

## EPR STUDY OF MAGNETIC $\text{Cu}^{2+}$ COMPLEXES IN CRYSTALS OF GUANIDINIUM ALUMINUM SULFATE HEXAHYDRATE

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Ferroelectric GASH crystal with ca. 0.01 per cent copper atoms were studied by EPR at room temperature and found to present tetragonal magnetic complexes  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  distributed in subordination to the  $C_3$  symmetry of GASH.

The structure of the complexes was observed to depend on the condition of growth. Parameters of the spin hamiltonian:  $g_{\parallel} = 2.380 \div 2.422$ ,  $g_{\perp} = 2.034 \div 2.08$ ,  $A_{\parallel} = (96 \div 108) \cdot 10^{-4} \text{cm}^{-1}$ ,  $A_{\perp} = (20 \div 30) \cdot 10^{-4} \text{cm}^{-1}$  as well as the orientation of principal directions of various complexes in the crystals are calculated from the measurements.

The introduction of defects in the form of admixture ions into ferroelectric crystals affects their ferroelectric properties, such as the spontaneous polarization, coercive force and Curie point. Admixtures of paramagnetic ions permit structural studies of the nearest neighbourhood by methods of electron paramagnetic resonance (EPR) [1, 2, 3]. By way of the EPR spectra, the magnetic complexes arising in the crystal inform us of the changes occurring in the crystal under the effect of temperature and pressure variations [4].

Crystals of guanidinium aluminum sulfate hexahydrate  $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (abbrev. GASH) present the relatively high symmetry  $C_{3v}$ -P31m. The group of such compounds, of the form:



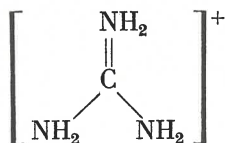
(where M is a trivalent ion  $\text{Al}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ) are ferroelectrics from  $4^\circ\text{K}$  to about  $400^\circ\text{K}$  *i. e.* up to a temperature at which crystallization water is rapidly set free and the crystal falls to pieces [5].

Spontaneous polarization ( $P_s$ ) is more or less the same for compounds with aluminum, gallium and chromium, ranging at room temperature from  $P_s = 0.35$  to  $0.38 \mu\text{C}/\text{cm}^2$ . If  $\text{SO}_4$  is replaced by  $\text{SeO}_4$ , the spontaneous polarization rises to  $0.48 \mu\text{C}/\text{cm}^2$ . Deuterized crystals are ferroelectric too.

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Stability of the trigonal structure depends on the presence of the plane guanidinium ion [5], having the structure:



Structural studies of these crystals have been performed on the compounds of gallium, aluminum and chromium [6, 7]. The elementary cell, of dimensions:  $a = 11.738 \text{ \AA}$ ,

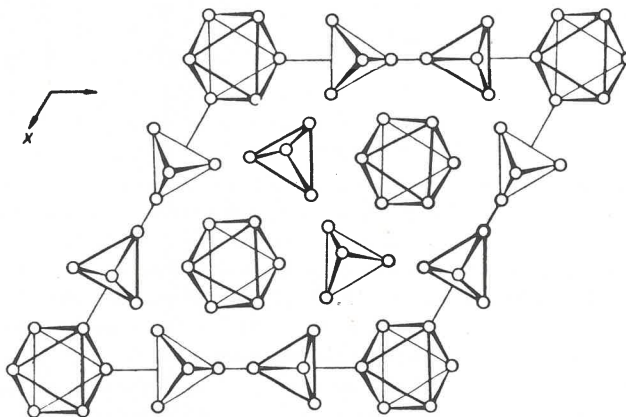


Fig. 1. GASH structure (schematically) viewed along the  $C_3$ -axis. Aluminum ions inside the octahedra and guanidinium ions below the octahedra are omitted [7]

$c = 8.951 \text{ \AA}$  [7], comprises three molecules of  $\text{C}(\text{NH}_2)_3 \text{ Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Trivalent ions, surrounded octahedrally by six water molecules, lie on the symmetry axis  $C_3$ , whereas the guanidinium groups are situated below and above the octahedra (Fig. 1). The hydrogen atoms contribute to forming hydrogen bonds  $\text{N}-\text{H}\dots\text{O}$  of a length exceeding  $3 \text{ \AA}$  connecting the guanidinium groups with the apices of the  $\text{SO}_4$  tetrahedra. The network of hydrogen bonds  $\text{O}-\text{H}\dots\text{O}$  between octahedra housing trivalent ions and the  $\text{SO}_4$  tetrahedra extends in planes perpendicular to the  $C_3$  axis of the crystal.

X-ray studies have permitted to establish with accuracy the positions of the various functional groups in the elementary cell as well as the differences in structure of the octahedral groups  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  [7]. Two axially deformed octahedra in the elementary cell have symmetry  $C_3$  whereas the remaining one has symmetry  $C_{3v}$ . The resulting slight deviation from cubicity consists in a compression of the  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  octahedra parallel to the three-fold axis.

