Lattice Relaxation and Order in the Low-Spin to High-Spin Transitions in Molecular Crystals

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ABSTRACT

A series of the d^6 iron(II) complexes with bulky organic ligands (like $[Fe(bipy)_2(NCS)_2]$) can exist in two spin forms: in the low-spin ($S = 0$) form at low temperature and in the high-spin ($S = 2$) form at high temperature. In the crystal phase, the transition between these two forms may be either smooth or abrupt. Recently, the abrupt spin transitions were identified with the first-order transitions between different ordered phases occurring in the binary mixtures of the two spin forms of the complex. Here, we apply the method widely used in the field of binary metal alloys to the analysis of the spin transitions. The molecules undergoing the spin transition are modeled by octahedra of variable size which interact when they are immediate neighbors in the crystal lattice. We show that some simple assumptions concerning the intermolecular interaction and crystal geometry relaxation allows one to get the desired first-order phase transitions together with a satisfactory description for the crystal compressibility as a function of temperature.

Introduction

Spin transition in the transition-metal complexes are known already for more than half a century, but only starting early 1960s did intense studies begin. Today, dozens of compounds are known which exhibit spin transitions under proper conditions. Largely, they are complexes of transition metals with the electronic configuration d^4, d^5, d^6, and d^7 [1]. These compounds can have both a high-spin (HS) and low-spin (LS) central ion. For example, the d^6 complexes of $Fe(II)$ can have both the ground-state spin 2 (HS) and 0 (LS). What spin form a complex actually acquires depends on the ratio of d-level splitting in the ligand field ($10Dq$), which in its turn depends on the details of the ligand environment of the central ion and the average energy of the Coulomb interaction of d-electrons (P) which is less sensitive to the environment [1–4]. If $10Dq \gg P$ (strong ligand field), the ground state is LS; if $10Dq \ll P$ (weak ligand field), the ground state is HS. If, however, $10Dq \cong P$

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(i.e., we are in the proximity of the break on the Tanabe–Sugano diagram), then even for slightly different geometries of the ligand environment, the central ion can have the ground states of different spin. In this case, the difference between the energy minima of the corresponding HS and LS terms becomes comparable to $k_B T$. Under these conditions, both the states will be populated [i.e., some fraction $0 < x < 1$ of all the molecules is in the HS state and the rest $(1 - x)$ in the LS state]. The fraction of the molecules in the different spin states is defined from the thermodynamic equilibrium conditions and depends on temperature and pressure. The processes where under variation of temperature (or pressure) the fraction of the molecules of different spin changes is called a spin transition.

Numerous experimental studies revealed three major types of the $x(T)$ curves: They can (1) increase smoothly with the temperature increase, (2) undergo an abrupt increase at some critical temperature T_c, and (3) exhibit hysteresis, i.e., undergo the abrupt changes of the HS fraction at different temperatures depending on the way the transition is induced—by heating the LS crystal or by cooling the HS crystal. The variation of the fraction of the HS molecules is accompanied by the variation of other thermodynamic parameters. For example, at T_c of the spin transition, the volume of the crystal abruptly changes (though the crystal structure as a whole except the lattice parameters is conserved) and the specific heat diverges. [1–4]. All these data suggest that at least the curves of types (2) and (3) correspond to some phase transitions. The finite volume change and the hysteresis in the spin transitions suggest the first order of the phase transition for the concentration curves of types (2) and (3).

For the spin transitions in the solid state, numerous phenomenological theories have been proposed which result in the first-order phase transitions [5–8]. The assumption concerning a specific intermolecular interaction making the molecules in the same spin state occupy the nearest-neighbor sites in the lattice is a general feature for all these models. The original Slichter–Drickamer (SD) model [5] proposes, e.g., the following form of the crystal free energy:

$$g = (\delta h - T\delta s)x + k_B T(x \ln x + (1 - x)\ln(1 - x)) + \Gamma x(1 - x),$$

where δh and δs are the parameters characterizing the spin transition in a separate molecule [1–4] and the positive Γ is a phenomenological intermolecular interaction parameter. The SD model manifests a first-order phase transition with an abrupt change of the fraction x of the HS isomer if $\Gamma \geq 2k_B T_c$, where the critical temperature of the spin transition satisfying the condition $x(T_c) = 1/2$ is defined by the intramolecular parameters of the transition $T_c = \delta h/\delta s$.

