

# Jahn-Teller Effect of Cu<sup>2+</sup> ions in a Zinc Selenate Hexahydrate Single Crystal

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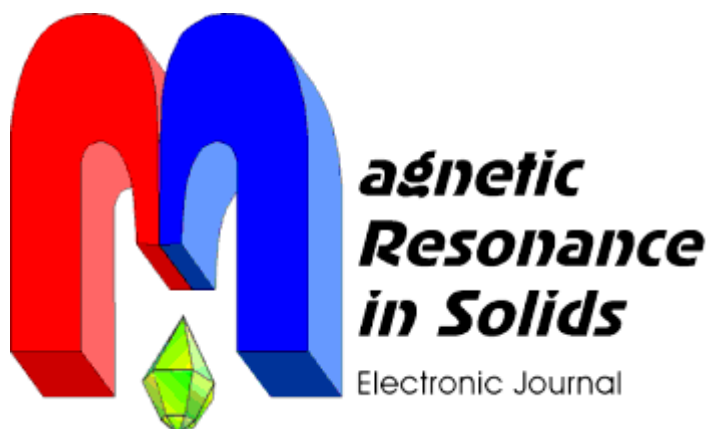
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*X*- and *Q*-band studies of Cu<sup>2+</sup> and Mn<sup>2+</sup> doped ZnSeO<sub>4</sub>·6H<sub>2</sub>O single crystals in the temperature range of 4.2 ÷ 300 K are carried out. Experimental data on EPR, spin-lattice relaxation time and optical absorption spectra are explained in the frame of the Jahn-Teller Effect of the Cu<sup>2+</sup> ion under the low- symmetry deformation of the nearest environment of the Cu<sup>2+</sup> ion.

## 1. Introduction

The problem of dynamics of multicomponent systems at a molecular level and the use of its properties in modern devices remains traditionally actual during last decades. The Jahn-Teller Effect (JTE) is a vivid example of the intramolecular dynamics in solid state and is due to the local deformations of the crystal lattice close to the paramagnetic center with degenerate or quasidegenerate ground orbital state. In this paper the properties of  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O} : \text{Cu}^{2+}$  single crystals studied by EPR, spin-lattice relaxation and optical spectroscopy are reported.

The Zinc Selenate Hexahydrate ( $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ ) is crystallized in monoclinic syngony with the space group of  $P4_12_12$  symmetry. Parameters of the unit cell are  $a = 0.6947(1)$  nm,  $c = 1.8592(1)$  nm,  $Z = 4$  [1].  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  single crystals were grown by slow evaporation of 35 % aqueous solution of the corresponding component at 273 K. Quality control of samples was carried out by X-ray of powders on a diffractometer DRON-3 and by measuring single crystal refraction parameters on a refractometer IRF-23 at room temperature. EPR spectra were investigated on a radiospectrometer RE-1301, "Thomson" at X-band in the temperature range of  $4.2 \div 300$  K and on a home-made radiospectrometer at Q-band at  $T = 300$  K. Optical absorption spectra were registered on a spectrophotometer NIR-61 at  $T = 300$  K in non-polarized and polarized light. Spin-lattice relaxation times of  $\text{Cu}^{2+}$  ions in the temperature range of  $4.2 \div 25$  K were measured at frequency 9.3 GHz by pulse saturation method on a relaxometer IRES-1003.

## 2. Results

### EPR spectra of $\text{Mn}^{2+}$ ions

EPR spectrum of  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  single crystals doped with  $\text{Mn}^{2+}$  ions in the temperature range  $4.2 \div 300$  K [2,3] is described by the spin-Hamiltonian:

$$H = g\beta HS + AIS + \frac{1}{3}b_2^0 O_2^0 + \frac{1}{3}b_2^2 O_2^2 + \frac{1}{60}b_4^0 O_4^0 + \frac{1}{60}b_4^2 O_4^2 + \frac{1}{60}b_4^4 O_4^4, \quad (1)$$

where  $g = 2.006 \pm 0.001$ ;  $b_2^0 = 553.8 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $b_2^2 = 52.4 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $b_4^0 = 4.3 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $b_4^2 = 1.3 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $b_4^4 = 1.8 \cdot 10^{-4} \text{ cm}^{-1}$ ;  $A = 88.4 \cdot 10^{-4} \text{ cm}^{-1}$ .

Angular dependences of the  $\text{Mn}^{2+}$  EPR spectrum reveal 4 types of centers having the same principal values of the spin Hamiltonian (1) parameters but differing in the orientation of fine structure tensors  $b_n^m$ . The principal direction ( $z$  axis) of the  $b_n^m$  coincides with the direction of the Zn(Mn) – O3 bond and makes an angle of  $41.7^\circ$  with the  $L_4$  axis. The  $x$  axis of the  $\text{Mn}^{2+}$  EPR spectrum coincides with the crystallographic direction  $[110]$ , and the  $Y$  axis lie in the  $(1\bar{1}0)$  plane and makes an angle of  $48.3^\circ$  with the  $L_4$  axis. The value of the covalency parameter  $C = 8.5\%$  was estimated from the value of the  $\text{Mn}^{2+}$  ion hyperfine structure parameters according to [2].

