

ELECTRONIC ABSORPTION SPECTRUM OF Cu^{2+} IONS DOPED IN ZINC CESIUM SULPHATE HEXAHYDRATE

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The optical absorption spectrum of Cu^{2+} ions doped in $\text{ZnCs}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ single crystals has been studied at room (300 K) and liquid nitrogen (77 K) temperatures. From the nature and positions of the bands observed, a successful interpretation of all the bands could be made assuming D_{2h} site for Cu^{2+} ions in zinc cesium sulphate hexahydrate. ESR studies of the sample confirm the site symmetry of the central metal ion. Taking ${}^2A_g(d_{x^2-y^2})$ as the ground state in D_{2h} symmetry, the four absorption bands at 77 K are attributed to the transitions to ${}^2A_g(d_{z^2})$, ${}^2B_g(d_{xy})$, ${}^2B_g(d_{xz})$ and ${}^2B_g(d_{yz})$, respectively, in the order of increasing energy.

ЭЛЕКТРОННЫЙ СПЕКТР ПОГЛОЩЕНИЯ ИОНОВ Cu^{2+} , ДОБАВЛЕННЫХ В ГЕКСАГИДРАТ СУЛЬФАТА ЦИНКО-ЦЕЗИЯ

В работе исследован оптический спектр поглощения ионов Cu^{2+} при комнатной температуре (300 К) и при температуре жидкого азота (77 К), которые добавлены в монокристаллы $\text{ZnCs}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. На основе характера и расположения наблюдаемых полос сделана успешная расшифровка всех полос в предположении, что ионы Cu^{2+} находятся в узле D_{2h} решетки гексагидрата сульфата цинко-цезия. Изучение электронного спинового резонанса в образцах подтвердило узловую симметрию иона центрального металла. Если считать ${}^2A_g(d_{x^2-y^2})$ основным состоянием в симметрии D_{2h} , то при температуре 77 К в переходы ${}^2A_g(d_{z^2})$, ${}^2B_g(d_{xy})$, ${}^2B_g(d_{xz})$ и ${}^2B_g(d_{yz})$ вносят вклад (в порядке возрастающей энергии) четыре полосы поглощения.

1. INTRODUCTION

The present study is a continuation of the investigation of the absorption spectra of the transition metal ions doped in zinc cesium sulphate hexahydrate, $\text{ZnCs}_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (referred to throughout as ZCSH) single crystals in our laboratories [1—4].

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ZCSSH belongs to the family of isomorphous compounds, known as Tutton's salts. The crystals are monoclinic and the unit cell contains two molecules related by the space group operation $P2_1/a$ [5, 6]. The divalent metal ion is situated at the positions (0, 0, 0) and (1/2, 1/2, 0) in the unit cell and is surrounded by a distorted octahedron of six water molecules. Jain et al. [7] and Jain [8] confirmed from their ESR studies of Mn^{2+} and VO^{2+} doped in ZCSSH that the divalent transition metal ions substitute the divalent cation sites in ZCSSH. Crystal structure data for ZCSSH, used as host in this work are not available, and for this reason we have included distances for some Tutton's salts in Table 1, from which we can argue by analogy that in ZCSSH, the bond Cu—O (7) is shorter than the Cu—O (8) one, the reverse of that found in the copper ammonium salt (CASH). However, the Cu—O (9) bond is the shortest in all the salts. The numbering of the coordinated water oxygen atoms in Table 1 is that given by most authors and illustrated, for example, in Fig. 1 of Ref. [9]. The tetragonalities of the corresponding potassium [10], rubidium [11, 12] and cesium [11] Tutton salts shown in the same Table are much more comparable and similar to the low temperature tetragonalities of CASH [13—16].

It is evident from Table 1 that for the ammonium salt a marked temperature variation is present, for the rubidium salt only a slight temperature variation is present and for the cesium salt very little temperature variation is present as confirmed by the neutron powder data for α -Cu(HCO₂)₂ [17], where $T = 0.756$, 0.758 and 0.762 at 296, 80 and 4 K, respectively, indicating very little variation of structure over the range of 292 K.

The present investigation is carried out with a view to verify the site symmetry of Cu^{2+} ions in ZCSSH, because it has already been studied in detail in zinc potassium sulphate hexahydrate [9, 18] and in many copper Tutton's salts [19, 20].

II. EXPERIMENTAL

Single crystals of ZCSSH were grown from an aqueous solution containing equimolar concentrations of Cs_2SO_4 and $ZnSO_4 \cdot 7H_2O$ to which 0.1 mole % of $CuSO_4 \cdot 5H_2O$ was added as impurity.

