EPR of exchange-coupled pairs of the Jahn-Teller Cu^{2+} ions in K_2ZnF_4

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EPR of exchange-coupled Cu^{2+} ion pairs in K_2ZnF_4 is investigated. Pairs of nearest neighbors produced by substituting Cu^{2+} ions for Zn^{2+} ions are ferromagnetic. It is shown that the local Jahn-Teller effect prevails over superexchange and interaction of Cu^{2+} ions via the lattice.

The close relation between the structural and magnetic properties of substances containing ions with orbital degeneracy has attracted much attention to these substances. The results of the investigations are summarized in a recent review by Kugel' and Khomskiĭ.[1] to understand the nature of the relation, it is urgent to investigate exchange-coupled ion pairs implanted in a diamagnetic matrix.

To explain structural and magnetic phase transitions it is necessary to take simultaneously into account the local Jahn-Teller effect, superexchange, cooperative interactions of ions via the lattice, and multipole-multipole interactions. The relative role of these interactions especially the first three, is not clear. As emphasized in Ref. 2, definite conclusions can be drawn even by determining whether exchange-coupled pairs of Jahn-Teller ions are ferromagnetic or antiferromagnetic under conditions of 180-degree superexchange. It follows from Refs. 3 and 4 that important information on this subject can be obtained from the hyperfine structure of the ESR spectrum.

Single crystals of K_2ZnF_4:Cu^{2+} are convenient research objects.1) They simulate to a full extent the competition between the interactions that take place in layered Jahn-Teller magnets (K_2CuF_4, K_2CrF_4, Rb_2CuCl_4, Rb_2CrCl_4 and others). The fact that ^{19}F has a nuclear moment permits additional information to be obtained on the distribution of the electron density (on the orbital structure) and on the transport integrals, which determine the indirect exchange, over the ligand hyperfine structure.

The crystals can be grown with different Cu^{2+} ion contents. This is an important circumstance. By varying the density of the Cu^{2+} ions in K_2ZnF_4 we have succeeded in proving the existence of a sufficiently strong interaction of the Jahn-Teller ions via the lattice: we observed in Ref. 6 a correlation of the local distortions of the Cu^{2+} magnetic centers in K_2ZnF_4 at distances exceeding the radius of the exchange interactions. In the present paper we shall pay principal attention to the study of pairs of nearest ions coupled by 180-degree superexchange via an intermediate F^- ion.

It is known[7] that in K_2ZnF_4 the ZnF_6 octahedra tetragonally compressed along the [001] axis form a layered structure, a fragment of which is shown in Fig. 1. K_2ZnF_4 crystals doped with Cu^{2+} were grown from a molten solution. The Cu^{2+} ion density ranged from 0.08 to 20% (as synthesized). Cu^{2+} and Zn^{2+} have equal charges and their ion radii are close. It is natural to assume that Cu^{2+} ions isomorphously replace Zn^{2+} ions.

The ESR spectra were investigated in the 3-cm band at temperatures from 2 to 300 K. In the study of single centers only one isotope, ^{63}Cu, was introduced to simplify the hyperfine-structure spectrum. The hyperfine structure, which includes splittings from the nucleus of the ^{63}Cu ion itself and from the ^{19}F nuclei, is distinctly resolved in the ESR spectrum of samples with low density of Cu^{2+} ions at $T = 4.2$ K and at a macrowave power level below 1 μW. The spectrum is described by the spin Hamiltonian

$$\mathscr{H}=\beta SgH+SA^{\mathrm{Cu}}I^{\mathrm{Cu}}+\sum_{i=1}^{6}\left(SA_i^{\mathrm{F}}I_i^{\mathrm{F}}-g_{\mathrm{JT}}\beta_{\mathrm{JT}}I_i^{\mathrm{F}}H\right), \qquad (1)$$

