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Molecular dynamics of spin crossover: The (P,T) phase diagram of [Fe(PM-BIA)₂(NCS)₂]

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The spin crossover properties and the domains of existence of the different phases for the [Fe(PM BIA)₂(NCS)₂] complex are obtained from combining DFT and classical molecular dynamics (MD). The potential energy surfaces expressed in the Morse form for Fe N interactions are deduced from molecular DFT calculations and they allow producing Infra Red and Raman frequencies. These Fe N potentials inserted in a classical force field lead from MD calculations to the relative energies of the high spin and low spin configurations of the orthorhombic structure. The MD investigations have also allowed assessing the experimental (P,T) phase diagram by showing the monoclinic polymorph in its two spin states, and generating two triple points.

1. Introduction

Few inorganic transition metal ion complexes exhibit two electronic states of their *d* electrons, the Low Spin state (*LS*) and High Spin state (*HS*). The switching between these two states is subjected to small energy magnitudes and the transitions can be achieved with external constraints such as temperature and pressure as well as by applying light. The observed behavior, referred to as Spin Crossover (*SCO*) and mainly studied in Fe^{II} complexes, has been widely investigated by research groups worldwide both from the fundamental and applied (display applications, ...) [1-4]. The transition temperature at which there is same proportion of *LS* and *HS* is called $T_{1/2}$. In the case of first order transition, the thermal hysteresis is described by $T_{1/2}\uparrow$ and $T_{1/2}\downarrow$ associated with the corresponding enthalpy change ΔH . One of these complexes, [Fe(PM BIA)₂(NCS)₂]¹, is characterized by iron surrounded by a distorted octahedron involving two *N* (2' pyridylmethylene) (PM) and two 4 aminobiphenyl (BIA) ligands and completed by two thiocyanate anions. It is known to undergo a gradual *SCO* at $T_{1/2} = 190$ K in the monoclinic polymorph (II phase, *Z* = 4, space group *P2₁/c*) [1-8]. A very abrupt transition is observed for the orthorhombic polymorph (I phase, *Z* = 4, space group *Pccn*) with $T_{1/2}\uparrow = 173$ K and $T_{1/2}\downarrow = 168$ K between the low spin (*LS*, *S* = 0) to the high spin state (*HS*, *S* = 2) of the Fe²⁺ ion [4]. Among its interesting magneto optical properties, this *SCO* may be light induced, the limit temperature

above which a photomagnetic effect in a material is erased the so called T_{LIESST} (for « Light Induced Excited Spin State Trapping ») depending strongly on the structural distortion of the 3d⁶ Fe²⁺ environment [9] and/or the nature of the ligand [10]. As often [8,11,12], pressure plays a role in the opposite sense of temperature in as far the starting spin state is the high spin: by increasing pressure, both I and II polymorphs of FePMBIA yield a *HS* → *LS* transition [13].

In such a complex compound, density functional theory (*DFT*) [14,15] approach is useful for understanding the property differences between the two spin states, namely ionic charges of the Fe²⁺ cation or the N atoms, geometric molecular building and magnetic properties, as shown in the study of Fe^{II} complexes: the *SCO* with a measurable $T_{1/2}$ originates from the crystal field around Fe^{II} which must be of medium strength such with use of *N* based ligands [16]. But *ab initio* methods cannot well explain intermolecular interactions in molecular crystals, because dispersion forces are insufficiently reproduced. Consequently, the obtained energy values may be far from experiments, leading sometimes to wrong hierarchy stability between the spin states. In view of this drawback the determination of the transition enthalpy $\Delta H_{LS \rightarrow HS}$ is made difficult.

For that, classical methods, such as molecular dynamics (*MD*), where van der Waals forces or hydrogen bonding may be modeled inside a generalized atom atom force field, are preferred. Nevertheless, the knowledge of atomic charges (q_i) and of the potential energy surface (*PES*) deduced from molecular *DFT* calculations, is very often used as a starting step in a *MD* approach, as in [17]; the quantum results allow evaluating force field parameters. In

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¹ [Fe(PM-BIA)₂(NCS)₂] complex will be called thereafter as FePMBIA.

this context we may define such an original methodology, combining *DFT* calculations and molecular dynamics, first in the molecular state and finally in the crystalline one, as “semi classical molecular dynamics”.

2. Methodology

Because the classical intramolecular force field comprises electrostatic forces acting between atomic charges, stretching 2 body interactions, bending 3 body forces and dihedral 4 body interactions, in order to model a molecule, the first step is a *DFT* procedure. *Ab initio* calculations applying the *GAUSSIAN* code to the FePMBIA molecule in its two spin states are firstly carried out, followed by a Mulliken analysis [18]. For this purpose, the hybrid *B3LYP** functional, with effective core potential *LANL2DZ* (*Los Alamos National Laboratory with Double Zeta* polarization) function, has been used for all atoms. For a reminder, in the original formulation of the *B3LYP* hybrid functional, one modification of the exchange weighting parameter called *B3LYP** was proposed by Reiher [19]. Resulting optimized molecular structure and point charges allow generating the *PES*. The curve is fitted with Morse $V_{\text{Fe-N}}$ and harmonic $V_{\text{Fe-C-N}}$ potentials, by varying alternatively one of the three Fe N_i distances of FePMBIA in each spin state while the two others remain constant. Only I phase whose vibration properties are experimentally known has been used.

In a second step, *MD* simulations are performed including other intramolecular interactions described by 2 body, 3 body and 4 body potentials at the level of the molecule. Internal van der Waals interactions occurring between pyridine and phenyl rings or describing $S \dots H$ hydrogen bonds must be added. All these parameters are adjusted with respect to the molecular geometry and the spectroscopic properties by using the *DL POLY* code [20] which yields a molecular field for each spin state.

Then these generalized force fields can be applied to the molecular crystal lattice. After a minimization step at 1 K for both spin states, *MD* simulations are performed up to 300 K by increasing temperature. Similar *MD* runs are done by cooling. Best van der Waals parameters are searched for, in order to reproduce structures both in *LS* state (25 K and 140 K) and *HS* state (298 K) [2,4,21].

With these final intermolecular force fields, the complete set of runs allow evaluating respectively $T_{1/2\uparrow}$ and $T_{1/2\downarrow}$ and transition enthalpy $\Delta H_{LS \rightarrow HS}$ at $T_{1/2}$, the so called $\Delta H_{1/2}$, $T_{1/2}$ and $\Delta H_{1/2}$ are related, as shown in a phenomenological thermodynamical view, by modeling the *LS HS* domain mixture as a regular solid solution [22]. In such a way, the Gibbs free energy $G_{LS \rightarrow HS}$, referred to the *LS* state, is expressed as a function of the molar fraction of *HS* state γ_{HS} in the crystal according to:

$$G_{LS \rightarrow HS} = \gamma_{HS} \Delta H_{LS \rightarrow HS} + \Omega \gamma_{HS} (1 - \gamma_{HS}) + RT \{ [\gamma_{HS} \ln \gamma_{HS} + (1 - \gamma_{HS}) \ln (1 - \gamma_{HS})] \Delta S_{LS \rightarrow HS} \} \quad (1a)$$

Ω is a constant, which may be related to the interacting energy between domains and the domain size [23]. $\Delta S_{LS \rightarrow HS}$ represents the transition entropy during the spin transition, and R the ideal gas constant. Searching the equilibrium condition in the crystal as:

$$\partial G_{LS \rightarrow HS} / \partial \gamma_{HS} = 0, \quad (1b)$$

a relationship is found in this model giving temperature as a function of thermodynamical functions:

$$T = [\Delta H_{LS \rightarrow HS} + \Omega (1 - 2\gamma_{HS})] / \{ R \ln [(1 - \gamma_{HS}) / \gamma_{HS}] + \Delta S_{LS \rightarrow HS} \}, \quad (1c)$$

At the so called $T_{1/2}$ temperature for which $\gamma_{HS} = 1/2$, Eq. (1c) implies that $T_{1/2}$ is Ω independent, as for an ideal mixture, and $T_{1/2} = \Delta H_{LS \rightarrow HS} / \Delta S_{LS \rightarrow HS}$. For other temperatures, $\gamma_{HS} \neq 1/2$, even if $\Omega = 0$; the enthalpy function will be evaluated by using Eq. (1c)

and assuming a Boltzman distribution of the *HS* domains. The variation enthalpy is then deduced as the enthalpic term of the Gibbs free energy:

$$\Delta H = \gamma_{HS} \Delta H_{LS \rightarrow HS} + \Omega \gamma_{HS} (1 - \gamma_{HS}) \quad (1d)$$

with an S shape, more pronounced when $\Omega \geq 2RT_{1/2}$.

