Hydrostatic pressure investigation of the spin crossover compound [Fe(PM–BiA)2(NCS)2] polymorph I using reflectance detection

Aurelian Rotaru, Francois Varret, Epiphane Codjovi, Kamel Boukheddaden, Jorge Linares, Alexandru Stancu, Philippe Guionneau, Jean-François Letard

Hydrostatic pressure investigation of the spin crossover compound $[Fe(PM-BiA)_2(NCS)_2]$ polymorph I using reflectance detection

Aurelian Rotaru,[1,2,a)] François Varret,[1,a)] Epiphane Codjovi,[1] Kamel Boukheddaden,[1] Jorge Linares,[1] Alexandru Stancu,[2] Philippe Guionneau,[3] and Jean-François Létard[3]
[1]*"Groupe d'Etude de la Matière Condensée" (GEMaC), CNRS-UMR 8635, UVSQ, 78035 Versailles Cedex, France*
[2]*Department of Physics, Faculty of Physics, "Alexandru Ioan Cuza" University, Blvd. Carol I, nr 11, Iasi 700506, Romania*
[3]*Institut de Chimie de la Matière Condensée de Bordeaux, ICMCB, UPR 9048 CNRS, Université Bordeaux I, 87 Avenue Dr. A. Schweitzer, 33608 Pessac, France*

(Received 11 May 2009; accepted 11 July 2009; published online 9 September 2009)

We investigated by diffuse reflectivity the effect of hydrostatic pressure (1–1800 bar) on the thermal spin transition of $Fe(PM-BiA)_2(NCS)_2$ polymorph I, where PM=*N*-2-pyridylmethylene and BiA =4-aminobiphenyl. We evidenced the onset of a progressive transformation into a phase of higher cooperativity which cannot be assigned to polymorph II. This result is discussed with respect to previous pressure investigations. © *2009 American Institute of Physics*. [doi:10.1063/1.3202385]

I. INTRODUCTION

Some $3d^{4-7}$ transition metal compounds of octahedral symmetry undergo a thermally induced crossover between a low-spin (LS) and a high-spin (HS) state, with their spin state being governed by temperature, pressure, light, and magnetic field effects (Refs. 1–4, respectively).

Application of an external pressure provides an important insight into the nature of the interaction between a transition-metal center and the surrounding ligands as well as into intermolecular interactions.[2] To summarize, pressure favors the LS state due to its lesser volume and shifts upward the transition temperature according to the Clapeyron relation $dT/dp=\Delta V/\Delta S$. Pressure usually results in a decrease in the width of the thermal hysteresis loop, which is explained through the usual two-level models[5] within the assumption of a constant interaction parameter. However, in a recent work[6] we observed a slight increase in the interaction parameter, qualitatively explained by the shortening of the interatomic distances under pressure. Of course this simple description fails when pressure induces additional structural reorganizations, leading to pressure-induced structural transitions such as that previously reported on the title compound $Fe(PM-BiA)_2(NCS)_2$, where PM is *N*-2-pyridylmethylene and BiA is 4-aminobiphenyl.

It is also worth mentioning that pressure effects also impact the electronic spectra usually through minor but sizable modifications in the positions and intensities of the optical absorption bands.[7]

$[Fe(PM-BiA)_2(NCS)_2]$ crystallizes in two nonconcomitant polymorphs. Polymorph I (P1) has orthorhombic crystal structure and polymorph II (P2) has monoclinic.[8] Polymorph I (under study here) undergoes a hysteretic spin transition around ~170 K and polymorph II a progressive one around ~200 K.[8] The pressure-induced transformation of polymorph I was previously investigated by superconducting quantum interference device measurements in a clamped cell[9] and by neutron diffraction in a hydrostatic pressure cell at room temperature.[10]

We briefly discuss these previous results. On one hand, in the clamped cell,[9] a neat change was observed at around 7 kbar, which led to a new phase with a wider thermal hysteresis loop. Due to its higher cooperativity evidenced by a larger width of the thermal hysteresis loop, this new phase was not be assigned to polymorph II. We outline here the bent character reported for the hysteresis loops reported in Ref. 9 (see Ref. 11 for a general discussion of inhomoge-

