

## Specific Heat of Cr(AA)<sub>3</sub> in the Region of Solid-Phase State Temperatures

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### Abstract

Specific heat at a constant volume  $C_V(T)$  and linear anharmonic contribution into specific heat  $AT$  for chromium *tris*-acetylacetonate Cr(AA)<sub>3</sub> within temperature range from 185 K till the melting point at 489 K are calculated. This calculation is based on experimental specific heat for this compound within the range of 5–320 K, analysis of the role of different regions of the phonon spectrum in the formation of crystal heat capacity and a special method to approximate the harmonic part of heat capacity on the basis of its high-temperature expansion (effective sum method).

### INTRODUCTION

Beta-diketonates of transition metals due to their high volatility are widely used in practice to deposit metal coatings, separate and purify metals and for some other purposes. For directed synthesis of beta-diketonates with the desirable characteristics it is necessary to know their physicochemical properties including specific heat. The data on specific heat in a wide temperature range are necessary to calculate reliably integral thermodynamic functions: enthalpy, entropy, *etc.* that in turn are necessary to investigate equilibrium characteristics of the crystal–gas system and the stability of these volatile compounds. However, till now there are no data available on specific heat of beta-diketonates in the whole range of solid phase existence.

Low-temperature specific heat is measured by means of adiabatic technique with a high accuracy. Modern methods that are applied to analyse its functional behaviour [1] allow one in some cases to calculate specific heat  $C_V(T)$  till the melting point. In the present work, specific heat  $C_V(T)$  is measured within the range of 5–320 K and constant-volume specific heat  $C_V(T)$  is calculated, along with linear anhar-

monic contribution into specific heat  $AT$  within 185–489 K temperature range (till the melting point). These calculations are based on our experimental data, some data on the phonon spectrum of the compound under consideration, and a special approximation technique for the harmonic part of specific heat, *i. e.* effective sum method (ESM) which is described in the Appendix.

### EXPERIMENTAL SPECIFIC HEAT

Specific heat  $C_p(T)$  of chromium *tris*-acetylacetonate Cr(AA)<sub>3</sub> is measured by adiabatic method in 103 points of the temperature range of 5–320 K using a set-up characterized in [2, 3]. Mean square deviation of experimental points from smoothed curve is 0.87 % within the range 5–14 K, 0.11 % within 14–105 K and 0.03 % for 105–320 K. Experimental specific heat is shown in Fig. 1. Specific heat of Cr(AA)<sub>3</sub> reaches about 42 % of the limiting value (according to Dulong and Petit). Debye temperature  $\theta_D(T)$  within the studied temperature range increases from ~205 to ~1470 K and exhibits the tendency to further increase with temperature growth.

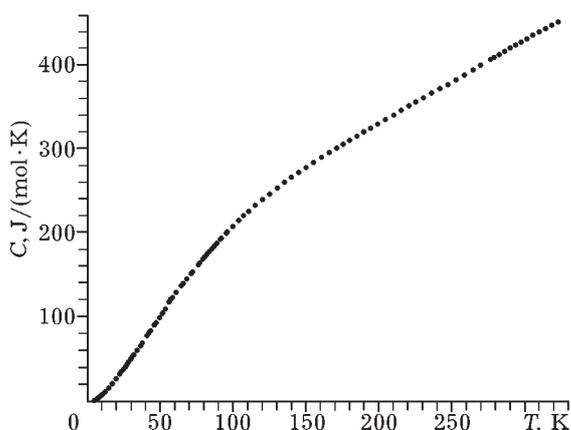


Fig. 1. Experimental specific heat of  $\text{Cr}(\text{AA})_3$ .

#### THE METHOD OF $C_V(T)$ CALCULATION FOR THE COMPOUND $\text{Cr}(\text{AA})_3$

At present, the most precise method to calculate  $C_V(T)$  is the effective sum method described in the Supplement. ESM is based on high-temperature expansion of specific heat and can be applied for temperature  $T$  above a definite temperature point  $T_1$  which depends on the upper limit of phonon spectrum  $\theta_*$  and is  $\theta_*/(2\pi)$ .

The calculation is done in two stages. At the first stage, the parameters of the phonon spectrum that are determined from the experimental specific heat of the crystal include characteristic temperatures connected with the second and fourth moments of the phonon spectrum and with its upper border  $\theta_2$ ,  $\theta_4$ ,  $\theta_*$ , and the parameter  $A$  which is the coefficient at the linear anharmonic contribution into specific heat  $AT$ . At the second stage, these parameters are used to calculate  $T > T_1$  constant-volume specific heat  $C_V(T, \theta_2, \theta_4, \theta_*)$  and linear anharmonic contribution into specific heat  $AT$ .

