INVESTIGATION OF VIBRONIC INTERACTION OF Cu(II) IONS IN CsMgCl₃ SINGLE CRYSTAL

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Abstract. The EPR spectra of Cu(II) ions in $CsMg_{1-x}Cu_xCl_3$ ($x = 0.005$–0.05) single crystals in the X band and in the temperature range 4.2–300 K are investigated. Three types of spectra are observed:

1. A low-temperature (4–40 K) tetragonal spectrum (six centres) with $g_\parallel^L = 2.320 \pm 0.001$; $g_\perp^L = 2.07 \pm 0.01$; $A_\parallel = 118 \times 10^{-4}$ cm⁻¹; $A_\perp < 15 \times 10^{-4}$ cm⁻¹;
2. A "quasi-powder" EPR spectrum with the principal axes non collinear to the low-temperature (LT) axes (40–200 K);
3. A high-temperature ($T > 200$ K) trigonal spectrum (one centre) with $g_\parallel^H = 2.147$; $g_\perp^H = 2.157$; $\Delta H_\parallel = 10.6$ mT; $\Delta H_\perp = 13.5$ mT. Two theoretical models for calculating the EPR spectra of Cu(II) centres in CsMgCl₃ single crystals are used.

i) Jahn–Teller reorientations are modelled as random jumps between three minima in terms of the stochastic Liouville equation (SLE) for the spin operator component parallel to the direction of the oscillating magnetic field;
ii) Temperature dependence of EPR spectra is interpreted as a change of the tunnel splitting and a continuous transition from "static" Jahn–Teller effect to the "intermediate" and the "dynamic" one. The results simulated by both these models are discussed.

Key words: EPR, Cu(II), Jahn–Teller effect, temperature dynamics.

INTRODUCTION

The investigation of the Jahn–Teller effect (JTE) in Cu²⁺ ion in a quasi-one-dimensional CsMgCl₃ crystal is a continuation of the investigations of Jahn–Teller (JT) centres in compounds of different composition and symmetry. The crystal under consideration is extremely interesting by the fact that its two neighbouring octahedra [1] have three common anions. In such structure, JT-active e-type deformations are to change considerably the type of distortion of the nearest neighbourhood of a paramagnetic ion.

Cooperative JTE in concentrated $CsCuCl_3$ magnetic leads to the displacement of Cu ions from the C_3-axis of the crystal and a strong monoclinic distortion of the nearest neighbourhood. There has been obvious interest in investigating the mechanism of this effect, proceeding from the studying of single JT centres.

EXPERIMENT

Single crystals of $CsMgCl_3$ doped with 0.5–5% Cu^{2+} were grown from the charge of the corresponding composition of Cs, Mg and Cu dehydrated halogenides in evacuated quartz ampoules according to the Bridgman method. EPR spectra were measured at the X band by using an ESR-230 spectrometer having a KPTI flow cryostat and a temperature controller to vary and record the temperature.

$CsMgCl_3$ is of a $CsNiCl_3$-type hexagonal perovskite structure (space group $P6_3/mmc$) whose peculiar feature is a linear chain of face-sharing octahedra of $MgCl_6$ along the c-axis [1]. The octahedra are slightly elongated along the C_3-axis and the angle between the bond Mg—Cl and C_3 is equal to 53°.

Six axial centres of Cu^{2+} having some angular dependences, like static JT centres, are observed at 4.2 K [2]. The angle between the principal axis of the $\{g\}$ tensor of each centre and the C_3-axis of the host crystal is equal to 56.5° (Fig. 1). EPR spectra of the centres are described by the axial spin-Hamiltonian

