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Optical and EPR studies of VO^{2+} and Cu^{2+} in $\text{Rb}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

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Abstract. The optical absorption and electron spin resonance spectra of vanadyl- and copper-doped rubidium cadmium sulphate hexahydrate are investigated at room and liquid nitrogen temperatures. From the analysis, the spectra are ascribed C_{4v} site symmetry in the case of VO^{2+} ions and D_{2h} site symmetry in the case of Cu^{2+} ions.

1. Introduction

Crystals of Tutton's salts form the basis of many spectroscopic investigations because of their well-defined growth characteristics and simplicity of structure. Rubidium cadmium sulphate hexahydrate, $\text{Rb}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, hereafter called RCSH, belongs to the family of Tutton's salts. These are monoclinic with the space group $P2_1/a$ and have two molecules per unit cell. The divalent metal sites are octahedrally coordinated by six water molecules [1–3]. In Tutton's salts doped with transition metal ions, they replace the divalent metal sites and exhibit slightly distorted octahedral site symmetry [4–18]. The present investigations on the vanadyl- and copper-doped RCSH crystals were undertaken with a view to studying the effect of the reduction in symmetry of the energy levels of the VO^{2+} and Cu^{2+} ions.

2. Experimental procedure

The single crystals of RCSH were grown at room temperature by slow evaporation of an aqueous stoichiometric solution of rubidium and cadmium sulphates. To grow the vanadyl- or copper-doped crystals 0.1 mol% of the respective sulphate was added to the growth solution. A number of crystals appeared in about a fortnight. For optical absorption studies, crystals 2 mm thick were chosen and the spectra were recorded on a Hitachi-U 3400 spectrophotometer in the wavelength region 300–1400 nm, at both laboratory and liquid nitrogen temperatures. In the case of copper-doped crystals the (010) faces were well developed. Therefore the spectra of the (010) face were also recorded with the incident polarised light with its electric vector parallel and perpendicular to the crystallographic a axis. The EPR spectra of the polycrystalline samples were recorded on a Varian E-112 X-band spectrometer, both at laboratory and liquid nitrogen temperatures.

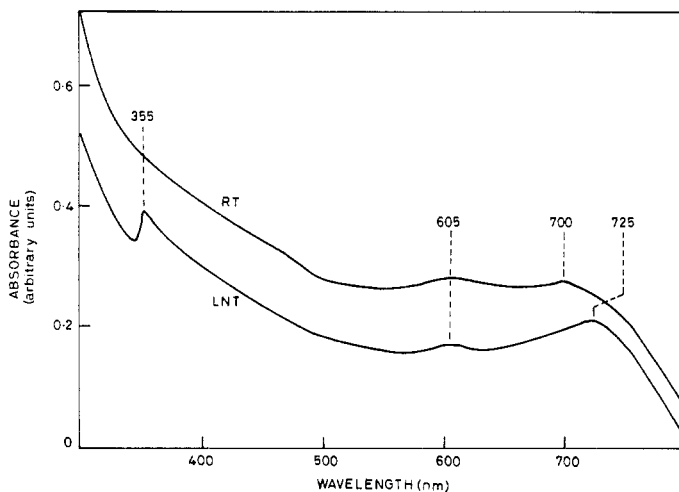


Figure 1. Optical absorption spectra of the VO^{2+} ion in RCSH (RT: room temperature; LNT: liquid nitrogen temperature).

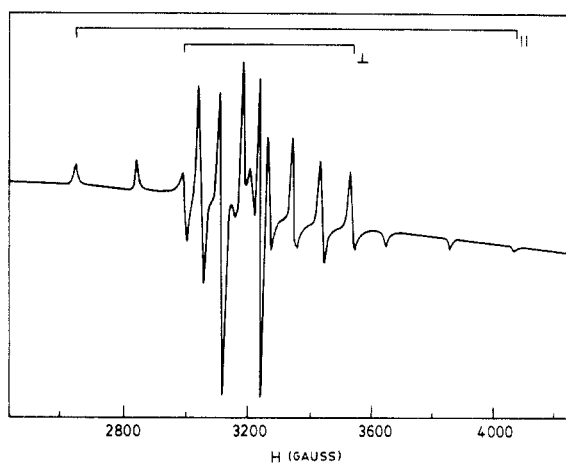


Figure 2. The EPR spectrum of the VO^{2+} ion in RCSH at LNT.

