

Pressure-induced hysteresis in the high spin \leftrightarrow low spin transition in bis(2,4-bis(pyridin-2-yl)thiazole) iron(II) tetrafluoroborate

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 026011

(<http://iopscience.iop.org/0953-8984/21/2/026011>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 17:04

Please note that [terms and conditions apply](#).

Pressure-induced hysteresis in the high spin \leftrightarrow low spin transition in bis(2,4-bis(pyridin-2-yl)thiazole) iron(II) tetrafluoroborate

A Bhattacharjee^{1,2,4}, V Ksenofontov¹, H A Goodwin³ and P Gülich^{1,4}

¹ Institut für Anorganische Chemie und Analytische Chemie, Johannes-Gutenberg Universität, D-55099 Mainz, Germany

² Department of Physics, Visva-Bharati University, Santiniketan 731235, India

³ School of Chemistry, University of New South Wales, Sydney, NSW 2052, Australia

E-mail: ashis.bhattacharjee@visva-bharati.ac.in and guetlich@uni-mainz.de

Received 17 July 2008, in final form 5 October 2008

Published 9 December 2008

Online at stacks.iop.org/JPhysCM/21/026011

Abstract

Studies of the spin transition behavior of the mononuclear compound $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ have been carried out under hydrostatic pressures up to 9.13 kbar in the 5–300 K temperature range. Under ambient pressure this compound exhibits an approximately half-step (incomplete) HS \leftrightarrow LS transition with $T_{1/2} = 146$ K without any thermal hysteresis. At pressures up to 4.5 kbar the behavior remains similar but with an upward displacement of $T_{1/2}$ and a slight decrease in the residual high spin fraction at low T . Application of higher pressures resulted in an almost complete two-step spin transition with several unusual pressure effects. Along with the expected pressure dependence of $T_{1/2}$ the surprising appearance of hysteresis in the spin transition curves was observed. It is suggested that the likely origin of this unprecedented behavior is a pressure-induced structural change.

1. Introduction

The phenomenon of a transition from low spin (LS) to high spin (HS) (or vice versa) has long been known for certain complexes of transition metal ions with d^4 , d^5 , d^6 and d^7 configurations but remains a property of high current interest due principally to the recognition of its potential for practical applications, especially for iron(II) (d^6) systems [1]. A spin transition may be physically induced by a change in temperature, pressure, by light irradiation or application of a magnetic field. The observation of a thermally induced spin transition requires that the difference in the zero point energies of the two spin states, $\Delta E_{\text{HL}}^0 = E_{\text{HS}}^0 - E_{\text{LS}}^0$, be of the order of the thermal energy, $k_{\text{B}}T$. In this case the LS state will be favored at very low temperatures or higher pressures, whereas at elevated temperatures or lower pressures an entropy-driven almost quantitative population of the HS state will generally occur. While the normal means

of characterizing a spin transition in iron(II) is to determine the magnetism or Mössbauer spectral details as a function of temperature and thereby produce a spin transition curve (γ_{HS} versus T), the generation of a related curve, γ_{HS} versus P , by measurement of the variation in physical properties with change in pressure can reveal additional significant aspects of the spin transition. The effect of pressure is generally obtained so as to yield both the effects of temperature and pressure, i.e. by the generation of a series of γ_{HS} versus T curves over a selected range of pressure values, as in the present work. Although the pressure dependence of the course of a spin transition has been studied by many groups over the years, and these studies have yielded much useful information, the development of special cells, which ensure the hydrostatic nature of the applied pressure, has broadened both the scope and reliability of the technique [2]. In contrast to the effect of an increase in temperature, which is to favor the low spin \rightarrow high spin conversion, that of an increase in pressure is to favor the reverse process, i.e. a high spin

⁴ Authors to whom any correspondence should be addressed.

→ low spin change. Generally the latter effect implies an increase in the transition temperature with increase in pressure and can be understood readily in terms of the molecular volume expansion accompanying the low spin → high spin change, requiring a work term $P\Delta V$ additional to the zero-point energy difference between the low spin and high spin states. The underlying reason for the pressure influence on the spin transition process is the large difference in the metal–donor atom bond lengths, $\Delta r_{\text{HL}} = r_{\text{HS}} - r_{\text{LS}} \approx 0.2 \text{ \AA}$, for Fe(II) spin crossover molecules. A schematic representation of the pressure influence on the LS and HS potential wells of Fe(II) is shown in figure 1. Application of pressure increases the relative vertical displacement of the potential wells; the additional minor horizontal displacement of the potential wells due to a slight decrease in bond length with an increase in pressure, independent of the change in spin state, has been neglected. Thus, application of pressure favors the LS state of the molecule and shifts the spin transition to higher temperatures because pressure increases the zero-point energy difference ΔE_{HL}^0 by the work term $P\Delta V_{\text{HL}}^0$ and decreases the activation energy ΔW_{HL}^0 , which finally favors the LS state. As a corollary to these effects, a high spin system which does not undergo a transition within a normally accessible temperature range at ambient pressure, may well do so under an increase in pressure. There are several reported instances of this but a particularly informative illustration is provided by the binuclear system $\{[\text{Fe}(\text{bpym})(\text{NCX})_2](\text{bpym})\}$ (bpym = 2, 2'-bipyrimidine). The system where X = S is high spin at ambient pressure and temperature remains so down to 4.2 K while that with X = Se undergoes an abrupt transition which is only 50% complete [3]. The effect of pressure induces a 50% transition in the X = S system and a complete (two-step) transition in the latter [4], demonstrating in both instances the increased stabilization of the low spin state with increasing pressure. More subtle effects may result from application of increased pressure to a spin crossover system. For example, the nature of the spin transition curve can change and if there is a hysteresis loop associated with a thermal transition it can be affected in unusual ways. For spin transitions with hysteresis which is due to the spin transition system and not accompanied by structural changes, a shift of the transition temperature towards higher temperatures and also a decrease of the width of the hysteresis loop are expected from model calculations. However, there are instances where the normal effects of an increase in pressure are not observed [2, 5–10]. There are reports where a shift of the transition to lower temperatures, equivalent to a stabilization of the HS state [9], and even stabilization of the HS state over the complete temperature range [2, 10] has been observed.

