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Heat capacity and Raman spectra of $Cr(C_5H_7O_2)_3$ at low temperature

V.N. Naumov *, M.A. Bespyatov, T.V. Basova, P.A. Stabnikov, I.K. Igumenov

Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, Prospect Akademika Lavrentieva 3, 630090 Novosibirsk, Russia

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Abstract

The heat capacity of $Cr(C_5H_7O_2)_3$ has been measured by the adiabatic method within the temperature range 5–320 K. An anomaly with a maximum at ∼60 K has been discovered which points to the phase transformation of the compound. Anomalous contributions to entropy and enthalpy have been revealed. The thermodynamic functions (entropy, enthalpy and reduced Gibbs energy) at 298.15 K have been calculated using the obtained experimental heat capacity data. The Raman spectra have been measured in the frequency range 60–400 cm^{-1} and in the temperature range 5–220 K. It has been discovered that a new line (109 cm^{-1}) appears at ∼60 K. The nature of these peculiarities in heat capacity and in Raman spectra is discussed.

Keywords: Heat capacity; Raman spectra; β-Diketonates; Phase transitions

1. Introduction

Tris-acetylacetonate (pentane-2,4-dionate) of chromium $Cr(C_5H_7O_2)_3$ belongs to the complex of transition metals and β-diketone. 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). Now 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 such knowledge is essential for optimizing MO CVD processes, calculating equilibrium characteristics and estimating the stability of crystal–gas systems. The reliable calculation of thermodynamic functions (enthalpy, entropy and other) requires the experimental data on heat capacity in the low temperature range. The predicting of this information from the results of other studies (empiric approaches, simulations within the framework of lattice dynamics [4,5], etc.) is difficult because of the complex structure of β-diketonates and possible phase transitions these compounds can undergo at low temperatures [5–7].

In [8] the heat capacity of $Cr(C_5H_7O_2)_3$ was obtained in the range 80–300 K. In this work, the investigations of heat capacity for this compound in the range 5–320 K and besides the Raman spectra in the range 5–220 K are presented.

2. Sample

Chromium tris-acetylacetonate (pentane-2,4-dionate) $Cr(C_5H_7O_2)_3$ (or $Cr(AA)_3$) was obtained by the method given in [9]. As initial materials, $CrCl_3{\cdot}6H_2O$ and acetylacetonate (of purity higher then 99%) were used. The final purification was carried out by double sublimation in a vacuum gradient furnace ($P = 10^{-1}$ Torr) with separating the precipitation zone of 140–150 °C.

By visual inspection the $Cr(AA)_3$ sample is a crystalline powder with a mean crystallite size 0.3–0.5 mm, dark violet at the room temperature. The melting point determined on a Boetius table is 216 °C (489 K), which is in good agreement with data obtained in [9]. According to X-ray phase analysis, the compound is single-phase; the structure of obtained crystals corresponds to the $Cr(AA)_3$ structure determined in [10] with lattice parameters $a = 14.031 \pm 0.009$ Å, $b = 7.551 \pm 0.005$ Å, $c = 16.379 \pm 0.011$ Å and $\beta = 99.06 \pm 0.02°$; space group $P2_1/C$. The measured density of $Cr(AA)_3$ is $1.374 \pm 0.003\ cm^{-3}$; the X-ray density (according to [10]) is $1.362 \pm 0.01\ cm^{-3}$. The derivatogram and the examination of IR spectra show

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[*] Corresponding author. Tel.: +7 3832 309765; fax: +7 3832 309489.
E-mail address: vn@che.nsk.su (V.N. Naumov).

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the obtained compound to correspond to the class of tris-acetylacetonate of metals.

3. Experimental results

The heat capacity $C_P(T)$ of the sample Cr(AA)$_3$ was measured by the adiabatic method on the installation described in [11] using the demountable calorimeter [12]. 7.539 g of substance was loaded into calorimeter. The calculated molecular weight (from the formula $Cr(C_5H_7O_2)_3$) is 349.324 g. The heat capacity has been measured at 107 points in the range 5–320 K. The obtained data are presented in Table 1.