3. Results

3.1. VO^{2+} ion

The electronic absorption spectra of the sample recorded at room temperature (RT) and liquid nitrogen temperature (LNT) are shown in figure 1. The RT spectrum shows the presence of two bands at 700 and 605 nm. At LNT, the band at 700 nm is shifted towards the longer-wavelength side and is observed at 725 nm. The band at 605 nm does not show any shift. An additional band is observed at 355 nm. The EPR spectra at RT and LNT are similar and therefore the LNT spectrum alone is shown in figure 2. It reveals the usual eight-line pattern, resulting from the hyperfine coupling of the single unpaired electron with the $I = \frac{7}{2}$ nucleus.

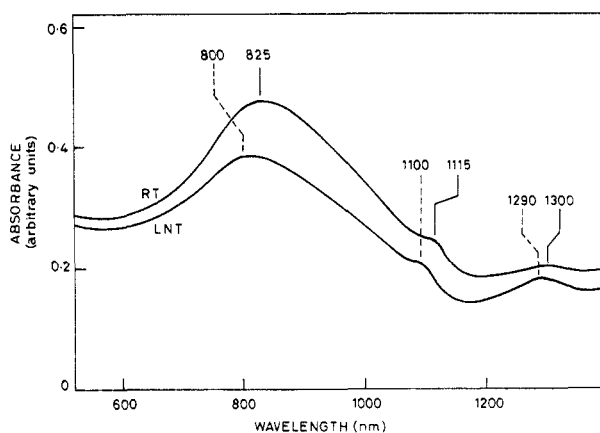


Figure 3. Optical absorption spectra of the Cu^{2+} ion in RCSH.

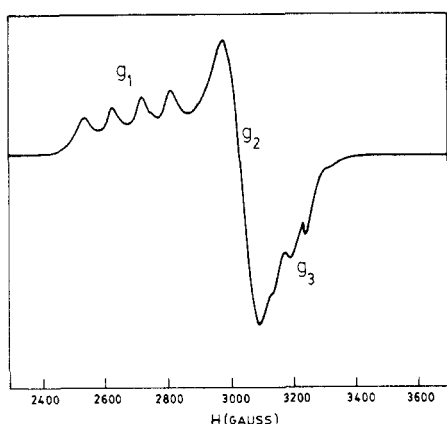


Figure 4. The EPR spectrum of the Cu^{2+} ion in RCSH at LNT.

3.2. Cu^{2+} ion

The optical absorption spectra of Cu^{2+} in RCSH, recorded at both RT and LNT, are shown in figure 3. The spectrum at RT exhibits three bands at 1300, 1115 and 825 nm. At LNT, all these bands exhibit shifts towards the shorter-wavelength side and are observed at 1290, 1100 and 800 nm respectively. In the polarised spectra, the band at 1300 nm is more intense and the band at 1115 nm is too weak to be recognised in the parallel-polarised light. The EPR spectrum of the polycrystalline sample at RT does not give any valuable information as it is unresolved. The spectrum recorded at LNT reveals four lines in the low field (corresponding to g_1), one broad line in the mid-field (corresponding to g_2) and four lines in the high field (corresponding to g_3). The spectrum is shown in figure 4.

4. Analysis

4.1. VO^{2+} ion

In an octahedral (O_h) crystal field, the free-ion term 2D of the VO^{2+} (d^1) ion splits into ${}^2T_{2g}$ and 2E_g terms, ${}^2T_{2g}$ being the ground state. Therefore, only one band, corresponding

Table 1. Assignments for the bands of VO²⁺ in RCSH.

