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Pressure-Controlled Plasticity of $Cu(H_2O)_6{}^{2+}$ Complex and Phase Transition in $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$

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The X-band EPR study of a polycrystalline $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ demonstrates a feature of plasticity of the Jahn–Teller $Cu(H_2O)_6$ complex in the crystal lattice of this compound. The temperature- and pressure-induced evolution of the spectra shows that the copper complex is extremely sensitive to these factors, which due to the ferroelastic properties of the compound studied modify the internal tetragonal and orthorhombic strains acting on the complex. It is supported by the analysis of the temperature dependencies of the principal values of the **g**-factor under various pressures, indicating that the complex varies its shape adapting it to the varied conditions. A pressure-induced phase transition is discovered.

Plasticity of the Jahn−Teller (JT) complex is a term describing a unique feature of the interrelated changes of the plane and axial bond lengths of the complex adapting it to the conditions determined by the crystal lattice.[1] This feature is responsible for the differences in the shape, symmetry, and dynamics of the JT complex in various crystals. Recently, we have observed the effect of plasticity in one specific compound. It was manifested as temperature induced dramatic changes of the shape and the elongation direction of the $Cu(H_2O)_6$ complex in the $Cs_2Cu(ZrF_6)_2 \cdot 6H_2O$ crystal.[2] The observed effects have been related to the ferroelastic phase transition discovered at $T_c = 320$ K. This type of phase transition produces a spontaneous temperature-dependent strain,[3] which in the case studied modifies the internal strains in the crystal and in this way influences the shape of the copper complex. The modification of the adiabatic potential surface resulting in the switch of the elongation direction of the $Cu(H_2O)_6$ complex was earlier observed only in the deuterated copper ammonium Tutton salt as induced by the hydrostatic pressure.[4] It is also known that in the ferroelastic material a relatively low external pressure could modify internal strains. Therefore, we have decided to check the influence of external pressure on the features of the $Cu(H_2O)_6$ complex in the title compound.

Our measurements were carried out on the powdered sample with the use of X-band EPR spectrometer and the high-pressure equipment described previously.[5] Spectra were analyzed by the standard methods. For the highly averaged spectra in the temperature range ∼250−325 K the characteristic *g*-values were chosen based on the comparison of Q-band[2] and X-band spectra under ambient pressure. We have carried out measurements in two regimes: under a constant pressure (Figure 1) and under a constant temperature (Figure 2). Recorded spectra yield essential information about changes of the $Cu(H_2O)_6{}^{2+}$ complex configuration.

The temperature dependencies of the spectrum under the pressure 100 and 150 MPa (Figures 1a,b and 3a) resemble those observed under ambient pressure. At high temperatures (265−320, 225−320, and 200−320 K for 0.1, 100, and 150 MPa, respectively) EPR spectra are strongly averaged, but their analysis reveals many similarities. (i) All three **g**-tensor components are temperature dependent, which points to small deformations of the octahedral complex. (ii) The *g*-values of the rhombic spectra practically coincide, and for pressures of 0.1, 100, and 150 MPa the differences between the largest and intermediate g-values are the same. (iii) The low-temperature values of the **g**-tensor indicate the tetragonal symmetry of the complex. The main difference between the spectra observed under elevated pressure and those under ambient pressure is the pressure-dependent shift of the temperature range in which the strong dependencies of the principal values of the *g*-factor are observed. The above analysis allows us to interpret the pressure-affected spectra analogously to those observed under ambient pressure.[2] Therefore, we can assume that, up to a pressure of 150 MPa, a transformation from the slightly deformed orthorhombic

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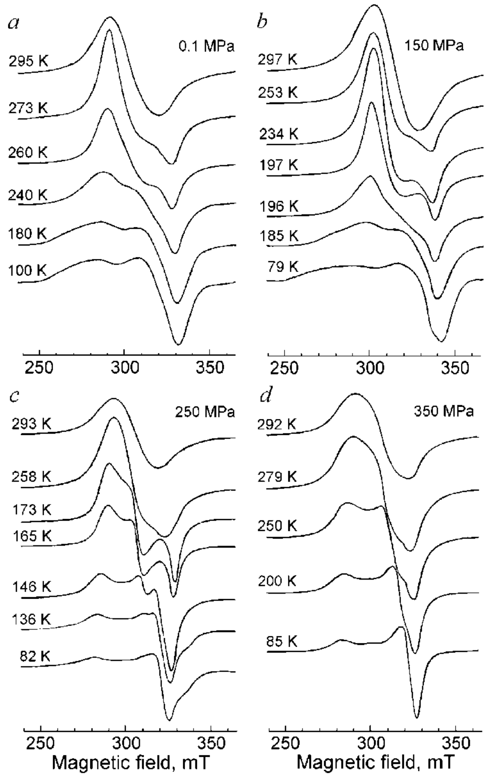

Figure 1. Temperature evolution of the X-band EPR spectra under various pressures. Spectra a and b correspond to Figure 3a and spectra c and d to Figure 3b. The pressure was applied at room temperature.

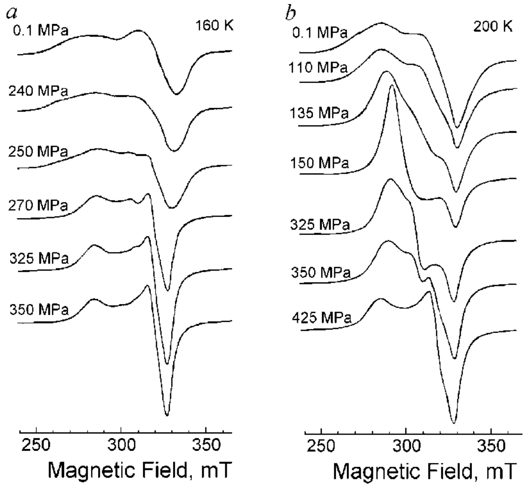

Figure 2. Pressure-induced evolutions of the EPR spectra at constant temperature, which was established at the ambient pressure.