where the principal axes of the g and A tensors coincide with the crystallographic axes (the z and y axes are directed along [001] and [100], respectively; $g_{\parallel} = 2.014 \pm 0.002$; $g_{\perp} = 2.381 \pm 0.002$; the hyperfine-structure parameters (in 10^{-4} cm^{-1}) are $A_{\parallel}^{\mathrm{Cu}} = 72.2 \pm 0.5$; $A_{\perp}^{\mathrm{Cu}} = 42.3 \pm 0.6$; the hyperfine-structure ligand parameters due to the axial and equatorial fluorine atoms are (in 10^{-4} cm^{-1}) $A_z^{\mathrm{Fa}} = 123.0 \pm 0.5$; $A_x^{\mathrm{Fa}} = A_y^{\mathrm{Fa}} = 31.6 \pm 0.6$; $A_z^{\mathrm{Fe}} = 13.9 \pm 0.5$; $A_x^{\mathrm{Fe}} = 33.7 \pm 0.7$; $A_y^{\mathrm{Fe}} = 6 \pm 4$ (for ligands 1 and 4); $A_x^{\mathrm{Fe}} = 6 \pm 4$; $A_y^{\mathrm{Fe}} = 33.7 \pm 0.7$ (for ligands 2 and 5).

The obtained relation between the g factors ($g_{\perp} > g_{\parallel}$) corresponds to the case of tetragonal compression of an octahedron with a ground state $|3z^2 - r^2\rangle$. For a static tetragonally compressed octahedron, however, we always have $g_{\parallel} < 2$. In our case $g_{\parallel} > 2$ so that the compressed CuF_6 center is of the dynamic Jahn-Teller type.[8,9] The states $|3z^2 - r^2\rangle$ and $|x^2 - y^2\rangle$ are intermixed by the ion-lattice interaction, and a definite minimum of the surface of the adiabatic potential of the center (Fig. 2a) corresponds to a rhombically distorted

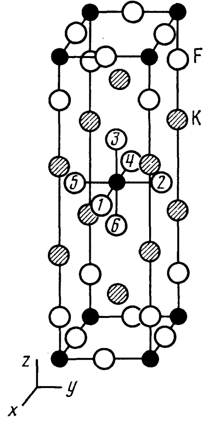

FIG. 1. Unit cell of K_2ZnF_4 crystal.

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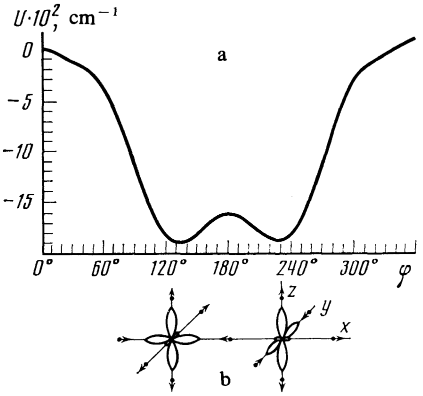

FIG. 2. Adiabatic potential of CuF_6 (a) and distribution of Cu^{2+} hole density at the minima (b). The adiabatic potential was numerically calculated using the equations of Ref. 9 and the vibronic constants of Refs. 11 and 12. $M\omega^2/2 = 90$ N/m, $\rho = 0.12$ Å, $\delta = 2930$ cm^{-1}.

octahedron configuration.[9,10] In experiment are observed g and A^{Cu} tensors of axial symmetry. It follows therefore that the frequency of the migration of the CuF_6 complex between the minima of the potential surface is higher than the ESR observation frequency. Assuming that the wave function is of the form

$$\Psi=C_1|3z^2-r^2\rangle+C_2|x^2-y^2\rangle+C_3|4s\rangle, \tag{2}$$

the experimentally observed values of g and A^F can be obtained at the following values of the coefficients C_i and of the parameters of the spin density at the fluorine nuclei

$$\begin{gathered}\overline{C_2^2}=0,025, \quad \overline{C_1C_3}=-0,08, \quad \overline{C_1C_2}=0, \\ f_\sigma^a=5.8\%, \quad f_s^a=0.55\%, \quad f_\sigma^e=5.4\%, \quad f_s^e=0,50\%.\end{gathered} \tag{3}$$

Here $\overline{C_iC_j}$ denotes an average over the motion of the nuclei; the ratio of the spin-density parameters of the axial and equatorial fluorines is assumed equal to the ratio of the corresponding overlap integrals.

