

# Phase transition in paramagnetic complexes of thiosemicarbazones of Fe(III)

V. I. Shipilov, V. V. Zelentsov, V. M. Zhdanov, and V. A. Turdakin

Moscow Physico-technical Institute

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We measured the magnetic susceptibility and the specific heat of the complexes  $Al_{0.33}[Fe(5-Clths\alpha)_2]$  (I) and  $H[Fe(5-Clths\alpha)_2]$  (II). A phase transition of the  $\lambda$  type is observed at  $T_c = 228^\circ K$  (I) or  $\sim 226^\circ K$  (II). The compounds have a low spin ( $\mu_{eff} = 2.45\mu_B$ ) at  $T < T_c$ , they have a high spin ( $\mu_{eff} = 5.62\mu_B$ ) and at  $T > T_c$ .

Compounds with anomalous magnetic properties that can be attributed to closely-lying levels with different spin multiplicities have been recently observed and actively investigated<sup>[1-13]</sup>. In this case the spin-pairing energy of the paramagnetic-ion electrons is comparable with the ligand field, and a change in the external conditions (temperature, pressure) noticeably influences the magnetic properties. Thus, Fe(III) compounds of the dialkyl-dithiocarbamate or monothio- $\beta$ -diketonate type<sup>[1-3]</sup> show a characteristic smooth decrease of the magnetic moment with decreasing temperature, which can be attributed to the presence of thermal equilibrium of low-spin and high-spin states, owing to the Boltzmann distribution of their energy levels. Some compounds of Fe(II), however, exhibit in addition to a smooth variation of the magnetic moment<sup>[4-6]</sup> a sharp transition (in the temperature interval  $10-30^\circ$ ) from a low-spin to a high-spin state. Compounds of this type include also the group of thiosemicarbazones of Fe(III), synthesized at the Chemistry Institute of the Moldavian Academy of Sciences, whose magnetic,  $\gamma$ -resonance, and radio-spectroscopic properties were investigated in<sup>[7-12]</sup>. The magnetic moment of most of them changes very abruptly, and the  $\gamma$ -resonance and EPR spectra show that inversion of the electronic levels with different multiplicity takes place near the transition temperature. The spin-equilibrium model does not describe the observed properties of such compounds, and it was therefore

proposed that a phase transition exists near the electronic-level inversion temperature.

One of the direct methods of ascertaining the presence, position, and character of the phase transition is the adiabatic method of measuring the specific heat. We chose for the measurements two polycrystalline samples of chlorine-substituted thiosemicarbazones of salicyl aldehyde of iron (III):  $Al_{0.33}[Fe(5-Clths\alpha)_2]$  (I) and  $H[Fe(5-Clths\alpha)_2]$  (II). In the temperature interval  $210-230^\circ K$ , the magnetic moment of these compounds varies very abruptly from  $2.5$  to  $5.6\mu_B$ .<sup>[7,12]</sup> The EPR spectra show that at low temperatures the ground state is  $^2T_2$ , which is split by the axial component of the ligand field into terms  $^2E$  and  $^2B_2$  in the case of tetragonal distor-

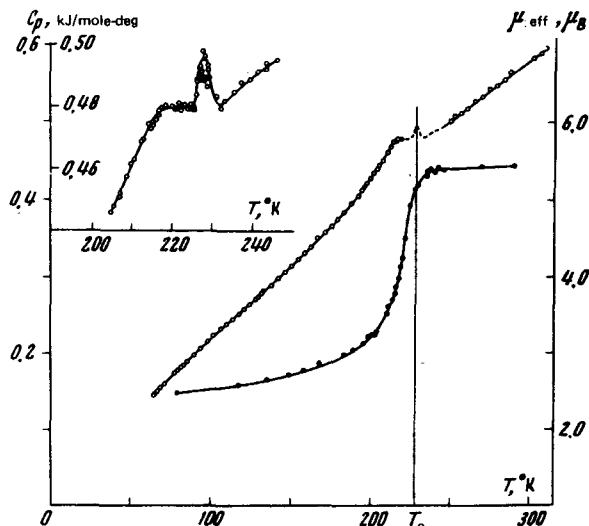


FIG. 1. Magnetic moment (●) and specific heat (○) of compound I:  $Al_{0.33}[Fe(5-Clths\alpha)_2]$ .

