

RESTRICTED VALIDITY OF THE TWO-STATE  
MODEL DESCRIBING A VIBRONIC EPR  
 $g$ -FACTORS AVERAGING IN  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$   
TUTTON SALT CRYSTALS  
DOPED WITH  $\text{Cu}^{2+}$  IONS

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Single crystals and powder EPR spectra of  $\text{Cu}^{2+}$  ions in  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  were recorded in the temperature range of 4.2–300 K and the  $g$ -factor temperature variations were determined. The  $g_z$  and  $g_y$  have the values of 2.443 and 2.134, respectively, at the rigid lattice limit below 20 K, and then continuously tend to an average value on heating. This vibronic averaging produced by reorientations of  $\text{Cu}(\text{H}_2\text{O})_6$ -complexes between Jahn-Teller distorted octahedral configurations is described in terms of a two-state Silver-Getz model which is known as a good model for diamagnetic non-ammonium Tutton salts. We found, however, that this model is only a crude approximation in  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  below 150 K. Above this temperature the model works better and describes the vibronic dynamics between the two lowest energy potential wells in the adiabatic potential surface differing in the energy of  $\delta_{12} = 318(9) \text{ cm}^{-1} = 3.7 \text{ kJ/mol}$ .

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## 1. Introduction

Silver and Getz have proposed a model [1] which describes the  $g$ -factor temperature variations due to jumps between two potential wells of different depths in an adiabatic potential surface produced by the Jahn-Teller effect. This model has been successfully used for a description of  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  vibronic complexes behaviour in  $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and after a generalization by Hitchman et al. [2] it was found as a good approximation in some diamagnetic Tutton salt crystals doped with  $\text{Cu}^{2+}$  ions [3]. However, a clear deviation from predictions of the model was found in ammonium Tutton salts [4], especially in  $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  [5]. It

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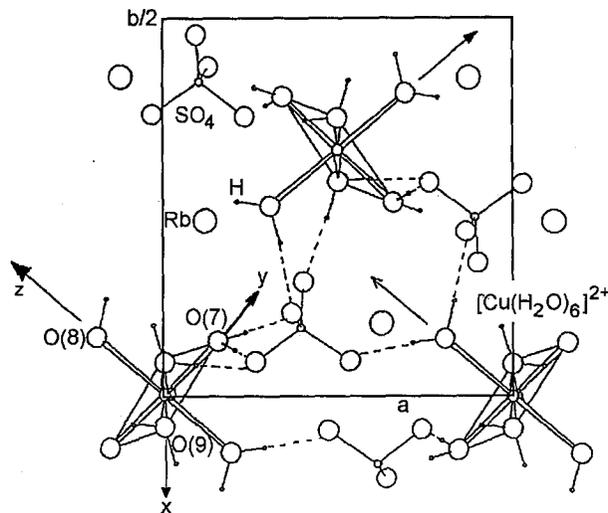


Fig. 1. Projection of the crystal structure of  $\text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  in the  $ab$ -plane. Broken lines show the hydrogen bonds between coordinated water molecules and  $\text{SO}_4$ -groups. The local  $x$ ,  $y$ ,  $z$  axes of  $\text{Cu}(\text{H}_2\text{O})_6$  complexes are marked by arrows.

was explained as due to hydrogen bonds between sulphate groups and  $\text{NH}_4$ -groups deforming additionally the adiabatic potential surface. In this paper we show that the validity of the Silver-Getz model is broken also for  $\text{Cu}(\text{H}_2\text{O})_6^{2+}$  complexes in a  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  crystal where ammonium groups are absent.

The crystal structure of  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  has been not exactly determined but the unit cell symmetry is  $P2_1/a$  with a ratio of the cell parameters  $a : b : c = 0.727 : 1 : 0.496$  and  $\beta = 107^\circ 1'$  [6]. These parameters indicate that the crystal structure is very similar to other Tutton salt crystals and very close to the structure of  $\text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  [7]. The deformation of the hexaaqua octahedra in diamagnetic salts is rather small but becomes large, due to the strong Jahn-Teller effect in  $\text{Cu}^{2+}$  doped salts. In  $\text{Cs}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  the molecular structure of the  $\text{Cu}(\text{H}_2\text{O})_6$ -complex is known [3] with  $\text{Cu}-\text{H}_2\text{O}$  distances: 0.2315 nm ( $\text{Cu}-\text{O}_8 = z$ -axis), 0.2004 nm ( $\text{Cu}-\text{O}_7 = y$ -axis) and 0.1966 ( $\text{Cu}-\text{O}_9 = x$ -axis), i.e. a strong axial deformation of the complex exists. A crystal unit cell of the Tutton salt crystals contains two molecules and a projection of the structure in  $ab$ -plane is shown in Fig. 1.

