Full Articles

A theory of spin-Peierls transitions in chains of exchange clusters

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A theoretical approach to analysis of magnetic structural phase transitions of chain polymer heterospin complexes is proposed. The approach is based on the model for spin-Peierls phase transition of chain exchange clusters. The type of the phase transition depends on the elastic constant of the chain.

Key words: spin-Peierls transition, exchange cluster, spin crossover, effective magnetic moment.

Heterospin complexes $Cu(hfac)_2L^R$ formed by $Cu(hfac)_2$ with pyrazole-substituted nitronyl nitroxides (L^R, R = Me, Et, Pr) have been the subject of intensive research.[1—3] On cooling, they exhibit unique structural rearrangements accompanied by magnetic anomalies similar to spin crossover.[4,5] The effective magnetic moments of the exchange clusters can abruptly change in a narrow temperature interval and change the sign of the exchange integral within a subensemble of spin clusters. The chain polymeric structure of such molecular complexes[1] allows one to describe the magnetic structural phase transitions of these systems using an approach based on the theory of spin-Peierls transitions.[6] Paramagnetic exchange clusters will be modeled by a two-spin system with the elastic constant q and the parameter of exchange interaction J.

The form of expression for the free energy of an elastically coupled spin chain is conventional to the concept of a "condensed" phonon mode with $q = 2k_F$ accepted in the theory of spin-Peierls transitions.[6,7] Traditionally, the theory of spin-Peierls transitions treats an infinite one-dimensional chain of spins coupled by antiferromagnetic exchange interaction between nearest neighbors. In our case the one-dimensional chain is naturally divided into paramagnetic clusters (inter-cluster exchange interaction is ignored). The overall pattern of the phenomenon is similar to a classical spin chain.[8] In this case the statistical sum of the system is represented by the product of corresponding integrals with respect to bonds between the nearest neighbors, *i.e.*, it can be calculated with ease in the general case.

Consideration of the phonon subsystem in the approximation, when only the static ("condensed") mode is considered, is also used in the analysis of conventional Peierls metal—semiconductor transition.[9,10]

The model for the spin chain

The model for a chain of paramagnetic clusters (Fig. 1) differs from the traditional spin-Peierls chain[6] in the ab-

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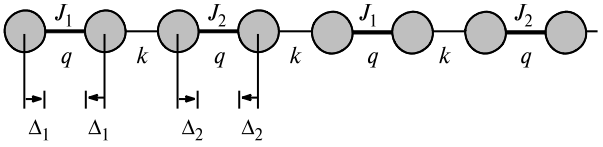

Fig. 1. Model for a chain of exchange clusters. Intra-cluster exchange integrals J_1 and J_2 depend on the spin displacements Δ_1 and Δ_2, respectively; no inter-cluster exchange occurs; and the parameters q and k are the intra-cluster and inter-cluster elastic constants.

sence of exchange interaction between clusters, which allows the free energy ε to be written in the form

$$\varepsilon/(N/2) = F(J_1) + F(J_2) + 2q(\Delta_1{}^2 + \Delta_2{}^2) + k(\Delta_1 + \Delta_2)^2. \quad (1)$$

Here N is the number of spin clusters in the chain and q and k are the intra-cluster and inter-cluster elastic constants, respectively. The spin free energies of the clusters have a conventional form $F(J) = -T\ln Z(J)$, where the statistical sum Z for the two-spin cluster ($S_1 = S_2 = 1/2$) is given by

$$Z(J) = \exp[-3J/(2T)] + 3\exp[J/(2T)]. \quad (2)$$

From this point on we will consider only two-spin clusters and use expression (2) for the statistical sum $Z(J)$. Following the theory of spin-Peierls transitions, we assume that intra-cluster exchange interaction is a linear function of cluster deformation, $2\Delta_1$ or $2\Delta_2$ (Δ_1 and Δ_2 are the displacements of particular paramagnetic centers, see Fig. 1):

$$J_1 = J_0 - \varepsilon\Delta_1,\ J_2 = J_0 - \varepsilon\Delta_2. \quad (3)$$

In the text below we will consider the thermodynamic behavior of a clumped chain ($L = Na$ = const, where a is the distance between centers of adjacent paramagnetic centers) in two limiting cases, namely, $k \to \infty$ ($\Delta_1 = -\Delta_2 = \Delta$) and $k = 0$ ($\Delta_1 = \Delta_2 = \Delta$).

In these cases the two-dimensional ordering parameter (Δ_1, Δ_2) is reduced to one-dimensional parameter Δ.

