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ELECTRON PARAMAGNETIC RESONANCE STUDIES OF COPPER(II)-DOPED TRIGLYCINE SELENATE CRYSTAL*

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EPR measurements of $^{63}Cu^{2+}$ complexes in triglycine selenate (TGSe) single crystal are reported. The spin Hamiltonian parameters at room temperature are $g_z = 2.2591$, $g_y = 2.0650$, $g_x = 2.0529$ and $A_z = 151.0$, $A_y = 2.5$, $A_x = 42.2$ (A — values in 10^{-4} cm^{-1}). By computer simulation of the EPR spectra, the copper (II) ion was found to be co-ordinated to two equivalent nitrogen atoms and two pairs of hydrogen atoms.

1. Introduction

Glycine crystals, irradiated as well as doped with paramagnetic ions, have been the subject of numerous EPR studies. In crystals of the triglycine sulphate (TGS) type, the electronic structure of paramagnetic admixture complexes has been studied, and a relationship has been found between the changes in EPR spectrum in the phase transition and the ferroelectric state parameters of the crystal. Such changes have been observed in the EPR spectra of Cr^{3+} [10, 11]. VO^{2+} [1], as well as in those of irradiated crystals [4]. EPR spectra of the Cu^{2+} ion have been investigated in TGS [2, 3, 6, 7, 12] and triglycine fluoroberyllate (TGFB) [8, 9[], though no influence of the phase transition on the spectrum was observed.

The aim of this paper is to report results on the electronic structure of the copper complexes in TGSe crystal.

2. Experimental

TGSe crystal was grown from saturated aqueous solution, containing 5% of $CuSO_4 \cdot 5H_2O$, by evaporation at constant temperature. The crystal used in the present work had been grown 3 years earlier; during the 3 years of aging its EPR lines underwent

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considerable narrowing and, in fact. were the narrowest ever observed for crystals of the TGS group.

The EPR study was carried out at room temperature using a RADIOPAN SE–X 201 spectrometer with rectangular TE_{102}-cavity and 100 kHz modulation.

3. *Results and discussion*

We measured the angular dependence of the EPR spectrum in two systems of coordinates: a^*, b, c and X, b, Z. The former is related with the system of crystallographical axes $a^* = b \times c$ whereas the latter is more directly related with the morphology of the crystal. In the reference frame X, b, Z, the Z-axis is perpendicular to the plane $(\bar{1}01)$, which,

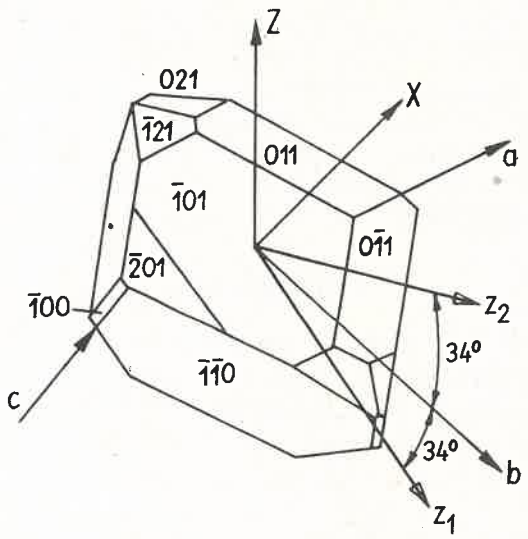

Fig. 1. Morphology of TGSe crystal. The axes of the reference frames a^*, b, c and x, b, z as well as the orientations of the principal z-axes of the Cu^{2+} complexes, are shown ($\pm 34°$ to the b-axis in the bZ-plane)

under natural conditions, is the largest face of the crystal. In TGSe, the angle between the axes X and a^* amounts to 15°40′. The axes of either reference frames, as well as the crystal morphology, are shown in Fig. 1. The EPR measurements were carried out in the two frames in order to determine the parameters of the spectrum univocally and to enhance the accuracy of their determination.