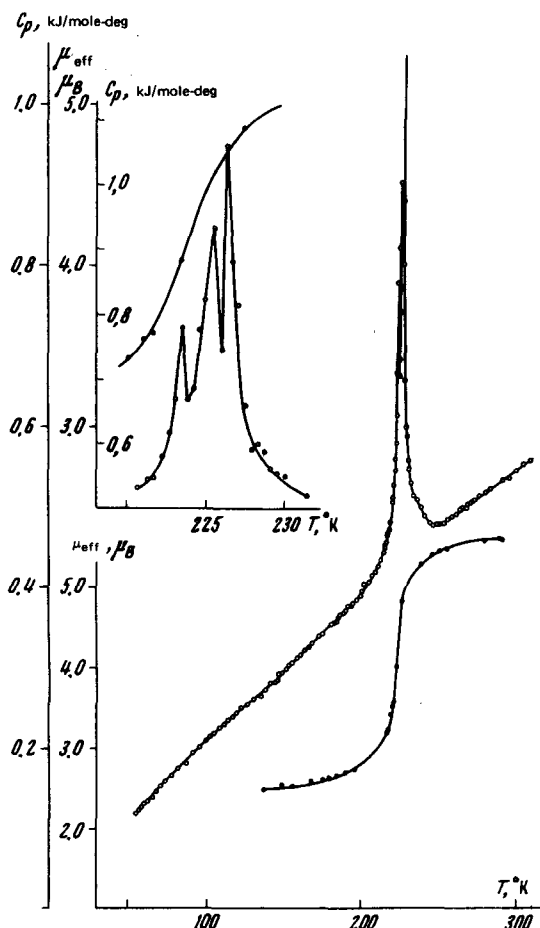


FIG. 2. Magnetic moment (●) and specific heat (○) of compound II:  $H[Fe(5-Clths\alpha)_2]$ .

Enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of the phase transition of compound I or II.

Compound	I	II
$\Delta H_{\text{tran}}^{\text{exp}}$ , kJ/mole	2.71	0.54
$\Delta H_{\text{tran}}^{\text{calc}}$ , kJ/mole	3.91	1.03
$\Delta S_{\text{tran}}$ , J/deg-mole	17.7 ± 1.4	16.2 ± 1.3

tions or  ${}^2E_1$  in the case of trigonal distortions. The lowest of them is the orbital singlet, and the  ${}^2E$  term lies 2000–3000  $\text{cm}^{-1}$  higher. In the high-spin state, the ground state is the  ${}^6A_1$  term. For the specific-heat measurements, the compounds were synthesized anew in amounts of 10  $\text{cm}^3$ . The newly measured dependences of the magnetic moment on the temperature (Fig. 1 and 2) coincide with those reported earlier.<sup>[7,12]</sup> Careful investigations have shown that the temperature dependence of the magnetic moment is fully reversible and is independent of the magnetic field in the interval 500–10 000 G.

The experimental curves of the specific heats of the compounds I and II are shown in Figs. 1 and 2. In the region of the abrupt variation of the magnetic moment, a weak smeared peak of the specific heat ( $T_c = 228^\circ\text{K}$ ) was observed for compound I, and a sharp peak with a clearly pronounced fine structure was observed for compound II ( $T_{c1} = 223.5$ ,  $T_{c2} = 225.5$ ,  $T_{c3} = 226.3^\circ\text{K}$ ). The peaks on the specific-heat curves correspond approximately to the instant of inversion of the electronic levels. For the simplest two-level model, the magnetic moment is given by

$$\mu^2 = \frac{\mu_1^2 + \mu_2^2 (g_2/g_1) \exp(-\Delta/kT)}{1 + (g_2/g_1) \exp(-\Delta/kT)},$$

where  $\mu_1$  and  $\mu_2$  are the magnetic moments of the low- and high-spin states, and  $g_1$  and  $g_2$  are their complete degeneracy, respectively, while  $\Delta$  is the distance between these energy levels.