## 2. Experimental

Single crystals were grown from a water solution of cesium and zinc sulphates and had the form of prisms with well-developed (011)-planes. The 0.1 mol percent of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was added to the mother solution resulting in about  $10^{19}$   $\text{Cu}^{2+}$  ions per gram in single crystals. Single crystals and powder EPR spectra were recorded in the temperature range of 4.2–300 K using a Radiopan SE/X-2437 spectrometer equipped with an Oxford ESR910 flow helium cryostat. Temperature variations of the EPR spectra were measured along  $z$ -axis and  $x$ -axis of the

$g^2$ -tensor, whereas  $g_y$  was determined by the computer simulation of the powder EPR spectrum since for  $B \parallel y$  the spectra from two magnetically inequivalent Cu-sites overlap and moreover the forbidden transition lines appear lowering accuracy of  $g$ -factor determination.

### 3. Results

Single crystal EPR spectra at room temperature consist of two broad lines from two inequivalent Cu-sites in the crystal unit cell of monoclinic symmetry. In some crystal orientations the low-field line is split into hyperfine quartet of Cu ( $I = 3/2$ ). At low temperatures, due to a line narrowing and shift, the spectrum consists of two well-resolved hyperfine quartets as is shown in Fig. 2, where the spectra along the principal  $x$ ,  $y$ ,  $z$  directions, defined in Fig. 1, are shown at 20 K. The angular variations of the resonance field, corresponding to the principal  $g$ -factors, in a crystal plane perpendicular to the  $[111]$  direction, are shown in Fig. 3 for 20 K and 295 K. All the three principal directions  $x$ ,  $y$ , and  $z$  are located in this plane as is marked in Fig. 3 and they are not affected by temperature whereas the resonance fields along the  $y$  and  $z$  axes depend on temperature. Spin-Hamiltonian parameters obtained from the rotational data are (hyperfine splittings  $A_i$  are in  $10^{-4} \text{ cm}^{-1}$ ) as follows:

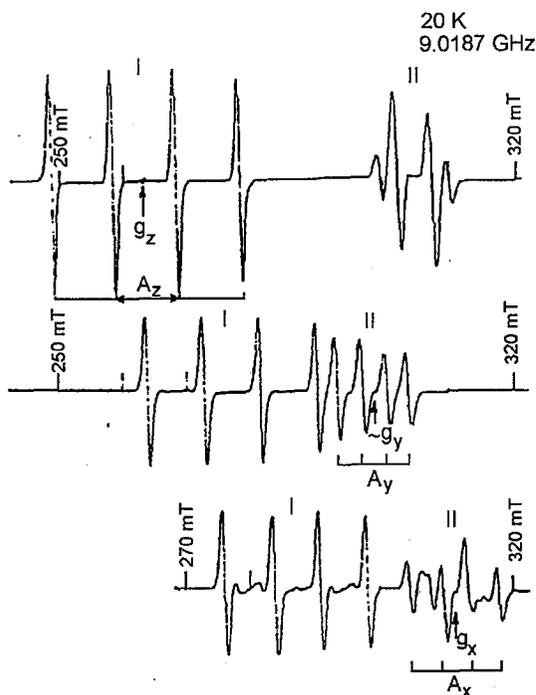


Fig. 2. Single crystal EPR spectra recorded along principal  $x$ ,  $y$ ,  $z$  axes at 20 K.

