Journal of Physics and Chemistry of Solids 75 (2014) 966–971

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

Pressure and temperature induced high spin–low spin phase transition: Macroscopic and microscopic consideration

G. Levchenko*, A. Khristov, V. Kuznetsova, V. Shelest

Donetsk Institute for Physics and Engineering, NASU, R. Luxemburg Str., 72, Donetsk, Ukraine 83114

ARTICLE INFO

Article history:
Received 5 November 2013
Received in revised form
28 March 2014
Accepted 8 April 2014
Available online 18 April 2014

Keywords:
C. High pressure
A. Spin crossover complex
D. Elastic interactions
D. Microscopic model
D. HL phase transition

ABSTRACT

The behavior under pressure of the high spin–low spin phase transition in the coordination compounds containing 3*d* ions is analyzed using thermodynamic and microscopic approaches. For thermodynamic approach the mean field model with interactions between spin-crossover molecules is considered. Microscopic model takes into account the interaction of *d* electrons of the transition metal ions with full symmetric distortions of the ligands. The relationship of the thermodynamic interaction parameters with microscopic ones is installed and shown how the quantum–mechanical interactions form the cooperativity of the system. Within the microscopic model the temperature and pressure dependences of the high spin fraction in 2-D compounds $\{Fe(3\text{-}Fpy)_2[M(CN)_4]\}$ ($M=Pd$, Pt) are simulated and microscopic parameters are evaluated. It is concluded that different experimental behaviors of the temperature and pressure induced spin transitions are determined by different variations of the inelastic and elastic energies under pressure, and vibrational component of the free energy drives the ST equally with electronic part.

1. Introduction

Spin crossover (SCO) phenomenon in the coordination compounds is of current interest in chemistry, physics and material science because of its intrinsic fundamental properties and potential applications [1–3]. The elucidation of the possibility to variate the spin transition (ST) behavior by external perturbations is an important goal of the modern studies of this phenomenon. As the change of the volume of the molecules and metal–ligand bond length are observed always at ST [4–8], the pressure as an external perturbation effectively influences the SCO. Moreover, the pressure is a powerful tool for investigation of the thermodynamic characteristics and microscopic aspects of the ST in molecular compounds and therefore the experimental study of the pressure effect on SCO causes a continued interest [9–19].

The thermodynamic [20,21], static microscopic Ising-like [22] and Landau-type models [23] were proposed for theoretical consideration of the SCO. Within these models the main aspects of the ST behavior, like the characteristics of the thermal spin transition (gradual and abrupt, with and without hysteresis), the two-step spin crossover phenomenon in mononuclear compounds, and the occurrence of irreversible or incomplete transitions have been successfully explained [24–26]. The interpretation of the interaction constants based on a elastic theory was developed in [27]. Later a kinetic version of the elastic model was developed using non-equilibrium Monte Carlo methods [28]. In [29] it was shown that a purely elastic model with periodic boundary conditions mediates effective long-range interactions. Moreover, it has been shown that thermodynamic and microscopic models are completely equivalent in the mean-field approximation and thermodynamic properties of the ST and charge transfer processes have been described by a unified model [30]. Pressure influence on spin interconversion has been studied on the basis of thermodynamic [9,12,20,28,31] and Ising-like models [32–34]. It was observed in the experiment that non-monotonic behavior of the spin transition temperature and hysteresis under pressure [11,12,13,15] were successfully reproduced in frame of thermodynamic [12,28] and 1D atom–phonon models [35,36], where the elastic field and intermolecular interactions were considered as pressure dependent. Pressure induced phase transition has been investigated numerically, using Monte Carlo simulations in the isothermal isobaric ensemble, and several important properties of pressure induced ST have been reproduced [28]. The study of pressure influence on ST gives access to the elastic properties of the system, in particular, the thermo-elastic coefficients.

The microscopic model [37–39] gives an understanding of the physical picture of the ST. But the description of the experimental behavior of the ST is problematic through a big amount of unknown parameters and because these parameters are difficult to relate to elastic and interaction energies of the mean field model.