The root-mean-square deviations of experimental points from a smoothed $C_P(T)$ curve are 0.87% (5–14 K), 0.11% (14–105 K) and 0.033% (105–320 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. The values of these functions at the reference temperature 298.15 K are:

$$C_P^\circ(298.15\,\mathrm{K}) = 430.34 \pm 0.14\,\mathrm{J\,mol^{-1}\,K^{-1}},$$

$$S^\circ(298.15\,\mathrm{K}) = 509.06 \pm 0.40\,\mathrm{J\,mol^{-1}\,K^{-1}},$$

$$H^\circ(298.15\,\mathrm{K}) - H^\circ(0\,\mathrm{K}) = 74,976 \pm 34\,\mathrm{J\,mol^{-1}},$$

$$\Phi^\circ(298.15\,\mathrm{K})^* = 257.59 \pm 0.32\,\mathrm{J\,mol^{-1}\,K^{-1}}.$$

$$\left({}^*\Phi^\circ(T) = S^\circ(T) - \frac{H^\circ(T) - H^\circ(0)}{T} \right)$$

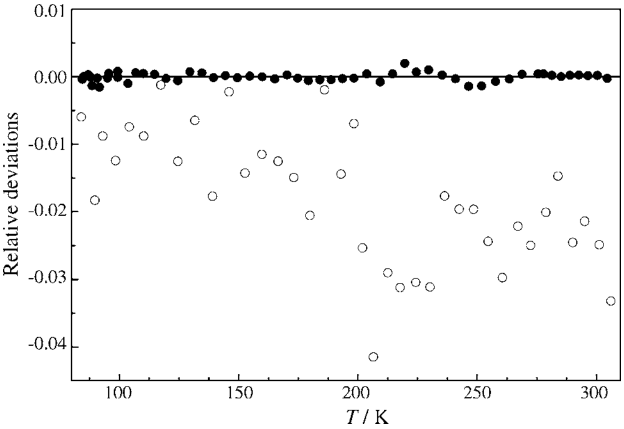

Fig. 1. Relative deviations of data [8] (the empty circles) from data obtained in the present work (the black circles).

Table 1
Experimental values of heat capacity for $Cr(C_5H_7O_2)_3$; molecular weight = 349.324 g

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})
4.90	1.148	64.15	136.960	159.87	289.93
6.17	2.135	65.54	139.617	165.11	295.59
7.27	3.324	67.85	144.650	170.26	301.31
8.70	5.192	70.92	150.922	174.76	305.92
10.37	7.709	71.78	152.869	179.21	310.45
12.37	11.292	75.78	161.568	184.02	315.44
14.67	15.813	75.84	161.530	188.75	320.27
17.00	20.742	76.87	164.109	193.51	325.12
19.75	26.829	79.05	168.715	198.29	329.94
22.21	32.260	80.06	170.690	203.71	335.55
23.22	34.529	81.28	173.158	209.36	340.75
24.48	37.466	82.06	175.055	214.53	346.27
24.55	37.584	83.26	177.408	219.64	351.86
25.99	40.946	84.38	179.572	224.51	356.22
27.39	44.233	84.96	180.827	229.67	361.44
27.85	45.338	86.91	184.813	235.31	366.76
29.83	50.223	87.94	186.773	240.88	372.10
30.57	52.013	88.47	187.582	246.38	377.18
31.91	54.954	90.71	192.115	251.83	382.68
34.08	60.062	91.61	193.563	257.71	388.87
36.42	65.822	94.95	200.008	263.50	394.88
37.30	68.088	95.50	201.141	268.77	400.54
41.15	77.448	99.24	207.839	275.50	407.45
42.87	81.837	99.28	207.718	277.87	409.89
43.47	83.185	103.58	214.817	281.32	413.33
45.92	89.529	106.80	220.428	285.19	417.22
46.92	92.225	110.04	225.532	288.93	421.14
49.30	98.412	114.71	232.636	292.64	424.92
51.32	103.881	119.52	239.528	296.43	428.72
53.16	108.898	124.45	246.370	300.42	432.75
55.97	117.049	129.50	253.520	304.53	436.63
57.04	120.291	134.54	260.040	308.77	440.79
58.09	122.636	139.45	266.030	313.07	444.86
60.55	128.556	144.36	272.099	317.49	448.89
60.56	128.908	149.43	278.014	321.88	453.39
63.91	136.267	154.65	284.092		

Here the uncertainties are due to experimental data scatter.

The heat capacity below 4.9 K was calculated from the formula: $C_P(T) = 2.4\pi^4 nR(T/\Theta_D)^3$, here n is the number of atoms in molecule, R the gas constant and $\Theta_D(0)$ is Debye temperature at 4.9 K. The obtained value $\Theta_D(0)$ is 204.6 K.

In Fig. 1, the deviations of data [8] from our smoothed values $C_P(T)$ are presented in the range 80–300 K. The heat capacities differ by ∼1% in the range 80–200 K and by ∼2.5% above 200 K.

