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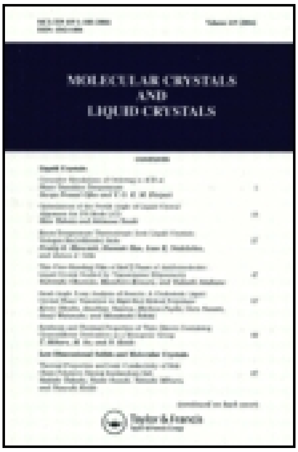

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Lattice Relaxation and Cooperativity in the Low-Spin to High-Spin Transitions in Molecular Crystals

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

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Abstract

We apply a model recently proposed for the analysis of the spin transitions in molecular crystals of the spin active complexes of Fe(II) to analysis of some experimental data. 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 if the crystal geometry is allowed to relax in the course of the transition the cooperative sign of the effective intermolecular interaction appears and thus the spin transition becomes a first order phase transition with the finite change of the fraction of the high spin molecules as a function of temperature. The magnitude of the effective interaction is estimated from the data on the crystal compressibility and within the assumption of the van der Waals character of the forces responsible for the effective interaction.

I. Introduction

The complexes of transition metals with the electronic configuration d^4, d^5, d^6, and d^7 can have both high spin (HS) and low spin (LS) central ions.[1] 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

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the ratio of the d-level splitting by 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 $10Dq >> P$ (strong ligand field) the ground state is LS; if $10Dq << P$ (weak ligand field) the ground state is HS. If, however, $10Dq \cong P$ (*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 the 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 are 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 $x(T)$ curves can either (1) increase smoothly with the temperature increase, or (2) undergo an abrupt increase at some critical temperature T_c, or (3) exhibit hysteresis *i.e.* undergo the abrupt changes of the HS fraction at different temperatures depending on the way how 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. The volume of the crystal changes (though the crystal structure as a whole except the lattice parameters is conserved); the specific heat diverges *etc.*[1-4] The finite volume variation and the hysteresis suggest that the spin transitions are the first order phase transitions at least for the concentration curves of the type (2) and (3). For the spin transitions in the solid state a phenomenological theory has been proposed by Slichter - Drickamer (SD) which results in a first order phase transition.[5] 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 crucial feature for this model. The SD model suggests the following form of the free energy for the crystal undergoing the transition:

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

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 at T_c if $\Gamma \geq 2k_B T_c$,

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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 $T_c = \delta h/\delta s$. However, the existence of the positive Γ has not been understood until recently[6] from the point of view of the microscopic properties of the constituent molecules. The purpose of the present work is to find the conditions when it is possible to have cooperative sign of the effective interaction between the molecules and to apply this result to the analysis of differences in the cooperative behavior of various iron(II) complexes exhibiting the spin transition in the solid phase.

II. Account of the model

A. Spin active molecules

For describing the spin transition on the molecular level a model has been recently proposed.[6] Within this model each molecule of an iron(II) complex undergoing the transition is represented by an octahedron formed by the central ion surrounded by the six point ligands placed on the octahedron axes. As it is evident from its name the spin of the central ion changes when the spin transition takes place. This change is possible only due to change in the positions of the surrounding ligands. The distances $Fe - N$ increase in the moment of the transition and respectively the crystal field 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 the approach[6,7] this feature is modeled by introducing the variation $\delta r_{HL} > 0$ of the distance between the metal and the point ligand. This distance is R in the LS state and it is $R + \delta r_{HL}$ in the HS state.

B. Crystal formed by the LS and HS isomers

1.Intermolecular forces

A simple cubic crystal formed by the octahedra introduced just above was proposed in Ref. 6 as a model for the crystal undergoing the spin transition. The axes of the octahedra are directed along the three axes of the simple cubic lattice. The intermolecular interaction which holds the molecules together in the crystal is due to the ligand - ligand interaction extended to the nearest neighbor ligand along the crystal axis. We assume following Refs. 6,7 that the interaction energy is a quadratic function of the separation 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: $K^{-1} = 3a/\kappa$, where a is the lattice constant of the crystal at ambient pressure ($a = d+2R$ in the LS crystal and $a = d + 2R + 2\delta r_{HL}$ for the crystal formed by the HS molecules).