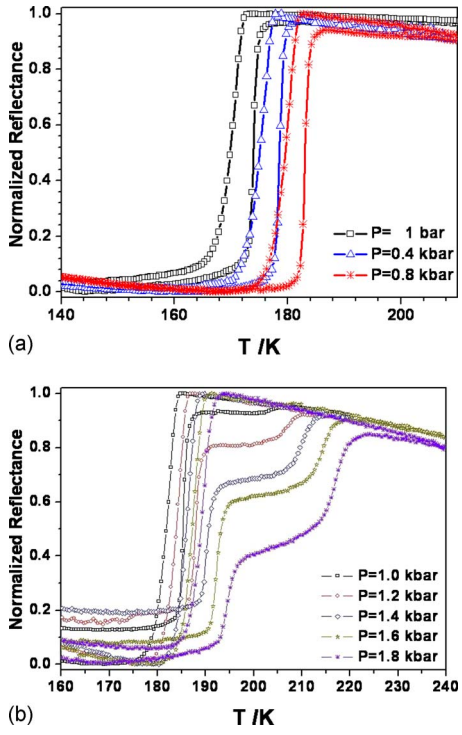

FIG. 1. (Color online) The spin transition of $Fe(PM-BiA)_2(NCS)_2$ polymorph I derived from reflectance data at different hydrostatic pressures.

[a)]Authors to whom correspondence should be addressed. Electronic addresses: aurelian.rotaru@gmail.com and varret_francois@yahoo.fr.

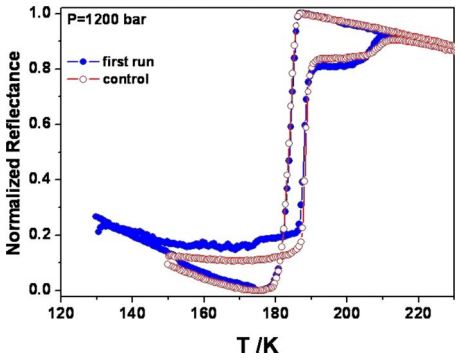

FIG. 2. (Color online) The reproducibility of the pressure effect: hysteresis loops recorded at 1200 bar during the first run of experiments (blue squares) and after release of the maximum pressure (red open circles).

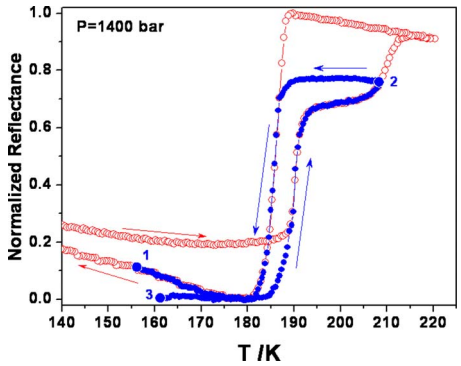

FIG. 3. (Color online) A minor hysteresis loop generated by temperature reversal at T_R=210 K on the heating branch (blue open circles) at 1400 bar compared to the major loop (red open circles) taken from Fig. 1(b).

neous effects on the thermal hysteresis loops). This bent character clearly indicates that pressure was not homogeneous and presumably nonhydrostatic due to the freezing of the transmitting medium. It is easily conceived that the anisotropic transformation of the compound embedded in an isotropic solid matrix may result in anisotropic stresses which add up to the external pressure. On the other hand, the neutron diffraction investigation at room temperature under hydrostatic pressure[10] revealed a structural change between 7 and 8 kbar, which was assigned to the transformation into polymorph II on the basis of an identical space group. We report here on a diffuse reflectance investigation using the hydrostatic pressure device (1–1800 bar) developed at the Versailles University,[12] which clears up the question by showing a pressure-induced phase which differs from polymorph II, and consequently is labeled here polymorph III.

II. EXPERIMENTAL

The sample (polymorph I) was synthesized using a preparation mode described in Ref. 13 and exhibited the reported thermochromism suitable for optical detection. The hydrostatic pressure device (transmitting medium is He gas) with diffuse reflectance detection was already described in Ref. 12. The powder samples have been thermally cycled at least ten times between the liquid nitrogen and room temperature before starting the measurements. The repeated application of such thermal shocks led to automilling of the sample into smaller crystals, which is thought to release internal stresses due to grain boundaries and definitely improves the reproducibility of the hysteresis loop. The light source was a 100 W QTH (quartz tungsten halogen) lamp with a (900 ± 50) nm interferential filter located ahead of the optical fibers which carry light to the pressure cell.

