# The plasticity of the $Cu(H_2O)_6^{2+}$ Jahn–Teller complex affected by lattice strains and cooperative interactions

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The EPR spectra evolution of $Cs_2Zn_{1-x}Cu_x(ZrF_6)_2 \cdot 6H_2O$ ($x = 0.01$, 0.6, 0.8, and 1.0) in the temperature range $4.2-330$ K and the $X$-ray structure analysis of the compound with $x = 1.0$ in the range $150-327$ K show that the Jahn–Teller (JT) complex $Cu(H_2O)_6$ coordination sphere undergoes a plastic deformation. The observed effect is due to the combined influence of small lattice strains existing in the para-phase and a new one appearing as a result of a ferroelastic phase transition and increasing with the temperature decrease below $T_c$. It is proved that both cooperative interactions between JT complexes and ferroelastic strain stabilise the some JT configuration. The problem of instability of a compressed at $T \sim 265$ K JT configuration is discussed.

EPR study of a series of compounds $Cs_2Zn_{1-x}Cu_x(ZrF_6)_2 \cdot 6H_2O$ $(0.01 \le x \le 1)$ for $x \ge 0.6$ has shown an extremely strong temperature dependence of resonance line positions [1]. Temperature dependencies of all the three principal values of the $g$-factor indicate very weak lattice deformations of the position occupied by the Jath–Teller (JT) $Cu(H_2O)_6^{2+}$ complex, i.e. very small differences in the energy of its possible JT configurations. Such situation remains weakly investigated and gives interesting possibilities for the study of JT dynamics.

Recently, a new light on this problem was thrown by structural and EPR studies [2,3]. It was found that the ferroelastic phase transition take plase in $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ at 320 K followed by the gradual change of $Cu(H_2O)_6$ configuration from tetragonal elongated along one $C_4$ $(Cu-O_3 \equiv R_3)$ direction through tetragonal compressed along another $C_4$ axis $(Cu-O_1 \equiv R_1)$ at $\sim 265$ K to elongated again along the third $C_4$ axis $(Cu-O_2 \equiv R_2)$ at $\sim 150$ K. The temperature dependencies of the $R_k$ are shown in Fig. 1 where the main structural results of the paper [3] are collected. On a basis of these data, the EPR results were interpreted in the framework of the continuous transformation of the adiabatic potential surface of the weakly deformed complex. Ferroelastic strains appearing after phase transitions and cooperative JT interactions were considered as the reasons of dramatic changes of structure and EPR parameters. We shall analyse here these processes in more detail focusing our attention on the reasons and mechanisms of the transformations in question. The EPR data of the diluted compounds will be taken into consideration. $X$- and $Q$-band EPR studies were performed in the temperature range of $4.2-330$ K.

## Results and discussion

The temperature dependencies of $g$-values for the compounds with $x = 0.8$ and 0.6 compared with data for $x = 1$ and 0.01 are shown in Fig. 2. We shall analyse them in the way described previously [3].

The universal factors stabilising the definite JT configuration and determining JT complex dynamics are low symmetry strains in the crystal and cooperative interactions between JT complexes [4]. The octahedral complex is elongated along $R_3$ in the para-phase of the $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ crystal with the symmetry *Pmnn*. The corresponding minimum on the adiabatic potential surface in the $\rho_0\varphi$ coordinate space corresponds to $\varphi = \varphi_0 = 0$ and is lower than two others by $\delta E_{3-1(2)} \equiv \delta_{31(2)} = 230$ cm$^{-1}$ (Fig. 3). The ferroelastic transition to the phase with the $P2_1/n$ symmetry leads to appearance of some additional deformation, which sharply arises at $T_c \cong 320$ K and then gradually increases in the temperature interval $320-(\sim 180-200)$ K and results in the smooth change of the $g_2(R_2)$ and $g_3(R_3)$ values. The spontaneous strain appearing below the ferroelastic phase transition has a certain component along $R_2$ with $\varphi = \varphi_0 + 120°$ and increases with the temperature decrease. The resulting deformation also increases with the temperature decrease. Its direction changes from $\varphi = 0$ and at about 265 K leads to the configuration compressed along $R_1$ (with $R_2 = R_3$) for $\varphi = 60°$. With further temperature decreasing, the resulting deformation changes resembling the behaviour of the $b$, $c$ and monoclinic angle $\beta$ (Fig. 1). The last one can be considered as the phase transition order parameter. At low temperatures, the $Cu(H_2O)_6$ complex configuration is again nearly tetragonal, but elongated along $R_2$ with
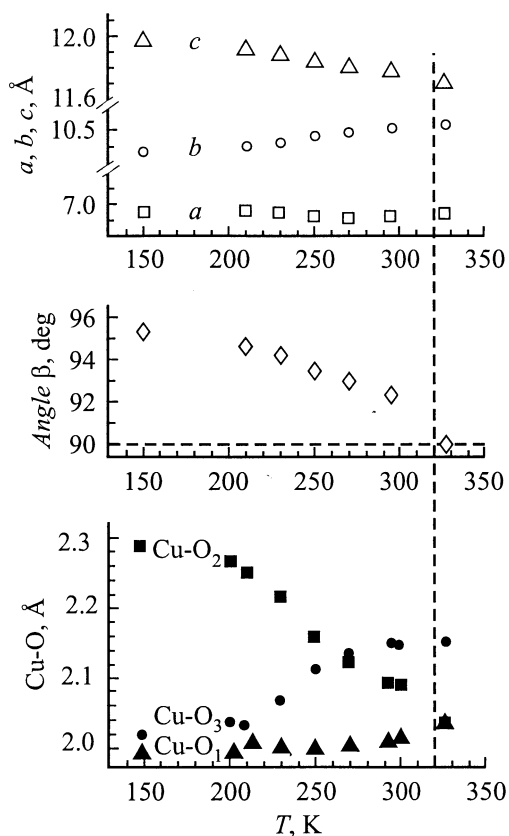
**Figure 1.** Temperature dependencies of the unit cell parameters and Cu−O distances.

