Phonon density of states and thermodynamic properties of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$

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Abstract. In the work, the phonon density of states of europium dipivaloylmethanate was calculated based on the experimental low-temperature heat capacity, and basic characteristic temperatures related to the moments of the $g(\omega)$ were obtained. The molar thermodynamic functions of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ at constant volume up to the melting point of 464 K were calculated: heat capacity, entropy, internal energy, and Helmholtz energy. The zero-point energy was determined, and total internal energy was obtained. Accuracy of the obtained results was estimated. The approach used to obtain the properties of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ is general, it can be used to study a wide range of solids.

1. Introduction

Currently, the direction associated with the development of emission materials for the manufacture of organic light emitting diodes (OLED) is actively developing in modern electronics and applied chemistry [1–3]. Lanthanide beta-diketonates are promising emission materials in OLED technologies [4,5]. Their unique optical properties, such as high luminescence efficiency, long excited-state lifetimes and monochromaticity make them of interest for a wide range of photonic applications. In this regard, these complexes are a source of increased scientific interest [6–9].

Europium dipivaloylmethanate (or tris(2,2,6,6,-tetranethyl-3,5-heptanedionato) europium) belongs to the class of metal beta-diketonates. In the condensed state, it exists as a dimer (Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ or Eu$_2$(thd)$_6$) and crystallizes in molecular lattices [10]. Much attention is paid to the development of synthesis methods [10] of these complexes, as well as the study of their structural [10,11], photophysical properties [12,13], and etc. However, the thermodynamic properties are poorly understood. Only information about the low-temperature heat capacity [14] and the enthalpy of sublimation [15] is known. The properties that can be obtained from the data on the heat capacity (temperature and heat of phase transitions [16–18], thermodynamic functions [19–21], phonon density of states and zero-point energy [22–24]) occupy an important place among thermodynamic properties. These data are extremely informative, since they are linked by thermodynamic relations with many other important properties of a substance [25].

In this work, the phonon density of states $g(\omega)$, the characteristic temperatures associated with the moments of $g(\omega)$, the zero-point energy, and the isochoric thermodynamic functions (entropy, internal energy, and Helmholtz free energy) in a wide temperature range were calculated.
2. Phonon density of states

We used the method described in [26,27] to calculate the phonon density of states of Eu2(C11H19O2)6. It is based on numerical solution of the inverse problem of reconstructing density of states \( g(\omega) \) from low-temperature heat capacity \( C_v(T) \). The method allows us to calculate the \( g(\omega) \) dependence with correct description of its shape and correct proportion of the number of vibrational modes in different frequency intervals.

2.1. Before calculations

Before doing the calculations, it is necessary to prepare and verify initial data and determine the boundary conditions. For example, to use experimental heat capacity, it is necessary to determine the region of correspondence between the isobaric \( C_p(T) \) and isochoric \( C_v(T) \) heat capacity. To determine the temperature range of validity of the calculated isochoric thermodynamic functions from \( g(\omega) \), we need to know information about the structural phase transitions. It is also necessary to determine the frequency interval for the cutoff frequency searching, and etc.

The phase transition testing was done using a differential scanning calorimeter Netzsch DSC 204 F1 Phoenix. We used the same sample Eu2(C11H19O2)6 (molar mass is 1403.54 g mol\(^{-1}\)) as in [14], and description of the sample characteristic are provided in [14]. The DSC profile presented one endothermic peak at 464.1 K (standard uncertainty for temperature is 0.5 K), which associated with the melting of Eu2(C11H19O2)6.

We considered the possibility of using experimental data [14] to reconstruct the density of states of Eu2(C11H19O2)6. Heat capacity at constant pressure \( C_p(T) \) and at constant volume \( C_v(T) \) below a certain temperature is almost the same for all solids. The heat capacity \( C_p(T) \) at room temperature is only \( \sim 37\% \) of the limit value corresponding to the Dulong-Petit law at high temperatures [28]. In view of the foregoing, anharmonic contribution of the heat capacity of up to \( \sim 300 \) K will be insignificant. Our estimation of this contribution is on the level of the experimental heat capacity uncertainty or less. Analysis [14] of the functional behavior of experimental curve \( C_p(T) \) gives indication for the existence of anomaly at 250–270 K, which is not associated with first-order structural phase transition. Crystalline europium dipivaloylmethanate is dielectric and paramagnetic in the studied temperature range. The Eu\(^{3+} \) ground state is a singlet (\( 7F_0 \)). Therefore, the total heat capacity includes only the phonon component and does not contain any other components (Schottky anomaly, magnetic, electronic, etc.). Therefore, to solve our inverse problem, experimental data on the heat capacity \( C_p(T) \) in the temperature range of 8–250 K can be used.