The observed difference in heat capacity can possibly be attributed to different methods of production and purification of investigated compound.

Entropy and enthalpy at 298.15 K obtained in [8] are less then our values by 2 and 1.7% correspondingly. We suppose there are two reasons for this difference. First, extrapolation of experimental heat capacity data [8] to 0 K was carried out by means of semi-empirical Krestov–Yacimirsky rule. Second, the above-mentioned difference between heat capacities in the range 80–300 K results in the difference between thermodynamic functions.

The Debye temperature $\Theta_D(T)$ increases from 204 to 1470 K within the temperature range 5–320 K. Such a strong dependence of Θ_D on temperature points to a large extension of vibration spectrum of Cr(AA)$_3$ crystal. At 320 K the heat capacity reaches only ∼40% of limiting value and continues to increase. This is an evidence of high boundary frequency and a considerable density of modes in a high-frequency region of phonon spectrum.

The anomaly with a maximum at ∼60 K has been discovered on the heat capacity curve below 90 K.

One more experimental series has been made in an interval 20–90 K which includes area of anomaly. Data of these two

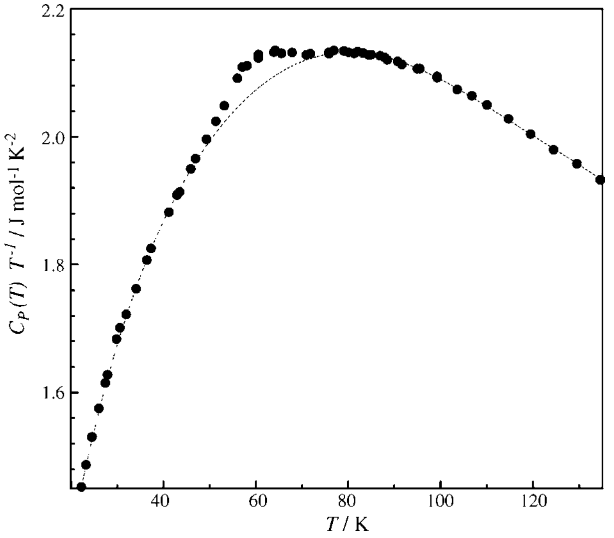

Fig. 2. Experimentally measured heat capacity plotted as $C_P(T)/T$ vs. T. The abnormal behaviour of heat capacity is observed in a neighbourhood 60 K.

series do not find out a regular deviation between them. We do not observe of explicit indications of first-kind phase transition. An anomaly is observed in Fig. 2 in coordinates (C/T)–T.

To extract the anomalous component the dependence $\Theta_D(T)$ was used. Debye temperature $\Theta_D(T)$ increases in the anomalous region. We compensated this increase by a linear function $L(T)$. The linear function is obtained by a least square method (in the range 30–90 K). She corresponds to carrying out direct through the points Θ_D(31.91 K) and Θ_D(84.38 K). The difference between $\Theta_D(T)$ and $L(T)$ is shown in Fig. 3. This difference shows a diversion from linear behaviour $\Theta_D(T)$.

The solid line presents the suggested regular run $\Theta_D(T)$. The anomalous contribution to heat capacity manifests itself as a sag in the range 45–70 K. The solid line in Fig. 3 shows a regular course, guessed by us, $\Theta_D(T)$. The regular heat capacity $C_{reg}(T)$ in the range 20–90 K was calculated using the regular values of Debye temperature. The difference between experimental and regular values $\Delta C(T)$ is presented in Fig. 4.

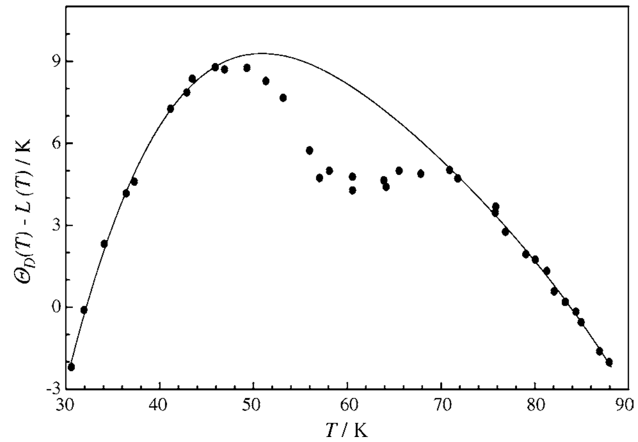

Fig. 3. Difference between Debye temperature $\Theta_D(T)$ and the linear curve $L(T)$. Points—experiment; a solid line—regular course $\Theta_D(T)$.