At the level crossing point at  $\mu_1 = 2.45$  and  $\mu_2 = 5.62$  we have  $\mu = 5.01 \mu_B$ . The experimental magnetic moments (in Bohr magnetons) at the phase-transition point, namely 5.2 (228°K) for I and 4.03 (223.5°K), 4.56 (225.5°K), and 4.71 (226.3°K) for II, are in good agreement with the calculated value.

The experimental and calculated values of the enthalpy ( $\Delta H_{\text{tran}}$ ) and entropy ( $\Delta S_{\text{tran}}$ ) of the transition are listed in the table.  $\Delta H_{\text{tran}}^{\text{calc}}$  and  $\Delta S_{\text{tran}}$  were calculated by numerical integration. The lattice part of the specific heat was determined by interpolating the linear sections of the specific-heat curve adjacent to the transition re-

gion. From the value of the transition entropy we can draw certain conclusions concerning the character of the phase transition from a low-spin to a high-spin paramagnet. The change in the magnetic component of the entropy, neglecting the population of the excited states, can be expressed in the form

$$\Delta S_{\text{tran}}^{\text{mag}} = R \ln(Z_2/Z_1),$$

where  $Z_1$  and  $Z_2$  are the partition functions of the states before and after the phase transition, and are proportional to the statistical weights of these states, while  $R$  is the universal gas constant.

In our case  $\Delta S_{\text{tran}}^{\text{mag}} = R \ln 3$ . The experimentally determined values  $\Delta S_{\text{tran}}^{\text{mag}} = R \ln(7-8)$  indicates that the fraction of the degrees of freedom "frozen" upon ordering is  $R \ln(2-3)$ , i.e., 2–3 vibrational degrees of freedom are "frozen."

The possible mechanism causing inversion of the electronic levels with different spin multiplicity may be the cooperative Jahn-Teller effect due to the interaction of trigonal or tetragonal vibrations in the octahedral environment of Fe(III) with the electronic state  ${}^2T_2$ . The collective interactions (the coherent form of which is not yet clear) increase the axial distortion of the crystal field with decreasing temperature, as a result of which the lower component of the  ${}^2T_2$  term turns out to be lower than the high-spin component  ${}^6A_1$ , and the Fe(III) ion becomes low-spin.

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<sup>1</sup>A.H. Ewald, R.L. Martin, I.G. Ross, and A.H. White, Proc. Roy. Soc. **A280**, 235 (1964)

<sup>2</sup>A.H. Ewald, R.L. Martin, E. Sinn, and A.H. White, Inorg. Chem. **8**, 1837 (1969).

<sup>3</sup>M. Cox, J. Darker, *et al.*, J.C.S. Dalton trans. **12**, 1192 (1972).

<sup>4</sup>D.C. Fisher and H.G. Drickamer, J. Chem. Phys. **54**, 4825 (1971).

<sup>5</sup>E. König, G. Ritter, *et al.*, Ber. Bunsenges **76**, 393 (1972).

<sup>6</sup>E. König, G. Ritter, *et al.*, J. Chem. Phys. **56**, 3139 (1972).

<sup>7</sup>E.V. Ivanov, Candidate's dissertation, Moscow Physicotech. Inst., 1970.

<sup>8</sup>V.V. Zelentsov, G.M. Darin, E.V. Ivanov, and N.V. Gerbeleu, Teor. Eksp. Khim. **7**, 798 (1971).

<sup>9</sup>K.H. Turta, A.V. Ablov *et al.*, Dokl. Akad. Nauk. SSSR **196**, 1383 (1971)

<sup>10</sup>A.V. Ablov, K.H. Turta, V.I. Gol'danskii *et al.*, *ibid.* **196**, 1101 (1971).

<sup>11</sup>E.V. Ivanov, V.V. Zelentsov, N.V. Gerbeléu, and A.V. Ablov, *ibid.* **191**, 827 (1970).

<sup>12</sup>V.I. Shipilov, Trudy MFTI, 1972.