PHYSICAL REVIEW B **70**, 184106 (2004)

Total free energy of a spin-crossover molecular system

H. Spiering,[1,*] K. Boukheddaden,[1] J. Linares,[1] and F. Varret[2]
[1]*Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, Staudinger Weg 9, D-55099 Mainz, Germany*
[2]*Laboratoire de magnétisme et d'optique, CNRS-université de Versailles-Saint-Quentinm 45, avenue des États-Unis, 78035 Versailles cedex, France*

(Received 20 April 2004; published 12 November 2004)

The free energy of spin-crossover molecular systems studied so far deal with the inner degrees of freedom of the spin-crossover molecules and a variety of interaction schemes between the molecules in the high spin (HS) and low spin (LS) states. Different types of transition curves, gradual, abrupt, hysteresis, and also two step transitions have been simulated or even satisfactorily fitted to experimental data. However, in the last decade spin transition curves were measured, especially under pressure, which could not be explained within these theoretical models. In this contribution the total free energy of an anharmonic lattice incorporating spin-crossover molecules which have a certain misfit to the lattice and interact elastically by their change in volume and shape has been constructed for a finite spherical crystal treated as a homogeneous isotropic elastic medium. The simulations demonstrate that already the knowledge of average properties of the crystal, as elastic constants and the anharmonicity of the potential of the lattice, and relative effective sizes of the molecules and their misfit to lattice is sufficient to interpret spin transition behavior. Almost all known anomalous spin transitions behaviors have been reproduced within reasonable limits of such parameters.

DOI: 10.1103/PhysRevB.70.184106 PACS number(s): 62.20.Dc, 64.30.+t, 64.60.Cn, 64.70.−p

I. INTRODUCTION

Several spin-crossover compounds show a dependency of spin transition curves on applied pressure which has to be denoted as unusual as the theoretical models so far developed cannot simulate the different behaviors observed. Generally it is expected that transitions shift to higher temperatures by the fact that the molecules in the low spin (LS) state are stabilized under pressure by its smaller size as compared to molecules in the high spin (HS) state. The few molecular crystals studied in detail by x-ray crystallography support these qualitative consideration as to a high accuracy a linear increase of volume with increasing HS fraction has been observed.[1–5] For spin transitions with hysteresis which is due to the spin transition system and not accompanied by structural changes, beside the change of the volume and shape proportional to the HS fraction, not only a shift to higher temperatures but also a decrease of the width of the hysteresis is expected from the model calculations. However, there are observations which do not fit to these expectations. With increasing pressure the following behaviors have been reported: diverse increase of transition temperatures,[6,7] increasing hysteresis width,[8,9] shift of the hysteresis at constant width,[10] decreasing to zero and again increasing width,[6] shift of the transition to lower temperatures, equivalent to a stabilization of the HS state,[11] and stabilization of the HS state over the whole temperature range.[7,12]

In order to give a brief description of the structure of the models developed so far it is useful to start with isolated spin changing molecules in the lattice as present in highly diluted systems.[13] The fraction of molecules in the HS state $\gamma_{\rm HS}$ is obtained by the partition functions $Z_{\rm HS}$ and $Z_{\rm LS}$ of the molecules in the HS and the LS electronic/vibronic states, respectively:

$$\gamma_{\rm HS} = \frac{Z_{\rm HS}}{Z_{\rm HS} + Z_{\rm LS}}. \tag{1}$$

The Boltzmann population of the vibronic states already leads to a transition, even though a very gradual one, by the fact of the large difference of the energies of vibronic states in the two spin states. Many examples show a HS fraction close to 1.0 already at room temperature,[13] such that the standard methods such as optical, magnetic, and Mössbauer measurements fail to detect the small fraction of molecules in the LS ground state.

Introducing the free energies $f_\alpha = -Nk_BT \ln Z_\alpha$ ($\alpha = {\rm HS}, {\rm LS}$) of N particles their difference $\Delta f_{\rm HL} = f_{\rm HS} - f_{\rm LS}$ is obtained according to Eq. (1) from the measurement of $\gamma_{\rm HS}$:

$$\Delta f_{\rm HL}(T) = -Nk_BT \ln\left(\frac{\gamma_{\rm HS}(T)}{1-\gamma_{\rm HS}(T)}\right). \tag{2}$$

The free energy $F_{x\to 0}$ (concentration x of spin crossover molecules—typical Fe) of the mixture of HS and LS molecules in a highly diluted mixed crystal system ($x \to 0$) is then given by ($f = F/N$)

$$f_{x\to 0}(T,\gamma_{\rm HS}) = \Delta f_{\rm HL} \cdot \gamma_{\rm HS} - Ts_{\rm mix}(\gamma_{\rm HS}), \tag{3}$$

where $s_{\rm mix} = -k_B[\gamma_{\rm HS}\ln(\gamma_{\rm HS}) + (1-\gamma_{\rm HS})\ln(1-\gamma_{\rm HS})]$ is the mixing entropy for a random mixture of HS and LS molecules. The minimum of $f_{x\to 0}(T,\gamma_{\rm HS})$ with respect to $\gamma_{\rm HS}$ gives back Eq. (1).

In several cases[13–15] the spin transition curves of the full mixed crystal series could be parametrized by only two further parameters, an energy shift Δ and an interaction constant Γ, which may be considered as the expansion coefficients of the linear and quadratic term in $\gamma_{\rm HS}$:

$$f(T,\gamma_{\mathrm{HS}}) = f_{x\to 0}(T,\gamma_{\mathrm{HS}}) + x\Delta\gamma_{\mathrm{HS}} - x\Gamma\gamma_{\mathrm{HS}}^2. \quad (4)$$

Originally Drickamer *et al.*[16] used for the interaction term the symmetric form $\gamma_{\mathrm{HS}}(1-\gamma_{\mathrm{HS}})$ and spoke of an interaction between HS and LS molecules. With the same right we can speak of an interaction only between LS molecules expressing γ_{HS} by the LS fraction $\gamma_{\mathrm{HS}}=1-\gamma_{\mathrm{LS}}$. All cases become equivalent after readjusting the linear term. How has pressure been introduced in Eq. (4)? The observation of a linear dependency of volume on the HS fraction has suggested the term $p\Delta v_{\mathrm{HL}}\gamma_{\mathrm{HS}}$. Δv_{HL} is known from x-ray studies. This way satisfying agreement has been obtained for some monomolecular crystals.[1,17,18]

Equation (4), which represents a mean-field free energy, has been extended and modified to go beyond the mean-field approximation.[19–27] In the approach of Kambara[28,29] modeled after cooperative Jahn-Teller theory the lattice strains of different symmetries are coupled to the ligand field Hamiltonian of the spin-crossover molecule. The mean-field free energy is minimized with respect to three strain parameters A_{1g}, E_g, and T_{2g}, so that there is no direct connection between the HS fraction and pressure p. Nevertheless only similar behaviors as predicted by Eq. (4) could be obtained. This approach is mathematically equivalent to the free energy from above if only A_{1g} strain is considered.[30] As there is no experimental evidence of strong strain coupling to the ${}^5T_{2g}$ electronic state of the molecule in the HS state[31] the generalized approach of Kambara cannot be expected to model the unusual pressure behaviors observed.

A first step in understanding the anomalous behavior under pressure, that is the increasing hysteresis width, has been done recently. The consequences of the volume dependence of the bulk modulus has been discussed for small pressures. Analytical relationships between the interaction parameter taken to be proportional to the bulk modulus, the energy separation and entropy change going from the LS to HS state could be evaluated from the equation of state and regions of parameters were given, where such an unusual behavior has to be expected.

Here we follow this idea setting up a complete free energy of the whole system, such that the HS fraction as well as the volume and anisotropic deformations are free variational parameters. Because of the lack of knowledge about the lattice potential and phonon frequencies the simple Debye approximation for the phonons and Grüneisen behavior for the lattice potential has been used in a self-consistent way.

II. SPIN CROSSOVER MOLECULES AS DEFECTS

The interpretation of the interaction constant based on elasticity theory provides the difference in energy of the lattice potential dependent on the fraction of molecules in the HS state and the metal dilution x. For these elastic energies there are analytical expressions if the molecules are approximated by point defects and the crystal by a homogeneous isotropic elastic medium of spherical shape with only two elastic constants, the bulk modulus K and the Poisson ratio $0\leqslant\sigma\leqslant\frac{1}{2}$. The lattice sum over all two center interaction is performed applying mean-field approximation. It is well known that the interaction of spherical defects is too small to explain the effective interaction constants observed. Therefore in a second step general elastic dipoles are introduced following the scheme of the following sections.

A. Spherical defects

In order to outline the different contributions of elastic interaction according to the procedure in elasticity theory[32] the interaction between spherical defects is described in more detail. The interaction scheme for spherical defects has the mean-field property. The reason is that there is no interaction between spherical defects embedded in an infinite medium (no direct interaction) consequently no contribution depending on the distance between the molecules. Spherical point defects interact only via the surface by the image pressure belonging to their strain field.

1. Molecules approximated by spherical elastic dipoles

In the following first step the molecules in a mixed crystal system are represented by spheres of volumes v_{HS}, v_{LS}, and v_M for the spin changing molecule in the HS,LS state and the molecule containing the metal ion M, respectively. The misfit of the molecules to the crystal lattice is expressed by $v_\alpha - v_0$, where α=LS,HS,M, and the volume v_0 fits to the lattice site, i.e., the volume provided by the lattice for its molecules. In the case of an isotropic and homogeneous medium the elastic energy needed to extend or shrink the volume v_0 to that of v_α is given by[32]

$$e_\alpha = \frac{1}{2}K(\gamma_0-1)\left[\frac{(v_\alpha-v_0)^2}{v_0} - \gamma_0\frac{(v_\alpha-v_0)^2}{V}\right]. \quad (5)$$

Eshelby introduced the constant $\gamma_0=3(1-\sigma)/(1+\sigma)$ (Eshelby constant) the meaning of which will be given later. The volume V is the volume of the crystal, so that V/v_0 is of the order of Avogadro's number. Both energy contributions in Eq. (5) depend on the square of the misfit, so that the sign of the misfit does not enter.

The second term vanishing in an infinite medium corrects for the effect of a free surface of the crystal. It is interpreted as the volume work according to the image pressure on the surface of the crystal. The image pressure is the result of the volume change of the crystal Δv_α upon incorporation of v_α

$$\Delta v_\alpha = \gamma_0(v_\alpha - v_0) \quad (6)$$

which is larger by the factor $1\leqslant\gamma_0\leqslant 3$ (Ref. 32) than the misfit volume $v_\alpha - v_0$. The additional volume change $\Delta v_\alpha - (v_\alpha - v_0) = (\gamma_0-1)(v_\alpha-v_0)$ is formally attributed to a pressure $p_I = -K(\gamma_0-1)(v_\alpha-v_0)/V$. The second term is then the integral of $p_I\gamma_0\,dv$, where dv is the volume changing from v_0 to v_α inside the crystal and $\gamma_0\,dv$ the change observed at the surface of the crystal the image pressure is acting on:

$$\int_{v_0}^{v_\alpha} p_I\gamma_0\,dv = -K\gamma_0\,(\gamma_0-1)\left(\frac{1}{2}v^2 - v_0 v\right)\Bigg|_{v_0}^{v_\alpha} = \frac{1}{2}p_I\Delta v_\alpha. \quad (7)$$

For spherical symmetry, i.e., a spherical defect at the center of a spherical crystal, the pressure is constant over the surface, as assumed for the integration of Eq. (7). Eshelby, however, could show that Δv_α remains valid irrespective of the shape of V and the position of the defect, such that for a homogeneous distribution of defects over a volume V (a constant density of defects) the pressure is again constant over the surface. It is positive, when ions with $v_\alpha < v_0$ are incorporated, and negative for bigger volumes $v_\alpha > v_0$. This effect is used to create positive or even negative pressures by replacing atoms by smaller or larger foreign atoms, respectively. The term "chemical pressure" is therefore in use. Although small for one defect, for one mole of defects (in spin crossover compounds every metal lattice site is treated as a defect) the pressure adds up to a finite entity which acts on all defects. For N sites in a crystal (defects randomly distributed in an isotropic homogeneous elastic medium) the total elastic energy is not simply the sum of e_α, but becomes[14]

$$E = \frac{1}{2}K(\gamma_0 - 1)\sum_{i=1}^{N}(v_i - v_0)^2/v_0 - \frac{1}{2}K\gamma_0(\gamma_0 - 1)\left[\sum_{i=1}^{N}(v_i - v_0)\right]^2 \Bigg/ V. \qquad (8)$$

The second term, the energy correction due to the free surface, does not sum the squares of the misfits $v_\alpha - v_0$ but squares the sum of the misfits. The first term represents the self-energy in an infinite medium and the second term shall be called surface energy. The simple proof by complete induction which gives good insight into the mechanism of the interaction is given in Ref. 18.

