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# Electron Paramagnetic Resonance Study of the $[(\text{CH}_3)_2\text{NH}_2]_5\text{Cd}_3\text{Cl}_{11}$ Monocrystal Doped with $\text{Cu}^{2+}$ ion

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The paper reports the electron paramagnetic resonance investigation of  $\text{Cu}^{2+}$  doped  $[(\text{CH}_3)_2\text{NH}_2]_5\text{Cd}_3\text{Cl}_{11}$  (DMACC) monocrystal. DMACC: $\text{Cu}^{2+}$  was studied in the temperature range (6 ÷ 293) K. We did not observe any anomalies of spin-Hamiltonian parameters of  $\text{Cu}^{2+}$  ion corresponding to the temperature anomalies observed in dielectric studies. The electron paramagnetic resonance anomaly recorded at about 40 K results from the subtle changes in bonds angles and Cu–Cl distances and suggests the smooth second order transition.

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## 1. Introduction

Crystals containing methyloammonium cations exhibit a number of phase transitions related to the dynamics of organic cations [1–4]. The crystal of general formula  $[(\text{CH}_3)_2\text{NH}_2]_2\text{MCl}_x$ , where  $\text{M} = \text{Cu}, \text{Co}$ ;  $x = 4$ , shows ferroelectric properties [3, 4]. The  $[(\text{CH}_3)_2\text{NH}_2]_5\text{Cd}_3\text{Cl}_{11}$  (DMACC) crystal ( $\text{M} = \text{Cd}$ ,  $x = 11$ ) at room temperature is orthorhombic with a space group  $Cmcn$ . The unit cell with lattice parameters  $a = 18.108 \text{ \AA}$ ,  $b = 11.413 \text{ \AA}$ ,  $c = 15.789 \text{ \AA}$  consists of four formula units,  $Z = 4$  [5].

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The crystal structure of DMACC is formed by two alternating layers parallel to (001) plane. One of the layers consists of dimethyloammonium cations with van der Waals interaction between them. The other layer comprises the chlorocadmate complexes linked in a chain by one of cations  $[\text{N}(1)\text{H}_2\text{C}(1)\text{H}_2]$ . The ammonium group of this cation connects two separate  $[\text{Cd}_3\text{Cl}_{11}]^{5-}$  anions by forming hydrogen bonds with the equatorial doubly bonded Cl(1) and Cl(2) atoms. The  $[\text{Cd}_3\text{Cl}_{11}]^{5-}$  unit consists of octahedrally coordinated Cd atoms with Cl atoms at the corner of the coordination polyhedron [5]. Each of three distorted octahedra is connected to the others by sharing faces in such a way that the Cl(3)–Cl(3)''' is common to all three polyhedra, while the corners Cl(1), Cl(1)', and Cl(2) are each shared by two. Thus each octahedron has two unshared corners, with two terminal chlorine atoms. The room-temperature X-ray studies showed an orientational disorder of one dimethyloammonium cation for which a flip-flop motion is allowed [5].

Dielectric measurements [6], dilatometric [7], and linear birefringence [8] studies of DMACC revealed the phase transitions at about  $T_1 = 260$  K,  $T_2 = 180$  K,  $T_C = 127$  K. The dielectric constant along the  $c$ -direction shows a broad maximum at  $T_1$  and cusp-like break on  $\epsilon_c$  at  $T_2$  and discontinuous change at  $T_C$  [6]. It is considered that the phase transition at  $T_C$  is promoted by ordering of the dimethyloammonium ions.

Unfortunately, because of marked first order transition the crystal cracked at  $T_C$  giving no chance for dielectric study below  $T_C$ . Fortunately, for electron paramagnetic resonance (EPR) measurements small monocrystals obtained after sample cracking are sufficient for low temperature studies, too.

EPR is usually sensitive to structural changes, therefore we were expecting the changes in EPR spectra which would correspond to the three anomalies of low frequency dielectric constant at  $T_1 = 260$  K,  $T_2 = 180$  K,  $T_3 = 127$  K.

## 2. Experimental details

The crystals  $[(\text{CH}_3)_2\text{NH}_2]_5\text{Cd}_3\text{Cl}_{11}$  were grown from solution containing stoichiometric quantities of  $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{CH}_3)_2\text{NH}_2\text{Cl}$  and about 12 mol percent  $\text{CuCl}_2$  was added.