III. RESULTS AND DISCUSSION

We recorded the thermal hysteresis loops at increasing pressure values (from 1 to 1800 bars by 200 bar steps), see Fig. 1. Temperature was scanned every 0.5 K in the heating and cooling modes, successively. We checked that the initial hysteresis loop at 1 bar was obtained again after releasing the maximum pressure and also controlled that the pressure effect was reproducible, see Fig. 2.

We also recorded a minor hysteresis loop generated by a single reversal curve on the heating branch, see Fig. 3. This "reversal curve" clearly showed that the pressure-induced phase, which will be called in the following polymorph III (P3), is also hysteretic over a temperature interval much wider than that of the initial phase.

Quantitative data derived from the present experiments are listed in Table I. They lead to the following statements: (i) the critical temperatures obtained here are in good agreement with Ref. 9; (ii) at low pressures (below 900 bars) the hysteresis loop is shifted toward higher temperatures with $dT/dP \sim 25$ K/kbar and little change in the hysteresis width; (iii) upon further pressure increase, the heating branch displays a double-step character which reveals the progres-

TABLE I. Transition temperature values and relative phase fractions assigned to the thermal hysteresis loops of Fig. 1 derived from the location of the inflection points. The temperatures that maximize dn_{HS}/dT are associated with the separate transition temperatures of the phases. The n_{HS} value associated with the minimum dn_{HS}/dT value on the heating branch approximately corresponds to the relative fraction of polymorph I at the given pressure.

P (bar)	T_{down} (K)	T_{up} P1 (K)	ΔT P1 (K)	T_{up} P3 (K)	ΔT P3 (K)	Fractions P1:P3 (%)
1	170.6	174.1	3.5	⋯	⋯	100:00
1000	182.5	185.6	3.1	204	21.5	93:07
1200	184.6	188.2	3.6	207	22.4	81:19
1400	186.8	190.2	3.4	210	23.2	69:31
1600	187.8	192.1	4.3	214.2	26.4	62:38
1800	189.8	194.6	4.8	217.1	27.3	44:56

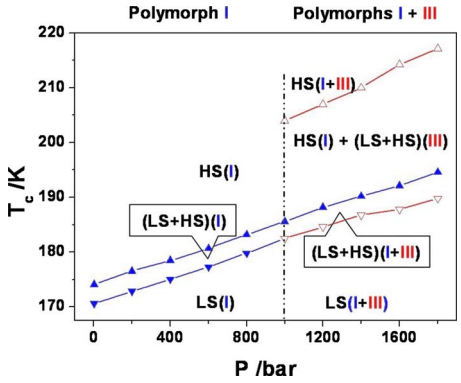

FIG. 4. (Color online) The temperature-pressure spin fraction phase diagram. The HS-to-LS branches of polymorphs I and III (full and open triangles, respectively) are not experimentally resolved.

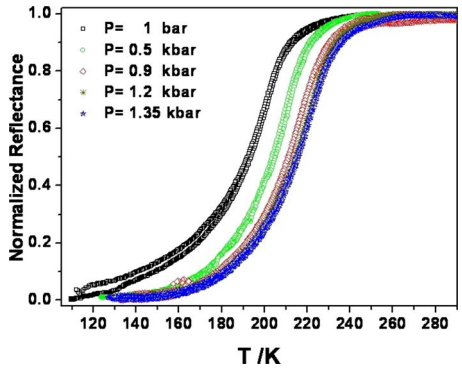

FIG. 6. (Color online) The spin transition of $Fe(PM-BiA)_2(NCS)_2$ polymorph II derived from reflectance data at different hydrostatic pressures.

sive onset of the pressure-induced phase; and with a hysteresis width in agreement with the previous work,[9] (iv) on the contrary, the cooling branch keeps a one-step character with remarkably steep variation. The spin state diagram derived from these data is shown in Fig. 4 and the pressure dependence of the structural fractions (derived from inflection point positions as explained in the caption of Table I) is reported in Fig. 5. These data rule out the assignment of the pressure-induced phase to polymorph II. This conclusion will be supported by a pressure investigation of polymorph II under pressure reported in Sec. IV.

