Russian Chemical Bulletin, International Edition, Vol. 66, No.2, pp. 201—207, February, 2017

Full Articles

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

V. A. Morozov[a,b]★ ***and R. Z. Sagdeev***[a,b]

[a]*International Tomography Center Institute, Siberian Branch of the Russian Academy of Sciences,*
3a ul. Institutskaya, 630090 Novosibirsk, Russian Federation
[b]*Novosibirsk State University,*
2 ul. Pirogova, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 333 1399. E-mail: moroz@tomo.nsc.ru

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 $Cu_{1-x}Ni_x(hfac)_2L^R$ (hfac is hexafluoroacetylacetonate anion, ligand L^R 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 $>N—O—Cu^{2+}—O—N<$ and coordination centers with isolated copper $>N—Cu^{2+}—N<$. "Breathing" crystals consisting of polymeric chains of two-spin exchange clusters $>N—O—Cu^{2+}—N<$ 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 $Cu^{2+}—O$ axial bond length is taken into account, then such models can

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 0201—0207, February, 2017.

describe both the cases of gradual temperature change of the mean distance Cu^{2+}—O and the sharp jumps, which have a phase transition-like character.[7] Apart from that, they qualitatively correctly describe the transformation of magneto-structural anomalies in "breathing" crystals when applying external hydrostatic pressure[8] and the specific features of self-decelerating kinetics of the relaxation of photoexcited states of "breathing" crystals at low temperature.[9] It was shown[9] 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 CuO_4N_2) is characterized by an elongated Cu^{2+}—N axial bond. The higher state 3, on the other hand, has an elongated Cu^{2+}—O axial bond in the octahedron CuO_6 of the three-spin exchange cluster and a shortened Cu^{2+}—N axial bond in the neighboring coordination center CuO_4N_2. In this work we will discuss the properties of "breathing" crystals which have a head-to-head motif of polymeric chains, *i.e.*, contain chains of three-spin exchange clusters.

The limitation of exactly solvable one-dimensional model equations[7,10] 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 the interaction of polymeric chains and different kinds of influence of solvent molecules, which can be quite easily integrated into the "breathing" crystal interchain space[11] and considerably alter the magneto-structural properties of the latter. In order to cover these phenomena, in the present work we will develop a new model by considering the influence of the surrounded crystal on a particular unit cell of a polymeric chain as a fluctuating field with some distribution function, which needs to be determined self-consistently. Such an approach to the Ising spin lattice was first suggested by H. Mamada and F. Takano.[12] In this case, the traditional mean-field theory approximation is the limit of the theory[12] under conditions of the fluctuating field distribution function being effectively replaced by one delta-function, *i.e.*, instead of a fluctuating field, its mean value is introduced.

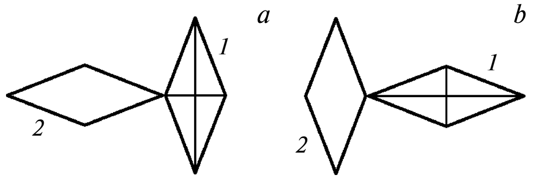

Fig. 1. Significant deformation states, the states 2 ($s = 1$, *a*) and 3 ($s = -1$, *b*), of the polymeric chain unit cell of Jahn—Teller exchange clusters: *1*, the coordination center CuO_6; *2*, the coordination center CuO_4N_2.

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:

$$\hat{H} = -h_0 \sum_i s_i - \frac{c_\parallel}{2} \sum_{(\parallel)} s_i s_j - \frac{c_\perp}{2} \sum_{(\perp)} s_i s_j, \tag{1}$$

where $h_0 = -\left(\tilde{E}_2 - \tilde{E}_3\right)/2$ 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 $k_B = 1$)

$$\tilde{E}_2 = E_2 - T\,\lg\left(\nu_2 Z_s^{(2)}\right),\ \tilde{E}_3 = E_3 - T\,\lg\left(\nu_3 Z_s^{(3)}\right). \tag{2}$$

The difference between the energies $\tilde{E}_2$ and $\tilde{E}_3$ 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 ν_2 and ν_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:

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

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

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 ν_2 and ν_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 ν_2 and ν_3 as being constant.