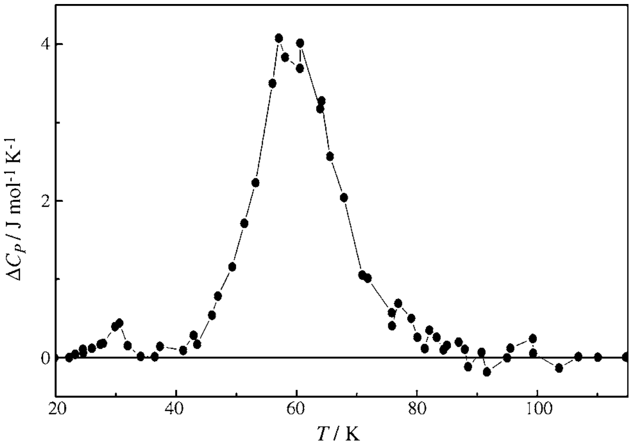

Fig. 4. Anomalous contribution to heat capacity of $Cr(AA)_3$ in the range 20–90 K.

The amplitude of anomaly is 3.2% of regular heat capacity. Anomalous contributions to entropy and enthalpy are $\Delta S = 1.2 \pm 0.05$ J mol^{-1} K^{-1} and $\Delta H = 72 \pm 1$ J mol^{-1}. One unit cell of $Cr(AA)_3$ contains four molecules. The anomalous entropy ΔS related to one unit cell is 4.8 J mol^{-1} K^{-1}. The anomaly is supposed to relate to the change in mutual arrangement of molecules in unit cell. Molecule contains six methyl groups. If the anomaly is bound to ordering methyl groups, then the value of entropy should be $\Delta S = 7.2$ J mol^{-1} K^{-1}.

Earlier we measured the static magnetic susceptibility $\chi(T)$ of studied compound $Cr(AA)_3$ in the temperature range 2–300 K [11]. In whole temperature range the obtained experimental data showed no deviation of $\chi(T)$ dependence from Curie–Weiss law. This means that there is no change in magnetic state of Cr^{3+} ion and the observed anomaly in heat capacity cannot be of magnetic nature.

To find out the nature of this anomaly the Raman spectra were investigated. The Raman spectra were recorded with a Triplemate, SPEX spectrometer equipped with an O-SMA, Si-diode array. The 633 nm, 50 mW line of a He–Ne-laser was used for the spectral excitation. The measurements were carried out in the frequency range 60–400 cm^{-1} and in the temperature range 5–220 K. For the measurements at low temperature the sample was placed on the cold finger of helium cryostat (APD Cryogenic Inc.). The temperature was fixed with the accuracy ±0.1 K. The obtained Raman spectra are presented in Fig. 5.

In the range 60–100 cm^{-1}, when temperature is decreasing, the wide lines are splitting into distinct components, their frequencies are shifting and their relative intensities practically are not decreasing which supports their belonging to the spectrum of crystal vibrations. Along with this, in the crystal modes we observed no changes pointing to a change in crystal structure of compound. Also, when temperature is decreasing, the intramolecular vibrations behave in usual manner; therefore, no change in structure of molecule happens.

In the range between crystal and molecular vibrations (100–150 cm^{-1}), when temperature decreases down to 60–70 K, a new line 109 cm^{-1} appears which was not observed at higher temperatures. In low-temperature Raman spectra of Ga- and Al-

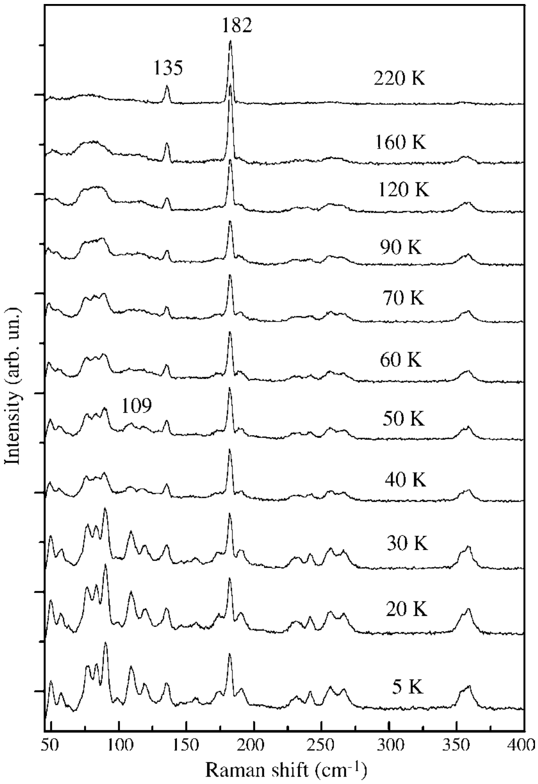

Fig. 5. Raman spectra of $Cr(AA)_3$.

