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THE NATURE AND DYNAMICS OF THE DISTORTIONS OF JAHN-TELLER CENTRES UNDER LOW-SYMMETRY PERTURBATIONS

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Abstract The results of the EPR study of the behaviour of Jahn-Teller (JT) $Cu(H_2O)_6$ centres in $ABF_6 \cdot 6H_2O$ type crystals under low-symmetry perturbations are reported. The following questions are considered: a)the nature of the distortions of JT fragments of structure and the symmetry of lattice; b)the correlation of the distortions of the nearest JT configurations; c)the dependence of the configuration of a pair of JT centres on lattice parameters; d)the dynamics of distorted JT systems.

Introduction It is known from the static problem of JT effect that if E orbital state splitting is small (of the order of local deformation) JT pseudo-effect is equivalent to the corresponding JT effect and at the intermediate splittings (of the order of square terms of electronic-vibrational interaction) the presence of the vibronic bonding may lead to essentially new and important results. The results of the EPR spectra analysis of Cu(II) in $Zn_{1-x}Cu_xBF_6 \cdot 6H_2O$ type crystals obtained serve as one of the confirmations of this idea.

Results and discussions In a series of compounds of the $ABF_6 \cdot 6H_2O$ type the structural phase transition of the first type takes place, as a result their symmetry lowers from rhombohedral to monoclinic /1/. In monoclinic crystals E levels of the doped Cu(II) ions split. However Cu(II) EPR spectra in the monoclinic phase of the crystals mentioned (the experimental data may be summarized as follows: 1)a static EPR spectrum with temperature dependent parameters is observed below $T_{ph.t.}$; 2)the spectrum remains axial after phase transition; 3)the curves $g_{\parallel}=g_{\parallel}(T)$ and $g_{\perp}=g_{\perp}(T)$ depend on Cu(II)concentration but tend to one limit at 4.2K; g_i values at 4.2K are equal to the values of static JT spectrum parameters in the same crystal without phase transition; all above-stated is valid for $\{A\}$; 4)the average $\langle g \rangle$ and $\langle A \rangle$ values are temperature independent) and their analysis have shown /2, present paper/that inspite of the influence of the low-symmetry external perturbation removing E level degeneracy the distortion of the $Cu(H_2O)_6$ remains JT and has a dynamic nature. In other words in this crystal phase of $Zn_{1-x}Cu_xBF_6 \cdot 6H\ O$ the intermediate situation actually realizes. Then the temperature and concentration dependence of the Cu(II) EPR spectra parameters in the crystal phase in question shows that the positions of the minimums of adiabatic potential in the space of normal coordinates of JT centres and hence the distortions of magnetic fragments connected with them depend on temperature and Cu(II) concentration. Even more interesting situation arises when low-symmetry perturbation removing E level degeneracy is connected with the presence of another magnetic centre in the nearest crystalline lattice site. In particular, the analysis of the EPR spectra of JT pairs of Cu(II) ions in $Zn_{1-x}Cu_xZrF_6 \cdot 6H_2O$ crystals has shown /3/ that in such cases JT distortions of the nearest centres are not independent. Besides it was proved that in $Zn_{1-x}Cu_xBF_6 \cdot 6H_2O$ type crystals the correlation character depends on the lattice parameter, changing from ferrodistortional in $Cu_x Zn_{1-x}ZrF_6 \cdot 6H_2O$ crystal to antiferrodistortional in $Zn_{1-x}Cu_xSiF_6 \cdot 6H_2O$ crystal. We have investigated the temperature dependence of the EPR spectra of JT pairs of Cu(II) ions in $Zn_{0.8}Cu_{0.2}ZrF_6 \cdot 6H_2O$ crystal. It was proved that as the temperature dependence of the width and position of the HFS lines in half-fields is concerned, the picture of the pair spectrum transformation is analogous to the temperature dependence of the Cu(II) single ion EPR spectrum in the same matrix. However the important differences were discovered. Firstly, the maximum temperatures (≃90K) at which the traces of ferrodistortional pair spectrum may be observed are essentially higher than the corresponding temperatures (≃50K) for the static JT copper single ion spectrum in the same matrix. Secondly, if the static JT spectrum of the single Cu(II) ion vanishes in the interval of 40÷50K, transforming into a new dynamic EPR spectrum, the ferrodistortional pair spectrum stops to be observed without creation of any new lines of absorbtion. In principle the temperature changes of the half-field Cu(II) pair EPR spectrum described above may have double origin. They may be connected either with the phonon-induced tunnelling between three equivalent potential wells to which the ferrodistortional ordering of the distortions corresponds or with the breaking of the distortion correlation itself. In any case it is clear that the difference between energies of stabilization of ferrodistortional or antiferrodistortional pairs in the matrix investigated is more or about 60 cm^{-1}.

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