The optical absorption spectra were recorded on a Cary-17D spectrophotometer. The 77 K spectrum was recorded with a suitable cryogenic arrangement. Since the crystal axes could not be identified exactly, polarization studies were not carried out. The oscillator strengths were determined by computing the area under the absorption curves.

ESR measurements were carried out on a JEOL FE 1X X-band spectrometer. Measurements were made on powder samples at 300 and 120 K using a variable temperature accessory.

III. THEORY

The Cu^{2+} ion has the electronic configuration $A 3d^9$ where 'A' stands for the closed argon shell.

In a crystal field of octahedral symmetry, the free ion 2D term splits into 2E_g and ${}^2T_{2g}$ levels, 2E_g being the lower level. Due to the Jahn-Teller effect, the 2E_g level generally splits and therefore the Cu^{2+} ion is rarely found in a regular octahedral environment.

In a tetragonal field, the ground state 2E_g splits into two levels ${}^2B_{1g}$ and ${}^2A_{1g}$ and similarly the upper ${}^2T_{2g}$ into ${}^2B_{2g}$ and 2E_g levels. One of the levels ${}^2B_{1g}$ or ${}^2A_{1g}$ forms the ground state. For an elongated octahedron the $d_{x^2-y^2}$ orbital will be lying lower than the d_z orbital corresponding to the ${}^2A_{1g}$ state. In a rhombic field [21], the lower 2E_g level splits into two levels ${}^2A_{1g}(d_{x^2-y^2})$ and ${}^2A_{1g}(d_z)$, whereas the upper ${}^2T_{2g}$ level splits into ${}^2B_{1g}(d_{xy})$, ${}^2B_{2g}(d_{xz})$ and ${}^2B_{2g}(d_{yz})$ levels. The relative energies of Cu^{2+} in an octahedral and rhombic fields are shown in Fig. 1.

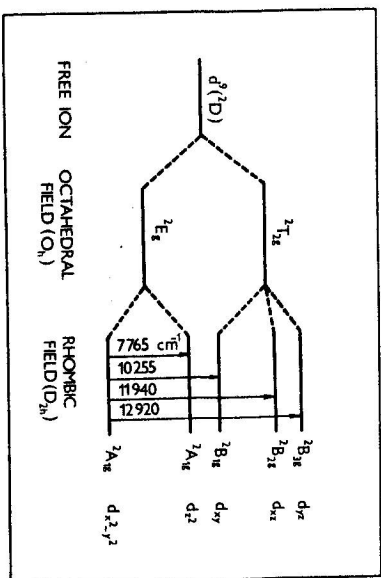


Fig. 1. Splittings of the energy levels for the d^9 configuration in octahedral and rhombic fields.

IV. RESULTS AND DISCUSSION

The optical absorption spectra have been recorded in the wavelength region of 600 nm to 1450 nm both at 300 K and 77 K and the spectra are shown in Fig. 2.

The spectrum recorded at 300 K consists of three bands, one in the near infrared at 7765 cm^{-1} and the two others in the visible at 10125 cm^{-1} and 11765 cm^{-1} . Of these three bands observed, the band at 11765 cm^{-1} is quite intense, while the 10125 cm^{-1} band is found in the form of a weak shoulder of the lower energy side of the intense band.

When the crystal is cooled to 77 K, changes in intensities of the bands as well as their positions are observed. In addition to the three bands observed at 300 K, a sharp band is seen on the higher energy side of the intense band. At 77 K, the bands are located at 7765, 10255, 11940 and 12920 cm^{-1} .

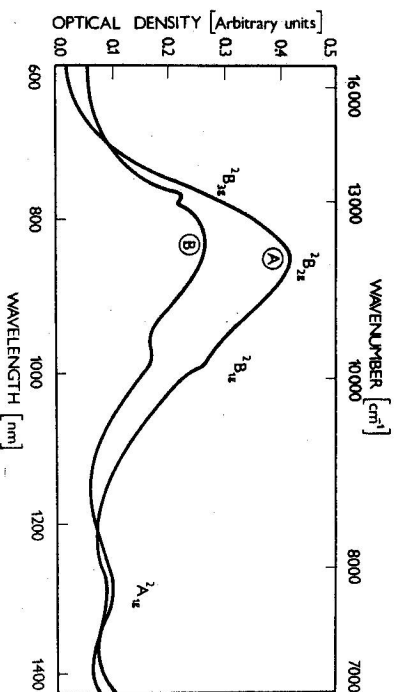


Fig. 2. Absorption spectra of Cu^{2+} in zinc cesium sulphate hexahydrate at 300 K (curve—A) and 77 K (curve—B).