A long-known mononuclear system which undergoes an incomplete thermal spin transition is $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$, where pythiaz = 2,4-bis(2-pyridyl)thiazole, an essentially planar NNN tridentate, structurally related to terpyridine [11, 12]. In the present work a study of the pressure dependence of the course of the transition in this system was initiated primarily to determine if the transition could be induced to go to completion and whether a two-step process was then involved. In the event, the study has revealed some quite unexpected aspects of the spin transition in this system.

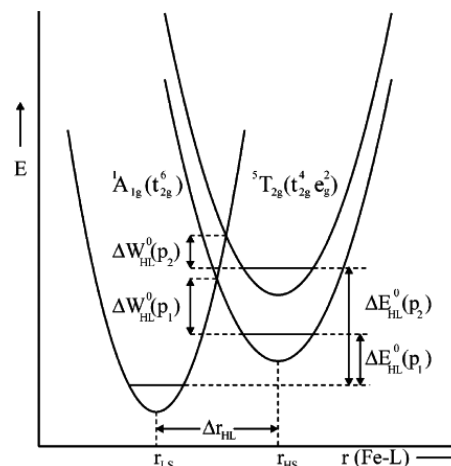


Figure 1. Schematic representation of the pressure influence ($p_2 > p_1$) on the LS and HS potential wells of Fe(II). The minor change in bond lengths Δr_{HL} under pressure is not considered. (Adapted from [18].)

2. Experimental details

Magnetic susceptibility measurements were performed on polycrystalline samples of $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ using a Quantum Design MPMS XL SQUID magnetometer with 1 T magnetic field in the 2–300 K range under different applied pressures. The hydrostatic pressure cell, made of hardened beryllium bronze with silicon oil as the pressure transmitting medium, is workable below 13 kbar pressure (1 kbar = 0.1 GPa). A cylindrically shaped powder sample holder with dimensions of 1 mm in diameter and 5–7 mm in length was used. External pressures were applied on the pressure cell at room temperature by using a hydraulic press, and after each pressurization the pressure cell was kept at ambient conditions for nearly 2 h. The applied pressure was measured using the pressure dependence of the superconducting transition temperature of a built-in pressure sensor made of high purity tin. The magnetic data were collected both in the cooling and heating directions with a cooling/heating rate of 1 K min^{-1} . The time interval between two successive series of measurements after pressurization was 1 day. Experimental data were corrected for diamagnetism using Pascal's constants.

Mössbauer spectra were measured for the sample in a bath cryostat using a conventional constant-acceleration spectrometer and $^{57}\text{Co}/\text{Rh}$ source. The hyperfine parameters were obtained by least-squares fitting of the data to Lorentzian lines using the Recoil (1.03a) Mössbauer Software Analysis program [13].

3. Results and discussion

3.1. Pressure-dependent magnetic measurements

In figure 2 the magnetism of polycrystalline $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$, measured under ambient pressure between 2 and 300 K and a 10 kOe magnetic field, is shown. Figure 2(a) shows the temperature variation of χ_m —the molar magnetic

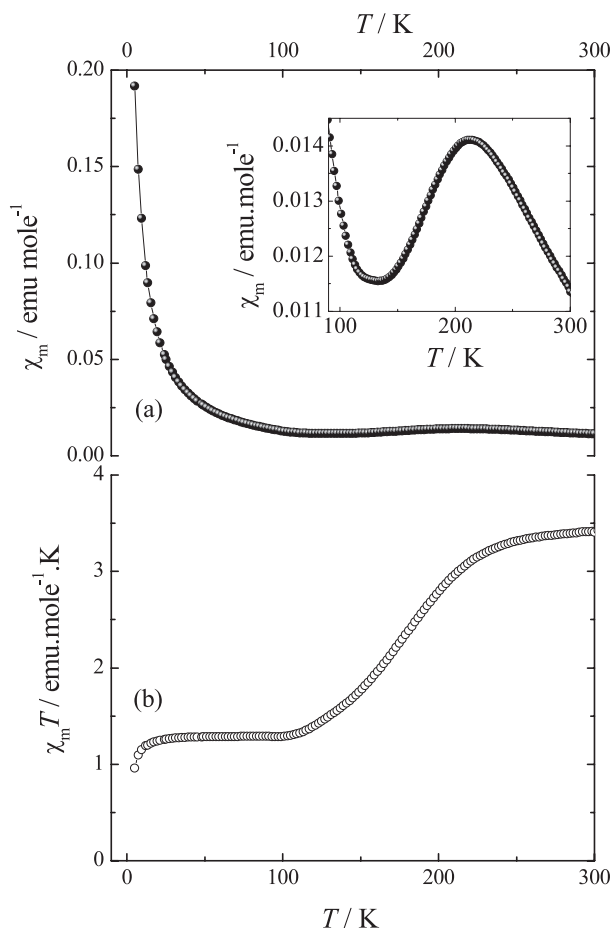


Figure 2. Temperature dependence of (a) χ_M and (b) $\chi_M \cdot T$ for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ at ambient pressure.

susceptibility. The temperature dependence of χ_m observed here resembles that shown in figure 1 of [11] within the common temperature range. Goodwin and Sylva [11] found that the magnetism of this compound obeyed the Curie–Weiss law within 363–250 K with θ equal to approximately -59 K, below which χ_m decreases rapidly with temperature down to about 100 K (see the inset in figure 2(a)), followed by Curie–Weiss law behavior again with $\theta = -25$ K, the magnetic moment becoming nearly independent of temperature. In the present study a similar trend in $\chi_m(T)$ has been observed, but the θ values estimated are -75 and -15 K in the $T > 245$ K and $T < 100$ K regions, respectively. Figure 2(b) shows the $\chi_m T$ versus T plot at atmospheric pressure. At 300 K the $\chi_m T$ product has a value of 3.407 emu mol $^{-1}$ K, which closely corresponds to the high spin (HS) state of the Fe II ions with $S = 2$ and a g factor of 2. The $\chi_m T$ value decreases gradually when the temperature is lowered below room temperature and reaches 1.29 emu mol $^{-1}$ K at 100 K. The $\chi_m T(T)$ plot shows a plateau within the ~ 100 – 20 K range. Below 20 K the $\chi_m T$ value starts to decrease with $\chi_m T = 0.959$ emu mol $^{-1}$ K at 5 K. When the sample is heated from 5 K the $\chi_m T(T)$ plot retraces the same path as that observed while cooling and thus no thermal hysteresis is observed. The spin transition in this complex was studied earlier by Mössbauer spectroscopy [12] and that study supported the interpretation of the magnetism

