



HAL
open science

Structural phase transition in the spin-crossover complex $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ studied by x-ray diffraction

Sabine Lakhroufi, Philippe Guionneau, Marie-Hélène Lemée-Cailleau, Patrick Rosa, Jean-François Letard

► **To cite this version:**

Sabine Lakhroufi, Philippe Guionneau, Marie-Hélène Lemée-Cailleau, Patrick Rosa, Jean-François Letard. Structural phase transition in the spin-crossover complex $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ studied by x-ray diffraction. *Physical Review B: Condensed Matter and Materials Physics (1998-2015)*, 2010, 82 (13), pp.132104. 10.1103/PhysRevB.82.132104 . hal-00545047

HAL Id: hal-00545047

<https://hal.science/hal-00545047>

Submitted on 16 Jun 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Structural phase transition in the spin-crossover complex $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ studied by x-ray diffraction

S. Lakhroufi,^{1,2} P. Guionneau,^{1,*} M. H. Lemée-Cailleau,² P. Rosa,¹ and J.-F. Létard¹
¹CNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr A. Schweitzer, Pessac, F-33608, France
²Institut Laue-Langevin, 6 rue Jules Horowitz, BP 156, Grenoble F-38042, France

(Received 22 July 2010; published 25 October 2010)

The spin-crossover system $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ has been studied for more than 25 years and is used as a model system to the understanding of the eponymous phenomenon in solid-state materials. However, the structural properties of the low-spin phase formed at low temperature after a slow cooling have never been elucidated due to a splitting of the Bragg peaks. We report here a reinvestigation of this low-spin phase by single-crystal x-ray diffraction. This study demonstrates the perfect matching between the structural and magnetic transitions temperatures and hysteresis width through careful unit-cell temperature dependence. The Bragg splitting is also unambiguously associated to the spin transition. Above all, this work reveals a reversible doubling of the unit-cell parameters a and b corresponding to the spin transition. A preliminary solution for the crystal structure of the low-spin phase notably shows the potential major role of the deformation of the n -propyl groups in the physical behavior of this material.

DOI: 10.1103/PhysRevB.82.132104

PACS number(s): 64.70.-p, 61.05.cp, 64.90.+b, 78.20.Ls

The fascinating spin-crossover phenomenon concerns many fields as diverse as the dynamics of Earth mantle,¹ human biology² and the race to new materials for the future with potential industrial applications in information storage, display devices, and molecular electronics, in general.³ To this end, the spin-crossover phenomenon in molecular materials has been extensively studied worldwide resulting in a large amount of data and a detailed knowledge of this phenomenon, revealing, in particular, the paramount influence of the structural features on the magnetic and optical properties.⁴ Among the most studied systems is the complex $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ (ptz=1-propyltetrazole) that has been investigated for more than 25 years.⁵ The reasons for this interest are multiple. One of them is certainly that this system has been the first to reveal a photoinduced spin-crossover phenomenon.^{5,6} The light irradiation effects on this material at low temperature have been very thoroughly investigated.⁷ It is also one of the rare spin-crossover materials that is transparent in the high-spin (HS) state, and strongly colored in the low-spin (LS) state, which has allowed, for instance, the use and the development of several optical means of investigation.⁸ Another reason is undoubtedly the complexity of the pressure, temperature, and light irradiation phase diagram^{7,9-12} as well as the question of synergy between spin and phase transitions and factors such as cooling mode, aging, and purity of the sample.¹³ Notably, the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ system is known to show a different structural phase in the LS state depending on the rate of cooling.⁷ The structural properties of the LS phase obtained by slow cooling have never been clearly identified. This work aims to shed light on this phase diagram by mean of single-crystal x-ray diffraction focusing on the thermal spin-crossover at or close to thermal equilibrium.