### Optical spectrum of $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O} : \text{Cu}^{2+}$

Two bands with the centers at  $\nu_1 = 9880 \text{ cm}^{-1}$  and  $\nu_2 = 11920 \text{ cm}^{-1}$  with relative intensities 4:3 and widths  $800 \text{ cm}^{-1}$  and  $880 \text{ cm}^{-1}$ , respectively, are observed in the optical absorption spectrum.

### Spin-lattice relaxation of $\text{Cu}^{2+}$ ions

In the temperature range of  $4.2 \div 300$  K the spin-lattice relaxation time of  $\text{Cu}^{2+}$  ion is described well by the following expression [3]:

$$T_1^{-1} = A_0 T + A_1 \exp\left(\frac{\delta_1}{T}\right) + A_2 \exp\left(\frac{\delta_2}{T}\right) + A_3 \exp\left(\frac{\delta_3}{T}\right), \quad (2)$$

where  $A_0 = 0.27 \text{ K}^{-1} \text{ s}^{-1}$ ;  $A_1 = 3.3 \cdot 10^5 \text{ s}^{-1}$ ;  $\delta_1 = 69.5 \text{ K}$ ;  $A_2 = 2.6 \cdot 10^7 \text{ s}^{-1}$ ;  $\delta_2 = 140 \text{ K}$ ;  $A_3 = 1.36 \cdot 10^{10} \text{ s}^{-1}$ ;  $\delta_3 = 735.6 \text{ K}$ .

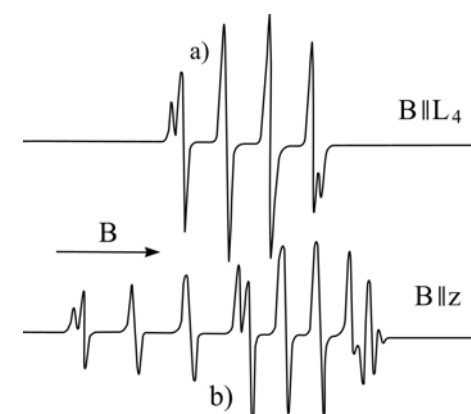


Fig. 1. The EPR spectrum of  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O} : \text{Cu}^{2+}$  single crystals. a)  $B \parallel L_4$ ; b)  $B \parallel z$ .

### EPR spectra of $\text{Cu}^{2+}$ ions

The EPR spectrum of  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  single crystals doped with  $\text{Cu}^{2+}$  ions (Fig.1) as well as the EPR spectrum of  $\text{Mn}^{2+}$  ions is described by the spin-Hamiltonian of rhombic symmetry

$$H = \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z \quad (3)$$

where  $A_z = (129 \pm 0.5)10^{-4} \text{ cm}^{-1}$ ;  $A_x = (22.3 \pm 0.5)10^{-4} \text{ cm}^{-1}$ ;  $A_y = (11.3 \pm 0.5)10^{-4} \text{ cm}^{-1}$ ;  $g_z = 2.427 \pm 0.001$ ;  $g_x = 2.097 \pm 0.003$ ;  $g_y = 2.095 \pm 0.003$ .

Angular dependences of the  $\text{Cu}^{2+}$  EPR spectrum reveal 4 centers with identical magnetic parameters but noncoincident principal axes of the  $g$  and  $A$  tensors (Fig.2). The  $z$  axis makes the angle  $43.3^\circ$  with  $L_4$  axis, instead of  $41.7^\circ$  as it was observed in the case of EPR of  $\text{Mn}^{2+}$  ions. In the  $(110)$  plane the  $x$  axis deviates from the  $[110]$  direction by the angle  $3^\circ$ . In the  $\text{Cu}^{2+}$  EPR spectrum the additional lines due to  $^{63}\text{Cu}$

isotope are also observed.

As the temperature increases from  $T = 4.2$  K to room temperature the EPR lines of  $\text{Cu}^{2+}$  ions move to the high field region, and their width increases. At room temperature the line width of different hyperfine structure components is unequal, decreasing as the magnetic field increases.