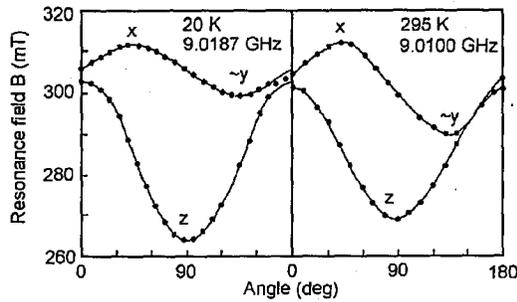


Fig. 3. Angular variations of the resonance field  $B = h\nu/g\mu_B$  in the crystal plane perpendicular to the  $[111]$  direction at 20 K and 295 K. The  $x$ ,  $y$ ,  $z$  axes are the principal directions of the  $g^2$ -tensor and are defined in Fig. 1.

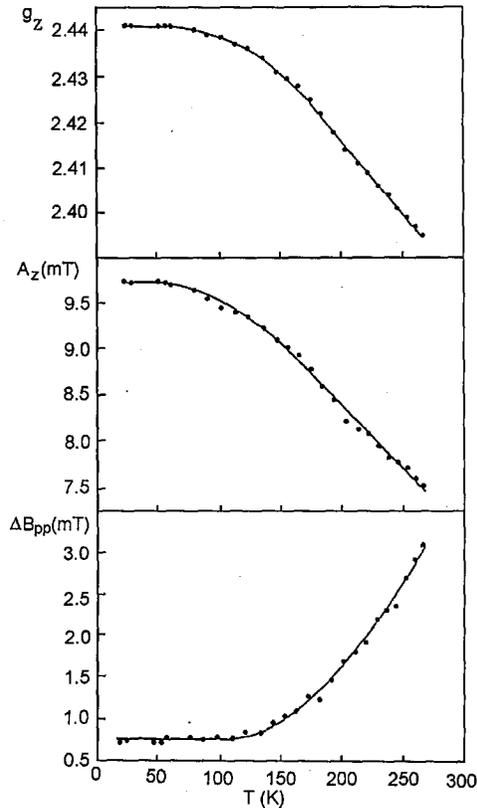


Fig. 4. Temperature variations of the  $g_z$ -factor, hyperfine splitting  $A_z$  and linewidth  $\Delta B_{pp}$  from the single crystal EPR data along the  $z$ -axis.

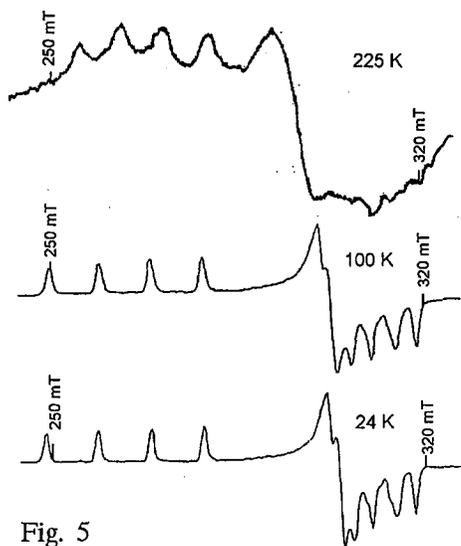


Fig. 5

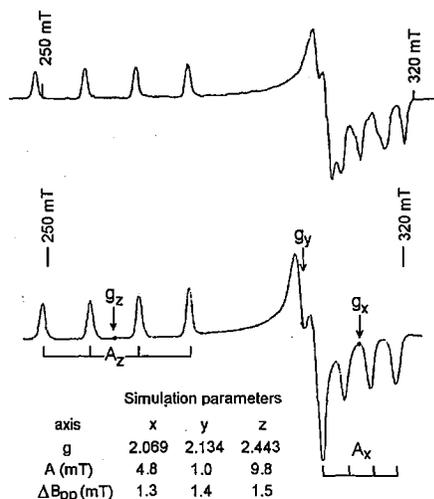


Fig. 6

Fig. 5. Powder EPR spectra recorded at various temperatures.

Fig. 6. Experimental and simulated powder EPR spectrum.