Assignments	Band positions			
	300 K		77 K	
	λ (nm)	ν (cm ⁻¹)	λ (nm)	ν (cm ⁻¹)
² B ₂ → ² E	700	14 282	725	13 789
² B ₂ → ² B ₁	605	16 524	605	16 524
² B ₂ → ² A ₁	—	—	355	28 161

to the transition ²T_{2g} → ²E_g, is expected for VO²⁺ in pure O_h symmetry. However, if the symmetry is lowered, the upper and lower levels split, giving rise to more bands. Generally the site symmetry reduces either to C_{4v} or C_{2v} because of the non-symmetrical alignment of the V–O bond along the symmetry axis. In the case of C_{4v} symmetry three bands are expected, whereas in the case of C_{2v} symmetry four bands are expected.

In the present investigation, two bands are observed at RT whereas three bands are observed at LNT. Generally the band on the high-energy side is obscured by the tail of the more intense charge transfer band. As temperature decreases the intensity of the charge transfer band reduces. Also the ligand vibrations that contribute to the width of the band lessen with the decrease in temperature. These factors explain the presence of a sharp band on the high-energy side at LNT. The observation of only three bands even at LNT suggests the site symmetry to be C_{4v}. Accordingly the bands observed at LNT at 725, 605 and 355 nm are attributed respectively to the transitions ²B₂ → ²E, ²B₂ → ²B₁ and ²B₂ → ²A₁ (table 1). The crystal field parameters *Dq*, *Ds*, *Dt* were evaluated using the formulae corresponding to the transitions:

$${}^2B_2 \rightarrow {}^2E: \quad -3 Ds + 5 Dt$$

$${}^2B_2 \rightarrow {}^2B_1: \quad 10 Dq$$

$${}^2B_2 \rightarrow {}^2A_1: \quad 10 Dq - 4 Ds - 5 Dt.$$

The following values were evaluated from the band data at LNT:

$$Dq = 1650 \text{ cm}^{-1} \quad Ds = -3635 \text{ cm}^{-1} \quad Dt = 575 \text{ cm}^{-1}.$$

The characteristic two-set eight-line pattern observed in the polycrystalline EPR spectrum supports the proposal of C_{4v} as the site symmetry of the VO²⁺ ion in RCSH. The following spin Hamiltonian parameters were observed for the EPR spectrum at LNT:

$$g_{\parallel} = 1.937 \quad A_{\parallel} = 183 \times 10^{-4} \text{ cm}^{-1}$$

$$g_{\perp} = 1.982 \quad A_{\perp} = 71 \times 10^{-4} \text{ cm}^{-1}.$$

These are in good agreement with those observed for the similar compound VO²⁺:Rb₂Co(SO₄)₂·6H₂O [17].

Using the values of *g*_∥, *g*_⊥, *A*_∥, *A*_⊥ obtained from the EPR spectrum and the free-ion value of the spin-orbit coupling constant $\lambda = 170 \text{ cm}^{-1}$, the dipolar hyperfine splitting constant $P = -123 \times 10^{-4} \text{ cm}^{-1}$ and Fermi contact term $K = 0.85$ were evaluated from the formulae given by Kivelson and Lee [19].

The EPR and optical absorption data were correlated to evaluate the molecular orbital coefficients β_1^{*2} and ϵ_π^{*2} using the following formulae [19–22]:

$$g_e - g_{\parallel} = 8\lambda\beta_1^{*2}/\Delta_{\parallel} \quad g_e - g_{\perp} = 2\lambda\epsilon_\pi^{*2}/\Delta_{\perp}$$

where $g_e = 2.0023$ and Δ_{\parallel} and Δ_{\perp} are the energies corresponding to the transitions ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$ respectively. The values evaluated for the parameters are as follows:

$$\beta_1^{*2} = 0.80 \quad \epsilon_\pi^{*2} = 0.83.$$

These values indicate that the in-plane σ -bonding and out-of-plane π -bonding are covalent to a large extent [21].

4.2. Cu^{2+} ion

In an octahedral (O_h) crystal field, the free-ion term 2D of the Cu^{2+} (d^9) ion splits into 2E_g and ${}^2T_{2g}$ terms, 2E_g being the ground state. However, the ground state 2E_g splits due to the Jahn–Teller effect and Cu^{2+} will never have regular O_h symmetry. In a rhombic field (D_{2h}) the lower state 2E_g splits into 2A_g ($d_{x^2-y^2}$) and 2A_g (d_{z^2}) whereas the upper level splits into ${}^2B_{1g}$ (d_{xy}), ${}^2B_{2g}$ (d_{xz}) and ${}^2B_{3g}$ (d_{yz}) states.