### 3. Discussion

To describe the properties of doped divalent copper centers in the  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  crystal, it is necessary to take into account the interaction of  $\text{Cu}^{2+}$  ions with the normal displacements  $Q_\theta$  and  $Q_\epsilon$  of the  $\text{Cu}(\text{H}_2\text{O})_6$  complexes. The interaction of the ion in the  $\Gamma_3$  ground state with the  $Q_\theta$  and  $Q_\epsilon$  deformations of the complex  $\text{Cu}(\text{H}_2\text{O})_6$  and with the low-symmetry crystal field which arises due to the static deformation of the environment of the dopant  $\text{Cu}^{2+}$  ion is described by the following Hamiltonian [4,5]:

$$H = V(Q_\epsilon U_\epsilon + Q_\theta U_\theta) + V_2(-Q_\theta^2 U_\theta + Q_\epsilon^2 U_\theta + 2Q_\theta Q_\epsilon U_\epsilon) + \frac{M\omega^2}{2}(Q_\theta^2 + Q_\epsilon^2)\mathbf{I} + V_3(Q_\theta^3 - 3Q_\theta Q_\epsilon^2)\mathbf{I} + \Delta U_\theta + \gamma U_\epsilon \quad (4)$$

where  $\mathbf{I}$ ,  $U_\theta$ ,  $U_\epsilon$  are Pauli's matrices, the first and the second terms correspond to linear and quadratic electron-phonon interaction, respectively; the third term is the potential energy of the nuclei; the fourth term accounts for the anharmonicity; the fifth and the sixth terms are the tetragonal and rhombic components of the crystal field, respectively. The bottom surface of the adiabatic potential is shown in Fig. 3. It is seen in Fig. 3 that instead of one minimum of energy with rhombic symmetry the complex  $\text{Cu}(\text{H}_2\text{O})_6$  has three minima, differing in energy. The value of the energy interval  $\Delta E$  up to the excited minima at  $\varphi \sim 120^\circ$  and  $\varphi \sim 240^\circ$  can be defined from the Hamiltonian (4) if for the crystal under study the constants  $V$ ,  $V_2, V_3$ ,  $\Delta$  and  $\gamma$  are known. If such data are absent the  $\Delta E$  value can be estimated from the following empirical formula:  $\Delta E_i \sim k \cdot \Delta R_i$  [5], where  $k$  is the factor of proportionality which for hydrate crystals can be accepted to be equal to  $k \approx 10^5 \text{ cm}^{-1}/\text{nm}$ , and  $\Delta R_i$  is the difference between the longest metal - ligand bond and other bonds. Let us estimate the  $\Delta E$  value for the compound under study. According to the crystallographic data for  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$  [1], the nearest environment of the  $\text{Zn}^{2+}$  ion, which is replaced by the dopant  $\text{Cu}^{2+}$  ion, has monoclinic symmetry. The structure of  $\text{Zn}(\text{H}_2\text{O})_6$  octahedra not perturbed by the dopant center has a monoclinic distortion, and its bond lengths Zn-O equal 0.2045 nm, 0.2088 nm and 0.2138 nm. The average deviation of the O-Zn-O bond angle from  $90^\circ$  is equal to  $0.85^\circ$  evidencing that the monoclinic distortion is small. The differences in the bond lengths are  $\Delta R_1 = 0.005$  nm,  $\Delta R_2 = 0.0093$  nm. The  $\Delta E$  values are  $\Delta E_1 \sim 500 \text{ cm}^{-1}$  and  $\Delta E_2 \sim 930 \text{ cm}^{-1}$ , respectively. These large values of the energy interval to the excited minima from the bottom surface of the adiabatic potential lead to their population being small even at room temperature and therefore only the ground minimum ( $\varphi = 0^\circ$ ) is mainly populated. Distortions of the complexes occupying this minimum do not have the rhombic character as for a matrix complex. They are mainly tetragonal, with a weak rhombicity, determined by the structure of the minimum along the  $\varphi$  coordinate. Thus it is possible to explain the experimental values of the  $g$  tensor components of  $\text{Cu}^{2+}$  ions which are in the sites with tetragonal symmetry within experimental accuracy. Excited minima can affect the temperature dependence of the  $g$  factors (basically  $g_z$  components), the relaxation characteristics of the system at temperatures of about room temperature and the width of the EPR lines due to the relaxation transitions between minima. The mainly tetragonal EPR spectrum of  $\text{Cu}^{2+}$  ions means that the difference between  $\Delta E_i$  value estimated above is close to zero and one can take as the  $\Delta E$  value the average of  $\Delta E_i$ , i.e.  $\Delta E \sim 715 \text{ cm}^{-1}$ .