Before calculating the density of states \( g(\omega) \), the component of the heat capacity due to stretching vibrations of hydrogen atoms was took into account [22–24]. The heat capacity without component associated with the stretching vibrations of hydrogen atoms was used to reconstruct \( g(\omega) \).

2.2. Density of states reconstruction

Reconstruction of the phonon density of states by method [26,27] is implemented in three steps: selecting zero approximation; obtaining a set of solutions by zero approximation refinement using iteration process with various parameters; averaging the set of solutions. As a zero approximation we used function \( g_0(\omega) \) which has constant density of modes below the cutoff frequency.

The calculation was made for the frequency resolution of 48 K. In total, we performed 18 calculations \( (k = 18) \) of the density of states \( g^{(k)}(\omega) \) with different algorithms of the iterative process implementation. Every calculation \( g^{(k)}(\omega) \) was made independently by starting from the selected zero approximation \( g_0(\omega) \). After that all obtained \( g^{(k)}(\omega) \) were averaged. The averaging procedure significantly reduces the random component, which is present in each instance. The density of states \( g(\omega) \), calculated in that way, was cutoff frequency of 2352 ± 96 K. As a result, phonon density of states \( g(\omega) \) of Eu2(C11H19O2)6 was obtained by include modes, connected with the stretching vibrations of hydrogen atoms. It is shown in figure 1. As it can be seen from the figure, spectrum \( g(\omega) \) has two main regions. The low-frequency part of this has few peaks, connected with both intramolecular and intermolecular vibrations. The high-
The frequency region is represented in the one-peak approximation; it is connected with only intramolecular vibrations.

2.3. Assessing accuracy of the results obtained

The peculiarity of the considered inverse problem is that it does not have a single uniquely determined solution. This is determined not only by the specifics of the inverse problem, but also by the uncertainty, with which the initial temperature dependence of the heat capacity is known. As a result, the obtained set of solutions $g^{(k)}(\omega)$ is located in a band determining the uncertainty of solutions to be obtained.

We calculated the absolute deviations $\Delta g^{(k)}(\omega)$ of all solutions $g^{(k)}(\omega)$ from the averaged $g(\omega)$ (horizontal axis); they are shown in figure 2 (the scales of vertical axes in figures 1 and 2 are the same). It can be seen that the calculated uncertainty of the density of states is random and, on the average, is an increase along with the frequency. The root mean square deviation was 0.05; 0.21; 0.4 at the frequencies of 24; 72; 120 K, and 0.7 from 144 to 1104 K, and 1.0 from 1104 to 2352 K.

![Figure 1](image1.png)

**Figure 1.** The phonon density of states of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$.

![Figure 2](image2.png)

**Figure 2.** Absolute deviations $\Delta g^{(k)}(\omega)$ of set of individual calculations $g^{(k)}(\omega)$ from the averaged density of states $g(\omega)$. Different symbols in the figure correspond to different calculation runs $k$.

![Figure 3](image3.png)

**Figure 3.** Relative deviation of the experimental values $C_p(T)$ [14] from the calculated heat capacity $C_V(T)$. Unfilled circles corresponds to values $C_p(T)$, which did not use to calculate $g(\omega)$.
2.4. Characteristic temperatures
For obtained phonon density of states $g(\omega)$ of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ with taking into account the stretching vibrations of hydrogen atoms, basic characteristic temperatures $\Theta_i$ for $i = 1; 2; 4; 6; -1; -2$ were calculated. They are related to the moments $\mu_i$ of the $g(\omega)$ and were calculated by the following formula:

$$\Theta_i = \frac{h}{k_B} \sqrt[1/i]{\int \frac{g(\omega) d\omega}{\int g(\omega) d\omega}} = \frac{h}{k_B} \left( \frac{\int g(\omega) d\omega^i}{\int g(\omega) d\omega} \right)^{1/i}$$

(1)

The calculated values of characteristic temperatures $\Theta_i$ are given in table 1.