Case $k \to \infty$ ($\Delta_1 = -\Delta_2 = \Delta$). The expression for the free energy per two adjacent clusters has the form:

$$\varepsilon = -T\ln\left\{Z(J_0)^2 + 6\exp(-\frac{J_0}{T})\left[\mathrm{ch}(\frac{2\varepsilon\Delta}{T}) - 1\right]\right\}T + 4q\Delta^2. \quad (4)$$

The extrema of E ($dE/d\Delta = 0$) meet the condition

$$\frac{2\varepsilon\Delta}{T} = \frac{\varepsilon^2}{2qT}\frac{\rho\,\mathrm{sh}(2\varepsilon\Delta/T)}{\left\{1 + \rho\left[\mathrm{ch}(2\varepsilon\Delta/T) - 1\right]\right\}}, \quad (5)$$

where $\rho = 2\xi/(1 + \xi)^2$, $\xi = (1/3)\exp(-2J_0/T)$. Equation (5) can have one ($\Delta = 0$) or three roots Δ. From Eq. (5) one can see with ease that the solution $\Delta = 0$ is unstable at $[\varepsilon^2/(2qT)]\rho \geq 1$, which corresponds to the classical pattern of second-order phase transitions. The Landau expansion in the vicinity of $\Delta = 0$ can be written as follows:

$$\varepsilon = (2\Delta^2\varepsilon^2/J_0)\{Q - f_0[T/(2J_0)]\} + O(\Delta^4), \quad (6)$$

where

$$Q = 2J_0q/\varepsilon^2,\ f_0[T/(2J_0)] = 3\exp(-J_0/T)/\{Z(J_0)^2[T/(2J_0)]\}.$$

A second-order phase transition is possible at $Q < \max\{f_0[T/(2J_0)]\} \approx 0.1$. The transition temperature T_Q is determined from the equation $Q = f_0[T/(2J_0)]$, which has the following approximate solution at $Q << 0.1$:

$$T_Q \approx J_0[(3/8)/Q - 1]. \quad (7)$$

The approximate solution to Eq. (5) for the nonzero root Δ gives

$$\Delta \approx \varepsilon/(4q)\ (\text{at } \varepsilon^2/(2qT) >> 1). \quad (8)$$

Thus, the exchange integrals in paramagnetic clusters after phase transition take the values

$$J_1 = J_0 - \varepsilon^2/(4q),\ J_2 = J_0 + \varepsilon^2/(4q). \quad (9)$$

For the initial ferromagnetic exchange integral ($J_0 > 0$) we get $J_1 < 0$ and $J_2 > 0$, *i.e.*, 50% of the spin clusters go to the singlet ground state and the effective magnetic moment, μ_{eff}, of the cluster abruptly decreases after the phase transition. Figure 2 shows the plot of μ_{eff} *vs.* temperature for the simplest case (equal g-factors of both electron spins in the cluster) where the magnetic susceptibility χ is given by[11]

$$\chi(J) = [(2\beta^2g^2)/T][3 + \exp(-2J/T)]^{-1} \quad (10)$$

(β is the Bohr magneton).

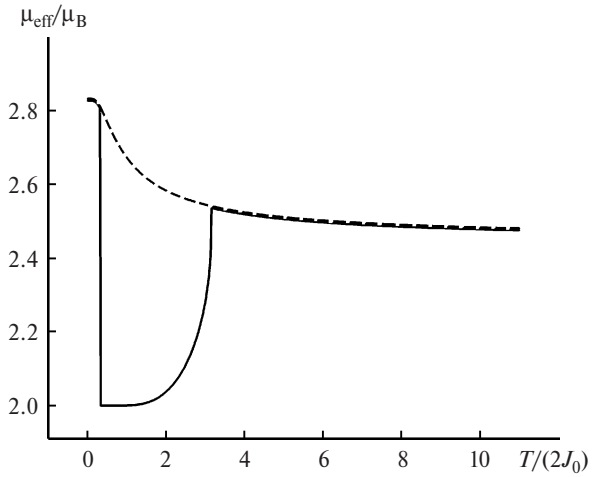

Fig. 2. Average effective magnetic moment of two-spin exchange cluster (equal g-factors; $g = 2$) plotted *vs.* temperature for the case $k \to \infty$. The parameter Q is 0.05 for the solid line and 0.2 for the dashed line. In the latter case, no phase transition occurs.