The EPR spectrum at LNT is characteristic of rhombic symmetry with three values. From the positions of the peaks and their separations, the following spectroscopic splitting factors and the hyperfine structure constants were obtained:

$$g_1 = 2.423 \quad g_2 = 2.132 \quad g_3 = 2.010$$

$$A_1 = 105 \times 10^{-4} \text{ cm}^{-1} \quad A_3 = 61 \times 10^{-4} \text{ cm}^{-1}.$$

From these values it is possible to extract valuable information on the electronic ground state of the Cu^{2+} ion. The signs of the A -values are tentative. If for the g -values ($g_1 > g_2 > g_3$) the quantity $R = (g_2 - g_3)/(g_1 - g_2)$ is greater than unity, the ground state is predominantly 2A_g (d_{z^2}), and if it is less than unity, it is 2A_g ($d_{x^2-y^2}$). In the present investigation the value of $R = 0.42$ is far less than unity and this strongly indicates the ground state to be 2A_g ($d_{x^2-y^2}$) [23].

The ordering of the energy levels for the Cu^{2+} ion in D_{2h} symmetry with 2A_g ($d_{x^2-y^2}$) as the ground state is as follows [7]:

$${}^2A_g (d_{x^2-y^2}) < {}^2A_g (d_{z^2}) < {}^2B_{1g} (d_{xy}) < {}^2B_{2g} (d_{xz}) < {}^2B_{3g} (d_{yz}).$$

Accordingly the optical absorption bands at 1290, 1100 and 800 nm are attributed to the transitions 2A_g ($d_{x^2-y^2}$) \rightarrow 2A_g (d_{z^2}), 2A_g ($d_{x^2-y^2}$) \rightarrow ${}^2B_{1g}$ (d_{xy}) and 2A_g ($d_{x^2-y^2}$) \rightarrow ${}^2B_{2g}$ (d_{xz}) respectively. The fourth band corresponding to the transition 2A_g ($d_{x^2-y^2}$) \rightarrow ${}^2B_{3g}$ (d_{xz}) is generally weak and is not observed in the present investigation. The band data are given in table 2. In the polarised spectra the band corresponding to the transition 2A_g ($d_{x^2-y^2}$) \rightarrow ${}^1B_{1g}$ (d_{xy}) shows a decrease in intensity and the band corresponding to the transition 2A_g ($d_{x^2-y^2}$) \rightarrow 2A_g (d_{z^2}) shows an increase in intensity in parallel polarisation. These observations are in tune with those reported earlier [7] in the case of a Cu^{2+} ion in D_{2h} symmetry and this lends a strong support to our assignments.

Table 2. Band data and assignments for the Cu²⁺ ion in RCSH.

Transition from	Band positions			
	300 K		77 K	
	λ (nm)	ν (cm ⁻¹)	λ (nm)	ν (cm ⁻¹)
² A _g (d _{x²-y²)}				
² A _g (d _{z²)}	1300	7690	1290	7750
² B _{1g} (d _{xy})	1115	8966	1100	9088
² B _{2g} (d _{xz})	825	12 118	800	12 497

From the EPR data, the bonding parameter (α^2) is calculated [24], assuming the value of the free-ion dipolar term P to be 0.036 cm⁻¹:

$$\alpha^2 = \frac{7}{6} [(A_3 - A_1)/P - (g_e - g_1) + \frac{11}{4}(g_e - g_3) - \frac{6}{14}(g_e - g_2)].$$

The value of α^2 is 0.41. This indicates that the bonding is partly covalent or partly ionic.

5. Conclusions

The salient features of the optical absorption and EPR spectra reported in the present paper are well explained on the basis of the change to a lower symmetry from the octahedral symmetry. From the results, it is reasonable to conclude that the octahedral coordination is tetragonally (C_{4v}) distorted in the case of the VO²⁺ ion and rhombically (D_{2h}) distorted in the case of the Cu²⁺ ion. The bonding between the metal ion and the ligands is found to be partly covalent and partly ionic in both the cases.

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