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INVESTIGATION OF THE FORMATION OF THE LOW-TEMPERATURE MAGNETIC AND STRUCTURAL ORDER IN A JAHN–TELLER $CsCuCl_3$ CRYSTAL BY THE EPR OF FRAGMENTS OF A MAGNETIC STRUCTURE

Violeta VORONKOVA[a], Dante GATTESCHI[b], Aleksandr USACHEV[a], and Yurii YABLOKOV[a]

[a] Физико-технический институт им. Е. К. Завойского КНЦ РАН (E. K. Zavoisky Physical-Technical Institute of RAS), Сибирский тракт 10/7, 420029 Казань, Татарстан, Российская Федерация (Russian Federation)
[b] Dipartimento di Chimica, Università di Firènze (University of Florence), Via Maragliano 75/77, I-50144 Firènze, Italia (Italy)

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Abstract. In order to investigate the nature of the low-temperature magnetic and structural order of a Jahn–Teller $CsCuCl_3$ crystal an isomorphous doping of $CsCuCl_3$ in a diamagnetic $CsMgCl_3$ and an EPR study of $CsMg_{1-x}Cu_xCl_3$ ($x = 0.005$–0.05) have been undertaken. The orientation of the $\{g_i\}$ tensors of single Cu^{2+} ions relative to the crystallographic axes of the $CsMgCl_3$ crystal have been determined. The types of pairs, the number of magnetically unequivalent pairs of each type and magnetic properties of the fragments of Cu^{2+}–Cu^{2+} pair in $CsMg_{1-x}Cu_xCl_3$ have been studied. A detailed analysis of the anisotropy of exchange interaction is presented for the nearest-neighbour Cu^{2+}–Cu^{2+} pairs in the $CsCuCl_3$ chain. The suppositions about the nature of odd distortion modes in a low-temperature phase, the character of the anisotropy of the exchange interactions and the correlation between the properties of the pair exchange interaction and the helical magnetic structure of $CsCuCl_3$ are given.

Key words: electron paramagnetic resonance, Jahn–Teller effect, exchange interaction.

INTRODUCTION

The $CsCuCl_3$ crystal is built up of linear chains of face-sharing $[CuCl_6]^{4-}$ octahedra. At room temperature it shows a helical structure. Each octahedron is elongated along one Cu–Cl direction below the transition temperature and Cu^{2+} ions are displaced by 0.42 Å from the 6_1-axis [1]. A structure phase transition has been discovered at 423 K [2, 3]. The space group at higher temperature is $P6_3/mmc$ (Fig. 1). The nature of

the phase transition associated with the realization of helically distorted chains has been actively investigated [4–19]. For example, the presence of helical deformations in the $CsCuCl_3$ crystal means that there exist both odd deformations of the octahedra and even deformations due to the E ⊗ e Jahn–Teller effect. Different models for the interpretation of this unusual situation have been proposed. It is impossible to decide unambiguously whether the odd distortion modes are determined by the nature of single Cu^{2+} ions [17] or they are due to a correlation effect of the deformations of neighbouring centres [19], since experimental data are absent.

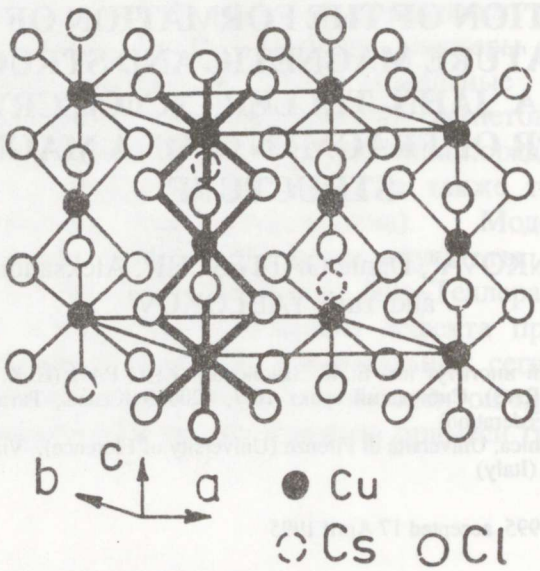

Fig. 1. The parent hexagonal perovskite lattice.