Numerous magnetic, optical, and spectroscopic investigations have shown that $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ undergoes a HS to LS thermal spin-crossover without hysteresis at ~ 130 K if rapidly cooled (>10 K min^{-1}) while, if slowly cooled (<1 K min^{-1}) it shows an abrupt thermal spin-crossover at

~ 125 K with a hysteresis of 7 K.⁷ $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ crystallizes in the $R\bar{3}$ (no. 148) space group in the high-temperature HS phase, denoted $HS-R\bar{3}$.¹⁴ The LS phase obtained by rapid cooling corresponds¹⁵ to a quenching of the high-temperature structure, denoted $LS\text{-ord}$ for ordered phase, and shows no major difference from $HS-R\bar{3}$, except with the usual iron coordination sphere modifications due to the spin-crossover.¹⁶ The case of the slowly cooled LS phase appears much more problematic. Indeed, a split of the Bragg peaks has been reported in the initial structural studies of this phase, and subsequently confirmed.^{7,17} This phase is denoted $LS\text{-dis}$ for disordered phase since the splitting was understood as a loss of the single-crystal character of the sample. A detailed structural study of the $LS\text{-dis}$ phase was done by Wiehl and co-workers about 20 years ago.¹⁷ The conclusions of this careful study were that the space group cannot be determined for the $LS\text{-dis}$ phase, due to the splitting of the Bragg peaks, but that most probably a lowering of the symmetry occurs in LS, provided the unit-cell volume does not change from HS to LS. Since the initial structural study was performed with photographs (Weissenberg method), we thought it deserved a reinvestigation with modern x-ray diffraction techniques.

Fresh single crystals of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ were obtained using the method initially described in the literature¹⁸ and its subsequent improvements.¹⁹ A single crystal of dimensions $1.22 \times 1.0 \times 0.1$ mm³ was selected and mounted on an x-ray diffractometer. First, the crystal structure in the $HS-R\bar{3}$ was solved and refined just before the spin transition, at 140 K.²⁰ This redetermination has allowed checking the nature and quality of the samples and incidentally the quality of the $HS-R\bar{3}$ crystal structure has been significantly improved in comparison with the one previously obtained at higher temperature.¹⁴ Then, 21 short data collections were run in the range (150–80 K) leading to 12 sets of data obtained by cooling from 150 to 80 K and nine sets of data obtained by warming from 112 to 150 K. These temperatures were cho-

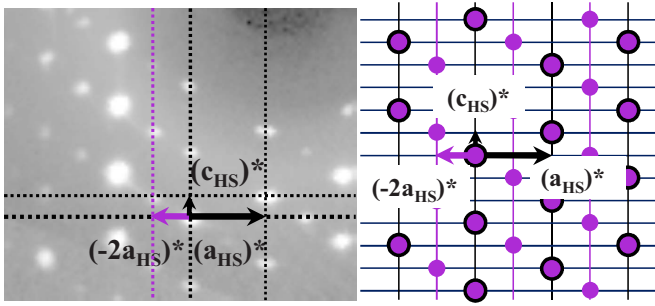


FIG. 1. (Color online) Partial view of the $(h0l)$ plane at 80 K in the LS - dis phase of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. The reciprocal parameter a^* is drawn in HS, a_{HS}^* to show the additional peaks corresponding to the doubling of a and respecting the $R\bar{3}$ symmetry. The same conclusions are reached for the b lattice parameter. The unit cell of the LS - dis phase is thus defined by $(-2a, -2b, c)$. These additional Bragg peaks appear at the HS to LS transition (125 K) and disappear at the LS to HS transition (132 K). Reversibility and reproducibility have been checked.

seen to follow the spin transition, anticipated around 125 K in the cooling mode and 132 K in the warming mode. In our experiments, the speed of cooling used was always 1 K min^{-1} . All these short data collection permit the determination of the unit-cell parameters temperature dependence as well as a significant coverage of reciprocal space to track additional reflections.²¹ A full data collection was also run at 80 K.²²