As in the preliminary report,[6] when the density of the Cu^{2+} ions is increased and the temperature is lowered, signals from two types of single centers of rhombic symmetry appear in the spectrum corresponding to single CuF_6 centers. The axes x and y of the principal directions of the g-tensors of these centers are mutually perpendicular, and the z axes coincide. The principal values of the g-tensors are:

$$\begin{gathered}g_x^{(1)}=2,46\pm0.01, \quad g_y^{(1)}\neq2,23\pm0,01, \quad g_z^{(1)}=2.10\pm0,01, \\ g_x^{(2)}=2,23\pm0,01, \quad g_y^{(2)}=2,46\pm0,01, \quad g_z^{(2)}=2,10\pm0.01.\end{gathered} \tag{4}$$

With increasing Cu^{2+} density the tunneling between the wells of the adiabatic potential is slowed down by the interaction of the Jahn-Teller centers via the phonon field and because of the onset of random stresses. The interpretation assumed is confirmed by an investigation of the temperature dependence of the restructuring of the ESR spectrum and by an estimate of the value of the interaction of the tunnel states via the phonon field.[6] From the measured principal values of the g-tensor (4) we can determine the coefficients C_1 and C_2 in (2), which correspond to static configurations at the minima of the adiabatic potential. A simple calculation shows that these positions correspond to $C_1 = 0.935$ and $C_2 = \pm 0.344$. The distribution of the hole density is shown in Fig. 2b.

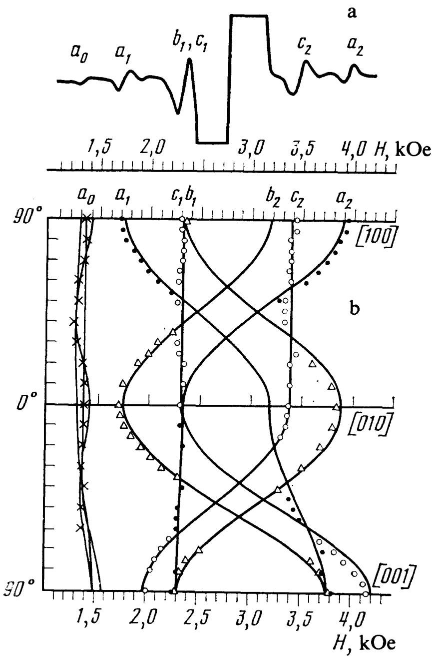

FIG. 3. ESR spectrum of $K_2Zn_{0.94}Cu_{0.06}F_4$ crystal in the orientation H‖[100] at a frequency $\nu = 9.2$ GHz and temperature $T = 4.2$ K (a) and angular dependence of the spectra of Cu^{2+}–Cu^{2+} pairs in the planes (010) and (001) (b). The solid lines in Fig. (b) show the theoretical relations calculated in accord with Eqs. (6) and (7); the symbols ●, △, and ○ are the experimental results for pairs I, II, and III, respectively.

Besides the lines of single rhombic centers, less intense lines from exchange-coupled pairs appear when the Cu^{2+} density is increased above 0.5%. The general form of the spectrum of the $K_2Cu_{0.06}Zn_{0.94}F_4$ crystal at **H**‖[100] is shown in Fig. 3a. The signals a_1, a_2, b_1, c_1, c_2, and a_0 belong here to exchange-coupled pairs, and the central signal corresponds to single centers. The relative intensity of the pair signals, compared with the intensity of the signal from the single centers, increases with increasing density. The angular dependence of the position of these signals is shown in Fig. 3b. It can be seen that the signals c_1 and c_2 belong to pairs with axial symmetry. The lines of pairs I and II (signals a_i and b_i) are transformed into each other when the magnetic field is rotated 90° in the (001) plane. The latter means that the connecting axes of pairs I and II are perpendicular (see Fig. 4). At half the magnetic field strength there is observed also a "forbidden" transition with a weak angular dependence. The position of the forbidden transition for the three

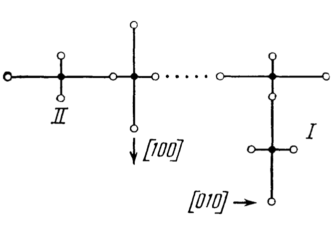

FIG. 4. Antiferrodistortion ordering of CuF_6 octahedra in pairs of type I and II in the $K_2Zn_{1-x}Cu_xF_4$ crystal.

types of pairs differ insignificantly, so that a single line α_0 is observed in the spectrum.