The magnetic properties of $CsCuCl_3$ have been described by a model in which the compound is built up of ferromagnetic chains and the triangular magnetic structure is stabilized by an antiferromagnetic interaction between the chains [20]. Helical modulated ferromagnetic chains along the *c*-axis have been discovered [9]. It has been proposed that helical modulation is due to the antisymmetric exchange. In order to elucidate which $CsCuCl_3$ properties are due to cooperative interactions and which due to the nature of single Cu^{2+} ions or pair exchange interactions, an isomorphous doping of $CsCuCl_3$ in diamagnetic $CsMgCl_3$ and an EPR investigation of $CsMg_{1-x}Cu_xCl_3$ ($x = 0.005 - 0.05$) have been undertaken.

In [21], the results of the investigation of the Jahn–Teller peculiarities of Cu^{2+} ions in $CsMg_{1-x}Cu_xCl_3$ ($x = 0.005 - 0.01$) have been described. This work is devoted to the studying of $CsMg_{1-x}Cu_xCl_3$ crystals with a higher concentration of Cu^{2+} ions when there is a probability for substituting Mg ions by Cu^{2+} ions in the nearest positions: in the chain and between the chains. It is necessary to obtain information on how many various types of Cu–Cu pairs are observable in $CsMg_{1-x}Cu_xCl_3$ to determine what types of

pairs are realized in the crystal and what is the character of pair interactions in it.

RESULTS AND DISCUSSION

The EPR spectra were recorded at $\nu_1 = 9.3$ GHz (X band) in the temperature range from 300 K to 4.2 K and at $\nu_2 = 37.2$ GHz (Q band) at 4.2 K. Beginning from T ~ 40–50 K the EPR spectra contain additional signals [22]. Their concentration and angular and frequency dependences enable us to attribute these to the spectra of exchange-coupled Cu–Cu pairs ($J\hat{S}_1\hat{S}_2$ $J<0$) [23, 24]. The angular dependence of the EPR spectra at ν_1 shows that the main part of additional signals is due to transitions in the states with the resultant spin $S = 1$ for the case $\Delta > h\nu_1$, Δ being the effective value of the splitting of the triplet state (Fig. 2). The form of the additional spectrum at ν_2 corresponds to the case $\Delta < h\nu_2$ (Fig. 3).

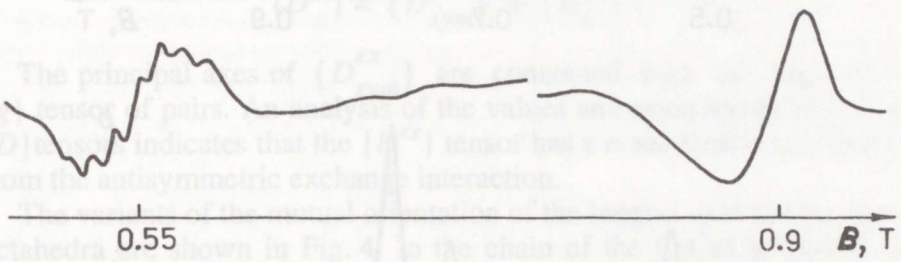

Fig. 2. The exchange spectrum of the $CsMg_{1-x}Cu_xCl_3$ crystal for $T = 4.2$ K, $\nu_1 = 9.3$ GHz. The orientation of $\boldsymbol{B}$ is close to C_3.

The angular dependences of the EPR spectra of the X band of $CsMg_{1-x}Cu_xCl_3$ ($x = 0.02$) at $T = 4.2$ K were studied in three mutually orthogonal planes, one of which coincided with the *ac* plane of the $CsMgCl_3$ crystal. The X-band spectrum can be interpreted as a sum of signals from six magnetically inequivalent centres with $S = 1$. The angular dependence of the transition fields of each centre is described by an effective spin-Hamiltonian:

$$\mathcal{H} = \beta \boldsymbol{B}\{g\}\hat{S} + \hat{S}\{D\}\hat{S},$$

where the total spin of the pairs $S = 1$, $\{g\}$ is the matrix of the parameters conventionally called the g tensor of the pair and $\{D\}$ is the fine-structure tensor. The $\{D\}$ tensor is determined by the anisotropic spin–spin interaction and it contains contributions from dipole and exchange interactions [23, 24]:

$$\{D\} = \{D^{d-d}\} + \{D^{ex}\}.$$

The principal values and orientations of the $\{D\}$ and $\{g\}$ tensors are obtained by fitting experimental and theoretical angular dependences of the transition fields of each centre:

$$D_{zz} = \pm (0.52 \pm 0.01)\ \text{cm}^{-1},$$
$$D_{xx} = \mp (0.29 \pm 0.01)\ \text{cm}^{-1},$$
$$D_{yy} = \mp (0.23 \pm 0.01)\ \text{cm}^{-1}.$$