The constants $c_{||}$ and $c_{\perp}$ in expression (1) characterize the elastic interaction of neighboring unit cells. This is underlined by the summation index, which is in parentheses. The summation in the expression (1) is carried out over only adjacent cells: in the second term, over two adjacent cells along the polymeric chain, in the third term, over adjacent cells from the side chains. Let us consider that these interactions can be characterized by only two parameters $c_{||}$ and $c_{\perp}$. Thus, the elastic interaction energy for each pair of adjacent unit cells is equal to $c_{||}s_is_j$ and $c_{\perp}s_is_j$ along and across the chain, respectively. The factor 1/2 before the summation signs in the expression (1) is in place because each pair of effective spins (unit cells) is taken into account twice. Up to this point, the theory of magneto-structural transitions in exchange cluster chains used only a part of the Hamiltonian (1), including the first and the second terms. The interchain interaction described by the third term in the expression (1) was ignored. The reason for this was that the strongest elastic interactions corresponded to interactions along the polymeric chain, while interchain interactions, which have most likely a van der Waals nature, are considerably weaker. Therefore, we expect that $|c_{||}| >> |c_{\perp}|$. At the same time, the study of single-chain problems allowed us to formulate a two-point approximation, which ignored the higher-lying states with strong deformation of the unit cell, which are negligibly thermally populated, though they play an important role in the processes of relaxation of the photoexcited states.[9,13] If the energy of elastic interaction of adjacent unit cells along the polymeric chain in states 2 and 2 (2 and 3) is written as $E_{||}(22)$ ($E_{||}(23)$), then it can be shown that

$$c_{||} = -(E_{||}(22) - E_{||}(23)). \tag{4a}$$

Similarly, for adjacent cells across the polymeric chain we have

$$c_{\perp} = -(E_{\perp}(22) - E_{\perp}(23)). \tag{4b}$$

It was shown[13] that the difference (4a) can be written as $c_{||} = k\Delta_0^2$, where k is the rigidity of intercluster interaction (in an elastic spring model), while Δ_0 is the deformation of the exchange cluster (the change of the Cu^{2+}—O axial bond length in a coordination center CuO_6). Let us consider $\rho_1(s)$ as the unit cell state distribution function. Then

$$\langle s\rangle = \Sigma s\rho_1(s) = \rho_1(1) - \rho_1(-1) = \rho(2) - \rho(3) \tag{5}$$

is the difference in the populations of states 2 and 3, while $\rho(2) + \rho(3) = 1$ according to the normalization condition. Knowing the values $\rho_1(1)$ and $\rho_1(-1)$, the magnetic properties of the crystal can be determined and the specific effective magnetic moment μ_{eff} for one coordination center can be calculated. The simplest approximation, which is the mean-field approximation allowing one to find $\rho_1(s)$, consists of exchanging the variable s_j in the expression (1) with a mean $\langle s\rangle$. This leads to an approximate Hamiltonian $\hat{H}_{\text{MF}}$

$$\hat{H}_{\text{MF}} = -\bigl(h_0 + \xi\langle s\rangle\bigr)\sum_i s_i = -\bigl(h_0 + h_{\text{MF}}\bigr)\sum_i s_i, \tag{6}$$

where $\xi = (z_{||}c_{||} + z_{\perp}c_{\perp})/2$ and $z_{||} + z_{\perp} = z$. Here $z_{||}$, $z_{\perp}$ are the number of cells adjacent to the given cell, along and across the polymeric chain, respectively. Usually $z_{||} = 2$, and below, for simplicity, we will consider $z_{\perp} = 2$ (two side chains). The roughness of the mean-field theory approximation is that the contributions of interactions along and across the chain are additive and cannot be taken out of the ξ value separately. This inaccuracy is compensated by the simplicity of determining $\hat{H}_{\text{MF}}$ from the expression (6). In fact, the effective field h, acting upon each "spin" (unit cell), is the same and equal to $h_0 + h_{\text{MF}}$. This means that $\rho_1(s)$ in this case is determined by the usual Boltzmann distribution:

$$\begin{aligned}\rho_1(\pm 1) &= \mathrm{e}^{\pm h/T}/\bigl(\mathrm{e}^{h/T} + \mathrm{e}^{-h/T}\bigr) = \\ &= \frac{1}{2}\bigl(1 \pm \mathrm{th}(\beta h)\bigr) = \frac{1}{2}\bigl(1 + s\,\mathrm{th}(\beta h)\bigr),\end{aligned} \tag{7}$$

where $\beta = 1/T$ is traditionally used for reciprocal temperature.