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

with $g_\parallel^{LT} = 2.320 \pm 0.001$; $g_\perp^{LT} = 2.07 \pm 0.01$; $A_\parallel = 118 \times 10^{-4}$ cm^{-1}; $A_\perp < 15 \times 10^{-4}$ cm^{-1}. The spectrum of Cu^{2+} at $H \parallel Z_i$ is shown in Fig. 2. When the temperature increases (range 40–200 K), the hyperfine (hf) structure lines broaden, split, and their peak-to-peak intensity decreases essentially. A new quasi-powder spectrum appears, whose principal axes are not along those of the low-temperature spectrum and whose orientation changes with temperature. Within the temperature range of 75–95 K a transformation of the form of two low-field hf lines has been observed like in a powder spectrum when the isotropic g tensor changes to axial with $g_\parallel < g_\perp$. Each hf line is split into two lines and the distance between them is about 3 mT. At $T > 95$ K the second lines are not observable and at $T > 130$ K the first ones begin to shift to higher magnetic field without changing their linewidths. The intensities of these lines are about 100 times less than at $T = 4$ K. At $T = 200$ K the common spectrum turns into one weak anisotropic line with unresolved hf structure: $g_\parallel^{HT} = 2.147$; $g_\perp^{HT} = 2.157$; $\Delta H_\parallel = 10.6$ mT; $\Delta H_\perp = 13.5$ mT and $Z \parallel C_3$.

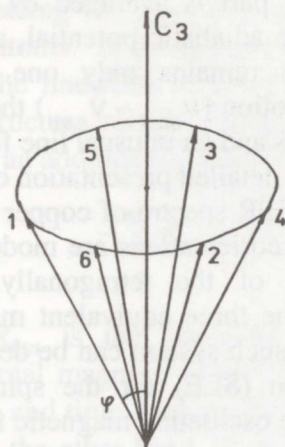Fig. 1. Orientations of the Z-axes of $\{g\}$ tensor (at low temperature).
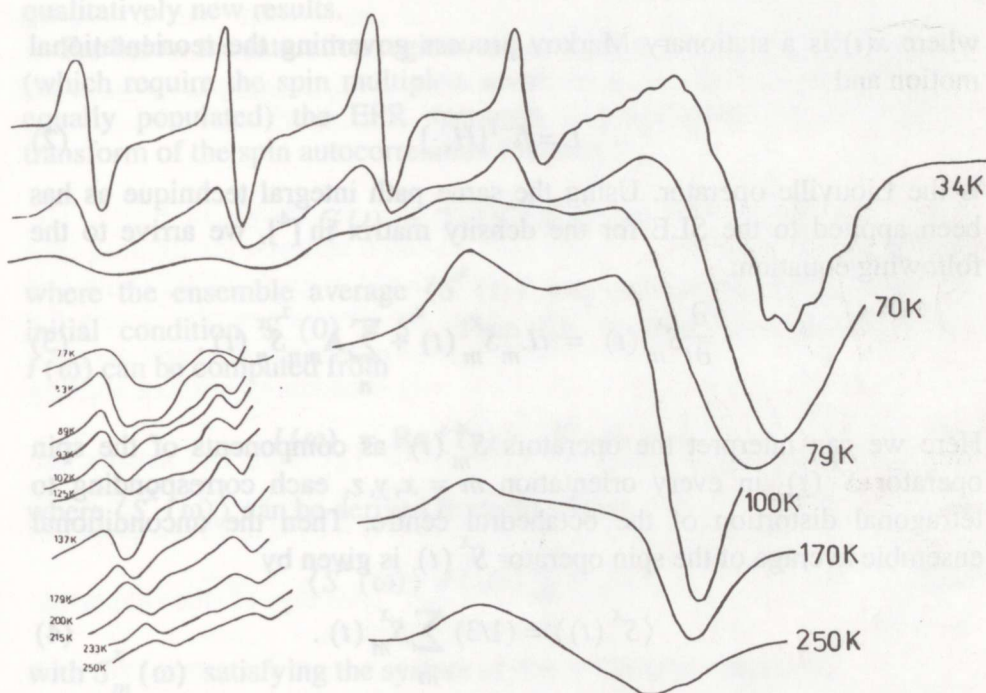

Fig. 2. Experimental spectra of $CsMgCl_3:Cu^{2+}$.

