Universal Interaction of Thermodynamical and Structural Characteristics in Molecular Crystals of Metal *β*-Diketonates

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In this paper we are observing the behavior of low-temperature heat capacity for metal β-diketonates to detect the relation between thermodynamic and structural characteristics of these metals. As a starting point, a correlation between the heat capacity and the molecule's effective size was detected for metal tris-β-diketonates: $Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3$, $Fe(C_{11}H_{19}O_2)_3$, and $Fe(C_5HF_6O_2)_3$. If we consider the nature of such an interrelation we can see how the observed correlation is connected with the changes of intermolecular interactions in a number of compounds under study. It is demonstrated that universal behavior of the heat capacity on a wide range of temperatures can be observed for metal β-diketonates with identical ligands. The explanation of the detected regularity is related to the identical structure in a short-range ordering, which initiates the coincidence in the vibration spectrum of these objects in a high frequency range. A simple equation has been put forward for the framework of detected regularities to describe heat capacity behavior in compounds considering a wide range of temperatures. The results obtained can be used in calculating and forecasting thermodynamic characteristics of unstudied objects of metal β-diketonate classes, for those where structural data are known. Observing the degree of generality of the results obtained, we came to think that the regularities that we detected can be observed within other classes of molecular crystals.

1. Introduction

Metal β-diketonates are representative of metal organic compounds possessing high volatility. Such compounds are widely used in modern technologies based on chemical substance deposition from the gaseous phase. Such technologies are used to obtain metal,[1] dielectric,[2] and other[3,4] coatings of high quality that do not have any limits on thickness minimization. Those capabilities are used when manufacturing and studying various nanomaterials.[5−7] Metal β-diketonates are used as catalysts, and they also have applications in medicine.[8,9]

It is not by chance that in the last few years the study of various physical and chemical properties of metal β-diketonates has obtained a high interest level.[10−12] Researching thermodynamic properties of such objects is also rather interesting. If we, for instance, speak about the practical aims when optimizing processes of gas-phased thermolysis, it is necessary to know all thermodynamic properties of these materials not only in the gaseous phase but also in their solid state. Our academic interest is awakened by the necessity of deepening our knowledge of the properties of volatile compounds. Among the properties of metal β-diketonates, an important place is occupied by those properties that can be obtained from data on a low-temperature heat capacity. The experimental data are now the main source of information about thermodynamic properties of such complex objects as metal β-diketonates.[13−20] Regular interrelations can be observed in this direction when studying the behavior of the various properties of these objects. Research in this direction is an important task of physical chemistry, because it can help in forecasting the properties of unstudied objects.

It is well-known that the crystal structure and energy of atom interaction in a lattice fully determine thermodynamic properties of solid bodies. It holds true for all substances including molecular crystals. A priori it is possible to await similar heat capacity behavior in the framework of solid phase existence when having an identical structure and characteristic energy of interatomic interaction. In complex compounds the crystal structure can be observed in an interatomic range, meaning short-range ordering, and in those ranges that are much wider than interatomic ones, meaning long-range ordering. It can be assumed that, having identical crystal structures in short-range ordering, the universal behavior of thermodynamic properties of the objects under study can be observed. In the work,[21] where the results of an experimental heat capacity investigation into zeolites in the range of temperatures of (5 to 300) K were presented, such behavior was discovered at medium and high temperatures. The heat capacity of all zeolites under study, when recounted on an identical number of degrees of freedom, coincides with a wide temperature area beginning with nitrogen temperatures and finishing with room temperatures. This kind of behavior can be explained by the presence of identical short-range ordering in all zeolite crystals that were formed by the initial structural elements, tetrahedrons $Si(Al)O_4$, from which in their turn various skeleton zeolite structures are formed.

It is possible to divide molecular crystals of the metal β-diketonate class into groups with an isoligand molecule structure. In the framework of the same group, molecules present the same structure on their periphery. This can be considered as evidence for the structure similarity in short-range ordering. Thus, it can be expected that when having identical molecule topology, that is, when molecules have identical ligand structures, some regularities will be observed in the behavior of

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thermodynamic properties that can be similar to the regularities observed in the work.[21]

In the present analysis we have considered all now-available experimental data on the low temperature heat capacity for tris-β-diketonates $Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3$, $Fe(C_{11}H_{19}O_2)_3$, and $Fe(C_5HF_6O_2)_3$[13−20] to detect regularities in thermodynamic property behavior and the interrelation of such properties with structural characteristics of these materials.

