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Two-step spin-crossover phenomenon under high pressure in the coordination polymer $\text{Fe}(\text{3-methylpyridine})_2[\text{Ni}(\text{CN})_4]$

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The temperature dependence of the magnetic susceptibility and Mössbauer spectra of the compounds $\text{FeL}_2[\text{Ni}(\text{CN})_4]$ ($L = 2, 3$ or 4-methylpyridine) have been investigated. In each case the iron(II) ions are high spin at room temperature, but in the 3-methylpyridine compound about half of the iron ions becomes diamagnetic around 90 K. The application of external pressure allowed to uncover the underlying two-step nature of this spin transition. For further increase of the pressure the plateau between the two steps disappeared. Both observations were successfully interpreted in the framework of an Ising-like model with two iron sites displaying different volume changes.

1. Introduction

Spin-crossover complexes of transition metal ions have attracted much attention from the fundamental point of view [1,2]. Some of these complexes exhibit a first-order spin transition accompanied by a large thermal hysteresis loop making them appealing also for potential applications in molecular display, memory and switching devices [3,4]. This cooperative phenomenon appears in these materials primarily due to long-range elastic interactions between the molecules, whose volume changes considerably with their spin-state [5]. To date, numerous spin-crossover materials displaying first-order transition have been obtained by different chemical synthetic techniques. One of the most successful strategy to obtain strongly cooperative systems with hysteresis loops around room temperature is the introduction of the spin crossover ions in coordination poly-

meric networks, in which the strong bonding forces may enhance the interactions between the active centres [6,7].

In this context, a number of two- and three-dimensional coordination polymers, the so-called Hofmann-type chlorates, have been synthesised using various metal ions and ligands [8–11]. Some of these complexes revealed remarkable thermal, piezo and photo-induced spin-crossover phenomena even at room temperature [12–17]. In our quest to explore the spin-crossover behaviour of this family of complexes we report here on the magnetic properties of the two-dimensional polymer compounds $\text{Fe}^{\text{II}}\text{L}_2\text{-}[\text{Ni}(\text{CN})_4]$ (L stands for 2-methylpyridine (**2**) or 3-methylpyridine (**3**) or 4-methylpyridine (**4**)), which were synthesised according to Ref. [10]. While compounds **2** and **4** were found to remain in the high-spin (HS) state between 2 K and 300 K at atmospheric pressure, the complex **3** displays an intriguing half-transition leading to a ca. 50% mixture of high-spin and low-spin (LS) states. The application of hydrostatic pressure on this compound revealed a hidden two-step transition and several unexpected pressure effects.

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2. Experimental

The variable-temperature magnetic susceptibility measurements were carried out using a Quantum Design MPMS2 SQUID magnetometer operating at 1 T magnetic field. The independence of the susceptibility with regard to the applied magnetic field was checked at room temperature for each compound. Experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants. Magnetic susceptibility measurements at high pressures have been carried out in 2 T magnetic field using a clamp-type, hardened beryllium bronze (CuBe) cell. Hydrostatic conditions are obtained by mixing the powder samples (ca. 15 mg) with a pressure transmitting mineral oil (Alcatel-100). The pressure inside the cell was determined from the pressure shift of the superconducting transition of a 99.99% purity Pb wire (Goodfellow) measured at a cooling rate of 0.005 K min^{-1} with a zero-field AC current of 2.2 Hz frequency and 3 Oe amplitude. Using the calibration curve of Bireckoven and Wittig [18] pressure can be calculated with an accuracy of $\pm 0.015 \text{ GPa}$. The hydrostatic conditions at high pressures and low temperatures were maintained as inferred from the abruptness of the lead superconducting transition. The temperature cycles were carried out at a rate of 1 K min^{-1} the pressure clamped at a fixed value at room temperature. The thermal variation of the clamped pressure was determined by four-wire measurements using a manganin gauge [19]. The pressure loss (ca. 0.15 GPa) between 295 K and 7 K was found comparable with that of the widely used Daphne-7373 oil [20]. The contribution from the pressure cell to the total susceptibility was subtracted out by carrying out dummy runs.