At the same time, cell parameter variations versus temperature may be directly compared to experiments [3]. Isotherm and isobar *MD* runs are also performed on the *LS* state (I phase) in order to study its instability, the resulting I \rightarrow II transition in both spin states and to assess the experimental (P, T) phase diagram [13,24].

3. Force field in the two spin states of a FePMBIA molecule

3.1. Potential energy surface fit

Fig.1 gives a molecular view of the FePMBIA complex. The numbering of the nitrogen atoms is the following: N_1 is attached to the pyridylmethylene group (PM), N_2 to the aminobiphenyl ring (BIA) and N_3 belongs to thiocyanate anion. *DFT* calculations are achieved for each spin state by a geometry optimization of this structure. The *PES* fit requires studying successively its sections by two of the Fe N_1 , Fe N_2 and Fe N_3 distances, in order to know its variation with Fe N_1 , Fe N_2 and Fe N_3 distances. Except the last case, the molecular geometry constraints imply that, when $d_{\text{Fe } N_1}$ distances vary, $\theta_{\text{Fe } N_2 \text{ C}}$ angles are not constant. In the same manner, $\theta_{\text{Fe } N_1 \text{ C}}$ angles vary with $d_{\text{Fe } N_2}$. Point Mulliken charges deduced from *DFT* calculations are given in Table 1. For Fe^{2+} , they show that $q_{LS} \approx 3/2 q_{HS}$. Thus, it will not be surprising that existence of point Mulliken charges devoted to one spin state will imply two different intramolecular force fields.

All Fe N_i ($i = 1, \dots, 3$) 2 body interactions are described by a Morse expression:

$$V_{\text{Morse}}(r_{ij}) = E_{ij}^0 \left[\left\{ 1 - \exp(-\rho_{ij}(r_{ij} - r_{ij}^0)) \right\}^2 - 1 \right] \quad (2)$$

where E_{ij}^0 is the potential depth, ρ_{ij} the electronic hardness and r_{ij}^0 the equilibrium distance between two i and j species. It needs to be mentioned here that for the commodity of the many parameters for the six fits, we chose to make constant the ρ_{ij} value to 1.33 \AA^{-1} independently from the nature of N_i and of the spin state. A constant value of ρ_{ij} is currently used in classical force field, even if the coordination polyhedra around a specific atom i are of different types and strongly distorted (see as an example, [25]).

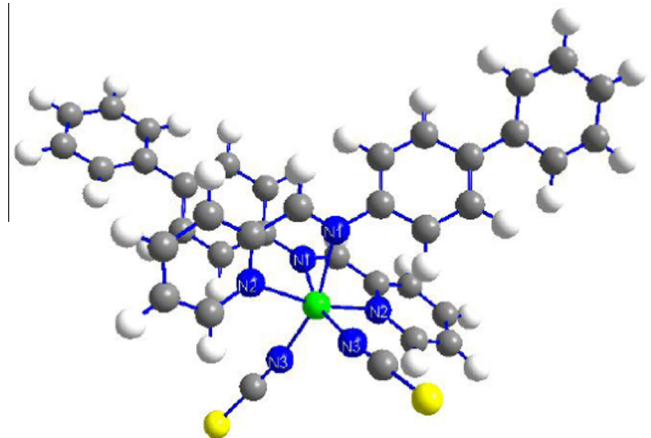


Fig. 1. Molecular view of the $\text{Fe}(\text{PM-BIA})_2\text{NCS}_2$ complex. The numbering of the nitrogen atoms is the one found within the text, figures and tables.

Table 1Mulliken charges of atoms in the Fe-(N)₆ octahedron (in e).

	LS	HS
Fe	1.5099	1.0442
N ₁	-0.7245	-0.7662
N ₂	-0.7678	-0.6936
N ₃	-0.7567	-0.7326

Furthermore we used harmonic 3 body interactions for the Fe N₁ C and Fe N₂ C angles:

$$V_{\text{harm}}(\theta_{ijk}) = 1/2k_{ijk}(\theta_{ijk} - \theta_{ijk}^0)^2 \quad (3)$$

where k_{ijk} is the stiffness constant of the angle θ_{ijk} and θ_{ijk}^0 the equilibrium angle.

Taking into account the Coulomb forces due to $q_{\text{Fe}^{2+}}$ and q_{N_i} charges, Fig. 2(a) (c) show the Morse fit of PES combined with angular harmonic potential (case of N₁ and N₂) when Fe²⁺ is in the LS state. Fig. 3(a) (c) give the same kind of results for the HS state. All the corresponding parameters are given in Table 2. It can be noted that the minimum position r_{min} is smaller than r_{ij}^0 as a consequence of the influence of the Coulomb field leading to a slightly modified curvature of the total potential $V(r_{ij}) = V_{\text{Morse}}(r_{ij}) + V_{\text{Coulomb}}(r_{ij})$ as seen by the 2nd order derivative:

$$\left[\frac{d^2 V(r_{ij})}{dr_{ij}^2} \right]_{\text{min}} = 2E_{ij}^0 \rho_{ij}^2 \exp[2\rho_{ij}(r_{\text{min}} - r_{ij}^0)] + 2kq_i q_j \times (1 - 0.5 \times \rho_{ij} r_{\text{min}}) / r_{\text{min}}^3 \quad (4)$$

where k is the Coulomb constant. From Table 2, the potential depths in the LS state ($E_{\text{FeN}_1}^{\text{o,LS}}$, $E_{\text{FeN}_2}^{\text{o,LS}}$, $E_{\text{FeN}_3}^{\text{o,LS}}$) are deeper than in the HS state ($E_{\text{FeN}_1}^{\text{HS}}$, $E_{\text{FeN}_2}^{\text{HS}}$, $E_{\text{FeN}_3}^{\text{HS}}$) and:

$$E_{\text{FeN}_1}^{\text{o,LS}} \sim 3E_{\text{FeN}_1}^{\text{o,HS}} \text{ and } E_{\text{FeN}_2}^{\text{o,LS}} \sim 3E_{\text{FeN}_2}^{\text{o,HS}}$$

3.2. Intramolecular force field

The force field devoted to a given spin state requires the input of:

- (i) all 2 body stretching harmonic interactions, such as C H, C C, C N, C S, N S, but also weak N N octahedron interactions;
- (ii) 3 body interactions, namely H C C, H C N, C C C, C C N, which will be described by bending harmonic potentials associated (Eq. (3)) and coupled potentials. There are two extra contributions needing to be accounted for in the coupling potentials; these are the coupling between adjacent bonds for species i, j and i, k in $V(r_{ij}, r_{ik})$:

$$V(r_{ij}, r_{kj}) = A_{ijk}(r_{ij} - r_{ij}^0)(r_{ik} - r_{ik}^0) \quad (5)$$

and the potential accounting for the bond and the angle $V(r_{ij}, \theta_{ijk})$:

$$V(r_{ij}, \theta_{jk}) = A_{ijk}(r_{ij} - r_{ij}^0)(\theta_{ijk} - \theta_{ijk}^0) \quad (6)$$

in both Eqs. (5), (6) A_{ijk} is a stiffness constant.