2. Materials and Methods

Samples of metal tris-β-diketonates were synthesized according to the methodology described in the following works: ref 22, tris(2,4-pentanedionato) aluminum(III), $Al(C_5H_7O_2)_3$; ref 23, tris(2,4-pentanedionato) chromium(III), $Cr(C_5H_7O_2)_3$; ref 24, tris(2,4-pentanedionato) iron(III), $Fe(C_5H_7O_2)_3$; ref 25, tris(2,4-pentanedionato) iridium(III), $Ir(C_5H_7O_2)_3$; ref 26, tris(2,2,6,6-tetramethyl-3,5-heptanedionato) iron(III), $Fe(C_{11}H_{19}O_2)_3$; ref 27, tris(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) iron(III), $Fe(C_5HF_6O_2)_3$. A more detailed description of the synthesis of the samples, which were studied in the present work, and their characteristics is presented in the articles.[13−20] The chemical analysis of the compounds showed that the carbon and hydrogen content corresponds to the rated one, when redistributing the analysis precision. All compounds were characterized by X-ray phase and X-ray structure methods. Measured IR spectra and derived graphs for the compounds obtained conform with those from literature.

Experimental data on the heat capacity of tris-β-diketonates at low temperatures are given in the following works: ref 20, $Al(C_5H_7O_2)_3$; refs 14 and 17, $Cr(C_5H_7O_2)_3$; ref 13, $Fe(C_5H_7O_2)_3$; ref 19, $Ir(C_5H_7O_2)_3$; refs 15 and 18, $Fe(C_{11}H_{19}O_2)_3$; ref 16, $Fe(C_5HF_6O_2)_3$. Heat capacity measurements $C_p(T)$[14−20] were conducted using an adiabatic method using a dismountable calorimeter ampule made of nickel. A dismountable calorimeter ampule and the methodology of filling an ampule with a substance, as well as the filling of the ampule with heat-exchange gas (helium), are all described in the work.[28] A description of the installation of its parts and its construction as well as its characteristics is given in the works.[14,29] The absolute uncertainty of heat capacity measurements below 30 K makes up ∼ 1 %, above 30 K: about ∼ 0.1 %. The relative uncertainty of the definition $C_p(T)$ makes up (0.1 to 0.01) % in the range from (80 to 320) K and (1.0 to 0.1) % below 80 K. The data we obtained earlier[14−20] as well as the data presented in another work[13] for $Fe(C_5H_7O_2)_3$ were used when analyzing the behavior of metal β-diketonate heat capacity.

Figure 1 presents values of molar heat capacity in the coordinates C_p/T versus T for all considered tris-β-diketonates within the range of (125 to 320) K. Molar mass was determined in accordance with the chemical formula of compounds per one molecule.

3. Results of Analysis

The experimental data, given in the Figure 1, demonstrate that for metal β-diketonates $Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, and $Ir(C_5H_7O_2)_3$ in a wide range of temperatures heat capacities practically coincide. It is worth noting that these four states have identical ligand structure, that is, they form an isoligand group of metal β-diketonates. We drew attention to the fact that effective volumes of a single molecule (V_m) in this group of compounds as well as the heat capacity possess the nearest value (see Table 1). Effective volumes of molecules (V_m) were calculated as a ratio of the elementary cell volume (V) to the amount of molecules (n_m) in an elementary cell. The volume of an elementary cell was calculated on the basis of the results obtained through X-ray research. Note that for $Fe(C_{11}H_{19}O_2)_3$ with the largest value of heat capacity (see Figure 1) molecule volume is also the largest. Taking into consideration the whole metal tris-β-diketonates row ($Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3$, $Fe(C_{11}H_{19}O_2)_3$, and $Fe(C_5HF_6O_2)_3$) and their structural characteristics (see Table 2), the correlation between the heat capacity and the molecule volume was detected. The analysis showed that heat capacity at the temperature of 298.15 K (C_p^o) is a linear function of the reverse molecule volume ($1/V_m$). Heat capacity for all compounds can be described using the following equation:

$$C_p^o = Ra\left(1 - \frac{V^*}{V_m}\right) \qquad (1)$$

where R is the universal gas constant, $a = 152.20$ is a nondimensional coefficient, $V_m = V/n_m$, V is the volume of the elementary cell (Å^3), n_m is the number of molecules in the elementary cell, and $V^* = 283.014$ Å^3 is a dimensional coefficient. As it can be seen from eq 1, the linear function can be definitely determined by the tangent of the inclination angle (RaV^*) and the free term (Ra). Quantities V^* and a can be calculated using it. Interrelation of heat capacity at the temperature of 298.15 K with an effective β-diketonate molecule volume is depicted in the Figure 2, and it corresponds to eq 1. Relative deviation of the experimental values C_p^o from eq 1 correlates with the experimental error when defining this quantity at a given temperature. Deviations of experimental values C_p^o from the results of the description using eq 1 are given in Table 1.

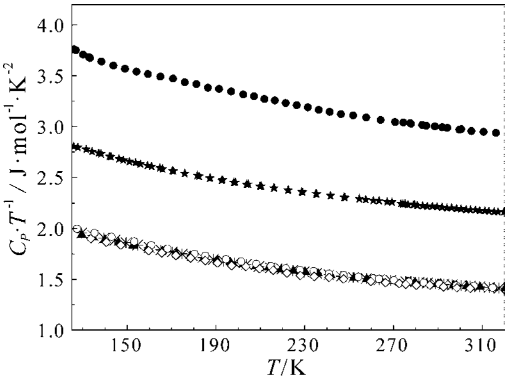

Figure 1. Experimental heat capacity of metal tris-β-diketonates in C_p/T vs T coordinates. ●, $Fe(C_{11}H_{19}O_2)_3$, refs 15 and 18; ★, $Fe(C_5F_6HO_2)_3$, ref 16; ○, $Fe(C_5H_7O_2)_3$, ref 13; ∗, $Cr(C_5H_7O_2)_3$, refs 14 and 17; ▲, $Al(C_5H_7O_2)_3$, ref 20; ◇, $Ir(C_5H_7O_2)_3$, ref 19.

The physical sense of V^* can be determined in the following way. We assume that the V^* quantity is the limiting value of the molecule volume (for the selected compound class) having maximum molecule convergence with each other with extremely powerful molecule attraction. Approximation to such a state can be achieved when applying high pressure to the sample so that the molecules in the crystal will converge to the maximum degree. Such a limiting case can be generated when the energy of molecule interaction works for an infinitely large quantity. In such a case, the possibility of vibrating degrees of freedom excitation will work for zero at the final temperature (298.15 K), when the vibrating degrees of freedom are connected with intermolecular and intramolecular interactions. Because of the fact that solid body heat capacity is proportional to the probability of degrees of freedom excitation in accordance with

Table 1. Volume of Elementary Cell (V), Number of Molecules in an Elementary Cell (n_m), Effective Volume of a Separate Molecule (V_m), and Heat Capacity at $T = 298.15$ K (C_p^o) for the Metal Tris-β-diketonates Studied

compound	V / Å^3	n_m	V_m[a] / Å^3	C_p^o/J·mol^{-1}·K^{-1} exptl[b]	C_p^o/J·mol^{-1}·K^{-1} calcd[c]	Δ[d]
$Ir(C_5H_7O_2)_3$	1693.11[25]	4	423.28	423.3 ± 1.1[19]	419.34	0.9
$Al(C_5H_7O_2)_3$	1694.41[30]	4	423.60	424.6 ± 0.2[20]	419.98	1.1
$Cr(C_5H_7O_2)_3$	1709.40[31]	4	427.35	430.34 ± 0.14[14,17]	427.40	0.7
$Fe(C_5H_7O_2)_3$	3479.47[32]	8	434.93	429.9 ± 0.9[13]	442.01	−2.7
$Fe(C_5HF_6O_2)_3$	2344.90[27]	4	586.23	654.9 ± 0.6[16]	654.53	0.06
$Fe(C_{11}H_{19}O_2)_3$	7577.30[33]	8	947.16	887.7 ± 0.8[15,18]	887.33	0.04

[a] $V_m = V/n_m$; the effective volumes of an individual molecule. [b] Experimental heat capacity at the temperature of 298.15 K. [c] Heat capacity at the temperature of $T = 298.15$ K calculated according to eq 1. [d] $\Delta = 100(C_p^o(\text{exptl}) - C_p^o(\text{calcd}))/C_p^o(\text{calcd})$.