Case $k = 0$ ($\Delta_1 = \Delta_2 = \Delta$). Here, the expression for the free energy is essentially simplified and has the form

$$\varepsilon = F(J) + 2q\Delta^2, J = J_0 - \varepsilon\Delta. \quad (11)$$

Relation (11) describes a single cluster, because in this case all clusters in the chain behave identically. For a two-spin cluster the extrema of free energy ($d\varepsilon/d\Delta = 0$) obey the equation

$$\exp(2J/T) = (b - \varepsilon\Delta/3)/(b + \varepsilon\Delta), b = \varepsilon^2/(8q). \quad (12)$$

Equation (12) always has a root $\Delta_- < 0$ corresponding to the high-temperature equilibrium. Two roots $\Delta > 0$ are possible at $J_0 < 3b$ ($Q < 3/4$); they correspond to the appearance of an additional minimum Δ_+ (Fig. 3). If Q is sufficiently small, the additional minimum Δ_+ can become deeper than the main minimum Δ_- on lowering the temperature; this corresponds to a second-order phase transition with discontinuity of the ordering parameter $\Delta_- \to \Delta_+$.

In this case the effective magnetic moment $\mu_{eff} = \sqrt{3\chi T}$ abruptly decreases to almost zero (Fig. 4), because the phase transition corresponds to the change in the sign of the exchange integral. The exchange integral changes identically for all clusters in the chain. Therefore, no doubling of the chain period will occur and, generally, this phase transition should not be treated as the spin-Peierls one.

Results and Discussion

The model for one-dimensional chain of paramagnetic clusters considered in this work has a single control parameter $Q = 2J_0q/\varepsilon^2$, which determines the character of thermodynamic behavior of the system. If Q is sufficiently small ($Q < 0.1$), the chain of paramagnetic clusters experiences a phase transition on lowering the temperature, the type of the transition being determined by the inter-cluster elastic constant. If this inter-cluster interaction is strong, the second-order spin-Peierls phase transition with doubling of the chain period occurs. In this case 50% of clusters change the sign of exchange interaction (it becomes antiferromagnetic in character) and the effective magnetic moment decreases by a factor of about $\sqrt{2}$. If the inter-cluster elastic interaction is weak, the phase transition becomes a first-order transition identically experienced by all spin clusters in the chain. As a result the effective magnetic moment μ_{eff} of the spin cluster tends to zero upon the change in the sign of the exchange integral after phase transition.

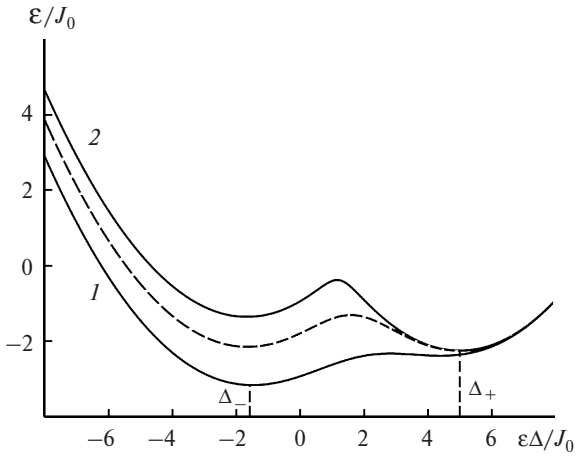

Fig. 3. Free energy ε (see Eq. (11)) plotted *vs.* spin displacement Δ in exchange cluster at different temperatures. Curve *1* corresponds to $T = 2J_0$ (above the transition temperature) and curve *2* corresponds to $T = 0.4J_0$ (below the transition temperature). The dashed line corresponds to the point of phase transition ($T \approx 1.12J_0$). The parameter Q has the same value (0.15) for all curves.

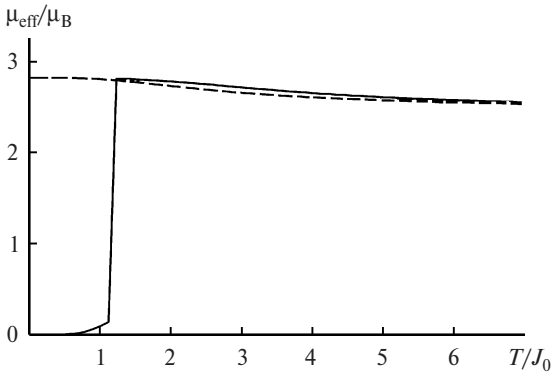

Fig. 4. Effective magnetic moment of two-spin exchange cluster with equal g-factors ($g = 2$) plotted *vs.* temperature at $k = 0$. The parameter Q is 0.15 for the solid line and 0.3 for the dashed line. No phase transition occurs in the latter case.

The model we have considered ignores weak inter-cluster antiferromagnetism, which becomes pronounced at low temperatures.[12] This phenomenon leads to vanishing of μ_{eff} at very low temperatures and helps to correct the behavior of μ_{eff} in the vicinity of $T = 0$ (see Fig. 2). The inclusion of cubic anharmonicity in the expression for the inter-cluster interaction would be yet another important refinement of the model. It is known[10] that the inclusion of anharmonicity in the theory of Peierls phase transitions leads to essential refinement of quantitative characteristics of the phenomenon.

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