The sums in Eq. (8) are expressed by the concentration x of spin changing molecules and the fraction γ_{HS} $(\nu = 1, 2)$:

$$\frac{1}{N}\sum_{i=1}^{N}(v_i - v_0)^\nu = x[\gamma_{\mathrm{HS}}(v_{\mathrm{HS}} - v_0)^\nu + (1 - \gamma_{\mathrm{HS}})(v_{\mathrm{LS}} - v_0)^\nu] + (1 - x)(v_M - v_0)^\nu. \qquad (9)$$

Comparing the phenomenological free energy of Eq. (4) with the energy per spin changing molecule E/Nx the terms proportional to $x\gamma_{\mathrm{HS}}^2$ and $x\gamma_{\mathrm{HS}}$ have to be interpreted as interaction constant Γ and the energy shift Δ:

$$\Gamma = \frac{1}{2}K\gamma_0(\gamma_0 - 1)v_{\mathrm{HL}}^2/v_m,$$

$$\Delta = K\gamma_0(\gamma_0 - 1)v_{\mathrm{HL}}v_{\mathrm{ML}}/v_m. \qquad (10)$$

The differences are written as $v_{\mathrm{HL}} = v_{\mathrm{HS}} - v_{\mathrm{LS}}, v_{\mathrm{LM}} = v_{\mathrm{LS}} - v_M$ such that $v_{\mathrm{ML}} = -v_{\mathrm{LM}}$. The volume per metal site of the crystal is denoted by $v_m = V/N$. The volume v_m is typically larger than v_0 because there are other molecules (anions, solvent molecules, etc.) per spin-crossover molecule in the crystal.

Note that v_0 is absent from Γ and Δ since only volume differences enter these equations of elastic energy differences. Thus all parameters can be experimentally determined. $\gamma_0 v_{\mathrm{HL}}$ is the volume increase on going from the LS to the HS state, which is accessible by structure determination at variable-temperatures or using the light-induced-excited-spin-state-trapping effect at low temperature if there are no structural changes. $\gamma_0 v_{\mathrm{ML}}$ is obtained by comparison of the unit cell volumes of the metal compound and the Fe compound in the LS state at the same temperature.

As the external pressure couples to the volume the contribution of the integral of Eq. (7) correcting for the free surface has to be considered more closely. The integral is the sum of two integrals which describe the energies involved in the procedure of taking out a finite (spherical) volume V out of the infinite medium:

$$\int_{v_0}^{v_\alpha} p_I\gamma_0\,dv = \int_{v_0}^{v_\alpha} p_I\,dv + \int_{v_0}^{v_\alpha} p_I(\gamma_0 - 1)\,dv. \qquad (11)$$

The negative of the first integral is the energy stored outside V. The negative pressure p_I at the surface of V moves the surface corresponding to $(v_\alpha - v_0)$ outside storing energy by the volume work inside the infinite volume. This energy has to be subtracted (the integral added) for the elastic energy of V. After removing the infinite part of the medium the remaining V further extends by $(\gamma_0 - 1)(v_\alpha - v_0)$ as the pressure $-p_I$ from the infinite medium balancing p_I is removed. Rewriting the second integral by substitution of the variable v according to $v' - [V + \gamma_0(v_\alpha - v_0) = (\gamma_0 - 1)(v - v_0)]$ the integral reads **(**$p_I'(v') = K\{v' - [V + \gamma_0(v_\alpha - v_0)]\}/V$ and $p_I' = -p_I$**)**:

$$\int_{v_0}^{v_\alpha} p_I(\gamma_0 - 1)dv = -\int_{V+\gamma_0(v_\alpha - v_0)}^{V+(v_\alpha - v_0)} p_I'(v')dv'. \qquad (12)$$

The pressure $p_I'(v') = -p_I(v')$ is similar to the external (positive) pressure at the surface which is zero at the final volume $v_f' = V + \gamma_0(v_\alpha - v_0)$ of the sphere. So the integral obviously represents the work compressing the volume to the size $v_i' = V + (v_\alpha - v_0)$ it has in the infinite medium. By the extension from v_i' to v_f' the volume energy decreases by the value of this integral.

Denoting the value of the integral (7) by e_{surf} and the two terms of the sum of Eq. (12) by appropriate superscripts [infinite (∞) and finite] the energy contributions are written as

$$e_{\mathrm{surf}}^{\infty} = -\frac{1}{2}Kv_m(\gamma_0 - 1)\left(\frac{\overline{v} - v_0}{v_m}\right)^2,$$

$$e_{\mathrm{surf}}^{\mathrm{fin}} = -\frac{1}{2}Kv_m(\gamma_0 - 1)^2\left(\frac{\overline{v} - v_0}{v_m}\right)^2, \qquad (13)$$

where $\overline{v} - v_0 = 1/N\Sigma(v_i - v_0)$ of Eq. (9).

2. Volume dependence of the free energy of a lattice

Recently the thermodynamical properties of silver metal have been successfully reproduced (Xie *et al.*[33]) calculating $u(a - a_0)$, the lattice potential dependent on the lattice constant a, by density functional perturbation theory (DFPT) and adding the phonon free energy as obtained from inelastic neutron scattering.

Here the phonon free energy is approximated by the Debye model with a Debye temperature Θ dependent on volume by the Grüneisen approximation

$$\frac{d\Theta}{\Theta} = -\gamma_G \frac{dV}{V},$$

$$\Theta(V) = \Theta_0 \left(\frac{V_0}{V}\right)^{\gamma_G}. \tag{14}$$

The reference volume V_0 shall be the volume per molecule v_m at zero temperature. The Grüneisen constant γ_G describes the change of the Debye frequency due to the anharmonicity of the lattice. For spin-crossover compounds it has been estimated in two cases to be around $\gamma_G = 3.0$.[34,35] In the second Eq. (14) the differential relationship is written in the integrated form for convenience (dV/V is of the order of 10^{-2}).

The static potential energy has to be chosen consistently with the Grüneisen approximation. This is achieved by the thermodynamical relationship for the bulk modulus (free energy f per volume V)

$$V \left.\frac{d^2 f}{dV^2}\right|_T = K(V) \tag{15}$$

and the dependency of the bulk modulus K on V in the Debye approximation.[34,36] K is proportional to

$$K(V) \propto \left(\frac{k_B\Theta}{\hbar}\right)^2 \rho \left(\frac{V}{18\pi^2}\right)^{2/3} \tag{16}$$

and to a function of γ_0. Taking the Eshelby constant independent of V the bulk modulus as a function of V is expressed by its value at $V_0 = v_m$ $[\Theta_0 = \Theta(V_0), K_0 = K(V_0)]$:

$$K(V) = K_0 \left(\frac{\Theta(V)}{\Theta_0}\right)^2 \left(\frac{V_0}{V}\right)^{1/3}. \tag{17}$$

The free energy f_0 at zero temperature is the sum of the potential energy u and the zero point vibrational energy $9/8 k_B \Theta$. The integration of Eq. (15) with the condition of a minimum at V_0 and an arbitrary choice of $f(V_0) = 0$ gives $\left(\xi = 2\gamma_G - \frac{2}{3}\right)$

$$f_0(V) = \frac{K_0 V_0}{\xi + 1} \left\{ \frac{1}{\xi} \left[\left(\frac{V}{V_0}\right)^{-\xi} - 1 \right] + \frac{V}{V_0} - 1 \right\}. \tag{18}$$

From the expansion of f_0 around V_0 as a function of the relative volume change $\nu = (V - V_0)/V_0$ up to the first anharmonic third order term

$$f_0(V) = K_0 V_0 \left[\frac{1}{2}\nu^2 - \frac{1}{3}\left(\gamma_G + \frac{2}{3}\right)\nu^3 + \cdots \right] \tag{19}$$

the dependency of this term on the Grüneisen constant is obtained. Obviously, f_0 has an anharmonic behavior even at $\gamma_G = 0$. At $\gamma_G = -2/3$ the anharmonic third order term vanishes. The fact that only a harmonic potential is left is directly seen from Eq. (18). Another special case is $\gamma_G = 1/3$ which gives $f_0(\nu) = K_0 V_0[-\ln(\nu + 1) + \nu]$. In Fig. 1 the potential curves are plotted. The thicker line is the harmonic potential at $\gamma_G = -2/3$. The potential curve for $\gamma_G = 3.0$ gives an impression of the anharmonicity introduced by the Grüneisen constant.

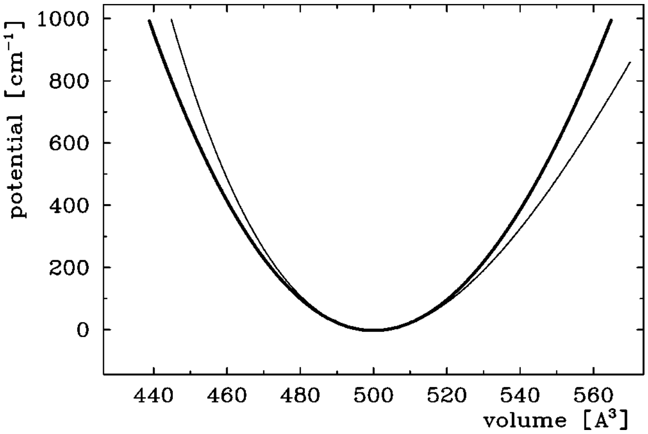

FIG. 1. The potential $f_0(V)$ versus volume for $\gamma_G = -2/3$ (thick curve) and $\gamma_G = 3.0$. At $\gamma_G = -2/3$ the potential is harmonic.

The total free energy $f(T, V)$ in the Debye approximation per volume V containing μ vibrating masses is given by [Debye function $D(x)$]

$$f = f_0(V) + \mu k_B T \left[3 \ln(1 - e^{-\Theta/T}) - D\left(\frac{\Theta}{T}\right) \right]. \tag{20}$$

The large intramolecular frequencies as compared to the low frequencies of the lattice with the cut off at the Debye frequency $\hbar\omega_D$ (corresponding to about $\Theta = 50$ K) justifies treating molecules as rigid units vibrating as a whole in the lattice. This means that the intra and extra molecular vibrations are assumed to be essentially decoupled. The number μ of vibrating molecules is adjusted to reproduce the experimentally observed lattice expansion versus temperature. Figure 2 shows the free energy versus volume at temperatures in the range from $T = 40$ to 310 K. The volume shift of the minima of the free energy corresponds to what typically is observed in spin crossover compounds.