Table 2. Optimal α and Θ Parameter Values That Were Obtained as a Result of Experimental Heat Capacity Approximation for Metal Tris-β-diketonates Using eq 8 in the Temperature Range of (T_1 to T_2) K

compound	n_a[a]	T_1 / K	T_2 / K	α	Θ / K	rmsd[b] %
$Al(C_5H_7O_2)_3$	43	260	315	1.14	424.54	0.04
$Cr(C_5H_7O_2)_3$	43	260	320	1.14	423.26	0.05
$Fe(C_5H_7O_2)_3$	43	270	315	1.14	422.84	0.30
$Ir(C_5H_7O_2)_3$	43	260	305	1.14	433.98	0.23
$Fe(C_5HF_6O_2)_3$	43	270	317	1.91	235.10	0.12
$Fe(C_{11}H_{19}O_2)_3$	97	240	316	1.14	481.55	0.20

[a] Number of atoms in a molecule. [b] Root-mean-square deviations (rmsd's) of the experimental data on heat capacity from the values obtained using eq 8 in the temperature range of (T_1 to T_2) K.

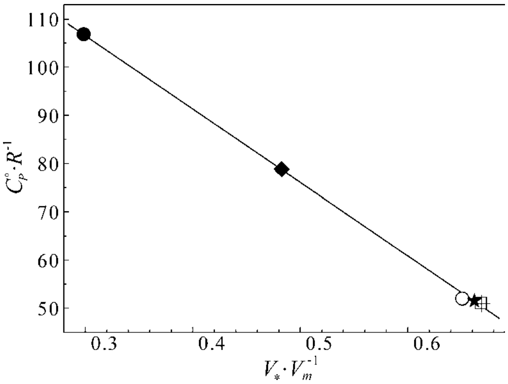

Figure 2. Connection of C_p^o, the metal tris-β-diketonate heat capacity, with effective molecule volume V_m. ●, $Fe(C_{11}H_{19}O_2)_3$; ◆, $Fe(C_5F_6HO_2)_3$; ○, $Fe(C_5H_7O_2)_3$; ★, $Cr(C_5H_7O_2)_3$; □, $Al(C_5H_7O_2)_3$; +, $Ir(C_5H_7O_2)_3$. $V^* = 283.014$ Å^3 is a dimensional coefficient.

the quantum statistics of Bose−Einstein, it will also work for zero. Thus, the V^* value can be determined as the volume value when $C_p^o = 0$ (see eq 1). It seems that V^* will be constant for some selected class of molecular crystals with similar molecule topology.

As a result we know that effective molecular volume is connected with heat capacity at a temperature of 298.15 K. However, as it follows from Figure 1, such interaction is observed at other temperatures, encompassing quite a wide temperature range.

The functional dependence of heat capacity $C_p(T)$ in the wide range of temperatures including a temperature of 298.15 K for all tris-β-diketonates can be described with high precision with the following equation:

$$C_p(T) = \frac{3Rn_a}{\Theta^{\alpha}T^{-\alpha} + 1} \tag{2}$$

where n_a is the number of atoms in a molecule, α is a dimensionless parameter, and Θ is a parameter that has temperature dimension. This equation can be obtained from having a massive simplification of the precise formula to describe harmonic heat capacity domain.[34,35] In this expression the sum of the alternate series (the aggregation of the even degree hyperboles) is substituted by one component:

$$\left(\frac{\Theta_2}{T}\right)^2 - \left(\frac{\Theta_4}{T}\right)^4 + ... + (-1)^n\left(\frac{\Theta^*}{T}\right)^{2n} \approx \left(\frac{\Theta}{T}\right)^{\alpha} \tag{3}$$

