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Spin Transition Diagram of (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] Studied by EPR

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The high-spin \leftrightarrow low-spin transition in (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] was studied by EPR under hydrostatic pressure in the temperature range of 80–310 K. Two modifications of the low-spin complexes: low-pressure (LS-1) and high-pressure (LS-2) ones were revealed. The low-spin complexes are associated in domains. Under atmospheric pressure LS-1 appears or disappears at 220 K. The hydrostatic pressure shifts the transition to high temperatures. Above 410 MPa the abrupt changes of the g -factor and width ΔB of the EPR line are observed. The pressure-induced transition LS-1 \leftrightarrow LS-2 is almost independent of T up to 275 K where under pressure 420 MPa a triple point is observed. When the pressure has been decreased the reverse transition from LS-2 to LS-1 or to high spin phase (at $T > 260$ K) occurs with a large hysteresis about 95 MPa.

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1. Introduction

There are many iron(II) and iron(III) complexes in solids, in which high-spin (HS) – low-spin (LS) transitions induced by temperature, pressure or light take place [1–5]. In particular, compounds with thermal or pressure hysteresis associated with the transition are the most attractive due to a memory effect [6].

Particularly interesting is the class of thiosemicarbazones of aromatic aldehydes of iron(III) with the general formula: $M^+[\text{Fe}(\text{Th-R-Sa})_2]$ [2], where $M = \text{H}$,

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Na, Cs or 2Me-5Et-PyH and R = Cl, Br. The variety of different spin transition types occurs in these compounds. Our recent EPR studies have been focused on the low spin domain formation in the process of spin transition in Na[Fe(Th-Sa)₂] [7, 8].

In this paper we present results of EPR study of spin transitions in polycrystalline 2-methyl-5-ethyl-pyridine 5-chloro-salicylaltiosemicarbazonatoferrate(III) (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] under high hydrostatic pressure in a wide temperature range. In the complex, the Fe³⁺ ion is coordinated by two tiosemicarbazone ONC-ligands in two mutually perpendicular planes with O and S atoms in *cis* and N atom in *trans* positions [2]. The Fe[O₂N₂S₂] co-ordination polyhedron in the HS state is larger than in the LS state and strongly distorted.

2. Experimental

The powder sample of (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] was prepared as described in [2]. EPR spectra of a powder sample were taken with an X-band RADOPAN SE/X spectrometer under atmospheric pressure in the temperature range of 80–300 K. Next, the same sample was used in high-pressure EPR measurements applying a special equipment previously described [9]. The measurements were carried out at different constant temperatures changing the pressure up and down between the atmospheric pressure and 550 MPa. The temperature changes in EPR spectra at some constant pressures were recorded, too.

3. Analysis of EPR spectra and results

Because of the spin transition of iron(III) between the high-spin and low-spin states the signal observed strongly depends on both temperature and pressure. The powder spectrum of HS iron(III) complexes ($t_{2g}^3 e_g^2$, $S = 5/2$), consists in a broad single line. In the corundum resonator, used in high pressure EPR measurements, this HS signal is additionally deformed by paramagnetic impurities [9]. The resulting signal forms a background that can be described to sufficient accuracy by superposition of two Lorentzian lines. This approximation has not any physical sense; it only allows a separation of the background signal from the LS spectrum by the numerical procedure.

On cooling under atmospheric pressure a signal assigned to the LS iron(III) complexes (t_{2g}^5 , $S = 1/2$) starts appearing at about $T_c = 220$ K (called the onset temperature). The intensity of the signal gradually rises with temperature decreasing down to 80 K. A relatively small value of the linewidth at EPR signal shows [7, 8] that LS iron(III) complexes are not randomly distributed in the crystal but combined into domains. On heating, the changes in the signal did not show any hysteresis. Increasing pressure shifts this onset temperature of the transition to higher temperatures.