The microscopic intermolecular interaction responsible for the positive sign of Γ is called cooperative. However, its existence has never been understood from the point of view of the microscopic properties of the constituent molecules. Moreover, it has been shown in [9] that (1) in the unrelaxed lattice the intermolecular interaction is anticooperative, i.e., the molecules having the same spin try to avoid each other, and (2) the cooperativity of an interaction is not necessary since even with the anticooperative [10] interaction between the molecules in the crystal the spin-phase transition of the first order is still possible if the free-energy function for the crystal has the form

$$g(T, x, \theta) = g_0(T, x) + \Delta g(T, x, \theta),$$

where

$$g_0 = (\delta h - T\delta s)x + k_B T(x \ln x + (1 - x)\ln(1 - x)) - \Gamma x(1 - x)$$

is the SD free energy, but with the negative interaction and the term

$$\begin{aligned}\Delta g(T, x, \theta) = k_B T(1 + s)^{-1} & \times (x(1 + s\theta)\ln(1 + s\theta) \\ & + (1 - x)(1 - ys\theta)\ln(1 - ys\theta) \\ & + s(x(1 - \theta)\ln(1 - \theta) \\ & + (1 - x)(1 + y\theta)\ln(1 + y\theta))) \\ & - sz_{eff}\Gamma x^2\theta^2,\end{aligned}$$

with $y = x/(1 - x)$, describes the sublattice order. However, neither in [9] nor in the earlier works [6–8] admitting the possibility of sublattice formation in the spin-transition systems, the reasons for their formation were not given and the parameters characterizing sublattices such as s—the ratio of the numbers of sites in different sublattices were not estimated. The purpose of the present work was to analyze the conditions when it is possible to have cooperative and anticooperative signs of the interactions between the constituent molecules. We also consider the elastic properties of the crystal undergoing the spin transition and make an approach to the problem of determination of the sublattices in a regular way accepted in the theory of binary alloys.

Model

SPIN-ACTIVE MOLECULES

The major part of the body of experimental data concerning the spin transitions is obtained on the six-coordinated molecular complexes of Fe(II) with bulky organic ligands containing nitrogen as a donor atom (like bipyridyl, phenantrolin, NCS^- anion, etc.). For describing the spin transitions on the molecular level, we present each molecule of an iron(II) complex undergoing the transition as an octahedron formed by the central Fe(II) ion surrounded by the six point ligands placed on the octahedron axes. As is evident from its name, the spin of the central ion changes when the spin transition happens. This change is possible only due to change in the positions of surrounding ligands. The distances Fe—N increase in the moment of the transition and, respectively, the crystal field (the value of $10\,Dq$) decreases and the HS state becomes the ground state of the molecule. All the remaining interatomic distances in the crystal stay unperturbed by the spin transition. Within our approach, we model this feature by introducing the variation of the metal–point ligand distance $\delta r_{HL} > 0$. This distance is R in the LS state and it is $R + \delta r_{HL}$ in the HS state.

CRYSTALS FORMED BY THE MOLECULES OF ONE TYPE

Now we consider a simple cubic crystal formed by the octahedra introduced just above. We assume that the axes of the octahedra are directed along the three axes of the simple cubic lattice. The crystals formed by such molecules are held together by the van der Waals forces. It is reasonable also to assume that the intermolecular interaction is due to the ligand–ligand interaction extended to the nearest-neighbor ligand along the crystal axis. We assume that the interaction energy is a quadratic function of the intermolecular separations between the closest ligands of the neighbor molecules: $\kappa(r - d)^2/2$, where κ is a force constant and d is the equilibrium (van der Waals) distance between the ligands in the neighbor molecules. One can easily check that the compressibility (reciprocal bulk modulus) of such a crystal is given by $K_{\mathrm{LS}}^{-1} = 3a/\kappa$, where a is the lattice constant of the crystal at zero (ambient) pressure and $a = d + 2R$, where R is the distance between the central ion and the point ligand in the LS complex. The equilibrium lattice constant for the crystal formed by the HS molecules within our model is $a + 2\,\delta r_{HL}$, and its compressibility $K_{\mathrm{HS}}^{-1} = 3(a + 2\,\delta r_{HL})/\kappa$.

CRYSTALS OF BINARY MIXTURES OF HS AND LS ISOMERS

Mechanical Energy

Let us consider now the mechanical potential energy of the crystal formed by a mixture of the HS and LS molecules. To do so, we [11] introduce the occupation number operators $\sigma_i(\mathbf{r})$ for the lattice sites. The $\sigma_i(\mathbf{r})$ equals 1 if the $\mathbf{r}$-th site of the lattice ($\mathbf{r}$ is a triple of integer numbers) is occupied by the molecule of the i-th type. In our case, when we have two types of the molecules (LS and HS), $i = 0$ or 1, respectively. The mechanical potential energy of the crystal then has the form

$$U = \sum_{ii'} \sum_{\mathbf{r},\alpha} \sigma_i(\mathbf{r})\sigma_{i'}(\mathbf{r} + \hat{\alpha})W_{ii'}^{\alpha}(\mathbf{r}), \qquad (1)$$

where $\alpha = x, y, z$; $\hat{\alpha}$ is the unit vector in the direction α; and $W_{ii'}^{\alpha}(\mathbf{r})$ is the potential energy of the interaction between the closest ligands of the molecules occupying the sites $\mathbf{r}$ and $\mathbf{r} + \hat{\alpha}$. According to our assumption concerning the intermolecular interaction, it is equal to $(\kappa/2)(r(i, i', \mathbf{r}, \alpha) - d)^2$, where

$$\begin{aligned} r(i, i', \mathbf{r}, \alpha) = a - 2R - (i + i')\,\delta r_{HL} \\ + \Delta + u_{\alpha}(\mathbf{r} + \hat{\alpha}) - u_{\alpha}(\mathbf{r}). \end{aligned}$$