DISCUSSION

The result of the joint action of the trigonal distortion of the host lattice and the tetragonal elongation of Cu octahedron due to JTE is that the $\{g\}$ tensor's principal axes do not coincide with the metal-ligand direction, two of them being in the plane including C_4- and C_3-axes of the anion octahedra. The angle φ between g_i and C_3 ($\varphi = 54.7°$ for undistorted octahedron) characterizes the relationship between the tetragonal and the trigonal part of the crystal field. At the temperature increase from 4 K to

300 K, the tetragonal (JTE) part is averaged by the relaxation motion between three minima of the adiabatic potential, and in the limit of fast ($\nu_{mot} \gg \nu_{epr}$) motion there remains only one trigonal part. At an intermediate frequency of motion ($\nu_{mot} \sim \nu_{epr}$) the appearance of mixed spectra with various φ-angles and an unusual line form are possible.

This section is aiming at a detailed presentation of the theoretical model we used for calculating the EPR spectra of copper II centres in $CsMgCl_3$ single crystals. Here the JT reorientations are modelled as random jumps between three orientations of the tetragonally distorted octahedral complex corresponding to the three equivalent minima of the adiabatic potential. The behaviour of such system can be described in terms of the stochastic Liouville equation (SLE) for the spin operator component parallel to the direction of the oscillating magnetic field [3],

$$\frac{\partial}{\partial t} S^x(t) = iL(x(t)) S^x(t),\tag{1}$$

where $x(t)$ is a stationary Markov process governing the reorientational motion and

$$L = \hbar^{-1}[H, \cdot]\tag{2}$$

is the Liouville operator. Using the same path integral technique as has been applied to the SLE for the density matrix in [4], we arrive to the following equation:

$$\frac{\partial}{\partial t} S_m^x(t) = iL_m S_m^x(t) + \sum_n \Lambda_{mn} S_n^x(t).\tag{3}$$

Here we can interpret the operators $S_m^x(t)$ as components of the spin operator $S^x(t)$ in every orientation $m = x, y, z$, each corresponding to tetragonal distortion of the octahedral centre. Then the unconditional ensemble average of the spin operator $S^x(t)$ is given by

$$\langle S^x(t) \rangle = (1/3) \sum_m S_m^x(t).\tag{4}$$

At each orientation $m = x, y, z$ the spin Hamiltonian H_m includes the Zeeman and the hyperfine term and, hence, it can be written as

$$H_m = B \cdot G_m \cdot S + I \cdot A_m \cdot S,\tag{5}$$

where $G_m = \beta g_m$ and A_m are the spectroscopic and hyperfine splitting tensor S, respectively. These tensors can substantially differ from one orientation to another.

The matrix elements Λ_{mn} can be defined by the intensity λ of reorientational jumps as

$$\Lambda_{mn} = \begin{cases} \lambda & \text{for } m \neq n \\ -2\lambda & \text{for } m = n. \end{cases}\tag{6}$$

So far we were neglecting the hyperfine splitting resulting from six neighbouring chlorine atoms. In our approach this interaction is assumed to contribute only to the linewidth of each component of the spectrum while the hyperfine structure remains unresolved. It can be taken into account by introducing an additional relaxation term,

$$-\sum_n R_{mn} S_n^x (t) ,$$ (7)

into Eq. (3), where R_{mn} is the linewidth tensor depending on the orientation of the external magnetic field. This procedure saves a lot of computational memory and time, making the problem appropriate for our computer facilities. On the other hand, there is no reason to expect that a detailed analysis of those hyperfine interactions would lead to qualitatively new results.

Far below the saturation regime and in high-temperature approximation (which require the spin multiplets involved in the EPR absorption to be equally populated) the EPR spectrum is proportional to the Fourier transform of the spin autocorrelation function [1]:

$$G(t) = \mathrm{Tr} [S^x \langle S^x (t) \rangle] ,$$ (8)

where the ensemble average $\langle S^x (t) \rangle$ was defined in Eq. (4) with the initial condition $S^x (0) = S^x$. Then the spectral line-shape function $I(\omega)$ can be computed from

$$I(\omega) = \mathrm{Re} \, (\mathrm{Tr} [S^x \langle S^x (\omega) \rangle]) ,$$ (9)

where $\langle S^x (\omega) \rangle$ can be derived from Eq. (4) as

$$\langle S^x (\omega) \rangle = (1/3) \sum_m S_m^x (\omega) ,$$ (10)

with $S_m^x (\omega)$ satisfying the system of linear algebraic equations

$$i(\omega - L_m) S_m^x (\omega) - \sum_n (\Lambda_{mn} - R_{mn}) S_n^x (\omega) = S^x .$$ (11)