where Θ_2, Θ_4, and Θ^* are characteristic temperatures connected with corresponding moments (second, fourth, and boundary) of phonon conditions density $g(\omega)$, and $n = 3$, 4, 5, and so forth. Thus, quantity Θ in eq 2 is the characteristic temperature connected with the effective middle moment of the function $g(\omega)$, and it characterizes some middle frequency of the crystal's vibrational spectrum. The parameter α is the degree with which heat capacity approaches the value $3Rn_a$. Equation 2 possesses correct asymptotics at high temperatures, because when $T \to \infty$ heat capacity works for the quantity of the Dulong−Petit law ($3Rn_a$). Equation 2 cannot be used at low temperatures (below the point of the curve bend $C_p(T)$); that is, it is true only when $\alpha > 0$. To facilitate the detection of the scalable parameters α and Θ, eq 2 may be given in the following form:

$$\frac{3Rn_a}{C_p} - 1 = \left(\frac{\Theta}{T}\right)^{\alpha} \tag{4}$$

Finding the logarithm of the both parts of eq 4, we obtain:

$$\ln\left(\frac{3Rn_a}{C_p} - 1\right) = \alpha \ln\left(\frac{\Theta}{T}\right) \tag{5}$$

Making a change in eq 5:

$$Y = \ln\left(\frac{3Rn_a}{C_p} - 1\right) \qquad X = \ln T \tag{6}$$

$$A = -\alpha \qquad B = \alpha \ln \Theta \tag{7}$$

we obtain a linear equation:

$$Y = AX + B \tag{8}$$

in which X and Y depend on the values calculated in the experiment and A and B are unknown parameters. A and B parameters can be found using the least-squares method when taking into account the experimental data for the temperature range in which heat capacity is adequately described by eq 8. Then values α and Θ can be obtained from eq 7.

The heat capacity of all compounds under consideration was described in the corresponding temperature range by eq 8, and the parameters α and Θ were calculated. Computational results and the uncertainty of the experimental data description by eq 8 are given in Table 2. Root-mean-square deviations of the experimental points from approximating straight lines in the temperature range under consideration did not go beyond the

