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The study of the spin transition process in Na[Fe(Th-Sa)$_2$] by electron paramagnetic resonance*

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The crossover phenomenon in Na[Fe(Th-Sa)$_2$], a representative of a large class of the Fe(III) thiosemicarbazonates, was examined by X-band EPR in temperature range of 80–300 K and magnetisation of a polycrystalline sample was collected in the temperature range of 1.8–300 K. The main results are as follows: The appearance of low-spin (LS) complexes requires the thermal population of the ^{2}A term but the transition process is ruled by other factors. The LS complexes formed are not statistically distributed among the high-spin (HS) ones but tend to assemble in restricted spaces of the crystal lattice (domains) in which both short-range and long-range interactions of the complexes occur. The increase of co-operative interactions between the LS complexes and the enlargement of domains occur gradually with two abrupt changes. Each of the jumps has a different character; the first one is related to a redistribution of the complexes in the domains and the other to a rapid increase of the LS phase volume.

1. Introduction

Spin transitions in compounds containing 3d^4–3d^7 ions are conditioned by the closeness of electronic terms of different multiplicity, which is determined by the ligand field strength and symmetry. The conditions allowing the appearance of low-spin (LS) complexes can be achieved by inducing the thermal population of the relevant term, light induction of the metastable state of LS or by other means such of LS stabilisation, like e.g. external hydrostatic pressure.

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An essential first requirement for the spin transition is to populate LS multiplet states. Two phenomena are discussed in the literature as the important features of the process of the spin transition: the correlations between the states of a definite multiplicity being the first stage of cooperative interaction [1, 2] and the appearance of domains of the LS complexes [3] as an element of the origin of a new phase. The research into the spin transitions has a long history and mechanisms of the spin transitions have been the subject of many experimental and theoretical studies [2, 4]. However, the mechanisms have not been fully recognised yet [2] and domains have not been observed directly, their presence being inferred from a qualitative conformity of the observed inner hysteresis loops to the common theory of the hysteresis phenomena [4].

Measurements of the magnetic susceptibility, X-ray analysis, Mössbauer spectroscopy are traditionally applied for the study of the spin transitions. EPR has also been applied but up to now its role has been limited to the detection of the crossover phenomenon. As the possibilities of this very sensitive and selective method are essentially larger we have used the EPR method for the study of the spin transitions in the vast class of the thiosemicarbazonates of aromatic aldehydes of $M^+[Fe(Th\text{-}R\text{-}Sa)_2]$ type [5]. The distorted $Fe[O_2N_2S_2]$ octahedron represents the coordination polyhedron in these compounds. The changes of M^+ and R lead to diverse types of the spin transition. In this paper, we present the results of the magnetic susceptibility and EPR study of the continuous spin transition in $Na[Fe(Th\text{-}Sa)_2]$.

2. Description of experimental results

Synthesis of the $Na[Fe(Th\text{-}Sa)_2]$. A stoichiometric amount of a hot aqueous solution of $Fe(NO_3)_3.9H_2O)$ was added to a boiling aqueous solution of Na-thiosemicarbazonate. The solution was rapidly filtered and the mother solution was left for cooling. The filtered off crystalline precipitate was washed with water, alcohol and ether.

Magnetic susceptibility. The magnetic susceptibility of the powdered sample of $Na[Fe(Th\text{-}Sa)_2]$ was measured over the temperature range of 1.8–300 K using a Quantum Design SQUID-based MPMSXL-5-type magnetometer. The superconducting magnet was generally operated at a field strength ranging from 0.1 to 5 T. The SQUID magnetometer was calibrated with a palladium rod sample for which the gram magnetic susceptibility was taken as 5.30×10^{-6} cm^3g^{-1} at $T = 293.1$ K. The corrections for diamagnetism were estimated from the Pascal constants [6]. The temperature dependence of magnetic moment of $Na[Fe(Th\text{-}Sa)_2]$ presented in Fig. 1 shows that the decrease of the magnetic moment starts at about 300 K and its value gradually and very slowly diminishes down to about 50 K, then sharply decreases. The HS–LS spin transition occurs in a very wide temperature interval and can be subdivided into two intervals: 300–50 K and 50–1.8 K but even at the lowest temperatures it is not completed. In this paper, we present the results of our EPR studies of the initial processes taking place in the high-temperature interval.