The linear variation in the high temperature branch above the hysteretic range (see Fig. 1) is not assigned to the change in spin populations but to the effect of temperature upon the optical properties of the sample. A possible account of this effect based on the pragmatic approximations would not significantly impact the numbers given in Table I and the subsequent discussion.

A. Polymorph II behavior under an external pressure

We also performed reflectance measurements on polymorph II. The thermal behavior of polymorph II at different pressures is presented in Fig. 6. As expected, increasing pressure shifts the equilibrium temperature toward higher temperatures but does not sizably change the shape of the thermal variation in the HS fraction without any tendency toward opening of the hysteresis loop up to 1350 bars. The latter value was limited due to an instrumental problem (leakage).

In Fig. 7 we directly compare the properties of polymorphs I and II at the same pressure. No doubt the present pressure-induced phase cannot be assigned to polymorph II.

IV. DISCUSSION

The present results quantitatively disagree with the previous pressure investigation using a clamped cell,[9] since the latter did not report any sizeable variation in the hysteresis width below 7 kbar. Among possible explanations for such a discrepancy, we mainly question the hydrostatic character of the clamped cell due to the freezing of the transmitting medium, as already noted in Sec. I. We also briefly comment on the result of the neutron diffraction study,[10] which assigned the room temperature pressure-induced phase to polymorph II. The hydrostatic character of pressure cannot be questioned, and if we rely on the quoted assignment, we are left with the assumption that the surface behavior—probed by diffuse reflectance—may sizably differ from that of the bulk. One indeed may conceive that the stress tensor involved in solid-state transformations differs from bulk to surface. Differences may also originate from the thermal history of the samples along the experiments since the neutron diffraction experiment has only been run at room temperature while numerous thermal variations were applied in the present experiment. In addition the pressure transformation from polymorph I to polymorph II reported in Ref. 10 was observed at a much higher pressure (6–7 kbar) than the pressure range reached in the present experiment.

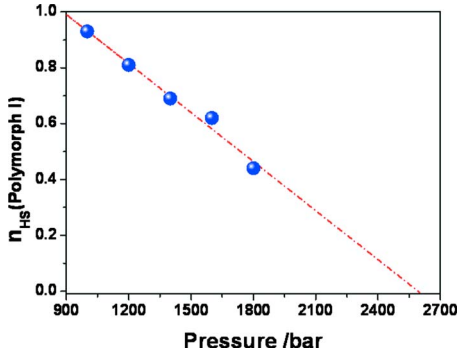

FIG. 5. (Color online) The pressure dependence of the structural phase fraction of polymorph I.

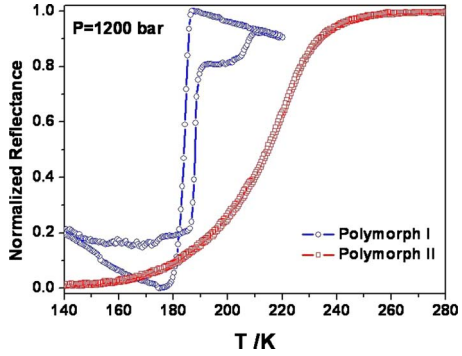

FIG. 7. (Color online) Thermal variation in the HS fraction of polymorphs I and II recorded at 1.2 kbar.

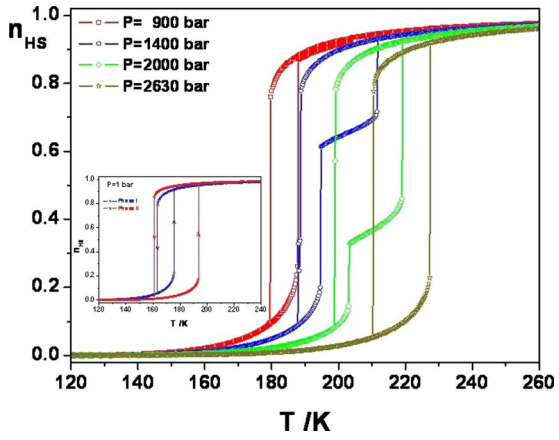

FIG. 8. (Color online) Simulated behavior assuming both hysteretic phases using Ising-like model.