Here, $u_{\alpha}(\mathbf{r})$ is the α-th component of the shift of the molecule in the $\mathbf{r}$-th site as a whole from its equilibrium position, and Δ, the uniform elongation of the parameters of the all unit cells. After taking into account the relation between the LS equilibrium lattice constant a and the equilibrium interligand separation d, the potential energy assumes the form

$$U = (\kappa/2) \sum_{ii'} \sum_{\mathbf{r},\alpha} \sigma_i(\mathbf{r})\sigma_{i'}(\mathbf{r} + \hat{\alpha}) \times (\Delta - (i + i')\,\delta r_{HL} + u_\alpha(\mathbf{r} + \hat{\alpha}) - u_\alpha(\mathbf{r}))^2. \quad (2)$$

Now, we introduce the average fraction of the molecules of the i-th type in the lattice according to

$$c_i = (1/N) \sum_{\mathbf{r}} \sigma_i(\mathbf{r}) \quad (3)$$

and the local deviations of the occupation numbers at the $\mathbf{r}$-th site $\gamma_i(\mathbf{r})$ according to

$$\sigma_i(\mathbf{r}) = c_i + \gamma_i(\mathbf{r}). \quad (4)$$

Provided that the terms higher than second overall order in u's and γ's are vanishing and that the molecular shifts and the occupation number deviations comply with the conditions,

$$\sum_{\mathbf{r}} u_\alpha(\mathbf{r}) = 0; \qquad \sum_{\mathbf{r}} \gamma_i(\mathbf{r}) = 0,$$

the expression for the energy takes the following form:

$$\begin{aligned} U = {} & 3N_\kappa/2\Big((1 - x)^2\Delta^2 + 2x(1 - x)(\Delta - \delta r_{HL})^2 \\ & + x^2(\Delta - 2\,\delta r_{HL})^2\Big) \\ & + N\kappa/2 \sum_{\alpha} \sum_{k} U_k^\alpha U_{-k}^\alpha\, |1 - \exp(ik_\alpha)|^2 \\ & + N\kappa\,\delta r_{HL} \sum_{\alpha} \sum_{k} \Gamma_k U_{-k}^\alpha (1 - \exp(ik_\alpha)) \\ & \times (1 + \exp(-ik_\alpha)) \\ & + N\kappa\,\delta r_{HL}^2 \sum_{\alpha} \sum_{k} \Gamma_k \Gamma_{-k} \exp(-ik_\alpha). \end{aligned} \quad (5)$$

Here, we passed to the Fourier transforms both for the shifts and for the local fraction deviations:

$$U_k^\alpha = (1/N) \sum_{\mathbf{r}} \exp(ik\mathbf{r}) u_\alpha(\mathbf{r});$$

$$\Gamma_k^i = (1/N) \sum_{\mathbf{r}} \exp(ik\mathbf{r}) \gamma_i(\mathbf{r}),$$

denoted the average fraction of the HS molecules c_1 by x and $c_0 = 1 - x$, and also mentioned that $\Gamma_k^1 = -\Gamma_k^0 = \Gamma_k$.

We see that the overall fraction of the HS molecules and the uniform deformation enter together the first term of the above expression for the mechanical potential energy, whereas the terms concerning the local lattice distortions coupled with the local fraction deviations are decoupled from the overall fraction/uniform deformation term. It is also worth noting that within the proposed approximation the acoustic phonon spectrum remains unchanged irrespective to the fractions of the component HS and LS molecules. The only effect on the phonons that could be expected on the basis of the proposed approach is the slight modification of the libron spectrum due to difference of the inertia moments of the LS and HS isomers. We, however, do not consider here the libration degrees of freedom.

Compressibility

Let us assume for a moment that the local terms containing U_k^α and Γ_k are not important and consider the global first term in the mechanical energy. It allows us to write down the Gibbs energy for the crystal undergoing the spin transition in the following form:

$$\begin{aligned} g = G/N = {} & (\delta h - T\delta s)x \\ & + k_B T(x \ln x + (1 - x)\ln(1 - x)) \\ & + 3\kappa/2(\Delta^2 - 4\Delta\,\delta r_{HL} x \\ & + 2\,\delta r_{HL}^2 x(1 + x)) + p(a + \Delta)^3. \end{aligned} \quad (6)$$

The equilibrium values of x and Δ are to be determined for each value of T and p from the standard thermodynamic relations: $\partial g/\partial x = \partial g/\partial \Delta = 0$.