When the trivalent ion  $\text{M}$  is a  $\text{Cr}^{3+}$  ion, the angles  $\text{O}-\text{Cr}-\text{O}$  amount to  $88.4^\circ$  for an octahedron with a neighbourhood of symmetry  $C_3$  (type 2) and  $88.0^\circ$  for one with a neighbourhood symmetry  $C_{3v}$  (type 1), respectively. This leads to the occurrence of two types of EPR spectra, since the fine structure of the spectrum is closely related with the axial deformation of the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  octahedron [8].

The two types of EPR spectra of the  $\text{Cr}^{3+}$  ion in GASH crystals differ as to the zero splitting value  $2D$  and present axial symmetry, with spectrum axis coinciding with the direction of the trigonal axis [9, 10].

The spin hamiltonian accounting for interaction between chromium ions and the crystal and external magnetic field is of the form:

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + D \left( S_z^2 - \frac{5}{4} \right) \quad (1)$$

with  $\mathbf{S}$ -ion spin,  $\beta$ -Bohr's magneton,  $g$ -spectroscopic splitting factor,  $D$ -fine structure constant, and  $\mathbf{H}$ -the external magnetic field.

The zero splitting parameter  $2D$  amounts to  $0.15 \text{ cm}^{-1}$  for type 1 and to  $0.12 \text{ cm}^{-1}$  for type 2. The EPR signal amplitudes from centres of type 1 and 2 are in the ratio 1:2.

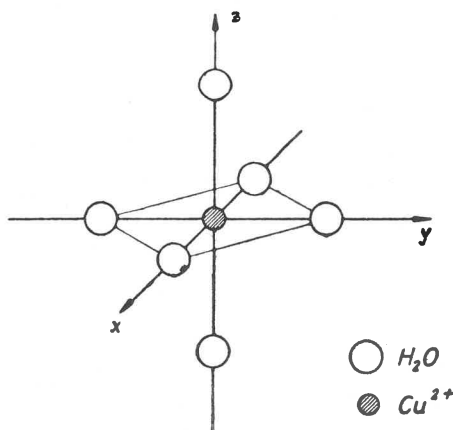


Fig. 2. Diagram of principal directions in the octahedral  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complex

With increasing temperature, the splitting factors  $D_1$  and  $D_2$  decrease; the mean steepness of the curves  $D(T)$  amounts first to  $1.9 \cdot 10^{-4} \text{ cm}^{-1} \text{ deg}^{-1}$  and then to  $1.4 \cdot 10^{-4} \text{ cm}^{-1} \text{ deg}^{-1}$  in the temperature range from  $200^\circ\text{K}$  to  $400^\circ\text{K}$  [11].

Ferroelectric properties of GASH crystals doped with copper ions were measured from  $240^\circ\text{K}$  to  $380^\circ\text{K}$  [12]. A copper admixture was found to lower the spontaneous polarization  $P_s$ , as well as the coercive force.

The formation of copper complexes perturbing the ferroelectric interactions in GASH crystals can be demonstrated by means of electron spin resonance.

Crystals for EPR were grown from saturated aqueous solutions of GASH containing from 1 to 10 per cent of cupric sulfate  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Crystals growing at slow evaporation, at a temperature of  $40^\circ\text{C}$  or  $70^\circ\text{C}$ , were colourless; the spectrophotometrically determined copper ion concentration ranged from 0.007 to 0.02 per cent weight. Although the temperature at which the crystals were grown had no effect on their ferroelectric properties, they nevertheless exhibited different types of complexes.

EPR measurements were carried out in the X-band, at room temperature, with a JES-3BX spectrometer from the Japanese makers JEOL. Magnetic complexes of copper

ions, of the form  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ , were shown to occur. Their orientation in the crystal is subordinated to the trigonal symmetry. The immediate neighbourhood of the copper ions consist of the tetragonally deformed octahedron of six water molecules (Fig. 2).

To within the experimentally attainable accuracy, EPR spectra from separate complexes can be said to present axial symmetry, and the spin hamiltonian describing the anisotropy of the spectrum is of the form:

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A_{\parallel}S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (2)$$

with  $g_{\parallel}$ ,  $g_{\perp}$  — principal values of the tensor  $g$ ;  $A_{\parallel}$ ,  $A_{\perp}$  — principal values of the hyperfine interaction tensor.

