Quasistatic long-range correlations of Jahn-Teller centers via the phonon field in K_2ZnF_4: Cu^{2+} at low temperatures

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Correlations are discovered between distortions of Jahn-Teller Cu^{2+} centers in a K_2ZnF_4 crystal at distances exceeding the range of indirect-exchange interactions.

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While studying electronic paramagnetic resonance of Cu^{2+} impurity centers in K_2ZnF_4 at low temperatures, we discovered an interesting effect.

In a $K_2Zn_{0.8}Cu_{0.2}F_4$ crystal (as synthesized) additional lines arise in the spectrum corresponding to single Cu^{2+} centers with decreasing temperature. At $T \gtrsim 60$ K, a signal is observed from single centers of the same type, characterized in the crystallographic system of coordinates (the $z||[001]$ axis by the principal values of the g tensor $g_x^I = g_y^I = 2.372, g_z^I = 2.04$. With decreasing temperature, in addition to the signal described, there were two more signals, which gradually increased in intensity. These signals are due to single centers with rhombic symmetry with the parameters: $g_x^{II} = 2.46$; $g_y^{II} = 2.23$; $g_z^{II} = 2.10$; $g_x^{III} = 2.23$; $g_y^{III} = 2.46; g_z^{III} = 2.10$. The restructuring of the spectrum as a function of temperature is shown in Fig. 1. It is evident that at $T = 4.2$ K, signals are observed in the spectrum primarily from rhombic II and III

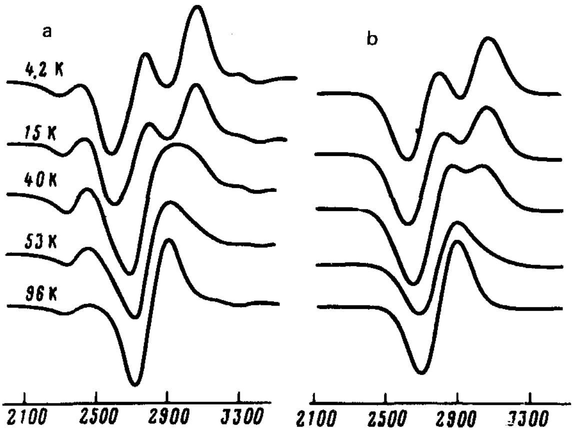

FIG. 1. Temperature dependence of the EPR spectrum of single centers in the crystal $K_2Zn_{0.8}Cu_{0.2}F_4$ $\nu = 9.3$ GHz; $H||[100]$. (a) Fragment of the experimental spectrum; (b) theoretical spectrum obtained by superimposing three EPR lines with a Gaussian shape with 200 Oe and with $g^{II} = 2.46$; $g^I = 2.372$; $g^{III} = 2.23$) varying their contribution to the total curve. The relative contribution of lines to the total curve was taken into account by introducing weighting coefficients. Their ratio $n^{II}:n^I:n^{III}$ was assumed to equal 41:18:41; 35:30:35; 27:46:27; 14:72:14; 0:100:0 for temperature 4.2 K, 15 K, 40 K, 53 K, 96 K respectively. The superposition of lines due to exchange-coupled pairs was not included.

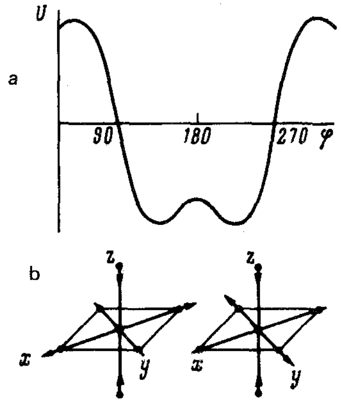

FIG. 2. Adiabatic potential (a) and the distortions of the fluorine octrahedra (b) corresponding to the minima in the potential for the crystal K_2ZnF_4:Cu^{2+}

centers. As the ion concentration decreases, additional lines disappear in the EPR spectrum, together with the disappearance of lines from exchange-coupled pairs.[1)]