Our EPR measurements of  $\text{Cu}^{2+}$  concentration in the crystal under investigation shows that  $\text{Cu}^{2+}$  concentration was about of 4 mol percent.

The good quality yellow monocrystals of DMACC: $\text{Cu}^{2+}$  were investigated by an X-band EPR spectrometer in the temperature range of (6 ÷ 293) K. The  $XYZ$  orthogonal laboratory frame chosen for the EPR anisotropy pattern was related to the  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}$  crystallographic axes as follows:  $\mathbf{X} \parallel \mathbf{a}$ ,  $\mathbf{Y} \parallel \mathbf{b}$ , and  $\mathbf{Z} \parallel \mathbf{c}$  [6].

## 3. Results and discussion

The EPR spectrum of  $\text{Cu}^{2+}$  ions in DMACC recorded at room temperature (RT) for external magnetic field parallel to the  $\mathbf{b}$ -crystal axis is shown in Fig. 1.

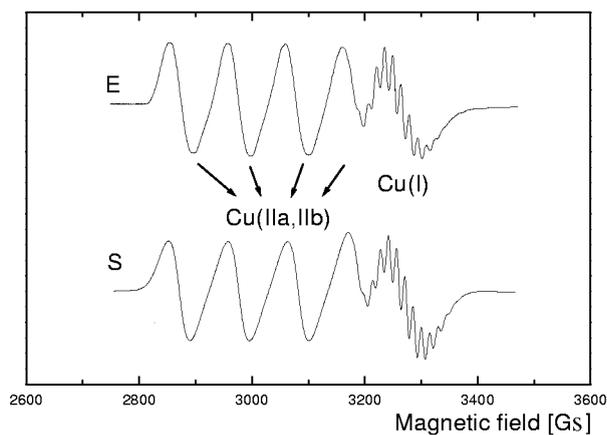


Fig. 1. The experimental (E) and simulated (S) EPR spectrum of  $\text{Cu}^{2+}$  ion in DMACC at room temperature. An external magnetic field  $B$  is parallel to the  $b$ -crystal axis.

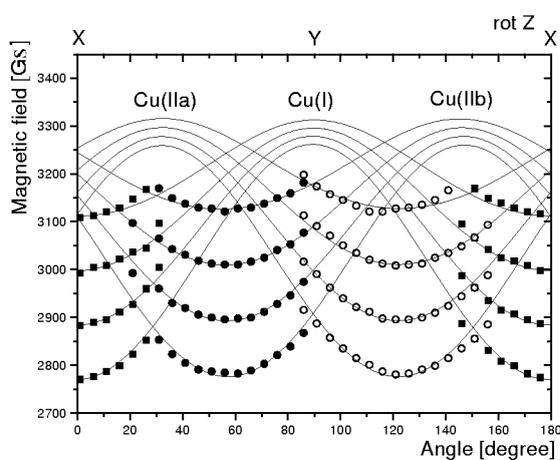


Fig. 2. The simplified angular dependence of the resonance fields for  $\text{Cu}^{2+}$  complexes in the  $(XY)$  plane which include only  $g$  and  $A_{(\text{Cu})}$  changes. The symbols represent the experimental data for Cu(I) (solid squares), Cu(IIa) (open circle) and Cu(IIb) (solid circle) complexes. The solid lines were calculated using Eq. (1).

Three kinds of  $\text{Cu}^{2+}$  complexes: one denoted as Cu(I), Cu(IIa) and Cu(IIb) were found. Figure 2 presents the full anisotropy pattern in the  $(XY)$  plane. The Cu(IIa) and Cu(IIb) complexes are magnetically equivalent but structurally nonequivalent and the Cu(I) complex is magnetically and structurally nonequivalent with respect to centers Cu(IIa) and Cu(IIb).