The variable temperature ^{57}Fe Mössbauer measurements were carried out by means of a constant-acceleration spectrometer with a 50 mCi $^{57}\text{Co}(\text{Rh})$ source on ca. 60 mg powder sample enclosed in a 12 mm diameter cylindrical plastic sample holder. Spectra were obtained at 5 K and 293 K for each compound. Additional spectra at intermediate temperatures have been recorded for sample 3 using a custom-designed, liquid helium flow-type cryostat. Cooling and heating rates were fixed at 1 K min^{-1} . A least-squares computer program was used to fit the Mössbauer parameters and to determine the standard deviations of statistical origin (given in parentheses) [21]. The isomer shift values are given with respect to metallic iron at room temperature.

3. Experimental results

The magnetic properties of the three samples have been measured at atmospheric pressure between 2 and 300 K (Fig. 1). At 300 K the $\chi_m T$ product, χ_m being the molar magnetic susceptibility, has a value of 3.71, 3.78 and $3.49 \text{ cm}^3 \text{ K mol}^{-1}$ for 2, 3 and 4, respectively, which corresponds to the high spin (HS) state of the Fe^{II} ions with $S=2$. The somewhat different $\chi_m T$ value determined for 4 might be due to a small impurity content. As the tempera-

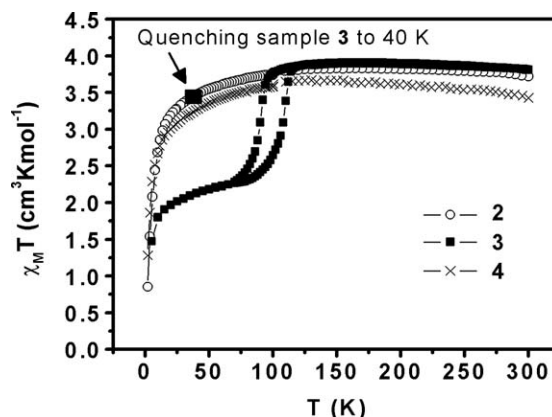


Fig. 1. Thermal variation of $\chi_m T$ for compounds 2, 3 and 4 at atmospheric pressure.

ture is lowered, the magnetic moment of 2 and 4 remains virtually constant, except at very low temperatures where the $\chi_m T$ product decreases strongly with decreasing T due to the zero-field splitting phenomenon. The HS state of the Fe^{II} ions in these complexes is confirmed also by the Mössbauer spectra recorded at 5 K and 293 K (Table 1). On the contrary, the $\chi_m T$ product in sample 3 drops considerably when the temperature is lowered below ca. 100 K and reaches a value of $2.30 \text{ cm}^3 \text{ K mol}^{-1}$ at 70 K indicating the formation of a mixture of HS and low spin (LS) states. Although the $\chi_m T$ product continues to decrease somewhat at lower temperatures, this can be attributed only to zero-field splitting effects (vide infra). The spin-crossover occurs with a large hysteresis since the pure HS state is restored only above ca. 120 K upon heating. ^{57}Fe Mössbauer spectra correspond well to the magnetic data. At room temperature the Mössbauer spectrum consists in a single doublet with quadrupole splitting (1.080 mm s^{-1}) and isomer shift (1.030 mm s^{-1}) values typical of Fe^{II} ions in the HS state. At 80 K a new absorption line appears with lower quadrupole splitting (0.18) and isomer shift (0.494 mm s^{-1}) values as expected for a LS state ($S=0$) of Fe^{II} ions. The HS fraction (n_{HS}) obtained from the Mössbauer area ratio is 58% at 80 K and remains constant (within the measurement error) down to 5 K (57%) proving thus that the decrease of the magnetic moment at low temperatures is indeed due to the zero-field splitting effects.