This system, another version of SLE, is solved by using some standard methods based on tridiagonalization and QL algorithms as applied to a complex symmetric matrix [3]. In a fast motion regime a simplified method based on the relaxation matrix approach can also be applied to solve the line-shape problem [5].
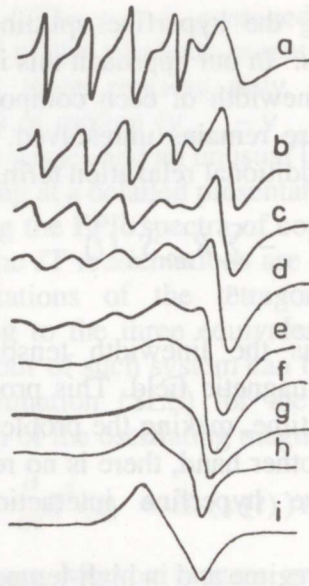
Fig. 3. Dependences of simulated spectra (SLE model) on the frequency of random jumps ν (Hz) : a, 10^7; b, 10^8; c, $10^{8.2}$; d, $10^{8.4}$; e, $10^{8.6}$; f, $10^{8.8}$; g, 10^9; h, 10^{10}; i, 10^{11}.

EPR spectra, simulated by this procedure, are shown in Fig. 3. The change of the frequency of reorientation motion between the minima over a temperature range of 60–120 K is proportional to $\exp(-\Delta E/kT)$ with ΔE ~500 cm^{-1}. One can notice that in general the spectra describe closely the experimental temperature dependence. Let us note some essential details:

i) the lines of hyperfine structure are only broadening without shifting in the frequency or in the magnetic field;

ii) the centres with higher anisotropy of $\{g\}$ and $\{A\}$ tensors are averaged at higher frequencies among six centres $H \parallel g_z$. EPR spectra of three centres in the orientations different from $H \parallel Z$ ($H \perp Z$) are averaged first and those of three others, afterwards;

iii) in principle one cannot obtain any splitting of the hyperfine structure without adding some new types of centres.

The fact that the averaging takes place over six centres in ground vibronic states with different orientations of Z-axes (frequencies or temperature dependences of these are slightly different) leads to the emergence of a quasi-powder spectrum both in the experiment and on modelling. However, in this case for the closest coincidence of the experiment with the result of simulation there is a lack of some averaged centres. The coincidence should be better if along with the centres mentioned at least six (or 12, 18) more centres will be added with the value of g factor anisotropy smaller than that for the centres in the ground state. Then the splitting of the lines in the experiment and some variation of spectra in the intermediate area could be described easily. This way we come to a conclusion about the need to introduce additional centres which could be interpreted as complexes in excited vibronic states with a larger life time compared with the characteristic time of the EPR experiment, ~ $1/\nu_{epr}$.

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On the other hand, the introduction of such excited states implies that the nuclear wave function of the system in this state is more strongly delocalized than the wave function for the system in the ground state. It means in turn that the overlapping of such functions of different minima of the "Mexican hat" increases, i.e. the tunnel splitting or the 3Γ value for this state increases. If the discussion is continued in the same way, one can see that every state is characterized with its own tunnelling or 3Γ value. Then the following mechanism of temperature dependence of tunnel splitting is possible. At the temperature increase the excited vibronic states are averaged by relaxation, which results in the average 3Γ value according to the Boltzmann statistics. From this stand-point the temperature averaging of the static JTE is the averaging at the cost of movement and a transition to the dynamic JTE. In our opinion the separation of these cases is not warranted.