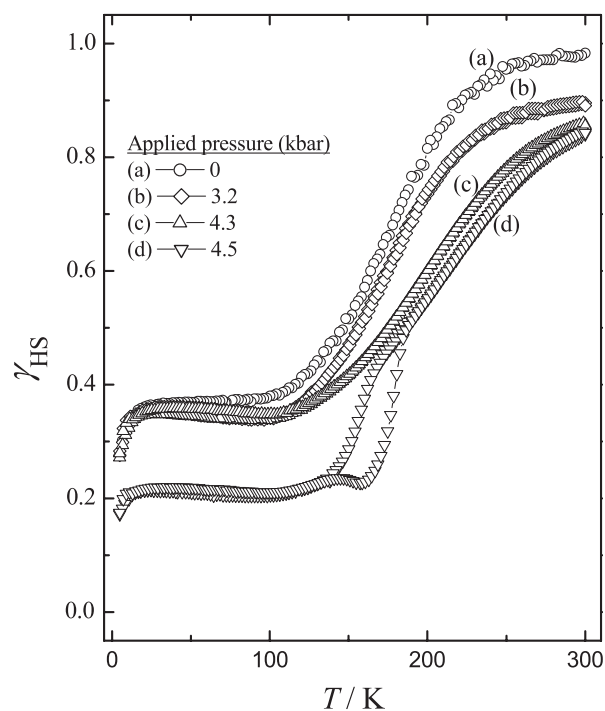


Figure 3. Temperature dependence of the molar high spin fraction γ_{HS} derived from the magnetic data for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ under different applied pressures (0–4.5 kbar) and over the temperature range 5–300 K.

and showed that both spin states were present at a more or less constant HS:LS ratio of $\sim 3:2$ below 100 K. Thus the plateau in the $\chi_m T(T)$ plot in the 20–100 K range is associated with this mixture of HS and LS states of Fe(II) at these temperatures and the decrease of $\chi_m T$ below 20 K is due to zero-field splitting effects in the HS fraction.

In an attempt to convert the low-temperature residual HS fraction of Fe(II) ions observed under ambient pressure into the LS state, external pressure was applied on the sample. Magnetic susceptibility values were recorded for the sample in the 2–300 K range with a 10 kOe magnetic field under different external pressures during cooling as well as heating (figures 3 and 4). The molar high spin fraction was evaluated from the experimental magnetic susceptibility data by application of the following relationship:

$$\gamma_{\text{HS}}(T) = [(\chi_M \cdot T)_{\text{observed}}(T) - (\chi_M \cdot T)_{\text{LS}}] / [(\chi_M \cdot T)_{\text{HS}} + (\chi_M \cdot T)_{\text{LS}}]. \quad (1)$$

The value of $(\chi_M \cdot T)_{\text{HS}}$ was calculated from the spin-only effective magnetic moment value for high spin Fe(II) [$\mu_{\text{eff}} = (8\chi_M \cdot T)^{1/2} = 2\sqrt{S(S+1)}$, where $S = 2$ for high spin Fe(II)], whereas the $(\chi_M \cdot T)_{\text{LS}}$ value was taken to be 2×10^{-4} emu mol $^{-1}$ K [14], which is very small when compared to the $(\chi_M \cdot T)_{\text{HS}}$ value. The $(\chi_M \cdot T)_{\text{HS}}$ value cannot be taken as the observed $(\chi_M \cdot T)$ value at 300 K, as the spin transition is not complete even at this temperature, as figure 3(a) shows there is still a small LS fraction at 300 K. Close examination of the Mössbauer spectrum measured at 298 K shown in [12] reveals an asymmetry in the doublet and it is at least feasible to ascribe this to a very small LS

Table 1. Estimated parameters from the $\gamma_{\text{HS}}(P)$ versus T plots obtained under different applied pressures for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$. (Note: γ_{HS} = molar high spin fraction, γ_{LS} = molar low spin fraction, T_{\downarrow} , T_{\uparrow} = temperatures where the $\gamma_{\text{HS}}(T)$ plots in cooling and heating directions bifurcate, respectively, ΔT = temperature interval between T_{\downarrow} and T_{\uparrow} , T' = temperature at which a small hump appears in the $\gamma_{\text{HS}}(T)$ plots, $T_{1/2\downarrow}$, $T_{1/2\uparrow}$ = temperatures at which γ_{HS} equals 0.5 in $\gamma_{\text{HS}}(T)$ plots in cooling and heating directions, respectively, $\Delta T_{1/2}$ = temperature interval between $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$, T_{R} = temperature range of the gradual spin transition.)

Applied pressure (kbar)	γ_{HS} at 300 K	γ_{LS} at 5 K	T_{\downarrow} (K)	T_{\uparrow} (K)	ΔT (K)	T' (K)	$T_{1/2\downarrow}$ (K)	$T_{1/2\uparrow}$ (K)	$\Delta T_{1/2}$ (K)	T_{R} (K)
0	0.98	0.28	—	—	0	—	146	146	0	0
3.2	0.89	0.275	—	—	0	—	157	157	0	0
4.3	0.85	0.27	—	—	0	—	177	177	0	0
4.5	0.84	0.17	185	136	49	136	189	189	0	0
6.3	0.83	0.03	216	158	58	172	200	208	8	62
7.45	0.81	0.015	240	185	55	194	218	226	8	100
8.48	0.75	0.00	259	203	56	211	234	242	8	125
9.13	0.73	0.00	275	211	64	220	241	249	8	142