---

* Corresponding author. Tel.: +380623429699; fax: +380623429699.
E-mail address: g-levch@ukr.net (G. Levchenko).

http://dx.doi.org/10.1016/j.jpcs.2014.04.006
0022-3697/

In [40], for the first time, the behavior of the high spin–low spin (HL) phase transition in 2D coordination compounds {Fe(3-Fpy)$_2$[M(CN)$_4$]} (M=Pd, Pt) induced separately by temperature and pressure was compared , and the disagreement between experimental P–T phase diagrams was observed. It is not clear why the correspondent points of phase P–T diagrams do not coincide with one another. It requires the explanation and, from our point of view, the application of the thermodynamic and microscopic models in a unified way is more preferable for that. The main advantage of the application of these models is to receive the opportunity to understand the physical nature of change of the spin interconversion driving forces.

In this paper we introduce the microscopic consideration, based on the Kambara model [37–39], for describing temperature induced ST (TIST) under invariable pressure and pressure induced ST (PIST) at invariable temperature and relate the microscopic interaction parameters in the ligand field approximation with the thermodynamic ones. The efficiency of this consideration is demonstrated by analyzing of TIST and PIST for 2D spin crossover coordination compounds studied in [40].

2. Microscopic model of the ST under pressure

Microscopic model developed here considers the system which is built up of N molecules, each of which contains a Fe(II) ion octahedrally surrounded by bulky ligand complexes. The model takes into account the influence on the spin state of the change under temperature and pressure of the totally symmetric deformation of the ligand complexes and the elastic medium. In contrast to Kambara model, the distortions of the complexes other than the totally symmetric are not considered. This approximation is justified by the fact that ST primarily is determined by the difference in volume of the ligand complexes in the HS and LS states regardless of the distortions of the SCO molecules.

According to microscopic theory developed in [37–39] the Hamiltonian of this spin crossover system is represented as

$$H = H_0 + H_M + H_{eM} + H_{eL} + H_L \tag{1}$$

The first term is the Hamiltonian for d electrons of Fe ions in the undistorted system and given by

$$H_0 = \sum_{i=1}^{N} [f_0(i) + V_0(i)] \tag{2}$$

where $f_0(i)$ is the Hamiltonian of the free Fe(II) ion in the molecule, $V_0(i)$ is the octahedral ligand field.

The second term is the Hamiltonian for the intramolecular displacements of the ligands, when the intermolecular coupling is considered. $P_\alpha(\mathbf{k})$ is the canonical conjugate momentum to $Q_\alpha(\mathbf{k})$ normal coordinate belonging to the α irreducible representations of the point group of $\mathbf{k}$ and written as

$$H_M = \frac{1}{2}\sum_{\alpha}\sum_{\vec{k}}\left[\frac{P^*_\alpha(\mathbf{k})P_\alpha(\mathbf{k})}{M_\alpha} + M_\alpha\omega^2_\alpha(\mathbf{k})Q^*_\alpha(\mathbf{k})Q_\alpha(\mathbf{k})\right] \tag{3}$$

The third term is the Hamiltonian of the interaction of d electrons with totally symmetric intramolecular displacement of the ligands and has a form

$$H_{eM} = \sum_{i=1}^{N} [\partial V(i)/\partial Q_{1i}]_0 Q_{1i} = \sum_{i=1}^{N} X_{1i} Q_{1i} \tag{4}$$

The fourth term is the Hamiltonian of the interaction between d electrons and the lattice strain U_1. This term is written as

$$H_{eL} = \sum_{i=1}^{N} [\partial V(i)/\partial U_1]_0 U_1 \tag{5}$$

The fifth term is the elastic energy and written as

$$H_L = \frac{1}{2} C_1 U_1^2 \tag{6}$$

where $C_1 = 3BV_0$ (B is the bulk modulus; V_0 is the average volume per SCO complex in the absence of deformation) and $U_1 = 1/\sqrt{3}(e_{x\,x} + e_{y\,y} + e_{z\,z})$ is a lattice strain, represented as the sum of the diagonal components of the strain tensor.