Table 1. Characteristic temperatures associated with the phonon density of states of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$.

| Quantity$^a$ | Value   | Quantity$^a$ | Value   |
|--------------|---------|--------------|---------|
| $\Theta_1$   | 1713 ± 11 K | $\Theta_{-1}$ | 464.7 ± 2.5 K |
| $\Theta_2$   | 2208 ± 15 K | $\Theta_{-2}$ | 196 ± 7 K   |
| $\Theta_4$   | 2865 ± 21 K | $\Theta_c$    | 2352 ± 96 K |
| $\Theta_6$   | 3236 ± 25 K | $\Theta_H$    | 4237 ± 30 K |

$^a$ $\Theta_i$, are the characteristic temperatures related to the relevant moments of the $g(\omega)$ (see Eq. (2)); $\Theta_c$ is the cutoff frequency of $g(\omega)$ without taking into account the stretching vibrations of hydrogen atoms; $\Theta_H$ is the characteristic temperature of stretching vibrations of hydrogen atoms.

3. Thermodynamic properties

3.1. Isochoric heat capacity
The reconstructed spectrum $g(\omega)$ of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ should describe the isochoric heat capacity $C_V(T)$ up to the melting point. We calculated the relative deviation of the experimental values $C_p(T)$ [14] from the calculated $C_V(T)$ (figure 3). The obtained deviation in the range of 20–250 K is at the level of experimental scatter, but below 20 K, the deviation increases rapidly with decreasing temperature.

Below 20 K, the calculated density of phonon states does not give a satisfactory description of the heat capacity, which is related both to frequency resolution of $g(\omega)$ and inadequate description of the Debye heat capacity within the framework of the Einstein model. The heat capacity below 20 K was calculated using the low-temperature expansion of the Debye characteristic temperature [29]. As a result, the obtained isochoric heat capacity in the entire range of solid phase existence is shown in figure 4. Relative combined standard uncertainty of the smoothed heat capacity is 0.012 in the temperature range of 0–20 K, 0.004 in the range of 20–80 K, and 0.0020 in the range of 80–464 K.

3.2. Isochoric thermodynamic functions
Using the heat capacity at constant volume $C_V(T)$, thermodynamic functions of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$: entropy $S_V(T)$, internal energy $\Delta U(T)$ and Helmholtz free energy $\Delta F(T)$ up to the melting point of 464 K were calculated. The results are shown in figures 4 and 5.
3.3. Zero-point energy

The data on the phonon density of states at zero temperatures makes it possible to calculate the zero-point energy of the crystal lattice. Zero-point oscillations of atoms of a condensed matter do not disappear when normal thermal vibrations are practically “frozen out”. According to [27], we can calculate the zero-point energy $E(0)$ using the first characteristic temperature $\Theta_1$ by the formula:

$$E(0) = \frac{3N_A n k_B}{2} \Theta_1$$

In this case, the uncertainty of $E(0)$ calculation will correspond to the uncertainty of obtaining $\Theta_1$.

We calculated molar zero-point energy of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ using obtained value of $\Theta_1$ as $E(0) = 4160 \pm 60$ kJ mol$^{-1}$ and $E^*(0) = 21.5 \pm 0.3$ kJ mol$^{-1}$ considering the molecule as a unit.

Taking into account the contribution of zero-point energy, the total internal energy of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ can be calculated as $U(T) = E(0) + \Delta U(T)$. It can be assumed that a significant value of the total energy results in reduced crystal lattice stability and influence on volatility of the molecular crystal. Therefore, when studying the factors affecting the stability (and volatility) of a solid it is necessary to take into account the contribution of zero-point energy.

Conclusion

For the first time phonon density of states $g(\omega)$ of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ was obtained, which has two areas: low frequency and high frequency. The low-frequency region of the spectrum shows a few peaks, while the high-frequency region has one-peak form. It can be assumed that the low-frequency part is connected with both intramolecular and intermolecular vibrations; and high-frequency part is associated with only intramolecular vibrations. We calculated the characteristic temperatures related to the basic moments of phonon density of states with high accuracy, it was possible due to the correct determination of the number of vibrational modes at different frequency intervals in $g(\omega)$.

We calculated isochoric heat capacity and thermodynamic functions (entropy, internal energy and Helmholtz free energy) of Eu$_2$(C$_{11}$H$_{19}$O$_2$)$_6$ in the entire region of solid phase existence based on obtained phonon density of states. Using the knowledge of the first moment of $g(\omega)$, the zero-point energy was obtained. The detailed analysis of uncertainties of the obtained characteristics was performed.

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