The inspection of the diffraction images first confirm a splitting of some Bragg peaks in the LS region. Moreover, comparison of the diffraction images reveals straightforwardly a new feature of the structural behavior of the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. Supplementary Bragg reflections corresponding to a doubling of the a and b unit-cell parameters are unambiguously observed at the lowest temperatures (Fig. 1). When cooling from 150 K, these supplementary Bragg peaks appear at 125 K and when warming from 80 to 150 K they disappear at ~ 132 K. These temperatures perfectly match the spin transition from HS - $R\bar{3}$ to LS - dis . Systematic extinction in LS - dis shows the space group remains $R\bar{3}$. The HS - $R\bar{3}$ to LS - dis transition is thus clearly identified as corresponding, in slow-cooling regime (1 K/min), i.e., quasiadiabatic, to a transition from a $(a, c) R\bar{3}$ phase to a $(-2a, c) R\bar{3}$ phase. The unit cell volume is consequently quadrupled in the low-spin phase. Note that, in their initial work,¹⁷ the diffracting images obtained by Wiehl and co-workers already contained additional reflections on photographs but no deeper analysis was technically possible at that time and such feature seems not to have been taken into account later. The doubling of the unit-cell parameter a (and b) associated with the spin transition demonstrates an important characteristic of the $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ compound, since all previous hypotheses considered no volume change at the spin-crossover, when in fact the unit cell is quadrupled. Note that numerous samples, including ones more than 5 years old, were cooled and investigated to successfully check the reproducibility of the quadrupling of the unit cell.

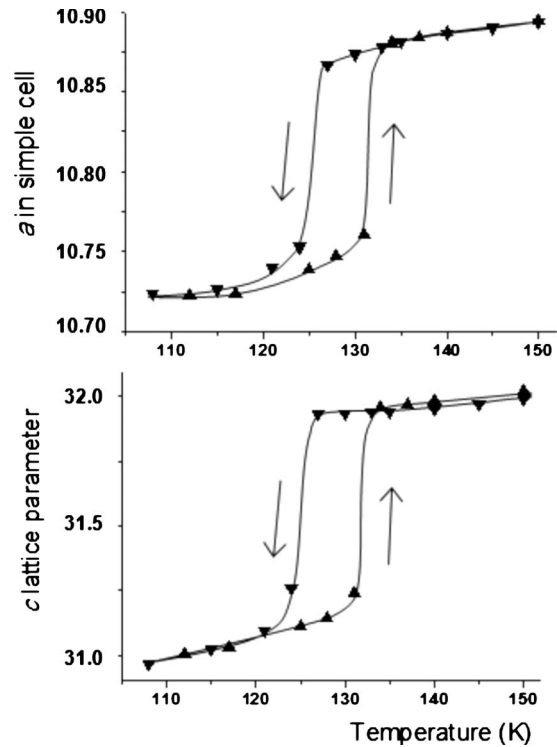


FIG. 2. Temperature dependence in the range (105–155 K) of the unit-cell parameters (\AA): (top) a represented in the simple lattice for comparison and (low) c . The structural transition temperatures and hysteresis match the spin-transition ones, 125 K when cooling and 132 K when warming. Drawn lines are guide for the eyes.

The temperature dependence of unit-cell parameters (Fig. 2) is represented in the simple (a, b, c) unit cell for comparison between HS and LS ranges. Temperatures of the structural phase transition [125(2) K when cooling and 132(2) K when warming] and hysteresis width (7 K) are in good agreement with magnetic and spectroscopic measurements on this compound. Considering the simple cell, in the abrupt domain of the transition, between 127 and 121 K, the a parameter decreases by 1.16% while the c parameter decreases by 2.63%. Consequently, despite the lattice being doubled in the a and in the b directions, large structural change is expected in the c direction within the crystal packing. Note that while the doubling of the a parameter induces a quadrupling of the unit-cell volume, the large decrease in the c parameter makes the volume being in fact slightly less than quadrupled in LS. Otherwise, if still considering the simple cell, the volume of the lattice decreases by 6.2% from fully HS (150 K) to fully LS (108 K) state. This value appears significantly higher than the usual unit-cell volume reduction observed as a consequence of the spin-crossover in Fe(II) molecular complexes (1–5%).¹⁶ Once again, large modifications are thus expected in the LS - dis crystal structure.