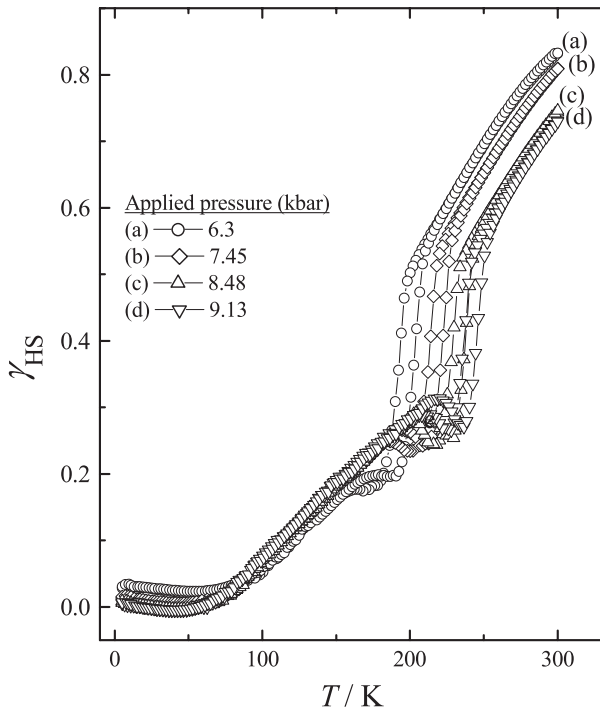


Figure 4. Temperature dependence of the molar high spin fraction γ_{HS} derived from the magnetic data for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ under different applied pressures (6.3–9.13 kbar) and over the temperature range 5–20 K.

fraction. In the initial report of this system [11] the magnetism was measured up to ~ 360 K and it is clear that there is a significant increase in the moment above room temperature, indicating the incomplete nature of the spin transition at that temperature. The temperature dependence of γ_{HS} derived from equation (1) is shown in figures 3 and 4 for some selected pressures. From figure 3(a) the γ_{HS} value under zero applied pressure ($P = 0$ kbar) is found to be 0.98 and 0.37 at 300 K and in the 20–100 K range, respectively. These values are in excellent agreement with those estimated from the earlier Mössbauer studies [12]. $\gamma_{\text{HS}}(T)$ variations during cooling and heating remain identical. The spin transition temperature at $\gamma_{\text{HS}} = 0.5$ for $P = 0$ is $T_{1/2\downarrow} = T_{1/2\uparrow} = 146$ K.

On application of an external pressure of 3.2 kbar, γ_{HS} shows an overall decrease, being 0.89 at 300 K and 0.35 at

~ 100 K followed by a plateau in the $\gamma_{\text{HS}}(T)$ curve similar to that observed with $P = 0$ (figure 3(b)). With further increase of applied pressure to $P = 4.3$ kbar γ_{HS} (300 K) falls to 0.85 and the spin transition becomes more gradual. However, the plateau in the 20–100 K range is retained with $\gamma_{\text{HS}} = 0.34$ (figure 3(c)). It is clear that external pressures up to 4.3 kbar do not result in any significant change in the LS \leftrightarrow HS conversion in the plateau region (20–100 K), but gradually changes its nature at temperatures above this region. Further increase in pressure induces a fundamental change in the nature of the transition. Remarkably, hysteresis appeared in the $\gamma_{\text{HS}}(T)$ plot when the external pressure was increased to 4.5 kbar (figure 3(d)). Under this pressure γ_{HS} (300 K) is 0.84 and the $\gamma_{\text{HS}}(T)$ plot shows a thermal hysteresis loop with $\Delta T = 49$ K and $T_{\downarrow} = 185$ K and $T_{\uparrow} = 136$ K, where the hysteresis width $\Delta T = T_{\downarrow} - T_{\uparrow}$, with T_{\downarrow} and T_{\uparrow} being the temperatures of the upper and lower bifurcation points of the $\gamma_{\text{HS}}(T)$ plots, respectively. It is clear from figure 3(d) that below T_{\uparrow} the $\gamma_{\text{HS}}(T)$ plot shows the plateau in the 15–115 K range with $\gamma_{\text{HS}} = 0.21$. It is significant that at this and higher pressures the high spin fraction in the plateau region is much smaller than at the lower pressures. This indicates that an effect of these relatively high pressures is certainly to instigate the transition in the residual high spin fraction evident in the relatively low pressure behavior. This effect becomes more pronounced as the pressure is further increased, and at 8.48 kbar (figure 4(c)) the transition to low spin is virtually complete at about 50 K. It is noteworthy that the spin transition curves at pressures ≥ 4.5 kbar indicate that three contributions to the overall spin change can be distinguished—a continuous change at high T , an abrupt change with associated hysteresis at intermediate T and a further continuous change at low T , giving rise to an overall change in three steps. These changes are evident in the various plots in figures 3 and 4 and are characterized by the parameters listed in table 1.

Application of 6.3 kbar pressure reduces γ_{HS} (300 K) to 0.83 and the thermal hysteresis in $\gamma_{\text{HS}}(T)$ appears with $T_{\downarrow} = 216$ K and $T_{\uparrow} = 158$ K (figure 4(a)). Noticeably, under this pressure the $\gamma_{\text{HS}}(T)$ plot below T_{\uparrow} exhibits a gradual change with temperature, reaching $\gamma_{\text{HS}} = 0.02$ at 65 K. Thus application of such a pressure is able to achieve a virtually complete conversion to the LS state of Fe(II) in this

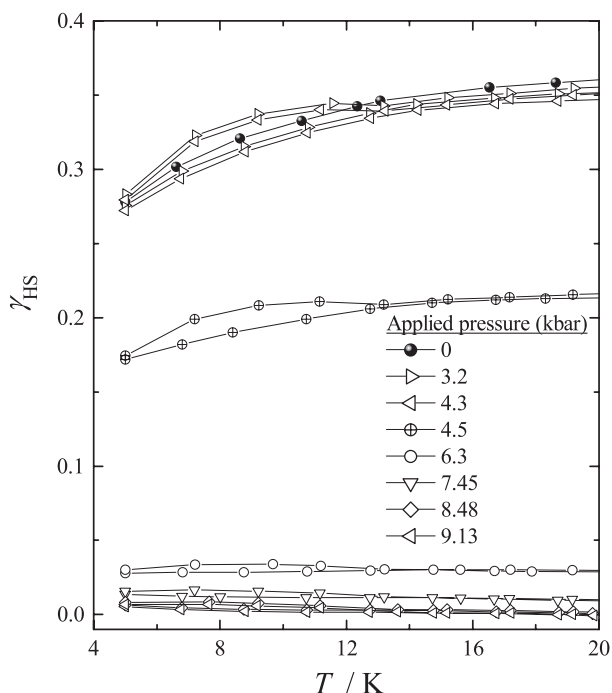


Figure 5. Temperature dependence of the molar high spin fraction γ_{HS} derived from the magnetic data for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ under different applied pressures at temperatures below 20 K.

compound at ~ 65 K. It is evident that under this pressure the $\gamma_{\text{HS}}(T)$ plot exhibits a two-step spin transition process—the first step being a comparatively abrupt process within 158 and 300 K associated with a thermal hysteresis $\Delta T = 58$ K and converting 80% of HS Fe(II) to LS, while the second is quite gradual over the temperature range 65–158 K and converts the remaining HS Fe(II) ions to LS at ~ 65 K. Further gradual increase of pressure resulted in similar $\gamma_{\text{HS}}(T)$ variations (figures 4(a)–(d)), but shifted the abrupt spin transition towards higher temperatures and also increased the temperature range (T_{R} —see table 1) of the gradual spin transition. The maximum pressure applied in the present work was 9.13 kbar.