The main idea of this approach consists[12] of the introduction of a distribution across possible fields h, which act upon the "spin" (a particular cell) from the closest surrounding. In our case this means the introduction of a distribution function $P(h)$ for effective elastic fields, which act on a particular unit cell of the exchange cluster chain. This function will be determined by the following expression:

$$P(h) = \sum_{s_1}\cdots\sum_{s_z}\delta\Bigl[h - h_{\Sigma}\bigl(s_1, \ldots, s_z\bigr) - h_0\Bigr]\rho\bigl(s_1, \ldots, s_z\bigr), \tag{8}$$

where $\rho(s_1,\ldots, s_z)$ is the probability of a configuration of effective spins $s_1,\ldots, s_z$ in the nearest surroundings around the given "spin" (unit cell), while the value h_{Σ}, which can be written as

$$h_{\Sigma} = \frac{c_{||}}{2}\sum_{j=1}^{z_{||}} s_j^{(||)} + \frac{c_{\perp}}{2}\sum_{j=1}^{z_{\perp}} s_j^{(\perp)},\ z_{||} + z_{\perp} = z, \tag{9}$$

determines the effective field, acting on a particular "spin" from the given configuration. The sum in the expression (8) is over all the possible configurations of effective spins (unit cells) in the nearest surroundings of a certain unit cell. The total number of such configurations is equal to 2^z. In this case, it is possible to reduce to the mean-field theory by using the following approximation:

$$\rho\bigl(s_1, \ldots, s_z\bigr) \approx \prod_{s_1}^{s_z}\rho\bigl(s_i - \langle s\rangle\bigr),\ \sum_{s_i} \to \int ds_i.$$

Then

$$P(h) \approx \int ds_1 \ldots \int ds_z \delta\left[h - h_\Sigma(s_1, \ldots, s_z) - h_0\right] \prod_{s_1}^{s_z} \delta\left(s_i - \langle s \rangle\right) = \\ = \delta\left(h - h_{\mathrm{MF}} - h_0\right),$$

where

$$h_{\mathrm{MF}} = (z_\| c_\| + z_\perp c_\perp)\langle s \rangle/2 = \xi\langle s \rangle.$$

The Mamada—Takano approximation is to use a more accurate distribution over the probability distributions of effective spins than the δ-function, which only fixes the mean value $\langle s \rangle$, while at the same time preserving the factorization

$$\rho(s_1, \ldots, s_z) \approx \prod_{j=1}^{z} \rho_1\left(s_j\right) \tag{10}$$

Factorization (10) means a full correlation break in the multiparticle configurations in the nearest surroundings of a particular unit cell, significantly simplifying the problem, since $P(h)$ is now determined through a single-particle distribution function, which needs to be equated with $\rho_1(s)$ after averaging with $P(h)$. For the Ising problem, the approximation (10) and the subsequent self-consistency procedure are equivalent to the Hartree approximation in quantum chemistry. Thus,

$$\overline{\rho_1(s)} = \int \rho_1(s) P(h) dh = \frac{1}{2}(1 + sX), \quad X = \int \mathrm{th}(\beta h) P(h) dh. \tag{11}$$

We remind that the value X is equivalent to $\langle s \rangle$, while the populations of the unit cell states 2 and 3 are expressed through it in a simple manner: $\rho(2) = (1 + X)/2$ and $\rho(3) = (1 - X)/2$. According to the Mamada—Takano approximation

$$P(h) = \sum_{s_1} \cdots \sum_{s_z} \delta\left[h - h_\Sigma\left(s_1, \ldots, s_z\right) - h_0\right] \prod_{j=1}^{z} \overline{\rho_1\left(s_j\right)} \tag{12}$$

The function $\overline{\rho_1(s)}$ is linear in X, while the distribution $P(h)$ according to expression (12) is dependent on the product of the functions $\overline{\rho_1(s)}$. Therefore, the Eq. (11) becomes closed for X and, by solving it, one can first find X, then $\overline{\rho_1(s)}$ and the populations $\rho(2)$ and $\rho(3)$ of unit cell states. We note that in the mean-field theory approximation, when $P(h) \approx \delta(h - h_{\mathrm{MF}} - h_0)$, the Eq. (11) provides a simple expression for X:

$$X = \int \mathrm{th}(\beta h)\delta(h - h_{\mathrm{MF}} - h_0) dh = \mathrm{th}\left(\beta\left(h_{\mathrm{MF}} + h_0\right)\right) = \\ = \mathrm{th}\left(\beta\left(h_0 + \xi\langle s \rangle\right)\right) = \mathrm{th}\left(\beta\left(h_0 + \xi X\right)\right). \tag{13}$$