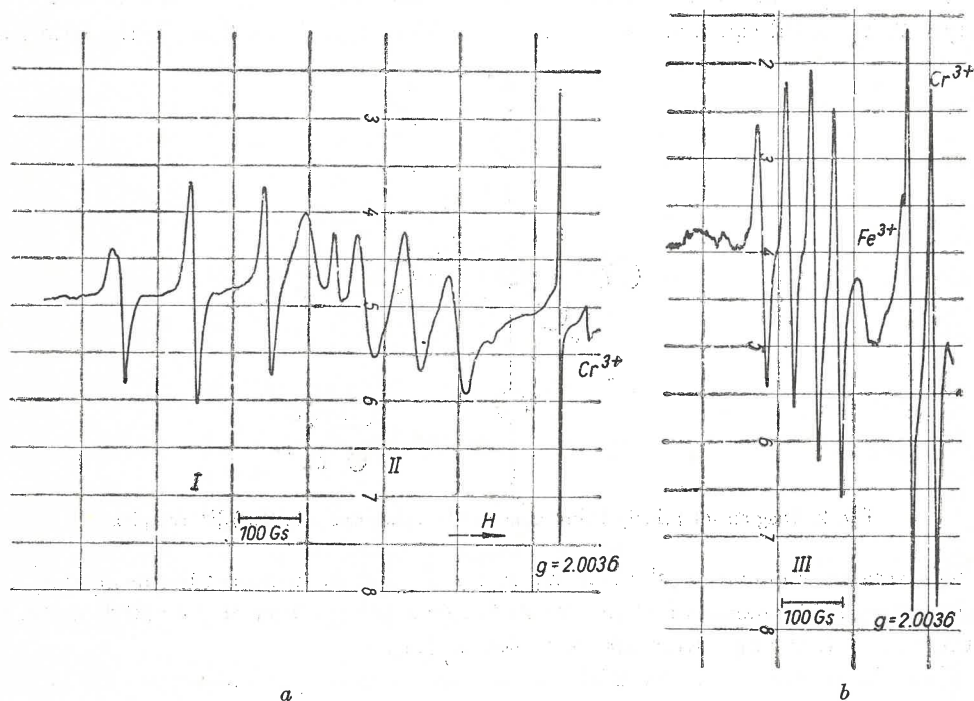


Fig. 3. *a* — EPR spectrum from complexes of types I and II in crystal A. *b* — EPR spectrum from complexes of type III in crystal B. Lines due to impurities ( $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$ ) are visible.

The first two terms in Eq. (2) account for the anisotropy of the factor  $g$ , whereas the remaining terms describe the anisotropy of hyperfine interaction between the electron spin  $S = 1/2$  of the copper ion and that of the nucleus of the odd isotopes  $\text{Cu}^{63}$  and  $\text{Cu}^{65}$  amounting to  $I = 3/2$ .

The observed EPR spectra occur in the form of quartets deriving from interaction between the unpaired electron and the spin of the nucleus (Figs 3*a* and 3*b*).

The formation of different types of complexes in crystals grown at the temperatures  $40^\circ\text{C}$  and  $70^\circ\text{C}$  is presumably due to the different rates of growth, as can be concluded from the temperature-dependence of the solubility of guanidinium aluminum sulfate [13].

Investigation of the EPR spectrum anisotropy permitted the determination of the principal directions for the magnetic complexes  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  as well as of the parameters of the spin hamiltonian (2).

Specimens in the form of hexagonal plates were fixed in a rotatable holder within the  $\text{TE}_{011}$  resonance cavity. Each crystal was rotated about the three mutually perpendicular directions of  $XYZ$ -coordinates. The  $Z$ -axis was perpendicular to the (0001) cleavage plane and parallel to the  $C_3$ -direction;  $X$ -was directed along the [1000] diagonal of the hexagon;  $Y$ -was perpendicular to the face (01 $\bar{1}$ 0) (Fig. 4a).

A. In crystal A, grown at  $40^\circ\text{C}$ , six magnetic complexes of two types differing by their orientation in the crystal and by the values of spin hamiltonian parameters were found.

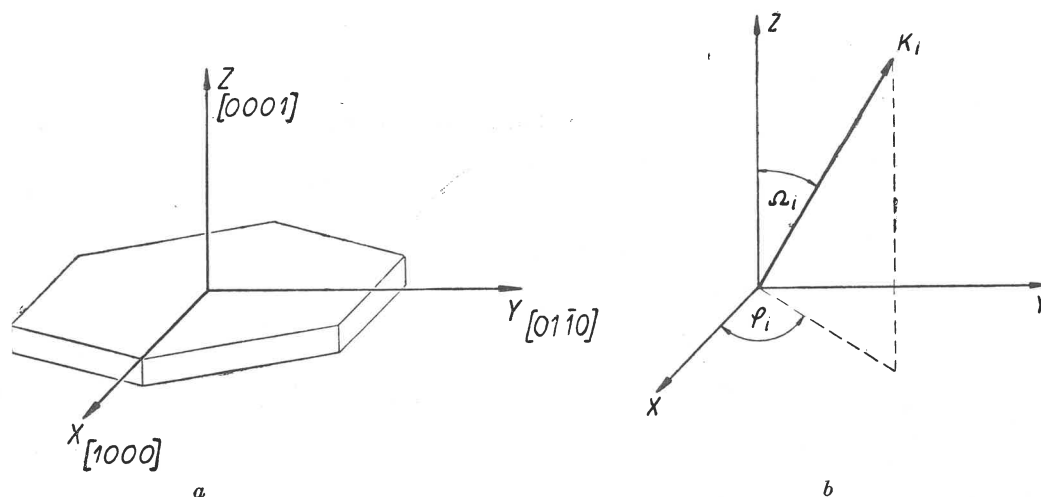


Fig. 4a. Orthogonal coordinates  $XYZ$  attached to the crystallographic axes of GASH.  $b$  — Principal directions of complex  $K_i$  in spherical coordinates  $\varphi_i, \Omega_i$

The principal  $z$ -directions of three complexes of type I subtend an angle of  $7^\circ$  with the threefold axis. Three complexes of type II subtend an angle of  $60^\circ$  with  $C_3$ . The EPR spectrum from the two types of complexes contains  $(3+3) \times 4 = 24$  lines.