Before passing to the equations determining the $x(T)$, we consider the compressibility of the crystal formed by the molecules undergoing the spin transition. According to the general definition, the compressibility is given by

$$K^{-1} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right) = -\frac{3}{a + \Delta}\left(\frac{\partial \Delta}{\partial p}\right).$$

Both x and Δ are defined by the above equations as the implicit functions of p and T:

$$\begin{aligned} \partial g/\partial x = {} & (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s) + k_B Tx/(1 - x) \\ & - 6\kappa\,\delta r_{HL}(\Delta - \delta r_{HL} x) = 0, \end{aligned}$$

$$\partial g/\partial \Delta = \kappa(\Delta - 2x\,\delta r_{HL}) + p(a + \Delta)^2 = 0. \quad (7)$$

Making use of the standard relations for the implicit functions, we get for the compressibility at $p = 0$ (ambient pressure)

$$K^{-1} = \frac{3(a+\Delta)}{\kappa} \times \left(1 - \frac{2}{1 + k_B T / 6\kappa\,\delta r_{HL}^2\, x(1-x)}\right)^{-1},$$

or after introducing the characteristic temperature related to the intermolecular interaction $2k_B T_i = 3\kappa\,\delta r_{HL}^2$,

$$K^{-1} = \frac{3(a+\Delta)}{\kappa}\,\frac{T + 4T_i x(1-x)}{T - 4T_i x(1-x)}. \qquad (8)$$

From Eq. (7), we can also find the relation between the equilibrium values of Δ and x:

$$\Delta = 2x\,\delta r_{HL} - pa^2/\kappa \cong 2x\,\delta r_{HL}. \qquad (9)$$

For the crystals composed of the molecules of one type ($x = 0$ or $x = 1$), we get just the above results for K_{LS}^{-1} and K_{HS}^{-1}, respectively. At the critical temperature of the spin transition at which $x(T_c) = 1/2$ holds, we get for the compressibility

$$K_c^{-1} = \frac{3(a+\Delta)}{\kappa}\,\frac{T_c + T_i}{T_c - T_i}.$$

The compressibility is obviously larger for the intermediate composition and has a maximum at the critical temperature when the fractions of the two components are equal. This feature is in a perfect agreement with the recent experimental findings [12]. The compressibility diverges and becomes negative if $T_c \leq T_i$.

Concentration Curves $x(T)$

Let us consider now the equation for $x(T)$. First, we study the case of the unrelaxed lattice with $\Delta = 0$, which is possible at high pressure. Then, the Gibbs energy takes the form

$$g = (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s)x + k_B T(x\ln x + (1-x)\ln(1-x)) - 3\kappa\,\delta r_{HL}^2\, x(1-x), \qquad (10)$$

which corresponds to the anticooperative interaction between the molecules of different spin. For this situation, it has been proposed in [9] to consider the sublattice order (see below) to describe possible first-order spin transitions.

Consider now the case of vanishing (ambient) pressure. Substituting to the Gibbs energy [Eq. (6)] the equilibrium value of Δ [Eq. (9)], one easily comes to the following form of the Gibbs energy dependent only on x:

$$g = (\delta h - T\delta s)x + k_B T(x\ln x + (1-x)\ln(1-x)) + 3\kappa\,\delta r_{HL}^2\, x(1-x), \qquad (11)$$

which is exactly the SD free energy with the positive (cooperative) interaction parameter $\Gamma = 3\kappa\,\delta r_{HL}^2$. This form of the Gibbs energy allows first-order spin transitions if the interaction characteristic temperature T_i is larger than the intramolecular characteristic temperature T_c. We see that even the sign of the effective intermolecular interaction drastically depends on the conditions of relaxation of the crystal geometry.

Concentration Waves

Let us continue the analysis of the unrelaxed crystal. We assume that the local deformations described by the variables U_k^{α} are vanishing as the uniform deformation variable Δ. In this case, the mechanical potential energy for the crystal with a nonuniform distribution of the molecules with different spin has the form

$$U = -3N\kappa\,\delta r_{HL}^2\, x(1+x) + N\kappa\,\delta r_{HL}^2 \sum_{\alpha}\sum_{k} \Gamma_k \Gamma_{-k} \cos k_{\alpha}. \qquad (12)$$