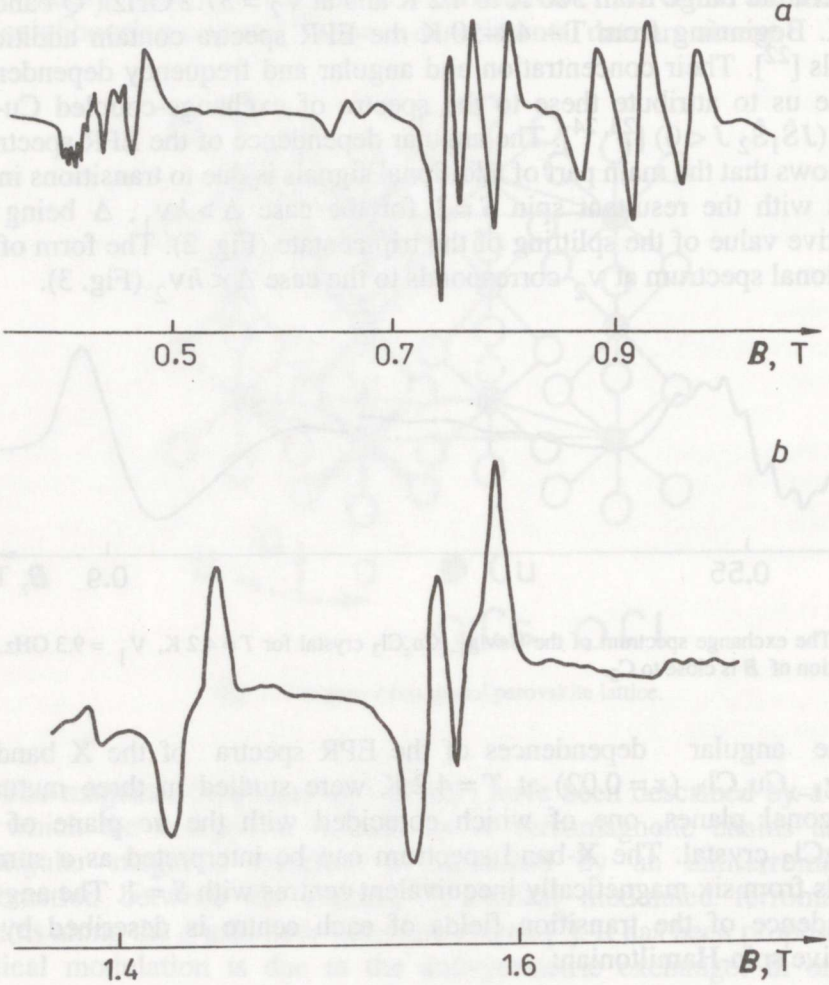

Fig. 3. The low-field (*a*) and high-field (*b*) parts of the exchange spectrum of the $CsMg_{1-x}Cu_xCl_3$ crystal for $T = 4.2$ K, $\nu_2 = 37.2$ GHz. The orientation of $\boldsymbol{B}$ is arbitrary.

The directions D_{zz} and D_{xx} are in the plane close to the *ac* plane. The direction D_{zz} makes an 18° angle with the *c*-axis, the direction g_z, being also in this plane, makes a 53° angle with the *c*-axis. The principal axes of magnetically inequivalent pairs are connected with each other by a 60° rotation. It has been shown earlier [21] that the principal axes of $\{g_i\}$ tensors of six magnetically inequivalent single Cu^{2+} ions in the chain are connected with each other by a 60° rotation about the *c*-axis. These

experimental results allow us to attribute the observed spectra to the nearest-neighbour Cu–Cu pairs in the chain. The point dipole approximation and the data for isolated Cu^{2+} allow us to estimate the dipole contribution to the $\{D\}$ tensor of these pairs. This contribution is small and the observed value of the noncoincidence of the principal axes of $\{g\}$ and $\{D\}$ tensors cannot be explained by dipole contribution.