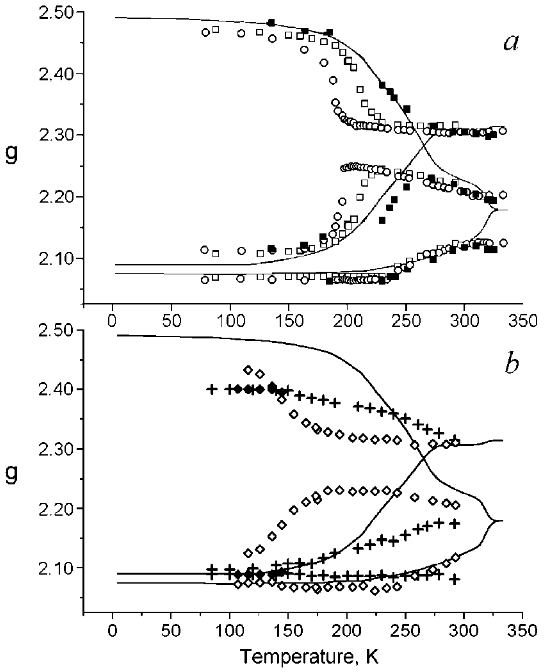

Figure 3. Temperature dependencies of the principal values of the **g**-tensor. (a) For ambient pressure: — (Q-band data[2]); ■ (X-band data). For 100 MPa: □. For 150 MPa: ○. (b) For 250 MPa: ◇ and ◆, the additional spectrum (◆) corresponding to the configuration compressed along the Cu−O$_1$ direction. For 350 MPa: +, the configuration compressed along the Cu−O$_1$ direction. For comparison: the Q-band data for the ambient pressure, lines (—) are drawn.

configuration with the longest Cu−O$_3$ bond to that elongated along the Cu−O$_2$ direction takes place. Due to the overlapping of the signals, we could not determine exactly the temperature of this transformation. However, we noted an extension of the temperature range in which EPR spectra correspond to the slightly deformed configuration.

The situation becomes more complicated and interesting at higher pressures. Figure 3b shows the $g(T)$ dependencies for 250 and 350 MPa. For 250 MPa at temperatures down to ~190 K a strong averaging of the two higher g-values takes place just as it was observed under lower pressures. A further temperature decrease results in the transformation (at ~173 K) to the rhombic spectra; then at ~146 K, a new tetragonal spectrum appears abruptly. Its parameters differ significantly from those of the low-pressure spectrum at the corresponding temperatures. However, some amount of complexes remains in the previous configuration, and below 146 K the spectrum gradually transforms into that similar to the low-pressure spectra. The coexistence of two spectra is observed down to low temperatures. In our opinion this indicates a pressure-induced phase transition.

The properties of the configuration corresponding to the tetragonal spectrum can be described on the basis of the temperature dependencies of the spectra recorded at 350 MPa (Figures 1d and 3b). Under this pressure the $g(T)$ dependencies do not show any anomalies. It can be noticed that the lowest g-value (the shortest Cu−O$_1$ bond) is not dependent on temperature and the low temperature tetragonal spectra resemble those appearing abruptly at 146 K at 250 MPa. We assume that the pressure of 350 MPa induces a transformation of the sample to a new phase already at room temperature. The $g(T)$ dependencies for this phase are similar to those observed for the Tutton salts and indicate the tetragonal compression along the Cu−O$_1$ direction.

The measurements performed at $T =$ constant have shown that the character of transformations strongly depends on temperature. At $T = 160$ K (Figure 2a) an abrupt transformation with a pressure hysteresis, from the spectrum characteristic of low pressures to that assigned to the new phase, is observed. But above 170 K (for $T = 200$ K, see Figure 2b) the spectra transformations are gradual going from those characteristic of the elongated configuration through the tetragonally compressed to the rhombic, and then the spectra characteristic of the tetragonally elongated configuration in the pressure-induced phase appear. The spectrum shown in Figure 2b for 350 MPa obviously differs from the spectrum shown in Figure 1d for 200 K, indicating that the sequence of transformations depends on the regime of the experiment.

For pressures up to 250 MPa we can notice the pressure-generated shift of the strong $g(T)$ change to the low-temperature region. In our case the appearance of this strong dependence is stipulated by the cooperative JT interactions.[2] It seems that the hydrostatic pressure changes the contribution of various vibrational modes participating in the cooperative JT interactions[6] and decreases the contribution of the ferrodistortive correlations stabilizing the ground state.

Initially the hydrostatic pressure increases T_c of the ferroelastic phase transition but does not strongly affect the complex deformations. However, a pressure of 250 MPa is high enough to induce an additional lattice deformation. It leads to the narrowing of the line width of the rhombic spectrum resulting from the tetragonally compressed complex and finally to a phase transition at 146 K**.** The pressure-induced transformations of the spectra at a constant temperature can be described in an analogous way. At 200 K a gradual increase of the hydrostatic pressure leads to the tetragonal spectrum of the slightly deformed complex; then the pressure produces additional deformation. This results first in the appearance of the rhombic spectra and then in a phase transition to the new phase. At 160 K the pressure necessary to modify the cooperative interactions is higher than the pressure inducing the phase transition.

Summarizing, we can conclude that the JT $Cu(H_2O)_6^{2+}$ complex in the crystal lattice of $Cs_2Cu(ZrF_6)_2{\cdot}6H_2O$ clearly manifests its feature of plasticity by changing the shape and adapting it to the conditions varied by the hydrostatic pressure and temperature.

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