In order to try to convert the low-temperature residual HS fraction into the LS state external pressure was applied on sample 3. Fig. 2 shows the $\chi_m T$ product as a function of T in the cooling and heating modes at different applied pressures. At 0.18 GPa the transition shifts to higher temperature, the hysteresis width decreases and the shape of the transition curve starts to develop towards a two-step transition since a small second loop appears as well. This two-step transition appears clearly under 0.3 GPa pressure with the two steps centred around 130 and 210 K and separated by a plateau of ca. 20 K. The transition at this pressure extends over a large temperature range (when compared to atmospheric pressure), but one can still observe two hysteresis

Table 1

Least-squares fitted Mössbauer data for compounds **2**, **3** and **4** at different temperatures in the cooling and heating (in *italic*) modes

T (K)	Sample	Spin	δ (mm s ⁻¹)	ΔE_q (mm s ⁻¹)	Γ (mm s ⁻¹)	A_{HS}/A_{tot}
5	2	2	1.238(1)	2.138(3)	0.201(2)	1.0
293		2	1.110(1)	1.486(2)	0.184(1)	1.0
5	4	2	1.195(1)	1.164(3)	0.256(2)	1.0
293		2	1.064(2)	0.579(3)	0.157(2)	1.0
5		2	1.208(1)	1.595(2)	0.166(2)	0.57(1)
		0	0.490(6)	0.19(1)	0.162(4)	0.43(1)
25		2	1.206(2)	1.495(3)	0.182(2)	0.55(1)
		0	0.501(6)	0.20(1)	0.150(6)	0.45(1)
50	2	1.204(2)	1.500(4)	0.165(2)	0.57(1)	
	0	0.50(1)	0.17(2)	0.19(1)	0.43(1)	
80	3	2	1.199(5)	1.493(9)	0.180(4)	0.58(1)
		0	0.494(8)	0.18(1)	0.147(6)	0.42(1)
100	2	1.188(1)	1.536(2)	0.171(2)	1.0	
150	2	1.165(1)	1.445(2)	0.168(2)	1.0	
293	2	1.080(1)	1.030(1)	0.158(1)	1.0	
100	2	<i>1.196(3)</i>	<i>1.486(6)</i>	<i>0.177(3)</i>	<i>0.68(1)</i>	
	0	<i>0.484(7)</i>	<i>0.18(1)</i>	<i>0.159(6)</i>	<i>0.32(1)</i>	

δ : isomer shift (with reference to metallic iron at 293 K), ΔE_q : quadrupole splitting, Γ : half-height width, A_{HS} : area of HS doublet, A_{tot} : total Mössbauer spectrum area. The error bars of statistical origin are given in parentheses.

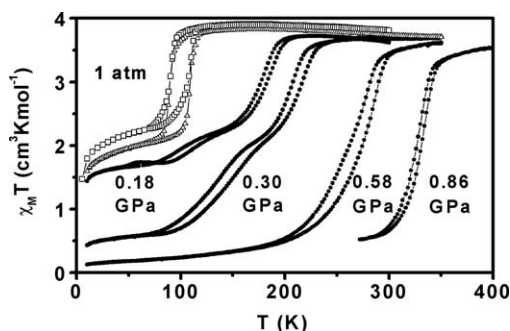


Fig. 2. Thermal variation of $\chi_m T$ for compound **3** at different pressures (closed circles). Open triangles (squares) correspond to the measurement before (after) compression at atmospheric pressure.

loops. At low temperatures a nearly complete transition is obtained as inferred from the $\chi_m T$ values and the absence of zero-field splitting effects at low temperatures. As the pressure increases to 0.58 GPa the transition becomes steeper, the hysteresis width increases and the plateau between the two steps decreases. Finally at 0.86 GPa the sample displays a relatively abrupt, one-step spin transition with a small hysteresis loop (4 K). When the pressure is released the sample shows a similar magnetic behaviour than before compression proving therefore that the effects of 0.86 GPa pressure are still reversible. (It is to be noted that while the transition temperatures are the same before and after compression, the $\chi_m T$ values are somewhat different, but this difference is not far from the experimental uncertainty induced by the pressure cell.)