3. Contribution of spherical defects to the potential energy

So far we have the lattice free energy $f_0(V)$ per unit volume V_0 of an infinite lattice containing molecules of size v_0. These molecules will be replaced in a first step by incompressible molecules of different volume v_{HS}, v_{LS}, and v_M. The infinite medium extends, such that the volume V_0 per molecule increases by $\overline{v}(x, \gamma_{\mathrm{HS}}) - v_0$ where $\overline{v}(x, \gamma_{\mathrm{HS}}) = x[\gamma_{\mathrm{HS}} v_{\mathrm{HS}} + (1 - \gamma_{\mathrm{HS}}) v_{\mathrm{LS}}] + (1 - x) v_M$ is the average volume of a concentration x of spin crossover molecules (here Fe) being a fraction of γ_{HS} in the HS state and a concentration $1 - x$ of other metal molecules. This extension changes the potential $f_0(V)$ twofold, the minimum energy and the position of the minimum from V_0 to $v' = V_0 + [\overline{v}(x, \gamma_{\mathrm{HS}}) - v_0]$. In order to modify the potential correspondingly, we make use of two integration constants A, B of Eq. (15) for a constant energy shift A and a linear term $B(V - V_0)/V_0$.

$$\varphi_0(V) = f_0(V) + B\frac{V - V_0}{V_0} + A. \tag{21}$$

The first derivative $d\varphi_0/dV$ vanishes at the minimum v' and determines the constant B dependent on x and γ_{HS}. With

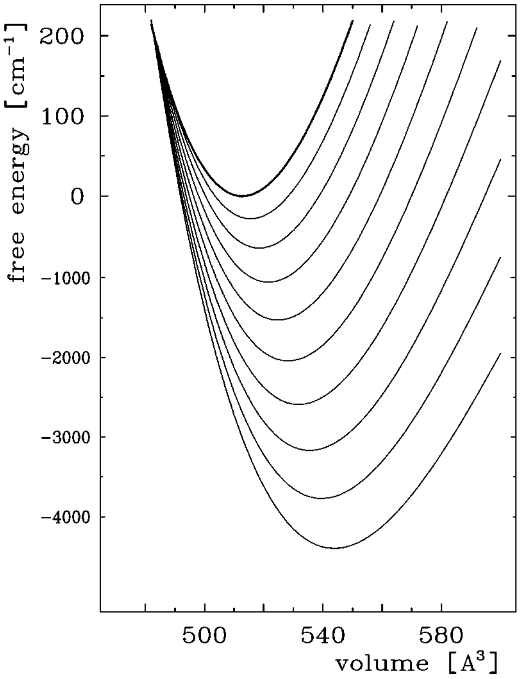

FIG. 2. The free energy $f(T,V)$ of Eq. (20) is plotted for a series of temperatures from $T=40$ K (thick curve on the top) up to 310 K versus volume V. The shift of around 30 Å^3 of the minimum of the free energy is about 6% of the voume. This volume expansion is typically observed in spin crossover compounds. Two scales are used. The free energy curves are plotted with respect to the upper scale (0–200 cm^{-1}). The energy difference of the minima belong to the lower scale (0 through -4000 cm^{-1}). The typical parameters used are $\Theta=50$ K and $\mu=3$.

the knowledge of $B(x,\gamma_{\rm HS})$ the constant $A(x,\gamma_{\rm HS})$ is obtained from the energy difference $\varphi_0(v')-\varphi_0(V_0)$ which is just the self-energy $e_{\rm self}(x,\gamma_{\rm HS})$ in an infinite medium [$\varphi_0(V_0)=0$ was chosen as reference energy]. Obviously, the product of $B(x,\gamma_{\rm HS})$ with $(V-V_0)/V_0$ represents a coupling between the HS fraction and the volume of the crystal.

In a next step the energy correction $e_{\rm surf}$ of Eq. (13) resulting from the free surface (cutting out a finite medium) has to be added. That is the energy stored in the infinite part $\int p_I dv$ of Eq. (11) and the decrease in energy increasing the volume by the image pressure. This part, however, cannot be simply added since the volume is an independent parameter of the free energy. The free energy has to be constructed in such a way that in the harmonic case the correct volume and shift in energy as derived from elasticity theory [Eqs. (6) and (13)] are obtained. The energy dependence on the volume V, the product of $p_I=-K(\overline{v}-v_0)(\gamma_0-1)/V_0$ times the volume change $(V-v')$ per molecule, added to the harmonic potential meet these requirements. The sum denoted by ϕ

$$\begin{aligned}\phi &= \frac{KV_0}{2}\left(\frac{V-v'}{V_0}\right)^2 - K\frac{\overline{v}-v_0}{V_0}(\gamma_0-1)(V-v')\\ &= \frac{1}{2}KV_0\left(\frac{V-(V_0+\gamma_0(\overline{v}-v_0)}{V_0}\right)^2\\ &\quad -\frac{1}{2}KV_0(\gamma_0-1)^2\left(\frac{\overline{v}-v_0}{V_0}\right)^2 \end{aligned} \tag{22}$$

represents a displaced oscillator, the energy and volume shift is directly read off. As elastic energies are derived in the harmonic approximation (by using elasticity theory for small deformations) the linear term used locally in the anharmonic potential remains a valid approximation.

B. General point defects

The interaction constant derived from experiment could be approximately reproduced by the theory when the anisotropy of the deformation of the crystal accompanying the change of the spin state of the molecules[37,38] has been included. The situation, however, becomes much more complicated although the crystal is still approximated by an isotropic homogenous medium. While isotropic defects do not interact directly (they "see" each other only by the surface image pressure) anisotropic defects interact directly (also with isotropic ones) in addition to the interaction by an anisotropic image stress. The direct interaction energy depends on the distance ($\sim 1/r^3$) and relative orientation of the defects and can give rise to deviations from random distribution (correlations) of the spin states of the molecules. Here we assume random distribution preserving mean-field approximation.

1. Infinite range interaction

The calculation of the elastic energies of the anisotropic lattice deformation accompanying the spin transition requires a deformation tensor of the lattice. It is described by a Cartesian tensor ϵ with components ϵ_{ik}, $(i=x,y,z)$, which are transformed to a real irreducible (with respect to the rotation group) basis. The trace of the Cartesian ϵ tensor $\epsilon_s=\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz}$ is the relative volume change of the lattice, such that, e.g., $\epsilon_s^{\rm HL}$ with the superscript HL is equal to $\epsilon_s^{\rm HL}=\gamma_0(v_{\rm HS}-v_{\rm LS})/v_m$:

$$\begin{aligned}\epsilon_0 &= \frac{1}{\sqrt{6}}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy}),\\ \epsilon_{1c} &= \sqrt{2}\epsilon_{xz},\quad \epsilon_{1s}=\sqrt{2}\epsilon_{yz},\\ \epsilon_{2c} &= \frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy}),\quad \epsilon_{2s}=\sqrt{2}\epsilon_{xy}.\end{aligned} \tag{23}$$

The tensor components are evaluated from the deformation of the unit cell due to the spin transition. Several examples have been studied.[2–4,39] Taking these deformations to be uniform throughout the crystal (approximated by homogeneous medium), the origin of the deformation is traced back to a uniform distribution of elastic point dipole tensors $\boldsymbol{P}$ (related by translational symmetry) with components P_s, P_M where $M=0,1c,1s,2c,2s$:[38]

$$\begin{aligned}P_s &= Kv_m\epsilon_s,\\ P_M &= \frac{3}{2}Kv_m(\gamma_0-1)\epsilon_M.\end{aligned} \tag{24}$$

The tensor has the dimension of an energy. In the case of one defect per molecular volume v_m the average values P_M of

Eq. (24) represent the dipole strength of the defect. The self-energy e_{self} of a defect stored in an infinite crystal outside the volume v_0 is given by (i.e., Ref. 40)

$$e_{\text{self}} = \frac{(\gamma_0 - 1)}{2\gamma_0^2 K v_0}\left[P_s^2 + \frac{(3\gamma_0^2 + 4\gamma_0 + 5)}{15(\gamma_0 - 1)^2}\sum_M P_M^2 \right]. \tag{25}$$

The interaction energy per molecule between the molecules (=defects) uniformly distributed over a sphere caused by the image pressure/stress at the free surface of the sphere is proportional to the square of the deformation tensor components [compare Eq. (8) (Ref. 38)]:

$$e_{\text{surf}} = -Kv_m \frac{(\gamma_0 - 1)}{2\gamma_0}\left[\epsilon_s^2 + \frac{3}{10}(2\gamma_0 + 1)\sum_M \epsilon_M^2 \right]. \tag{26}$$

For a mixed crystal spin crossover system the self-energies just add up such that P_M^2 in Eq. (25) is replaced by $\overline{P_M^2}$ following the definition of Eq. (9). The deformation tensor results from the sum of the contibutions of all molecules. This sum is equivalent to the average tensor $\overline{\epsilon_M}$ of the deformation tensor for each species of molecules. In Eq. (26) ϵ_M^2 is replaced by $\overline{\epsilon_M^2}$.

The $M=s$ terms are the spherical contributions already discussed. In order to obtain the linear term of the anisotropic deformations leading to the energy contribution of the expanding surface as has been done for the spherical part in Eq. (22), the surface energy has to be split into the infinite and finite contribution. Before doing this Eq. (22) shall be rewritten using ϵ tensors. These are the variable $\epsilon_s=(V-V_0)/V_0$, the total deformation $\overline{\epsilon_s}=\gamma_0(\overline{v}-v_0)/V_0$, the deformation of the infinite medium $\overline{\epsilon_s^\infty}=\overline{\epsilon_s}/\gamma_0$, and the deformation by the image pressure $\overline{\epsilon_s^I}=(\gamma_0-1)/\gamma_0\overline{\epsilon_s}$:

$$\begin{aligned}\phi &= \frac{1}{2}KV_0(\epsilon_s - \overline{\epsilon_s^\infty})^2 - KV_0\overline{\epsilon_s^I}(\epsilon_s - \overline{\epsilon_s^\infty}) \\ &= \frac{1}{2}KV_0(\epsilon_s - \overline{\epsilon_s})^2 - \frac{1}{2}KV_0(\overline{\epsilon_s^I})^2. \end{aligned}\tag{27}$$

In terms of ϵ_s tensors the calculated energy shift by the relaxing surface is obtained at the minimum $\overline{\epsilon_s}=(\overline{\epsilon_s^I}+\overline{\epsilon_s^\infty})$ of the harmonic potential. For the corresponding expressions of the energy corrections of anisotropic deformations proportional to $\overline{\epsilon_M}$ the splitting into the contribution $\overline{\epsilon_M^\infty}$ and $\overline{\epsilon_M^I}$ is needed. Comparing the total displacement $\mathbf{U}=\mathbf{U}^\infty+\mathbf{U}^I$ at the surface of a spherical medium (crystal) of radius R_a expressed by spherical vector harmonics $\mathbf{Y}_{LM}^J$ (see Ref. 37)

$$\mathbf{U}(R_a) = -\frac{4\pi}{3}R_a\frac{\mathbf{Y}_{00}^1}{\sqrt{4\pi}}\overline{\epsilon_s} + 2\pi R_a\sum_M \frac{\mathbf{Y}_{2M}^1}{\sqrt{3\pi}}\overline{\epsilon_M},$$

$$\mathbf{U}^I(R_a) = -\frac{4\pi}{3}R_a\frac{\mathbf{Y}_{00}^1}{\sqrt{4\pi}}\frac{\gamma_0 - 1}{\gamma_0}\overline{\epsilon_s} + 2\pi R_a\sum_M \frac{\mathbf{Y}_{2M}^1}{\sqrt{3\pi}}\frac{2\gamma_0 + 1}{5\gamma_0}\overline{\epsilon_M}, \tag{28}$$

and $\mathbf{U}^\infty(R_a)$, the partial deformation tensors for the anisotropic deformations $\overline{\epsilon_M^I}=(2\gamma_0+1)/5\gamma_0\overline{\epsilon_M}$ caused by the image stress field and $\overline{\epsilon_M^\infty}=(3\gamma_0-1)/5\gamma_0\overline{\epsilon_M}$ are also obtained. The energy corrections $e_{\text{surf}}^{\text{finite}}$ are the displacements $\mathbf{U}(r=R_a)$ multiplied by the image stress $\sigma^I\mathbf{e}_r$ in radial direction $\mathbf{e}_r$ (Ref. 37)

$$\sigma^I(R_a)\mathbf{e}_r = -K4\pi\frac{\mathbf{Y}_{00}^1}{\sqrt{4\pi}}\overline{\epsilon_s^I} + K\frac{3}{2}(\gamma_0 - 1)\sum_M 2\pi\frac{\mathbf{Y}_{2M}^1}{\sqrt{3\pi}}\overline{\epsilon_M^I} \tag{29}$$

and integrated over the surface of the sphere:

$$\begin{aligned} &-\frac{1}{2}\int_\Omega \mathbf{U}^{\mathbf{I}}(\sigma^I\mathbf{e}_r)R_a^2\,d\Omega \\ &\quad = -\frac{1}{2}Kv_m(\overline{\epsilon_s^I})^2 - \frac{1}{2}Kv_m\frac{3}{2}(\gamma_0 - 1)\sum_M(\overline{\epsilon_M^I})^2. \end{aligned}\tag{30}$$

