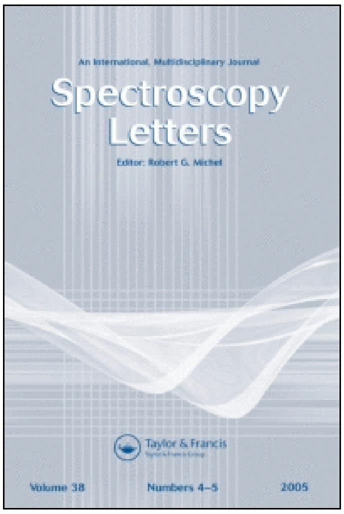

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Hedewy, S. and Issa, M. A. A.(1978) 'E. P. R Study Of Copper (II) - Doped Triglycine Selenate (TGSe)', Spectroscopy Letters, 11: 12, 987 — 995

To link to this Article: DOI: 10.1080/00387017808063470

URL: http://dx.doi.org/10.1080/00387017808063470

SPECTROSCOPY LETTERS, 11(12), 987-995 (1978)

E.P.R Study Of Copper (II) - Doped Triglycine Selenate

(TGSe)

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The angular dependence of EPR of the Cu^{2+} ion in the ferroelectric TGSe crystal has been investigated. The coordination of the Cu^{2+} ion and the number of complexes were found to be the same as in the isomorphous copper - doped TGS crystal. The spin density on the central metal ion indicates a more covalent nature of the Cu-ligand bond in TGSe. The spectroscopic splitting factor exhibits an anomaly near the ferroelectric transition point.

1. INTRODUCTION

Paramagnetic probes were used extensively for EPR studies of ferroelectric crystals. Triglycineselenate belongs to the family of ferroelectric crystals with the formula : $(NH_2\,CH_2\,COOH)_3 \cdot H_2BX_4$, where $BX_4 = SO_4$ (TGS) ; BeF_4(TGFB), SeO_4 (TGSe) . TGSe undergoes a second order phase transition(1) in the region of 22.5°C . Above T_c , the crystal belongs to the centerosymmetric point group 2/m while it is in the polar group below T_c .

The coordination of Cu^{2+} ion was previously studied in both the two isomorphous crystals TGS (2-5) and TGFB (6,7). EPR study of TGFB : Cu^{2+} revealed the existence of both isolated and aggregated complexes with spin S = 1/2 and 2 respectively. On the other hand, only one kind of X - band spectrum was observed for $^{63}Cu^{2+}$ ion into TGS corresponding to the isolated complexes (4). Terumasa et al (5) succeeded using K - band to observe at 77 °K two kinds of spectra with intensity ratio dependent on temperature. The aim of this study is to ascertain the coordination of Cu^{2+} ion in TGSe as well as the determination of the values of the spin - Hamiltonian parameters.

2. EXPERIMENTAL

Anisotropic study of the X-band spectrum was performed using a Varian E - 12 spectrometer at the temperature 16°C . Spectra were also recorded at other temperatures including the liquid nitrogen temperature. Sample temperature was regulated by a Varian - variable temperature controller.

This anisotropy of the EPR was described in the previously used (4) orthogonal coordinate system arbitrary attached to the crystal. The Y - axis is perpendicular to the cleavage plane , and the Z - axis subtends an angle of $-15^{\circ}\ 40'$ with the Wood-Holden c' - axis (8) or $180^{\circ} + 15^{\circ}\ 40'$ with Hoshino, Okaya - Pepinsky c - axis (9) and is perpendicular to the natural crystallographical plane (001)

3. RESULTS AND DISCUSSION

The angular dependence of the spectrum in the YZ - plane , Fig.(1) , and in other planes revealed the same number of copper