For 4.5 kbar pressure a small but noticeable increase in the $\gamma_{\text{HS}}(T)$ plot at 136 K (say, T') in the heating mode has been recorded (figure 3(d)). This small increase and the similar but more pronounced increases seen under higher pressures (see figures 4(a)–(d)) may be due to a phase change at the temperature at which hysteresis emerges and this structural rearrangement may be relatively slow compared to the rate of data collection. As this superheated phase is heated further it is able to relax back to a stable phase and this accounts for the dip in the curve before the heating branch of the hysteresis loop is reached. However, this consideration would not be relevant in the cooling mode since the structural change begins at a higher temperature, thus with a lower kinetic barrier.

The observed decrease of $\chi_{\text{m}}T$ values below ~ 20 K due to zero-field splitting effect of the HS Fe(II) sites is reflected in the $\gamma_{\text{HS}}(T)$ variations below 20 K (figures 3 and 4). Figure 5 represents the $\gamma_{\text{HS}}(T)$ plots in the temperature region where the zero-field splitting effect dominates the magnetic behavior of the present compound. This figure reveals that the effect

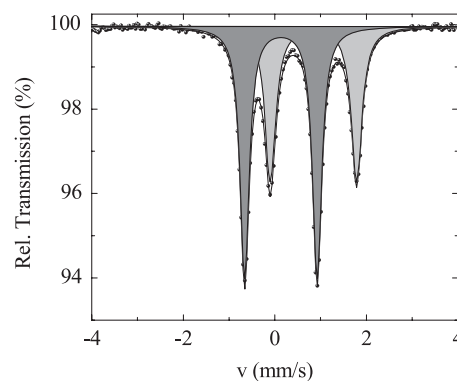


Figure 6. Mössbauer spectrum of $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ at 4.2 K under ambient pressure.

of increasing pressure is to move the zero-field splitting effect towards lower temperature, as is usually expected. To the best of our knowledge this is the first ever evidence of the effect of pressure on the zero-field splitting effect in spin crossover compounds. It is interesting to note that a very small hysteresis appears in the $\gamma_{\text{HS}}(T)$ plots below 13 K, which decreases with increasing pressure. However, at present we do not have any explanation for that.

3.2. Mössbauer spectroscopy

In order to cast some light on the origin of the stepwise nature of the transition observed in $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ its Mössbauer spectrum, shown in figure 6, has been measured at 4.2 K and ambient pressure. Such spectra are sensitive to minor lattice variations and can indicate the presence, for example, of more than one lattice site for the Mössbauer nuclide, a likely origin of a stepwise transition. The spectrum shown in figure 6 could be satisfactorily fitted with only two quadrupole-split doublets, which can be characterized by the isomer shift $\delta = 0.95$ mm s $^{-1}$ (relative to α -iron) and quadrupole splitting, $\Delta E_{\text{Q}} = 1.88$ mm s $^{-1}$, and $\delta = 0.24$ mm s $^{-1}$ and $\Delta E_{\text{Q}} = 1.58$ mm s $^{-1}$, respectively. The former doublet corresponds to the high spin ground state of Fe(II), whereas the latter originates from the low spin Fe(II) fraction. The hyperfine parameters obtained for the present compound at 4.2 K are in excellent agreement with those reported earlier for this compound at 5 K ($\delta = 0.96$ mm s $^{-1}$ and $\Delta E_{\text{Q}} = 1.90$ mm s $^{-1}$; $\delta = 0.26$ mm s $^{-1}$ and $\Delta E_{\text{Q}} = 1.59$ mm s $^{-1}$ for HS and LS Fe(II), respectively) by König *et al* [12]. The quantitative determination of the HS or LS fraction (γ) from Mössbauer spectra is based on the estimation of the area fractions n_{HS} and n_{LS} of the resonance lines. These are proportional to the products $f_{\text{HS}} \cdot \gamma_{\text{HS}}$ and $f_{\text{LS}} \cdot \gamma_{\text{LS}}$, respectively, where γ and f are the molar fraction and Lamb–Mössbauer factor, respectively, of the corresponding spin states. The area fractions of the resonance signal in the Mössbauer spectra do not necessarily reflect the actual concentration of the different iron spin states, as different bonding interactions of the Mössbauer nuclide in its two different spin states can lead to different Lamb–Mössbauer factors, which in turn give rise to different intensities of the corresponding Mössbauer

resonance signals [15, 16]. König *et al* derived different Lamb–Mössbauer factors ($f_{\text{HS}} < f_{\text{LS}}$) for the HS and LS states of Fe(II) in the present compound, at least over the temperature range 77–298 K [12]. However, in the present work we have assumed that at 4.2 K the Lamb–Mössbauer factors are the same for the two spin states and the high spin and low spin fractions correspond to their area fractions n_{HS} and n_{LS} , respectively. The error involved in this assumption is unlikely to be high (<5%) [16]. The area population ratio of the HS and LS doublets at 4.2 K under this condition are calculated to be 42% and 58%, respectively (i.e. $\gamma_{\text{HS}} = 0.42$).

3.3. Effect of pressure on spin transition

In table 1 are listed the estimated values of γ_{HS} (300 K), T_{\downarrow} , T_{\uparrow} , $\Delta T (= T_{\downarrow} - T_{\uparrow})$, T' , $T_{1/2\downarrow}$, $T_{1/2\uparrow}$, $\Delta T_{1/2} (= T_{1/2\downarrow} - T_{1/2\uparrow})$ and T_{R} obtained under different external pressures in the present study for comparison. Figure 7(a) represents the pressure variation of $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$, whereas the variation of ΔT with pressure is shown in figure 7(b). It is interesting to note that, after the appearance of thermal hysteresis, the spin transition temperatures ($T_{1/2\downarrow}$, $T_{1/2\uparrow}$) and the hysteresis width (ΔT) vary linearly with pressure. Consistent with previously reported observations of the effect of increased pressure on the degree to which the transition is gradual, both steps of the spin transition extend over larger temperature ranges with gradually increasing pressure, and one can still observe a two-step spin transition process at the highest applied pressure. When the pressure was released from the highest applied pressure, the sample showed similar magnetic behavior to that observed before compression, showing that the effects of pressurization were reversible within this range of pressure.