The application of ESM to the compound under investigation  $\text{Cr}(\text{AA})_3$  has some peculiarities. It follows from temperature dependence of experimental specific heat (see Fig. 1) and Debye temperature  $\theta_D(T)$  that the energy range of the phonon spectrum is rather broad, and its upper border is surely above 1470 K. This conclusion agrees with the data on the frequencies of vibrational spectrum of  $\text{Cr}(\text{AA})_3$  crystal [4, 5]. It is known from those studies that the upper border of vibrational spectrum of the

compound under consideration is  $\sim 3100 \text{ cm}^{-1}$  ( $\sim 4400 \text{ K}$ );  $T_1 = \theta_*/(2\pi)$  is equal to  $\sim 700 \text{ K}$ . This means that our experimental points (5–320 K) are out of the region of ESM applicability.

In the present study we use a special procedure (see below) that allows us to use the ESM method in spite of this limitation to calculate  $C_V(T)$  of the compound under investigation. The procedure is based on the known data on phonon spectrum of  $\text{Cr}(\text{AA})_3$  [4, 5] and a strict account of the number of vibrational modes contributing into specific heat of the compound within temperature range of 5–320 K.

#### VIBRATIONAL MODES AND SPECIFIC HEAT

Intra- and intermolecular vibrational spectra of the  $\text{Cr}(\text{AA})_3$  crystal have been calculated theoretically in [4]. The spectrum of intermolecular vibrations lies within the range of 0–140  $\text{cm}^{-1}$  while the spectrum of intramolecular vibrations spreads till 3100  $\text{cm}^{-1}$ . The histogram of the frequencies of intramolecular vibrations is shown in Fig. 2. The monograph [5] presents attributions of different frequencies in the spectrum of  $\text{Cr}(\text{AA})_3$  to the vibrations of specific groups of atoms. A substantial feature of the spectrum is energy gap within the range of 1900–2800  $\text{cm}^{-1}$ .

The fraction brought into specific heat at a temperature  $T$  by a separate mode with the frequency  $\omega$  can be calculated using the Einstein function  $\Psi$  [6]:

$$\varphi(z) = \frac{z^2 e^{-z}}{(1 - e^{-z})^2} \quad (1)$$

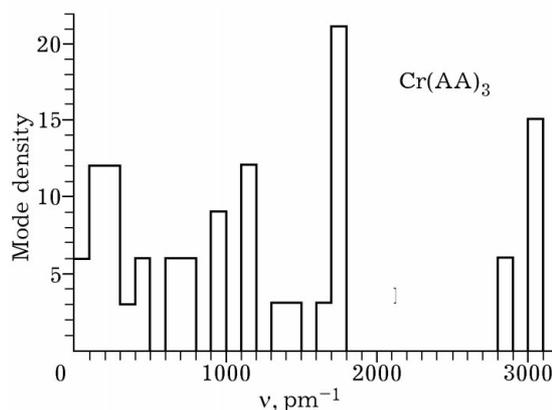


Fig. 2. Histogram of the frequencies of intramolecular vibrations of  $\text{Cr}(\text{AA})_3$ .

where  $z = \hbar\omega/(kT)$ . This calculation shows that a substantial part of the vibrational spectrum of Cr(AA)<sub>3</sub> (high-frequency part) is not excited at temperatures of 5–320 K. For example, the contribution into specific heat from the frequency range of 1300–3100 cm<sup>-1</sup> (54 vibrational modes) at 320 K accounts for only 2.5 % of the experimental specific heat while the contribution into specific heat from high-frequency stretching vibrations of CH and CH<sub>3</sub> groups (frequency range of 2800–3100 cm<sup>-1</sup>, 21 vibrational modes) is only 0.03 % at 320 K.

Taking this fact into account let us conventionally separate the measured specific heat  $C_{\text{meas}}(T)$  into two terms,  $C_{\text{h}}(T)$  originating from the high-frequency region of the spectrum (1300–3100 cm<sup>-1</sup>, 54 vibrational modes), and  $C_1(T)$  originating from the low-frequency region of the spectrum (0–1300 cm<sup>-1</sup>, 75 vibrational modes):

$$C_{\text{meas}}(T) = C_{\text{h}}(T) + C_1(T) \quad (2)$$

High-frequency part of the vibrational spectrum starting from ~1300 cm<sup>-1</sup> can be represented as a set of 18 Einstein frequencies (see [4]), 54 vibrational modes as a total. Then specific heat  $C_{\text{h}}(T)$  will be represented by the sum of 18 Einstein terms  $C_j(E_j, T)$  with the corresponding energy  $E_j$  and factors  $v_j$ :

$$C_{\text{h}}(T) = \sum_{j=1}^{18} v_j C_j(E_j, T) \quad (3)$$

Thus calculated  $C_{\text{h}}(T)$  is the harmonic part of specific heat which depends on high-frequency modes excitation.