Preliminary electron spin resonance studies are needed to analyse and discuss the optical absorption data. As no ESR studies are reported in literature on Cu^{2+} ions doped in ZCS_2SH , the authors have taken up the study. ESR studies were carried out for Cu^{2+} in ZCS_2SH at 300 K and 120 K and Fig. 3 shows the spectra taken at the two temperatures. The principal g values are found to be:

$g_1 = 2.384$	$g_2 = 2.164$	$g_3 = 2.050$	at 300 K
$g_1 = 2.402$	$g_2 = 2.127$	$g_3 = 2.050$	at 120 K.

The g values in the present work are consistent with the values reported for Cu^{2+} ions doped in some Turton salts [18, 22, 23] and in many copper Turton salts [20, 24]. The observed g values indicate that the Cu^{2+} in ZCS_2SH is also under the influence of a rhombic distortion. Also, the g factors indicate that the ground state of the copper ion is either $d_{x^2-y^2}$ or d_{z^2} , since g_1 is greater than $(g_2 + g_3)/2$ [25]. The values of $(g_2 - g_3)/(g_1 - g_2)$ is 0.52 and 0.28 at 300 K and 120 K respectively. These values are clearly less than one and indicate that the ground state is $d_{x^2-y^2}$ with the z axis along the long $\text{Cu}-\text{O}$ (8) bond [26]. It is interesting to find that the value of g_1 increases, g_2 decreases and g_3 remains invariant as the temperature is lowered from 300 K to 120 K. This temperature dependence of g values is due to the dynamic Jahn-Teller effect as suggested by Silver and Getz [18].

The observed absorption bands in the present investigation are therefore attributed to Cu^{2+} in an elongated rhombic site (D_{2h}) with $d_{x^2-y^2}$ as the ground state. In most copper compounds having a distorted octahedral structure, the transition ${}^2A_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ lies in energy close to the other "d-d" trans-

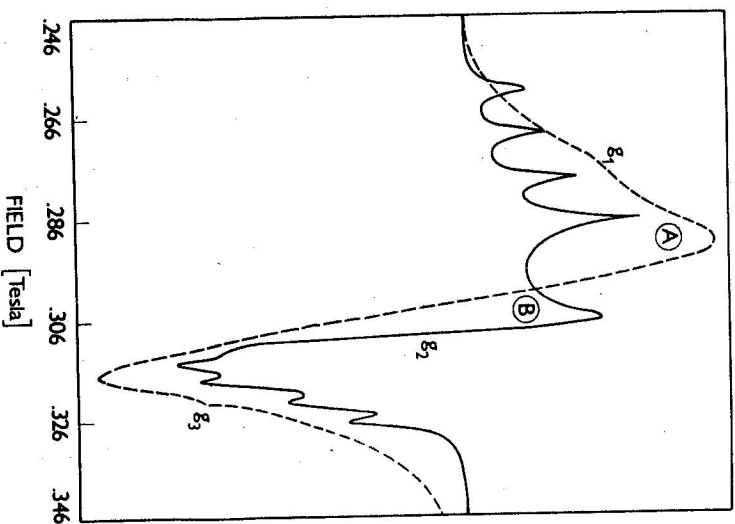


Fig. 3. ESR spectra of Cu^{2+} in zinc cesium sulphate hexahydrate at 300 K (curve—A) and 120 K (curve—B).

itions, i.e., at ~ 10000 to 14000 cm^{-1} and it has been assigned within this range in a number of copper complexes containing $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ or similar ions [27-29]. Indeed, the spectra of some of the Turton salts have previously been assigned on this basis [30, 31]. However, the spectra of deuterated complexes presented by Hitchman et al. [19] strongly suggest that in the Turton salts the transition ${}^2A_{1g}(d_{x^2-y^2}) \rightarrow {}^2A_{1g}(d_{z^2})$ occurs at a much lower energy ($6000-8000 \text{ cm}^{-1}$). In the present work a band is observed at 7765 cm^{-1} both at 300 K and 77 K and is assigned to the above said transition. The low energy of this transition is probably

Table 1

The Cu—OH₂ bond distances of (NH₄)₂Cu(OH₂)₆(SO₄)₂ at various temperatures and (M²⁺)₂Cu(OH₂)₆(SO₄)₂ at room and low temperatures