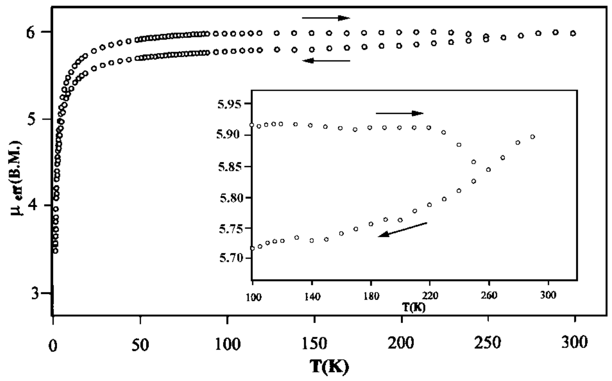

Fig. 1. The temperature dependence of the magnetic moment of Na[Fe(Th-Sa)$_2$]. Arrows indicate directions of the temperature changes. In the insert, the results in the magnetic scale are shown for the temperature range studied by EPR

Electron paramagnetic resonance. EPR measurements of Na[Fe(Th-Sa)$_2$] powder sample were performed with an X-band RADIOPAN SE/X-2547 spectrometer with 100 kHz magnetic field modulation and a home-made nitrogen cryostat in the temperature range of 80–300 K. A weak broad signal with $\Delta B \sim 120$ mT was observed at a room temperature. When the temperature is lowered, a narrower signal appears. This signal is definitely due to LS Fe(III) complexes. We begin to detect it from $T = 254$ K when its width becomes $\Delta B = 56$ mT (see Fig. 2).

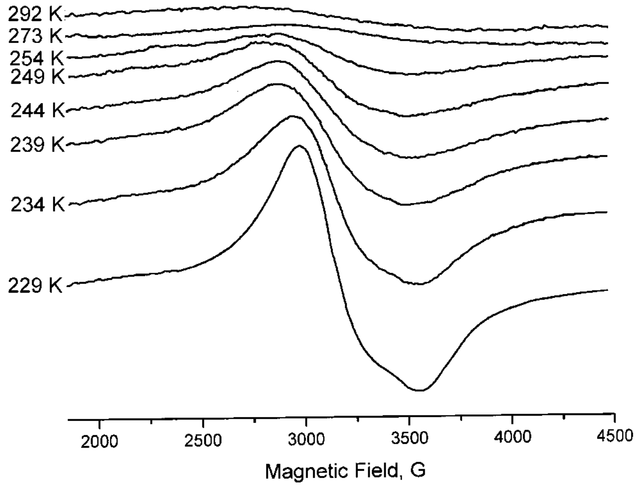

Fig. 2. Transformation of the EPR spectrum of the Na[Fe(Th-Sa)$_2$] complexes at the HS–LS transition with decreasing temperature

With decreasing temperature, the intensity of this signal increases and its linewidth decreases. Hereafter we refer to the width of an individual EPR line obtained in the procedure of fitting of the observed experimental anisotropic spectrum. The parameters of the fit are the *g*-factor components, the line shape and the width of individual components as well as the control parameter – a full width at a half maximum measured for the low field side of the signal. A line width ΔB_{pp} measured between the maximum and minimum of the first derivative of EPR signal has been chosen to characterise wide symmetrical EPR signals at high temperatures. To assess the abundance of the LS complexes, we have estimated the relative values of integral intensities of the signals. Therefore, the nature of the spin transition process can be inferred from examination of the temperature dependencies of ΔB, the signal integral intensity I and the *g*-tensor.