The exchange interactions between Cu^{2+} ions in face-sharing octahedra have practically not been investigated. Since the inversion centre is absent, the spin–spin interaction has an antisymmetric part [25],

$$d\,[\hat{S}_1 \times \hat{S}_2].$$

The $\{D\}$ tensor contains contributions from both the symmetric and antisymmetric interactions. In the strong exchange limit the effect of the antisymmetric term on the energy levels of a S spin manifold can be represented by a symmetric tensor, $\{D^{ex}_a\}$, which gives an additional contribution to the zero field splitting [23, 24]:

$$\{D^{ex}\} = \{D^{ex}_{sym}\} + \{D^{ex}_a\}\,.$$

The principal axes of $\{D^{ex}_{sym}\}$ are connected with the axes of the $\{g\}$ tensor of pairs. An analysis of the values and orientations of $\{g\}$ and $\{D\}$tensors indicates that the $\{D^{ex}\}$ tensor has a considerable contribution from the antisymmetric exchange interaction.

The variants of the mutual orientation of the longest axes in two nearest octahedra are shown in Fig. 4. In the chain of the $CsCuCl_3$ crystal, one sequence of the changes in distortion is realized. However, in the diamagnetic $CsMgCl_3$ lattice one can expect the formation of Cu–Cu pairs in which, when going from the first octahedron to the second one, the longest axes are rotated by $\pi/3$ and $-\pi/3$ around the C_3-axis, since all variants are energetically equivalent. If the Cu^{2+} ion is situated on the 6_1-axis, the Cu–Cu direction will coincide with the 6_1-axis and only six magnetically inequivalent centres can be observed. If the Cu^{2+} ion is displaced from the 6_1-axis in the pair fragment, the Cu–Cu directions for the left and the right chain will differ and two sets of six magnetically inequivalent centres can be distinguished by rotation of the $\{D\}$ tensors.

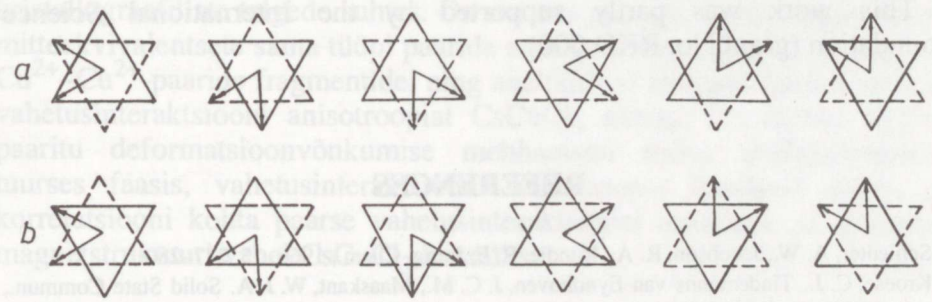

Fig. 4. Projections of two face-sharing octahedra (common face is shown by a broken line) on the *ab* plane. All possible variants of the orientations of long axes in two octahedra are shown. When going from the first octahedron to the second one, the orientation of the long bond is rotated by 60° clockwise (*a*) and anti-clockwise (*b*).

The preliminary investigation at the Q band showed that for some single-crystal orientations a small splitting of each signal is detectable. The observed spectra allow us to assume that twelve Cu–Cu centres are realized, i.e. there exist two sets of six magnetically inequivalent pairs with close magnetic axes. This shows that the Cu^{2+} ion is displaced from 6_1-axis in the pair fragment. Note that the results of the studying of single Cu^{2+} ions in $CsMg_{1-x}Cu_xCl_3$ [21] show that no displacement of the Cu^{2+} ion from 6_1-axis is detected in an isolated octahedron fragment. Since the displacement of the Cu^{2+} ion from the 6_1-axis is one of the manifestations of odd distortion modes, the obtained EPR data allow us to propose that the presence of odd modes is due to the correlation effect of the deformations of the neighbouring centres [19].

