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The heat capacity and vibration spectra of tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III)

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Abstract

The heat capacity of compound tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III) has been measured by the adiabatic method within the temperature range 4.8–321 K. The thermodynamic functions: entropy, enthalpy and reduced Gibbs' energy have been calculated. The components of heat capacity related to intermolecular and intramolecular vibrations have been analyzed.

An anomaly has been discovered in the heat capacity with a maximum at 44.6 K. A critical change in spectral density of phonon states has been marked at the same temperature.

Keywords: Adiabatic calorimetry; Beta-diketonates; Low-temperature heat capacity; Vibration spectra; Phase transitions

1. Introduction

In solid state, beta-diketonates of metals are the crystals of molecular type. Due to their high volatility they are used in solving some important applied problems. A wide application of beta-diketonates of metals in metal–organic chemical vapor deposition techniques (MOCVD) [1] explains the interest in study of their structure, stability and thermal properties. Beta-diketonates of metals are utilized as precursors for chemical vapor deposition of different coatings and films at moderate temperatures (for example, metal and metal oxide thin films, high-T_c superconducting films) [2–6]. The data on thermodynamic functions are important for governing the equilibrium and stability characteristics of crystal–gas systems and for controlling the gas-phase technological processes.

A reliable calculation of thermodynamic functions requires the experimental data for heat capacity over a wide range of temperatures. Literature offers data on the heat capacity of only few beta-diketonates of metals (see, for example, [7–9]). Nowadays data are required on many more such compounds.

Along with obtaining thermodynamic functions by experimental measurements it is also interesting to predict them through adequate theoretical models.

This work makes a contribution to both aspects of investigating the beta-diketonates of metals. Firstly, the results are presented concerning the thermodynamic properties for the compound tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III) ($Fe(hfac)_3$ or $Fe(O_2C_5HF_6)_3$). These results were obtained by means of low-temperature adiabatic calorimetry. Secondly, the modeling of contributions to heat capacity from intermolecular and intramolecular vibrations was carried out. The best match to the experimental heat capacity was taken as the criterion of optimum at this modeling.

2. Experimental results

The complex tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III) was obtained by boiling the solution of hex-

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afluoroacetylacetone H-HFA in carbon tetrachloride CCl_4 and anhydrous $FeCl_3$. After cessation of HCl evolution, the solution was filtered and evaporated. For purification, the dry residue was recrystallized: it was dissolved in chloroform, the solution was filtered and the compound was precipitated with another solvent heptane. The precipitated beta-diketonate of metal was separated, washed with heptane and dried in a vacuum drier.

The resulting complex was additionally purified by sublimation in vacuum gradient furnace at a residual pressure of $P = 10^{-2}$ Torr with allocation of the deposition zone near 50 °C. Visually, the $Fe(hfac)_3$ sample at room temperature is a cherry-red crystal powder of mean crystallite size ~0.3 mm. The melting point determined with Boetius table is 328 K.

Chemical analysis of the purified complex for the carbon, hydrogen and fluorine content gave the following results (mass%): C, 26.55 (26.61); H, 0.28 (0.45); F, 50.28 (50.51). Within the accuracy of analysis, this gives evidence of a correspondence between the obtained composition and the formula $Fe(O_2C_5HF_6)_3$.

The results of a diffraction study shows that the sample is uniphase and its crystal structure corresponds to the $Fe(hfac)_3$ structure established in [10] with the unit cell parameters $a = (9.057 \pm 0.004)$ Å, $b = (13.424 \pm 0.005)$ Å, $c = (21.591 \pm 0.016)$ Å, $\beta = (116.71 \pm 0.02)^\circ$, space group $P2_1/C$. There are four $Fe(hfac)_3$ molecules per unit cell.

The heat capacity $C_p(T)$ has been measured by the adiabatic method within the temperature range 4.8–321 K on the installation described in [9]. The mass of sample loaded into the calorimetric ampoule was 8.9289 g. The mass of mole used in the calculation of molar heat capacity was determined from formula $Fe(O_2C_5HF_6)_3$ and equals 677.00 g. In the stepwise heating mode, 141 experimental points of the heat capacity have been obtained. Experimental values of heat capacity are presented in Table 1.

The root-mean-square deviations of experimental points from a smoothed $C_p(T)$ curve are 1.2% (5–12 K), 0.16% (12–85 K) and 0.09% (85-321 K). Entropy $S^\circ(T)$, difference of enthalpies $H^\circ(T) - H^\circ(0\,K)$ and reduced Gibbs' energy $\Phi^\circ(T)$ within the range 5–320 K were obtained by numerical integration of the smoothed $C_p(T)$ dependence. In doing this, it was assumed that below 4.8 K, where experimental data are absent, the heat capacity has no anomalous contributions and obeys the limiting Debye law (see Fig. 1).