In the general case of the approximation (12) the expression for X is much more complex. In the right side, it contains a z degree polynomial with variable X. Thus, under the simplest conditions, when $z_\| = 2$ and $z_\perp = 2$ (two side chains), $z = z_\| + z_\perp = 4$. Below is the explicit form of equation for this case:

$$\begin{aligned} X = {} & w_+^4 \mathrm{th}\left(\beta\left(h_0 + c_\| + c_\perp\right)\right) + \\ & + 2w_+^3 w_-\left[\mathrm{th}\left(\beta\left(h_0 + c_\|\right)\right) + \mathrm{th}\left(\beta\left(h_0 + c_\perp\right)\right)\right] + \\ & + w_+^2 w_-^2\left[\mathrm{th}\left(\beta\left(h_0 + c_\| - c_\perp\right)\right) + 4\mathrm{th}\left(\beta h_0\right) + \mathrm{th}\left(\beta\left(h_0 - c_\| + c_\perp\right)\right)\right] + \\ & + 2w_+ w_-^3\left[\mathrm{th}\left(\beta\left(h_0 - c_\|\right)\right) + \mathrm{th}\left(\beta\left(h_0 - c_\perp\right)\right)\right] + \\ & + w_-^4 \mathrm{th}\left(\beta\left(h_0 - c_\| - c_\perp\right)\right), \end{aligned} \tag{14}$$

where we used the values $w_+ = (1 + X)/2$ and $w_- = (1 - X)/2$. From the expression (14) it can be seen that despite $c_\|$ and $c_\perp$ being included in the equation symmetrically, the solution for X is determined by the values $c_\|$ and $c_\perp$ separately and not by their sum, as is the case in mean-field theory (see Eq. (13)), when $\xi = c_\| + c_\perp$ for $z_\| = z_\perp = 2$. Therefore it can be expected that the Eq. (14) will describe the temperature of the system more accurately than mean-field theory (Eq. (13)).

Another interesting feature of the Mamada—Takano method is that it allows one to take into account random impurities in the crystal, their influence on critical behavior of Jahn—Teller clusters. In fact, if a unit cell next to the one in question is not a Jahn—Teller cell, then most likely it has a thermal stiffness. Its geometry is weakly dependent on temperature, magneto-structural transitions are absent, and it can be suggested that such a cell is characterized by the same interaction energy with a specific Jahn—Teller cell both in the state 2 ($s = 1$) and in the state 3 ($s = -1$). In the Hamiltonian (1), the presence of such an "inert" impurity cell provides some general shift in energy proportional to the concentration of random impurities, which is insignificant when calculating partition functions. An important factor is the appearance of effective field h configurations, where some positions of adjacent cells are substituted with "inert" (Jahn—Teller inactive) impurity cells, which do not contribute to $P(h)$. A change of the $P(h)$ calculation procedure is needed when such "inert" unit cells are present in the polymeric chain. Now, when calculating the $P(h)$ distribution function it is necessary to also average over all the possible configurations of random impurities around a certain cell. We label this distribution function over random impurity configurations as F_{mix}. In the simplest case of isotropic and uncorrelated distribution of impurities, this function depends only on the number of impurity cells n around the one in question ($0 \le n \le z$) and has the following form:

$$F_{\mathrm{mix}}(n) = Q_n = C_z^{\,n} p^n (1 - p)^{z-n}, \tag{15}$$

where $C_z^{\,n}$ is the number of combinations of z over n. Thus, in the simplest case $F_{\mathrm{mix}}(n)$ is the usual binomial distribution. If $P^{(n)}(h)$ is the random field distribution when there are n impurity cells in the vicinity, then for averaging over all the impurity configurations of the distribution function $\langle P(h) \rangle_Q = P_Q(h)$ we obtain the ratio

$$P_Q(h) = \sum_{n=0}^{z} Q_n \cdot P^{(n)}(h). \tag{16}$$

The function $P_Q(h)$ replaces $P(h)$ in the Eq. (11), which in the presence of uncorrelated random impurities can be written as

$$X = \int \mathrm{th}(\beta h)P(h)dh = \sum_{n=0}^{z} Q_n \cdot \int \mathrm{th}(\beta h)P^{(n)}(h)dh. \tag{17}$$