Table 1. Parameters of the EPR signal at selected temperatures[1]

T	ΔB_{pp}, mT	$\Delta B_{\mathrm{individ}}$, mT	$g_\perp$	$g_{\vert\vert}$
254	68	56.0	$\langle g \rangle = 2.17$	
249	63	54.0		
244	61	48.3	2.248	1.948
239	59	48.0		
234		42.0	2.248	1.948
229		32.7	2.240	1.945
224		30.0		
190		26.9	2.239	1.945
185		22.2	2.236	1.936
163		21.2	2.242	1.937

[1] A linewidth ΔB_{pp} is measured between the maximum and minimum of the first derivative the wide symmetrical EPR signals at high temperature, the $\Delta B_{\mathrm{individ}}$ corresponds to the width of an individual EPR line obtained in the procedure of fitting of the observed experimental anisotropic spectrum.

Selected data are shown in Table 1 and in Figs. 2–4. In the temperature range of 254–244 K a nearly symmetrical signal is observed with its width constantly decreasing on decreasing temperature. Starting from $T \sim$ 244–239 K the signal becomes asymmetric. Sharp decreases of $\Delta B(T)$ are observed in the T-interval 234–229 K (we shall call it the first critical temperature interval and characterise it by the mean T-value, $T_{\mathrm{c}}^{(1)} = 232$ K) and at T near 187 K (the second critical T-interval, characterised by $T_c^{(2)}$). Moreover, the changes of $\Delta B(T)$ are accompanied by changes in *g*-tensor components: in the vicinity of $T_{\mathrm{c}}^{(1)}$ the $g_\perp$ changes from 2.248±0.002 to 2.240±0.002 and $g_{\vert\vert}$ changes from 1.948±0.002 to 1.945±0.002. At 185 K $g_\perp = 2.236$ and $g_{\vert\vert} = 1.936$ and transforms correspondingly to 2.245 and 1.938 below $T_{\mathrm{c}}^{(2)}$. In the temperature intervals of 229–190 K and 185–82 K the line width ΔB (T) continues to decrease. These intervals differ in the slopes of the $\partial(\Delta B)/\partial T$ dependency (cf. Fig. 3).

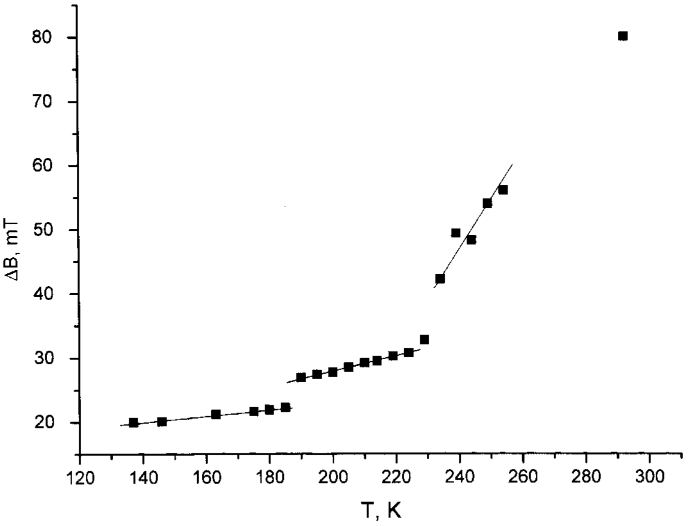

Fig. 3. The temperature dependence of the EPR line width in LS complexes

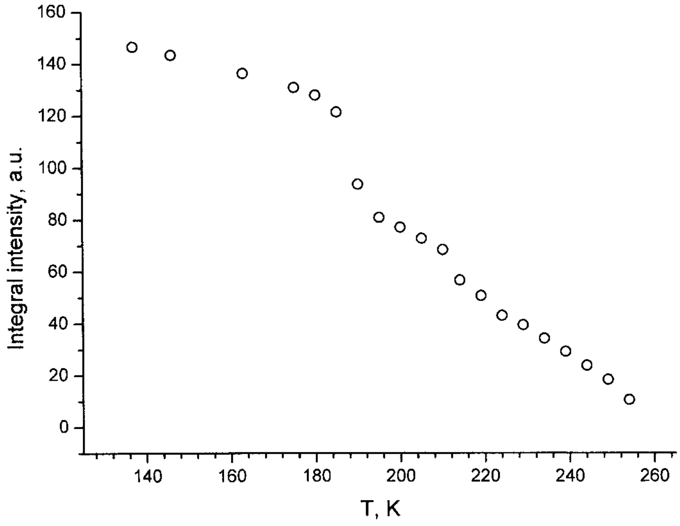

Fig. 4. The temperature dependence of the integral intensity of the EPR signal in LS complexes