4. Theoretical approach and discussion

Thermal spin-crossover phenomena are known to occur gradually over a large range of temperature (10–100 K) or

abruptly with or without a hysteresis loop. In a few complexes the temperature dependence of the high-spin fraction displays an interesting two-step behaviour [22–25]. This staging phenomenon has received much attention from the theoretical point of view [26–29]. Two-step curves can be obtained trivially by considering two crystallographically different metal ions, but two-step behaviour can also be predicted for structurally equivalent sublattices [26] or binuclear molecules [28] if the model combines negative and positive interactions (long and short range, respectively).

Examples for half transitions have also been reported in the literature [1,2]. At low temperatures it is generally thought to occur due to the slow kinetics. Indeed, below ca. 50–70 K the spin conversion rate for many iron(II) complexes becomes very slow and the system can be maintained in a metastable HS state during several days [30]. In order to verify this hypothesis we have quenched the sample **3** from room temperature to 40 K in the magnetometer. The magnetic susceptibility of this quenched sample at 40 K equals that of sample **2** (Fig. 1), i.e., the system remains in the HS state. It appears therefore that the incomplete nature of the transition in sample **3** has most likely a kinetic origin. Only the application of external pressure can reveal the underlying two-step character of such an incomplete transition, since under pressure the LS state with smaller volume is stabilised and therefore the spin transition is shifted to higher temperatures where the conversion rates are faster. The Mainz team reported a few examples for this kind of experiments, but it is usually difficult to discuss the evolution of the two steps due to the gradual nature of the transition [31–33]. Our case is different because the interactions in the polymeric system are sufficiently strong and we can clearly observe under pressure the appearance of a large plateau dividing the two stages of the transition and we can even observe two hysteresis loops.

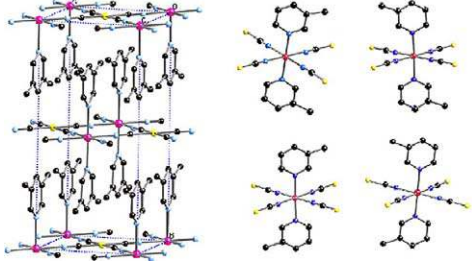


Fig. 3. Structure and possible location disorder of methyl groups in compound **3**.

Unfortunately, we were unable to grow single crystals of **3** with sufficient quality so as to determine the X-ray structure below the transition temperature. We were also unable to observe the transition by Raman spectroscopy, because the exciting laser light induces LIESST effect below 90 K. Therefore we cannot establish unambiguously the structural origin of the two-step transition. Though Mössbauer spectroscopy could not resolve the presence of different lattice sites, it seems reasonable to assume that at least two different iron(II) atoms exist in the polymer structure of **3** (Fig. 3) in the same way as in the isostructural $\text{Fe}(\text{3-chloropyridine})_2\text{Ni}(\text{CN})_4$ complex [9]. Therefore, we assign tentatively the two-step transition in **3** to crystallographically inequivalent iron sites and we propose to analyse the experimental observations by means of an Ising-like model adapted for the case of two different iron sites [26].

In this model, pressure effects can be included as follows. The two-level Hamiltonian for different iron sites, including cooperativity, is given as:

$$\hat{H} = \sum_i \frac{1}{2} \Delta_i \hat{\sigma}_i + \sum_{(i,j)} J_{ij} \hat{\sigma}_i \cdot \hat{\sigma}_j \quad (1)$$

with the energy gap $\Delta_i = E_{i,\text{HS}} - E_{i,\text{LS}}$ of a iron site i , $\hat{\sigma}_i$ a fictitious spin operator taking as eigenvalues -1 (LS) and $+1$ (HS), J_{ij} the interaction parameter. In our case, two iron sites A and B are considered and the total HS fraction is obtained in the mean-field approach as:

$$n_{\text{HS}} = \frac{1}{2} + \frac{1}{4} (\langle \hat{\sigma}_A \rangle + \langle \hat{\sigma}_B \rangle) \quad (2)$$