The spectra of the ESR pairs are described by spin Hamiltonian

$$\mathcal{H}=\beta SgH+SDS \tag{5}$$

with effective spin $S=1$ and with parameters

$$\begin{gathered}
g_z{}^{\mathrm{I}}=g_z{}^{\mathrm{II}}=g_z{}^{\mathrm{III}}=2{,}10\pm0.01, \quad g_{x,y}^{\mathrm{I}}=g_{x,y}^{\mathrm{II}}=2.30\pm0{,}01,\\
g_{x,y}^{\mathrm{III}}=2.24\pm0.01,\\
D_{xx}{}^{\mathrm{I}}=D_{yy}{}^{\mathrm{II}}=-774\pm10, \quad D_{yy}{}^{\mathrm{I}}=D_{xx}{}^{\mathrm{II}}=300\pm10,\\
D_{zz}{}^{\mathrm{I}}=D_{zz}{}^{\mathrm{II}}=474\pm10,\\
D_{xx}{}^{\mathrm{III}}=D_{yy}{}^{\mathrm{III}}=368\pm10, \quad D_{zz}{}^{\mathrm{III}}=-736\pm10.
\end{gathered} \tag{6}$$

The values of D_{ij} were determined accurate to the sign and are given in units of 10^{-4} cm^{-1}. Within the limits of measurement error, the spin-Hamiltonian parameters are independent of temperature and of the Cu^{2+} ion density. The hyperfine structure in the pair spectra is not resolved. The observed lines have a width ~150 Oe. When the temperature is lowered right down to 2 K the pair line intensity increases. This is evidence that $S=1$ is the ground state, i.e., all three pair types are ferromagnetic. Models of pairs I and II are shown in Fig. 4. Pairs with tetragonal symmetry are probably produced when the ions Zn^{2+} and K^+ are simultaneously replaced by Cu^{2+}, or else are of the defect type.

The Hamiltonian constructed by the method of Refs. 13 for the exchange interaction of Cu^{2+} $({}^2E_g)$ ions through an intermediate F^- ion is given by

$$\begin{aligned}
\mathcal{H}_{\text{ex}}=J_1\{&[1-\tau_{\theta a}-\tau_{\theta b}+\tau_{\theta a}\tau_{\theta b}](S_aS_b)\\
&+{}^1/_4[-3+\tau_{\theta a}+\tau_{\theta b}+\tau_{\theta a}\tau_{\theta b}]\}\\
&+J_2[{}^1/_4+(S_aS_b)](1-\tau_{\theta a}-\tau_{\theta b}+\tau_{\theta a}\tau_{\theta b})\\
+J_3\{&[8-5\tau_{\theta a}-5\tau_{\theta b}+2\tau_{\theta a}\tau_{\theta b}](S_aS_b)+{}^5/_4(\tau_{\theta a}+\tau_{\theta b})-{}^5/_2\tau_{\theta a}\tau_{\theta b}\}\\
&+J_4(1-\tau_{\theta a}-\tau_{\theta b}+\tau_{\theta a}\tau_{\theta b}).
\end{aligned} \tag{7}$$

Here and elsewhere τ_θ and τ_ε are operators that act in the space of the orbital doublet $|\theta\rangle=|3z^2-r^2\rangle$, $|\varepsilon\rangle=|x^2-y^2\rangle$ in accordance with the rule

$$\tau_\theta=\begin{vmatrix}-1 & 0\\ 0 & 1\end{vmatrix}, \quad \tau_\varepsilon=\begin{vmatrix}0 & 1\\ 1 & 0\end{vmatrix}. \tag{8}$$