The linear terms to be added to a harmonic potential with the property of the correct displacements and energy shifts are readily constructed according to Eq. (27):

$$\begin{aligned}\phi = {}&\frac{1}{2}KV_0(\epsilon_s - \overline{\epsilon_s^\infty})^2 - KV_0\overline{\epsilon_s^I}(\epsilon_s - \overline{\epsilon_s^\infty}) + \sum_M \frac{1}{2}Kv_m\frac{3}{2}(\gamma_0 - 1) \\ &\times(\epsilon_M - \overline{\epsilon_M^\infty})^2 - Kv_m\frac{3}{2}(\gamma_0 - 1)\overline{\epsilon_M^I}(\epsilon_M - \overline{\epsilon_M^\infty}). \end{aligned}\tag{31}$$

For the value of the average deformation tensor $\overline{\epsilon_M}$ the knowledge of the misfit of the molecules to the lattice is required. The misfit has to be expressed by deformation tensor components instead of the volume and shape of the defect minus volume and shape provided by the lattice. With the deformation ϵ_M^α of each species $\alpha=\text{HS},\text{LS},M$, each representing an unknown misfit to the lattice, the unknown values are reduced to one value for each component M if all differences ($\epsilon_M^{\text{HL}}=\epsilon_M^{\text{HS}}-\epsilon_M^{\text{LS}}$, etc.) being experimentally accessible are inserted. In case of the spherical component s not the volume difference v_{L0} but the tensor component $\epsilon_s^{\text{LS}}=\gamma_0(v_{\text{LS}}-v_0)/V_0$ has been taken as unknown misfit.

The energy e_{surf}^∞ stored outside the spherical volume in the infinite medium (to be subtracted from the energy of the infinite medium)

$$e_{\text{surf}}^\infty = \frac{1}{2}Kv_m(\gamma_0 - 1)\left[(\overline{\epsilon_s^\infty})^2 + \frac{3}{2}\frac{2\gamma_0 + 1}{3\gamma_0 - 1}\sum_M(\overline{\epsilon_M^\infty})^2\right], \tag{32}$$

is the integral $+\frac{1}{2}\int_\Omega \mathbf{U}^\infty(\sigma^\infty\mathbf{e}_r)R_a^2\,d\Omega$.

The coupling of the deformation of the lattice to the HS fraction determining the average values of the tensor components is established by two ways, the dependency of these energies on the bulk modulus $K(V)$ and new minima values in the anharmonic potential which has the same shape as $f_0(V)$ of Eq. (18). Replacing ϵ_s by ϵ_M and the prefactor K_0V_0 by $3/2K_0V_0(\gamma_0-1)$ the contribution of mode M is given by

$$f_{0M}(\epsilon_M) = \frac{3}{2}K_0V_0(\gamma_0 - 1)\frac{1}{\xi + 1} \times \left\{ \frac{1}{\xi - 1}((\epsilon_M + 1)^{1-\xi} - 1) + \epsilon_M \right\}. \quad (33)$$

The same Grüneisen constant is taken for all modes of deformation.

2. Elastic interaction in an infinite medium

The elastic interaction energy between two dipoles $\mathbf{P}_M^a$ and $\mathbf{P}_M^b$ in an infinite medium separated by a distance R on the z axis of a coordinate system (Shuey and Beyeler[40]) consists of two types of terms

$$e_{\mathrm{int}}^{\infty} = \frac{1}{4\pi}\frac{1}{R^3}\frac{1}{K\gamma_0}\left\{ \sqrt{6}(\mathbf{P}_0^a \cdot \mathbf{P}_s^b + \mathbf{P}_0^b \cdot \mathbf{P}_s^a) + \frac{2(\gamma_0 + 1)}{\gamma_0 - 1}\mathbf{P}_0^a \cdot \mathbf{P}_0^b - \frac{2}{\gamma_0 - 1}(\mathbf{P}_{1c}^a \cdot \mathbf{P}_{1c}^b + \mathbf{P}_{1s}^a \cdot \mathbf{P}_{1s}^b) - (\mathbf{P}_{2c}^a \cdot \mathbf{P}_{2c}^b + \mathbf{P}_{2s}^a \cdot \mathbf{P}_{2s}^b) \right\}. \quad (34)$$

The first is an interaction term between a spherical defect $\mathbf{P}_s$ and the component $M=0$ of an anisotropic defect $\mathbf{P}_0$. All other terms are of the second type, namely products between components describing the anisotropic part of the defects.

The sum over all pairs of defects, that is the sum over all molecular sites (the position of the defect being inside the molecule), is treated in mean field approximation, such that the averages of $\mathbf{P}_M$ are replaced by the strain tensor components $\overline{\epsilon_M}(x, \gamma_{\mathrm{HS}})$. Then we can define two types of interaction constants

$$e_{\mathrm{int}}^{\infty} = -\Gamma_s\overline{\epsilon_s\epsilon_0} - \sum_M \Gamma_M\overline{\epsilon_M^2} \quad (35)$$

the size of which are determined by the relative positions and orientation of the spin-crossover molecules in the crystal. The first interaction term proportional to Γ_s represents a coupling between isotropic and anisotropic deformations so that the volume change accompanied by the spin transition will depend on the anisotropy of the deformation.

This direct interaction is proportional to $1/R^3$, that means it has the property of long-range interaction (not infinite range as the interaction due to the free surface). So far it was calculated for three compounds [Fe(picolylamine)3](ClO4)2 · Sol (Sol=EtOH, MeOH) (Ref. 38) and $[\mathrm{Fe(propyltetrazole)}_6](\mathrm{BF}_4)_2$.[15] The absolute size amounts 30–60 % of the interaction parameter obtained from a fit to Eq. (4). In the monoclinic picolylamine compound the direct interaction adds to the interaction constant whereas in the axial symmetric propyltetrazole compound it has the opposite sign. Therefore the interaction constants $\Gamma_{s,M}$ cannot be put into limits from general considerations.

It is well known that there are spin crossover transitions with very large interaction constants.[24] Interaction of elastic origin are limited by the typical K values being less than 10 Gpa and the size of the observed deformation tensor components. Larger values are attributed to short range interaction between molecular units interacting by π bonding or metal atoms sharing ligand entities. Such a contribution is not proportional to the bulk modulus K and therefore not affected by the anharmonicity of the crystal lattice. As this interaction is also treated using mean field approximation a term proportional to the square of γ_{HS}, a linear one in γ_{HS}, and a constant are obtained. The constant energy shift does not matter, the linear term contributes to a constant (independent of volume and temperature) energy separation between the HS and LS state of the molecule. When simulating metal dilution series the dependency of the constants on concentration x and especially the relative size of the interaction constant as compared to the energy shift is important. Considering only two center interactions a general expression for the mean field approximation has been written as[39]

$$\frac{E_{\mathrm{int}}}{N^2} = \frac{1}{2}x^2\gamma_{\mathrm{HS}}^2 p^{\mathrm{HL}}\overline{A}p^{\mathrm{HL}} + \gamma_{\mathrm{HS}}(-x^2p^{\mathrm{HL}}\overline{A}p^{\mathrm{ML}} + xp^{\mathrm{HL}}\overline{A}p^{M}) + \frac{1}{2}[(1-x)p^{\mathrm{ML}} - p^{\mathrm{LS}}]\overline{A}[(1-x)p^{\mathrm{ML}} - p^{\mathrm{LS}}]. \quad (36)$$

The letter p stands for some tensor property of the molecule such that the interaction between two molecules i,j can be written as p_iAp_j with a tensor $A(i,j)$. If there are only three different molecules with properties p^{HS}, p^{LS}, and p^M the lattice sum over all sites i,j is expressed by the average tensor $\overline{A}=1/N^2\Sigma_{i\neq j}A(i,j)$ and tensor differences $p^{\mathrm{HL}}=p^{\mathrm{HS}}-p^{\mathrm{LS}}$ and $p^{\mathrm{ML}}=p^M-p^{\mathrm{LS}}$.

The last term in Eq. (36) is independent of γ_{HS}. The meaning of the term proportional to $x\gamma_{\mathrm{HS}}$ is an energy shift of each spin crossover molecule in the HS state. This shift has been already mentioned above. The two energies proportional to x^2 (these contributions decrease linearly for each spin crossover molecule) $p^{\mathrm{HL}}\overline{A}p^{\mathrm{HL}}$ and $p^{\mathrm{HL}}\overline{A}p^{\mathrm{ML}}$ would be the same if the properties of the molecule with the metal ion M is the same as the spin crossover molecule in the HS state. This is approximately the case for Fe and Zn molecules where the difference of deformation tensors for the crystal in the HS state and the Zn crystal are very small as compared to the crystal in the LS state. Denoting $\Gamma=-Np^{\mathrm{HL}}\overline{A}p^{\mathrm{HL}}/2$ and $\Delta=-p^{\mathrm{HL}}\overline{A}p^{\mathrm{ML}}$ the direct interaction per metal atom is given by

$$e_{\mathrm{int}}^{\infty} = -\Gamma_s\overline{\epsilon_s\epsilon_0} - \sum_M \Gamma_M\overline{\epsilon_M^2} + x^2\Delta\gamma_{\mathrm{HS}} - x^2\Gamma\gamma_{\mathrm{HS}}^2. \quad (37)$$

Note that Γ is not only determined by the HS property p^{HS} of the molecules but by the difference p^{HL} although the square of γ_{HS} looks similar to an interaction between HS molecules [see comment on Eq. (4)]. The typical ratio $\Delta/\Gamma \sim 2$ found from experiment of metal dilution series with $M=\mathrm{Zn}$ is used for simulations because the energy shift vanishes at $\gamma_{\mathrm{HS}}=\frac{1}{2}$ preserving the transition temperature with an increase of Γ.

III. TOTAL FREE ENERGY

We are now in the position to set up the total free energy $f(\epsilon_s, \epsilon_M, T, \gamma_{\mathrm{HS}})$. For each mode M the potential of the infinite crystal is constructed in the same way as for the spherical mode s. For clarity the functions $A(x,\gamma_{\mathrm{HS}})$ and $B(x,\gamma_{\mathrm{HS}})$ get a subscript s and M. The sum over M practically will be restricted to one or utmost two M modes:

$$\begin{aligned} f = {} & f_{0s}(\epsilon_s) + B_s\epsilon_s + A_s + \sum_M f_{0M}(V) + B_M\epsilon_M + A_M + e^{\infty}_{\mathrm{int}} \\ & - e^{\infty}_{\mathrm{surf}}[x,\gamma_{\mathrm{HS}},K(\epsilon_s)] - K(\epsilon_s)v_m\overline{\epsilon}^{I}_s(\epsilon_s - \overline{\epsilon}^{\infty}_s) + pv_m\epsilon_s \\ & - K(\epsilon_s)v_m\frac{3}{2}(\gamma_0 - 1)\sum_M \overline{\epsilon}^{I}_M(\epsilon_M - \overline{\epsilon}^{\infty}_M) + f_{\mathrm{Debye}}[T,\Theta(\epsilon_s)] \\ & + x\cdot f_{x\to 0}(T,\gamma_{\mathrm{HS}}). \end{aligned} \quad (38)$$

The first two lines of the free energy (enthalpy) describe the potential energy of an infinite medium/crystal. The next three lines correct for the surface and include the external pressure p where the constant energy pv_m of $pV = pv_m\epsilon_s + pv_m$ has been omitted. The free energy of the lattice phonons and the spin crossover molecules introduce the temperature dependence. The minimum of the free energy with respect to all variables ϵ_s, ϵ_M, and γ_{HS} determine these variables, the HS fraction and especially the volume ϵ_s, in thermal equilibrium:

$$\left.\frac{\partial f}{\partial \gamma_{\mathrm{HS}}}\right|_T = 0, \qquad \left.\frac{\partial f}{\partial \epsilon_s}\right|_T = 0, \qquad \left.\frac{\partial f}{\partial \epsilon_M}\right|_T = 0. \quad (39)$$

Several contributions to the free energy are coupled by the bulk modulus because all elastic energies are proportional to K, these are A_s, A_M, Γ_s, Γ_M, and $e^{\infty}_{\mathrm{surf}}$. Thereby K is defined by Eq. (15), the second derivative of f, which function as an extra condition and reads in terms of ϵ_s instead of V:

$$Kv_m = (1+\epsilon_s)\left.\frac{\partial^2 f}{\partial \epsilon_s^2}\right|_{T,\epsilon_M}.$$

In a numerical solution this condition is simultaneously reached within the iteration procedure to the minimum of f.

