalline parameters. Thus the smaller the nearest neighbor distance, the larger will be the value of D_q [10]. The observed and calculated values of energies are well in agreement for $D_q = 900 \text{ cm}^{-1}$ except for the ${}^4T_{1g}(G)$, and ${}^4T_{1g}(P)$ levels. These differences in the observed and calculated energies suggest that only the inclusion of Trees correction matrices is not

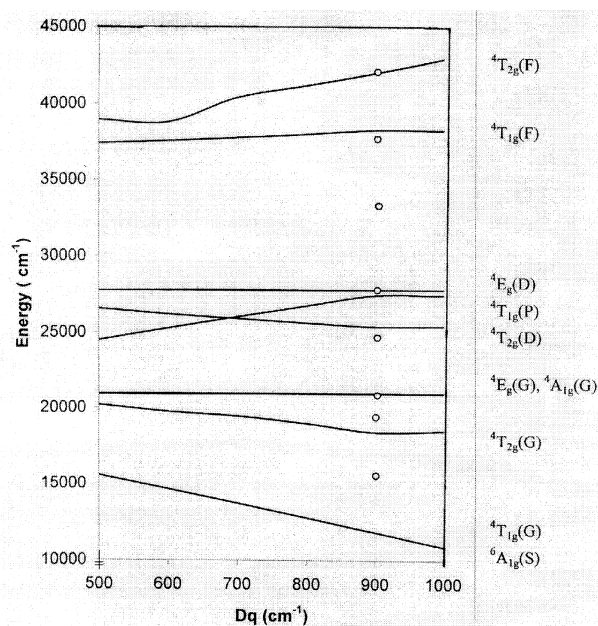


Figure 5. The energy level diagram of Mn^{2+} showing the variation of the level with D_q for a case with $B = 1124 \text{ cm}^{-1}$, $C = 1637 \text{ cm}^{-1}$, and $\alpha = 76 \text{ cm}^{-1}$. The circles show the experimental energies.

Table 1. Observed and calculated energies and assignments for the bands of Mn^{2+} in diammonium hexaaquamagnesium(II) sulfate ($B = 1124 \text{ cm}^{-1}$, $C = 1637 \text{ cm}^{-1}$, $D_q = 900 \text{ cm}^{-1}$ and $\alpha = 76 \text{ cm}^{-1}$).

Band number	Transition from ${}^6A_{1g}(S)$	Observed		Calculated (cm^{-1})
		(nm)	(cm^{-1})	
1	${}^4T_{1g}(G)$	638	15582	11831
2	${}^4T_{2g}(G)$	505	19801	18415
3	${}^4E_g(G)$	478	20920	20920
	${}^4A_{1g}(G)$			20945
4	${}^4T_{2g}(D)$	405	24691	25381
5	${}^4E_g(D)$	360	27777	27774
6	${}^4T_{1g}(P)$	301	33222	27426
7	${}^4T_{1g}(F)$	270	37037	38266
8	${}^4T_{2g}(F)$	239	41841	41997

sufficient and seniority correction [10] also seems necessary to be included. The parameter α which we have taken equal to 76 cm^{-1} is a free ion value and is expected to differ in crystals [10]. This may also be one of the reasons for the disagreement between the observed and calculated values of some of the levels. Ionic radii of magnesium and manganese are 0.66 and 0.80 \AA respectively, which may

be accounted for lattice distortion [11]. The states ${}^4A_{1g}(G)$, ${}^4E_g(G)$ are normally degenerate, but their degeneracy is lifted by covalency in the crystal [9]. Lifting of degeneracy of ${}^4A_{1g}(G)$, ${}^4E_g(G)$ level depends on various perturbing factors [12]. The band assigned to ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$, ${}^4E_g(G)$ is sharp but does not show splitting. Therefore we propose trigonal distortion [11] in diammonium hexaaquamagnesium(II) sulfate.

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References

- [1] P D Pathinettam, C Mulhukrishanan and R Murugesan, *Spectrochim. Acta* **A58**, 509 (2002)
- [2] J P Renault, C Beaur, I Badarau, F Yamakura and M Gerloch, *Inorg. Chem.* **39**, 2666 (2000)
- [3] P Prakash, A Murali and J L Rao, *Mod. Phys. Lett.* **B16**, 143 (2002)
- [4] Y Tanabe and S Sugano, *J. Phys. Soc. Jpn.* **9**, 753 (1954)
- [5] E N Maslen, S C Ridous and K J Watson, *Acta Crystallogr.* **C44**, 409 (1988)
- [6] C J Ballhausen, *Introduction to ligand field theory* (McGraw Hill, New York, 1962)
- [7] A B P Lever, *Inorganic electronic spectroscopy* (Elsevier, Amsterdam, 1968) p. 296
- [8] J L Rao and K Purandar, *Solid State Commn.* **37**, 983 (1981)
- [9] J L Rao, M R Reddy and S V J Laxman, *Z. Natureforsch.* **44a**, 19 (1989)
- [10] D Curie, C Barthou and B Canny, *J. Chem. Phys.* **61**, 3048 (1974)
- [11] S N Rao and Y P Reddy, *Solid State Commun.* **82**, 419 (1992)
- [12] J W Stout, *J. Chem. Phys.* **31**, 709 (1959)