When the crystal is oriented so that  $C_3 \parallel H$ , the principal directions "z" of complexes I and II form angles of respectively  $7^\circ$  and  $60^\circ$  with the magnetic field  $H$ . Hence, with  $C_3 \parallel H$ , the spectrum consists of eight lines, namely four lines of the hyperfine structure of type I complexes and four lines of that of complexes II (Fig. 3a).

The orientation of the principal directions of a complex with respect to orthogonal  $XYZ$ -coordinates is described by giving the polar coordinates  $\Omega$  and  $\varphi$ , with  $\varphi$  measured with reference to the  $X$ -axis in the  $XY$ -plane (Fig. 4b).

When rotating the crystal about the  $X$ -axis in the external magnetic field  $H$ , the angle  $\Theta_i$  subtended by the principal direction of the  $i$ -th complex and the direction of  $H$  can be determined from the relation:

$$\cos \Theta_i = (\sin \Omega \cos \varphi_i) \sin \Theta' + \cos \Omega \cos \Theta' \quad (3)$$

$\Theta'$ -denoting the angle between the  $Z$ -axis and the field  $H$  during rotation of the crystal about the  $X$ -axis of coordinates.

The angular dependence of the resonance field for the complex of type I is plotted in Fig. 5, where the continuous line shows the dependence of the resonance field strength  $H_i$  for the  $i$ -th complex as a function of the rotation angle of the crystal  $\Theta'$ :

$$H_i = \frac{h\nu}{g_i\beta} = \frac{h\nu}{\beta} [(g_{\parallel}^2 - g_{\perp}^2) \cos^2 \Theta_i + g_{\perp}^2]^{-1/2} \quad (4)$$

with  $h$ -Planck's constant and  $\nu$ —the microwave frequency. Values of  $g_{\parallel}$  and  $g_{\perp}$  were adjusted so that the curve of Eq. 4. should pass through the experimental points. The number of these

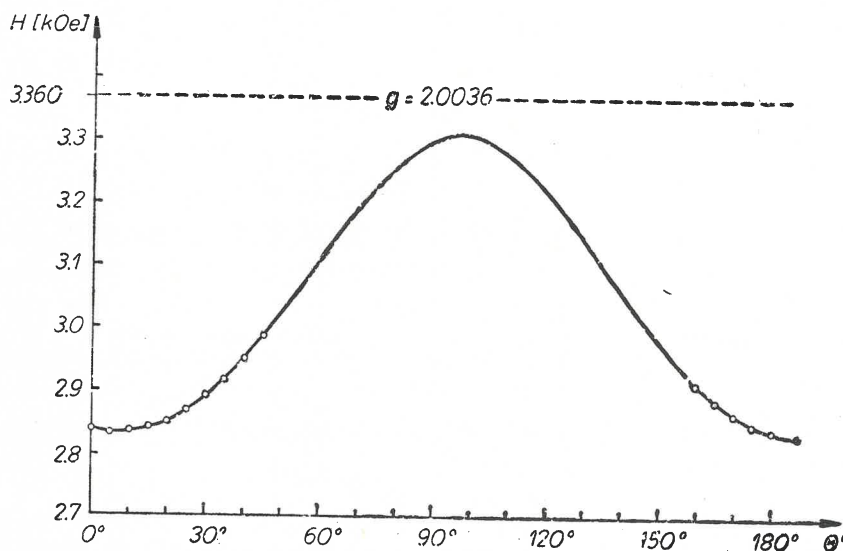


Fig. 5. Angular dependence of the resonance field for a chosen complex of type I at rotation of the crystal A about the  $X$ -axis.  $\Theta'$  — is the angle between the crystal  $C_3$ -axis and the magnetic field  $H$

points is restricted by the presence of a great number of mutually overlapping lines; the centre of a quartet can be found only if orientation of the principal direction  $z$  of the particular complex in the magnetic field is close to parallel *i. e.* if  $\Theta_i$  is close to zero. This situation implies a minimal value of the resonance field strength, and maximal hyperfine splitting.

Crystal A contains three complexes of type I, with azimuth  $\varphi$  amounting respectively to:  $\varphi_1 = 90^\circ$ ,  $\varphi_2 = 210^\circ$ ,  $\varphi_3 = 330^\circ$ , and angles  $\Omega_1 = \Omega_2 = \Omega_3 = \Omega = 7^\circ$ . Parameters of the spin hamiltonian are:  $g_{\parallel} = 2.380$ ,  $g_{\perp} = 2.034$ ,  $A_{\parallel} = 108 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp} = 20 \cdot 10^{-4} \text{ cm}^{-1}$ .