The EPR resonance lines of the crystal are very narrow (about 0.15 mT); hence, the isotopic structure and superhyperfine structure from interaction with nitrogen nuclei and protons are well resolved. The splitting of the resonance lines of the superhyperfine (shfs) and hyperfine (hfs) structures is dependent on the orientation of the crystal in the magnetic field; this, jointly with changes due to g-factor anisotropy, leads to a highly complex shape of the angular dependence of the spectrum. The latter is shown in Fig. 2 for the hfs lines, in the bc-plane of the crystal. Angle-dependent studies show that the tensors g and

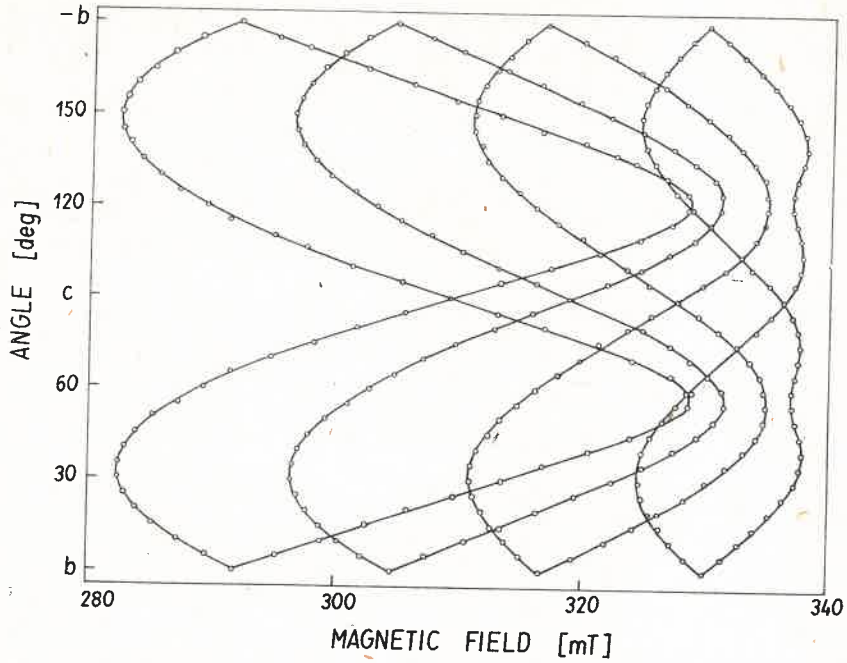

Fig. 2. Angular dependence of the spectrum of Cu^{2+} in TGSe in the *bc*-plane. Continuous lines show the theoretical plot derived from the data of Table I

A of the spin Hamiltonian are non-axially symmetric and that their principal axes coincide. Moreover, second-order shifts of the hfs lines affect the angular dependence essentially. As in the case of other crystals of the TGS group, we observed no quadrupole effects. Thus, the position of each hfs line (with given quantum number m) in the magnetic field is described by the formula, [5]

$$H = H_0 - Am - \varepsilon/H_0, \tag{1}$$

where

$$\varepsilon = \frac{(15/4-m^2)}{4A^2A_\perp^2}\left[A_z^2A_\perp^2+A^2(A_xA_y)^2+A_z^2(A_x^2-A_y^2)\,(g_xg_yg_z/gg_\perp^2)^2(\sin\varphi\cos\varphi\cos\theta)^2\right]$$

$$+\frac{m^2}{2A}\left[(A_z^2-A_\perp^2)\,(g_zg_\perp/g^2)^2\sin^2\theta\cos^2\theta+A_\perp^2(g_xg_y/gg_\perp)^2(\sin\varphi\cos\varphi\sin\theta)^2\right],$$

with

$$g^2 = (g_x\sin\theta\cos\varphi)^2+(g_y\sin\theta\sin\varphi)^2+(g_z\cos\theta)^2,$$

$$A^2g^2 = (A_xg_x\sin\theta\cos\varphi)^2+(A_yg_y\sin\theta\sin\varphi)^2+(A_zg_z\cos\theta)^2,$$

$$g_\perp^2 = g_x^2\cos^2\varphi+g_y^2\sin^2\varphi,$$

$$A_\perp^2g_\perp^2 = (A_xg_x\cos\varphi)^2+(A_yg_y\sin\varphi)^2.$$

In Eq. (1), the first two terms result from the first-order perturbation theory, whereas the last term is a second-order correction, due to which the hfs lines are non-equidistant. The quantity m is the magnetic quantum number of the copper nucleus ($I = 3/2$), whereas θ and φ are the polar and azimuthal angles of the field H in the reference frame of principal axes of the g and A tensors.