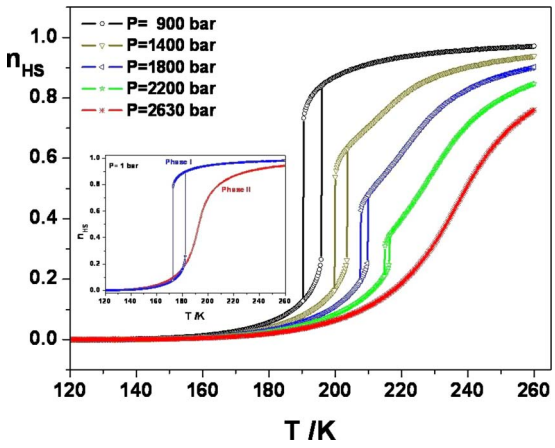

FIG. 9. (Color online) Simulated behavior of two independent phases in the assumption of a noncooperative pressure-induced phase.

A detailed analysis of the present data might also throw some light on the mechanism of the pressure-induced transition. A striking feature of the present investigation is that the HS→LS transitions of the two structural phases cannot be distinguished. Of course, this may be pure coincidence. However, we showed by suited simulations that an elastic coupling between the two phases may result in the collapse of the spin-transition temperatures when they are close to each other. This coupling also contributes to the variations in the spin transition temperatures, which then depend on the structural phase fractions, and might be responsible for the significant pressure dependence of the hysteresis width of polymorph III. The said model will be presented in a further work including designed experiments.

At last, we merely show that a simple biphasic model based on independent phases provides a qualitative simulation of the experimental data, see Fig. 8. We used here the simple two-level Hamiltonian Ising-like treated in mean-field approximation.[5] The molecular energy gap was written $\Delta_i = \Delta_i(P=0) - k_B T \ln g_i + P\Delta V_i$, with J_i as the effective interaction parameter and ΔV_i as the molecular volume increase upon complete spin crossover. The effective degeneracy factor $\ln g$ was derived from calorimetric data on polymorph I (Ref. 14) and assumed to have the same value in polymorph III. The parameter values which reproduce at best the spin-state diagram are $J_1=230$ K, $J_2=300$ K, $\ln g_1=7.09$, $\ln g_2=7.09$, $\Delta_1(P=0)=1208$ K, $\Delta_2(P=0)=1282$ K, $\Delta V_1=10.94$ Å^3, and $\Delta V_2=10.65$ Å^3. For comparison we show in Fig. 9 hysteresis loops computed in the assumption of a noncooperative pressure-induced phase (that is to say, assumed to be polymorph II).

V. CONCLUSION

We showed that under the effect of a moderate hydrostatic pressure (~1–2 kbar), $Fe(PM-BiA)_2(NCS)_2$ polymorph I progressively transforms into a structural phase which exhibits a wider hysteresis loop and for this reason has to be assigned to an new structural phase, here denoted as polymorph III. We have some cues that the spin transition and the structural transformation are coupled to each other, but further experiments are needed for documenting this point.

We found a quantitative disagreement with the data reported in the previous investigation by Ksenofontov *et al.*,[9] which we assigned to the nonhydrostatic character of pressure in the said investigation. In contrast, the use of helium as pressure transmitting medium ensured a highly homogeneous and isotropic pressure in the present work. Our conclusion concerning the nature of the pressure-induced phase that differs proved that it cannot be assigned to polymorph II contrary to what have been extrapolated from previous room temperature neutron diffraction.[10] However, the possibility of a specific surface behavior in the present study cannot be excluded. A variable temperature diffraction investigation under high pressure should be done to throw light on this open possibility.

ACKNOWLEDGMENTS

The financial supports of CNRS, Bordeaux and Versailles Universities, Région Aquitaine and Région Ile de France, European network of excellence MAGMANet, Romanian government for contract CNCSIS-IDEI 1994 FASTSWITCH, and Agence Universitaire de la Francophonie (AUF) are acknowledged. P.G. thanks ANR for granting project ANR-08-JCJC-0049-01.