IV. SIMULATIONS

We want to explore in this study general properties of the free energy of the spin-crossover system in order to recognize some of the unusual behavior found experimentally. The transition curves have been called unusual as the theoretical approaches so far discussed could not reproduce such transitions although the theories going beyond the mean-field approach provide a lot of parameters to be adjusted. The present mean-field theory introduces one new type of parameter, the space in the lattice provided for the molecule expressed by the misfit of one species, i.e., ϵ^{LS}_M for each component $M = s, 0, 1s, 1c, 2s, 2c$. So far these misfits are not experimentally accessible. Their influence on the spin transition curves is not known and this will be one subject to be studied.

In order to reduce the parameters to play with only one M component in addition to the spherical s component is used and the misfits for these components are related to each other by a fixed ratio $\epsilon^{\mathrm{LS}}_s/\epsilon^{\mathrm{LS}}_M = 1$. Since all M components, but the one with $M = 0$, contribute to the interaction energy in the same way, the index M is used excluding the $M = 0$ component for simplicity which has a product with the s component in the interaction energy. The direct elastic interaction constant Γ_M of this component, which for a given crystal structure can be calculated carrying out a lattice sum,[15,38] and the

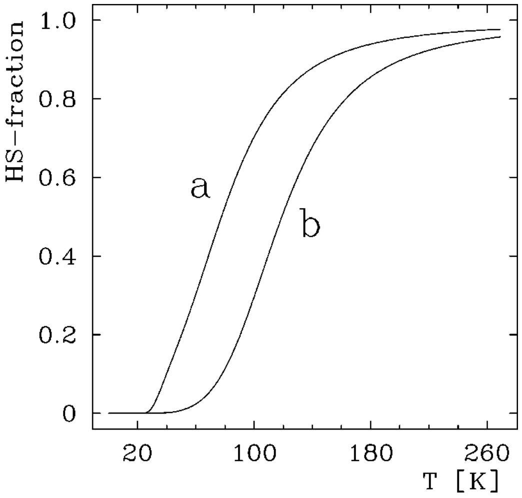

FIG. 3. The spin transition (Boltzmann population) of noninteracting molecules as obtained from the highly diluted mixed crystal (a) of $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{picolylamine})_3]\mathrm{Cl}_2\cdot\mathrm{EtOH}$ [$x = 0.003$ (Ref. 42)] according to the free energy of Eq. and (b) of the same partition functions of the HS and LS states but an increased energy separation between HS and LS state of $\Delta_{\mathrm{electr}} = 120\ \mathrm{cm}^{-1}$ in order to shift the transition temperature $T_{1/2}$ to 120 K.

TABLE I. Theory parameters used for the calculation of the spin transition curves of all the figures. The image interaction Γ_I and the effective direct interaction Γ_d of the mode of deformation M are derived from the calculated transition curve. The parameter Γ_M/K_0V_0 is a dimensionless number.

Figure	$v_{\mathrm{LS}} - v_0$	γ_G	Γ_M/K_0V_0	Δ_{elect}	Γ	Γ_I $[\mathrm{cm}^{-1}]$	Γ_d
4[a]	0	3	0.5	130	0	45.6	55.9
4	0	3	0.5	200	0	71.6	34.9
5	0	$-\frac{2}{3}$	0.9	65	0	47	123
5	0	3	1.25	106	0	71	91
5	$-v_{\mathrm{HL}}$	3	0.75	255	0	57	108
7	$\frac{1}{2}v_{\mathrm{HL}}$	$-\frac{2}{3}$	1.55	0	−50	50	209
7	$\frac{1}{2}v_{\mathrm{HL}}$	1.0	1.55	−15	10	62	152
7	$\frac{1}{2}v_{\mathrm{HL}}$	1.8	1.55	−20	35	62	131
7	$\frac{1}{2}v_{\mathrm{HL}}$	2.5	1.55	−28	50	58	113
8	$\frac{1}{2}v_{\mathrm{HL}}$	1.7	1.55	−20	5	66	128
8	v_{HL}	2.2	1.0	−90	74	71	83
9	v_{HL}	2.5	2.0	−225	20	70	130
9	$2v_{\mathrm{HL}}$	1.2	1.9	−425	10	67	138
11[b]	$2v_{\mathrm{HL}}$	1.9	1.8	0	230	50	145

[a] Transition is calculated without Debye free energy.

[b] In this special case ϵ^{LS}_M has been increased by $1/2\epsilon^{\mathrm{HL}}_M$ and the ratio of the volume per molecule divided by the molecular volume v_m/v_0 has been decreased from 2.0 to 1.73.

short range interaction constant Γ are chosen such that hysteresis widths of around 10 K at zero pressure are obtained. Γ_M is increased close to the critical value for a hysteresis and with a small value of Γ the width of 10 K is adjusted. The volume difference $v_{\mathrm{HL}}=10$ Å^3, the crystal volume per molecule $v_m=500$ Å^3, the Eshelby constant $\gamma_0=1.5$ and bulk modulus $K=0.6\times10^{10}\,\mathrm{N\,m^{-2}}$ are fixed as typical values found in spin crossover compounds. In the case of the compound $[\mathrm{Fe}(ptz)_6](\mathrm{BF}_4)_2$ the elastic constants K and γ_0 were measured by Brillouin scattering.[41] The difference of anisotropic deformation ϵ_M^{HL} in the HS and LS state of the crystal is fixed to the same value of 0.03 as the isotropic deformation $\gamma_0 v_{\mathrm{HL}}/v_m$. Similar values were found by x-ray structure determination.[15,38] The absolute value of v_0 is needed for the calculation of the self-energy e_{self}. It determines the relative size of the self-energy and the other elastic energy contributions. In the present simulations v_0 is fixed to $1/2v_m$. Further parameters of the total free energy will be fixed throughout the simulations. There is, as shown in Fig. 3 curve a, the Boltzmann population of noninteracting spin-crossover molecules. This transition curve was measured on the highly diluted mixed crystal $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(\mathrm{picolylamine})_3]\mathrm{Cl}_2\cdot\mathrm{EtOH}$ [$x=0.003$ (Ref. 42)].

In this compound a Debye temperature of about 50 K was found. The number μ of vibrating masses is fixed to 3 giving typical temperature dependence of the lattice as shown in Fig. 2. An energy difference Δ_{electr} between the HS and LS state of electronic and elastic origin, given by the energy eigenvalues of the free molecule and constant elastic energies possibly introduced by short range interaction (see above), is used to adjust the spin transition temperature $T_{1/2}$ to 120 K in order to simulate comparable spin transition curves. In Fig. 3, curve b at a transition temperature of 120 K is obtained by adding $\Delta_{\mathrm{electr}}=120\ \mathrm{cm}^{-1}$ to the energy separation between the HS and LS state.

The anharmonicity parameter γ_G will be varied up to $\gamma_G=3$ for the strong anharmonic situation. The value $\gamma_G=-2/3$ at which the potential is exact harmonic is used to show the transition curves obtained by the standard mean-field free energy (4) for comparison.

Table I collects all parameter sets used. Metal dilution effects have not been simulated ($x=1$ and $x=0$ for reference $M=\mathrm{Zn}$ compound). The parameters of the first two columns, the misfit and Grüneisen constant, have been set, of the next two, additional energy splitting between HS and LS state of the molecule and a direct interaction of mode M, have been varied to obtain a steep transition close to the hysteresis loop at 120 K, and the short range interaction Γ to obtain a hysteresis width of about 10 K. The interaction Γ_s between spherical and anisotropic elastic dipoles has been set to zero. The next two columns list effective interactions which have been derived from the simulated transition curves. The curves have been used as input for a determination of the interaction parameter of the phenomenological free energy of Eq. (4). The equilibrium condition $\partial f/\partial\gamma_{\mathrm{HS}}=0$ of Eq. (4) is written as ($\Gamma_{\mathrm{eff}}=\Gamma$)

$$\Delta-2\Gamma_{\mathrm{eff}}\gamma_{\mathrm{HS}}=\Delta f_{\mathrm{HL}}(T)-k_BT\ln\left[\frac{1-\gamma_{\mathrm{HS}}(T)}{\gamma_{\mathrm{HS}}(T)}\right]\qquad(40)$$

such that the effective interaction is half of the slope of the right-hand side of the equation. The image interaction is obtained separately by putting the direct interaction to zero. The short-range interaction turns out to be simply additive (it does not depend on the bulk modulus). This fact has been used to simulate curves without a hysteresis in order to obtain a well-defined slope. The sum of the columns $\Gamma+\Gamma_I+\Gamma_d$ is the total interaction.

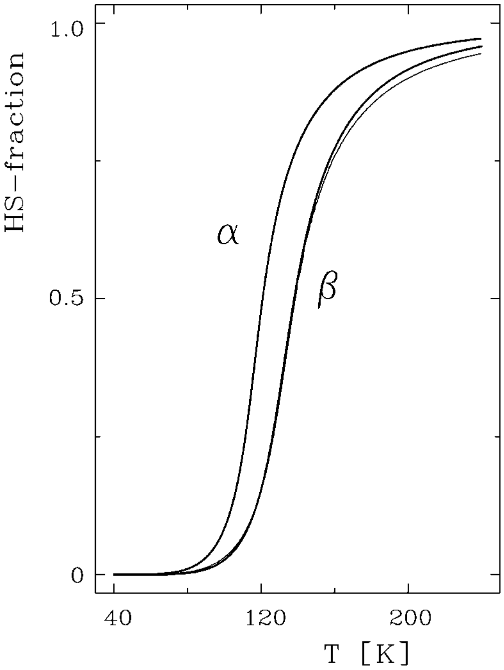

FIG. 4. Comparison of spin transitions calculated with (α curve) and without (thin β curve) lattice phonons. In order to have the same transition temperature for the transition curve with lattice phonons as without lattice phonons the energy separation Δ_{electr} is increased by 70 cm^{-1}. The two curves almost match besides the region of large HS fractions.

A. Phonon contribution

The lattice phonon contribution to the interaction between spin crossover molecules was first discussed by Zimmermann and König.[43] From the difference of the Debye temperatures of the crystal in the HS and LS state they estimated a considerable contribution of around 20% of the interaction constant. Later on this size was questioned.[13] These estimations can now be replaced by a comparison of simulations of transition curves with and without lattice phonons. The result is shown in Fig. 4.