Let us estimate the energy interval up to the excited minima on the basis of the temperature dependence of  $g$  - factors. From formulas (13) in ref. [5] one can write:

$$\Delta E(T) = kT \cdot \ln \left\{ \frac{2[g_z(T = 4.2\text{K}) - g_z(T)]}{g_z(T) - g_x(T = 4.2\text{K})} \right\} \quad (5)$$

In the compound under investigation  $g_z(4.2\text{K}) = 2.427$ ;  $g_x(4.2\text{K}) = 2.095$ ;  $g_z(293\text{K}) = 2.4144$ ;  $g_z(253\text{K}) = 2.4194$ ;  $g_z(193\text{K}) = 2.424$ , so  $\Delta E(293\text{K}) = 740 \text{ cm}^{-1}$ ;  $\Delta E(200\text{K}) = 770 \text{ cm}^{-1}$ .

This value agrees well enough with the value obtained from the spin-lattice relaxation times of the  $\text{Cu}^{2+}$  ion data ( $\Delta E = 735 \text{ K}$ ) and also with the above value from crystallographic data ( $\Delta E \sim 715 \text{ cm}^{-1}$ ). Such good agreement of the results of two various experiments and theoretical estimates allows us to conclude that the largest energy interval determined in spin-lattice relaxation experiments is due to the relaxation transitions between nonequivalent minima of the bottom surface of the adiabatic potential. These minima arise when the vibronic effects and the low-symmetry components of the deformation of the environment of dopant  $\text{Cu}^{2+}$  ion are taken into account. Two other energy

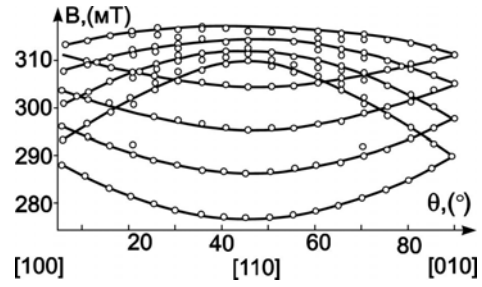


Fig. 2. Angular dependences of  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}:\text{Cu}^{2+}$  EPR spectrum.

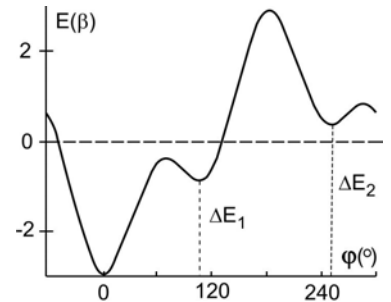


Fig. 3. The bottom surface of the complex  $\text{Cu}(\text{H}_2\text{O})_6$  adiabatic potential.

intervals at 69 and 140  $\text{cm}^{-1}$  should be attributed to the intervals between vibronic levels of the ground minimum with  $\varphi = 0^\circ$ .

The values of the energy interval between the bottom surface of the adiabatic potential (Fig.3) and the top surface characteristic for the hydrate crystal lie in the range of 6000÷10000  $\text{cm}^{-1}$ . The experimental optical band at 9880  $\text{cm}^{-1}$  can be probably attributed to transitions between these two surfaces of the adiabatic potential. As at  $\varphi = 0^\circ$  almost pure  $|x^2 - y^2\rangle$  orbital function corresponds to the bottom surface and the  $|z^2\rangle$  orbital function corresponds to the top surface this band corresponds to the transitions between the levels of the orbital doublet  ${}^2E$  split by the tetragonal component of the crystal field enhanced by JTE according to (4). Then the second optical band at 11920  $\text{cm}^{-1}$  can be attributed in these terms to transitions between  $|x^2 - y^2\rangle$  orbital doublet function and one of the  $|xy\rangle$  functions of the orbital triplet state.

An additional evidence of the molecular motion of the complexes  $\text{Cu}(\text{H}_2\text{O})_6$  is the linewidth dependence on  $m_I$  (projections of the nuclear magnetic quantum number). At room temperature the line widths ( $\Delta B$ ) decrease as the magnetic field increases (1:0.97:0.947:0.92), and the peak-to-peak intensity (85:90:95:100) accordingly grows. Depending on type of the intramolecular movement the line width is described by the expression [6]:  $\Delta B = A + B \cdot m_I + C \cdot (m_I)^2$ . The linear term with factor  $B$  results in the asymmetric EPR spectrum as observed experimentally. The sign of factor  $B$  depends on the sign of the product  $\Delta g \cdot \Delta A$ , where  $\Delta g$  and  $\Delta A$  are the anisotropy of the  $g$  and  $A$  tensors, respectively, of different states participating in averaging. The experimental field dependence of the line width can be explained with the factor  $B > 0$ . This sign of the product  $\Delta g \cdot \Delta A$  corresponds to the case when the copper octahedral complex moves between the ground-state and the excited minima of the adiabatic potential.

Thus, our result confirm that the Jahn-Teller Effect considerably contributes to the EPR spectra and spin-lattice relaxation times of  $\text{Cu}^{2+}$  ions in  $\text{ZnSeO}_4 \cdot 6\text{H}_2\text{O}$ .

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