The smoothed values of the heat capacity and the thermodynamic functions are listed in Table 2. The values of these functions at the reference temperature 298.15 K are equal to:

$$C_p^\circ(298.15\,K) = 654.9 \pm 0.6\,J\,mol^{-1}\,K^{-1},$$
$$S^\circ(298.15\,K) = 827 \pm 1\,J\,mol^{-1}\,K^{-1},$$
$$H^\circ(298.15\,K) - H^\circ(0\,K) = 113400 \pm 100\,J\,mol^{-1},$$
$$\Phi^\circ(298.15\,K) = 447 \pm 1\,J\,mol^{-1}\,K^{-1}.$$

Here, the uncertainty is due to experimental data scatter.

Table 1
Experimental heat capacity of the $Fe(hfac)_3$ complex (tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III)) (T, K; $C_p(T)$, $J\,mol^{-1}\,K^{-1}$; mol mass = 677.00 g)

T	C_p	T	C_p	T	C_p
4.800	3.993	87.777	278.0	209.723	506.1
5.863	6.492	88.448	279.5	210.317	508.2
7.561	12.53	91.985	287.0	215.989	517.7
8.932	18.83	93.246	289.3	216.271	518.6
10.248	24.98	94.616	292.2	222.376	527.8
11.830	33.50	97.180	297.3	222.561	529.2
13.815	44.16	99.440	302.3	228.589	539.6
14.671	48.88	101.636	306.2	229.034	539.5
15.387	52.80	104.130	310.7	235.006	550.4
16.457	58.38	106.555	316.4	235.332	550.0
16.893	60.51	109.536	322.6	241.525	561.2
18.403	68.35	111.727	326.3	241.544	560.7
18.527	69.23	114.875	332.9	247.675	571.5
20.089	76.80	116.994	336.3	248.051	571.2
20.370	77.97	120.315	343.6	248.053	571.6
21.796	84.61	122.657	347.7	254.486	583.6
22.468	87.84	125.850	353.1	257.460	588.5
23.705	93.82	127.723	357.1	260.832	593.9
24.661	98.17	131.486	365.1	263.395	599.1
25.923	103.9	134.088	369.5	267.091	604.3
27.002	108.4	137.079	375.8	269.262	608.9
28.713	115.6	138.144	377.3	273.276	613.7
29.330	118.5	141.939	384.3	274.163	614.8
31.633	128.3	142.645	386.0	275.167	616.9
32.014	130.5	146.280	392.5	276.466	618.4
33.936	137.9	148.193	396.1	278.929	622.9
34.446	140.5	150.937	400.9	279.381	625.0
35.163	143.2	153.733	406.6	280.586	625.4
36.201	147.4	155.892	410.4	283.035	629.6
36.866	150.8	159.138	416.7	285.158	632.7
37.538	152.8	160.941	419.8	287.494	638.1
38.787	157.7	164.666	427.1	289.585	641.1
39.253	159.2	165.891	428.8	291.837	644.9
39.855	162.1	170.321	437.2	294.034	647.7
41.703	169.2	170.795	437.8	296.136	652.9
42.289	171.0	175.857	446.4	298.372	655.5
44.594	179.3	175.870	446.9	300.399	658.7
47.655	187.5	181.526	457.5	302.655	661.7
50.504	194.9	182.351	458.2	304.618	665.4
53.403	201.8	187.154	466.4	306.896	670.2
56.817	208.8	187.311	467.7	308.797	672.3
60.416	218.3	192.481	475.7	311.116	677.0
64.217	226.8	192.991	477.7	312.936	679.5
68.223	235.5	197.921	485.1	315.290	683.0
72.801	246.1	198.682	487.4	317.037	686.1
77.905	256.8	203.703	495.4	319.691	691.7
82.640	267.2	204.496	498.1	321.015	693.0

3. Examination of heat capacity

The Debye temperature $\theta_D(T)$ was found to increase from 132 to 990 K within the temperature range 4.8–300 K and to continue to increase further. Such a behavior points to a substantial extension of vibration spectrum of $Fe(hfac)_3$ crystal over the frequency scale.