The investigations of K_2ZnF_4 crystals with concentrations of impurity Cu^{2+} atoms up to 0.5% (as synthesized) showed that the copper ions replace the Zn^{2+} ions and are found, as are the metal ions in a diamagnetic matrix, in an octahedron slightly compressed along the direction [001] and consisting of F^- ions. The values of the g factors and the hyperfine structure constants, owing to the F^- nuclei, can be described by assuming that due to the strong electron-vibrational interaction the CuF_6 complex rapidly migrates between two minima of the adiabatic potential (Fig. 2). One of the minima corresponds to stretching of the octahedron along the x axis ([100] direction), and the other corresponds to stretching along the y axis ([010] direction).

As the concentration of Cu^{2+} ions increases, the following apparently occurs. Because of the interaction of Jahn-Teller centers via the phonon field, tunneling between the wells of the adiabatic potential ceases. When in a separately chosen pair of Jahn-Teller centers the tunneling frequency is less than the frequency for observing EPR, instead of a single EPR line, two lines should be observed (ignoring the hyperfine structure). Jahn-Teller centers are distributed randomly in the crystal. Since the interaction between them via the phonon field depends on the distance,[1] thermal vibrations do not destroy the correlated nature of the distortions at the same time for all centers. For this reason, three EPR signals are observed in the spectrum at the given temperature.

This model of hindered tunneling due to interactions of Jahn-Teller centers via the phonon field permits understanding in a natural manner the ratio of the g factors of single centers and their observed temperature independence.

The qualitative considerations presented above, of course, are valid if the interaction of Jahn-Teller centers via the phonon field is sufficiently strong. It is well known[2] that for purely electronic states, its order of magnitude does not exceed that of the dipole-dipole interactions. We shall show, however, that when tunneling states interact, its magnitude is comparable to kT under the conditions of the experiments described (k is Boltzmann's constant).

The energy of interaction of tunneling states with the strain field can be written in the form

$$\mathcal{H}^{(i))}_{\text{eff}} = (g_x^{(i)} - g_y^{(j)})\, q\frac{\Delta}{8\lambda} V \tau_x^{(i))}(e_{xx} - e_{yy}), \tag{1}$$

where $g_x^{(i)}$ and $g_y^{(j)}$ are the values of the g factors of the impurity center at the minimum of the adiabatic potential, q is the vibronic reduction factor, λ is the spin-orbital interaction constant, Δ is the magnitude of the splitting of the d states of the Cu^{2+} ion by the cubic crystal field, V is the constant of the strain potential,[3] e_{xx} and e_{yy} are the components of the strain tensor, $\tau_x^{(i)}$ is a Pauli matrix defined in a basis of symmetrical and antisymmetrical tunneling states.[4]

Using next the theory of interactions via the phonon field,[1] we easily obtain for the interaction energy of the ith and jth Jahn-Teller centers situated in (110) planes

$$U_{ij} = [(g_x^{(i)} - g_y^{(j)})\, q\frac{\Delta}{4\lambda} V]^2 \tau_x^{(i)} \tau_x^{(j)} (16\pi\rho v^2 r_{ij}^3 \cdot)^{-1}, \tag{2}$$

where ρ is the density, v is the average velocity of sound, and r_{ij} is the distance between the impurity ions. From here, with the usual values $V \cong 20000$ cm^{-1} and $\lambda/\Delta = -0.064$, we find that for $r_{ij} = 12$ Å, the quantity $u_{ij} \sim 7$ cm^{-1}. Thus the estimate shows that the interaction of Jahn-Teller centers and more precisely, of the inversion states, via the phonon field is quite strong and can explain the observed restructuring of the EPR spectrum with decreasing temperature.

It is obvious that the phenomenon of long-range correlation of distortions gives a new nontrivial possibility for studying the nature of interaction of Jahn-Teller centers. As far as we know, this is the first quite distinct, but masked by other interactions, spectroscopic observation of the interaction via the phonon field.

[1)] For Cu^{2+} concentrations greater than 3%, exchange-coupled pairs, which we shall not discuss here, were also observed in the EPR spectrum.

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