$\varphi = 120°$. All these transformations result in the change of the adiabatic potential surface, and this change can be treated as a manifestation of plasticity of the JT complex coordination sphere [4].

In the discussed transformations, the cooperative JT interactions are also taken into consideration. Their existence is proved directly by the differences in the temperature dependencies of $g_k(T)$ for various copper concentrations (Fig. 2). Decreasing of the JT ion concentration moves the interval of strong $g_{2,3}(T)$ changes from the $180-250$ K region for $x = 1$ to regions of $80-180$ K for $x = 0.8$ and of $70-170$ K for $x = 0.6$ respectively. According to [1], the cooperative interactions in $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ occur through the phonon field, i.e. through the vibrations of the crystal lattice. They diminish because of increase of the distances between JT ions and thermal vibrations of the crystal lattice.

In the $Cs_2Zn_{1-x}Cu_x(ZrF_6)_2 \cdot 6H_2O$ crystals with $x < 1.0$, the cooperative interactions stabilise the same configuration elongated along $R_2$ as in the crystal with $x = 1.0$. It was shown by X-ray investigations of the crystals with $x = 1$ [3] and by the EPR study of the crystal with $x = 0.01$ [5]. The equality of the low temperature $g_i(T)$-values (at 4.2 K) and nearly equal high temperature $g_i(T)$-values (at 300 K) in all considered crystals allows us to spread this conclusion

on $x = 0.6$ and $0.8$ cases. These facts lead to the conclusion that both ferroelastic strains and cooperative JT interactions stabilise the same configuration of the JT $Cu(H_2O)_6$ complex. The ferroelastic deformation does this smoothly, the cooperative interactions result in the sharp dependencies of $g_k(R_r)$ parameters. This action of the cooperative interaction was confirmed by the theoretical analysis [1]. Energy of the cooperative interactions, $E_{coop}$, can be estimated due to the analysis of temperature behaviour of the intervals between different JT configurations [3]. As it is shown in Fig. 3, the values of $\delta_{23}$ (between the ground and first excited configuration), diminish from $\approx 420$ cm$^{-1}$ in $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$, $E_{coop}$ down to $\sim 200$ cm$^{-1}$ in the crystal with $x = 0.8$ and down to $\sim 180$ cm$^{-1}$ in a for $x = 0.6$.

As the crystal with $x = 0.01$ has shown ferroelastic properties [5], the character of $g_k(T)$ dependencies (the intermediate $g$-value increases up to $225-250$ K and then decreases above 250 K) allow us to postulate the existence of a hypothetical phase transition at $T_c \sim 550$ K in this crystal. The collected EPR data suggest a presence of such a phase transition also in the crystals with $x = 0.8$ and 0.6. First of



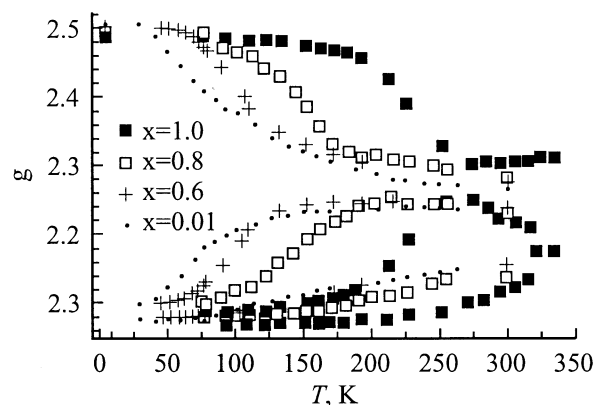**Figure 2.** Temperature dependencies of principal values of $g$-factor in $Cs_2Zn_{1-x}Cu_x(ZrF_6)_2 \cdot 6H_2O$ with $x = 0.01, 0.6, 0.8$ and $1.0$.
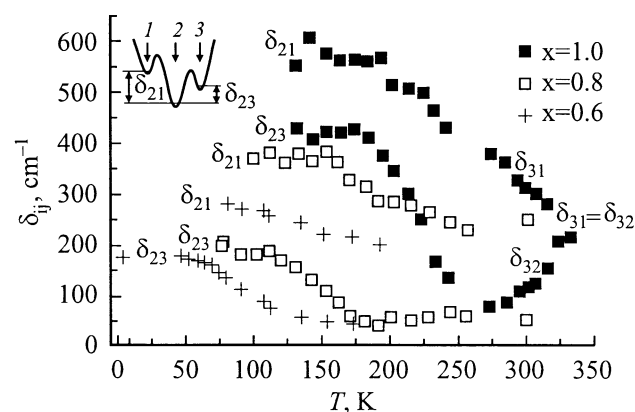