Bond	(NH ₄) ₂ Cu(OH ₂) ₆ (SO ₄) ₂			
	295 K	215 K	145 K	M ²⁺ =K, M ²⁺ =Rb, M ²⁺ =Cs
Cu—O (7)	2.219	2.250	2.278	2.069 2.031 (2.000)* 2.004
Cu—O (8)	2.095	2.041	2.012	2.278 2.307 (2.317)* 2.315
Cu—O (9)	1.961	1.967	1.970	1.943 1.957 (1.978)* 1.966
Tetragonality	0.914	0.891	0.874	0.881 0.864 (0.858)* 0.858

* Low temperature data (77 K)

Table 2

Band data and assignments for Cu²⁺ in zinc cesium sulphate hexahydrate

Band positions (cm ⁻¹)	Oscillator Strengths			Transition from ² A _{1g} (d _{x²-y²) to}
	300 K	77 K	300 K	
7765	7765	1.47 × 10 ⁻⁵	2.08 × 10 ⁻⁵	² A _{1g} (d _z)
10125	10255	—	9.33 × 10 ⁻⁵	² B _{1g} (d _{xy})
11765	11940	4.64 × 10 ⁻⁴	2.66 × 10 ⁻⁴	² B _{2g} (d _{xz})
—	12920	—	7.79 × 10 ⁻⁵	² B _{2g} (d _{yz})

due to the unusually short Cu—O bond along the z axis in the Tutton salts. The remaining three bands in the present work are assigned as transitions from the ground ²A_{1g}(d_{x²-y²) to the excited ²B_{1g}(d_{xy}), ²B_{2g}(d_{xz}) and ²B_{2g}(d_{yz}) states, respectively, in the order to increasing energy.}

On cooling the crystal to 77 K, the absorption peaks show a considerable decrease in intensity, in agreement with the vibronic origin of the intensity. The electronic spectra show no large shifts in peak positions on cooling, which proves that no great change in the tetragonality occurs when the temperature is lowered.

The observed band positions along with their oscillator strengths and assignments are given in Table 2. A comparison of the observed band positions in the present work along with those observed in copper Tutton salts are presented in Table 3.

The spin-orbit reduction parameters are evaluated with the following expressions given for a rhombic field [32].

$$[k_1]^2 = [(\theta_1 - 2) \Delta E_1] / [-8\lambda \cos^2 \theta]$$

$$[k_2]^2 = [(\theta_2 - 2) \Delta E_2] / [-2\lambda (\cos \theta + \sqrt{3} \sin \theta)^2]$$

$$[k_3]^2 = [(\theta_3 - 2) \Delta E_3] / [-2\lambda (\cos \theta - \sqrt{3} \sin \theta)^2]$$

Table 3

Comparison of absorption band positions
Transition energy and assignment of the excited state with respect to the ground state ²A_{1g}(d_{x²-y²)}

Compound	Transition energy and assignment of the excited state with respect to the ground state ² A _{1g} (d _{x²-y²)}						Ref.		
	² A _{1g} (d _z)	² B _{1g} (d _{xy})	² B _{2g} (d _{xz})	² B _{2g} (d _{yz})	² B _{3g} (d _{yz})				
(NH ₄) ₂ Cu(SO ₄) ₂ ·6H ₂ O	6400	7350	10650	10900	11760	12200	12350	12720	[19]
·6H ₂ O	7140	7580	10000	10200	10270	12900	—	—	[19]
K ₂ Cu(SO ₄) ₂ ·6H ₂ O	7630	7750	10000	10200	12350	12740	—	—	[19]
Rb ₂ Cu(SO ₄) ₂ ·6H ₂ O	8000	8260	10200	10400	12500	13160	—	—	[19]
Tl ₂ Cu(SO ₄) ₂ ·6H ₂ O	9820	—	10650	—	12350	—	13200	—	[31]
Cs ₂ Cu(SO ₄) ₂ ·6H ₂ O	7765	7765*	10125	10255*	11765	11940*	—	12920*	Present work