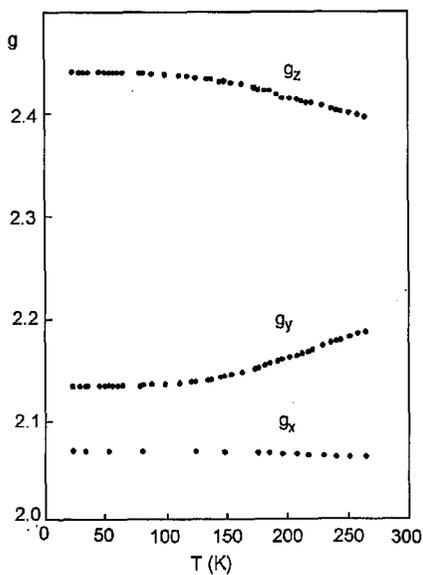


Fig. 7. Temperature variations of the  $g$ -factors.

$$T = 20 \text{ K} : g_x = 2.069(1), g_y = 2.134(2), g_z = 2.443(1), A_x = 46(5),$$

$$A_y = 10(2), A_z = 112(2);$$

$$T = 295 \text{ K} : g_x = 2.062(1), g_y = 2.183(3), g_z = 2.395(2), A_x = 46(5),$$

$$A_y \text{ — nonmeasurable, } A_z = 85(3).$$

Temperature variations of the spectral parameters along  $z$ -axis are shown in Fig. 4 and temperature dependences of the powder EPR spectra, from which  $g_y$ -factor was determined, are shown in Fig. 5. Since an accuracy of the  $g_y$  determination from single crystal data was very small due to the overlap of the spectra above *ca.* 100 K, we have use Bruker's SIMFONIA computer programme for powder spectra simulations. The single crystal data for  $g_z$ ,  $g_x$ ,  $A_z$ , and  $A_x$  were used as the input parameters and  $g_y$ ,  $A_y$  were varied to obtain the best peak positions. The experimental and simulated spectra are compared in Fig. 6. The resulting  $g$ -factors temperature dependence is shown in Fig. 7.

#### 4. Discussion

The Jahn–Teller effect of  $E \otimes \varepsilon$ -type in octahedral symmetry produces three minima in the adiabatic potential energy surface corresponding to the three distorted octahedron configurations [8]. Transitions between these configurations affect EPR spectra. The  $g$ -factor temperature variations in  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$  show that the  $g_x$  which appears along the shortest Cu–O bond is practically not affected by temperature, whereas the  $g_z$  and  $g_y$  display a tendency to averaging on heating. This is a typical behaviour for  $\text{Cu}^{2+}$  ions in Tutton salt crystals with three inequivalent potential wells (Fig. 8) although the  $g_i$  variations are here relatively weak. The independence of  $g_x$  on temperature indicates that the highest energy well is not involved in the reorientation process between the wells. The exci-

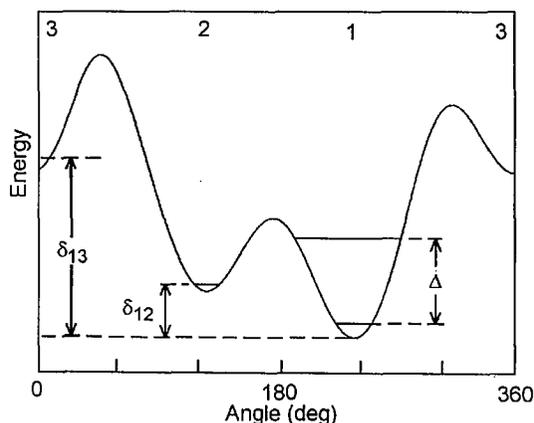


Fig. 8. A cross-section through the adiabatic potential surface with the three potential wells 1, 2, 3 and vibronic levels typical for  $\text{Cu}^{2+}$  in Tutton salt crystals.

tations of  $\text{Cu}(\text{H}_2\text{O})_6$  to the higher energy configuration and rapid back relaxation to the deepest potential well produce a mixing of the configurations observed as an averaging of the  $g$ -factors corresponding to these two wells.