After subtracting the calculated  $C_{\text{h}}(T)$  from the experimental specific heat according to equation (2) we obtain the function  $C_1(T)$  in numerical form. Thermal excitation of only 75 low-frequency vibration modes has an effect on the specific heat  $C_1(T)$ . The corresponding low-frequency part of the spectrum is limited from above by a frequency of ~1300 cm<sup>-1</sup>. The values corresponding to this border are  $\theta_* \approx 1800$  K and  $T_1 = \theta_*/(2\pi) = 285$  K. This  $T_1$  is much below 320 K, the upper limit of our measurements, so the ESM can be used to approximate the specific heat  $C_1(T)$ . We found that the approximation range can be broad-

ened without any loss of parameter stability down till 185 K.

Within the 185–320 K range, specific heat  $C_1(T)$  normalized for 75 vibrational modes can be approximated by the equation (8) (see the Appendix) with least squares. This approximation allows one to determine the parameters  $\theta_2$ ,  $\theta_4$ ,  $\theta_*$  and  $A$  corresponding to the low-frequency part of spectrum (till ~1300 cm<sup>-1</sup>). Using the parameters  $\theta_2$ ,  $\theta_4$ , and  $\theta_*$  we calculate the harmonic part of specific heat  $C_{\text{har}}(T, \theta_2, \theta_4, \theta_*)$  for the low-frequency part of spectrum. The parameter  $A$  allows one to calculate the anharmonic part of specific heat  $AT$ . As a result, specific heat  $C_1(T)$  at  $T > 185$  K is presented as a sum of two terms, harmonic and anharmonic ones:

$$C_1(T) = C_{\text{har}}(T, \theta_2, \theta_4, \theta_*) + AT \quad (4)$$

Value  $A$  was found to be 3.6 mJ·mol<sup>-1</sup>·K<sup>-2</sup> which gives a very small anharmonic contribution into specific heat: 0.2 % in the range of 200–300 K (scattering of experimental points being ~0.03 %).

Constant-volume specific heat  $C_V(T)$  is a sum of  $C_{\text{har}}(T, \theta_2, \theta_4, \theta_*)$  (equation (4)) and  $C_{\text{h}}(T)$ (equation (3)):

$$C_V(T) = C_{\text{har}}(T) + C_{\text{h}}(T) \quad (5)$$

Shifting the border that conventionally separates low-frequency and high-frequency parts

TABLE 1  
Constant-volume specific heat  $C_V(T)$  for Cr(AA)<sub>3</sub> from 185 K till melting point 489 K

$T$ , K	$C_V(T)$ , J·mol <sup>-1</sup> ·K <sup>-1</sup>	$T$ , K	$C_V(T)$ , J·mol <sup>-1</sup> ·K <sup>-1</sup>
185	316.3	340	469.8
190	321.1	350	479.3
200	330.8	360	488.7
210	340.6	370	498.0
220	350.5	380	507.1
230	360.5	390	516.2
240	370.6	400	525.1
250	380.7	410	533.9
260	390.8	420	542.6
270	400.9	430	551.2
280	410.9	440	559.7
290	421.0	450	568.0
300	430.9	460	576.3
310	440.8	470	584.4
320	450.6	480	592.5
330	460.3	490	600.4

of the phonon spectrum by  $\pm 150 \text{ cm}^{-1}$  we obtain calculated  $C_V(T)$  at melting point (489 K) differing by less than  $\sim 1\%$ . The calculated  $C_V(T)$  within 185–489 K temperature range are shown in Table 1.

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## APPENDIX

### Approximation of the harmonic part of specific heat according to the Effective Sum Method (Naumov's method).

A well-known analysis method allows one to separate specific heat of a solid within the middle and high temperature range into harmonic and linear contributions using a truncated high-temperature expansion of specific heat to describe the harmonic contribution (see, for example, [7, 8]). This analysis allows one to determine the first even moments of the phonon spectrum and the factor  $A$  of the linear contribution.