From this equation, it is clearly seen that the excitation of the concentration waves with the wave vectors $Q = (\pm\pi, \pm\pi, \pm\pi)$ diminishes the mechanical energy of the crystal. The wave vector Q corresponds to the alternation of the HS and the LS molecules in the cubic lattice. That means that the HS molecules have higher concentration on the sublattice formed by the sites complying the condition: $\exp(irQ) = 1$ and the LS molecules concentrate preferably on the sublattice with the condition $\exp(irQ) = -1$ or vice versa. The free energy for the crystal formed by the molecules of two types in the case when the concentration waves are allowed to appear acquires a more general form [11]:

$$g = (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s)x - 3\kappa\,\delta r_{HL}^2 x(1-x) + (k_B T/N)\sum_{\mathbf{r}}(n(\mathbf{r})\ln n(\mathbf{r}) + (1-n(\mathbf{r}))\ln(1-n(\mathbf{r}))) + \kappa\,\delta r_{HL}^2 \sum_{\alpha}\sum_{k}\Gamma_k\Gamma_{-K}\cos k_\alpha, \quad (13)$$

where the local concentrations $n(\mathbf{r})$ of the HS molecules are defined by the condition

$$n(\mathbf{r}) = x + \gamma(\mathbf{r}),$$

with

$$\gamma(\mathbf{r}) = \sum_{\mathbf{r}} \exp(-i k\mathbf{r})\Gamma_k.$$

It should be noted that the overall fraction of the HS molecules and the local deviations $\gamma(\mathbf{r})$ are understood now as ensemble averages. With the only allowed concentration wave vector Q, the expression for the Gibbs energy per molecule acquires the form

$$\begin{aligned} g = {} & (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s)x \\ & - 3\kappa\,\delta r_{HL}^2 x(1-x) - 3\kappa\,\delta r_{HL}^2\Gamma_Q^2 \\ & + (1/2)k_B T\big((x+\Gamma_Q)\ln(x+\Gamma_Q) \\ & + (x-\Gamma_Q)\ln(x-\Gamma_Q) \\ & + (1-x-\Gamma_Q)\ln(1-x-\Gamma_Q) \\ & + (1-x+\Gamma_Q)\ln(1-x+\Gamma_Q)\big). \quad (14) \end{aligned}$$

It is convenient to introduce a new concentration variable ξ by the relation $x = 1/2 + \xi$ since the point $\xi = 0$ corresponds then to the critical concentration of the HS molecules 1/2. Then, the Gibbs energy becomes

$$\begin{aligned} g = {} & (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s)(1/2 + \xi) \\ & - 3\kappa\,\delta r_{HL}^2\big((1/4 - \xi^2) + \Gamma_Q^2\big) \\ & + (1/2)k_B T\big((1/2 - \xi + \Gamma_Q)\ln(1/2 - \xi + \Gamma_Q) \\ & + (1/2 - \xi - \Gamma_Q)\ln(1/2 - \xi - \Gamma_Q) \\ & + (1/2 + \xi - \Gamma_Q)\ln(1/2 + \xi - \Gamma_Q) \\ & + (1/2 + \xi + \Gamma_Q)\ln(1/2 + \xi + \Gamma_Q)\big). \quad (15) \end{aligned}$$

Differentiating this expression with respect to two variables ξ and Γ_Q, we get for the extrema of the Gibbs energy functional the following conditions:

$$6\kappa\,\delta r_{HL}^2\xi - (1/2)k_B T\ln \times \frac{(1/2-\xi)^2 - \Gamma_Q^2}{(1/2+\xi)^2 - \Gamma_Q^2} + \mu(T) = 0$$

$$-6\kappa\,\delta r_{HL}^2\Gamma + (1/2)k_B T\ln \times \frac{(1/2+\xi+\Gamma_Q)(1/2-\xi+\Gamma_Q)}{(1/2-\xi-\Gamma_Q)(1/2+\xi-\Gamma_Q)} = 0,$$

with $\mu(T) = (\delta h + 6\kappa\,\delta r_{HL}^2 - T\delta s)$. One can easily see that at $T = T_c$ [defined by the condition $\mu(T_c) = 0$] the point ($\xi = 0$; $\Gamma_Q = 0$) is an extremum of the Gibbs energy. That justifies our choice of the variable ξ. Expanding g in the Taylor series with respect to ξ and Γ_Q up to the fourth order, we get for the entropy term

$$(1/2)k_B T\big(-2\ln 2 + 4(\xi^2 + \Gamma_Q^2) + (16/3)(\xi^4 + 6\xi^2\Gamma_Q^2 + \Gamma_Q^4)\big).$$