When the LS state of iron(III) complexes is observed the summary spectrum can be approximated by a superposition of two components:

1. LS state polycrystalline spectrum, obtained assuming the axial symmetry of g -factor and linewidth, Lorentzian line shape of the individual EPR line, and taking into account only Zeeman term in a spin Hamiltonian, and
2. the background signal represented by a superposition of two Lorentzian lines. The numerical fitting procedure is applied, from which the LS state values

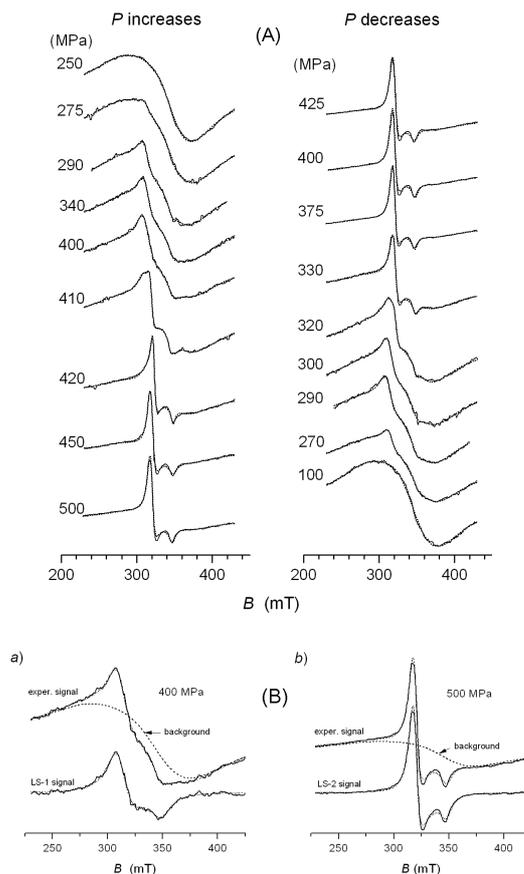


Fig. 1. (A) Pressure evolution of the experimental EPR spectrum of $(2\text{Me-5Et-PyH})[\text{Fe}(\text{Th-5Cl-Sa})_2]$ with the fitted one (dotted line) at 260 K. The left column — changes in the EPR spectrum on increasing pressure, the right column — on decreasing pressure. Fitting parameters are presented in Fig. 2. (B) Analysis of the EPR spectra recorded at 260 K under pressure 400 MPa (a) and 500 MPa (b). The experimental spectra is given by solid upper line. The lower solid line shows the LS spectrum obtained by subtraction of the background (dashed line) from the experimental curve. The dotted lines represent the best fitting data to the experimental spectrum. The fitting parameters are: $g_{\parallel} = 1.983$, $g_{\perp} = 2.216$, $\Delta B_{\parallel} = 10.9$ mT, $\Delta B_{\perp} = 15.3$ mT for 400 MPa and $g_{\parallel} = 1.989$, $g_{\perp} = 2.166$, $\Delta B_{\parallel} = 7.6$ mT, $\Delta B_{\perp} = 6.5$ mT for 500 MPa.

of g_{\perp} and g_{\parallel} , slope linewidth (ΔB_{\perp} and ΔB_{\parallel}) and intensity as well as the background data are obtained.

As an example, the pressure evolution of the spectrum at 260 K is shown in Fig. 1A. The dotted line is the best fit of a theoretical line shape to the experimental curve. The subtraction procedure of the background signal from the experimental one is shown in Fig. 1B for 400 MPa and 500 MPa. The beginning of the spin transition from HS to LS state occurs at $P_c = 275$ MPa with a similar g -factor and linewidth as that under atmospheric pressure. A further pressure increase causes a gradual rise of the intensity of LS signal, whereas g and ΔB suddenly change at 410 MPa. This indicates structural changes of domains with the LS Fe(III) complex in the LS state. The low-pressure LS-1 phase is transformed into the high-pressure LS-2 phase, which is visible in g -factor and ΔB changes (see Fig. 2). The content of the LS-2 phase quickly raises with increasing pressure and at about 450 MPa the contribution of the LS-1 phase can be neglected. On decreasing the pressure, a reverse transition from LS-2 to LS-1 occurs at a significantly lower pressure, 320 MPa, and then a transition to HS state takes place at 270 MPa. From the fitting procedure (dotted lines in Fig. 1A) the values of g_{\perp} , g_{\parallel} , and ΔB_{\perp} are obtained and shown in Fig. 2. The values of g_{\perp} complexes and ΔB_{\perp} in the LS-1 state are greater than in the LS-2 state.