* at 77 K

Table 4

Comparison of g and spin-orbit reduction parameters

Compound	Temperature T (K)	g values			Spin-orbit reduction parameters		Ref.
		g ₁	g ₂	g ₃	k ₁	k ₂	
(NH ₄) ₂ Cu(SO ₄) ₂ ·6H ₂ O	295	2.363	2.209	2.071	0.77	0.97	[19]
K ₂ Cu(SO ₄) ₂ ·6H ₂ O	295	2.403	2.154	2.055	0.78	0.86	[19]
Rb ₂ Cu(SO ₄) ₂ ·6H ₂ O	295	2.420	2.109	2.074	0.80	0.82	[19]
Tl ₂ Cu(SO ₄) ₂ ·6H ₂ O	295	2.418	2.116	2.070	0.80	0.83	[19]
Cs ₂ Cu(SO ₄) ₂ ·6H ₂ O	300	2.407	2.194	2.075	—	—	[24]
Cu ²⁺ ·K ₂ Co(SO ₄) ₂ ·6H ₂ O	210	2.330	2.227	2.053	—	—	[22]
Cu ²⁺ ·(ND ₄) ₂ Zn(SO ₄) ₂ ·6H ₂ O	77	2.425	2.127	2.064	—	—	[23]
·6H ₂ O	295	2.310	2.260	2.020	—	—	[18]
Cu ²⁺ ·K ₂ Zn(SO ₄) ₂ ·6H ₂ O	120	2.340	2.230	2.030	—	—	[18]
Cu ²⁺ ·ZnCs ₂ (SO ₄) ₂ ·6H ₂ O	300	2.384	2.164	2.050	—	—	Present work
	120	2.402	2.127	2.050	0.79	0.79	Present work

where λ , the spin-orbit constant, is -829 cm^{-1} for the free copper (II) ion, Θ is the angle related to the rhombic perturbation of the axial field and is nearly equal to zero since Θ is usually small. The energies ΔE_1 , ΔE_2 and ΔE_3 refer to the ${}^2A_{1g} \rightarrow {}^2B_{1g}$, ${}^2A_{1g} \rightarrow {}^2B_{2g}$ and ${}^2A_{1g} \rightarrow {}^2B_{3g}$ transitions, respectively. It is assumed that $k_1 = k_{||}$ and $(k_2 + k_3)/2 = k_{\perp}$, the data yield $k_{||} = 0.79$ and $k_{\perp} = 0.79$. These values are comparable with the values reported for those of the copper Tutton salts [20] in which the rhombic perturbation is observed. A comparison of these parameters is given in Table 4 along with g values.

The bonding parameter α^2 is obtained with the expression given by Kato and Abe [33].

$$\alpha^2 = 7/6 \{ [(A_3 - A_1)/P] - \Delta g_1 + \{11/14(\Delta g_3)\} - \{6/14(\Delta g_2)\} \}$$

where

$$P = [(14/17)(A_2 - A_3)] / [(\Delta g_3 - \Delta g_2)]$$

$$\Delta g_i = (g_e - g_i) \quad (g_e \text{ being } 2.0023).$$

At 120 K, the principal A values are found to be $A_1 = 97 \times 10^{-4} \text{ cm}^{-1}$, $A_2 = 22 \times 10^{-4} \text{ cm}^{-1}$ and $A_3 = 38 \times 10^{-4} \text{ cm}^{-1}$, α^2 , which shows that the bonding between copper and its ligands has a value of 1 if the bond is totally ionic and 0.5 if it is completely covalent. The α^2 calculated in the present work is ~ 0.9 , which indicates that the bonding between Cu—O is ionic. The ionic bonding between Cu—O is further supported by the large $g_{||}$ value [34].

From the analysis of the ESR data, it is established that the Cu^{2+} ion in ZCSSH is in the elongated rhombic environment with the largest bond along the z axis. The ground state is also established to be ${}^2A_{1g}(d_{x^2-y^2})$. With this term as the ground state, the various observed absorption bands in the present investigation are given approximate assignments which are consistent with the order proposed by Billing and Hathaway [35]. The spin-orbit reduction parameters calculated by making use of both optical and ESR data are in agreement with the reported values for the Tutton salts under the influence of a rhombic field. Thus the present study confirms the elongated rhombic environment for Cu^{2+} in ZCSSH and the bonding between Cu and O is ionic, as observed in diluted and undiluted copper Tutton salts [10—20, 22—24, 31].

ACKNOWLEDGEMENTS

The authors wish to express their sincere thanks to Professor Mihir Chowdhury, Calcutta for giving permission to record the absorption spectra on a Cary 17D spectrophotometer. The technical help rendered by Mr. Bikas Ghosh (Calcutta) is greatly acknowledged. The authors express their sincere thanks to the

authorities of DST, New Delhi, for providing finance for purchase of the JEOL ESR spectrometer. One of the authors (KP) is greatly obliged to the UGC, New Delhi, for the financial assistance. Finally the authors wish to thank the referee for his valuable comments on this paper.

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Received July 12th, 1982