- (iii) 4 body dihedral and inversion interactions for maintaining the planarity of pyridine and of phenyl rings as well as for describing low vibration modes. The 4 body dihedral potential is:

$$V_{\text{cos}} = A_{ijkl}[1 + \cos(m\phi_{ijkl} - \delta_{ijkl})] \quad (7)$$

where A_{ijkl} is a stiffness constant, ϕ_{ijkl} is the dihedral angle and δ_{ijkl} the reference dihedral angle acting as an out of phase. Interactions due to inversion (with the ϕ_{ijkl} angle) correspond to the following expression:

$$V_{\text{plan}} = A_{ijkl}[1 - \cos(\phi_{ijkl})] \quad (8)$$

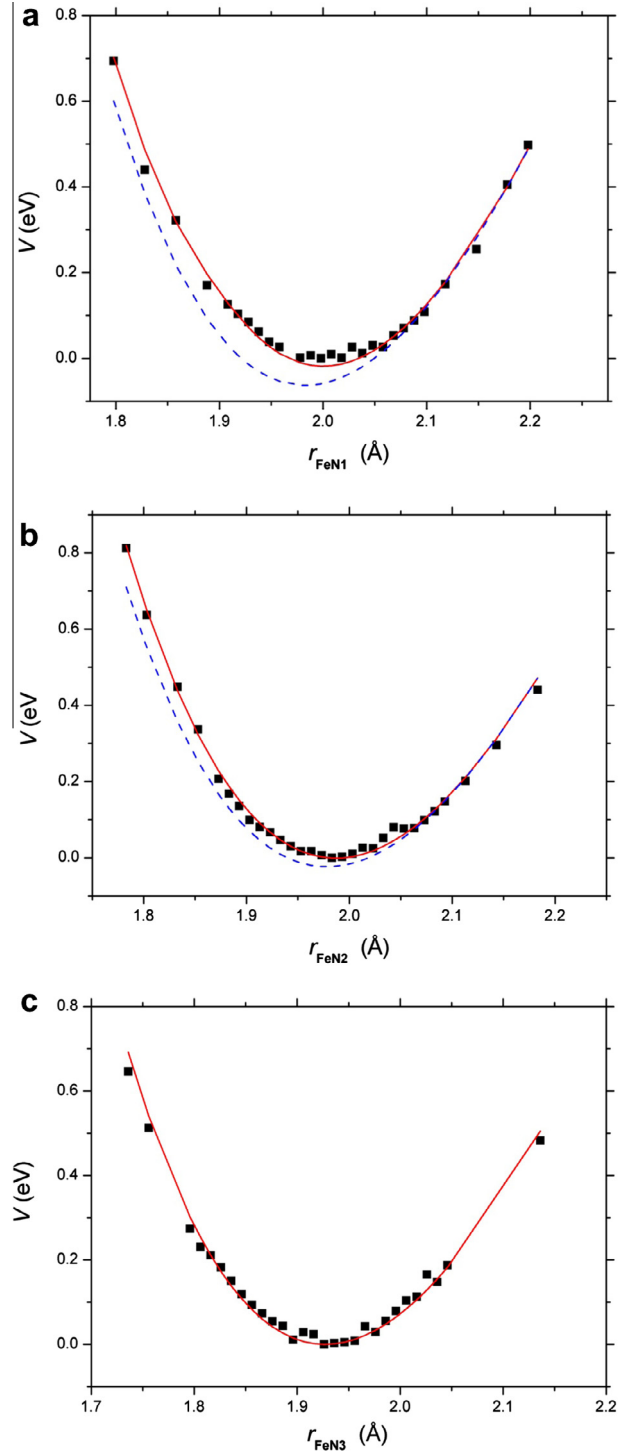


Fig. 2. Fit of the quantum potential energy surface (PES) in the LS spin state by combining Fe-N₁ Morse and Coulomb potentials with (straight red line in a) or without N₂-Fe-C harmonic potential (dotted blue line); by combining Fe-N₂ Morse and Coulomb potentials with (straight red line in b) or without N₁-Fe-C harmonic potential (dotted blue line); by using Fe-N₃ Morse and Coulomb potentials (straight red line in c). Black squares symbolize the PES values.

Starting values for parameters involved in all these intramolecular potentials, i.e. Eqs. (2), (3), (5) (8), come from the COMPASS force field which is devoted to organic molecules [26].

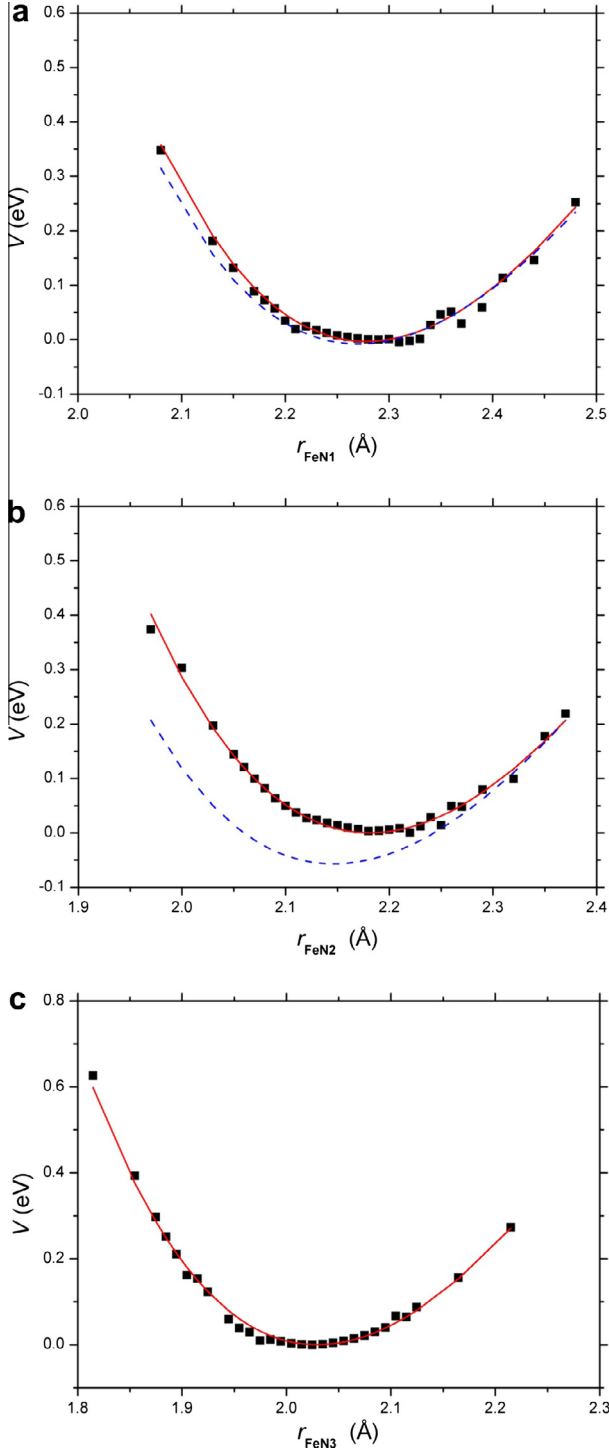


Fig. 3. Fit of the quantum potential energy surface (PES) in the HS spin state. Symbols have the same meaning as in Fig.2.

- (iv) long range potentials in a Lennard Jones form $V_{LJ}(r_{ij})$ have to be accounted for to describe the van der Waals interactions between adjacent phenyl rings and S...H hydrogen bonds and to reproduce the deformation modes involving two ligands connected to Fe^{2+} :

$$V_{LJ}(r_{ij}) = 4\epsilon_{ij}^0 \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (9)$$

ϵ_{ij}^0 is the potential depth, σ_{ij} the distance at which the long range $i-j$ interaction vanishes. The corresponding parameter values are extracted from [27].

The r_{ij}^0 equilibrium Morse values are changed in order to match the MD geometry (r_{min}) with experiment. In the same way the stiffness constants in the other 2 body potentials and in the 3 body potentials, as well as in the coupled ones, are modified according to the vibration modes. For both spin states, the complete force fields are given as [Supplementary informations](#) (Tables S1 and S2).

3.3. Application to the molecule in LS and HS spins states

The established force fields are applied to the FePMBIA molecule in MD runs by using DL POLY code. All simulations are performed at 0 K in the NVT ensemble coupled to a Berendsen thermostat (relaxation time constant = 0.1 ps) [28], with a long range distance cut off equal to 12 Å when calculating Coulomb forces by the Ewald method [29] or van der Waals interactions. As a result, Table 3 provides a comparison between experimental and MD octahedral FeN_6 geometries for the two spin states. The $d_{\text{Fe-N}}$ distance magnitudes are well reproduced together with the $\theta_{\text{N-Fe-N}}$ angles. The expected trend for a greater distortion in HS octahedron versus LS is found as exhibited by distance and angle extrema:

$$\Delta d_{HS} = 0.21 > \Delta d_{LS} = 0.03 \text{ \AA}; \quad \Delta \theta_{HS} = 26.4 > \Delta \theta_{LS} = 13.7 \text{ deg}$$

Low frequency vibration modes are well reproduced. Table 4 shows that the difference Δv_{MD} between measurements of Hoeffler [30] and MD results does not exceed 23 cm^{-1} for octahedral Fe N stretching modes, whereas DFT agreement is better ($\Delta v_{DFT} < 12 \text{ cm}^{-1}$). The position of the bending modes of the N C S group appear below experimental values ($\Delta v_{MD} < 35 \text{ cm}^{-1}$ in LS state, $< 10 \text{ cm}^{-1}$ in HS state); agreement is better for stretching C S and C N modes in both states ($\Delta v_{MD} < 24 \text{ cm}^{-1}$). In the high frequency region due to the C H modes, well matching values are found upon comparing with DFT calculations; for these modes, $0 < v_{LS} < v_{HS} < 49 \text{ cm}^{-1}$, smaller than with DFT values (Table S3 as supplementary informations).