Using canonical transformation and taking into account the random-phase approximation giving the ratio $X_i X_j \Rightarrow \langle\overline{X}\rangle X_i + \langle\overline{X}\rangle X_j - \langle\overline{X}\rangle\langle\overline{X}\rangle$ (where $\langle\overline{X}\rangle$ is the quantum and thermal average), the terms of the Hamiltonian ($H_M + H_{eM}$) are reduced to the harmonic part and to three terms per molecule complex

$$-\frac{1}{2} j_1 X_{1i}^2 - K_1\langle X_1\rangle X_{1i} + \frac{1}{2N} K_1 \langle X_1\rangle^2 \tag{7}$$

where $X_1 = [\partial V(i)/\partial Q_1]_0$ is the operator of the interaction of d electrons of the metal ion with ligand field.

$j_1 = 1/N\sum_k 1/M_1\omega_1^2(\mathbf{k})$ and $K_1 = (1/M_1\omega_1^2(0)) - j_1$ are the electronic coupling strengths.

The first term in Eq. (7) corresponds to the energy gained from the individual distortions of each molecule, second term corresponds to the energy gained from the individual molecular distortions in the mean field $\langle X_1\rangle$ and third term indicates the energy for the cooperative molecular distortions.

The eigenvalues of the transformed Hamiltonian on the basis of low spin state $|\Psi_{HS}\rangle$ E_{LS} and high spin state $|\Psi_{HS}\rangle$ E_{HS} are defined as

$$E_{LS} = \frac{1}{2}q_1^2 + b_1 q_1 + \frac{1}{2}u_1^2 + b u_1 \tag{8}$$

$$E_{HS} = E_0 + \frac{1}{2}q_1^2 + \lambda_1 b_1 q_1 + \frac{1}{2}u_1^2 + b\lambda\, u_1 \tag{9}$$

Here

$$E_0 = \Delta\varepsilon_0 - \frac{1}{2}\omega_0 b_1^2(\lambda_1^2 - 1) \tag{10}$$

$$\Delta\varepsilon_0 = \langle\psi_{HS}|(f_0(i) + V_0(i))|\psi_{HS}\rangle - \langle\psi_{LS}|(f_0(i) + V_0(i))|\psi_{LS}\rangle \tag{11}$$

and

$$\omega_0 = \frac{j_1}{K_1} = \frac{K_0}{\langle K\rangle - K_0} \tag{12}$$

In Eq. (12) K_0 is a force constant in the long-wavelength limit ($\mathbf{k}\to 0$) and $\langle K\rangle$ is the averaged value over the entire $\mathbf{k}$-space.

The variable parameter q_1, which describes the totally symmetric distortions of the complexes (inelastic interactions), and u_1, which describes elastic interactions of the lattice, are written as

$$q_1 = -\sqrt{K_1}\langle X_1\rangle \tag{13}$$

$$u_1 = \sqrt{C_1}U_1 \tag{14}$$

The main parameters of the model are

$$b = \langle\psi_{LS}\left|\left(\frac{\partial V(i)}{\partial U_1}\right)_0\right|\psi_{LS}\rangle/\sqrt{C_1}; \tag{15}$$

$$\lambda b = \langle\psi_{HS}\left|\left(\frac{\partial V(i)}{\partial U_1}\right)_0\right|\psi_{HS}\rangle/\sqrt{C_1}; \tag{16}$$

$$b_1 = \sqrt{K_1}\langle\psi_{LS}|X_1|\psi_{LS}\rangle; \tag{17}$$

$$\lambda_1 b_1 = \sqrt{K_1}\langle\psi_{HS}|X_1|\psi_{HS}\rangle. \tag{18}$$

The equilibrium values of q_1 and u_1 satisfy the thermodynamic equilibrium conditions $\partial G/\partial q_1 = 0$ and $\partial G/\partial u_1 = 0$. Gibbs free energy G is

$$G(T,P) = F_1 + F_{vib} + PV \tag{19}$$