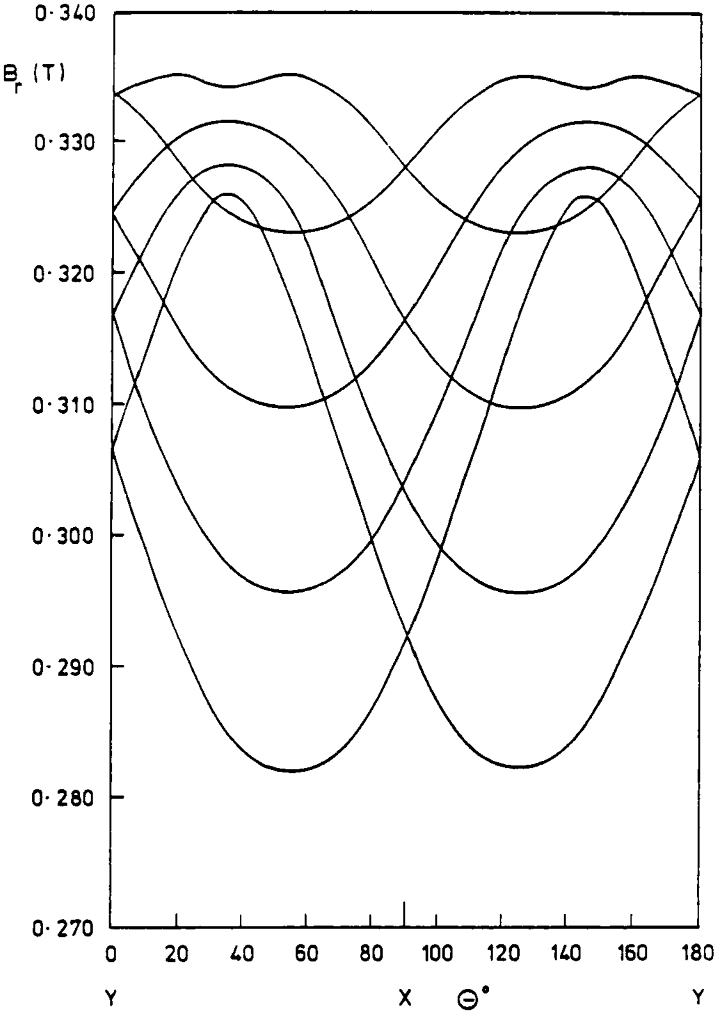

Fig. (1) : Angular dependence of copper hyperfine components in the YZ plane.

glycinate complexes as in TGS. The two magnetically equivalent complexes have the same type of symmetry as in TGS but with -differing values of the crystal field parameters. The principal axes subtend an angle 35° with the Y - axis. These complexes were the only detected ones even at $77^\circ K$.

The anomalous dip in the angular dependence for the hyperfine component $M_I = -3/2$; which was previously detected and interpreted for TGS : $^{63}Cu^{2+}$ in Ref.(4) ; extends only over an angular range of about ± 15° on both sides of the perpendicular orientation compared with ± 20° for TGS. The other hyperfine components with $M_I = \pm ½$ and $+ 3/2$ did not show such an anomalous behaviour. The spin Hamiltonian parameters corrected to second order are given in Table (1) .

Applying Bleaney's equation(10) for the resonance fields of the hyperfine components calculated to second order written in the form ;

$$B_m = B_o - A M_I - (A_\perp^2 / 4 B_o) \left[(A_{11}^2 + A^2) / A^2 \right] \left[I (I + 1) - M_I^2 \right]$$

$$- (1/2B_o) \left[(A_{11}^2 - A_\perp^2) / A \right]^2 \left[g_{11} g_\perp / g^2 \right]^2 M_I^2 \sin^2\theta \cos^2\theta$$

The expression giving the angles corresponding to extremum is as follows:

$$\cos^2\theta_{\text{max.}} = \left[1 + \frac{g_{11}^2}{g_\perp^2} \cdot \frac{A_{11}^2 - A^2}{A^2 - A_\perp^2} \right]^{-1}$$

Where: $$A = \frac{h\nu}{4 M_I} + 1/4 \left[(h\nu / M_I)^2 + \frac{8 (A_{11}^2 g_{11}^2 - A_\perp^2 g_\perp^2}{g_{11}^2 - g_\perp^2} \right]^{1/2}$$

Utilizing the values of the parameters listed in Table (1), the double extremum can be detected at the angles $\theta = 90^\circ \pm 15^\circ$ which is in agreement with that observed experimently.