For each spin state, the total energy found at 0 K ($E_{LS} = 26.11 \text{ eV}$, $E_{HS} = 25.99 \text{ eV}$) yields directly the molecular total energy difference between the two spin states $\Delta E_{LS \rightarrow HS}$:

$$\Delta H_{LS \rightarrow HS} = \Delta E_{LS \rightarrow HS} + P \Delta V_{LS \rightarrow HS} \quad (10)$$

Because MD runs of a single molecule are only done under the NVT ensemble in the DL POLY code [20], $\Delta V_{LS \rightarrow HS} = 0$ in this expression, and therefore, $\Delta E_{LS \rightarrow HS}$ gives directly the transition enthalpy: $\Delta H_{LS \rightarrow HS} = 0.12 \text{ eV} = 11.2 \text{ kJ/mol}$. Incidentally, this value is close to the experimental one determined by differential scanning analysis (DSC) on FePMBIA crystalline powders, obtained under atmospheric pressure (NPT conditions): (i) in the 160–190 K range, by [2] $\Delta H_{LS \rightarrow HS} = 10.06 \text{ kJ/mol}$; (ii) more recently by [31] $\Delta H_{LS \rightarrow HS} = 11.5 \text{ kJ/mol}$. Consequently, rigorously speaking, these two obtained values cannot be compared and another simulation method will be preferred calling for the whole crystal system which is modeled in the NPT ensemble as detailed in the following.

4. I-FePMBIA crystal in the two spin states

4.1. Intermolecular field in the crystal phase

At this step, molecular force field in one of the two spin states may be applied in MD runs to the crystal. For this purpose, the experimental structure corresponding with its three cell parameters (a , b and c), determined at 25 K and at room temperature, is used as a starting configuration and repeated in each crystallographic direction. The resulting 8 cell « box » is optimized at 0 K

Table 2Parameters for Morse potentials describing the 2-body Fe-N_i interactions and harmonic potentials of 3-body Fe-N_i-C interactions deduced from the *DFT* potential energy surface.

	E^0 (eV)	ρ (Å ⁻¹)	r^0 (Å)	$r_{\min}^{(opt)}$ (Å)	$r_{\min}^{(DFT)}$ (Å)	k (meV/deg ²)	$\theta_{\min}^{(opt)}$ (deg)	$\theta_{\min}^{(DFT)}$ (deg)
<i>LS</i>								
Fe-N ₁	1.54(1)	1.33	2.34(1)	2.000(5)	1.998	1.0	119(1)	114.5
Fe-N ₂	1.33(1)	1.33	2.38(1)	1.990(5)	1.983	0.52	119(1)	114.3
Fe-N ₃	1.23(2)	1.33	2.355(5)	1.925(5)	1.936			
<i>HS</i>								
Fe-N ₁	0.44(2)	1.33	2.78(1)	2.280(5)	2.28	0.52	119(1)	117.0
Fe-N ₂	0.405(5)	1.33	2.68(1)	2.180(5)	2.170	0.92	119(1)	113.5
Fe-N ₃	0.92(2)	1.33	2.41(2)	2.03(1)	2.014			

Table 3Octahedral geometry of the Fe²⁺ environment: comparison between experiments and molecular dynamics.

Distances (Å)	LS			HS		
	r^0	exp ^a	MD	r^0	exp ^b	MD
Fe-N ₁	2.105	1.965	1.967	2.586	2.251	2.250
Fe-N ₂	2.100	1.964	1.967	2.640	2.230	2.229
Fe-N ₃	2.067	1.938	1.934	2.288	2.040	2.041
N ₁ -N ₁		2.695	2.695		2.850	2.850
N ₁ -N ₂		2.546	2.552		2.707	2.707
"		2.896	2.893		3.246	3.246
N ₁ -N ₃		2.831	2.828		3.191	3.191
N ₂ -N ₃		2.837	2.844		3.030	3.030
"		2.781	2.780		3.293	3.293
N ₃ -N ₃		2.695	2.694		2.969	2.970
<i>Angles (deg)</i>						
N ₁ -Fe-N ₁		86.58	86.47		78.58	78.60
N ₁ -Fe-N ₂		80.79	80.86		74.37	74.40
"		94.98	94.61		92.90	92.93
N ₁ -Fe-N ₃		92.98	92.90		95.97	95.96
N ₂ -Fe-N ₃		90.88	90.89		90.33	90.30
"		93.27	93.54		100.86	100.84
N ₃ -Fe-N ₃		88.08	88.29		93.36	93.35

^a [21].^b [2].

in the *NVT* ensemble coupled to a Berendsen thermostat (relaxation time constant = 0.1 ps) with the same cut off as in Section 3.3 (12 Å). Then, isotherm simulations are made in the isostress *NσT* ensemble coupled to a Berendsen barostat (relaxation time constant = 1.0 ps): (i) to ensure that the average system pressure is maintained to the atmospheric one; (ii) to allow *b/a* and *c/a* ratios to vary; (iii) to ensure that the orthorhombic symmetry is conserved (the angles α , β and γ of the simulated cell ought to be very close to 90°). Contrary to an isobar simulation run performed in the *NPT* ensemble, isostress *NσT* ensemble implies that pressure does not rigorously conserve the angles within the cell. Each run is followed by a new simulation in the isobar *NPT* ensemble with the same relaxation time constants as in the *NVT* or *NσT* runs.

Table 4Fe-N and NCS group frequencies (in cm⁻¹): comparison between experiments of Höffer [30], molecular dynamics and *DFT*.

	LS			HS		
	exp	MD	DFT	exp	MD	DFT
			I.R.			I.R.
Fe-N	237	250		151	128	
	342	346	339	207	197	
	364	369	363	246, 259, 271	225	241, 257, 271
	368		369	326	327, 334	
δ (N-C-S)	447, 453, 458, 473, 487	418, 431, 446, 452		438, 469, 478	429, 460, 488	
C-S	809, 831, 847	825, 845	770, 775	840	837, 846	
C-N	2124	2148, 2161	2098, 2109	2074, 2081		2093, 2111

Table 5

Intermolecular interactions in the two spin states (For "chemical" clarity, the weak potential depths are given in kJ/mol units instead of eV).

	ϵ_{ij}^0 (kJ/mol)	LS	HS
		σ_{ij} (Å)	σ_{ij} (Å)
C...C	0.393	3.040	3.420
C...N	0.357	3.043	3.570
C...S	0.752	3.040	3.741
C...H	0.208	2.900	2.900
N...N	0.324	3.220	3.662
N...S	0.685	3.400	3.846
N...H	0.208	2.900	2.913
S...S	1.439	4.030	4.030
S...H	0.234	2.470	2.900
H...H	0.038	2.150	2.150

It is clear that cell volume and structure will be sensitive to the most numerous van der Waals interactions, that is C...C, C...H and H...H interactions, but also to the more energetic hydrogen bonds (N...H and S...H). Without compressibility data, it is impossible to adjust all the corresponding Lenard Jones potentials (Eq. (9)). Therefore, we introduce the constraint that each potential depth ϵ_{ij}^0 does not depend on the spin state and we modify C...C, C...N, C...S, N...N, N...S, N...H and S...H parameters by looking for their influence on the crystal data at 25 K (*LS* state) and 298 K (*HS* state) and on the corresponding van der Waals contacts. Table 5 gives the complete set of parameters (ϵ_{ij}^0 and σ_{ij}) for both spin states. Between the *LS* and *HS* states, some differences may be noted, mainly for C...S and S...H interactions where respectively ${}^{LS}\sigma_{S\ H} = 3.040$ Å is smaller than ${}^{HS}\sigma_{S\ H} = 3.741$ Å and ${}^{LS}\sigma_{S\ S} = 2.470$ Å smaller than ${}^{HS}\sigma_{S\ S} = 2.900$ Å: this means that S...H hydrogen bonds are stronger in the *LS* phase than in the *HS* phase, in agreement with the evolution of corresponding intermolecular distances with T (${}^{LS}d_{C\ \dots\ S} = 3.796$ Å, ${}^{HS}d_{C\ \dots\ S} = 3.901$ Å, and ${}^{LS}d_{S\ \dots\ H} = 2.94$ Å, ${}^{HS}d_{S\ \dots\ H} = 3.03$ Å), given by [4,32]. The van der Waals part of the energy E_{vdw} represents a little more of the 1/10 of the total energy (${}^{LS}E_{vdw} = 281.25$ kJ/mol, ${}^{HS}E_{vdw} = 278.90$ kJ/mol); but if these intermolecular terms are disregarded, $\Delta H_{LS \rightarrow HS}$ will be underestimated of ~ 2.3 kJ/mol.