In the framework of mean-field theory of phase transitions in SCO compounds [17] the pressure dependence of the spin transition temperature obeys the Clausius–Clapeyron equation:

$$\frac{\partial T_{1/2}}{\partial P} = \frac{\Delta V_{\text{HL}}}{\Delta S_{\text{HL}}}. \quad (2)$$

This relation reflects the scaling of the transition temperature $T_{1/2}$ and the volume change ΔV . Thus the transition temperature increases with increasing pressure. Furthermore, the mean-field approach predicts a decrease of the hysteresis width and of the slope of the transition curve with increasing pressure [2, 18]. In addition, the thermal hysteresis vanishes at a critical pressure, and at even higher pressures the transition transforms to the gradual type belonging to the overcritical region of the phase diagram. Figure 7(c) represents the observed pressure variation of $\Delta T_{1/2}$ —the hysteresis width at $\gamma_{\text{HS}} = 0.5$ for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$. Clearly, the presently observed pressure effects on the spin transition in $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ contradict the expectations following from the mean-field theory of phase transitions in SCO compounds. The parallel shift of the transition curve and the behavior of the hysteresis width under pressure observed here cannot be described by this theory.

To demonstrate the pressure effect on the hysteresis during spin transition Ksenofontov *et al* [7] extended the mean-field approximation of the free energy for SCO compounds

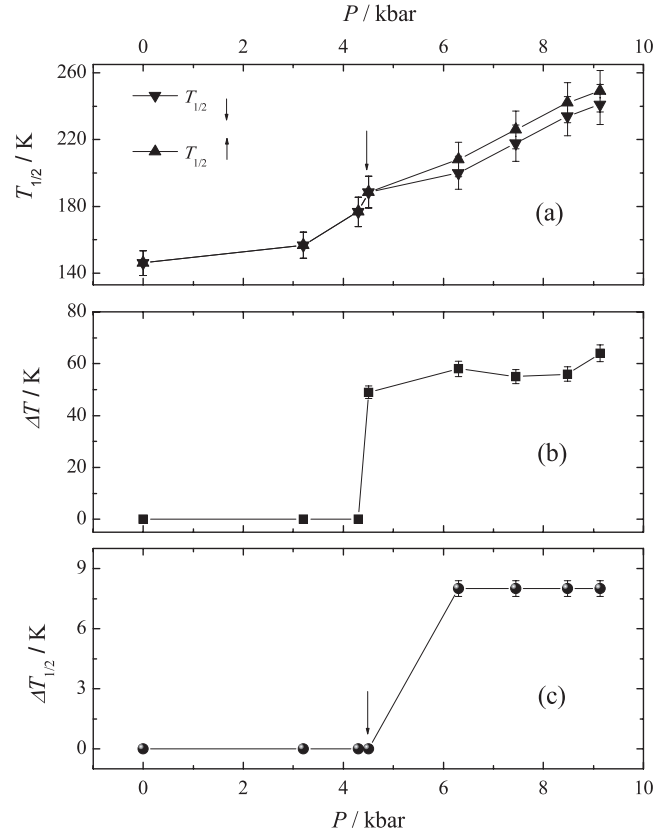


Figure 7. Pressure dependences of (a) the spin transition temperature $T_{1/2}$, (b) the hysteresis width ΔT , the temperature interval between T_{\downarrow} and T_{\uparrow} and (c) $\Delta T_{1/2}$, the hysteresis width at $\gamma_{\text{HS}} = 0.5$, the temperature interval between $T_{1/2\downarrow}$ and $T_{1/2\uparrow}$ for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$. Arrows indicate the onset pressure for thermal hysteresis.

assuming a direct coupling between the pressure and the order parameter as there is a volume change of the crystal proportional to the fraction of the molecules of either spin states, as is known experimentally. In the present case one can see a linear dependence of $T_{1/2}$ with P during cooling as well as heating, but only after the occurrence of hysteresis (figure 7(a)). At lower pressures (before the hysteresis appeared) the $T_{1/2}$ versus P plot deviates from linearity remarkably and is not in agreement with the expression for $\frac{\partial T_{1/2}}{\partial P}$ predicted in [7]. Also the $\Delta T_{1/2}$ versus P relation observed for $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ is significantly different from that predicted by the expression for $\frac{\partial \sqrt{\Delta T_{1/2}}}{\partial P}$ of [7]. In the present case, $\Delta T_{1/2}$ is independent of the pressure applied. A later theoretical formulation [19] of the total free energy of an anharmonic lattice incorporating spin crossover molecules which have a certain misfit to the lattice and interact elastically by their change in volume and shape, constructed for a finite spherical crystal being treated as a homogeneous isotropic elastic medium, could simulate many of the known anomalous spin transition behaviors. The parallel shift of the spin transition curve can be described by this theory, but not the behavior of the hysteresis width under pressure observed here in $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$. An interpretation of the curious pressure effects associated with the SCO phenomenon in this

system is not possible without the knowledge of the thermal and pressure dependences of the elementary cell volume of $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ and the possibility of a change in the elementary cell volume of the present material in the pressure range up to ~ 4.5 kbar cannot be excluded.