The EPR spectra of Cu^{2+} in TGS-like crystals are typically characterized by a very small value of the hyperfine splitting in the y-axis direction of the copper complex. The magnitude of this splitting is by no means easy to measure since the overlapping of many

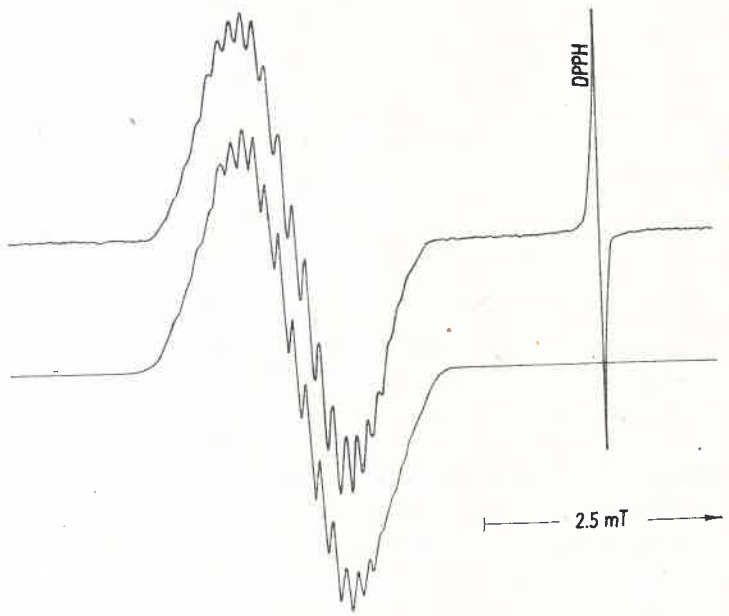

Fig. 3. Experimental spectrum (upper), and spectrum obtained by computer simulation (lower), as observed in the x-axis direction of the TGSe crystal

resonance lines generally leads to a diffuse structure of the spectrum at this orientation. In the case of our crystal, with regard to the narrowness of the lines, we observed a well resolved structure of the spectrum in the direction of the y-axis of the copper complex, coinciding practically with the X-axis of the crystal. The EPR spectrum observed in the X-axis direction is shown in Fig. 3. Computer analysis showed the spectrum to consist of 23 resonance lines, with the intensity ratios 1:2:4:8:13:20:27:36:44:50:55:56:55:50: ... etc. The individual resonance line is Lorentzian in shape, with a width of $\Delta H_{pp} = 0.153$ mT. The spectrum is the result of superposition of hfs lines of Cu^{2+} and shfs lines from two equivalent ^{14}N nuclei and two pairs of equivalent ^{1}H nuclei, with the splittings: $a_{Cu} = 0.252$ mT, $a_N = 0.252$ mT, $a_{H_1} = 0.126$ mT and $a_{H_2} = 0.378$ mT. The spectrum obtained by computer simulation is shown in Fig. 3.

A spectrum identical with the preceding one is also obtained if the splitting ratios of the lines are $a_{Cu}:a_N:a_{H_1}:a_{H_2} = 2:1:3:3$, i.e. on the assumption that all four hydrogen

atoms cause the same splitting of the shfs lines. By considerations of crystal symmetry, the last hypothesis is much less plausible. We also performed a similar computer analysis of the spectrum for other orientations of the crystal in order to resolve the isotopic structure.

By fitting the experimental angular dependence plots to Eq. (1) for all six studied orientations of the rotation axis of the crystal, we obtained the tensors g^2 and gA^2g for the spectrum of the isotope $^{63}Cu^{2+}$. The principal values and direction cosines derived by diagonalisation of these tensors are shown in Tables I and II, respectively. For comparison, we give in Table I the parameters of the EPR spectrum of the Cu^{2+} ions in TGS and TGFB crystals.

