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Thermochimica Acta 463 (2007) 90–92
thermochimica acta
www.elsevier.com/locate/tca

Short communication

Phase transition in $Fe(C_{11}O_2H_{19})_3$ at 115.25 K

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Abstract

The heat capacity for tris-dipivaloylmethanate of iron $Fe(C_{11}O_2H_{19})_3$ within a temperature range 57–316 K has been measured by the adiabatic method. An anomaly of heat capacity has been discovered with a maximum at ∼115 K, which points to the phase transformation of the $Fe(C_{11}O_2H_{19})_3$ complex. Anomalous contributions to entropy and enthalpy have been revealed. The anomalous entropy equals $R \ln 2$ in the limits of experimental accuracy. The possible reason of phase transition is considered.

Keywords: Heat capacity; β-Diketonates; Phase transitions

1. Introduction

Tris-dipivaloylmethanate of iron $Fe(C_{11}O_2H_{19})_3$, or $Fe(DPM)_3$, belongs to the class of complex of the transition metals with β-diketones. In solid state these compounds form molecular crystals. Due to their high volatility, β-diketonates of metals are used as precursors in the processes of chemical deposition of coatings from vaporous phase (MO CVD), and MO CVD is a promising technique for production of superconducting materials [1,2], nano-sized coatings [3], etc.

As of today, thermodynamic and other physico-chemical properties of β-diketonates have not been thoroughly studied, although understanding them is crucial for optimizing MO CVD processes, calculating equilibrium characteristics and estimating stability of crystal/gas systems, etc. Reliable calculation of thermodynamic functions (enthalpy, entropy and other) requires experimental data about the heat capacity in the range of low temperatures. Predicting this information from the results of other studies (empiric approaches, simulations within the framework of lattice dynamics [4,5], etc.) is problematic because of the complex structure of β-diketonates and possible phase transitions these compounds can undergo at low temperatures [5–7].

The present work discusses the results of experimental study of the heat capacity of iron tris-dipivaloylmethanate $Fe(C_{11}O_2H_{19})_3$ in the range of low temperatures, which indicate a phase transition at 115.25 K in this compound.

2. Experimental

The $Fe(C_{11}O_2H_{19})_3$ complex was synthesized in aqueous alcohol medium by reaction of $FeCl_3{\cdot}6H_2O$ with the neutralized by NaOH ligand $HC_{11}O_2H_{19}$, all taken in stoichiometric amounts. The formed $Fe(DPM)_3$ crystals were filtered off and washed with distilled water and then recrystallized in acetone–water system. The final purification of the product was performed by sublimation in a vacuum gradient furnace at a pressure of 10^{-2} mmHg allocating the deposition zone 120–130 °C.

Visually, the $Fe(DPM)_3$ sample at room temperature is brick-red crystalline powder with a mean crystallite size of ∼0.3 mm. The melting point determined on Boetius table is 437 ± 1 K, which is in good agreement with data obtained in the literature [8]. The IR spectra and derivatogram support the conformity of the obtained compound to tris-dipivaloylmethanate of iron. According to the X-ray phase analysis, the compound is single-phase; the structure of the obtained crystals corresponds to the $Fe(DPM)_3$ structure determined in the paper [9], with lattice parameters $a = (20.325 \pm 0.008)$ Å, $b = (17.350 \pm 0.007)$ Å, $c = (23.171 \pm 0.009)$ Å, $\beta = (111.98 \pm 0.03)^\circ$; space group $C2/c$; coordination number $Z = 8$. The calculated X-ray density,

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doi:10.1016/j.tca.2007.07.004

Table 1
Experimental heat capacity of $Fe(C_{11}O_2H_{19})_3$ (molar mass: 605.659 g/mol)

T (K)	C_P (J mol^{-1} K^{-1})	T (K)	C_P (J mol^{-1} K^{-1})	T (K)	C_P (J mol^{-1} K^{-1})
57.62	210.66	111.82	472.38	211.77	692.95
61.26	225.01	115.01	505.42	216.49	705.33
64.56	237.69	115.25	511.59	221.38	715.42
67.60	248.90	118.74	484.40	226.33	727.01
70.44	260.38	120.73	475.36	231.34	738.01
73.11	271.00	122.36	473.66	236.30	747.97
75.64	280.87	125.92	473.63	241.21	758.83
78.06	290.64	126.84	475.88	246.29	769.10
80.55	299.05	130.02	482.45	251.74	783.11
82.60	309.22	132.74	489.11	257.67	796.50
84.72	316.26	133.19	489.57	264.14	809.77
84.75	317.65	138.32	503.69	270.65	824.16
86.41	323.33	143.72	517.66	274.38	834.45
87.16	326.67	148.98	531.92	277.47	842.17
89.09	333.42	154.12	545.91	277.79	841.35
89.70	337.22	159.30	560.42	282.88	853.43
94.11	353.84	164.90	575.85	284.75	857.03
94.16	354.74	170.57	592.61	288.57	866.69
98.42	372.16	175.85	604.32	291.86	873.77
99.26	375.27	181.11	619.26	294.18	879.10
101.67	383.76	186.30	630.44	299.64	890.12
104.47	396.73	191.27	644.76	300.43	893.87
104.81	399.82	196.79	658.54	305.03	902.20
108.22	418.79	202.27	670.89	310.49	915.56
109.75	432.55	207.11	683.35	316.08	929.02