4.2. Intermolecular interactions in the crystal state: towards thermoinduced transition $LS \rightarrow HS$

After this van der Waals interaction determination, we are able to simulate an orthorhombic phase cell in its two spin states at 0 K under atmospheric pressure: the total HS energy ($E_{HS} = 28.65$ eV = 2674.0 kJ/mol) is found to be slightly lower than in the LS state ($E_{LS} = 28.29$ eV = 2640.4 kJ/mol). By constraining the van der Waals potential depths to be independent of the spin state, these total energy values are certainly not correct. Moreover, quantum effects prevail at low temperatures. At these temperatures, because the difference between these values is of the order of their numerical fluctuation (± 10 kJ/mol), the transition enthalpy cannot be evaluated precisely through an equation similar to Eq. (10), even if *DL POLY* code gives us both total energy E and enthalpy H during each step of a NPT or $N\sigma T$ run.

A better value for $\Delta^{MD}H_{LS \rightarrow HS}$ must be determined in another manner. For this purpose, the molecular crystal system has to be studied by varying its thermodynamic state through isotherm isobaric runs. Increasing temperature runs are made on LS phase at 0 K minimized by applying LS field; this field is also used for the resulting room temperature phase but with decreasing temperature, in order to study the hysteresis behavior near the $T_{1/2}$ temperature. Similar approach is used for HS phase starting in the 0–298 K temperature range with increasing and decreasing step runs.

As argued in the preceding section, the octahedral geometry and the molecular packing depend strongly of the spin state, yielding a transition of the first kind. During the LS HS spin state transition, cell parameters and, at least, cell volume will therefore undergo discontinuities, allowing to understand the $T_{1/2}$ transition temperature through crystallographic considerations. Figs. 4(a)–(c) give the respective variation of a , b and c cell parameters as a function of T . The three curve sets show different behaviors. The a curve, obtained when HS force field is applied to the HS phase, shows the instability of this phase below 100 K, whereas the c curves is too imprecise for extracting transition informations. However, the crossing of the b curves, obtained with LS and HS force fields and applied with increasing temperature, specifies more precisely the $T_{1/2}$ temperature ($T_{1/2}^{\uparrow} = 120$ K), which is 50 K lower than the experimental one (173 K, [2]). As a result, the effect of the instability of the HS state below 100 K, shown in the evolution of the a cell parameter, is found again in the cell volume: by increasing temperature a cell volume expansion occurs at 100 K (Fig. 4(d)). At this temperature, the difference of the cell volume between LS and HS phases ($\Delta V_{cell} = 121 \text{ \AA}^3$) may be compared to the experimental value deduced from crystal data ($\Delta V_{cell} = 57.4 \text{ \AA}^3$, [3]). The observed relatively large differences in temperature and in volume can be accounted for by the drawbacks of a purely classical model in view of the prevailing quantum effects in this temperature region.

At each run step, the total energy and therefore the enthalpy given by the *DL POLY* code are spin state dependent. Because of the fluctuations of enthalpy, both for the LS configuration with LS field on one hand and for the HS one with HS field on the other hand, the enthalpy difference $\Delta^{MD}H_{LS \rightarrow HS}$ cannot be accurately determined by the corresponding difference. For this purpose, MD runs combining increasing and decreasing temperature in the two states will be accurate, because of the possibility to use Eq. (1d). The enthalpy difference $\Delta^{MD}H_{LS \rightarrow HS}$ between the two states is obtained by acting the LS field on LS and HS configurations at increasing temperature, as reported on Fig.5 (lower points): a sharp transition occurs between 140 and 160 K, when γ_{HS} content increases according to Eq. (1a), (1b), (1c), (1d). By using now the HS field on both spin state phases during cooling runs (Fig.5, upper points), $\Delta^{MD}H_{LS \rightarrow HS}$ is found not to depart from 14 ± 1 kJ/mol, which corresponds to the absence of LS crystal domains ($\gamma_{HS} = 1$). Therefore, $\Delta^{MD}H_{1/2}$ may

be taken as the value of $\Delta^{MD}H_{LS \rightarrow HS}$, that is $\Delta \Delta^{MD}H_{1/2} \sim 14 \pm 2$ kJ/mol (the slightly lower accuracy is due to the fluctuations of the LS background around zero). This MD value lies a little above the data arising from *DSC* ($\Delta^{DSC}H_{LS \rightarrow HS} = 10.06$ kJ/mol, [2]; 11.5 kJ/mol, [31]). A more precise determination of $\Delta^{MD}H_{1/2}$ would be certainly obtained through the evaluation of the Gibbs free energy variation $\Delta^{MD}G_{LS \rightarrow HS}$ resulting from the integration of the hybrid classical Hamiltonian which contains potential and kinetic terms and which describes both LS and HS spin states (see [20,27]). Nevertheless, the evolution of $\Delta^{MD}H_{LS \rightarrow HS}$ with T leads to a transition temperature value ($T_{1/2} = 150$ K), more precise and higher than the one deduced from the structural results (see above), and therefore in better agreement when compared to the experiments ($T_{1/2}^{\uparrow} = 173$ K and $T_{1/2}^{\downarrow} = 168$ K, [2]).

The results of simulations presented here allow also comparisons with experimental structures (25 K, 140 K and 298 K). Then, in the LS spin state, Table 6 shows that the b parameter is larger by 7.2% at 25 K and 12.5% at 140 K, but this is compensated by a c parameter with a lower value (–11.7% at 140 K). This is even better shown for the HS spin state where the small differences on the three cell parameters compensate perfectly when looking for the V_{cell} cell volume: $\Delta V_{cell}/V_{cell} = 0.7\%$. All this result set leads to prefer the more precise thermodynamical value $T_{1/2} = 150$ K.

5. Pressure stability of I-FePMBIA crystal: the pressure induced I \rightarrow II phase transition

The influence of pressure on FePMBIA has been studied by magnetic susceptibility measurements [13], optical reflectivity [8] and completed by a recent neutron diffraction study [24]: the orthorhombic I phase undergoes a transition towards the monoclinic II phase, independently of the spin state. This expectedly means that the (P,T) phase diagram must involve four solid phases LS_I , HS_I , LS_{II} and HS_{II} , and therefore two triple points between three of these four phases. Because it would be difficult to study experimentally these last parts of the (P,T) phase diagram, in particular the respective positions of the triple points, MD is helpful for assessing it. Therefore, simulations have been performed in the $N\sigma T$ ensemble in different isotherm isobar conditions from 25 to 300 K with pressure up to 20 kbar. All these processes were carried out for orthorhombic $[\text{Fe}(\text{PMBIA})_2(\text{NCS})_2]$ in order to exhibit its instability with increasing pressure. Furthermore, simulating the monoclinic phase in both spin states would have required establishing not only a new intramolecular parameter set, but also to select appropriate van der Waals force field in II phase. It is well admitted to use the same force field for room pressure and high pressure phases, as in B_2O_3 [25]. Because of the symmetry breaking between I and II structures, the corresponding phase transition will be of the first kind and therefore better detected in modeling processes. At low temperature, the cell volumes of I and II in their LS state are known to differ ($V_{cell,LS_I} = 3339 \text{ \AA}^3$ at 140 K, $V_{cell,LS_{II}} = 3294 \text{ \AA}^3$ in metastable state at 120 K, [4]); this means increasing pressure will favor more strongly the $LS_I \rightarrow LS_{II}$ phase transition.