A substantial improvement of this method has been proposed by V. N. Naumov [9]. Instead of cutting short an endless row representing high-temperature expansion of specific heat, the author proposed to represent specific heat by the efficient complete but not cut-off row. In [1, 9] the residue of the row is replaced by the analytical term with the single parameter  $\theta_*$  that efficiently characterizes the upper border of phonon spectrum.

As a result, temperature dependence of the analytical harmonic contribution is described by the equation that contains (in the most widely used version) three parameters:  $\theta_2$ ,  $\theta_4$ , and  $\theta_*$ . These are characteristic temperatures connected with the second and fourth moments of the phonon spectrum and with its upper limit. With regard for linear anharmonic contribution ( $AT$ ), analytical equation for complete specific heat contains four parameters:  $\theta_2$ ,  $\theta_4$ ,  $\theta_*$  and  $A$  ( $A$  is the coefficient at the linear anharmonic term) (see [9]):

$$\frac{C(T) - AT}{3Nk} = 1 - \frac{\theta_2^2}{12T^2} - \frac{\theta_4^4}{\theta_*^4} + \frac{\theta_4^4}{T^2\theta_*^2} \left[ \frac{1}{12} + \frac{1}{\varphi(z)} \right] \quad (6)$$

Here  $\varphi(z) = e^z + e^{-z} - 2$ ,  $z = \theta_*/T$ ;  $3N$  is the number of modes contributing into specific heat;  $k$  is the Boltzmann constant.

It is proposed in [1, 9, 10] to represent (6) in parametric form through special coordinates  $X$  and  $Y$ :

$$Y(T, C, A) = 12T^2 \left[ 1 - \frac{C(T) - AT}{3Nk} \right] \quad (7)$$

$$X(T, \theta_*) = \frac{1}{\theta_*^2} \left[ 1 - \frac{12T^2}{\theta_*^2} + \frac{12}{\varphi(\theta_*/T)} \right]$$

The dependence  $Y(X)$  is a straight line. Its equation coefficients are the parameters of the phonon spectrum:

$$Y(T, C, A) = \theta_2^2 - \theta_4^4 X(T, \theta_*) \quad (8)$$

In order to test the efficiency of the proposed method, we performed approximations of model curves of specific heat with known spectra (Debye, Einstein, *etc.*, see, for example, [1, 10]) which allowed a high-accuracy test. This procedure showed that the proposed coordinates  $X$  and  $Y$  have a substantial advantage over the coordinates  $T$  and  $C(T)$ . Due to nonlinear transformation of coordinates (7) the points of  $C(T)$  at different temperatures gain different weight, the weight of higher temperature points being more than that of low-temperature ones. This definition of weights corresponds to the idea of high-temperature expansion which describes specific heat the better the higher temperature is. Because of this, when determining the parameters  $\theta_2$ ,  $\theta_4$ ,  $\theta_*$  and  $A$  in the coordinates  $X$  and  $Y$  their numerical values are stable within a wide temperature range while when determined in the coordinates  $T$  and  $C(T)$  the region of their stability is much more narrow and they are strongly dependent on approximation range.

Representations (6) and (8) for describing experimentally specific heat are true within a definite temperature range. The lower border of this range  $T_1 = \theta_*/(2\pi)$  is determined by the convergence limit of high-temperature expansion. The upper limit of this range  $T_h$  is the temperature at which the square anharmonic contribution into specific heat becomes important. At temperatures above  $T_h$  the two terms (harmonic and linear with respect to temperature) become insufficient to describe experi-

mental specific heat, so experimental points will deviate from the straight line  $Y(X)$ .

Within  $T_1 - T_h$  temperature limits, an optimal choice of the parameters  $\theta_*$  and  $A$  means that in the coordinates of (7) experimental points fall well within the straight line  $Y(X)$ . The parameters  $\theta_2$  and  $\theta_4$  are determined by the coefficients of this straight line equation (by means of least squares). After having determined the parameters  $\theta_2$ ,  $\theta_4$ ,  $\theta_*$  and  $A$ , they are used to calculate separately the harmonic and linear contributions: equation (6) describes the harmonic lattice specific heat while the parameter  $A$  describes the linear contribution.

The introduction of efficient sum instead of truncated series and the use of special coordinates  $X$  and  $Y$  give a new reliable method for precise determination of the moments of phonon spectrum, harmonic and linear contributions into specific heat, provide a substantial shift high-temperature expansion of the applicability region to lower temperatures and al-

low one to obtain one more characteristic of a solid, *i. e.* effective upper limit of the phonon spectrum  $\theta_*$ .

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