The local z axes are chosen along the pair axis. The parameters J_1, J_2, J_3, and J_4 are expressed in terms of the transport integrals M_s and M_σ and of the charge-transport energy Δ as follows:

$$\begin{gathered}
J_1=\frac{(M_s{}^2\Delta_s-M_\sigma{}^2\Delta_\sigma)^2}{\Delta_{ab}}, \quad J_2=2\frac{M_\sigma{}^4\Delta_\sigma{}^2}{|\Delta_{appb}|}-\frac{(\Delta_\sigma+\Delta_s)^2M_s{}^2M_\sigma{}^2}{|\Delta_{apsb}|},\\
J_3=-\frac{4B+C}{3}\frac{(M_s{}^2\Delta_s-M_\sigma{}^2\Delta_\sigma)^2}{\Delta_{ab}{}^2},\\
J_4=\frac{1}{2}M_\sigma{}^4\left[\Delta_\sigma-\frac{2\Delta_\sigma{}^2}{|\Delta_{appb}|}+\frac{3F_2\Delta_\sigma{}^2}{|\Delta_{appb}|^2}\right].
\end{gathered} \tag{9}$$

Here B and C are the Racah parameters for the $3d$ shell of Cu^{2+}; F_2 is the Slater parameter that characterizes the Coulomb repulsion of the $2p$ electrons of F^-. The first two terms of (9) differ from zero when the orbitals of the Cu^{2+} ions are not orthogonal, and always contribute to antiferromagnetic ordering of the spins. The third term is always negative (ferromagnetic coupling). It is smaller than the first two by a value on the order of $(4B+C)/3\Delta_{ab}$ and determines the sign of the exchange integral J in the Hamiltonian $J(S_aS_b)$ only when the orbitals of the Cu^{2+} ions are orthogonal or approximately orthogonal. We define the transport integrals in terms of the mean values of the spin densities (3) with the aid of the relation[13]

$$f_\sigma=(M_\sigma-{}^1/_2S_\sigma)^2, \quad f_s=(M_s-{}^1/_2S_s)^2, \tag{10}$$

where S_σ and S_s are the overlap integrals. At $S_\sigma=-0.057$, $S_{2s}=0.045$, and $f_\sigma=5.4\%$ we obtain $M_\sigma=0.20$ and $M_s=-0.048$. At the transport energies $\Delta_{ab}=60000$ cm^{-1} and $\Delta_\sigma=72000$ cm^{-1} typical of fluorides (the remaining values can be readily determined from the ionization potentials) we get from (9) (in cm^{-1})

$$J_1=98, \quad J_2=45, \quad J_3=-5, \quad J_4=26. \tag{11}$$

From this we find, in particular, for $\mathrm{KCuF_3}$ with account taken of the real ordering of the orbitals,[1] that the exchange integral in the Heisenberg Hamiltonian $\mathcal{H}=J(S_aS_b)$ for Cu^{2+} ions antiferromagnetically coupled along the c axis is equal to $J_a=257$ cm^{-1}, while for ions in the ab plane we have $J_e=20$ cm^{-1}. They agree in order of magnitude and in sign with the experimental data.[14]

Our observed g-factors of pairs I and II are close to the arithmethic means of the corresponding g components of single rhombic centers: $g_\alpha^{\mathrm{I}}=g_\alpha^{\mathrm{II}}\approx(g_\alpha^{(1)}+g_\alpha^{(2)})/2$, where $\alpha=x, y, z$. It can be assumed that the ground states of the Cu^{2+} ion in a pair are approximately the same as in single rhombic centers:

$$\begin{gathered}
\Psi_a=0{,}935|\theta_a\rangle-0{,}344|\varepsilon_a\rangle-0{,}08|4s\rangle,\\
\Psi_b=0{,}935|\theta_b\rangle+0{,}344|\varepsilon_b\rangle-0.08|4s\rangle.
\end{gathered} \tag{12}$$

It follows then from (7) and (11) that the ground state of the pairs actually corresponds to $S=1$ (is ferromagnetic). The exchange integrals for pairs of type I and II are $J_{ab}^{\mathrm{I}}=J_{ab}^{\mathrm{II}}=-9.4$ cm^{-1}. This value should be regarded as an order-of-magnitude estimate. We note that direct determination of the exchange integral by measuring the temperature dependence of the ESR spectra is difficult. When the temperature is raised the ESR line intensities referred to the pair spectrum decrease more rapidly than might be expected even if a strong temperature dependence of the exchange integral were assumed. This effect is apparenlty due to reversible clustering of the pairs on account of "attraction" of the Jahn-Teller centers.