β-diketonates investigated in [13], the torsion vibrations of CH_3 methyl groups were identified in the same frequency diapason (100–150 cm^{-1}). We can suppose that a new line appearing at low temperature is the line of methyl group torsion vibrations. This new line appears just at temperature which is close to maximum of anomaly in heat capacity (∼60 K).

From a temperature dependence of probability of thermal excitement of vibration modes with energy E (from Einstein function), it follows that this probability changes most quickly at temperature $T = E/3$ (see [14]). The mean energy of investigated methyl group torsion vibrations is ∼180 K. The most quick change of their thermal excitement probability falls on temperature 180/3 = 60 K. So, as temperature decreases down to ∼60 K, the torsion vibrations of methyl groups die out sharply.

Phase transitions of structural ordering happen just at that temperature where the thermal excitement of corresponding degrees of freedom changes sharply. Just at this temperature the anomaly in heat capacity of $Cr(AA)_3$ was found. Thus one can believe that at ∼60 K the phase transition resulting from ordering methyl groups (or molecules) occurs (under some weak interaction in this substance).

4. Conclusion

The experimental heat capacity of $Cr(AA)_3$ in the temperature range 5–320 K is presented for the first time. The thermodynamic functions (entropy, enthalpy and reduced Gibbs energy) are calculated at reference temperature 298.15 K. In the range 20–90 K the anomaly in heat capacity was discovered pointing to the phase transition.

The Raman spectra of $Cr(AA)_3$ have been investigated in the frequency range 60–400 cm^{-1} and in the temperature range 5–220 K. It was established that when temperature decreases down to ∼60 K, the new line at 109 cm^{-1} appears in the spectrum. This line can be attributed to the torsion vibrations of CH_3 methyl groups.

The assumption is given on the nature of observed peculiarities in the heat capacity and Raman spectra.

References

[1] Yu.D. Tretyakov, E.A. Goodilin, Russ. Chem. Rev. 69 (2000) 1–34.
[2] H. Zama, N. Tanaka, T. Morishita, J. Cryst. Growth 221 (2000) 440–443.
[3] Won-Jun Lee, Sa-Kyun Rha, Seung-Yun Lee, et al., Thin Solid Films 305 (1997) 254–258.
[4] V.P. Shpakov, J.S. Tse, V.R. Belosludov, R.V. Belosludov, J. Phys. Condens. Matter 9 (1997) 5853.
[5] V.N. Naumov, G.I. Frolova, M.A. Bespyatov, N.A. Nemov, P.A. Stabnikov, I.K. Igumenov, Thermochim. Acta 436 (2005) 135–139.
[6] M.N. Zhilina, N.V. Karyakin, V.A. Maslova, K.G. Shvetsova, G.I. Busygina, P.N. Nikolaev, Russ. J. Phys. Chem. 61 (1987) 1633–1634.
[7] V.N. Naumov, A.V. Seryakov, G.I. Frolova, V.V. Nogteva, P.A. Stabnikov, I.K. Igumenov, M.A. Bespyatov, Chem. Sustainable Dev. 10 (2002) 733–738.
[8] T.P. Melia, R. Merrifield, J. Chem. Soc. (A) 11 (1968) 2819–2820.
[9] B.E. Bryant, W.C. Fernelius, Inorg. Synth. 5 (1951) 188.
[10] B. Morosin, Acta Cryst. 19 (1965) 131.
[11] V.N. Naumov, G.I. Frolova, V.V. Nogteva, P.A. Stabnikov, I.K. Igumenov, Russ. J. Phys. Chem. 74 (2000) 1579.
[12] V.N. Naumov, V.V. Nogteva, Instrum. Exp. Techn. 28 (1985) 1194–1199.
[13] B.A. Kolesov, I.K. Igumenov, Spectrochim. Acta A 40 (1984) 233.
[14] V.N. Naumov, G.I. Frolova, V.V. Nogteva, P.A. Stabnikov, V.A. Nadolinny, Y.G. Shvedenkov, I.K. Igumenov, Chem. Sustainable Dev. 8 (2000) 231–235.