In the case of two side chains, this equation takes the following explicit form:

$$\begin{aligned}
X = {} & (1-p)^4 \cdot \int \mathrm{th}(\beta h)P^{(0)}(h)dh + \\
& + 2p(1-p)^3 \cdot \int \mathrm{th}(\beta h)\left[P_{\|}^{(1)}(h) + P_{\perp}^{(1)}(h)\right]dh + \\
& + p^2(1-p)^2 \cdot \int \mathrm{th}(\beta h)\left[P_{\|,\|}^{(2)}(h) + 4P_{\|,\perp}^{(2)} + P_{\perp,\perp}^{(2)}(h)\right]dh + \\
& + 2p^3(1-p) \cdot \int \mathrm{th}(\beta h)\left[P_{/\|}^{(3)}(h) + P_{/\perp}^{(3)}(h)\right]dh + \\
& + p^4 \cdot \int \mathrm{th}(\beta h)P^{(4)}(h)dh.
\end{aligned} \tag{18}$$

In this expression, $P_{\|}{}^{(1)}(h)$ and $P_{\perp}{}^{(1)}(h)$ are the distributions over effective fields for configurations with one random impurity in the vicinity of a particular cell (the impurity can be incorporated into the polymeric chain, represented by the subscript $\|$, or be located in the side chain, represented by the subscript $\perp$). The functions $P_{\|,\|}{}^{(2)}(h)$, $P_{\|,\perp}{}^{(2)}(h)$, and $P_{\perp,\perp}{}^{(2)}(h)$ describe similar distributions for situations with two impurities and their possible configurations around a certain cell, the functions $P_{/\|}{}^{(3)}(h)$ and $P_{/\perp}{}^{(3)}(h)$ correspond to the case of three impurity cells. In these circumstances, two cases are distinguished: when one remaining Jahn—Teller neighbor is placed along the polymeric chain (indicated as $/\|$) or is located in the side chain (indicated as $/\perp$). If $c_{\|} = c_{\perp}$, then the difference between these distributions for finding impurities located along the polymeric chain or in the side chain disappears. Finally, $P^{(4)}(h)$ is related to the configuration when all the surrounding unit cells are impurity cells. The first integral in the expression (18) containing the function $P^{(0)}(h)$, is applied to the case when there are no impurities in the vicinity of a specific cell. It is the same as the right side of the Eq. (14), while for the remaining integrals similar expressions can be obtained, which we ignore due to their cumbersomeness. The Eq. (18), same as (14), is difficult to study in the analytical form, therefore, we will limit ourselves to qualitative results of their numerical analysis.

Interchain interaction in temperature transitions of Jahn—Teller exchange clusters

Assuming $c_{\|} = 0$ in the expression (14), a distribution function for the one-dimensional case of a chain of exchange clusters can be obtained within the framework of the used method. Such a one-dimensional model in the two-point approach, which accounts for two structural states of the exchange cluster, the low-temperature (LT) and the high-temperature (HT) states, has an exact solution.[13] Figure 2 shows the result of the comparison of the temperature dependence of the effective magnetic moment for the two-point model and the calculations by the formula (14) with the same set of optimal parameters, which were used in the two-point model for the fitting in the Cu(hfac)$_2$L$^{\mathrm{Et}}$ experiment (hfac is hexafluoroacetylacetonate anion, ligand L$^{\mathrm{Et}}$ is nitronyl nitroxide radical with pyrazol substituent in the second position of the imidazoline ring). This compound stands somewhat apart in the "breathing" crystal family, since for it the schemes in Fig. 1 exchange places, and the ground state corresponds to a three-spin cluster elongated along the polymeric chain. From Fig. 2, it can be seen that the difference between the results of the two models is very small. Below, to simplify analysis, we will deal with the temperature dependence of state $n_{\mathrm{HT}} = \rho(3)$ population corresponding to the high-temperature conformation of the exchange cluster. Knowing this value and the magnetic interactions (the exchange integrals) in the states 2 and 3, all the magnetic properties of exchange clusters can be calculated.

Now let us describe the role of the interaction of polymeric chains. In the model in question this means taking into account the parameter $c_{\perp}$. Figure 3, *a* shows the temperature dependence $n_{\mathrm{HT}}(T)$ for three sets of parameters $c_{\|}$ and $c_{\perp}$, corresponding to one value $c_{\Sigma} = c_{\|} + c_{\perp}$, calculated using the expression (14). We remind that in the two-dimensional case the results obtained within the framework of the mean-field theory (13) are dependent only on the value c_{Σ}. Our calculations showed that this is not the case. At a constant c_{Σ}, the transition slope increases with