3.4. Nature of the spin transition

In a few mononuclear complexes the temperature dependence of the high spin fraction displays an interesting two-step behavior [20–23]. This stepped spin transition phenomenon has received much attention from the theoretical point of view [24–27]. Two-step curves can be obtained trivially by considering two crystallographically different metal ion environments, but two-step behavior can also be predicted for structurally equivalent sublattices [24]. Examples for half-transitions have also been reported in the literature [1, 22]. The mononuclear compound $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2 \cdot \text{EtOH}$ (2-pic = 2-aminomethylpyridine = 2-picolyamine), which exhibits a two-step spin transition process, undergoes two first-order phase transitions on cooling from a HS phase via an intermediate phase to an LS phase, where the HS and LS phases are isostructural, indicating that the two-step spin transition is due to two crystallographically different iron sites [23]. However, while $[\text{Fe}(\text{HC}(3, 5\text{-Me}_2\text{pz})_3)_2](\text{BF}_4)_2$, with tris(pyrazolyl)methane ligands, has one crystallographically unique Fe(II) site at 220 K, 50% of Fe(II) undergoes an LS \leftrightarrow HS transition at 206 K and the other 50% of Fe(II) sites remain in the HS state down to 10 K [28]. In this case, the crystal system changes from monoclinic to primitive triclinic with $Z = 2$ (i.e. yielding two crystallographically independent Fe(II) sites) along with a shortening of Fe–N bond distances for 50% of the molecules. The mononuclear $[\text{Fe}(\text{5-NO}_2\text{-sal-N}(1,4,7,10))][\text{5NO}_2\text{-sal-N}(1,4,7,10)\text{H}_2 = \text{bis}(5\text{-nitrosalicylidene)triethylenetetramine}]$ compound exhibits a 1:1 two-step LS \leftrightarrow HS transition associated with two structural phase transitions [22]. $[\text{Fe}(\text{btzb})_3](\text{PF}_6)_2$, (btzb = 1,4-bis(tetrazol-1-yl)butane) with one crystallographically independent Fe(II) site exhibits a sharp two-step spin transition behavior between 164 and 182 K with $T_{1/2} = 174$ K [29], where two distinguishable HS Fe(II) sites could not be observed. The thermodynamic stabilization of an alternating ordering of the HS and the LS Fe(II) sites around T_{SCO} has been held responsible for this two-step spin transition in $[\text{Fe}(\text{btzb})_3](\text{PF}_6)_2$ system. In another mononuclear complex $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ (mtz = 1-methyl-tetrazole) the Fe(II) ions occupy two non-equivalent crystallographic sites with 1:1 population ratio, and the Fe(II) complex molecules of only one site undergo thermal spin transition at ambient pressure, whereas those in the other site remain in the HS state down to 4.2 K [30]. The ^{57}Fe Mössbauer spectra of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ above ~ 160 K, however, show only one quadrupole doublet typical of Fe(II) in the HS state. This obviously indicates that the two sites of Fe(II) HS states are only minutely different in energy. A pressure effect study on this complex reveals that the Fe(II) ions occupy two non-equivalent crystallographic sites with 1:1 population ratio [31]. Poganiuch *et al* [32] have shown

that at low temperatures the ground state of iron(II) in both sites of $[\text{Fe}(\text{mtz})_6](\text{BF}_4)_2$ can be converted by light into long-lived metastable spin states: the LS state of A site molecules to HS with green light, and the HS state of B site molecules to LS with red light.

In view of the observed partial LS \leftrightarrow HS transition in $[\text{Fe}(\text{pythiaz})_2](\text{BF}_4)_2$ under ambient pressure, the following possibility can be considered. Though in the present case Mössbauer spectroscopy gave no indication of the presence of two different Fe(II) lattice sites in the present compound, it is tempting to ascribe the two-step nature of the transition to the presence of two such sites. It should be noted that the temperature at which the structure (tetragonal, space group— $P\bar{4}2_1C$, $Z = 2$) [33] of the present compound was solved corresponds to the high temperature region of the spin transition curve, but the nature of the structure at the intermediate plateau as well as the lowest region of the spin transition curve are unknown. It should also be pointed out that, primarily because of the quality of the crystal, the precision of the structure determination was not high. In addition, because of disorder, the structure solution required the imposition of constraints on both the ligands and the anion. Thus it is feasible that the appearance of hysteresis is associated with a phase change that (with decreasing T and increasing P) is instigated by a disorder–order transition. The lack of structural information on the present compound at lower temperatures does not allow us to give any further explanation along this direction and the origin of the two-step process or of the hysteresis remains unresolved.

4. Conclusions

The appearance of hysteresis in the χ_{HS} versus T curves at relatively high pressures strongly suggests the occurrence of a thermally induced phase change and this is supported by the anomalous nature of the heating branch of the curves which is indicative of a kinetically controlled process. It may well be that at ambient pressure and even slightly higher pressures where no hysteresis has been observed in the χ_{HS} versus T curve the phase transition would be displaced to such a low temperature that it is kinetically highly unfavorable, even in the cooling mode. It is relevant in this regard that the residual high spin fraction at low temperatures remains more or less constant until the pressure is raised to such an extent that hysteresis (and presumably a phase change) appears (figures 3 and 4). Any rationale for the nature of the phase change at this stage is speculative but it is feasible that it is instigated or associated with a disorder–order transition on cooling. Disorder is certainly evident in the structure under ambient conditions. Ordering of the ligand orientations within the coordination sphere or of the anions in the lattice under the combined effects of an increase in pressure and a decrease in temperature (both effects tending to stabilize the low spin state) is feasible. The association of disorder–order transitions with spin transitions and related phenomena has long been proposed [34] and some novel instances have been reported recently [35].

There are several SCO systems in which the effect of pressure on the SCO behavior cannot be adequately described by the existing theory [2, 7, 17, 36]. Occurrence of structural phase transitions and a change in the bulk modulus of the materials under applied pressure have been proposed for the anomalous behavior observed, e.g. nonlinear $T_{1/2}(P)$ behavior and pressure-independent hysteretic behavior. An understanding of the remarkable and unexpected pressure effects reported here for $[\text{Fe}(\text{pythiaz})_2][\text{BF}_4]_2$ will require additional structural studies at variable temperatures and under applied pressure. Pressure- and temperature-dependent synchrotron powder diffraction experiments have been planned and it is hoped that these will be diagnostic of the interplay between the lattice properties and the effects of applied pressure on the nature and extent of the spin transition in this compound.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (Priority Program No. 1137 ‘Molecular Magnetism’), the Fonds der Chemischen Industrie and the Materialwissenschaftliches Forschungszentrum of the University of Mainz are gratefully acknowledged, as is the support of the Australian Research Council.