Fig. 6(a)–(c) give the respective variations of a , b and c cell parameters as a function of P for different isotherms between 25 K and 160 K, when LS_I force field is acting: with increasing P , a and c show a sudden decrease in the range 7–12 kbar for 25 K, 50 K, 80 K, whereas a small b jump is observed; a departure of the β angle from 90° increases. Because the resulting volume variation is negative, SCO must not occur and therefore, as argued before, a $LS_I \rightarrow LS_{II}$ transition is assumed. For upper isotherms, the a and c curves have smaller discontinuities, one at lower P values, namely around 3 kbar, and the second one at 9 kbar. By comparison with the experiments of [13], two transitions must be taken into account: (i) for the lower transition, by combining SCO with

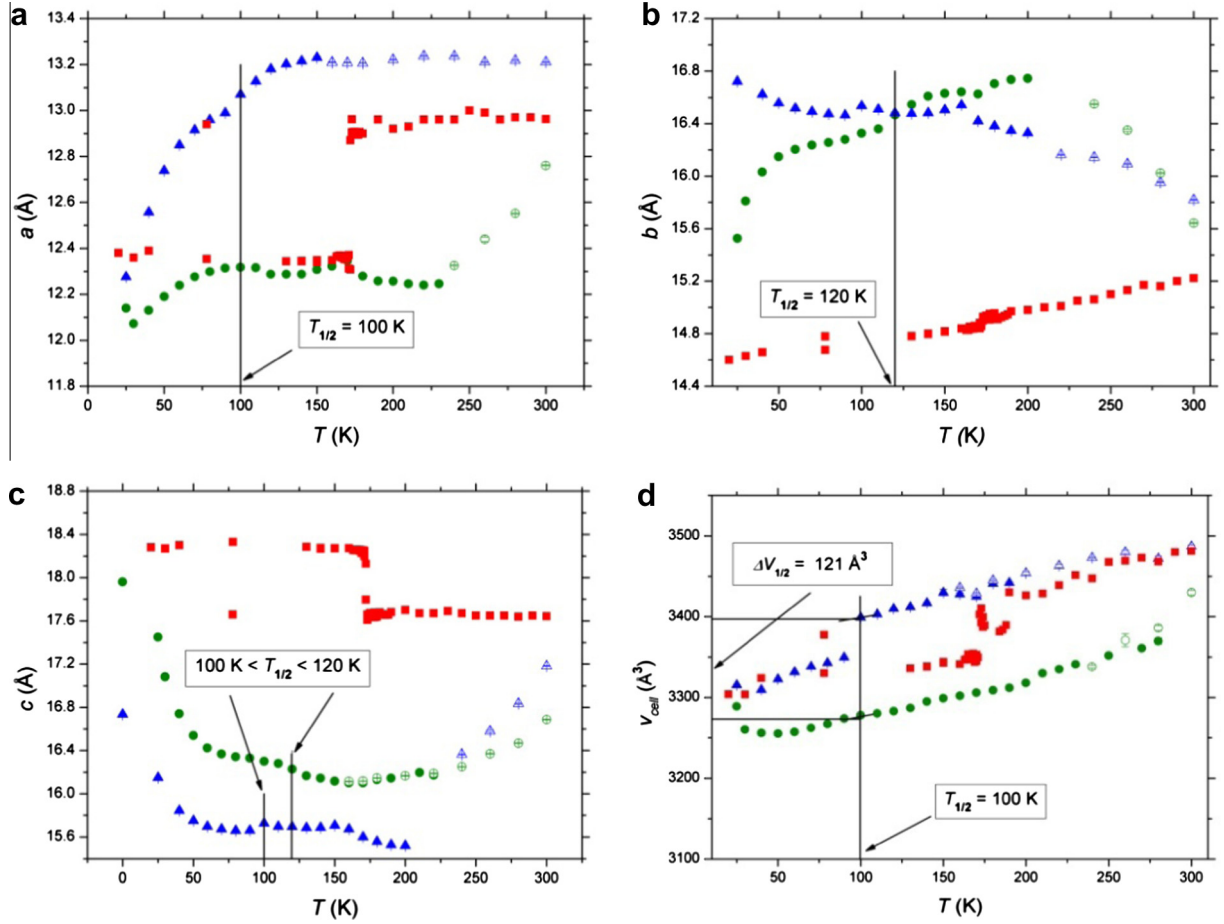


Fig. 4. Evolution of the a cell-parameter with temperature in the two spin states and comparison with diffraction data of [3] (a); evolution of the b cell-parameter with temperature in the two spin states (b); evolution of the c cell-parameter with temperature in the two spin states (c); evolution of the cell volume V_{cell} with temperature in the two spin states (d). Symbol notations are: filled green circles: LS -field acting on LS -phase at 0 K with increasing temperature; filled blue triangles: HS -field acting on HS -phase with increasing temperature; empty symbols correspond to runs but in decreasing temperature from 298 K; filled red squares correspond to diffraction data.

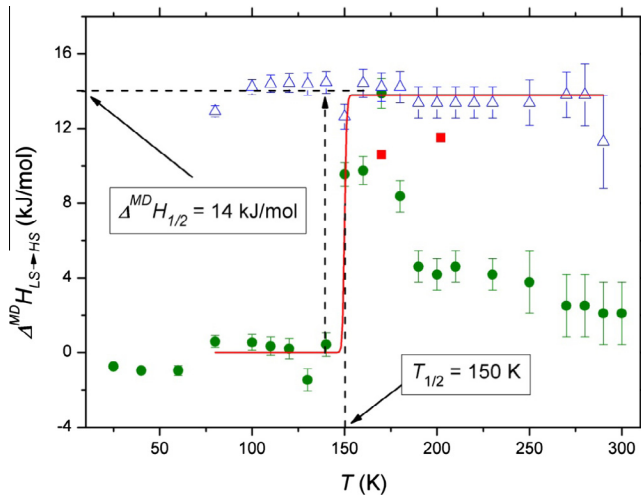


Fig. 5. Evolution of the difference enthalpy between the two spin states versus temperature (heating runs: filled green circles; cooling-down runs: empty blue triangles). Comparison with DSC measurements (filled red squares [2,31]).

Table 6

Cell parameters and cell volume in MD for the LS -state (25 K and 140 K) and for the HS -state (140 K and 300 K); comparison with experiments.

	LS			HS		
	MD	exp	diff. (%)	MD	exp	diff. (%)
25 K						
a (Å)	12.1393(4)	12.224(3) ^a	-0.7			
b (Å)	15.5257(6)	14.484(4) ^a	7.2			
c (Å)	17.4516(6)	18.130(5) ^a	-3.7			
V (Å ³)	3289.1(4)	3210(1) ^a	2.5			
140 K						
a (Å)	12.287(1)	12.370(3) ^b	-0.7	13.216(2)		
b (Å)	16.610(2)	14.764(3) ^b	12.5	16.481(2)		
c (Å)	16.146(2)	18.281(4) ^b	-11.7	15.688(2)		
V (Å ³)	3295(1)	3339(2) ^b	-1.3	3417(1)		
298 K						
a (Å)	13.211(3)	12.949(7) ^b	2.0			
b (Å)	15.818(3)	15.183(2) ^b	4.2			
c (Å)	16.688(3)	17.609(5) ^b	-5.2			
V (Å ³)	3487(2)	3462(2) ^b	0.7			

^a [21].

^b [2].

