Influence of the interaction of polymeric chains on thermal transitions of Jahn—Teller exchange clusters in compounds of "breathing" crystal family

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Based on the method of random field distribution functions in Ising magnets, for the first time a theoretical description of thermal transitions in Jahn—Teller exchange clusters is suggested, which takes into account the interactions of polymeric chains in "breathing" crystal compounds. It was shown that the inclusion of this interaction can lead to both an intensification of spin-crossover type cooperative transitions in exchange clusters and their deceleration. The approach in question is generalized to include non-Jahn—Teller metal impurities in "breathing" crystals, which suppress cooperative effects in thermal transitions of Jahn—Teller exchange clusters. The obtained results qualitatively reproduce the temperature dependencies of magnetic properties of solid solutions Cu1—xNix(hfac)2LR (hfac is hexafluoroacetylacetonate anion, ligand LR is nitronyl nitroxide radical with pyrazole substituent at the second position of the imidazoline ring) when R = Et.

Key words: molecular magnetics, exchange cluster, spin-crossover, effective magnetic moment.

Intensive studies of "breathing" crystal compounds have been going on for over 10 years.1—4 An enduring interest towards these compounds is caused by a large variety of magneto-structural properties which they demonstrate under changing temperature, application of external pressure, or irradiation with light. "Breathing" crystals are polymeric chain complexes based on copper(II) hexafluoroacetylacetonate with stable nitroxide radicals, which are characterized by a strongly pronounced Jahn—Teller instability of coordination units. The polymeric chains of "breathing" crystals are a sequence of alternating three-spin exchange clusters >N—O—Cu2+—O—N< and coordination centers with isolated copper >N—Cu2+—N<. "Breathing" crystals consisting of polymeric chains of two-spin exchange clusters >N—O—Cu2+—N< also exist. Earlier, the possibility of sharp thermal rearrangement of exchange clusters of "breathing" crystals was studied theoretically using one-dimensional models.5,6 If the dependence of the exchange interaction on the Cu2+—O axial bond length is taken into account, then such models can...
describe both the cases of gradual temperature change of the mean distance Cu²⁺—O and the sharp jumps, which have a phase transition-like character. Apart from that, they qualitatively correctly describe the transformation of magneto-structural anomalies in "breathing" crystals when applying external hydrostatic pressure and the specific features of self-decelerating kinetics of the relaxation of photoexcited states of "breathing" crystals at low temperature. It was shown that to describe the temperature properties of a chain of three-spin exchange clusters, one can be restricted to the states of unit cells 2 and 3 (Fig. 1). The two other states, corresponding to flattened or elongated states of both coordination centers of the chain unit cell, are higher in energy by several thousands of reciprocal centimeters than the state shown in Fig. 1. Later we will assign an effective Ising spin value \( s = 1 \) to the state 2, and \( s = -1 \) to the state 3. The state 2 is characterized by a three-spin exchange cluster octahedron flattened along the polymeric chain, which is most often the ground state of the unit cell (see Fig. 1). The neighboring copper coordination center within the cell (octahedron CuO₄N₂) is characterized by an elongated Cu²⁺—N axial bond. The higher state 3, on the other hand, has an elongated Cu²⁺—O axial bond in the octahedron CuO₆ of the three-spin exchange cluster and a shortened Cu²⁺—N axial bond in the neighboring coordination center CuO₄N₂. In this work we will discuss the properties of "breathing" crystals which have a head-to-toe motif of polymeric chains, i.e., contain chains of three-spin exchange clusters.