Combining that with the terms of the mechanical energy and that of the molecular part of the Gibbs energy, we get

$$\begin{aligned} g \cong {} & \mu(T)\xi + 3\kappa\,\delta r_{HL}^2(\xi^2 - \Gamma_Q^2) \\ & + 2k_B T\big[(\xi^2 + \Gamma_Q^2) + (4/3) \\ & \times(\xi^4 + 6\xi^2\Gamma_Q^2 + \Gamma_Q^4)\big] \\ = {} & \mu(T)\xi + (2k_B T + 3\kappa\,\delta r_{HL}^2)\xi^2 \\ & + (2k_B T - 3\kappa\,\delta r_{HL}^2)\Gamma_Q^2 \\ & + (8/3)k_B T(\xi^4 + 6\xi^2\Gamma_Q^2 + \Gamma_Q^4). \quad (16) \end{aligned}$$

We see that the multiplier at ξ^2 is always positive, whereas the multiplier at Γ_Q^2 becomes negative for the temperatures below $T_0 = 3\kappa\,\delta r_{HL}^2/2k_B$. The critical points of the above Landau expansion are

$$\partial g/\partial\xi = \mu(T) + 2(2k_B T + 3\kappa\,\delta r_{HL}^2 + 16k_B T\Gamma_Q^2)\xi + (32/3)k_B T\xi^3 = 0$$

$$\partial g/\partial\Gamma = 2(2k_B T - 3\kappa\,\delta r_{HL}^2 + 16k_B T\xi^2)\Gamma_Q + (16/3)k_B T\Gamma_Q^3 = 0.$$

The only possible solution of the first equation at $\mu(T_c) = 0$ is $\xi = 0$, though for Γ_Q, the nontrivial solutions are possible below the ordering temperature T_0. They present the ordered states of the binary solution of the two spin forms of the considered complex. These two solutions are always minima and have lower Gibbs energy than that of the uniform (disordered) solution with $\Gamma_Q = 0$. Unfortunately, these two minima are characterized by the same equilibrium concentration of the HS isomer, and for that reason, any transition between them cannot account for the observed abrupt change of the HS fraction. This also does not correspond directly to the sublattice order model of spin transitions [9] where the HS isomer concentration changes abruptly.

Concentration Waves with Lattice Relaxation

We consider now the case of the partial relaxation when only Δ is allowed to relax, whereas U_k^α are kept zero. The only difference with the above formulas is the change of the sign at the $(1/4 - \xi^2)$ term which is now positive. That means that at the temperature below $T_0 = T_i$ the uniform mixture with $\xi = \Gamma_Q = 0$ loses its stability with respect to both variables ξ and Γ_Q. We see that the ordering temperature T_0 now coincides with the temperature of the second-order transition in the SD model, below which the first-order transitions between the phases with the different content of the HS component occur. Making respective changes in the above Landau expansion Eq. (16), we get two pairs of nontrivial minima of the Gibbs energy for the temperatures below the ordering temperature T_0: $\Gamma_Q = 0$, $\xi_u^2 = (3/16)(3\kappa\,\delta r_{HL}^2 - 2k_B T_c)/k_B T_c$—two uniform phases with $\xi_u = \pm\sqrt{\xi_u^2}$ and two ordered phases with

$$\Gamma_Q^2 = (3/68)(3\kappa\,\delta r_{HL}^2 - 2k_B T_c)/k_B T_c$$

and

$$\xi_0 = \pm\sqrt{\xi_0^2}\,;$$
$$\xi_0^2 = (15/272)(3\kappa\,\delta r_{HL}^2 - 2k_B T_c)/k_B T_c.$$

One can easily check that at least for the critical temperatures close to the ordering temperature the equilibrium Gibbs energy is lower for the uniform phase.

The transition between the uniform phases $\xi_u = \pm\sqrt{\xi_u^2}$ is obviously the first-order transition known for a long time for the SD model [5]. We see also that the ordering not only increases the Gibbs energy, but also diminishes the amplitude of the variation of the HS fraction. The increase of the Gibbs energy in the ordered phase with respect to that of the uniform stable phase can be easily understood. The reason is a combination of the cooperative sign of the effective intermolecular interaction in the relaxed crystal and the opposite sign of the interaction in the concentration wave term. The concentration waves with the wave vector Q when excited force each molecule to be surrounded by those of the different spin. Meanwhile, the cooperative sign of the interaction favors for each molecule the surrounding by the molecules of the same spin. A collision of these two interactions leads to the overall energy increase in the ordered phase.