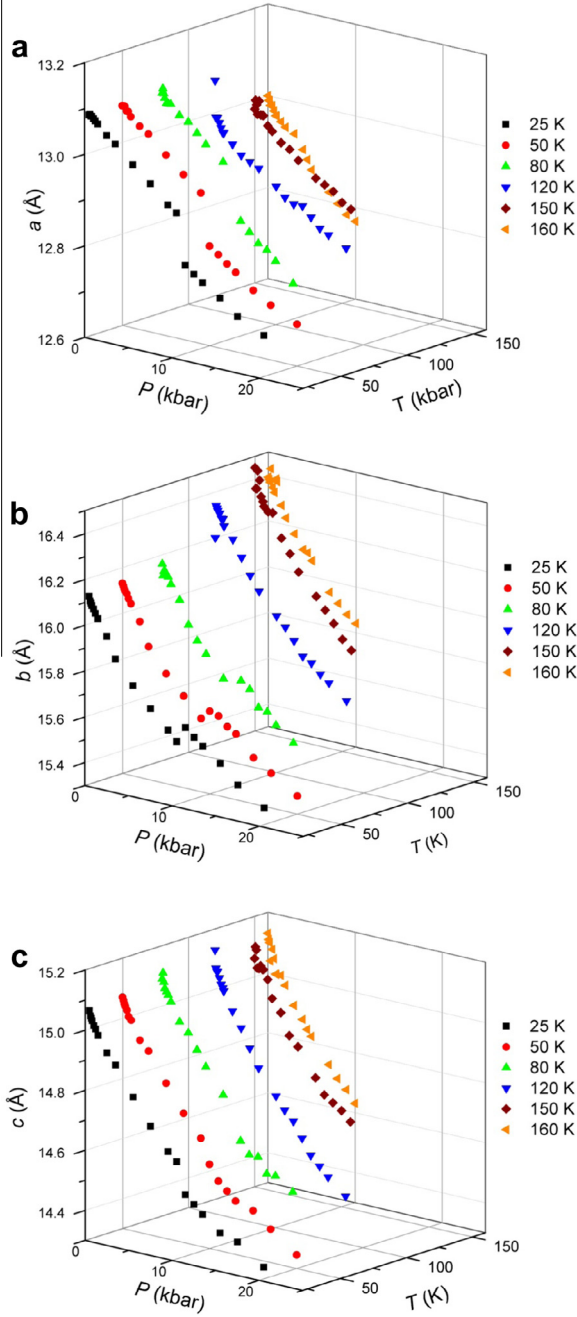


Fig. 6. Evolution of the a cell-parameter with increasing pressure between 25 K and 170 K (LS_1 -field acting during MD runs) (a); evolution of the b cell-parameter (b); evolution of the c cell-parameter (c).

a change of symmetry, pressure may authorize a phase in the HS state, but more compact than the LS_1 polymorph (here $\Delta V_{cell} = 35 \text{ \AA}^3$), leading to a $LS_1 \rightarrow HS_{II}$ transition; (ii) because pressure will favor a transition from HS to LS state, the upper transition will be $HS_{II} \rightarrow LS_1$.

When HS_1 force field is applied during MD runs, HS_1 phase will transform logically into a monoclinic HS_{II} polymorph. Fig. 7(a) (c) give the respective variations of a , b and c cell parameters as a function of P for different isotherms between 190 K and 300 K: the discontinuities appearing on the a and b curves, leading to a cell volume contraction, show that the expected $HS_1 \rightarrow HS_{II}$ transition occurs at $P \approx 3$ kbar below 280 K, at significantly higher pressure at 300 K ($P \approx 5$ kbar where $\Delta V_{cell} = 70 \text{ \AA}^3$).

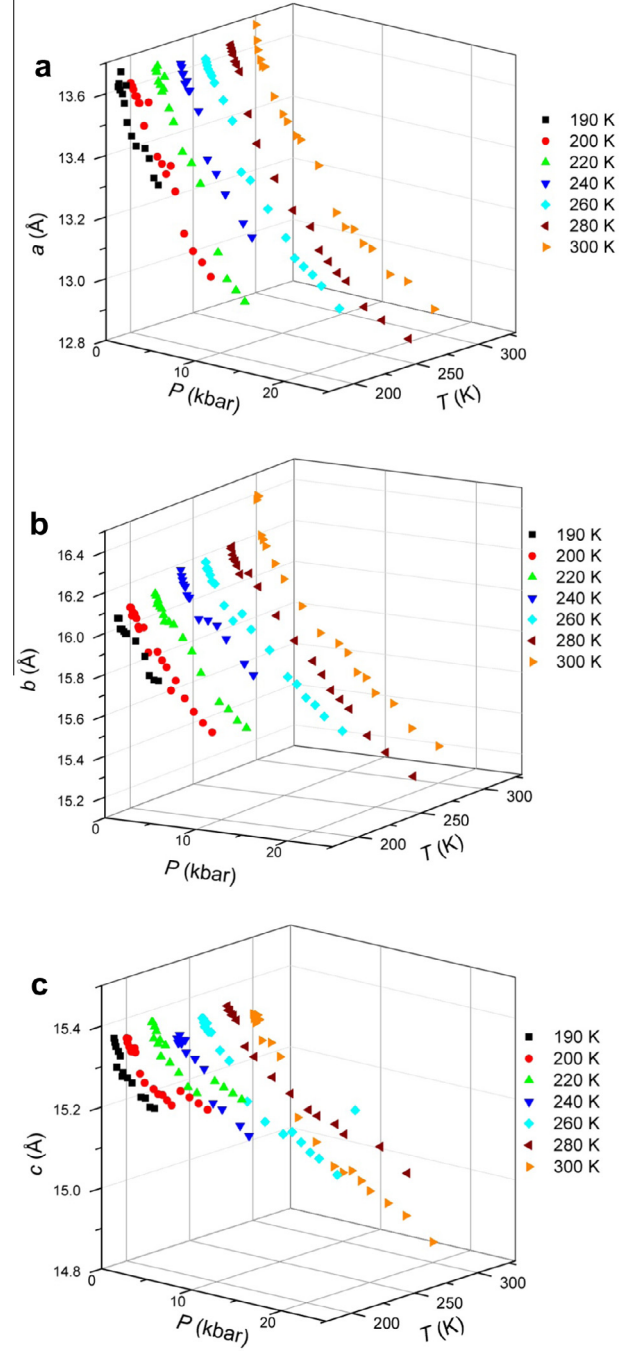


Fig. 7. Evolution of the a cell-parameter with increasing pressure between 190 K and 300 K (HS_1 -field acting during MD runs) (a); evolution of the b cell-parameter (b); evolution of the c cell-parameter (c).

Knowing both enthalpy and volume variations during the $LS_1 \rightarrow HS_1$ transition at $T_{1/2}$, as given in Section 4.2 ($\Delta H_{1/2} = 14.0 \text{ kJ/mol}$, $\Delta V_{cell} = 121 \text{ \AA}^3$), the use of the Clausius Clapeyron relation in its form valid for the transitions of the first kind:

$$\left(\frac{dP}{dT}\right)_{T_{1/2}} = \frac{\Delta H_{LS_1 \rightarrow HS_1}}{T \Delta V_{LS_1 \rightarrow HS_1}} \quad (11)$$

allows estimating the slope of the curve corresponding to the $LS_1 \rightarrow HS_1$ transition at 1 bar: $(dP/dT)_{T_{1/2}} = 0.08 \text{ kbar/K}$. Therefore, Eq. (11) may be used as a guide for the curve delimiting LS_1 and HS_1 area. One may remark that the value found is 1/2 of the one deduced from the experimental slope of a straight line separating LS_1 and HS_1 regions built from data of [24] ($(dP/dT)_{T_{1/2}} = 0.16 \text{ kbar/K}$).

Nevertheless, this difference is acceptable if we keep in mind the uncertainties found in the evaluation of $\Delta H_{1/2}$, $T_{1/2}$ and ΔV_{cell} . Moreover, the present MD value of $(dP/dT)_{T_{1/2}}$ is of the same order to the one found for the $[\text{Fe}(\text{sal}_2 \text{ trien})][\text{Ni}(\text{dmit})_2]$ complex which is known to have its SCO near 245 K ($(dP/dT)_{T_{1/2}} = 0.06 \text{ kbar/K}$, [11]).

From an experimental point of view, by putting the respective values of $T_{1/2}$ (170 K) and ΔV_{cell} (57.4 \AA^3) and knowing the slope dP/dT (0.16 kbar/K), $\Delta H_{1/2}$ can be evaluated from Eq. (11) ($\Delta^{CC}H_{1/2} = 23.5 \text{ kJ/mol}$). This value is twice the DSC one ($\Delta^{DSC}H_{LS \rightarrow HS} = 10.06 \text{ kJ/mol}$ [2], 11.5 kJ/mol [31]). In fact, this procedure is certainly incorrect, because in the pressure range involved (1 bar to 6 kbar) the true limiting curve between LS_I and HS_I domains is probably not a straight line, as a consequence of the evolution of the compressibility with pressure in each phase. This means that the slope dP/dT should be smaller than 0.16 kJ/mol, and therefore, the deduced $\Delta^{CC}H_{1/2}$ value closer to the DSC ones.