Table (1)

Parameter	TGSe	TGS (4)
g_{11}	2.241	2.261
$g_{\perp}$	2.05	2.054
A_{11}^{Cu}	$133.2 \times 10^{-4} cm^{-1}$	$150.1 \times 10^{-4} cm^{-1}$
$A_{\perp}^{Cu}$	$32.4 \times 10^{-4} cm^{-1}$	$30 \times 10^{-4} cm^{-1}$
A_{11}^{N}	$6.5 \times 10^{-4} cm^{-1}$	$7.4 \times 10^{-4} cm^{-1}$
$A_{\perp}^{N}$	$9.1 \times 10^{-4} cm^{-1}$	$11.4 \times 10^{-4} cm^{-1}$
A^{H}	4.6 gauss	4.6 gauss
α^2	0.67	0.73

It is clear from Table (1) that the value of the spin density α^2 on the central ion in TGSe , calculated from the formula(11) ,

$$\alpha^2 = -(A_{11}/P) + \Delta g_{11} + 3/7 \Delta g_{\perp} + 0.04$$

is smaller than the corresponding one for TGS pointing to a more covalent nature for the Cu - ligand bond in the former and to a more ionic nature in the latter.

The 13 - lines spectrum with intensity ratios 1 : 4 : 8 : 12 : 16 : 20 : 22 : 20 : 16 : 12 : 8 : 4 : 1 shown in Fig. (2) indicates the coupling between the unpaired 3d electron and the two equivalent nitrogen atoms directly attached to the central metal ion, in addition to a further coupling with four protons. This number of lines can be deduced from the relation :

$$N = 2 I^N n^N \eta + 2 I^H n^H + 1$$

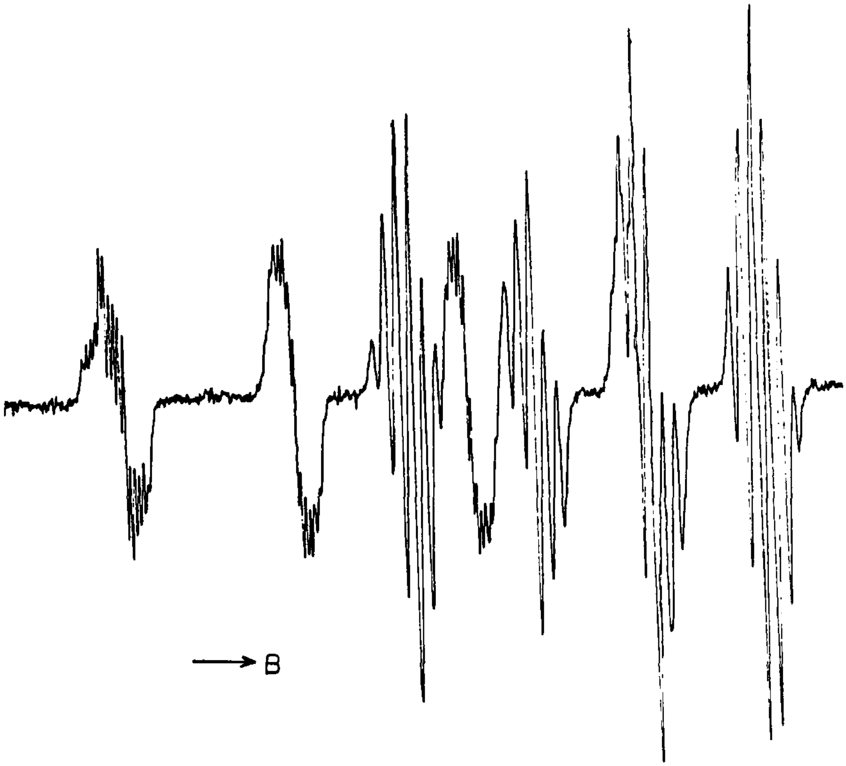

Fig. (2) : EPR spectrum of Cu^{2+} ion in TGSe showing SHFS from both nitrogen and hydrogen nuclei

with the assumption that the nitrogen coupling constant to be twice that of hydrogen i.e $\eta = 2$. Such ratio has been identified experimently. Refering to the spectrum of $^{63}Cu^{2+}$: TGS given in Ref.(4) - Fig.(10)- which is in exact resemblance with that shown in Fig.(2), it is possible without deuteration of TGSe crystal to attribute the proton splittings to the hydrogen atoms of the amine groups.