It should by stressed that measurements of the angular dependence of the spectrum in only one orthogonal reference frame do not permit the univocal determination of the principal values and directions of the g and A tensors. This is so because our crystal, of

TABLE I

Spin Hamiltonian parameters of $^{63}Cu^{2+}$ complexes in TGS-group crystals

Crystal	g_z	g_y	g_x	A_z	A_y	A_x	Remarks
TGSe	2.2591	2.0650	2.0529	151.0	2.5	42.2	A_N = 0.52–0.90 mT A_H = 0.123–0.25 mT this work
TGS	2.261	2.064	2.054	150.1	5.0	30.0	A_N = 0.74–1.14 mT A_H = 0.46 mT [7]
	2.259	2.092	2.027	165.4	24.2	84.8	A_N = 1.00 mT A_H = 1.00 mT [3]
TGFB	2.240	2.060	2.060	132	10	32	A_N = 0.68–1.05 mT [8,9]

Error in g-value for TGSe is ±0.008. A — values in 10^{-4} cm^{-1}; errors for TGSe are ±0.9 in A_z and A_x, ±0.1 in A_y.

TABLE II

Direction cosines of the principal axes of the g and A tensors in reference frames X, b, Z and a^*, b, c

Axis	X, b, Z			a^*, b, c		
	l	m	n	l	m	n
z	0.0297	±0.8320	−0.5540	0.1774	±0.8311	−0.5271
y	0.9464	±0.1550	0.2836	0.8216	±0.1699	0.5442
x	0.3218	±0.5327	−0.7827	0.5384	±0.5302	−0.6560

monoclinic symmetry, presents two identical but differently oriented copper complexes in the unit cell, yielding symmetrical shapes of the $H(\theta)$-function (see Fig. 2). This excludes the univocal choice of signs for the off-diagonal elements g_{ab}^2 and g_{bc}^2 of the spectroscopic splitting tensor, whereas $g_{ac}^2 < 0$.

Choosing identical signs i.e. $g_{ab}^2 g_{bc}^2 > 0$ (I) one obtains other principal values of g^2 than when taking different signs, $g_{ab}^2 g_{bc}^2 < 0$ (II). This is especially apparent with regard to the values of g_x and g_y, as in our case we obtain

(I) $g_z = 2.2591$, $g_y = 2.0650$, $g_x = 2.0529$,

(II) $g_z = 2.2551$, $g_y = 2.0916$, $g_x = 2.0302$.

The direction cosines are also different in the two cases. Supplementary measurements of the angular dependence in the orthogonal reference frame X, b, Z solved the problem in favour of case (I).

The above discussion, apparently, indicates the reason for the discrepancy between the experimental results of EPR for Cu^{2+} in TGS as reported by the two groups of authors in spite of the complete similarity of the spectra (see Table I). The similarity between the results of [3] and the set of our values (II) suggests an incorrect choice of signs for the off-diagonal elements of the g tensor previous to diagonalisation. This surmise is supported by the value $g_x = 2.027$, quite unusually low for spectra of the copper ion.

Diagonalization of the tensors g and A in both reference frames a^*, b, c and X, b, Z permits the evaluation of the accuracy with which the g-factors and direction cosines are determined. Error in the g-values and principal axis positions amounts to ± 0.0008 and ± 0.6 deg, respectively. We refrained from performing a strict analysis of shfs tensors for ^{14}N and ^{1}H, but only determined the maximal and minimal shfs splitting as: 0.90 and 0.52 mT for ^{14}N, and, 0.25 and 0.123 mT for ^{1}H.

The results reported above show the Cu^{2+} ion to be coordinated to two glycine molecules. Compensation of the charge of the Cu^{2+} ion occurs by deprotonation of the two NH_3 groups, as indicates by the interaction of Cu^{2+} with the remaining two pairs of protons. The direction cosines of the principal axes of the complex do not differ strongly from those found for TGS and TGFB pointing to a similar position of the copper ion in the unit cell of all crystals of the TGS group. The direction of the z-axis of our complex coincides to within 5° with the normal to the plane containing glycines GII and GIII in TGSe crystal. The z-axes of the two differently oriented complexes lie almost exactly in the bZ-plane and subtend $\pm 34°$ with the crystallographical b-axis (Fig. 1).

An interesting feature of the EPR spectrum in TGSe and the other glycine crystals resides in the dependence of the linewidth on the value of the nuclear magnetic quantum number m. The high-field lines are narrower than the low-field ones, leading to the asymmetry of the spectrum well apparent in Fig. 3. The effect resembles that observed for the spectra of solutions, but is considerably weaker. It points to an influence of dynamical effects (similar to the strong Jahn-Teller effect) on the electronic structure of the complex.

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