Besides the quadrupling of the unit cell, another feature observed is a splitting of Bragg peaks in the low-spin temperature range, such a feature being already known.⁷ The temperature dependence of the splitting confirms its concomitance with the HS to LS transition (Fig. 3). In addition, it is also reversible on a single crystal when warming back to

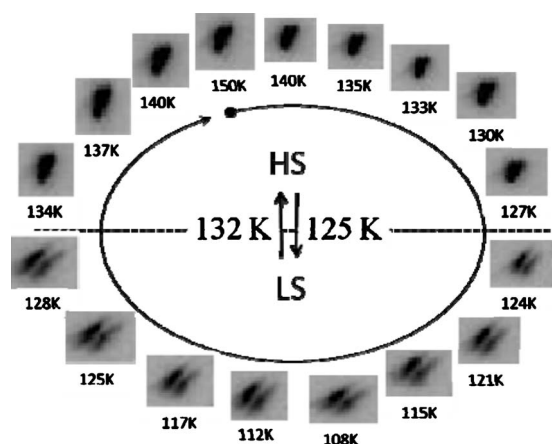


FIG. 3. Temperature dependence of the splitting of a Bragg peak showing the reversibility and the concomitance with the spin-transition features. The single crystal was cooled from 150 to 108 K then warmed back to 150 K.

HS. This feature is of importance since it proves the splitting does not correspond to physical cracking of the crystal. Co-existence of LS and HS phases would be possible since the splitting seems not to affect superstructure reflections but single crystal magnetic measurements show that residual HS phase cannot account for more than a few percent at 100 K.²³ Inspection of the diffraction images show that Bragg reflections are essentially split in the c^* direction.

The splitting of the reflections makes almost impossible a good quality crystal structure refinement of the *LS-dis* phase for $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$. However, based on the different features presented here, a preliminary crystal structure can be determined ($R=0.19$) and some comments can be made (Fig. 4), taking into account that such crystal structure represents an average one. Indeed, in an accurate description, a small structural disorder, responsible for the Bragg splitting, should arise. Since c^* is a privileged direction for such splitting, we assume the corresponding disorder affects layers perpendicular to such direction. One of the main consequences of the quadrupling of the unit cell is that the *LS-dis* asymmetric unit contains $2/3$ of one iron atom instead of $1/6$ in *HS-R $\bar{3}$* . The latter corresponds to one iron lying on the -3 axis. Meanwhile in *LS-dis*, the asymmetric unit contains one iron atom lying on a -3 axis ($1/6$ occupancy) and one iron atom lying on a center of inversion ($1/2$ occupancy). For both iron atoms, iron-nitrogen bond lengths clearly indicate a low-spin

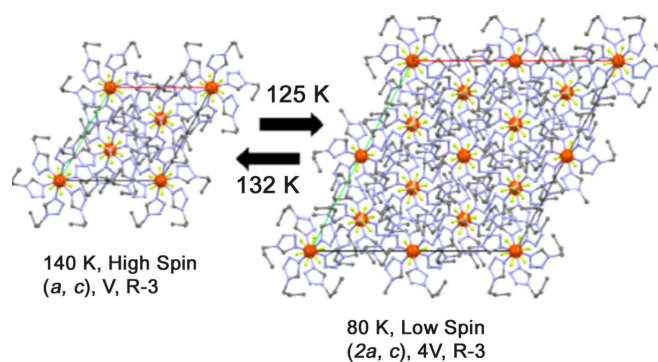


FIG. 4. (Color online) View of the crystal packing along c^* in *HS-R $\bar{3}$* (left) and *LS-dis* (right) showing the reversible quadrupling of the unit cell and the different iron symmetry sites (balls).