The nitrogen hyperfine splitting tensor $\hat{A}^N$ exhibited a smaller anisotropic behaviour compared with TGS. In TGSe, likewise in TGS, the largest anisotropy ($8.24 - 6.5 \times 10^{-4}$ cm^{-1}) was observed in the YZ plane. The slight nonaxiality ($9.1 - 8.93 \times 10^{-4}$ cm^{-1}) in the complex plane was characterized by a more definite maximium and minimium as shown in Fig.(3), which enable more accurate determination of the orientations of the tensor principal axes. Ignoring this slight anisotropy in the complex plane, the nitrogen hyperfine tensor possesses axial symmetry with its direction of maximium splitting lying in the plane of the complex and subtends an exact angle of 61° with the X - axis. The proton splitting observed for some angular ranges was nearly isotropic and amounts the value 4.6×10^{-4}cm.$^{-1}$.

As it is well known from NMR studies(12) the NH_3^+ group of the glycine ion is in a rotational motion which becomes hindered at low temperatures. One can expect that this rotational motion may affect the SHFS arising from the protons of this group.

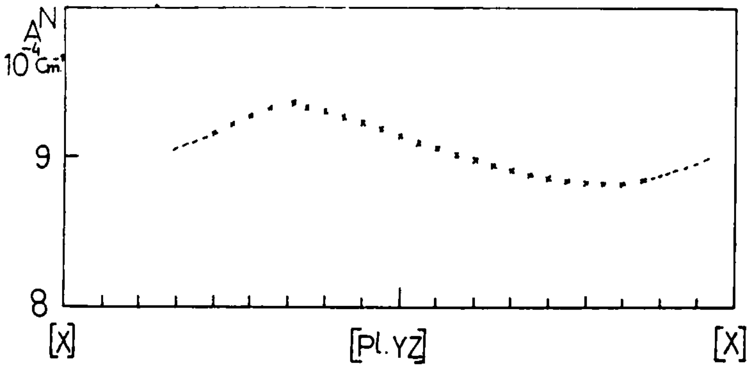

Fig. (3) : Angular dependence of splitting from nitrogen in the complex plane.

With the crystal oriented in a well - resolved proton direction, the measurements were performed throughout the temperature range from - 20° C to + 40°C. Measurements failed to detect any changes in the SHFS .

During the same temperature range, the measurements were repeated with the magnetic field directed along the principal axis of one of the complexes in TGSe crystal to detect the existence of the unconfirmed observed small anomaly (13) in the g - parameter for TGS : $^{63}Cu^{2+}$ at T_c . The measurements were also performed to study the direction of the principal axis as a function of temperature and was found to be temperature independent . Fig. (4) represents a plot of g_{11} versus temperature. It exhibits a marked anomaly near the ferroelectric Curie point which is an evidence for the phase transition occurring at this

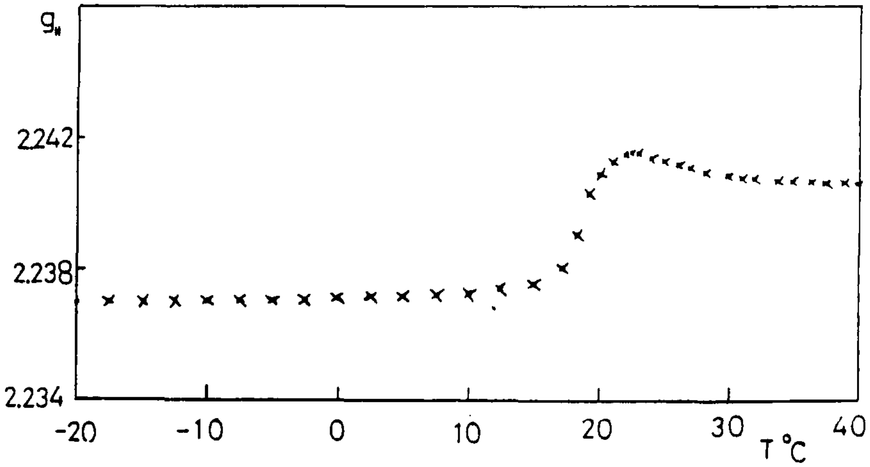

Fig. (4) : Temperature dependence of the spectroscopic splitting factor of Cu^{2+} ion in TGSe .

temperature. The hyperfine coupling constant A_{11} was unchanged through the whole temperature range. Thus, not only the fine structure parameters for the aggregated complexes of some copper-doped TGS type crystals which exhibit anomalies near T_c, but also the g - parameter of the simple complexes in some of these crystals.

This work has been carried out at Physics Dept. Riyad University, Saudi Arabia. The authors would like to thank Professor Dr. J.Stankowska - Institute of Physics, A.Mickiewicz University,Poznan- for growing the crystals.

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