The spin-Hamiltonian used for full EPR of  $\text{Cu}^{2+}$  spectra description has the following form:

$$\hat{H} = g\beta H\hat{S} + \hat{S}A_{(\text{Cu})}\hat{I}_{(\text{Cu})} + \hat{I}_{(\text{Cu})}A_{(\text{Cl})}\hat{I}_{(\text{Cl})}, \quad (1)$$

where  $g$  is the spectroscopic tensor;  $A_{(\text{Cu})}$ ,  $A_{(\text{Cl})}$  are the hyperfine and superhyperfine tensors, respectively;  $\hat{S}$ ,  $\hat{I}_{(\text{Cu}),(\text{Cl})}$  are the electron and nuclear spin operators, respectively.

The spin-Hamiltonian parameters, which give the best fit between calculated and experimental line positions in anisotropy pattern and direction cosines of crystal field gradient with respect to the  $XYZ$  system are presented in Table.

TABLE

The direction cosines and the spin-Hamiltonian parameters of  $\text{Cu}^{2+}$  ion in DMACC crystal.

Complex	Principal $g$ -values	Principal $A_{(\text{Cu})}$ -values in [Gs]	Principal $A_{(\text{Cl})}$ -values in [Gs]	Direction cosines of principal direction of $g$ -values		
				$X$	$Y$	$Z$
Cu(I)	2.060(2)	17(2)	12	0	0	1
	2.054(2)	15(2)	15	0	1	0
	2.296(2)	114(2)	< 4	1	0	0
Cu(IIa)	2.060(2)	17(2)	12	0	0	1
	2.054(2)	15(2)	15	-0.866	0.5	0
	2.284(2)	113(2)	< 4	0.5	0.866	0
Cu(IIb)	2.060(2)	17(2)	12	0	0	1
	2.054(2)	15(2)	15	-0.866	-0.5	0
	2.282(2)	113(2)	< 4	-0.5	0.866	0

In DMACC crystal the  $\text{Cu}^{2+}$  ion replaces  $\text{Cd}^{2+}$  and is octahedrally coordinated with Cl atoms at the corners of the coordination polyhedron. Crucial argument for such a site place of  $\text{Cu}^{2+}$  ion is the presence of superhyperfine structure from four chlorine nuclei with  $I_{\text{Cl}} = 3/2$ . Figure 3 shows the view on structure of the  $[\text{Cu}_3\text{Cl}_{11}]^{5-}$  anion, where complexes and their principal directions  $g_{zz}$  are marked.

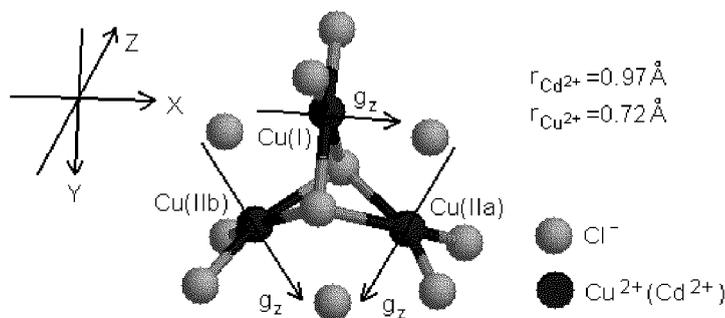


Fig. 3. The view on structure of the  $[\text{Cu}_3\text{Cl}_{11}]^{5-}$  anion and the principal direction of the  $g_{zz}$ -tensor component in the  $XYZ$  orthogonal system.

Since we have expected to observe some anomaly near the phase transition, we have made the EPR investigation in the temperature range (6 ÷ 293) K. The crystal was oriented in this way that magnetic field was directed along the  $a$ -crystal axis. Note that the complexes Cu(IIa) and Cu(IIb) are equivalent at this orientation of crystal. This means that there are no differences for position of resonance lines belonging to both complexes (see Fig. 2). One can observe a lot of clear separate resonance lines for Cu(IIa) and Cu(IIb) complexes due to a higher value of superhyperfine constants  $A_{(Cl)} = 13$  Gs with respect to the line width (8 Gs) at this orientation. On the contrary the spectrum of complex Cu(I) consists of only four broad lines because the superhyperfine splitting constant  $A_{(Cl)}$  from Cl nuclei has a small value at this orientation ( $A_{(Cl)} < 4$  Gs). We did not observe any anomalies in the spin-Hamiltonian parameters versus temperature for the complex of type-I.