The main effect of the lattice phonons is a shift of the transition (thin β curve) to lower temperature (thick line curve α) which is due to the lattice expansion of the anharmonic lattice and the coupling of the spin transition to the volume. In Fig. 4 there is also plotted the transition with lattice phonons (thick line curve β) at the same transition temperature by increasing the electronic energy separation between HS and LS states. The thick line and thin line transition curves almost match. Only at HS fractions larger than 0.75 the thick line curve (calculation with lattice phonons) is above the curve without phonons. This relative increase of the HS fraction represents a small contribution of the lattice

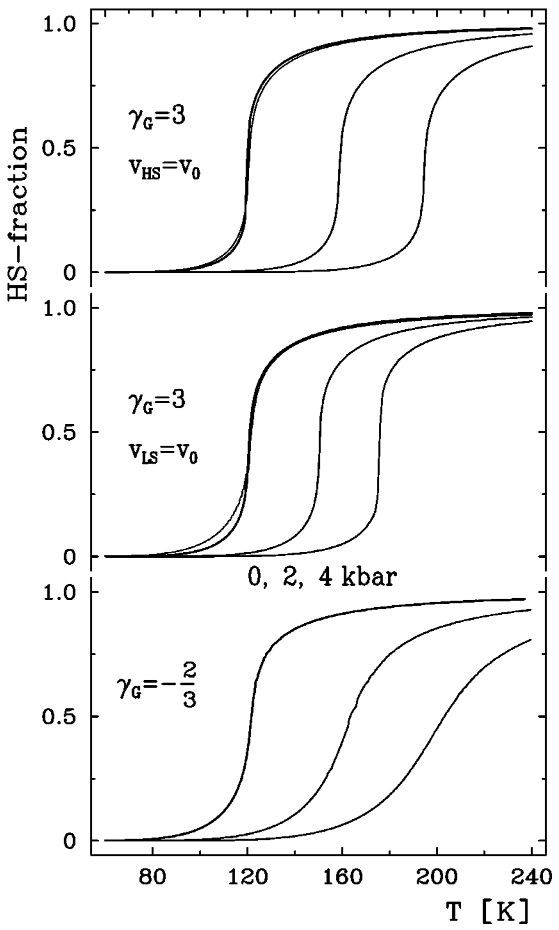

FIG. 5. Pressure dependence of spin transitions in an anharmonic lattice with a Grüneisen constant of $\gamma_G=3$ for two different sizes of molecular volumes with respect to the volume v_0 provided by the crystal for a molecule and in the artificial harmonic lattice $\gamma_G=-\frac{2}{3}$. At zero pressure the transition curves are very similar which is shown by the thinner curves at $T_{1/2}=120$ K. The thinner curve at $v_{\mathrm{LS}}=v_0$ is that of the harmonic lattice and at $v_{\mathrm{HS}}=v_0$ that of the transition curve at $v_{\mathrm{LS}}=v_0$. Although the transition curves at zero pressure are hardly to be differentiated their pressure dependence shows large differences.

phonons to the interaction. The total interaction constants as listed in Table I are different by about 5 cm^{-1}.

B. Shift of $T_{1/2}$ versus pressure

The pressure dependence of the transition temperatures $T_{1/2}$ observed so far[7] could be hardly commented on because of the lack of temperature-dependent x-ray diffraction data from which the volume change accompanying the spin transition could have been derived. The very different dependencies observed concerning the slope and the change of slope of $dT_{1/2}/dp$ did not offer any correlation with any other properties of the transition curve. The three series of simulated transition curves at 0, 2, and 4 kbar in Fig. 5 demonstrate this situation.

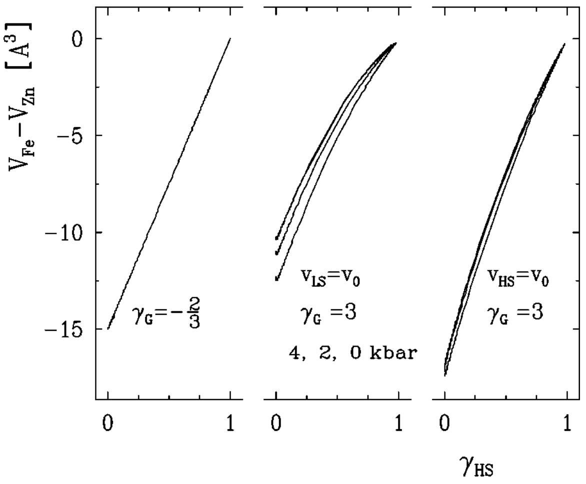

FIG. 6. The difference of the volumes per molecule of the crystal containing Fe spin crossover molecules and M=Zn molecules (assumed to be equal to Fe molecules in the HS state) plotted versus the HS fraction. Although the difference of the volumes of the molecules v_{HL} in the HS and LS state is fixed to 10 Å the change of the crystal volume $V_{\mathrm{Fe}}-V_{\mathrm{Zn}}$ depends on the misfit of the molecules to the space provided by the crystal. The three cases correspond to the cases in Fig. 5. In the harmonic case $\gamma_G=-2/3$ the volume change is linear and the difference between HS and LS states is equal to $\gamma_0 v_{\mathrm{HL}}=15$ Å. In case of $v_{\mathrm{LS}}=v_0$ the volume difference decreases considerably with increasing pressure.

The essential parameters are the misfit v_{LS} of the molecules and the Grüneisen constant γ_G. The anisotropic interaction Γ_M and the electronic energy difference Δ_{electr} are chosen in order to obtain very similar shapes close to a hysteresis transition (see text belonging to the figure) and the same transition temperature. At $\gamma_G=-2/3$, the harmonic potential, there is no dependence on the misfit. The free energy reduces to the phenomenological free energy of Eq. (4). This series shows the largest change of $T_{1/2}$ with pressure p. The different responses to p are expected from the dependence of the volume on the HS fraction. In Fig. 6 the difference $V_{\mathrm{Fe}}-V_{\mathrm{Zn}}$ is plotted versus the HS fraction γ_{HS}.

Here the Zn molecule is taken to be identical with the Fe molecule in the HS state, that means the same misfit to the crystal with the same Debye temperature. The temperature dependence of the Zn crystal serves as a reference as done in experimental work.[3,4] A linear dependence is obtained for the harmonic crystal with a difference of $\gamma_0 v_{\mathrm{HL}}=15$ Å between the crystal in the HS and LS state. The anharmonic crystal show larger volume change if the HS molecule fits to the lattice and smaller volume change with a pronounced pressure dependence if the LS state fits. The shifts of the transition temperatures are almost proportional to the volume differences neglecting the change of around 10% with pressure in the $v_{\mathrm{LS}}=v_0$ case. However, this proportionality is not at all fulfilled comparing the three cases. Such a discrepancy has been first reported for the iron pic=picolylamine compounds in 1990.[17] In this compound the hydrogen bridges between the spin crossover molecules were deuterated resulting in a shift of the transition temperature by 15 K. From the point of view of the elastic properties of the compound the lower vibrational amplitudes of the deuterium will shrink the space in the lattice provided for its molecules which is in line with the smaller volume change by more than 10%.

C. Pressure dependence of hysteresis transitions

1. Increase of hysteresis width

The first observation of an anomalous increase of the hysteresis width with increasing pressure was published by König *et al.*[8] and discussed in the frame of Landau theory developed by Das and Ghosh.[44] The compound $[\mathrm{Fe(phy)_2}](\mathrm{BF_4})_2$ (phy=1,10-phenanthroline-2-carbaldehyde phenylhydrazone) was later remeasured up to 5.8 kbar confirming the old data up to 2.5 kbar.[11] The anomalous behavior was now interpreted in the frame of the standard free energy of Eq. (4) allowing for a volume dependence of the bulk modulus K as a prefactor of the interaction constant and the energy separation between the HS and LS state. The authors already pointed out that the equations are not complete since the free energy of the lattice itself was not considered such that volume and HS fraction are both variational parameters. Over the years the Mainz group published several pressure data and found new anomalies from the point of view of standard spin crossover free energy equation. Most of them could be now reproduced as will be demonstrated by the following figures. In Fig. 7 we start with hysteresis in the harmonic case and increase the Grüneisen parameter up to $\gamma_G=2.5$. The misfit is fixed to $v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}/2$ and the direct elastic interaction to $\Gamma_M/K_0V_0=1.55$. To preserve the hysteresis width and $T_{1/2}$ at $p=0$ the energy separation Δ_{elect} and the short-range interaction Γ are adjusted (see Table I). In the harmonic potential the hysteresis already vanish at 2 kbar. The width at 2 and 4 kbar increase with increasing γ_G. Furthermore the width increase with p such that at $\gamma_G=1.8$ the widths are almost the same for 2 and 4 kbar and at $\gamma_G=2.5$ the above cited situation of an increasing hysteresis width with increasing p is simulated. At the same time the shift of $T_{1/2}$ decreases monotonously.

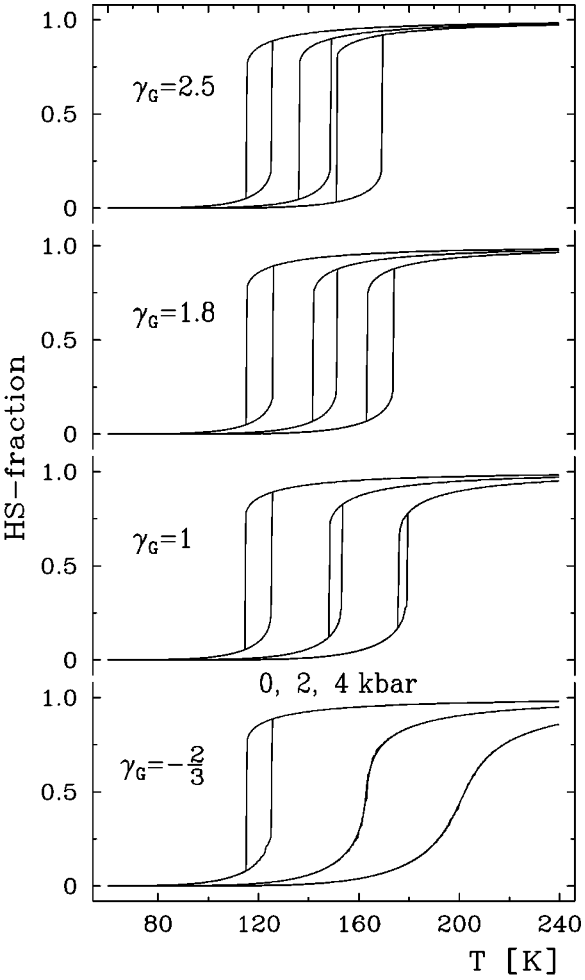

FIG. 7. Four spin transitions with a hysteresis width of 10 K at a transition temperature of $T_{1/2}=120$ K and their behavior under pressure up to 4 kbar are simulated. The misfit of the spin crossover molecule to the lattice is $v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}/2$ in all cases. With increasing anharmonicity [γ_G from harmonic $(-2/3)$ to 2.5] pressure favors the hysteresis behavior. At $\gamma_G=1.8$ the width of the hysteresis is almost independent of pressure and at the higher anharmonicity of $\gamma_G=2.5$ the figure shows and increasing width with increasing pressure.

2. Narrow hysteresis width

A narrow hysteresis was observed under pressure which shifts at constant width to higher transition temperatures.[10] Starting with the parameter of the transition of constant hysteresis width shown in the preceding Fig. 7 a decrease of the interaction by adding a short range interaction $\Gamma=-20\ \mathrm{cm}^{-1}$ and a small decrease of the Grüneisen constant from 1.8 to $\gamma_G=1.7$ give the transition curves at 0, 2, and 4 kbar in Fig. 8. The case of a vanishing small hysteresis which reappears at higher pressure[6] could be also almost reproduced as shown in the upper part of Fig. 8.

3. Stabilization of the HS fraction

At the large misfit of $v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}$ used for the transition of the previous figure and a Grüneisen constant of $\gamma_G=2.5$ two new situations are met. First the branch of the hysteresis curve of decreasing temperature at 1 kbar shifts to lower T. The general accepted argument that pressure favors the smaller LS molecules obviously is not valid for all properties of the crystal. Since such a case has indeed been observed[11] we take as a working hypothesis that this parameter set still catches real properties of a crystal. In the experiment of Ksenofontov *et al.*[11] on the compound $\mathrm{Fe(PM{-}PEA)_2(NCS)_2}$ the hysteresis curves shift as whole to lower T (shift of the center of gravity), however, the shift was irreversible at least for $p \geqslant 1.6$ kbar indicating a phase transition to a more stable state which is very likely driven by reducing the stress energy introduced by a large misfit.