2. Mechanical energy

Let us consider now the mechanical potential energy of the crystal formed by the HS and LS molecules. To do so we following[7,8] introduce the occupation number operators $\sigma_i(\mathbf{r})$ for the lattice sites. The $\sigma_i(\mathbf{r})$ equals to 1 if the $\mathbf{r}$-th site of the lattice is occupied by the molecule of the i-th type. In our case there are two types of the molecules (LS and HS) with $i = 0$ and 1, respectively. The mechanical potential energy of the crystal then has the form:[7]

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

where $\alpha = x, y, z; \hat{\alpha}$ is the unit vector along the axis α; and $W^{\alpha}_{ii'}(\mathbf{r})$ is the potential energy of the interaction betweenthe 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 the distance between the closest ligands of these molecules is given by:

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

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; Δ is the uniform elongation of the parameters of the unit cells. After taking into account the relation between the equilibrium lattice constant a for the completely LS crystal and the equilibrium interligand separation d the potential energy assumes the form:

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

Now we introduce the average fraction x of the HS molecules in the lattice according to:

$$x = (1/N) \sum_{\mathbf{r}} \sigma_1(\mathbf{r}) \tag{3}$$

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

$$\sigma_0(\mathbf{r}) = 1 - x - \gamma(\mathbf{r})$$
$$\sigma_1(\mathbf{r}) = x + \gamma(\mathbf{r}).$$

Provided 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 the conditions:

$$\sum_{\mathbf{r}} u_\alpha(\mathbf{r}) = 0; \sum_{\mathbf{r}} \gamma(\mathbf{r}) = 0$$

the expression for the energy assumes the form:

$$\begin{aligned} U = {} & 3N\kappa/2((1-x)^2\Delta^2 + 2x(1-x)(\Delta - \delta r_{HL})^2 + x^2(\Delta - 2\delta r_{HL})^2) \\ & + N\kappa/2 \sum_{\alpha} \sum_{k} U_k^\alpha U_{-k}^\alpha \mid 1 - \exp(ik_\alpha) \mid^2 + \\ & + N\kappa\delta r_{HL} \sum_{\alpha} \sum_{k} \Gamma_k U_{-k}^\alpha (1 - \exp(ik_\alpha)(1 + \exp(-ik_\alpha)) + \\ & + N\kappa\delta r_{HL}^2 \sum_{\alpha} \sum_{k} \Gamma_k \Gamma_{-k} \exp(-ik_\alpha) \end{aligned} \tag{4}$$

where the Fourier transforms for both the shifts and the local fraction deviations are given by:

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

From Eq. (4) one can easily 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 containing the local lattice distortions coupled with the local fraction deviations are decoupled from the overall fraction/uniform deformation term.

Let us consider the uniform case when U_k^α and Γ_k are vanishing and the global first term in the mechanical energy works. The Gibbs energy for the crystal undergoing the spin transition acquires the following form:

$$g = G/N = (\delta h - T\delta s)x + k_BT(x\ln x + (1-x)\ln(1-x)) +$$
$$+3\kappa/2(\Delta^2 - 4\Delta\delta r_{HL}x + 2\delta r_{HL}^2 x(1+x)) + p(a+\Delta)^3 \tag{5}$$

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

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

$$\begin{gathered}\partial g/\partial x = (\delta h + 6\kappa\delta r_{HL}^2 - T\delta s) + k_BTx/(1-x) - 6\kappa\delta r_{HL}(\Delta - \delta r_{HL}x) = 0,\\ \partial g/\partial\Delta = \kappa(\Delta - 2x\delta r_{HL}) + p(a+\Delta)^2 = 0\end{gathered} \tag{6}$$

The relation between the equilibrium values of Δ and x reads:

$$\Delta = 2x\delta r_{HL} - pa^2/\kappa \cong 2x\delta r_{HL} \tag{7}$$

Let us consider now the equation defining $x(T)$. Substituting to the Gibbs energy Eq. (5) the equilibrium value of Δ Eq.(7) one easily comes to the following form of the Gibbs energy dependent only on x:

$$g = (\delta h - T\delta s)x + k_BT(x\ln x + (1-x)\ln(1-x)) +$$
$$+3\kappa\delta r_{HL}^2 x(1-x) \tag{8}$$

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 $\Gamma/2k_B$ is larger than the intramolecular characteristic temperature T_c.

III. Discussion and conclusion

The result obtained just above shows that the ideal relaxation of the crystal lattice parameter Δ 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. By contrast, in Ref. 7 the effective interaction in a similar model turned out to be anticooperative since the lattice relaxation has not been allowed. The absolute values of Γ obtained here and in Ref. 7 coincide, however. That allows us to use the estimates[7] of Γ in terms of the independently measurable experimental

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quantities: compressibility of the crystal and the lattice constant variation under the transition instead of the estimates of the present paper given in terms of the microscopic characteristics (κ and δr_{HL}).

Using the data of Refs. 7, 9 we get for the effective interaction in the [Fe(phen)$_2$(NCS)$_2$] crystal (phen stands for phenanthroline) an estimate $\Gamma/2k_B$ = 180K,which is pretty close to the experimental critical temperature T_c = 176K for this compound. This accounts for the abrupt increase of the fraction of the HS isomer at the critical temperature observed experimentally (sometimes even a very narrow hysteresis loop is reported for this compound[1]).

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