[1] *Spin Crossover in Transition Metal Compounds*, Topics in Current Chemistry, edited by P. Gütlich and H. A. Goodwin (Springer-Verlag, Berlin, 2004), Vol. 233–235.
[2] E. Koenig, G. Ritter, S. K. Kulshreshtha, J. Waigel, and H. A. Goodwin, Inorg. Chem. **23**, 1896 (1984); E. Koenig, G. Ritter, H. Gruensteudel, J. Dengler, and J. Nelson, *ibid.* **33**, 837 (1994); J. Jeftic, H. Romstedt, and A. Hauser, J. Phys. Chem. Solids **57**, 1743 (1996); E. Codjovi, N. Menendez, J. Jeftic, and F. Varret, C.R. Acad. Sci., Ser. IIc: Chim **4**, 181 (2001); A. Bousseksou, G. Molnar, J. P. Tuchagues, N. Menendez, E. Codjovi, and F. Varret, *ibid.* **6**, 329 (2003); P. Gütlich, A. B. Gaspar, V. Ksenofontov, and Y. Garcia, J. Phys.: Condens. Matter **16**, S1087 (2004).
[3] S. Decurtins, P. Gütlich, C. P. Köhler, H. Spiering, and A. Hauser, Chem. Phys. Lett. **105**, 1 (1984).
[4] A. Bousseksou, N. Negre, M. Goiran, L. Salmon, J.-P. Tuchagues, M.-L. Boillot, K. Boukheddaden, and F. Varret, Eur. Phys. J. B **13**, 451 (2000).
[5] C. P. Slichter and H. G. Drickamer, J. Chem. Phys. **56**, 2142 (1972); J. Wajnflasz and R. Pick, J. Phys. Colloq. **32**, C1 (1971); A. Bousseksou, J. Nasser, J. Linares, K. Boukheddaden, and F. Varret, J. Phys. I **2**, 1391

(1992); F. Varret, S. A. Salunke, K. Boukheddaden, A. Bousseksou, E. Codjovi, C. Enachescu, and J. Linares, C. R. Chim. **6**, 385 (2003).
[6]A. Rotaru, Thesis, University of Versailles et Saint Quentin-en-Yvelines, 2009.
[7]J. Jeftic and A. Hauser, Chem. Phys. Lett. **248**, 458 (1996).
[8]M. Marchivie, P. Guionneau, J. F. Létard, and D. Chasseau, Acta Crystallogr., Sect. B: Struct. Sci. **59**, 479 (2003); J.-F. Létard, G. Chastanet, O. Nguyen, S. Marcen, M. Marchivie, P. Guionneau, D. Chasseau, and P. Gütlich, Monatsch. Chem. **134**, 165 (2003).
[9]V. Ksenofontov, G. Levchenko, H. Spiering, P. Gütlich, J.-F. Létard, Y. Bouhedja, and O. Kahn, Chem. Phys. Lett. **294**, 545 (1998).
[10]V. Legrand, F. Le Gac, P. Guionneau, and J.-F. Létard, J. Appl. Crystallogr. **47**, 637 (2008).
[11]V. Mishra, R. Mukherjee, J. Linares, C. Baldé, C. Deplanches, J. F. Létard, E. Collet, L. Toupet, M. Castro, and F. Varret, Inorg. Chem. **47**, 7577 (2008); H. Mishra, V. Mishra, F. Varret, R. Mukherjee, C. Baldé, C. Deplanches, and J. F. Létard, Polyhedron **28**, 1678 (2009).
[12]J. Jeftic, N. Menendez, A. Wack, E. Codjovi, J. Linares, A. Goujon, G. Hamel, S. Klotz, G. Syfosse, and F. Varret, Meas. Sci. Technol. **10**, 1059 (1999); J. Jeftic, U. Kindler, H. Spiering, and A. Hauser, *ibid.* **8**, 479 (1997); R. Tanasa, A. Stancu, J. F. Létard, E. Codjovi, J. Linares, and F. Varret, Chem. Phys. Lett. **443**, 435 (2007).
[13]J. F. Létard, P. Guionneau, L. Rabardel, J. A. K. Howard, A. E. Goeta, D. Chasseau, and O. Kahn, Inorg. Chem. **37**, 4432 (1998).
[14]J. A. Rodriguez-Velamazan, M. Castro, E. Palacios, R. Burriel, J. Sanchez Costa, and J. F. Létard, Chem. Phys. Lett. **435**, 358 (2007).