CONCLUSIONS

It was found that only one type of pairs is distinctly detectable in $CsMg_{1-x}Cu_xCl_3$. The angular dependence of the transition fields in the X band indicates the presence of six magnetically inequivalent pairs. The measurements in the Q band showed that there are two sets of six magnetically inequivalent pairs. The observed spectra were attributed to the nearest neighbour Cu^{2+}–Cu^{2+} pairs in the chain. It was established that the exchange interaction between the nearest neighbouring Cu^{2+} ions in the chain has an anisotropic character and the observed value of the noncoincidence of $\{g\}$ and $\{D\}$ tensors is not explainable by the dipole contribution. It was shown that the $\{D^{ex}\}$ tensor of the pair fragments from which $CsCuCl_3$ chains are built up has a considerable contribution from the antisymmetric exchange interaction. An experimental indication was obtained that the displacement of the Cu^{2+} ion from the 6_1-axis is realized already in the pair fragment.

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JAHNI–TELLERI TÜÜPI $CsCuCl_3$ KRISTALLI MADALATEMPERATUURSE MAGNETILISE JA STRUKTUURSE KORRASTUSE UURIMINE MAGNETSTRUKTUURI FRAGMENTIDE EPR-i ABIL

Violeta VORONKOVA, Dante GATTESCHI, Aleksandr USATŠEV, Juri JABLOKOV

$CsCuCl_3$ kristalli madalatemperatuurse magnetilise ja struktuurse korrastuse uurimiseks on $CsCuCl_3$ isomorfselt manustatud diamagnetilisse $CsMgCl_3$-sse ja EPR-i abil uuritud segukristalli $CsMg_{1-x}Cu_xCl_3$. On määratud Cu^{2+} üksikioonide g_i-tensorite orientatsioonid $CsMgCl_3$ kristallograafiliste telgede suhtes. On uuritud paaride tüüpe, magnetiliselt mitteekvivalentsete sama tüüpi paaride arvu ja nende magnetilisi omadusi Cu^{2+}–Cu^{2+}-paaride fragmentidel ning analüüsitud lähimate naaberioonide vahetusinteraktsiooni anisotroopiat $CsCuCl_3$ ahelas. On tehtud oletusi paaritu deformatsioonvõnkumise mehhanismi kohta madalatemperatuurses faasis, vahetusinteraktsiooni anisotroopia karakteri kohta ja korrelatsiooni kohta paarse vahetusinteraktsiooni omaduste ja spiraalse magnetstruktuuri vahel $CsCuCl_3$ kristallis.

ИССЛЕДОВАНИЕ ФОРМИРОВАНИЯ НИЗКОТЕМПЕРАТУРНОГО МАГНИТНОГО И СТРУКТУРНОГО ПОРЯДКА ЯН–ТЕЛЛЕРОВСКОГО КРИСТАЛЛА $CsCuCl_3$ НА ОСНОВАНИИ ИЗУЧЕНИЯ ЭПР ФРАГМЕНТОВ МАГНИТНОЙ СТРУКТУРЫ

Виолета ВОРОНКОВА, Данте ГАТТЕСКИ, Александр УСАЧЕВ, Юрий ЯБЛОКОВ

Для исследования природы низкотемпературного магнитного и структурного порядка ян–теллеровского кристалла $CsCuCl_3$ предприняты изоморфное разбавление $CsCuCl_3$ в диамагнитном $CsMgCl_3$ и изучение смешанного кристалла $CsMg_{1-x}Cu_xCl_3$ методом ЭПР. Определены ориентации $\{g_i\}$-тензоров изолированных ионов Cu^{2+} относительно кристаллографических осей $CsMgCl_3$ и изучены парные фрагменты Cu^{2+}–Cu^{2+} в $CsMg_{1-x}Cu_xCl_3$: тип пар, число магнито-неэквивалентных пар данного типа, их магнитные свойства. Представлен анализ анизотропии обменного взаимодействия для пар, образованных ближайшими соседними ионами меди в цепочке $CsCuCl_3$. Сделаны предположения о природе нечетной моды искажения кристалла $CsCuCl_3$ в низкотемпературной фазе, характере анизотропии обменного взаимодействия и корреляции свойств парных обменных взаимодействий с геликоидальной магнитной структурой $CsCuCl_3$.