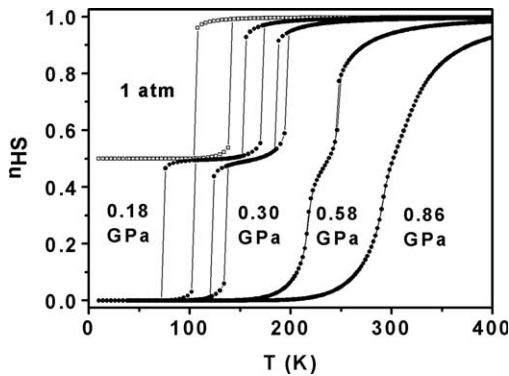


Fig. 4. Thermal variation of the high-spin fraction at different pressures computed using Eqs. (2)–(4) with $\delta V_A = 32 \text{ \AA}^3$, $\delta V_B = 22 \text{ \AA}^3$, $\Delta_{0A} = 1072 \text{ K}$, $\Delta_{0B} = 1370 \text{ K}$, $J_A = -194 \text{ K}$, $J_B = -248 \text{ K}$, $J_{AB} = 40 \text{ K}$ and $\ln(r_A) = \ln(r_B) = 7.6$.

The deduced mean-field equations are:

$$\begin{aligned} \langle \hat{\sigma}_A \rangle &= \frac{-1 + r_A e^{-\beta(\Delta_A + 2J_A \langle \hat{\sigma}_A \rangle + 2J_{AB} \langle \hat{\sigma}_B \rangle)}}{1 + r_A e^{-\beta(\Delta_A + 2J_A \langle \hat{\sigma}_A \rangle + 2J_{AB} \langle \hat{\sigma}_B \rangle)}} \\ \langle \hat{\sigma}_B \rangle &= \frac{-1 + r_B e^{-\beta(\Delta_B + 2J_B \langle \hat{\sigma}_B \rangle + 2J_{AB} \langle \hat{\sigma}_A \rangle)}}{1 + r_B e^{-\beta(\Delta_B + 2J_B \langle \hat{\sigma}_B \rangle + 2J_{AB} \langle \hat{\sigma}_A \rangle)}} \end{aligned} \quad (3)$$

with the ratio $r = g_{\text{HS}}/g_{\text{LS}}$ of the degeneracies of each spin state and $\beta = (kT)^{-1}$. J_A , J_B and J_{AB} stand for the intra- and inter-sublattice interaction parameters, respectively.

In a first approximation, no pressure dependencies of J and g will be considered. The effect of pressure can be included by replacing the term of the energy gap $\Delta_i = E_{i,\text{HS}} - E_{i,\text{LS}}$ in (3) for each iron site by:

$$\Delta_i = \Delta_{0i} + P \delta V_i \quad (i = A, B) \quad (4)$$

with Δ_{0i} the energy gap of each iron site at atmospheric pressure and δV_i the volume change of an iron site.

Fig. 4 shows the variation of the HS fraction as a function of temperature for different values of external pressure computed using Eqs. (2)–(4). It should be noted that the parameter values have been chosen in order to try to simulate the overall experimental observations, but curve fitting has not been carried out because the mean-field approximation is known to be inaccurate to reproduce hysteresis loops. Furthermore, the experimentally determined $\chi_m T$ values are difficult to convert accurately into n_{HS} values without Mössbauer spectroscopic calibration of the residual spin fractions under pressure. At 0 GPa the model predicts a half-transition because the second step is blocked at absolute zero temperature (i.e., the transition temperature ($T_{1/2}^A$) is below 0). When increasing the pressure, as expected, the transition curves are shifted towards higher temperatures due to the increase of the energy gap Δ_i by the work term $P \delta V_i$. As a result a second spin-crossover step appears at 0.18 GPa and the partial transition becomes complete with two steps. (Of course, by assuming a blocking temperature of ca. 70 K the second step would not yet appear at this pressure, but only at 0.3 GPa).