The anisotropy of the EPR spectra for complexes of type II at rotation of crystal A about the directions  $X$  and  $Z$  is shown in Figs 6 and 7. Azimuths amount respectively to:  $\varphi_1 = 30^\circ$ ,  $\varphi_2 = 150^\circ$ ,  $\varphi_3 = 270^\circ$  and polar angles are:  $\Omega_1 = \Omega_2 = \Omega_3 = 60^\circ$ . Parameters of the spin hamiltonian are:  $g_{\parallel} = 2.422$ ,  $g_{\perp} = 2.08$ ,  $A_{\parallel} = 103 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp} = 30 \cdot 10^{-4} \text{ cm}^{-1}$ .

As is easily checked from Eqs (3) and (4), the angular dependences of the resonance field for the first two of these complexes ( $\varphi_1 = 30^\circ$  and  $\varphi_2 = 150^\circ$ ) have to coincide.

Fig. 7 shows the position of EPR lines in polar coordinates. At rotation of the crystal about the Z-axis,  $\Theta'$  — is the angle between the X-axis and the field  $H$  in the XY-plane.

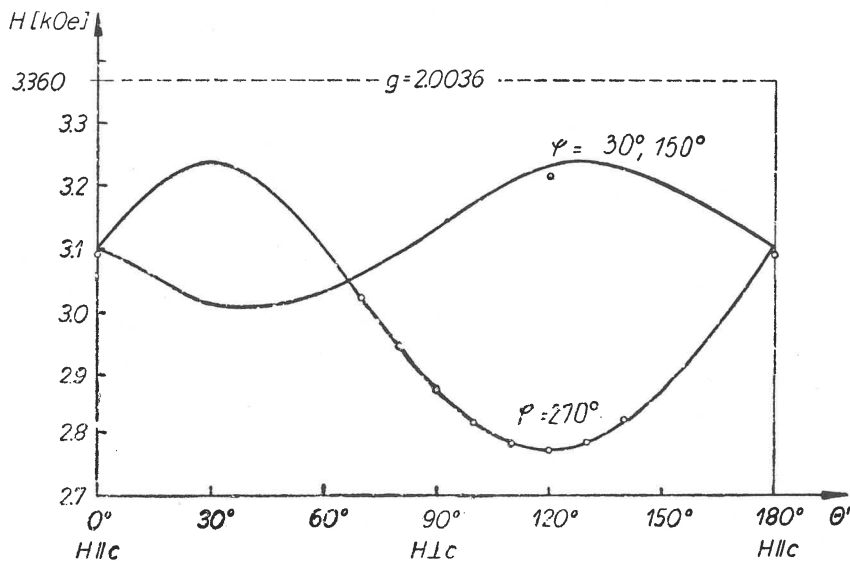


Fig. 6. Angular dependence of the resonance field for the three complexes of type II at rotation of the crystal A about the X-axis. The complexes with  $\varphi = 30^\circ$  and  $\varphi = 150^\circ$  present the same angular dependence

The angle between the principal direction of the  $i$ -th complex and  $H$  is determined from the relation:

$$\cos \Theta_i = \sin \Omega \cos (\Theta' - \varphi_i) \quad (5)$$

B. Crystals B, grown at  $70^\circ\text{C}$ , revealed six magnetically equivalent complexes III. Parameters of the spin hamiltonian in this case, are:  $g_{\parallel} = 2.387$ ,  $g_{\perp} = 2.063$ ,  $A_{\parallel} = 96 \cdot 10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp} = 23 \cdot 10^{-4} \text{ cm}^{-1}$ .

With regard to their orientation in the crystal, two groups of complexes can be distinguished:  $K_1, K_2, K_3$  with coordinates respectively:  $\varphi_1 = 8^\circ$ ,  $\varphi_2 = 128^\circ$ ,  $\varphi_3 = 248^\circ$ ,  $\Omega = 70^\circ$  and  $K'_1, K'_2, K'_3$  with  $\varphi'_1 = -8^\circ$ ,  $\varphi'_2 = -128^\circ$ ,  $\varphi'_3 = 248^\circ$ ,  $\Omega' = 110^\circ$ .

When the threefold crystal axis coincides with  $H$ , the EPR signal is a superposition of the six signals from the complexes III and the spectrum consists of four components of hyperfine structure (Fig. 3b).

The distribution of all six complexes in the crystal presents the symmetry  $C_2$  with regard to the crystallographical [1000] axes. Hence, at rotation of the crystal about the X-axis, the angular functions  $H(\Theta')$  of the complexes:  $K_1$  and  $K'_1$ ;  $K_2$  and  $K'_2$ ;  $K_3$  and  $K'_3$  are identical (cf. Eqs (3) and (4)), so that the spectrum consists of three quartets the amplitude of which is twice that of the EPR signals observed when rotating crystal B about Y or Z (Fig. 8).