The intensity of the EPR signal of the LS complexes, which, as a whole, increases with decreasing temperature, should also be sensitive to the above-mentioned changes and peculiarities in the $\Delta B(T)$ dependence. Fig. 4 shows a distinct discontinuity in $I(T)$ at $T = 187$ K. However, we were not able to detect any peculiarities in this dependence near 232 K.

3. Discussion

The main source of the information in our study is the linewidth ΔB of the EPR signal. As the LS complex has the electron spin $S = 1/2$, the line width is determined, in general, by three factors: time of paramagnetic relaxation, dipole-dipole interactions with magnetic neighbours and exchange interactions with the LS and HS partners. Our preliminary experiments under the hydrostatic pressure [7] showed that ΔB increases when the pressure is applied to the sample just at low temperatures. For example at $T = 180$ K, ΔB increases from ~ 20 mT at atmospheric pressure to 45 mT at $P = 500$ MPa. This shows directly that we do not need to analyse here a possibility of a relaxation broadening of the EPR line.

Low-spin Fe(III) complexes appear among the high-spin ones. The distance between the iron ions is of 0.63–0.64 nm. Magnetic moment of HS Fe(III) is 5.92 μ_B. Supposing a sixfold environment of LS complex and regarding that the value of its high temperature $\Delta B \sim 56$ mT, the LS complexes are considered as subject to strong enough dipole-dipole interactions with the HS complexes and to relatively weak exchange interactions. These two types of interactions are temperature independent. However, Table 1 and Figs. 2 and 3 show that ΔB essentially decreases with temperature. For example, $\Delta B = 42$ mT at 234 K, i.e. the line width decreases by 14 mT with the T decreasing by 20 K. The only reason for this ΔB narrowing can be a strengthening of the exchange interactions between the LS complexes.

An estimation of the EPR signal intensity shows that at $T = 254$ K the concentration of the LS complexes does not exceed 0.0005–0.001 mol % and, as follows from Fig. 4, the content of the LS complexes increases no more than five times after the temperature lowering down to 234 K. Such a small increase of the LS complexes concentration cannot lead to the observed increase in the exchange interactions if the LS complexes are distributed evenly. This allows us to draw an important conclusion that the appearing LS complexes are not distributed statistically in the crystal lattice of the compound but have a tendency to aggregate in limited areas (domains). This process of aggregation starts simultaneously with the onset of the HS to LS transition. Neglecting possible defects in the crystal lattice, we can consider the appearing LS complexes as not attached to any fixed positions in the structure. More than that, we can suppose that in the conditions of a definite balance between the thermal energy and stabilising factors and due to the translational symmetry of the crystal lattice, the LS state can migrate between the iron complexes. As was shown by the experiment, the aggregation of the LS complexes in domains is energetically efficient, and their amount in some limited areas of the structure increases with decreasing temperature. The enhancement of the exchange interactions allows a conclusion that the LS complexes do not occupy the neighbouring positions in the structure. We can only say that the mean distance between the LS Fe(III) complexes decreases. An availability of the structural bridges – hydrogen bonds – between complexes promotes the strengthening of exchange interactions.

A sharp increase in the LS complexes density in domains takes place at $T_c^{(1)}$. It is accompanied not only by a sharp increase in the exchange interactions, but also by a change in parameters of isolated LS complexes, already different from those of the HS complexes, and in the vicinity of T_c undergoing further changes due to the co-operative interactions between the complexes in domains. Unfortunately, no structural data are available for $Na[Fe(Th\text{-}Sa)_2]$ but we can use some parameters known for related compounds. For example, the length of the Fe-S and Fe-N bonds in $K[Fe(Th\text{-}3,5\text{-}Cl\text{-}Sa)_2]$ changes at the transition from HS compound to LS, from 0.238 nm and 0.227 nm to 0,205 nm and 0.190 nm, respectively [4]. The structural parameters of the iron complexes change at their transformation from HS into LS state. We can suppose that the structural parameters of the LS complexes in domains can differ from those in the bulk crystal being in LS state. As a result at $T_c^{(1)}$ the ligand field on the Fe(III) ion is changed. The supposition is confirmed by the above-mentioned changes in the g_i-values. It should be emphasised that this transformation occurs as a result of redistribution of the LS complex without changing their quantity, which is indicated by the fact that no anomaly is observed in the signal intensity near $T_c^{(1)}$ (see Fig. 4).

