Short Notes

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Kazan Physico-Technical Institute, Academy of Sciences of the USSR, Kazan (a), and Institute of Chemistry, Far-East Research Centre, Academy of Sciences of the USSR, Vladivostok (b)

The Depression of the Dynamic Jahn-Teller Effect

By

A.M. ZIATDINOV (a), M.M. ZARIPOV (a), YU.V. YABLOKOV (a), and R.L. DAVIDOVICH (b)

The phenomena connected with the Jahn-Teller distortion of complexes in the presence of degenerate electronic states result in consequences important in solid state physics (1, 2). The study of transitions between the potential minima of Jahn-Teller centres gives, in particular, rich information on the dynamics of the crystal lattice. Special interest might have the controllable depression of the Jahn-Teller effect by means of external action, for example, of uniaxial pressure as one obtains artificially a non-equivalency of the energy of the centres. But all attempts to carry out such experiments were unsuccessful.

In this note we report results of similar investigations of the distortion of $Cu(H_2O)_6^{2+}$ octahedra which appear during the structural phase transition in $Zn_{1-x}Cu_xGeF_6{\cdot}6H_2O$ (x = 0.01, 0.1, 0.2). The electron spin resonance (ESR) of $Zn_{1-x}Cu_xZrF_6{\cdot}6H_2O$ in which the phase transition is absent has been studied, too. Both matrices refer to the space group $R\bar{3}$ with Z = 1.

It has been proved experimentally that in $(Zn, Cu)ZrF_6{\cdot}6H_2O$ at 4.2 K $Cu(H_2O)_6^{2+}$ octahedra are fixed by local deformation of the crystal lattice in three equivalent potential wells, to which distortions along the <100> directions correspond. The ESR spectrum parameters at a given temperature are equal to: $g_\perp = 2.102$, $g_\parallel = 2.470$, $A_\perp = 17$ Oe, $A_\parallel^{63} = 91$ Oe, $A_\parallel^{65} = 97$ Oe.

The increase of relaxational transition probabilities between vibronic energy levels leads to an averaging of the static ESR spectrum in the interval 4.2 to 48 K. Above 48 K the weak anisotropic dynamic spectrum ($g_\perp = 2.221$, $g_\parallel = 2.234$, $A_\perp = 26$ Oe, $A_\parallel = 22$ Oe) is observed which consists of a hyperfine structure quartet of lines which widens to one signal after 100 K.

The similar picture is observed in $Zn_{1-x}Cu_xGeF_6 \cdot 6H_2O$ crystals but in this case for the first time the transition of the dynamic spectrum into a static one has been discovered for Jahn-Teller centres at an unusually high temperature and occupying an anomalously large interval. The dynamic spectrum is observed while cooling of the crystal to 191 K ($g_\perp = 2.225$, $g_\parallel = 2.219$, $A_\perp = 25$ Oe, $A_\parallel = 19$ Oe), then its intensity sharply reduces and in the interval 191 to 194 K it is transformed into a new spectrum which corresponds to six crystallographically non-equivalent centres. This spectrum has the following peculiarities: a) the components of g and A tensors greatly depend on T in the interval 40 to 180 K (Fig. 1), but the average $(g_\parallel + 2g_\perp)/3$ and $(A_\parallel + 2A_\perp)/3$ values remain constant; b) the $g_i(T)$ and $A_i(T)$ curves are saturated at $T \approx 40$ K taking $g_\perp = 2.104$; $g_\parallel = 2.471$, $A_\perp = 16$ Oe, $A_\parallel = 93$ Oe (Fig. 1).

It is possible to freeze a high-temperature phase of $Zn_{1-x}Cu_xGeF_6 \cdot 6H_2O$ (with $x \gtrless 0.1$) crystals by means of sharp cooling up to 77 K or 4.2 K. Then the Jahn-Teller centres at low temperatures behave as in $(Zn, Cu)ZrF_6 \cdot 6H_2O$ and their ESR parameters at 4.2 K coincide with the quantities to which g_i and A_i tend at lowering T beyond $T_{ph.t.}$

The paramagnetic resonance evidences that one of the directions of the tetragonal distortion of the $Cu(H_2O)_6^{2+}$ octahedron becomes energetically more favourable than the two others at phase transition and the octahedron is localised in a corresponding state. But the strong dependence of $g_i(T)$ and $A_i(T)$ indicates the ability of octahedra to change the orientation of distortion. In fact, if one of the potential wells is lower than two others by Δ , then due to the relaxational reorientation of the distortion axes of complexes the observed values of g and A tensors are defined in the following form if the form of the ESR lines is not taken into account:

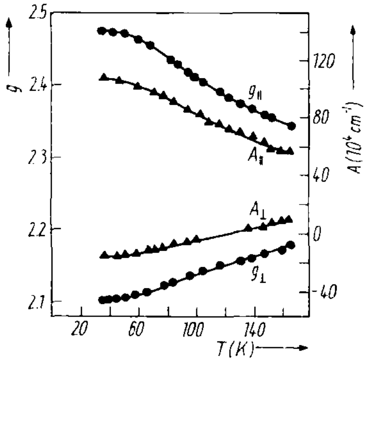

Fig. 1. The temperature dependence of ESR spectra parameters of the Cu(II) ion in $Zn_{0.9}Cu_{0.1}GeF_6 \cdot 6H_2O$ crystals after phase transition. Symbols ● and ▲ refer to the experimental values of g and A tensors, respectively

$$g_{\parallel}(T) = (K/K+2)g_{\parallel}^{*} + (2/K+2)g_{\perp}^{*};$$
$$g_{\perp}(T) = (K/K+2)g_{\perp}^{*} + (1/K+2)(g_{\parallel}^{*} + g_{\perp}^{*}),$$
$$A_{\parallel}(T) = (K/K+2)A_{\parallel}^{*} + (2/K+2)A_{\perp}^{*},$$
$$A_{\perp}(T) = (K/K+2)A_{\perp}^{*} + (1/K+2)(A_{\parallel}^{*} + A_{\perp}^{*}).$$

Here $K = (N_1/N_2) = \exp(\Delta/kT)$, N_1 and N_2 is the population of the lower and each of the two higher potential wells. g_i^* and A_i^* equals g_i(4.2 K) and A_i (4.2 K), respectively. The identity of the low temperature ESR spectrum parameters of $Zn_{1-x}Cu_xGeF_6 \cdot 6H_2O$ after the phase transitions and in the frozen state shows that during the phase transition only one of the potential wells is distinguished; the value and the character of octahedron distortion remain Jahn-Teller like. Using the low temperature g and A values we find $\Delta = 154\ cm^{-1}$.

Taking the correlation $\Delta = kT\ln K = V(e_{zz} - e_{xx})$, where V is the bonding parameter $\approx 15000\ cm^{-1}$/(unit strain) (3), e_{jj} are the strain coefficients, and using for elastic constants their values in $ZnSiF_6 \cdot 6H_2O$ (4) we can estimate the quantity of the axial pressure P (3 to 4 kbar) for the <100> directions which can lead to the observed non-equivalency of minima.

Taking into consideration the great demands to the mechanic strength of crystals and considering the non-effectiveness of the hydrostatic pressure we conclude that the study of the Jahn-Teller complexes in the conditions of phase transition is the most real experiment for investigation of minimisation conditions of the energy of systems with electronic degeneracy (in our case it is the only possible way).

References

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