The existence of two distinctly oriented groups of complexes is clearly apparent when rotating the crystal about the Y-direction (Fig. 9); where continuous and dashed lines show

$H(\theta')$  for complexes  $K_1, K_2, K_3$  and  $K'_1, K'_2, K'_3$ , respectively. For a chosen complex III, of coordinates  $\varphi_i, \Omega_i$ , the angle between its principal direction and the magnetic field at rotation of the crystal about  $Y$  can be determined from the formula:

$$\cos \theta_i = (\sin \Omega_i \sin \varphi_i) \sin \theta' + \cos \Omega_i \cos \theta' \quad (6)$$

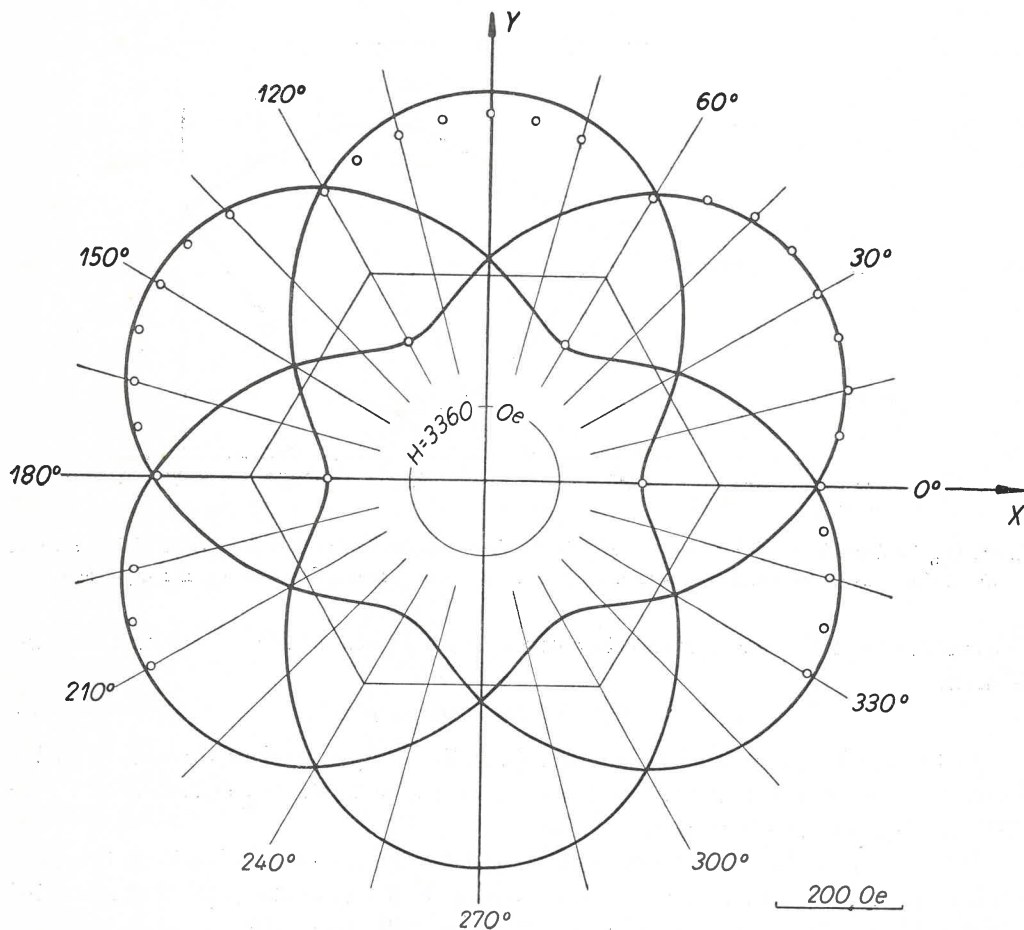


Fig. 7. Angular dependence of the resonance field for the three complexes of type II at rotation of crystal A about the  $Z$ -axis. Here,  $\theta'$  is the angle between the  $X$ -axis and  $H$  in the  $XY$ -plane

The positions of EPR lines for complexes  $K_1$  and  $K'_1$  at rotation about  $Z$  is plotted in Fig. 10 (continuous and dashed lines show  $H(\theta')$  calculated from Eqs (4) and (5) for complexes  $K_1$  and  $K'_1$ , respectively; to avoid overcrowding the graph, the remaining four complexes are omitted).

The experimental results are assembled in Table I together with values of  $g_{\parallel}$  and  $g_{\perp}$ , hyperfine splitting factors  $A_{\parallel}$  and  $A_{\perp}$ , as well as angles  $\varphi$  and  $\Omega$  for the complexes found in the various crystals.