Finally, we turn to the case of the completely relaxed crystal formed by the two spin isomers. First, we have to find the Gibbs energy as a function of the concentration variables (x and Γ_k) only. In differentiating the expression for the mechanical energy U [Eq. (5)] with respect to U_k^α, one finds from the condition $\partial U/\partial U_k^\alpha = 0$ for the mechanical equilibrium the equilibrium value for the Fourier transforms of the local deformations related to the local fraction deviations:

$$U_k^\alpha = -\delta r_{HL}\,\frac{1 + \exp(ik_\alpha)}{1 - \exp(-ik_\alpha)}\,\Gamma_k \tag{17}$$

for all α and k. Inserting this into the mechanical energy [Eq. (5)], we get finally

$$\begin{aligned} U = {} & 3N\kappa\,\delta r_{HL}^2\,x(1 - x) \\ & - 3N\kappa\,\delta r_{HL}^2 \sum_k \Gamma_k \Gamma_{-k}. \end{aligned} \tag{18}$$

This result is to be used in the formula for the Gibbs energy in the same manner as previous ones. Assuming that the local fraction deviations are small as compared to the fractions of the both HS and LS components of the binary mixture, we get by expanding the mixing entropy term up to the second order in Γ_k

$$\begin{aligned} g = {} & (\delta h - T\delta s)x + 3\kappa\,\delta_{HL}^2\,x(1 - x) \\ & - 3\kappa\,\delta r_{HL}^2 \sum_k \Gamma_k \Gamma_{-k} \\ & + k_B T(x \ln x + (1 - x)\ln(1 - x)) \\ & + \frac{k_B T}{2x(1 - x)} \sum_k \Gamma_k \Gamma_{-k}. \end{aligned} \tag{19}$$

Rewriting this with the use of the variable ξ and expanding up to the second order in it gives

$$g = \mu(T)\xi + (2k_BT - 3\kappa\,\delta r_{HL}^2) \times \left(\xi^2 + \sum_k \Gamma_k \Gamma_{-k} \right). \quad (20)$$

This expression obviously loses stability at $T = T_0$ which should be accompanied by the excitation of the concentration waves with all wave vectors k. It is clear that the oversimplified model adopted for the intermolecular interaction does not allow us to get the correct dispersion law for the concentration waves. Most probably, the anharmonic terms in the crystal energy must be taken into account (see also the discussion below).

Discussion and Conclusion

In the present article, two major unsolved problems concerning the spin transitions in the molecular crystals were addressed. The first one was the question concerning the role of the crystal structure relaxation for the whole process of the spin transition. It turned out that we can successfully describe the experimental features of the crystal volume increase and the behavior of the compressibility with temperature in the undercritical parameter region, i.e., in the area where the intermolecular interaction is weaker than that required for the first-order phase transition in the phenomenological SD model. We also have found that the ideal relaxation of the crystal lattice parameter is necessary for getting the cooperative sign of the intermolecular interaction required by the SD model for explanation of the cooperativity effects in the spin transitions. As far as we know, it is the first time that the parameter of the SD model is expressed in terms of the microscopic characteristics (κ and δr_{HL}). These parameters can be also related to the independently measurable quantities: compressibility of the crystal and the lattice constant variation under the transition (see below).

When the interaction becomes that strong that the spin transition is a first-order transition ($T_i = 3\kappa\,\delta r_{HL}^2/2k_B > T_c = \delta h/\delta s$), the compressibility diverges and becomes negative. That feature of the model can be related to the observation that the crystals exhibiting hysteresis in the spin transition (i.e., those that for sure manifest the first-order transition and thus have the intermolecular interaction temperature T_i higher than T_c) do not survive the operation and are always broken [12].

We have undertaken also an attempt to reproduce the intuitive results of [9] on a regular basis and by that to find the conditions to be imposed on the lattice structure and on the intermolecular interactions in the crystal formed by the spin-active transition-metal complexes in order to get first-order phase transition between the ordered phases of the corresponding binary mixture of the two-spin isomers with nonvanishing difference between the fractions of the HS form in these two phases. Though our attempt was not particularly successful, we nevertheless can extract some useful information from the results obtained. First of all, we should mention that the model that we used in our study is oversimplified in two respects: First, it contains only two energy parameters k_BT_c and $k_BT_i = k_BT_0$ and all the behavior of the system depends on their ratio only. Whatever changes in the system behavior occur only when the critical temperature defined by the molecular properties of the complexes forming the crystal and the ordering (interaction) temperature defined by the intermolecular forces become equal. Accidentally, the effective parameter (and the respective temperature) governing ordering and that governing cooperativity coincide, which is hardly the case for any real crystal composed of rather complex molecules (see the Introduction and [1–4]. Thus, a successful treatment should involve a more detailed description of the intermolecular interaction, since it is unrealistic to load on the single parameter κ the elastic properties of the whole crystal and the reaction of the neighbor molecules on the variation of the intramolecular coordinates δr_{HL} occurring in the course of the spin transition.