state at 80 K [$\langle\text{Fe-N}\rangle=1.97(1)$ Å and $1.99(1)$ Å, respectively]. The main general features of the crystal packing known in *HS-R $\bar{3}$* remain unchanged in *LS-dis*. No deeper analysis can be done due to the poor crystal structure refinement quality. However, it is worth noting that one of the main limitations in the atomic parameters refinement process arises from the terminal *n*-propyl group atoms, a fact that indicates a strong disorder of this part of the complex. As a consequence, one of the features of the structural phase transition that $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ undergoes at the *HS-R $\bar{3}$* to *LS-dis* transition concerns the *n*-propyl groups. Recent nuclear scattering experiments and density functional theory (DFT) calculations²⁴ have concluded that a deformation of the *n*-propyl groups should go together with the Fe-N stretching due to the spin transition. The present structural study tends to confirm this assumption.

To sum up, the single-crystal x-ray diffraction reinvestigation of $[\text{Fe}(\text{ptz})_6](\text{BF}_4)_2$ reveals a reversible quadrupling of the unit cell corresponding to the HS/LS transition in the slowly cooled mode. In addition, the reversibility of the Bragg-peak splitting on this material in single-crystal form clearly infirms that the split can be attributed to a macroscopic crack of the samples. Finally, a preliminary crystal structure solution for the *LS-dis* phase has been proposed, showing two different symmetry sites. These distinct features reveal a unique aspect of the spin-crossover phenomenon in this model material.

Acknowledgments are made to Ministère de la Recherche for S.L. grant and to S. A. Mason for English language corrections.

*Author to whom correspondence should be addressed; guio@icmcb-bordeaux.cnrs.fr

¹C. McCammon, I. Kantor, O. Narygina, J. Rouquette, U. Ponkratz, I. Sergueev, M. Mezouar, V. Prakapenka, and L. Dubrovinsky, *Nat. Geosci.* **1**, 684 (2008).

²M. F. Perutz, *Nature (London)* **228**, 726 (1970).

³J.-F. Létard, P. Guionneau, and L. Goux-Capes, *Top. Curr. Chem.* **235**, 221 (2004).

⁴*Spin Crossover in Transition Metal Compounds*, Topics in Current Chemistry Vol. 233, edited by P. Gülich and H. A. Goodwin (Springer-Verlag, Berlin, New York, 2004), p. 235.

⁵S. Decurtins, P. Gülich, M. L. Hasselbach, H. Spiering, and A. Hauser, *Inorg. Chem.* **24**, 2174 (1985).

⁶A. Hauser, *Chem. Phys. Lett.* **124**, 543 (1986).

⁷J. Kusz, P. Gutlich, and H. Spiering, *Top. Curr. Chem.* **234**, 129 (2004).