according to the data of the paper [9], is (1.061 ± 0.001) g/cm^3, the experimental density (picnometric density at ambient temperature) is (1.060 ± 0.003) g/cm^3. According to the results of elemental analysis, the carbon content in the sample is 51.08% (the calculated is 51.02%), the hydrogen content is 6.03% (the calculated is 5.99%) which corresponds to the stoichiometric composition $Fe(C_{11}O_2H_{19})_3$ within the experimental accuracy.

A heat capacity of the sample within temperature range 57–316 K was measured by the adiabatic method using the installation described in the literatures [7,10]. The substance in amounts of 4.326 g was loaded into calorimetric ampoule. The molar mass (605.659 g/mol) for the molar heat capacity calculating was obtained using the formula of $Fe(C_{11}O_2H_{19})_3$. In the pulse heating mode 75 experimental points of heat capacity were measured. The obtained data are presented in Table 1. Root-mean-square deviation of the experimental points of heat capacity from the smoothed curve $C_P(T)$ is 0.13% within temperature range 57–115 K and 0.08% for 115–316 K. In the neighborhood of the phase transition (105–120 K) the 124 points have been measured by the continuous heating method. The heat capacity has been calculated using a thermogram (the time dependence of calorimeter temperature while heating in adiabatic conditions with a constant power).

The anomaly with a sharp maximum at $T_c = 115.25$ K can be observed on the experimental heat capacity $C_P(T)$ (see Fig. 1). The appearance of the anomaly testifies about the phase transformation in the compound $Fe(DPM)_3$.

The anomalous part in a maximum (76.32 J mol^{-1} K^{-1}) accounts for 17.5% of the regular heat capacity $C_{reg}(T)$ (Fig. 1). For revealing the nature of anomaly, the static magnetic susceptibility of investigated compound $\chi(T)$ has been measured by SQUID magnetometer in the range 2–300 K. In Fig. 2 it is presented in coordinates $1/\chi(T)$ and T.

As it can be seen in Fig. 2 no deviations of experimental points has been observed from Curie–Weiss law: $\chi(T) = C/(T - \Theta)$, where C is a Curie constant (4.400 ± 0.002 K cm^3 mol^{-1}), Θ is a paramagnetic Curie temperature (−0.2264 ± 0.0001 K).

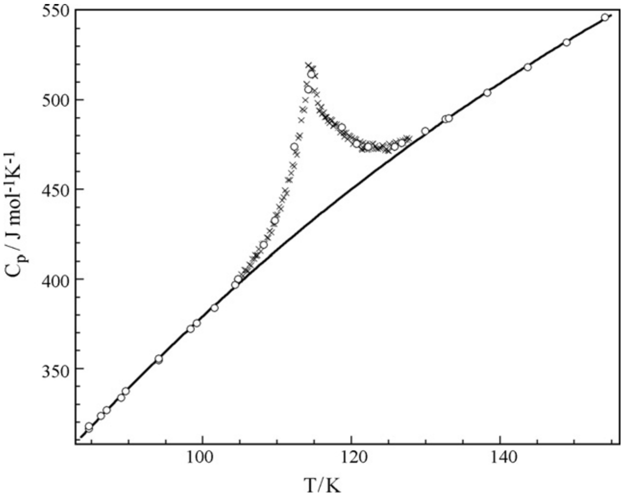

Fig. 1. Heat capacity $C_P(T)$ of compound $Fe(C_{11}O_2H_{19})_3$ in the neighborhood of phase transition: circles are experimental points obtained by the pulse heating method; crosses are experimental points obtained by the continuous heating method; solid line presents the regular heat capacity $C_{reg}(T)$.