**Figure 3.** Temperature dependencies of the energy intervals $\delta_{mn}$ between JT configurations corresponding to minimums of the adiabatic potential surface for $x = 0.6, 0.8$ and $1.0$.

all we take into consideration the analogous convergence of the $g_{2,3}$ (g-latge and g-intermediate) components in these crystals with $x = 0.6$, 0.8 and 1.0 and the mentioned tendency of the diminishing of g-intermediate (it should be equal to $g_1$ (g-small) at $T > T_c$). EPR does not allow to determine directly would the change of the axes directions occur in these crystals. This can be done only by structural studies which are in progress. However, the positive answer to this question can be obtained in the indirect way from the other data. We shall discuss this situation in more detail.

Structural studies of $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ show the equalising and reversing of $R_2$ and $R_3$ bond lengths but EPR studies do not show the expected equalising of $g_{2,3}$-components. It would appears that the compressed configuration with $R_2 = R_3$ is stable in the conditions of the structure determination but it is not stable from the EPR point of view, tumbling down into configurations with $R_2 > R_3$ or $R_3 > R_2$. Let us return to the $x = 1$ crystal. From $T_c$ down to of about 280 K, the $g_3$-value decreases when the $g_2$-value increases. The $g_1$-value decreases also but we concentrate onto two first values. Then, with in the interval of about 20 degrees these g-components are relatively close but without observable crossing. We shall name this interval as the range of instability. Here, the configuration of the octahedron is very close to a compressed one and we postulate that the configuration of the compressed octahedron is unstable. One can conclude that this is manifestation of a more general feature of the instability in the conditions of degeneration. As concerned the X-ray diffraction data, we should point out that this method can not distinguish between the dynamic and space averaging. If the instability results in the simultaneous existence weakly deformed complexes with different elongation direction the diffraction averages out this difference to zero giving the same result as the dynamic averaging. The supposition that the similar situation repeats for the crystals with $x = 0.8$ and 0.6 is reasonable. It is obvious that at low temperatures $Cu(H_2O)_6$ octahedrons are elongated along $R_2$ in all crystals. It does not seem realistic that at high temperatures the configuration of the $Cu(H_2O)_6$ complex elongated along $R_3$ for $x = 1$ (the hypothetic configuration for paraelastic phase for $x = 0.01$) would be different for crystals with $x = 0.8$ and 0.6. Transition from the high temperature to the low temperature configuration requires the existence of the transitional range with a principal compression along $R_1$. The character of $g_k(T)$ dependencies in the corresponding ranges in the crystals with $x = 0.8$ and 0.6 are very similar. It is no wonder as the temperature changes of the ferroelastic deformations are very small in these compounds and the cooperative stabilisation starts at lower temperatures.

Thus, the main result of the study of the $Cs_2Zn_{1-x}Cu_x(ZrF_6)_2 \cdot 6H_2O$ crystals is the discovery of the continuos changes of the JT complex configuration initiated by temperature dependent ferroelastic strains and supported by cooperative vibronic interactions. This fact is the manifestation of the plasticity of the JT complex

coordination sphere as one of the fundamental properties of its behaviour. The concept of plasticity was introduced to describe the JT complex unusual abilities to adapt to the conditions produced by various crystal lattices [4,6] when changes of axial and plane bond lengths are mutually depended. In the crystal studied, the plasticity of the coordination sphere was firstly observed directly as a modification of the complex shape reflecting the lattice changes.

The correlated influence of ferroelastic strains and cooperative JT interactions on the stabilisation of the definite JT configuration in the crystal in question should be accented. It was also concluded that cooperative JT interactions in the crystal studied are not the reason of the ferroelastic phase transition. But at the same time, the JT $Cu(H_2O)_6$ complexes were shown to influence extremely strong the temperature of the phase transition.

Of special interest is the question about the structural instability of the JT configuration compressed in the result of the external factors. Of course, the reasons of non-averaging of two rhombic configurations at relatively high temperature should be analysed. We suppose that this effect is connected with the ferroelastic properties of the compounds studied. The existence of the ferroelastic domains and boundaries between them can produce heterogeneous or random strains, which strongly influence the EPR spectra of the JT ion [7]. It is important that the conditions of the formal degeneration of two JT configurations can be exactly fulfilled in the crystals studied. This allows the accurate consideration of the posed problem.

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