This was described by Silver and Getz [1] in the case of  $\text{Cu}^{2+}$  in  $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Their two-well model assumes: (i) the  $g$ -factors are identical in both distorted configurations and an excitation results in the interchange of the  $y$  and  $z$  axes only; (ii) the population of the both wells is described by Boltzmann statistics; (iii) the shape of the adiabatic potential surface and thus the energy difference between two configurations is temperature independent. This is a very simple model but was successfully used for description of the vibronic  $g$ -factor averaging in various crystals. If the populations of the two wells are  $N_1$  and  $N_2$  ( $N_1 + N_2 = 1$ ) and the corresponding  $g$ -factors at the rigid limit for  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O} : \text{Cu}^{2+}$  (below 20 K) are  $g_z^0 = 2.243$  and  $g_y^0 = 2.134$  then the experimentally observed  $g$ -factors are weighted average due to the jumps between the wells

$$g_z(T) = N_1 g_z^0 + N_2 g_y^0, \quad g_y(T) = N_1 g_y^0 + N_2 g_z^0. \quad (1)$$

The populations can be calculated as

$$N_2 = \frac{g_z(T) - g_z^0}{g_y^0 - g_z^0} = \frac{g_y(T) - g_y^0}{g_z^0 - g_y^0}, \quad N_1 = 1 - N_2. \quad (2)$$

The population ratio calculated from the experimental data is shown by points in Fig. 9, where it is compared with the ratio calculated from Boltzmann statistics for different energy differences  $\delta_{12}$  between the wells. The energy  $\delta_{12}$  can be directly calculated from the population ratio as  $\delta_{12} = -kT \ln(N_2/N_1)$ . The result of the calculations is shown in Fig. 10.

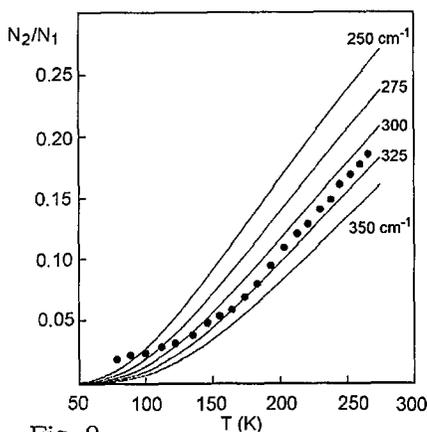


Fig. 9

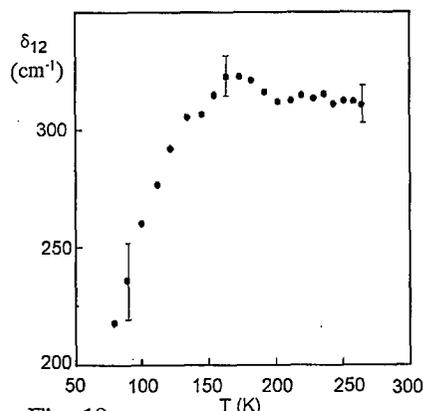


Fig. 10

Fig. 9. Population ratio of the two lowest energy potential wells of  $\text{Cu}^{2+}$  in  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  calculated from the EPR data (points). The solid lines represent  $N_2/N_1$  calculated from the Boltzmann statistics for different  $\delta_{12}$  values.

Fig. 10. Temperature variations of the energy difference  $\delta_{12}$  between two potential wells calculated from the Silver-Getz model for  $\text{Cu}^{2+}$  in  $\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .

The results presented in Figs. 9 and 10 clearly show that the two-state Silver-Getz model is not able to describe precisely the experimentally observed vibronic  $g$ -factor averaging. At low temperatures, where the  $g$ -factors variations are measured with a lower accuracy, the experimental  $N_1/N_2$  values are higher than expected and the "effective" energy difference between the potential wells apparently increases. Above 150 K a slow but clear decrease in effective  $\delta_{12}$  is observed, whereas according to the model the  $\delta_{12}$  value should be temperature independent in the whole temperature range. The average energy difference  $\delta_{12}$  above 150 K is  $\delta_{12} = 318(9) \text{ cm}^{-1} = 0.04 \text{ eV} = 3.7 \text{ kJ/mol}$ .

Our data show that the Silver-Getz model which was questioned for  $\text{Cu}^{2+}$  in ammonium Tutton salts is also an approximation only in non-ammonium salt  $\text{Cs}_2\text{Zn}(\text{SO}_4)_6 \cdot 6\text{H}_2\text{O}$ . It seems that the all assumptions of the model can be questioned but most probably the other excited vibronic levels should be included in an analysis of experimental  $g$ -factor data.

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