The second observation is the complete transition to the HS state at 4 kbar. Experimentally observed is a hysteresis shifting to higher temperatures at 0.8 and 3 kbar as usual but at $p=6$ kbar 50% of the molecules switch to the HS state down to 4 K.[12] This fraction increases to almost 80% at 10.5 kbar. The fact that there is not a complete transition to the HS state can have reasons such as nonequivalent lattice sites with different HS/LS energy separations or imperfections of the crystal. As for the example above there are irreversible changes. Releasing the pressure about 30% remain in the HS state at low temperatures. In the upper part of Fig. 9 this behavior could be partially modeled. At an even higher misfit

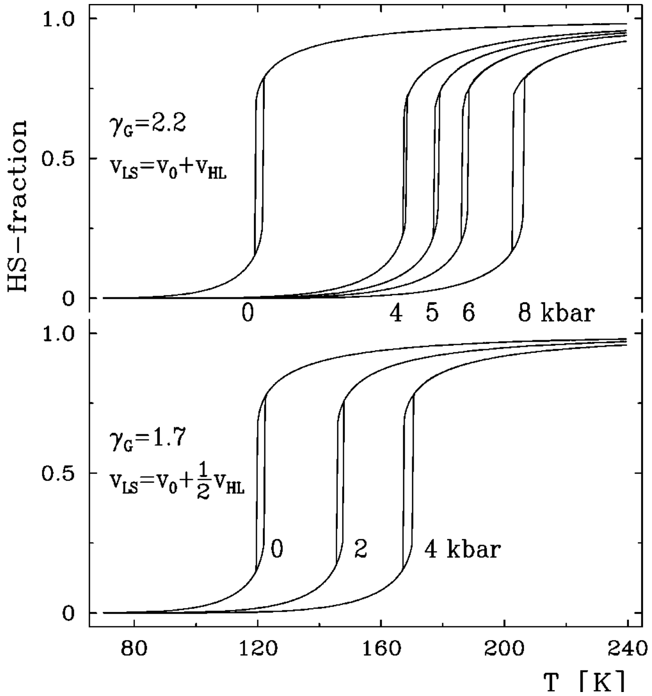

FIG. 8. Two behaviors of small hysteresis width of around 5 K as observed experimentally are simulated. A shift at constant width has been obtained starting from the parameter of Fig. 7 ($v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}/2$) and a slightly lower Grüneisen constant of $\gamma_G=1.7$. At the larger misfit of $v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}$ the situation of a small hysteresis width is obtained which almost vanishes at 4 kbar and recovers at 8 kbar to an even larger width than at zero pressure.

of $v_{\mathrm{LS}}=v_0+2v_{\mathrm{HL}}$ but only a comparably small anharmonicity of $\gamma_G=1.2$ the hysteresis shifts to higher temperatures at 1 kbar and jumps to the HS state over the whole temperature range (there is a small fraction of LS molecules around 80 K) at 8 kbar. It is worthwhile to look at the volume difference versus the HS fraction for these extreme cases. In Fig. 10 three cases are shown with an increasing misfit.

The first plot with the volume dependence for 0 and 4 kbar belongs to the increasing hysteresis width of Fig. 7. The volume dependence is reduced by about a factor of $\frac{1}{2}$ as compared to the harmonic case, but does not show the anomalies of the two other plots belonging to Fig. 9. Here under pressure the crystal in the LS state has a larger volume than the crystal in the HS state. According to Clausius-Clapeyron $dp/dT=\Delta S_{\mathrm{HL}}/\Delta V_{\mathrm{HL}}$ a negative shift in T requires a negative ratio of the difference in entropy ΔS_{HL} and crystal volume ΔV_{HL} between the crystal in the HS and LS state. The entropy difference of the systems is positive and mainly determined by the higher intra molecular frequencies in the LS state as compared to the HS state. The entropy difference is the driving force for the spin transition. This fact became evident by specific heat measurements,[45,46] measuring phonon spectra by nuclear inelastic scattering,[47] and also theoretical calculations.[48] Experimental observations of negative temperature shifts, therefore, require a negative volume change of the crystal going from an HS to LS state.

The basic mechanism for the dependence of ΔV_{HL} on the misfit can be easily isolated from the free energy equation. All elastic energies are proportional to the bulk modulus K which depends on the volume expressed by ϵ_s according to Eq. (19) as $K\sim 1-2(\gamma_G+\frac{2}{3})\epsilon_s$. This means that a linear term in ϵ_s is introduced which leads to a shift of the equilibrium

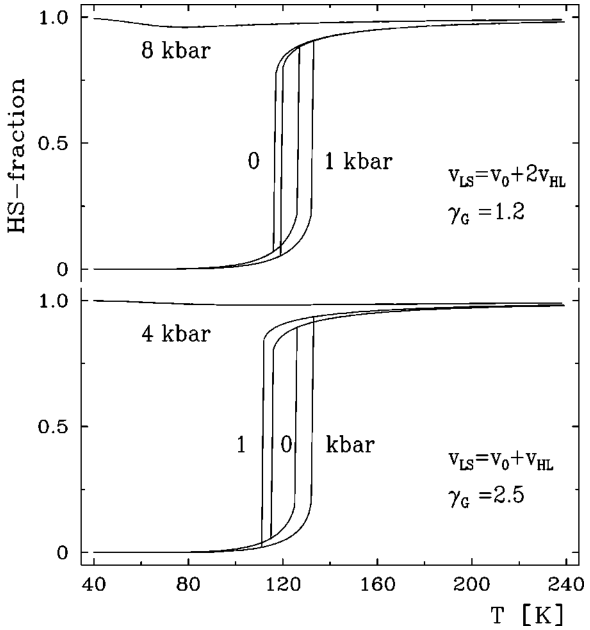

FIG. 9. The interesting case of a transition from LS to the HS state under pressure is reproduced. At large anharmonicity $\gamma_G=3$ a misfit of $v_{\mathrm{LS}}=v_0+v_{\mathrm{HL}}$ is sufficient in order to obtain a transition to the HS state over the whole temperature range at 2 kbar. At 1 kbar the anomalous behavior is already indicated by shift of center of gravity of the hysteresis to lower temperature. At a larger misfit but small anharmonicity $\gamma_G=1.2$ the hysteresis shifts to higher temperatures as usual but at 8 kbar the system stays again in the HS state.

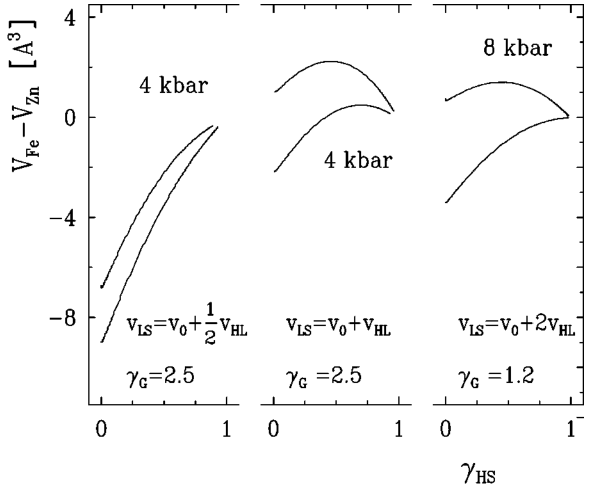

FIG. 10. The difference of the volumes per molecule of the crystal containing Fe spin crossover molecules and M=Zn molecules plotted versus the HS fraction (see Fig. 6). All three cases showing pressure dependence belong to the increasing hysteresis width in Fig. 7 and the two cases of Fig. 9 of induced HS state by external pressure, respectively. In the latter two cases the volume difference changes sign (finally under pressure) which gives rise to the stabilization of the HS state.

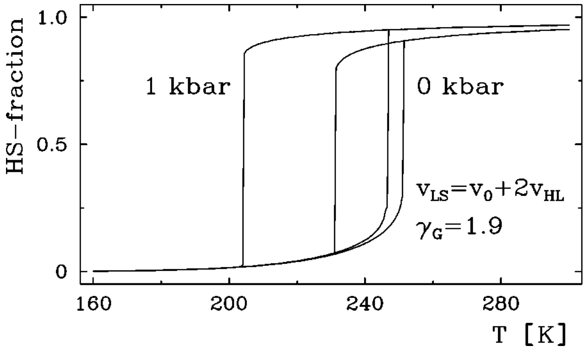

FIG. 11. A shift of the hysteresis under pressure to lower temperature as a whole (not only the center of gravity) has been simulated at a transition temperature of 240 K and a large misfit. In order to obtain the around 5 K shift of the $T_{1/2}^{\downarrow}$ temperatures the misfit of the anisotropic deformation has an extra increase by $\Delta\epsilon_M=0.015$ and the ratio v_m/v_0 is 1.73 instead of 2.

position in the potential energy $f_0(V)$. Considering the spherical part of the self energy $\sim(v_\alpha-v_0)^2$ the linear term is proportional to $-(v_\alpha-v_0)^2(\gamma_G+\frac{2}{3})\epsilon_s$. The difference (say δ) between the α=Zn compound and the LS state is then given by ($v_{\rm Zn}=v_{\rm HS}$)

$$\delta\sim-[(v_{\rm HS}-v_0)^2-(v_{\rm LS}-v_0)^2]\left(\gamma_G+\frac{2}{3}\right)\epsilon_s$$

$$=-(v_{\rm HS}+v_{\rm LS}-2v_0)v_{\rm HL}\left(\gamma_G+\frac{2}{3}\right)\epsilon_s. \qquad (41)$$

As a negative term shifts to a larger equilibrium value ϵ_s (larger volume) the larger volume difference $|V_{\rm Fe}-V_{\rm Zn}|$ with Fe in the LS state obtained for the misfit $v_{\rm HS}=v_0$ as compared to $v_{\rm LS}=v_0$ becomes obvious from this Eq. (41) and is in agreement with Fig. 10. One has to keep in mind, however, that different elastic energies contribute and the result of the iteration procedure to the minimum of the free energy cannot be easily estimated. The dependency of the volume change on pressure, which may cause even a change of sign (at 8 kbar in Fig. 10), is not easy to rationalize.

The last simulated hysteresis transition curve at 1 kbar shown in Fig. 11 is shifted to lower temperature, not only the branch of decreasing T but also the branch of increasing T. This situation, as already mentioned, seemed to be found experimentally.[12] In the first instance a simulation of it was not successful. Sticking to the idea that the free energy catches essential properties, the temperature has been changed from T=120 K to that of the experiment in order to keep the relative sizes of energies also with respect to the thermal energy. The effect could be a little increased by testing all parameters (see Table I). The corresponding volume difference plotted in Fig. 12 is about +8 Å^3. Although the experiment[12] cannot be interpreted by such a data set, because of the structural changes (see below), it guided to this interesting situation of Fig. 11.

4. The Fe(PM−PEA)$_2$(NCS)$_2$ compound

We have to state here, that positive $\Delta V_{\rm HL}$ values have not been observed yet, not for the compound Fe(PM−PEA)$_2$(NCS)$_2$ either.[49] The x-ray data show the volume difference between the HS and LS state to be 2.4% of the volume and positive so that a negative shift seems to be in contradiction to the law of Clausius Clapeyron. The way out is revealed by the present simulations. We have to consider the situation here more closely. The spin transition is accompanied by a structural phase change from $P2_1/c$ (HS) to the higher symmetric space group *Pccn* in the LS state and the authors observed a rearrangement of the topology of the network interactions and also of the shape of the molecule. This means that there are further inner degrees of freedom of the molecule allowing also to adjust to the misfit to its environment. So it is not unlikely that the stress field of the strain caused by a large misfit in the HS phase relaxes by the phase transition. Experimentally a positive value of $\Delta V_{\rm HL}$ in the HS phase at least under pressure cannot be excluded. Let us focus on the stabilization of the HS phase in the high-temperature structure following the branch of the hysteresis curve of decreasing temperature. A pressure dependence of a hysteresis curve taking place in the high-temperature structure as simulated in Fig. 9 at 1 kbar with a misfit of $v_{\rm LS}=v_0+v_{\rm HL}$ and γ_G=2.5 explains the negative temperature shift of the low-temperature branch.

The branch of the hysteresis curve of increasing temperature takes place in another structure which is even different from that at ambient pressure and, therefore, cannot be related to the negative temperature shift in the original structure of the crystal in the HS state. This is the way out of the contradiction to the relation of Clausius Clapeyron.