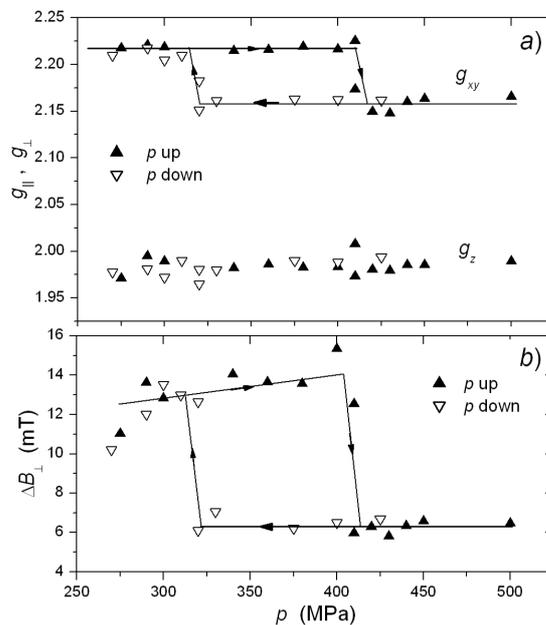


Fig. 2. The pressure dependence of the axial compounds of g -factor (a) and perpendicular slope linewidth (b) for $(2\text{Me-5Et-PyH})[\text{Fe}(\text{Th-5Cl-Sa})_2]$ at 260 K. g -factors and ΔB_{\perp} were obtained from the fitting procedure.

The pressure measurements at room temperature (294 K) at 460 MPa reveal a direct transition to the high-pressure LS-2 phase whose amount increases. When the pressure is reduced, the LS-2 signal disappears suddenly between 390 and 380 MPa.

4. Spin transition diagram

The studies of the HS \leftrightarrow LS transition at various pressure and temperature have been done. The following phase diagram of (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] has been obtained, Fig. 3. With increasing pressure, the temperature of the spin transition HS \leftrightarrow LS-1 increases with a slope coefficient (7.7 ± 0.3) MPa/K obtained from the linear regression. In the LS-1 phase, the values of $g_{\parallel} = 1.987$ and $g_{\perp} = 2.214$ are not dependent on temperature and pressure. Above 410 MPa, a new

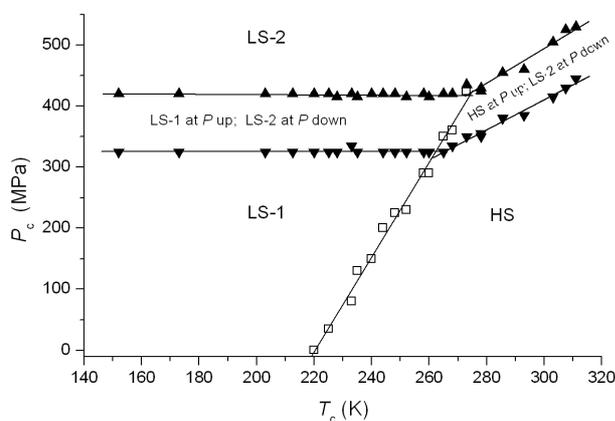


Fig. 3. The spin transition diagram of (2Me-5Et-PyH)[Fe(Th-5Cl-Sa)₂] (see the text).

low-spin phase LS-2 appears with different g -factors ($g_{\parallel} = 1.991$, $g_{\perp} = 2.164$). As shown, the transition pressure is almost independent on temperature up to 275 K and $P = 420$ MPa. This is a triple point, at which all phases exist. Above that point, the transition from the high spin phase HS to LS-2 phase is observed with a visible dependence on temperature, (2.6 ± 0.3) MPa/K. A large hysteresis (95 MPa for both LS-2 \rightarrow LS-1 and for LS-2 \rightarrow HS) is observed when the reverse transition from LS-2 to LS-1 or to HS occurs.

5. Discussion

The most unusual feature of the studied Fe(III) complex compound is the presence of the pressure-induced new crystallographic phase in the low-spin state (LS-2), both in low and high temperatures. The large hydrostatic pressure hysteresis about 100 MPa allows a superposition of specific structural changes. The latter

can be stipulated by two reasons: change in the structure fragments arrangement or change of the conformation of the co-ordination polyhedron. We suppose that the strong hydrostatic pressure reorganises the system of the hydrogen bonds in the crystal lattice and this leads to the change of the complex conformation. Inside the hysteresis the system is in a meta-stable state LS-2 or HS (LS-1), depending on the state of the sample.

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