An anomaly has been discovered in the heat capacity within the temperature range 30–60 K. In order to isolate this anomaly the temperature dependence of Debye temper-

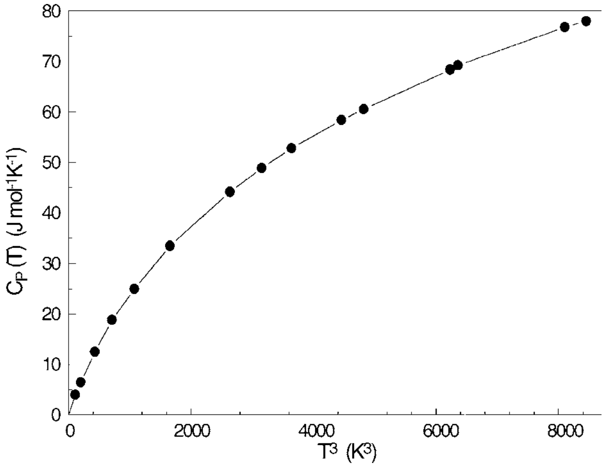

Fig. 1. Experimental heat capacity plotted as C_p(T) vs. T^3 within the range 5–20 K. Debye temperature Θ_D at $T = 4.8$ K calculated from the heat capacity according to the formula $C_p(T) = 2.4\pi^4 nR(T/\Theta_D)^3$ is 132.3 K (here n is the number of atoms in molecule and R is the gas constant).

ature θ_D(T) has been used (Fig. 2). The regular behavior of Debye temperature within the range 15–90 K has been obtained graphically. The anomalous contribution reveals itself as a flexure within the range 30–60 K with a minimum at 44.6 K. The regular heat capacity C_{reg}(T) within the temperature range 15–90 K has been calculated using the regular values of Debye temperature. The anomalous contribution ΔC_{int}(T) (Fig. 3, curve a) has been obtained as a difference between the experimental values and the regular heat capacity $\Delta C_{int}(T) = C_p(T) - C_{reg}(T)$. The amplitude of the anomaly accounts for 3% of regular heat capacity (the scattering being 0.16% within this temperature range). The anomalous contributions to entropy and enthalpy are: $\Delta S = 1.9 \pm 0.1$ J mol^{-1} K^{-1} and $\Delta H = 75 \pm 4$ J mol^{-1}.

Previously [9] an anomaly at ~60 K has also been discovered in the heat capacity of another beta-diketonate Cr(acac)$_3$ (or $Cr(O_2C_5H_7)_3$) (Fig. 3, curve b). The anomalies in heat capacities of both compounds (molecular crystals of the same

Table 2
Thermodynamic functions of the Fe(hfac)$_3$ complex (tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III)) (T, K; C°_p, S° and Φ°, J mol^{-1} K^{-1}; H°(T) – H°(0), J mol^{-1}; mol mass = 677.00 g)

T	C°_p (T)	S° (T)	H°(T) – H°(0)	Φ° (T)
5	4.51	1.50	5.64	0.37
10	23.96	9.59	70.7	2.52
15	50.67	24.26	256.2	7.18
20	76.34	42.41	574.8	13.67
25	99.64	61.96	1015	21.36
30	121.6	82.07	1568	29.80
35	142.6	102.4	2229	38.72
40	162.4	122.8	2993	47.95
45	180.0	143.0	3851	57.39
50	193.7	162.7	4787	66.94
55	205.2	181.7	5785	76.51
60	216.9	200.0	6839	86.05
65	228.8	217.9	7953	95.50
70	239.6	235.2	9125	104.9
80	261.1	268.6	11630	123.3
90	282.7	300.6	14350	141.2
100	303.0	331.5	17280	158.7
110	323.2	361.3	20410	175.8
120	342.5	390.2	23740	192.4
130	361.8	418.4	27260	208.7
140	381.0	445.9	30970	224.7
150	399.4	472.8	34870	240.3
160	418.2	499.2	38960	255.7
170	436.4	525.1	43240	270.8
180	454.3	550.6	47690	285.6
190	472.1	575.6	52320	300.2
200	490.0	600.3	57130	314.6
210	507.3	624.6	62120	328.8
220	524.6	648.6	67280	342.8
230	541.5	672.3	72610	356.6
240	558.3	695.7	78110	370.3
250	575.1	718.8	83770	383.7
260	593.0	741.7	89620	397.1
270	608.9	764.4	95630	410.3
280	624.7	786.9	101800	423.3
290	641.6	809.1	108100	436.2
298.15	654.9	827.3	113400	446.7
300	657.9	831.1	114600	449.0
310	674.8	852.9	121300	461.7
320	691.2	874.6	128100	474.3