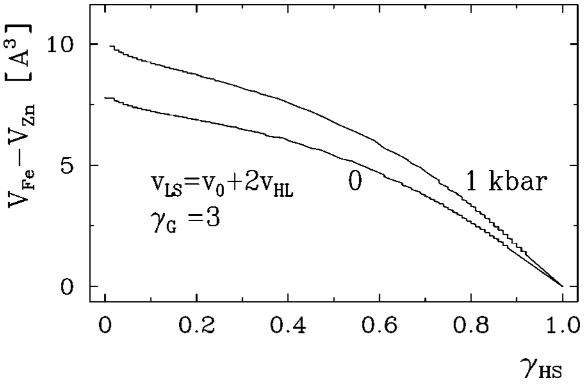

FIG. 12. The volume difference versus the HS fraction (see Fig. 10) for the anomalous hysteresis shift of Fig. 11 is already positive at zero pressure.

V. CONCLUSION

The total free energy of a spin crossover system has been constructed. Starting with an infinite crystal described within the Debye approximation and allowing for anharmonicity by the Grüneisen approximation the fictitious molecules of this crystal with volume v_0 and some anisotropic shape are replaced by spin crossover molecules and/or other metal molecules having a misfit with respect to the volume and the shape described by tensor components ϵ_s^α and ϵ_M^α (α=LS,HS,M), respectively. The potential energy of the infinite system is derived straightforwardly including the contributions of elastic energies of the molecular defects treated as elastic dipoles their strength being proportional to their misfit to the space of the fictitious molecules. The step to a crystal of finite size having a free surface introduces further contributions to the potential energy by elastic energies due to the displacement of the surface when the balance of forces at the surface is removed by removing the infinite part of the crystal. The latter contributions are typically not included in potential energies obtained from first principals calculations of the crystal potential since periodical boundary conditions are used in order to obtain a finite number of variables.

Two distortive modes have been included in the present calculation, the volume change and one anisotropic distortion, which has not been specified but is different from the axial component ϵ_0. These modes lead to two contribution to the interaction between the spin crossover molecules, the image interaction Γ_I being of "infinite" range and a direct long-range interaction Γ_d between the spin-crossover molecules in different spin states. A short-range interaction, which can be of ferroelastic or antiferroelastic type, is added to adjust the width of the hysteresis curves at zero pressure. The total free energy has three variational parameters, the HS fraction and the two distortion modes, which minimize the free energy under the constrain of the thermodynamic equation of the bulk modulus K. The proportionality of all elastic energies to K requires a self-consistent iteration procedure.

The essential result of this work is the importance of the misfit for the behavior of the spin transition under pressure. The volume change ΔV_{HL} of the crystal accompanying the spin transitions so far studied is positive as expected from the larger bond length of the molecules in the HS state. Consequently the crystal with its molecules in the LS state should be favored under pressure. The observation of stabilizing the HS state under pressure, switching to the HS state over the whole temperature range or just shifting a transition to lower temperatures, could not be rationalized. We consider the finding that a decreased or even negative volume change $\Delta V_{\mathrm{HL}} < 0$ is compatible with an increase of the molecular volume $(v_{\mathrm{HL}} > 0)$ as the main aspect of the present work. This unexpected behavior has been simulated within the scope of the elastic continuum theory of a finite crystal. The elastic energies of the anharmonic lattice are of such a size as compared to the potential energies and the thermal energies that with parameters within the limits of accessible experimental values the main features of anomalous transition curves could be simulated. The misfit of the molecule to the lattice, it is embedded, plays a crucial role for the relative size of elastic energies suited to obtain the extreme cases of stabilized HS state and negative temperature shift of the transition under pressure.

The large number of parameters of the free energy expression should not lead to the impression that sufficient flexibility is provided to account for any experimental observation such that predictive power is very limited. We stress that the free energy is well defined by the Debye and Grüneisen approximation and elasticity theory. The parameters of the Debye solid can be measured, that are the Grüneisen and elastic constants. From temperature-dependent x-ray structure the deformation tensors are obtained. There is also access to the self-energy comparing the electronic energies of the free molecule (say the molecule dissolved in a noninteracting liquid) with that of the molecule dissolved in the solid.[13] The forces due to the deformation of elastic medium (the lattice) are balanced by the molecule the electronic energy levels of which are appropriately changed. The self energy provides indirect information about the absolute value of volume and shape provided by the lattice. Only two parameters, the misfit of the molecule in one of the spin states and the short-range interaction, are left to reproduce the spin transition curve and its pressure dependence. The transition curves of a metal dilution series can already be predicted by the theory. So far the relevant parameters (elastic constants, Debye temperature, deformation tensor, etc.) of the spin transition compounds under discussion have not been determined. The present theory may stimulate the spin crossover community to collect the required data.

We are covinced that the consequences of the misfit of a molecule with respect to its lattice and of the finite size of the crystal is not only important for spin-crossover transitions. In any molecular crystal where molecules change size and shape of the order of 0.01 as a result of their inner degrees of freedom the contributions of elastic energies which will be of the order of 0.01 eV may influence phase transitions of the system. Candidates are cooperative Jahn Teller transitions and charge transfer transitions in molecular crystals.

ACKNOWLEDGMENT

One of the authors (H.S.) thanks for the opportunity to spend several months at the CNRS Institute in Versailles granted by CNRS.

---

*Electronic address: spiering@iacgu7.chemie.un-mainz.de

[1] E. Meissner, H. Köppen, H. Spiering, and P. Gütlich, Chem. Phys. Lett. **95**, 163 (1983).

[2] L. Wiehl, G. Kiel, C. P. Köhler, H. Spiering, and P. Gütlich, Inorg. Chem. **25**, 1565 (1986).

[3] J. Kusz, H. Spiering, and P. Gütlich, J. Appl. Crystallogr. **33**, 201 (2000).

[4] J. Kusz, H. Spiering, and P. Gütlich, J. Appl. Crystallogr. **34**, 229 (2001).

[5] J. Kusz, H. Spiering, and P. Gütlich (unpublished).

[6] Y. Garcia, V. Ksenofontov, and P. Gütlich, Hyperfine Interact. **139/140**, 543 (2002).

[7] V. Ksenofontov, A. Gaspar, and P. Gütlich, *Spin Crossover in Transition Metal Compounds*, Vol. 235 of Topics in Current Chemistry (Springer, Berlin, 2004), Chap. 22.

[8] E. König, G. Ritter, J. Waigel, and H. A. Goodwin, J. Chem. Phys. **83**, 3055 (1985).

[9] V. Ksenofontov, H. Spiering, A. Schreiner, G. Levchenko, H.

Goodwin, and P. Gütlich, J. Phys. Chem. Solids **60**, 393 (1999).

[10] Y. Garcia, P. van Koningsbruggen, R. Lapuyade, L. Fournès, L. Rabardel, O. Kahn, V. Ksenofontov, G. Levchenko, and P. Gütlich, Chem. Mater. **10**, 2426 (1998).

[11] V. Ksenofontov, G. Levchenko, H. Spiering, P. Gütlich, J.-F. Létard, Y. Bouhedja, and O. Kahn, Chem. Phys. Lett. **294**, 545 (1998).

[12] Y. Garcia, V. Ksenofontov, G. Levchenko, G. Schmitt, and P. Gütlich, J. Phys. Chem. B **104**, 5045 (2000).

[13] P. Gütlich, A. Hauser, and H. Spiering, Angew. Chem. **106**, 2109 (1994).

[14] H. Spiering, E. Meissner, H. Köppen, E. W. Müller, and P. Gütlich, Chem. Phys. **68**, 65 (1982).

[15] J. Jung, G. Schmitt, A. Hauser, L. Wiehl, K. Knorr, H. Spiering, and P. Gütlich, Z. Phys. B: Condens. Matter **100**, 523 (1996).

[16] H. Drickamer and C. Frank, *Electronic Transitions and the High Pressure Chemistry and Physics of Solids* (Chapman and Hall, London, 1973).

[17] C. P. Köhler, R. Jakobi, E. Meissner, L. Wiehl, H. Spiering, and P. Gütlich, J. Phys. Chem. Solids **51**, 239 (1990).

[18] P. Gütlich, H. A. Goodwin, and D. Hendrickson, Angew. Chem. **106**, 441 (1994).

[19] K. Boukheddaden and F. Varret, Hyperfine Interact. **72**, 349 (1992).

[20] J. Linares, J. Nasser, A. Bousseksou, K. Boukheddaden, and F. Varret, J. Magn. Magn. Mater. **140**, 1503 (1995).

[21] T. Kohlhaas, Master's thesis, Johannes Gutenberg-Universität, Mainz, 1995.

[22] H. Romstedt, A. Hauser, and Spiering, J. Phys. Chem. Solids **59**, 265 (1998).

[23] H. Romstedt, H. Spiering, and P. Gütlich, J. Phys. Chem. Solids **59**, 1353 (1998).

[24] J. Linarès, H. Spiering, and F. Varret, Eur. Phys. J. B **10**, 271 (1999).

[25] K. Boukheddaden, J. Linares, H. Spiering, and F. Varret, Eur. Phys. J. B **15**, 317 (2000).

[26] J. Jeftic, A. Hauser, F. Varret, and C. Ecolivet, High Press. Res. **18**, 195 (2000).

[27] E. Codjovi, N. Menendez, J. Jeftic, and F. Varret, C.R. Acad. Sci., Ser. IIc: Chim **4**, 181 (2001).

[28] T. Kambara, J. Chem. Phys. **74**, 4199 (1981).

[29] T. Kambara, J. Phys. Soc. Jpn. **50**, 2257 (1981).

[30] T. Kambara, J. Chem. Phys. **70**, 4199 (1979).

[31] H. Köppen, E. Meissner, L. Wiehl, H. Spiering, and P. Guetlich, Hyperfine Interact. **52**, 29 (1989).

[32] J. Eshelby, *Solid State Physics* (Academic, New York, 1956), Vol. 3, p. 79.

[33] J. Xie, S. de Gironcoli, S. Baroni, and M. Scheffler, Phys. Rev. B **59**, 965 (1999).

[34] E. Meissner, H. Köppen, C. P. Köhler, H. Spiering, and P. Gütlich, Hyperfine Interact. **36**, 1 (1987).

[35] J. Jung, Ph.D. thesis, D77, Johannes Gutenberg-Universität Mainz, 1995.

[36] W. Ludwig, in *Springer Tracts in Modern Physics*, edited by G. Höhler (Springer, Berlin, 1967), Vol. 43.

[37] N. Willenbacher and H. Spiering, J. Phys. C **21**, 1423 (1988).

[38] H. Spiering and N. Willenbacher, J. Phys.: Condens. Matter **1**, 10089 (1989).

[39] H. Spiering, T. Kohlhaas, H. Romstedt, A. Hauser, C. Bruns-Yilmaz, J. Kusz, and P. Gütlich, Coord. Chem. Rev. **190–192**, 629 (1999).

[40] R. Shuey and H. Beyeler, Z. Angew. Math. Phys. **19**, 278 (1969).

[41] J. Jung, F. Bruchhäuser, R. Feile, H. Spiering, and P. Gütlich, Z. Phys. B: Condens. Matter **100**, 517 (1996).

[42] R. Jakobi, H. Romstedt, H. Spiering, and P. Gütlich, Angew. Chem. **104**, 214 (1992).

[43] R. Zimmermann and E. König, J. Phys. Chem. Solids **38**, 779 (1977).

[44] A. Das and B. Ghos, J. Phys. C **16**, 1799 (1983).

[45] M. Sorai, Kikan Kagaku Sosetsu **3**, 191 (1988).

[46] R. Jakobi, H. Spiering, and P. Gütlich, J. Phys. Chem. Solids **53**, 267 (1992).

[47] H. Paulsen, H. Winkler, A. X. Trautwein, H. Grünsteudel, V. Rusanov, and H. Toftlund, Phys. Rev. B **59**, 975 (1999).

[48] H. Paulsen, L. Duelund, H. Winkler, H. Toftlund, and A. X. Trautwein, Inorg. Chem. **40**, 2201 (2001).

[49] P. Guionneau, J. F. Letard, D. S. Yufit, D. Chasseau, G. Bravic, A. E. Goeta, J. A. K. Howard, and O. Kahn, J. Mater. Chem. **9**, 985 (1999).