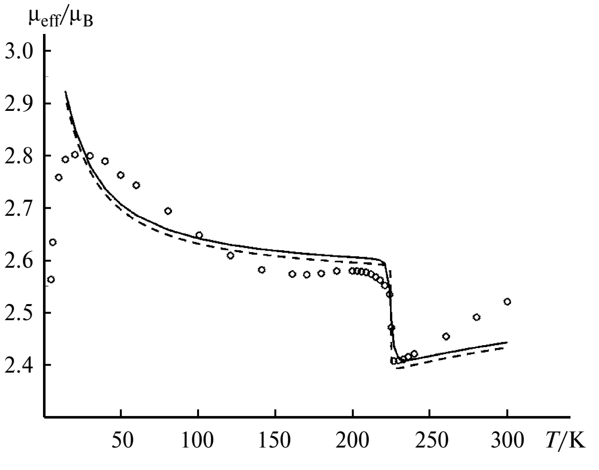

Fig. 2. A comparison of the results of the two-point exactly solvable model (solid curve) and the distribution function method (dashed curve) for the fitting of the experimental data (circles) on the effective magnetic moments μ_{eff} for the compound Cu(hfac)$_2$L$^{\mathrm{Et}}$. The value μ_{eff} is given in Bohr magnetons (μ_{B}). Here and in Fig. 3 the exchange integrals for the ground and the high-temperature states are: $J^{(2)}$ = 12 K, $J^{(3)}$ = –55 K, $E^{(2)}$ = 1750 K, $E^{(3)}$ = 2000 K, $\nu^{(3)}/\nu^{(2)}$ = 2.9.

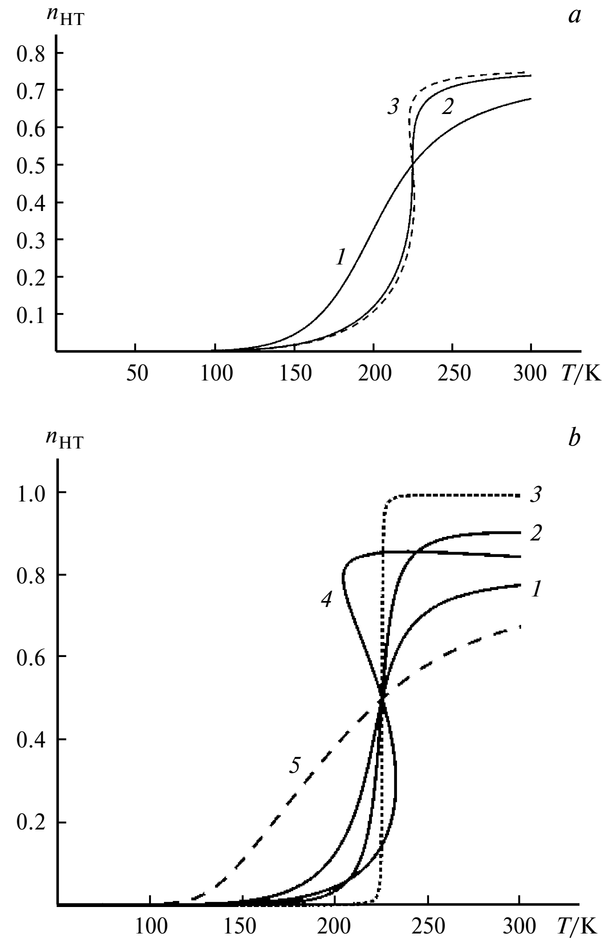

Fig. 3. (*a*) The influence of the interaction of polymeric chains on the slope of the thermal magneto-structural transition: curve *1* : $c_{\|} = 300$ K, $c_{\perp} = 0$ K; *2*: $c_{\|} = 200$ K, $c_{\perp} = 100$ K; *3*: $c_{\|} = 150$ K, $c_{\perp} = 150$ K. (*b*) The influence of the intensity and the unit cell interaction sign on the character of the thermal magneto-structural transition: curve *1*: $c_{\|} = 400$ K, $c_{\perp} = 10$ K; *2*: $c_{\|} = 600$ K, $c_{\perp} = 0$ K; *3*: $c_{\|} = 1000$ K, $c_{\perp} = 0$ K; *4*: $c_{\|} = 400$ K, $c_{\perp} = 40$ K; *5*: $c_{\|} = 400$ K, $c_{\perp} = -40$ K.

$c_{\perp}$ and reaches the maximum for isotropic interactions ($c_{\perp} = c_{\|} = c_{\Sigma}/2$).