The changes of the properties of the compound studied at $T = T_c^{(2)}$ are of a completely different character. At this temperature, a new sharp increase in the exchange is accompanied by a strong increase in the number of LS complexes, confirmed by an increase in the signal intensity shown in Fig. 4. The process in question can be treated as related to an enlargement or aggregation of domains leading to the extension of the phenomena responsible for the arrangement of LS and HS complexes in domains and the electron structure of domains in large volumes of the crystal. The relative concentration of the LS complexes remains not too high and we can state, in the accordance to the magnetic susceptibility data that only a small part of the complexes are in the LS state. In the temperatures above $T_c^{(1)}$, between $T_c^{(1)}$ and $T_c^{(2)}$, and below $T_c^{(2)}$ the increase in the LS complexes number and exchange interactions in domains, has a continuous character but its rate is different.

The evolution of the EPR spectra of the LS complexes observed in the process of the spin transition allows a conclusion that the exchange interactions between LS complexes become apparent already at their smallest concentrations. On the other hand, the exchange interactions are possible only after the appearance of some LS aggregates in the crystal lattice, i.e. the exchange only allows a detection of conglomeration of LS complexes in domains. The existence of domains has not been proved earlier [3], however, an evolution of the LS state in the crossover process was certainly analysed both experimentally and theoretically [2]. We shall mention some of the works. In [1, 8] the model of the static intermolecular interactions taking into account the molecular vibrations was developed. Spiering, Willenbacher et al. [9, 10] discussed the elastic interaction between the LS ions via the image pressure. The starting point of all considerations was the observed volume change and deformations of the lattice accompanying the transition of the ions from the HS to the LS state. We assume that these approaches can be used for analysis of the phenomena in domains to show an important role of the short-range correlations between LS complexes. At present we cannot infer about the character of these correlations. The Lorentz line shape observed for EPR of the LS complexes confirms that a large number of LS complexes are involved into exchange interactions in domains. The existence of the intermolecular contacts in the structure of Na[Fe(th-Sa)$_2$] explains both possibility of the mutual influence between the iron complexes being in a definite spin state and the exchange interactions between all complexes (LS–LS, HS–HS and LS–HS). At the same time, long-range interactions have also been proved to be significant, as demonstrated by the anomalies at $T_c^{(1)}$ and $T_c^{(2)}$.

4. Conclusions

The study of the diffuse HS−LS transition in Na[Fe(Th-Sa)$_2$] by EPR allowed a direct observation of some important features of the transition, which have hitherto been questionable.

The process of transition of Fe(III) complexes to the low spin state is shown to involve the formation of domains comprising a finite number of the LS complexes. The complexes do not necessarily occupy the nearest-neighbour positions in the crystal lattice. Just opposite, it is shown that the mean density of the LS complexes in a domain increases with their total concentration.

We consider the process of the growth of domains (i.e., inclusion of new LS complexes into a domain) as being ruled by short-range interactions. These interactions, at the beginning of the HS–LS transition, have a character of pair correlations and can show some the features inherent to the co-operative system. (In the same way the pair Jahn–Teller correlations in the doped pair of JT complexes are shown to model the co-operative interactions in the concentrated JT crystal [11, 12]). And indeed, the merging of domains, or their growth and reorganisation are cooperative process and stimulated by long- range interactions. Additional weak changes in the LS complexes parameters accompany the transformation of the domain structure of the HS–LS system.

All the above-mentioned observations should be a subject of further investigation.

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