The exchange-interaction parameter of the copper ions in the $\mathrm{K_2CuF_4}$ crystal, determined in Ref. 15 from the dispersion law of the spin wave, is equal to -16 cm^{-1}. This is somewhat larger than the value calculated by us with the functions (12). We note that J depends substantially on the values of the coefficients C_1, C_2, and C_3 in (3) and (12). Thus, if we use the values $C_1=\sqrt{3/2}$, $C_2=\frac{1}{2}$, and $C_3=0$ assumed in Ref. 16 for $\mathrm{K_2CuF_4}$, we obtain $J=-22$ cm^{-1}.

We now estimate the values of the D tensor within the framework of the assumption made concerning the structure of exchange-coupled pairs of type I and II. In particular, for a pair aligned with the x axis the components D_{ij} are given by

$$D_{zz}=\frac{g_z^{(1}g_z^{(2)}}{2R^3}\beta^2+\left(\frac{\lambda}{\Delta_\zeta}\right)^2(J_{b\zeta}+J_{a\zeta})C_2^2,$$

$$D_{yy}=\frac{g_y^{(1)}g_y^{(2)}}{2R^3}\beta^2+\frac{1}{4}\left(\frac{\lambda}{\Delta_\eta}\right)^2 \times[(C^2+\sqrt{3}C_1)^2J_{b\eta}+(C_2-\sqrt{3}C_1)^2J_{a\eta}], \tag{13}$$

$$D_{xx}=-\frac{g_x^{(1)}g_x^{(2)}}{R^3}\beta^2+\frac{1}{4}\left(\frac{\lambda}{\xi}\right)^2 \times[(C_2-\sqrt{3}C_1)^2J_{b\xi}+(C_2+\sqrt{3}C_1)^2J_{a\xi}].$$

The first terms represent here the contributions of the dipole-dipole interaction, and the second those of the anisotropic exchange interaction.[2)] By ζ, η, and ξ are denoted respectively. The hole states d_{xy}, d_{xz}, and d_{yz}, which are connected with the ground states Ψ_a and Ψ_b because of the spin-orbit interaction, Δ_i are the excitation energies discussed in Ref. 12, and λ is the spin-orbit interaction parameter. At $M_\sigma = 0.2$ and $M_\pi = -0.12$ the exchange parameters calculated with the equations of Ref. 13 are equal to (in cm^{-1})

$$J_{a\zeta}=-14.7,\quad J_{a\eta}=-13.4,\quad J_{a\xi}=-15.5, \\ J_{b\zeta}=-4.7,\quad J_{b\eta}=-4.2,\quad J_{b\xi}=-1.4. \tag{14}$$

Substituting the indicated values of the g factors and of C_i in (13), we obtain at $R = 4$ Å (disregarding the isotropic part), in cm^{-1}:

$$D_{zz}=161+446=607,\quad D_{yy}=198+25=223, \\ D_{xx}=-359-470=-829. \tag{15}$$

The dipole-dipole and exchange contributions are quantities of the same order. The resultant values of the components D_{ij} are in fair agreement with the measured ones.

Thus, the presented interpretation of the ESR data is evidence that the "single-center" energy that determines the distortion of the CuF_6 octahedron exceeds the exchange-interaction energy (7) and the energy of the interaction of the Jahn-Teller centers via the lattice. Let us obtain a numerical estimate of the latter.

The interaction $\mathscr{H}_{\text{lat}}$ of the ions via the lattice was discussed in a number of papers. Estimates show that the direct interaction of the electrostatic multipoles is in this case negligibly small. A detailed analysis of the interaction through the phonon field is given in Refs. 17 and 18. A survey of the papers on this question is given in Refs. 19 and 20. This interaction was discussed in Refs. 21 and 22 in the elastic-medium approximation, when the Jahn-Teller ions are located at sufficiently large distances. Attempts to consider cooperative distortion of two neighboring octahedra in the quesimolecular model were undertaken in Refs. 23–25. Owing to the different approximations used for the potential energy of the local lattice deformation, different authors arrived at different results. To obtain more definite information on the local distortion of a pair of octahedral complexes (of a bioctahedron), we used the following calculation procedure. We assumed that with replacement of Zn^{2+} by Cu^{2+} only local displacements take place from the equilibrium positions near the Cu^{2+} ions. The energies of the displaced atoms were written as is customary in the theory of lattice dynamics. The effective charges and the parameters of the Born-Mayer potentials were taken in accord with the data of Refs. 26 and 27. Minimizing the energy with respect to the strains and choosing the x axis along the pair axis, we obtained