With an increase of $c_{\|}$ (with $c_{\perp} = 0$) the slope of the transition to the high-temperature state (cooperativity) in the exchange cluster chain increases (see Fig. 3, *b*, curves *1*—*3*). However, at high values of $c_{\|}$ the addition of $c_{\perp} > 0$ (interchain interactions) leads to a new phenomenon, namely, the appearance of a first-order phase transition with a hysteresis loop (see Fig. 3, *b*, curve *4*). The phenomenon in question was absent in the one-dimension chain of exchange clusters and is caused entirely by the interaction of polymeric chains.

The size of the hysteresis temperature interval is determined by the distance along the *T* axis between the vertical tangents to the curve *4* (see Fig. 3, *b*). As it was indicated above, $c_{\|} = k\Delta_0^2 \geq 0$. At the same time $c_{\perp}$, determined by the formula (4b), can be either more or less than 0, due to this value characterizing the van der Waals interactions of adjacent side unit cells of polymeric chains. If $c_{\perp} < 0$, then the dependence $n_{HT}(T)$ becomes more gradual then in the case of $c_{\perp} = 0$ (see Fig. 3, *b*, curve *5*). In this case, the influence of polymeric chains on each other consists of the deceleration of thermal transition processes in Jahn—Teller exchange clusters as compared to the case of a particular chain. Such an unusual result remotely resembles the effect of "anticooperativity" recently discovered**[14]** experimentally for spin-crossover of the cobalt(II) clathrochelate complex on transition from the liquid to the solid phase.

Let us consider the magnetic properties of different metal solid solutions of "breathing" crystals such as $Cu_{1-x}M_x(hfac)_2L^R$. For the case of M = Ni, it is known**[1,15]** that Ni^{2+} ions are mainly incorporated into the MO_4N_2 coordination units (see Fig. 1). The $Ni(hfac)_2L^R$ compounds themselves do not demonstrate magneto-structural transitions, because the Ni^{2+} ions with the configuration d^8 are not Jahn—Teller in octahedral surroundings. Therefore, we will consider the unit cell containing a nickel ion of the polymeric chain in the compound $Cu_{1-x}Ni_x(hfac)_2L^R$ as being structurally rigid and not possessing Jahn—Teller activity. In order to calculate magneto-structural transitions (the function $n_{HT}(T)$) in typical unit cells with two Cu^{2+} ions, we will use the formula (18). Figure 4 shows the results of the final (non-linear) superposition of magnetic contributions into the effective magnetic moment for copper and nickel subsystems of the solid solution of compound $Cu_{1-x}M_x(hfac)_2L^{Et}$.

We note that due to the structural selectivity of substitution of copper ions by nickel ions, as indicated above, in

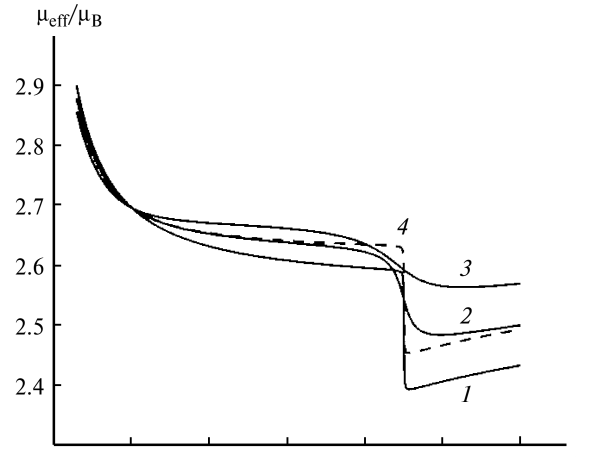

Fig. 4. The calculated transformation of the temperature dependence of the effective magnetic moment μ_{eff} (in Bohr magnetons, μ_B) with an increase of the impurity fraction *x* for compound $Cu_{1-x}Ni_x(hfac)_2L^{Et}$: curve *1*: *x* = 0, *2*: *x* = 0.04, *3*: *x* = 0.08, *4*: a simple statistical mixture of contributions of $Cu_{0.5}Ni_{0.5}(hfac)_2L^{Et}$ and $Cu(hfac)_2L^{Et}$.