- ⁸A. Goujon, F. Varret, K. Boukheddaden, C. Chong, J. Jeftic, Y. Garcia, A. D. Naik, J. C. Ameline, and E. Collet, *Inorg. Chim. Acta* **361**, 4055 (2008).
- ⁹M. H. Lemée-Cailleau, C. Ecolivet, B. Ouladdiaf, F. Moussa, and J. F. Létard, *Physica B* **404**, 379 (2009).
- ¹⁰A. Goujon, B. Gillon, A. Gukasov, J. Jeftic, Q. Nau, E. Codjovi, and F. Varret, *Phys. Rev. B* **67**, 220401(R) (2003).
- ¹¹J. Jeftic, H. Romstedt, and A. Hauser, *J. Phys. Chem. Solids* **57**, 1743 (1996).
- ¹²N. O. Moussa, G. Molnar, X. Ducros, A. Zwick, T. Tayagaki, K. Tanaka, and A. Bousseksou, *Chem. Phys. Lett.* **402**, 503 (2005).
- ¹³C. Chong, H. Mishra, K. Boukheddaden, S. Denise, G. Bouchez, E. Collet, J. C. Ameline, A. D. Naik, Y. Garcia, and F. Varret, *J. Phys. Chem. B* **114**, 1975 (2010).
- ¹⁴L. Wiehl, *Acta Crystallogr., Sect. B: Struct. Sci.* **49**, 289 (1993).
- ¹⁵Y. Moritomo, K. Kato, A. Nakamoto, N. Kojima, E. Nishibori, M. Takata, and M. Sakata, *J. Phys. Soc. Jpn.* **71**, 1015 (2002).
- ¹⁶P. Guionneau, M. Marchivie, G. Bravic, J. F. Létard, and D. Chasseau, *Top. Curr. Chem.* **234**, 97 (2004).
- ¹⁷L. Wiehl, H. Spiering, P. Gülich, and K. Knorr, *J. Appl. Crystallogr.* **23**, 151 (1990).
- ¹⁸L. P. Franke, G. J. Haasnoot, and P. A. Zuur, *Inorg. Chim. Acta* **59**, 5 (1982).
- ¹⁹J. Kusz, H. Spiering, and P. Gülich, *J. Appl. Crystallogr.* **33**, 201 (2000).
- ²⁰Experimental data for the crystal structure at 140 K in the HS phase. A single crystal was mounted on a Bruker-Nonius k-CCD diffractometer Mo $K\alpha$ radiation (0.71073 Å) and cooled to 140 K. Data collection was run by means of ω and φ scans, 1° per rotation frame, 40 s per frame, and a crystal-detector distance of 40.0 mm. Results: space group $R\bar{3}$, $a=10.8804(2)$ Å, $c=31.9402(6)$ Å, $V=3274.6(1)$ Å³, 13 767 reflections measured, 2773 unique ($R_{int}=0.030$) for 128 refined parameters. Final R indices were $R[I>2\sigma(I)]=0.036$ and $R(\text{all data})=0.040$. Full details are given in Supplementary Information as CIF file. The final quality criterions are much better in the present case than in the earlier published data for the $HS-R\bar{3}$ phase. Consequently these new data are used for the discussion.
- ²¹Experimental data for the unit-cell parameter temperature dependence were obtained on the same sample and diffractometer as the 140 K data collection. Between each of the short data collections in the range (150–80 K) the sample was cooled at the rate of 1 K min⁻¹ then the temperature was unchanged during the data collection duration of two and a half hours. Short data collections were run by means of φ scans, 2° per rotation frame, 120 s per frame, and a distance crystal detector of 40.0 mm leading to 77 images per temperature.
- ²²Experimental data for the data collection at 80 K in the LS phase were obtained on the same sample and the same diffractometer. The sample was cooled to 80 K at the rate of 1 K min⁻¹, note that subsequent trials at slower cooling mode gave the same result. Data collection was run by means of ω and φ scans and a distance crystal detector of 40.0 mm. Results: space group $R\bar{3}$, $a=21.473(2)$ Å, $c=30.875(4)$ Å, $V=12329(2)$ Å³. Final R indices were $R[I>2\sigma(I)]=0.19$ and $R(\text{all data})=0.29$. The final crystal structure is of poor quality due to the Bragg peak splitting. If the rough crystal structure can be determined, it cannot be reliably refined in detail, this is notably the case for the tetrafluoroborate and the n -propyl groups (see text). Many attempts at lower temperature, on other samples and with different experimental setups gave the same results. However, further work is in progress.
- ²³See supplementary material at <http://link.aps.org/supplemental/10.1103/PhysRevB.82.132104> for magnetic measurements.
- ²⁴L. H. Böttger, A. I. Chumakov, C. M. Grunert, P. Gülich, J. Kusz, H. Paulsen, U. Ponkratz, V. Rusanov, A. X. Trautwein, and J. A. Wolny, *Chem. Phys. Lett.* **429**, 189 (2006).