In order to simulate the experimental observations where the transition temperature for the site A shifts more than for the site B (ca. 340 K/GPa vs. 230 K/GPa) we have introduced into the model different δV values for the two iron sites. This condition allows a more important pressure effect for the first iron site and with the parameters $\delta V_A = 32 \text{ \AA}^3$ and $\delta V_B = 22 \text{ \AA}^3$ the experimental shifts of the two transition temperatures can be closely reproduced. It should be noted that these theoretically predicted values are close to the range obtained from crystallographic data for spin-crossover complexes with $\text{Fe}^{\text{II}}\text{N}_6$ core [1]. Furthermore, the introduction of different values for δV_A and δV_B allows us to reproduce a second important experimental observation, which is the disappearance of the plateau between the two steps on further compression. In fact, if the volume changes are similar for the two iron sites, the theory predicts no change for the separation of the two transition stages even if the gradual character of the curves may actually hide the plateau. The introduction of the different volume

changes has another interesting consequence. Theoretically at very high pressures the two-step transition should reappear, but this time it is the site B that transits before (i.e., at lower temperatures) the site A. Unfortunately, the highest temperature (400 K) that we can reach in our experimental set-up makes impossible to confirm this prediction.

On the whole, it appears that the model displayed in Fig. 4 describes qualitatively most of the experimental observations. However, a few features are not well reproduced. The theoretically generated hysteresis loops are always abrupt, while the experimental ones extend over a relatively large temperature range. Such behaviour is due to a distribution of certain parameters (energy gap, etc.) and, to some extent, due to the variation of the external pressure with the temperature (see above). One may note also that in the experiments the transition remains relatively abrupt at high pressures and the hysteresis width varies non-monotonously with increasing pressure. This behaviour is very unusual and bears a resemblance to the case of a one-dimensional polymeric spin-crossover system reported in Ref. [34]. Theoretically, these curves cannot be reproduced even if one allows for a pressure dependence of the interaction parameter and needs a more sophisticated treatment, which is out of the scope of the present paper [5].

5. Conclusions

We have measured the magnetic moment and Mössbauer spectra of a series of coordination polymers. The compound $\text{Fe}(\text{3-methylpyridine})_2[\text{Ni}(\text{CN})_4]$ revealed an intriguing half-step spin transition. By applying external pressure on this sample a two-step transition has been uncovered. To our knowledge this is only the second example for the observation of a two-step spin transition with two hysteresis loops. However, for further increase of the pressure this behaviour was progressively converted into a one-step transition. We rationalised these observations within the framework of an Ising-like model and predicted significantly different volume changes for the different iron sites in the polymeric lattice. On the other hand, a number of observations could not be explained within the limits of this theoretical model. Pressure and temperature dependent synchrotron powder diffraction experiments are planned to better understand the interplay between the lattice properties and pressure effects in this compound. Such structural data is essential for the development of more elaborated theoretical models.

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References

[1] P. Gütllich, H.A. Goodwin (Eds.), *Spin Crossover in Transition Metal Compounds I-III*, Topics in Current Chemistry, vol. 233-235, Springer, Berlin, 2004.