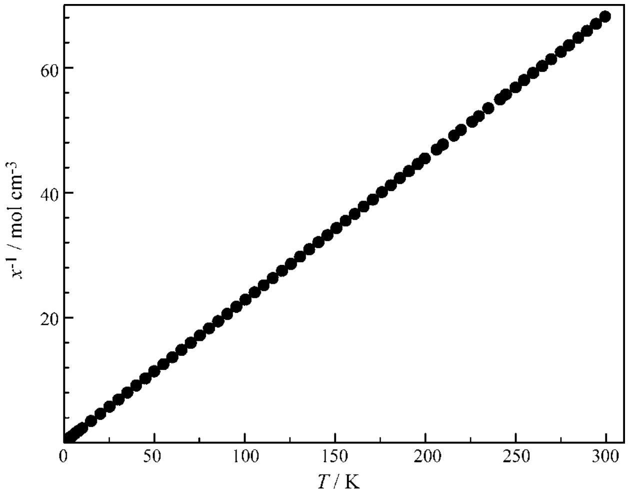

Fig. 2. Experimental reverse magnetic susceptibility $1/\chi(T)$ of the compound $Fe(C_{11}O_2H_{19})_3$ in the range 2–300 K.

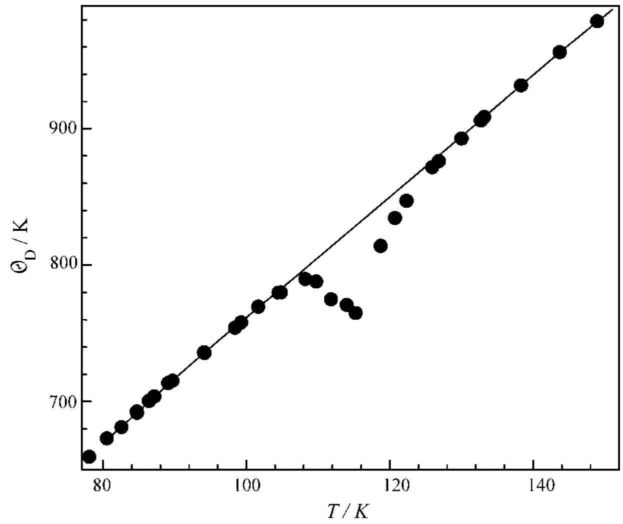

Fig. 3. Debye temperature $\Theta_D(T)$ for $Fe(C_{11}O_2H_{19})_3$ in the vicinity of phase transition: points are experimental values; a solid line is a regular behavior of $\Theta_D(T)$ Debye temperature, K.

3. Extracting anomalous contribution

From experimental $C_P(T)$ data in the range from 57 to 316 K the Debye temperature $\Theta_D(T)$ was calculated (see Fig. 3). One can see that the regular dependence $\Theta_D(T)$ is well described by a linear function, and no jump in the Debye temperature at the point of phase transition is observed. The linear dependence $\Theta_D(T)$ was taken as the regular component, from which C_{reg} was calculated. Subtracting C_{reg} from experimental heat capacity we obtain the anomalous contribution $\Delta C_P(T)$. The entropy ΔS and the enthalpy ΔH of the anomaly can be obtained by integrating $\Delta C_P(T)$ and amount to 5.75 ± 0.11 J mol^{-1} K^{-1} and 663 ± 12 J mol^{-1}, respectively. Here the uncertainties are due to experimental data scatter and uncertainty of calculation C_{reg}.

4. Conclusion

The absence of the jump in the Debye temperature at T_c together with the fact that the thermogram shows no signs of first-kind phase transition suggest that what we observe is necessarily a second-kind phase transition. Since the temperature dependence of magnetic susceptibility shows no deviation from the Curie–Weiss law (Fig. 2), we can leave out of consideration the change of the state of the magnetic ion Fe^{3+} as a cause of the observed phase transition. In other words, the observed phase transition cannot be of magnetic nature. The entropy ΔS of the transition coincides within good accuracy with the value $R \ln 2$ (5.76 J mol^{-1} K^{-1}). This ΔS of phase transition is the evidence of a possible transformation of two equally probable states (low-temperature phase) into a single state (high-temperature phase) or about phase transition of type order-disorder. One can observe phase transition with the value $R \ln 2$ for entropy normalized by one molecule. This excludes participation of methyl groups in organizing the transition, because recalculation of the value ΔS by one methyl group gives the value ΔS, which is smaller than $R \ln 2$. We suppose that in this case the phase transition can be analyzed as phase transition related to a change in the (structural or energetic) state of molecule as a whole. Whilst in the high-temperature phase molecules are indistinguishable, in the low-temperature phase they acquire distinguishing features. One of the variants may be spatial re-orientation of molecules in the low-temperature phase. The specific mechanism of this process may be related, for example, to different proton ordering in individual molecules or different ordering of methyl group orientation in different molecules.

For detailed analysis of the nature of the observed phase transition, one needs to conduct special research (X-ray, NMR, etc.).

Acknowledgement

The authors thank V.N. Ikorsky for carrying out experiment with SQUID magnetometer.

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