The limitation of exactly solvable one-dimensional model equations is the impossibility of their use to describe hysteresis magneto-structural transitions in a chain of exchange clusters, unless the equations are based on mean (deformation) field theory. Apart from that, in the one-dimensional case it is impossible to take into account interaction of the vibrational-rotational degrees of freedom \( \nu_2 \) and \( \nu_3 \), and the spin partition functions \( Z_s^{(2)} \) and \( Z_s^{(3)} \). Spin partition functions are determined by the spin-Hamiltonian of the unit cell in states 2 (effective Ising spin \( s = 1 \)) and 3 (\( s = -1 \)) and in the case of three-spin exchange clusters have the following form:

\[
Z_s^{(2)} = \exp \left[ -2J^{(2)} \left( \hat{S}_{Cu} \cdot \left( \hat{S}_{R_1} + \hat{S}_{R_2} \right) / T \right) \right] = 2e^{-2J^{(2)} T} \left( 1 + e^{2J^{(2)} T} + 2e^{3J^{(2)} T} / T \right),
\]

\[
Z_s^{(3)} = \exp \left[ -2J^{(3)} \left( \hat{S}_{Cu} \cdot \left( \hat{S}_{R_1} + \hat{S}_{R_2} \right) / T \right) \right] = 2e^{-2J^{(3)} T} \left( 1 + e^{2J^{(3)} T} + 2e^{3J^{(3)} T} / T \right),
\]

where \( \hat{S}_{Cu} \), \( \hat{S}_{R_1} \), and \( \hat{S}_{R_2} \) are the electron spin operators of the copper ion and radicals 1 and 2 of the exchange cluster, while \( J^{(2)} \) and \( J^{(3)} \) are the exchange integrals in the states 2 and 3, respectively. The factors \( \nu_2 \) and \( \nu_3 \) characterize the vibrational-rotational statistical sums of the states 2 and 3 of the unit cell and, in general, can be dependent on temperature and isotopic composition. To simplify calculations, we will not take this dependence into account and will consider \( \nu_2 \) and \( \nu_3 \) as being constant.

**Model of interacting chains**

Using the ground state (2) and the deformation state (3) of the polymeric chain unit cell closest to it in energy (see Fig. 1), the effective spin-structural Hamiltonian of a single crystal of the "breathing" crystal compound is written in the Ising form:

\[
\hat{H} = -\hbar_0 \sum \hat{s}_i - \frac{b}{2} \sum \hat{s}_i \hat{s}_j - \frac{c}{2} \sum \hat{s}_i \hat{s}_j ,
\]

where \( \hbar_0 = -\left( \bar{E}_2 - \bar{E}_3 \right) / 2 \) is the internal "field" measured in energy units. In this approach it determines the energy gap between possible deformation states of the unit cell, which have the energy (for brevity, below assuming the Boltzmann constant \( k_B = 1 \))

\[
\bar{E}_2 = E_2 - T \ln \left( \nu_2 Z_s^{(2)} \right), \quad \bar{E}_3 = E_3 - T \ln \left( \nu_3 Z_s^{(3)} \right).
\]

The difference between the energies \( \bar{E}_2 \) and \( \bar{E}_3 \) in the Hamiltonian \( \hat{H} \) in the expression (1) and the energies of the unit cell \( E_2 \) and \( E_3 \), which can, for example, be calculated by quantum chemistry methods, is related to the contributions of the vibrational-rotational degrees of freedom \( \nu_2 \) and \( \nu_3 \), and the spin partition functions \( Z_s^{(2)} \) and \( Z_s^{(3)} \). Spin partition functions are determined by the spin-Hamiltonian of the unit cell in states 2 (effective Ising spin \( s = 1 \)) and 3 (\( s = -1 \)) and in the case of three-spin exchange clusters have the following form:

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\[
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where \( \hat{S}_{Cu} \), \( \hat{S}_{R_1} \), and \( \hat{S}_{R_2} \) are the electron spin operators of the copper ion and radicals 1 and 2 of the exchange cluster, while \( J^{(2)} \) and \( J^{(3)} \) are the exchange integrals in the states 2 and 3, respectively. The factors \( \nu_2 \) and \( \nu_3 \) characterize the vibrational-rotational statistical sums of the states 2 and 3 of the unit cell and, in general, can be dependent on temperature and isotopic composition. To simplify calculations, we will not take this dependence into account and will consider \( \nu_2 \) and \( \nu_3 \) as being constant.

**Fig. 1.** Significant deformation states, the states 2 (\( s = 1 \), a) and 3 (\( s = -1 \), b) of the polymeric chain unit cell of Jahn—Teller exchange clusters: 1, the coordination center CuO₆; 2, the coordination center CuO₄N₂.