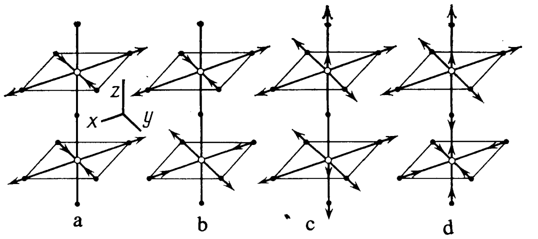

FIG. 5. Cooperative distortions of bioctahedron and corresponding signs of the constants of the interaction of the Jahn-Teller ions: a—$b_{2g}K_{\varepsilon\varepsilon} < 0$, $K_{\theta\theta} = 0$; b—$b_{1u}K_{\varepsilon\varepsilon} > 0$, $K_{\theta\theta} = 0$; c—a_{1g} $K_{\varepsilon\varepsilon} = 0$, $K_{\theta\theta} < 0$; d—a_{2u}: $K_{\varepsilon\varepsilon} = 0$, $K_{\theta\theta} > 0$, ○—Cu^{2+}, ●—F^-.

$$\mathscr{H}_{\text{lat}}=K_{\theta\theta}\tau_{\theta a}\tau_{\theta b}+K_{\varepsilon\varepsilon}\tau_{\varepsilon a}\tau_{\varepsilon b}+K_{\theta a}\tau_{\theta a}+K_{\theta b}\tau_{\theta b}+K, \tag{16}$$

where

$$K_{\theta\theta}=470\,\text{cm}^{-1},\quad K_{\varepsilon\varepsilon}=7\,\text{cm}^{-1},$$

$$K_{\theta a}=K_{\theta b}=-113\,\text{cm}^{-1},\quad K=170\,\text{cm}^{-1}.$$

It is interesting to note that there exist only four types of cooperative local bioctahedron distortions through which this interaction is mainly effected. They are shown in Fig. 5, where the signs, corresponding to these distortions, of the parameters $K_{\theta\theta}$ and $K_{\varepsilon\varepsilon}$ are also indicated. Specifically for our case, all four types of deformation are important. In particular, interactions via b_{1u} and b_{2g} deformations are approximately of the same order of magnitude, but of opposite sign. Both contributions are large (343.5 and 352 cm^{-1}), but cancel each other strongly. This agrees qualitatively with the study of cooperative distortions of the Jahn-Teller complexes $Cu(H_2O)_6^{2+}$ in the crystals $ZnZrF_6 \cdot 6H_2O$ and $ZnSiF_6 \cdot 6H_2O$ (Refs. 28 and 29). When the Zr ions are replaced by Si, the cooperative distortions of the ferrodistortion type are replaced by antiferrodistortion ones.

Comparison of (11) and (16) with the energy of the local distortions of individual copper ions shows that the latter indeed predominates. The tetragonal field at single Cu^{2+} ions in the K_2ZnF_4 lattice, without allowance for the six nearest fluorine ions, amounts to $\delta \approx 2930\ \text{cm}^{-1}$.

Thus, the results of our investigation offer unambiguous evidence that in layered structures such as K_2CuF_4 the local Jahn-Teller effect predominates over superexchange and over the interaction of orbitally degenerate ions via the lattice. It is important that in such structure the adiabatic potential is a two-well one. This is precisely why the local distortions of the individual centers in each pair turn out to be in mutual correspondence. The minimum of the energy of the local distortions in the systems is reached at as minimum value of the energy of each of the centers.

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1) The previously investigated[5] $K_2Zn_{1-x}Cu_xF_4$ were mainly polycrystalline.

2) Calculation of the antisymmetric exchange interaction $\mathbf{D}\cdot\mathbf{S}_a\times\mathbf{S}_b$ has shown it to be negligibly small in this case.

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