References

- [1] Gütlich P and Goodwin H A (ed) 2004 *Topics in Current Chemistry* vols 233–235 (Berlin: Springer)
- [2] Ksenofontov V, Gaspar A B and Gütlich P 2004 *Topics in Current Chemistry* vol 235, ed P Gütlich and H A Goodwin (Berlin: Springer) p 23
- [3] Real J A, Zarembowitch J, Kahn O and Solans X 1987 *Inorg. Chem.* **26** 2939
- [4] Gaspar A B, Ksenofontov V, Spiering H, Reiman S, Real J A and Gütlich P 2002 *Hyperfine Interact.* **144/145** 297
- [5] Garcia Y, Ksenofontov V and Gütlich P 2002 *Hyperfine Interact.* **139/140** 543
- [6] König E, Ritter G, Waigel J and Goodwin H A 1985 *J. Chem. Phys.* **83** 3055
- [7] Ksenofontov V, Spiering H, Schreiner A, Levchenko G, Goodwin H A and Gütlich P 1999 *J. Phys. Chem. Solids* **60** 393
- [8] Garcia Y, van Koningsbruggen P J, Lapouyade R, Fournès L, Rabardel L, Kahn O, Ksenofontov V, Levchenko G and Gütlich P 1998 *Chem. Mater.* **10** 2426
- [9] Ksenofontov V, Levchenko G, Spiering H, Gütlich P, Létard J-F, Bouhedja Y and Kahn O 1998 *Chem. Phys. Lett.* **294** 545
- [10] Garcia Y, Ksenofontov V, Levchenko G, Schmitt G and Gütlich P 2000 *J. Phys. Chem. B* **104** 5045
- [11] Goodwin H A and Sylva R N 1968 *Aust. J. Chem.* **21** 2881
- [12] König E, Ritter G and Goodwin H A 1973 *Chem. Phys.* **1** 17
- [13] Lagarec K and Rancourt D G 1997 *Nucl. Instrum. Methods Phys. Res. B* **129** 266
- [14] Boudreaux E A and Mulay L N 1976 *Theory and Applications of Molecular Paramagnetism* (New York: Wiley)
- [15] Garcia Y, Ksenofontov V, Mentior S, Dírto M M, Gieck C and Bhattacharjee A 2008 *Chem. Eur. J.* **14** 3745
- [16] König E, Ritter G and Goodwin H A 1974 *Chem. Phys.* **5** 211
- [17] Jung J, Spiering H, Yu Z and Gütlich P 1995 *Hyperfine Interact.* **95** 107
- [18] Meissner E, Köppen H, Spiering H and Gütlich P 1983 *Chem. Phys. Lett.* **95** 163
- [19] Spiering H, Meissner E, Köppen H, Müller E W and Gütlich P 1982 *Chem. Phys.* **68** 65
- [20] Adler P, Wiehl L, Meissner E, Köhler C P, Spiering H and Gütlich P 1987 *J. Phys. Chem. Solids* **48** 517
- [21] Gütlich P, Ksenofontov V and Gaspar A B 2005 *Coord. Chem. Rev.* **249** 1811
- [22] Spiering H, Boukhehdaden K, Linares J and Varret F 2004 *Phys. Rev. B* **70** 184106
- [23] Köppen H, Müller E W, Köhler C P, Spiering H, Meissner E and Gütlich P 1982 *Chem. Phys. Lett.* **91** 348
- [24] Real J A, Bolvin H, Bousseksou A, Dworkin A, Kahn O, Varret F and Zarembowitch J 1992 *J. Am. Chem. Soc.* **114** 4650
- [25] Boinnard D, Bousseksou A, Dworkin A, Savariault J-M, Varret F and Tuchagues J-P 1994 *Inorg. Chem.* **33** 271
- [26] Chernyshov D, Hostettler M, Törnroos K W and Bürgi H-B 2003 *Angew. Chem. Int. Edn* **42** 3825
- [27] Bousseksou A, Nasser J, Linares J, Boukhehdaden K and Varret F 1992 *J. Physique I* **23** 1381
- [28] Jacobi R, Spiering H and Gütlich P 1992 *J. Phys. Chem. Solids* **53** 267
- [29] Bousseksou A, Varret F and Nasser J 1993 *J. Physique I* **3** 1463
- [30] Boukhehdaden K, Linares J, Codjovi E, Varret F, Niel V and Real J A 2003 *J. Appl. Phys.* **93** 7103
- [31] Reger D L, Little C A, Young V G and Pink M 2001 *Inorg. Chem.* **40** 2870
- [32] Grunert C M, Schweifer J, Weinberger P, Linert W, Mereiter K, Hilscher G, Müller M, Wiesinger G and van Koningsbruggen P J 2004 *Inorg. Chem.* **43** 155
- [33] Wiehl L 1993 *Acta Crystallogr. B* **49** 289
- [34] Wiehl L, Spiering H, Gütlich P and Knorr K 1990 *J. Appl. Crystallogr.* **23** 151
- [35] Kusz J, Spiering H and Gütlich P 2001 *J. Appl. Crystallogr.* **34** 229
- [36] Kusz J, Gütlich P and Spiering H 2004 *Topics in Current Chemistry* vol 234, ed H Spiering, P Gütlich and H A Goodwin (Berlin: Springer) p 129
- [37] Poganiuch P, Decurtins S and Gütlich P 1990 *J. Am. Chem. Soc.* **112** 3270
- [38] Childs B J, Craig D C, Scudder M L and Goodwin H A 1998 *Inorg. Chim. Acta* **274** 41
- [39] König E, Ritter G, Kulshreshtha S K and Nelson S M 1982 *Inorg. Chem.* **21** 3022
- [40] Kaji K and Sorai M 1985 *Thermochim. Acta* **88** 185
- [41] Matouzenko G S, Luneau D, Molnár G, Ould-Moussa N, Zein S, Borshch S A, Bousseksou A and Averseng F 2006 *Eur. J. Inorg. Chem.* **2671**
- [42] Jeannin O, Clerac R and Fourmigue M 2007 *Cryst. Eng. Commun.* **9** 488
- [43] Holland J M, McAllister J A, Lu Z, Kilner C A, Thornton-Pett M and Halcrow M A 2001 *Chem. Commun.* **577**
- [44] Galet A, Gaspar A B, Muñoz M C, Bukin G V, Levchenko G and Real J A 2005 *Adv. Mater.* **17** 2949
- [45] Galet A, Gaspar A B, Muñoz M C, Levchenko G and Real J A 2006 *Inorg. Chem.* **45** 9670
- [46] Galet A, Gaspar A B, Agustí G, Muñoz M C and Real J A 2007 *Chem. Phys. Lett.* **434** 68