The model is also oversimplified with respect to its overall geometry. The lattice that we use is the simple cubic lattice with the nearest-neighbor interaction. It is very difficult to imagine any other sublattice separation of the cubic lattice rather than its separation in two sublattices defined by the conditions of the section Concentration Waves. However, for these two sublattices, the ratio s of the numbers of the sites within the sublattices equals unity, whereas the theory [9] predicts the first-order transition with the finite change of the fraction of the HS isomers only for s strictly larger than 1. Only in this case, the terms of the form $\xi\Gamma^2$ and $\xi\Gamma^3$ which are responsible for the nonvanishing equilibrium values of ξ in the ordered phases even for the anticooperative sign of the intermolecular interaction appear in the Landau expansion for the free energy. Even in the context of the metal binary alloys [11], the ordered phases appear for the more complex face-centered cubic lattice. The real crystals exhibiting the cooperative spin transitions have much more complex crystal structure which can alone be responsible for appearance of additional terms in the free energy and thus for possible nontrivial ordered phases in the molecular crystals undergoing the spin transitions. Work along these lines is now in progress.

Finally, we discuss the relations between the model proposed in this article and that due to Spiering and co-workers [13, 14]. The results of these two approaches look very similar since they both try to relate the cooperativity of the spin transitions in molecular crystals with the elastic properties of the latter. However, the two approaches differ by the means they use to reduce one class of observables (those related to the spin transitions) to another one (those related with the elastic properties). The approach [13, 14] considers the crystal composed by the molecules undergoing the spin transition as an elastic medium with defects of different volume representing the HS, LS, and nonmagnetic matrix ions embedded in it. Then, the formulas of the elasticity theory are applied in order to describe such defects and their interactions. However, the elasticity theory is by definition a long-range theory and its formulas are valid only for the characteristic distances much longer than the lattice constant. It may well be the case if the spin-active molecules represent a small fraction of the whole number of the molecules and the average distance between them is of the order of many intermolecular spacings, whereas the rest of the lattice is filled by the molecules which are not spin-active. In this case, the elasticity formulas apply and the result is expressed in terms of the *experimental* elastic moduli K and σ [or of the Eshelby constant $\gamma_0 = 3(1 - \sigma)/(1 + \sigma)$] and of the *experimental* crystal volume change *per* molecule ΔV_{HL}. Our approach, however, explores the opposite limit: We try to express simultaneously the elastic modulus K, the crystal volume change, the lattice constant itself, and the cooperative interaction in terms of the *microscopic* parameters of the intermolecular potential κ and d and of the molecular parameter δr_{HL} characterizing the spin transition in a separate molecule. Within the proposed model, the approximate relations between the macroscopic and microscopic quantities are established which allowed us to exclude the microscopic values from the final answers. However, the theory itself has a different characteristic length, namely, the intermolecular separation and thus relates all the effects to the nearest-neighbor interactions and to their renormalization if the crystal is allowed to relax. Incidentally, the results of the two approaches do *not* coincide. In the approach [13, 14], the phenomenological interaction parameter Γ (see the Introduction) is proportional to $(1 - \gamma_0)$. In our simple cubic model, γ_0 apparently equals to unity so that the effective interaction of the elastic origin vanishes. By contrast, the short-range interactions do not depend on the Eshelby constant and, probably, also give some contribution to the observed cooperativity of the spin transitions.

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References

1. E. König, Struct. Bond. **76**, 51 (1991).
2. E. König, G. Ritter, and S. K. Kulshreshtha, Chem. Rev. **85**, 219 (1985).
3. M. Bacci, Coord. Chem. Rev. **86**, 245 (1988).
4. P. Gütlich, Struct. Bond. **44**, 83 (1981).
5. C. P. Slichter and H. G. Drickamer, J. Chem. Phys. **56**, 2142 (1972).
6. R. A. Bari and J. Sivardiére, J. Phys. Rev. B **5**, 4466 (1972).
7. P. Gütlich, H. Koppen, R. Link, and H. G. Steinhäuser, J. Chem. Phys. **70**, 3977 (1979).

8. A. Bousseksou, J. Jasser, J. Linares, K. Boukheddaden, and F. Varret, J. Phys. I Fr. **2**, 1381 (1992).
9. A. L. Tchougréeff, Chem. Phys. Lett. **214**, 627 (1993).
10. J.-A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, and J. Zarembovitch, J. Am. Chem. Soc. **114**, 4650 (1992).
11. A. G. Khachaturian, *The Theory of Phase Transformation and Structure of Solid Solutions* (Moscow, Nauka Publ., 1974) (in Russian).
12. J. Zarembowitch, Private communication.
13. H. Spiering, E. Meissner, H. Köppen, E. W. Müller, and P. Gütlich, Chem. Phys. **68**, 65 (1982); P. Adler, L. Wiehl, E. Meissner, C. P. Köhler, H. Spiering, and P. Gütlich, J. Chem. Phys. Solids **48**, 517 (1987).
14. N. Willenbacher, and H. Spiering, J. Phys. C **21**, 1423 (1988); H. Spiering and N. Willenbacher, J. Phys. Condens. Mat. **1**, 10089 (1989).