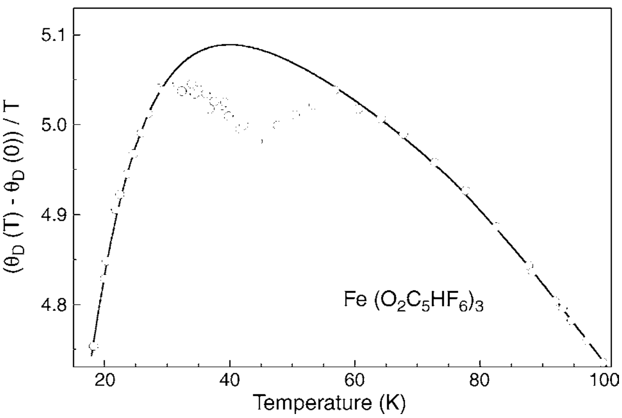

Fig. 2. The experimental heat capacity in coordinates $[\Theta_D(T) - \Theta_D(O)]/T$ on T (circles). The line is a suggested regular behavior.

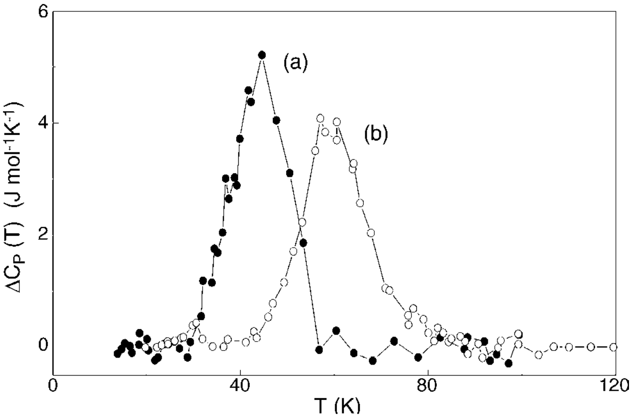

Fig. 3. The anomalies in the heat capacity of Fe(hfac)$_3$ (curve a) and Cr(acac)$_3$ (curve b).

type, containing the different metal atoms and the different substituents in ligand) are similar in the shape of $\Delta C_{int}(T)$ dependence.

It is possible that the anomalies in both compounds are of the same origin.

4. Examination of vibrations

In this work, the analysis of the intermolecular and intramolecular vibration spectra of investigated compound $Fe(hfac)_3$ is carried out, using the obtained thermodynamic data. The analysis is performed with the assumption that there is no interaction between the intermolecular and intramolecular vibrations.

The spectrum of intermolecular vibrations is calculated theoretically by means of the lattice dynamics method with optimization of the unit cell shape and the positions of molecules in the cell to the equilibrium shape at given temperature and normal pressure (for details, see [11,12]). The initial parameters necessary to calculations (the relative coordinates of mass centers and the angular variables describing the orientation of all molecules in a unit cell) were obtained from original structural data [10]. Using the optimal parameters, the dynamic matrix has been built and the spectra of intermolecular (external) vibrations at different temperatures within the range 5–320 K have been found.

These spectra have been used for calculating the corresponding contribution to heat capacity $C_{ext}(T)$. The calculated heat capacity $C_{ext}(T)$ approaches its limit (Dulong and Petit value) at ~50 K already. At 320 K, it amounts to ~15% of total heat capacity $C_p(T)$.

The contribution to heat capacity $C_{int}(T)$ from intramolecular vibrations has been obtained as a difference:

$$C_{int}(T) = C_p(T) - C_{ext}(T) \qquad (1)$$

(which is true in the absence of interaction between intermolecular and intramolecular vibrations). The contribution $C_{int}(T)$ increases from 0 (at 0 K) and reaches ~85% of total heat capacity $C_p(T)$ at 320 K. In this temperature range it is still far from the Dulong and Petit limit.

The vibration spectrum of molecule $Fe(hfac)_3$ (intramolecular spectrum) has been obtained by solving the Schrödinger equation in the harmonic approximation (for the method, see [11,12]) with subsequent variation of parameters. As the initial parameters, the data for isostructural compounds of this class have been taken (coordinates of atoms in molecule and force constants of interatomic interactions [10,13,14]).

The solution of Schrödinger equation gives the first approximation: 123 frequencies corresponding to internal vibrations of $Fe(hfac)_3$ molecule. Further, the variation was carried out for those force constants of interatomic interaction which are responsible for the frequency range below ~250 cm^{-1} (because only those frequencies contribute to heat capacity in the investigated temperature range). On variation, the best agreement between the contribution $C_{int}(T)$ obtained as a difference (1) and heat capacity calculated from intramolecular spectrum in the range 5–320 K was taken as the criterion of optimum.