the calculations we assumed that the random portion $p = 2x$. The presence of random impurities of unit cells which are not Jahn—Teller decreases the cooperative properties of exchange clusters in "breathing" crystals. The effect in question cannot be obtained by a simple static superposition of the contributions of two sub-ensembles $Cu_{0.5}Ni_{0.5}(hfac)_2L^{Et}$ and $Cu(hfac)_2L^{Et}$ with weighted values p and $(1 - p)$, as it can be seen from Fig. 4. The dependencies obtained from calculations qualitatively correctly reproduce the transformation of magnetic properties of solid solutions $Cu_{1-x}M_x(hfac)_2L^{Et}$, available from the experiment.[1,15]

In conclusion, the interaction of polymeric chains is one of the important physical factors, affecting magnetostructural transitions in the family of "breathing" crystal compounds. In the present work, it was shown that taking into account this interaction can lead to both an increase of cooperative transitions of the spin-crossover type in exchange clusters and the appearance of hysteresis phenomena and to an unexpected deceleration of these transitions. The developed approach to modeling the distribution function was generalized for the presence of non-Jahn—Teller random metal impurities in "breathing" crystals. The impurities in question 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 $Cu_{1-x}Ni_x(hfac)_2L^R$ for the case of R = Et. A quantitative comparison of theory with experiment requires a more precise calculation of the energies of unit cell interaction and a generalization of the calculation scheme for a realistic case of four and more nearest neighbors in the surrounding of the polymeric chain in the "breathing" crystal.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 14-03-00057) and Federal Agency on Science Organizations of Russia (Project No. 0333-2014-0001).

References

1. V. I. Ovcharenko, K. Yu. Maryunina, S. V. Fokin, E. V. Tret´yakov, G. V. Romanenko, V. N. Ikorskii, *Russ. Chem. Bull.* (*Int. Ed.*), 2004, **11**, 2406 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2004, **11**, 2304].
2. V. I. Ovcharenko, S. V. Fokin, G. V. Romanenko, Yu. G. Shvedenkov, V. N. Ikorsky, E. V. Tret´yakov, S. F. Vasilevsky, *Russ. J. Struct. Chem.* (*Engl. Transl.*), 2002, **43**, 153 [*Zh. Struktur. Khim.*, 2002, **43**, 163].
3. V. I. Ovcharenko, E. G. Bagryanskaya, in *Spin-Crossover Materials. Properties and Applications*, Ed. M. A. Halcrow, Wiley, 2013, p. 239.
4. M. V. Fedin, S. L. Veber, E. G. Bagryanskaya, V. I. Ovcharenko, *Coord. Chem. Rev.*, 2014, **289—290**, 3416.
5. V. A. Morozov, N. N. Lukzen, V. I. Ovcharenko, *Russ. Chem. Bull.* (*Int. Ed.*), 2008, **57**, 863 [*Izv. Akad. Nauk*, *Ser. Khim.*, 2008, 849].
6. V. A. Morozov, N. N. Lukzen, V. I. Ovcharenko, *J. Phys. Chem. B,* 2008, **112**, 1890.
7. V. A. Morozov, N. N. Lukzen, V. I. Ovcharenko, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13667.
8. V. A. Morozov, *Russ. J. Struct. Chem.* (*Engl. Transl.*), 2014, **55**, 1033 [*Zh. Struktur. Khim.*, 2014, **55**, 1098].
9. V. A. Morozov, *Russ. J. Struct. Chem.* (*Engl. Transl.*), 2016, **57**, 1523 [*Zh. Struktur. Khim.*, 2016, **57**, 1587].
10. V. A. Morozov, N. N. Lukzen, V. I. Ovcharenko, *Dokl. Phys. Chem.* (*Engl. Transl.*), 2010, **430**, Pt. 2, 33 [*Dokl. Akad. Nauk*, 2010, **430**, 647].
11. V. I. Ovcharenko, G. V. Romanenko, K. Yu. Maryunina, A. S. Bogomyakov, E. V. Gorelik, *Inorg. Chem.*, 2008, **47**, 9537.
12. H. Mamada, F. Takano, *J. Phys. Soc. Japan*, 1968, **25**, 675.
13. V. A. Morozov, *Phys. Chem. Chem. Phys.*, 2013, **15**, 9931.
14. V. V. Novikov, I. V. Ananyev, A. A. Pavlov, M. V. Fedin, K. A. Lyssenko, Y. Z. Voloshin, *J. Phys. Chem. Lett.*, 2014, **5**, 496.
15. K. Yu. Maryunina, S. V. Fokin, V. I. Ovcharenko, G. V. Romanenko, V. N. Ikorskii, *Polyhedron*, 2005, **24**, 2094.

Received May 25, 2016;
in revised form October 11, 2016