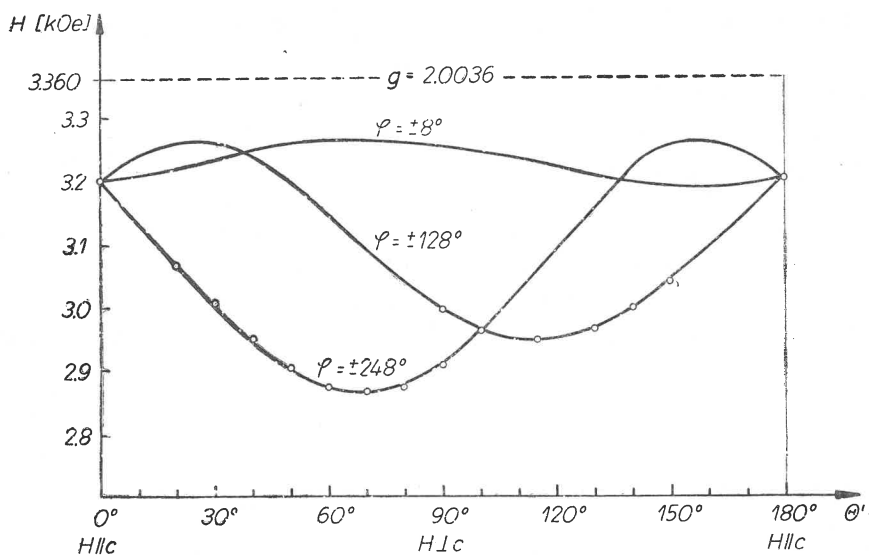


Fig. 8. Angular dependence of the resonance field for the six complexes of type III at rotation the crystal B about the  $X$ -axis of coordinates. The EPR signals from complexes  $K_1, K_2, K_3$  coincide with those from  $K'_1, K'_2, K'_3$  respectively

The fact that the complexes are distributed in a manner to present the symmetry  $C_3$  proves that the copper ions are built into the GASH crystal with regularity. The difference in electric charge between the aluminum ion  $Al^{3+}$  and the copper admixture ion  $Cu^{2+}$  makes it impossible to achieve arbitrarily high concentrations of the paramagnetic ion. The

TABLE I

	Complex of type	$g_{  }$	$g_{\perp}$	$A_{  }$ $10^4 \text{ cm}^{-1}$	$A_{\perp}$ $10^4 \text{ cm}^{-1}$	$\Omega$ [deg]	$\varphi$ [deg]
Crystal A	I	2.380	2.034	108	20	7	90 210 330
	II	2.422	2.08	103	30	60	30 150 270
Crystal B	III	2.387	2.063	96	23	70	8 128 248  -8 -128 -248

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complexes present in aqueous solution occupy positions in the lattice sites of GASH in the process of growth of the crystal.

Compensation of electric charge in the crystal can be presumed to consist in a replacement of a guanidinium group  $[\text{C}(\text{NH}_2)_3]^+$  and one  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  octahedron by two  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  groups or by the formation of interstitial defects  $\text{Cu}^{2+}$  in the lattice.

From what we know about the structure of GASH crystal, the directions of the electric field gradient acting on the  $\text{Cr}^{3+}$  ions (and consequently those of the tensor  $g$ ) should be expected to coincide with the threefold axis of the crystal.

However, in the case of the ion  $\text{Cu}^{2+}$ , which has the electron configuration  $3d^9$ , a neighbourhood of trigonal symmetry can not arise. The stable copper complex has the tetragonal

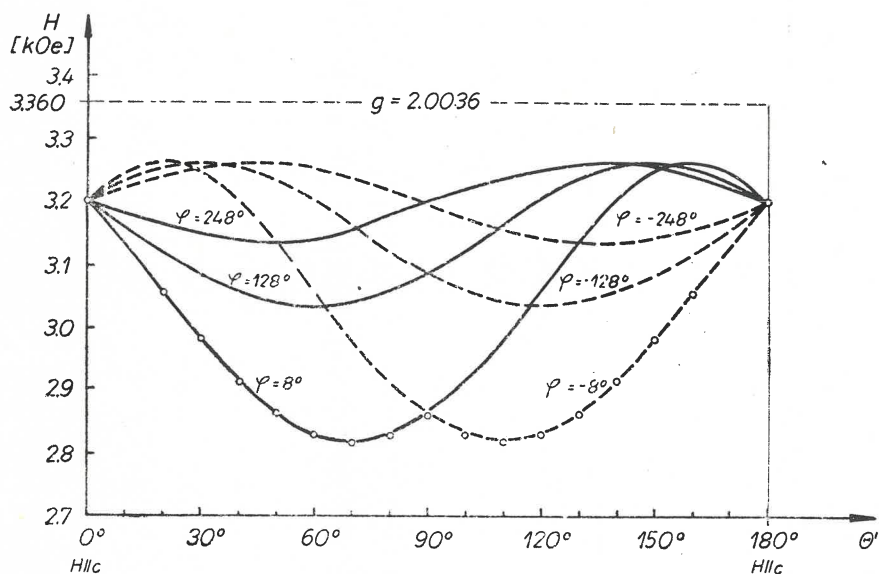


Fig. 9. Angular dependence of the resonance field for the six complexes of type III at rotation of crystal B about the  $Y$ -direction. Continuous lines correspond to complexes  $K_1, K_2, K_3$

symmetry, since this symmetry provides for the condition that the ground state of  $\text{Cu}^{2+}$  shall be a singlet orbital state [14].

In the trigonally symmetric crystal, the copper ions form three equivalent complexes presenting tetragonal or rhombic symmetry of the crystal field [15].