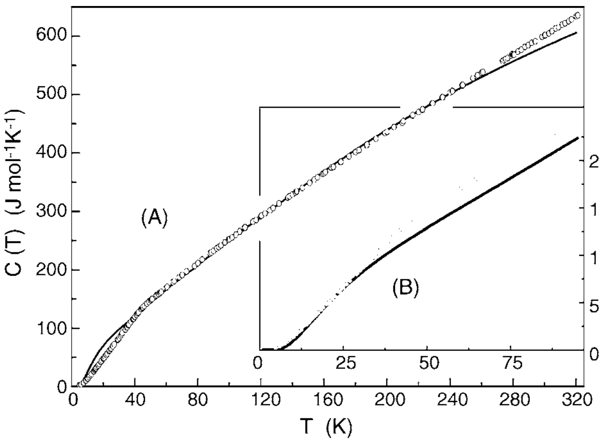

Fig. 4. The heat capacity due to intramolecular vibrations. Continuous curve presents the heat capacity calculated using the optimal force constants. Points present the contribution $C_{int}(T)$. Plot A shows the agreement with representative points for the range ~40–280 K; plot B shows the agreement with representative points for the range ~5–40 K.

As a result the spectrum A has been obtained which gives a good agreement with representative points in the temperature range 40–280 K (Fig. 4, plot A). (The deviation above 280 K comes from anharmonic vibrations in low frequency region of intramolecular spectrum.)

Another spectrum B gives a good agreement with representative points in the range 5–40 K (Fig. 4, plot B).

Hence, two solutions have been found which adequately depict the temperature dependence of contribution $C_{int}(T)$ within two ranges: just above the anomaly in heat capacity

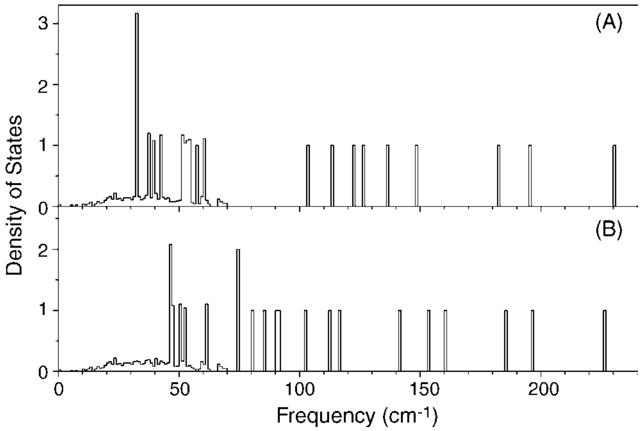

Fig. 5. Total density of states per 1 cm^{-1} (for intermolecular and intramolecular vibrations) in low frequency range normalized to number of modes for one molecule. The plot A presents the intramolecular spectrum for the temperature range 40–280 K. The plot B presents the intramolecular spectrum for the temperature range 5–40 K. The intermolecular spectrum calculated at 45 K can be seen on both plots as a solid background at the lower left.

and below. The corresponding densities of states (in the frequency range below ∼250 cm^{-1}) are presented in Fig. 5.

5. Phase transition

The performed analysis of both the heat capacity and the vibrations has revealed that the molecular crystal Fe(hfac)_3 shows separate values of parameters in temperature ranges ∼5–40 and ∼40–320 K. Two different intramolecular spectra have been determined within these two ranges. The change from one spectrum to another is accompanied by the anomaly in heat capacity.

Hence, it might be concluded that there are two distinct phases within two temperature ranges. The anomaly in heat capacity marks a phase transition at 44.6 K. Tentatively the observed phase transition is assumed to be a manifestation of some interatomic modification.

6. Summary

The heat capacity of molecular crystal tris(1,1,1,5,5,5-hexafluoro 2,4-pentanodionate) iron(III) has been measured.

Based on the experimental data, the Debye temperature and thermodynamic functions (entropy, enthalpy and reduced Gibbs' energy) have been calculated in the range 5–320 K.

The analysis of intermolecular and intramolecular vibration spectra for this molecular crystal has been carried out.

The phase transition has been discovered in the investigated molecular crystal. This phase transition revealed itself by the change of intramolecular vibration spectrum and the anomaly in heat capacity at 44.6 K.

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