At this step, the (P,T) phase diagram may be built and compared to experiments (Fig.8). MD points are shifted to lower pressure and to lower temperature. Consequently, the calculated triple points are more separated than the ones estimated from experiments: the low pressure triple point which defines the LS_I , HS_I and HS_{II} equilibrium is located at 170 K and a pressure of $\sim 3.0 \text{ kbar}$, the second triple point corresponding to the LS_I , LS_{II} and HS_{II} equilibrium is close to 100 K at $\sim 6.8 \text{ kbar}$. These results may be compared to the experiments [13]. By studying the pressure effect on the hysteresis loop, these authors concluded that the data in the 6–8 kbar range correspond to a SCO coupled to a crystallographic phase transition. The present investigation confirms these findings and further provides the nature of the spins states according to the natures of the polymorphs, I and II. In other words, because the data of Ref. [13] take into account the metastability of the LS_I phase in the corresponding thermodynamic conditions which transforms into the HS_{II} phase, the line delimiting HS_I and HS_{II} phase domains in Fig.8 would be located at pressures lower than 7 kbar and at lower temperatures, as found by MD.

Another interest in this phase diagram is found by inspecting the slopes of the curves corresponding to the two transitions $LS_I \rightarrow LS_{II}$ and $HS_I \rightarrow HS_{II}$ which are on opposite directions: $(dP/dT)_{LS_I \rightarrow LS_{II}}$ is clearly negative, whereas $(dP/dT)_{HS_I \rightarrow HS_{II}}$ is slightly positive below room temperature. Because pressure favors more compact II phases (LS_{II} or HS_{II}) with a smaller molar volume as shown by [4] ($V_{cell,LS_{II}} = 3294 \text{ \AA}^3 < V_{cell,LS_I} = 3399 \text{ \AA}^3$), Eq. (11) implies

that pressure and temperature play antagonist roles during the $LS_I \rightarrow LS_{II}$ transition with a positive enthalpy variation $\Delta H_{LS_I \rightarrow LS_{II}}$. On the other hand, the $HS_I \rightarrow HS_{II}$ transition will correspond to a small negative enthalpy variation $\Delta H_{HS_I \rightarrow HS_{II}}$, associated, or not, to a small cell volume variation at room temperature, and to a significant cell volume contraction for T below 280 K. This last assumption is confirmed by the behavior of the corresponding experimental cell volumes [4,24,32]: starting from nearly equal values at 293 K ($V_{cell,HS_{II}} = 3464 \text{ \AA}^3$; $V_{cell,HS_I} = 3462 \text{ \AA}^3$), the two volume values diverge with decreasing temperature ($\Delta V_{cell} = 20 \text{ \AA}^3$ at 250 K, $\Delta V_{cell} = 30 \text{ \AA}^3$ at 225 K), until 210 K where HS_{II} phase becomes unstable ($\Delta V_{cell} = 40 \text{ \AA}^3$).

It will kept in mind that all discrepancies appearing in this section arise partly from assuming one force field for I and II, in particular for long range van der Waals interactions. Nevertheless, the observed trends should not be changed.

6. Conclusions

Starting from the potential energy surface of the $[\text{Fe}(\text{PM BIA})_2(\text{NCS})_2]$ complex obtained by DFT calculations on its distorted molecular geometry, Morse two body Fe–N interactions have been evaluated for both spin states of the orthorhombic polymorph (I). The potential wells and the equilibrium distances depend both of the nature of the bound N atom and of the spin state of the Fe^{2+} ion. An adjustment of other two body potentials, combined with van der Waals interactions, allow then to calculate vibration modes (I.R. and Raman) of the molecule in its two spin states by molecular simulation. In agreement with the experimental molecular geometry, the FeN_6 octahedron is found more distorted in the high spin state than in the low spin one, as exhibited by distance ($\Delta d_{HS} = 0.21 > \Delta d_{LS} = 0.03 \text{ \AA}$) and angle extrema ($\Delta \theta_{HS} = 26.4 > \Delta \theta_{LS} = 13.7 \text{ deg}$). Transferring the two obtained fields to the crystal state, molecular simulations give structural informations on the crystal lattice of the orthorhombic phases. Intermolecular interactions show evidence of hydrogen bonding between NCS sulfur end atoms with nearest neighbors hydrogen belonging to the aromatic cycles. The evolution of the structure with temperature shows that the $LS \rightarrow HS$ transition occurs at $T_{1/2} = 120 \text{ K}$ which is 50 K lower than the experimental value. The corresponding volume change of the unit cell, $\Delta V_{cell} = 121 \text{ \AA}^3$, may be compared to the crystallographic data at 170 K ($\Delta V_{cell} = 57.4 \text{ \AA}^3$).

The change of the transition enthalpy, $\Delta^{MD}H_{1/2} = 14 \pm 2 \text{ kJ/mol}$ corresponds to the transition temperature $T_{1/2} = 150 \text{ K}$. If $T_{1/2}$ agrees with experiments ($T_{1/2} \uparrow = 173 \text{ K}$ and $T_{1/2} \downarrow = 168 \text{ K}$), the MD enthalpy value lies a little above experimental measurements ($\Delta^{DSC}H_{LS \rightarrow HS} = 10.06 \text{ kJ/mol}$ and 11.5 kJ/mol). A more precise determination of $\Delta^{MD}H_{1/2}$ would certainly be obtained through the evaluation of the Gibbs free energy variation $\Delta^{MD}G_{LS \rightarrow HS}$ resulting from the integration of the hybrid classical Hamiltonian which contains potential and kinetic terms and which describes both LS and HS spin states.

The relative disagreement for $\Delta^{MD}H_{1/2}$ and for the structural results can also be accounted for by the drawbacks of a purely classical model in view of the prevailing quantum effects accounting below 100 K.

The molecular simulations have led to assess and complete the experimental (P,T) phase diagram of $[\text{Fe}(\text{PM BIA})_2(\text{NCS})_2]$. This is relevant to showing the domains of existence of the monoclinic polymorph (II) generated by its two spin states. Furthermore the delimitation of the different domains allowed generating two triple points:

- for LS_I , HS_I and HS_{II} equilibrium: at 170 K and $\sim 3.0 \text{ kbar}$,
- for LS_I , LS_{II} and HS_{II} equilibrium, at 100 K and $\sim 6.8 \text{ kbar}$.

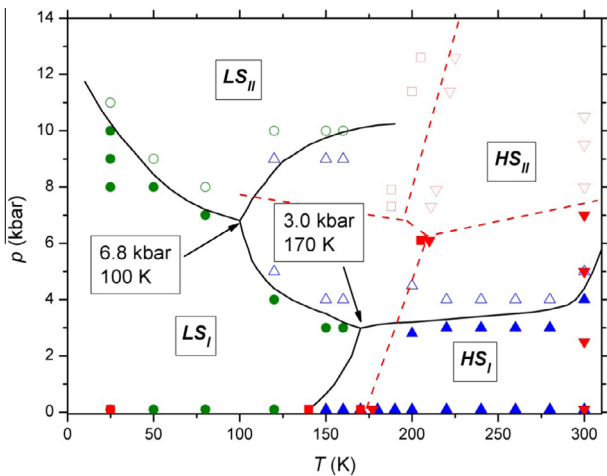


Fig. 8. (P,T) phase diagram showing four solid phases (LS_I : filled green circles; HS_I : filled blue triangles; LS_{II} : empty green circles; HS_{II} : empty blue triangles). Domains delimited by straight curves generate two triple points. Experimental points from [13,24] are also shown for comparison (LS_I : filled red squares; HS_I : filled red down triangles; LS_{II} : empty red square; HS_{II} : empty red up triangles).

On the other hand, the lack of data at low temperature leads us to provide neutron diffraction experiments on the LS_1 phase, in order to precise the (P,T) phase diagram below 175 K, in particular the stability range of this phase. These experiments are underway.

Indirectly, this work contributes to the general efforts done to identify the factors allowing to control the existence of the SCO phenomenon in molecular materials. This demonstrates how the packing may affect the geometry of a ligand and then the SCO properties. All the present results would be improved by using specific force field derived for each one of the four phases. This implies obtaining new van der Waals force field parameters as a function of the spin state and of the symmetry.

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