On the other hand, if such model of temperature dependence of tunnel splitting is true, then it can be confirmed by direct modelling. In our calculation we followed the method for the intermediate JTE case [6]. Model spectra at various $3\Gamma/\Delta$ relationships are shown in Fig. 4. It can be seen that on the whole the coincidence is satisfactory.
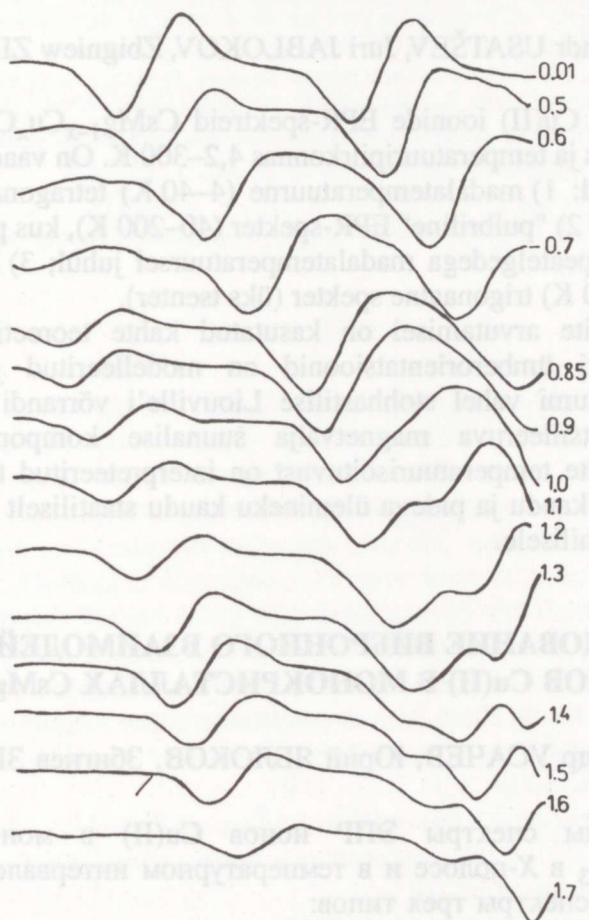

Fig. 4. Dependences of two low-field hyperfine lines on $3\Gamma/\Delta$ value.

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Cu(II) IOONIDE VIBROONINTERAKTSIOONI UURIMINE CsMgCl₃ MONOKRISTALLIDES

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On uuritud Cu(II) ioonide EPR-spektreid $CsMg_{1-x}Cu_xCl_3$ monokristallides X-ribas ja temperatuuripiirkonnas 4,2–300 K. On vaadeldud kolme tüüpi spektreid: 1) madalatemperatuurne (4–40 K) tetragonaalne spekter (kuus tsentrit); 2) "pulbriline" EPR-spekter (40–200 K), kus peateljed pole kollineaarsed peatelgedega madalatemperatuursel juhul; 3) kõrgtemperatuurne ($T > 200$ K) trigonaalne spekter (üks tsenter).

EPR-spektrite arvutamisel on kasutatud kahte teoreetilist mudelit: a) Jahni–Telleri ümberorientatsioonid on modelleeritud juhuhüpetena kolme miinimumi vahel stohhastilise Liouville'i võrrandi järgi spinn-operaatori ostsilleeruva magnetvälja suunalise komponendi tarvis; b) EPR-spektrite temperatuurisõltuvust on interpreteeritud tunnellõhenemise muutuse kaudu ja pideva ülemineku kaudu staatiliselt Jahni–Telleri efektilt dünaamilisele.

ИССЛЕДОВАНИЕ ВИБРОННОГО ВЗАИМОДЕЙСТВИЯ ИОНОВ Cu(II) В МОНОКРИСТАЛЛАХ CsMgCl₃

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Исследованы спектры ЭПР ионов Cu(II) в монокристаллах $CsMg_{1-x}Cu_xCl_3$ в X-полосе и в температурном интервале 4,2–300 K. Наблюдались спектры трех типов:
1) низкотемпературный (4–40 K) тетрагональный спектр (шесть центров);

2) "порошковый" спектр ЭПР (40–200 K) с главными осями, неколлинеарными осям в низкотемпературном случае;

3) высокотемпературный ($T > 200$ K) тригональный спектр (один центр).

При расчете спектров ЭПР использовались две теоретические модели: а) ян–теллеровские переориентации моделировались случайными прыжками между тремя минимумами в терминах стохастического уравнения Лиувилля для компоненты спинового оператора, параллельной направлению осциллирующего магнитного поля; б) температурная зависимость спектров ЭПР интерпретировалась через изменение туннельного расщепления и через непрерывный переход от статического эффекта Яна–Теллера к динамическому.