Figure 4 shows the evolution of the EPR spectrum for complexes of II-type versus temperature. There is a clear visible smearing of all EPR lines below 40 K, which is especially emphasised on edges of the spectrum. Figure 5 presents the

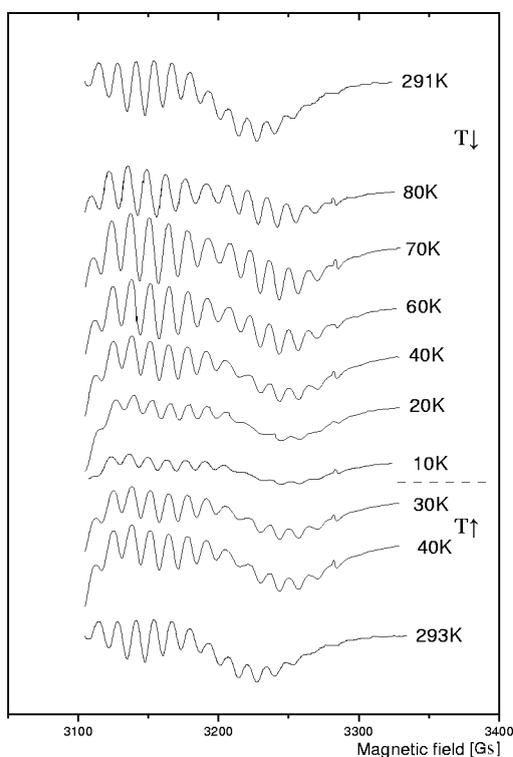


Fig. 4. The evolution of the fragment of the EPR spectra versus temperature. An external magnetic field is directed along the  $a$ -crystal axis.

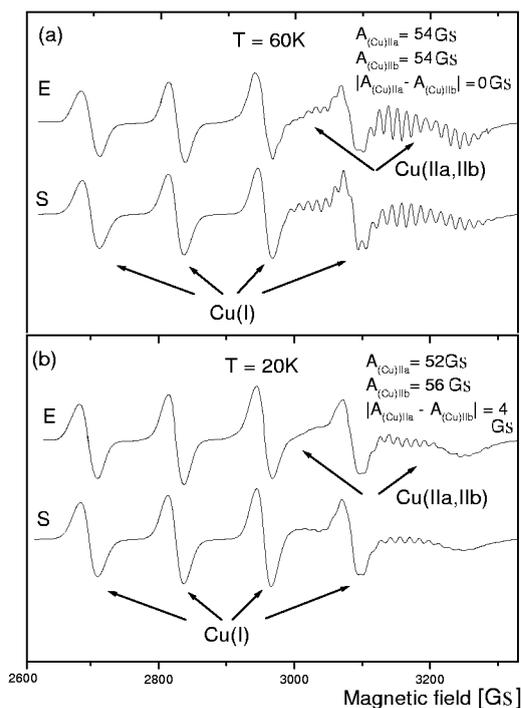


Fig. 5. The experimental (E) and simulated (S) EPR spectra of  $\text{Cu}^{2+}$  ion in DMACC crystal for temperature 60 K (a) and 20 K (b). An external magnetic field is directed along the  $a$ -crystal axis.

experimental and simulated EPR spectra at temperature 60 K and 20 K, respectively. The simulation indicates the difference in line positions belonging to Cu(IIa) and Cu(IIb) complexes below 40 K. We must keep in mind that complexes Cu(IIa) and Cu(IIb) are equivalent at this orientation at an external magnetic field above 40 K. Below this temperature the complexes Cu(IIa) and Cu(IIb) become nonequivalent. Nonequivalency of II-types complexes means the difference in coordination environment of Cu(IIa) and Cu(IIb) ions; the changes in the bond angles and/or distances within polyhedra.

Finally, our EPR results and spectra simulations suggest the smooth second order transition below about 40 K. Dielectric measurements of DMACC: $\text{Cu}^{2+}$  confirm the appearance of anomalies at temperature as for pure DMACC crystals [6]. Unfortunately,  $\text{Cu}^{2+}$  ion is not enough sensitive to detect these phase transitions. We combine the reason of this with a large difference radius of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  (see Fig. 3) and a strong molecular Cu-Cl bonding, which causes the partially decoupling of copper from the crystalline network.

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