[2] P. Gütllich, A. Hauser, H. Spiering, *Angew. Chem. Int. Ed. Engl.* 33 (1994) 2024.
 [3] O. Kahn, J. Kröber, C. Jay, *Adv. Mater.* 4 (1992) 718.
 [4] A. Bousseksou, G. Molnár, G. Matouzenko, *Eur. J. Inorg. Chem.* (2004) 4353.
 [5] H. Spiering, K. Boukheddaden, J. Linares, F. Varret, *Phys. Rev. B* 70 (2004) 184106.
 [6] J. Kröber, E. Codjovi, O. Kahn, F. Grolière, C. Jay, *J. Am. Chem. Soc.* 115 (1993) 9810.
 [7] Y. Garcia, V. Niel, M. Carmen Munoz, J.A. Real, *Top. Curr. Chem.* 233 (2004) 229.
 [8] T. Kitazawa, Y. Gomi, M. Takahashi, M. Takeda, M. Enomoto, A. Miyazaki, T. Enoki, *J. Mater. Chem.* 6 (1996) 119.
 [9] T. Kitazawa, M. Takahashi, M. Takahashi, M. Enomoto, A. Miyazaki, T. Enoki, M. Takeda, *J. Radioanal. Nucl. Chem.* 239 (1999) 285.
 [10] T. Kitazawa, M. Eguchi, M. Takeda, *Mol. Cryst. Liq. Cryst.* 341 (2000) 527.
 [11] V. Niel, J.M. Martinez-Agudo, M. Carmen Munoz, A.B. Gaspar, *J.A. Real, Inorg. Chem.* 40 (2001) 3838.
 [12] S. Bonhommeau, G. Molnár, A. Galet, A. Zwick, J.A. Real, J.J. McGarvey, A. Bousseksou, *Angew. Chem. Int. Ed.* 44 (2005) 2.
 [13] K. Hosoya, T. Kitazawa, M. Takahashi, M. Takeda, J.F. Meunier, G. Molnar, A. Bousseksou, *Phys. Chem. Chem. Phys.* 5 (2003) 1682.
 [14] G. Molnár, V. Niel, A.B. Gaspar, J.A. Real, A. Zwick, A. Bousseksou, J.J. McGarvey, *J. Phys. Chem. B* 106 (2002) 9701.
 [15] G. Molnar, V. Niel, J.A. Real, L. Dubrovinsky, A. Bousseksou, J.J. McGarvey, *J. Phys. Chem. B* 107 (2003) 3149.
 [16] G. Molnar, T. Kitazawa, L. Dubrovinsky, J.J. McGarvey, A. Bousseksou, *J. Phys.: Condens. Matter* 16 (2004) S1129.
 [17] T. Tayagaki, A. Galet, G. Molnár, M. Carmen Muñoz, A. Zwick, K. Tanaka, J.A. Real, A. Bousseksou, *J. Phys. Chem. B* 109 (2005) 14859.
 [18] B. Bireckoven, J. Wittig, *J. Phys. E* 21 (1988) 841.
 [19] M. Eremets, *High Pressure Experimental Methods*, Oxford University Press, 1996.
 [20] J. Kamarad, Z. Machatova, Z. Arnold, *Rev. Sci. Instr.* 75 (2004) 5022.
 [21] F. Varret, *Proceedings of the International Conference on Mössbauer Effect Applications*, Jaipur, India, 1981, Indian National Science Academy, New Delhi, 1982.
 [22] H. Köppen, E.W. Müller, C.P. Köhler, H. Spiering, E. Meissner, P. Gütllich, *Chem. Phys. Lett.* 91 (1982) 348.
 [23] J.A. Real, H. Bolvin, A. Bousseksou, A. Dworkin, O. Kahn, F. Varret, J. Zarembowitch, *J. Am. Chem. Soc.* 114 (1992) 4650.
 [24] D. Boinnard, A. Bousseksou, A. Dworkin, J.-M. Savariault, F. Varret, J.-P. Tuchagues, *Inorg. Chem.* 33 (1994) 271.
 [25] D. Chernyshov, M. Hostettler, K.W. Törnroos, H.-B. Bürgi, *Angew. Chem. Int. Ed.* 42 (2003) 3825.
 [26] A. Bousseksou, J. Nasser, J. Linares, K. Boukheddaden, F. Varret, *J. Phys. I, France* 23 (1992) 1381.
 [27] R. Jacobi, H. Spiering, P. Gütllich, *J. Phys. Chem. Solids* 53 (1992) 267.
 [28] A. Bousseksou, F. Varret, J. Nasser, *J. Phys. I, France* 3 (1993) 1463.
 [29] K. Boukheddaden, J. Linares, E. Codjovi, F. Varret, V. Niel, *J.A. Real, J. Appl. Phys.* 93 (2003) 7103.
 [30] A. Hauser, *Top. Curr. Chem.* 234 (2004) 155.
 [31] C.P. Köhler, R. Jakobi, E. Meissner, L. Wiehl, H. Spiering, P. Gütllich, *J. Phys. Chem. Solids* 51 (1990) 239.
 [32] V. Ksenofontov, A.B. Gaspar, J.A. Real, P. Gütllich, *J. Phys. Chem. B* 105 (2001) 12266.
 [33] V. Ksenofontov, A.B. Gaspar, P. Gütllich, *Top. Curr. Chem.* 235 (2004) 23.
 [34] Y. Garcia, V. Ksenofontov, P. Gütllich, *Hyperfine Interact.* 139 (2002) 140.