In GASH, trigonal ordering stems from the  $\text{SO}_4$  groups, and the tetragonally symmetric copper complexes  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  can assume three orientations, differing by  $120^\circ$ , in the elementary cell of GASH.

As a result, each type of copper complex arising in the crystal is represented by three distinctly oriented  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  complexes. With regard to the fact that an admixture introduced into the crystal perturbs locally the crystal field, the positions of the complexes can be determined but approximately from structural data relating to the non-doped crystal.

Nevertheless, a comparison of the symmetry of the neighbourhood of the  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  and the symmetry with which the principal directions of the copper complexes are distributed in the crystal leads to the conclusion that the complexes of types I and II occupy positions with local symmetry  $C_{3v}$ . It is now established that the intensity of EPR signals from type I and type II varies according to the concentration of copper ions in the solution from which the crystals are grown.

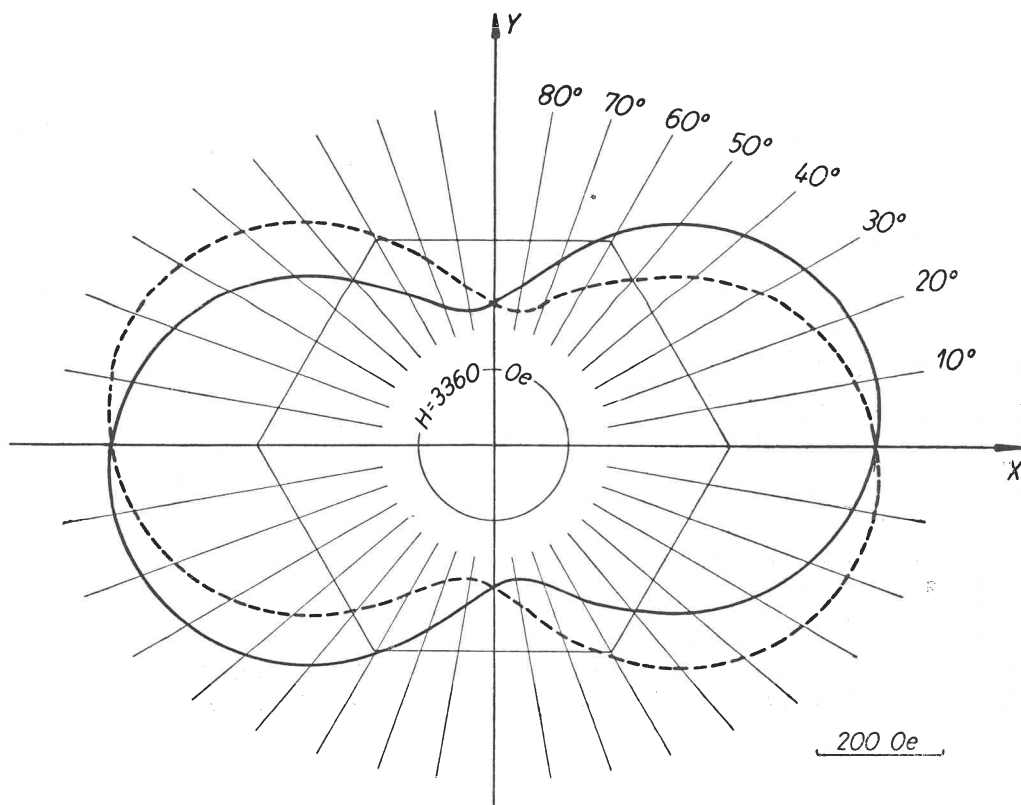


Fig. 10. Angular dependence of the resonance field for complex  $K_1$  (continuous line) and complex  $K_1'$  (dashed line) at rotation about the  $Z$ -direction

In crystal B, the copper complexes occupy positions of symmetry  $C_3$ . The apices of the  $\text{SO}_4$  tetrahedra in GASH are tipped by several degrees (Fig. 1); this gives rise to the existence of two varieties of complexes within type III, namely complexes  $K_1, K_2, K_3$  that are twisted to the right with respect to the  $[1000]$  direction and complexes  $K_1', K_2', K_3'$  twisted to the left. The signal amplitudes from the "dextro-" and "levogyric" complexes were found to be the same in all crystals investigated, in accordance with the presence of two equivalent positions of  $C_3$  in the elementary cell of GASH.

None of the crystals exhibited complexes of types I, II and III simultaneously, showing the formation of complexes to depend on the conditions of growth (thus, on the rate of growth, pH etc.) [13].

A comparison of data obtained when studying the chromium ion  $\text{Cr}^{3+}$  and copper ion  $\text{Cu}^{2+}$  in  $\text{C}(\text{NH}_2)_3\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  by electron paramagnetic resonance points to differences in the kind of deformation depending on the electron configuration of the complex-forming admixture ion.

With the parameters of the spin hamiltonian available, conclusions can be made concerning the amount of trigonal deformation of the  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  octahedra and the tetragonal deformation in  $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  ones. In the former, the deformation direction coincides with that of the trigonal crystal axis; in the latter, it is defined by the possible positions of axes of the octahedra in the elementary cell of GASH.

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