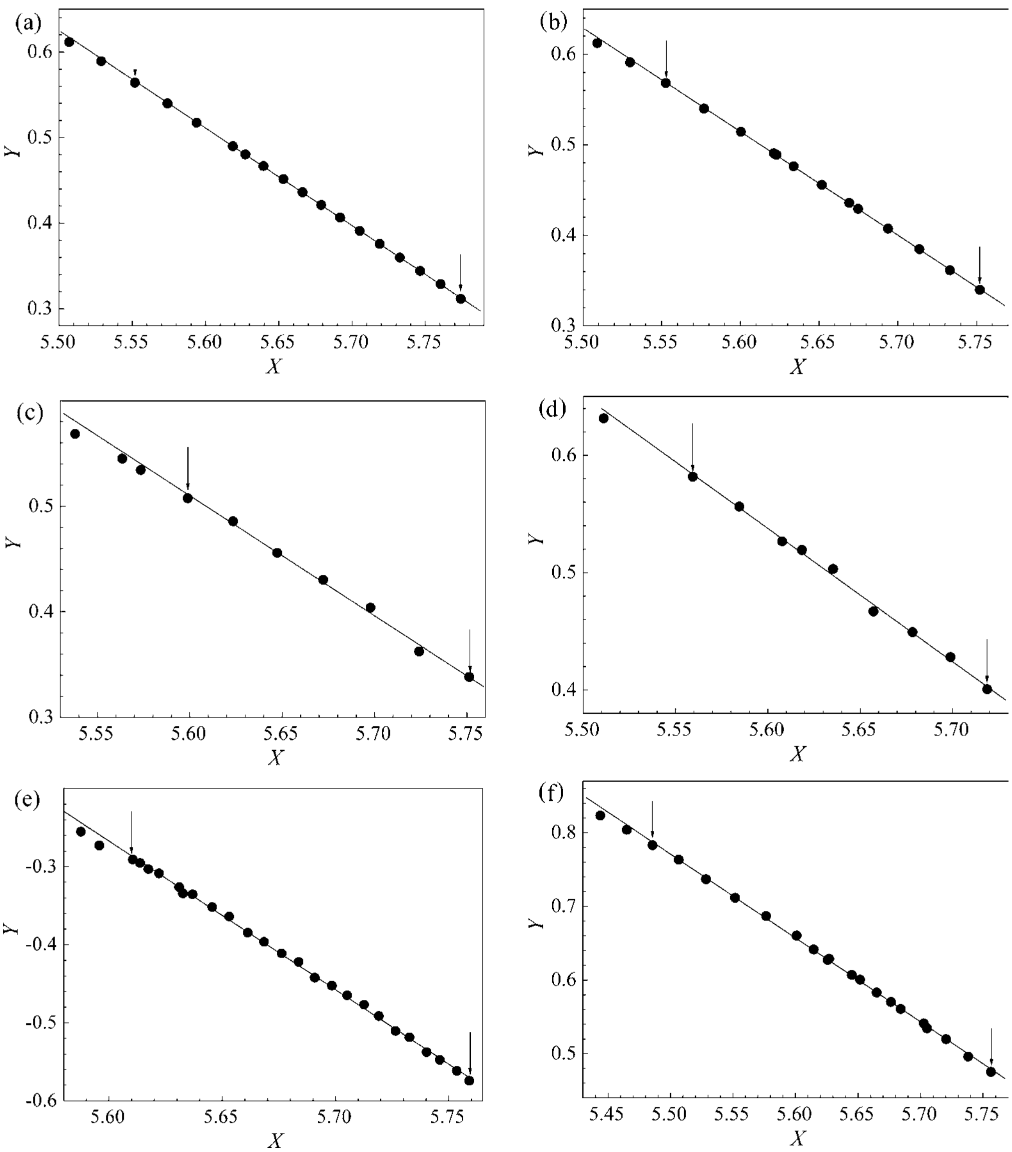

Figure 3. Description of the experimental heat capacity of metal tris-β-diketonates according to eq 8. Root-mean-square deviations of the experimental heat capacity values from the values obtained from eq 8 in the temperature range of (T_1 to T_2) K (arrows on the figure) are presented in Table 2. (a) $Cr(C_5H_7O_2)_3$; (b) $Al(C_5H_7O_2)_3$; (c) $Fe(C_5H_7O_2)_3$; (d) $Ir(C_5H_7O_2)_3$; (e) $Fe(C_5F_6HO_2)_3$; (f) $Fe(C_{11}H_{19}O_2)_3$.

scope of the experimental spread. The heat capacity of $Cr(C_5H_7O_2)_3$ in X versus Y coordinates as well as the approximating straight line corresponding to the minimum of the square deviations are presented in the Figure 3a. The experimental points with high precision are described with the equation of the straight line (eq 8) in the range of (260 to 320) K. A similar description is observed for other three isoligand metal β-diketonates: $Al(C_5H_7O_2)_3$ (Figure 3b), $Fe(C_5H_7O_2)_3$ (Figure 3c), and $Ir(C_5H_7O_2)_3$ (Figure 3d). As it follows from Table 2, identical α values and rather close Θ values are observed for this group of compounds, explained by the proximity of their heat capacity functional behavior (Figure 1).

Metal β-diketonate $Fe(C_5HF_6O_2)_3$ is different from the earlier considered isoligand group by the fact that in the ligand CH_3 groups were substituted by CF_3 groups. A description of this compound's heat capacity with eq 8 in the range of (270 to 317) K is given in the Figure 3e in X versus Y coordinates. The obtained parameters, α and Θ values, and the description precision are given in Table 2.

The results of the approximation of experimental points by eq 8 for $Fe(C_{11}H_{19}O_2)_3$ are depicted in the Figure 3f. The best description of the straight line was obtained in the range of (240 to 316) K.

It is worth noting that for the compound $Fe(C_5HF_6O_2)_3$ values $\alpha = 1.91$ and $\Theta = 235.10$ are noticeably different from α and Θ values for other compounds under study (see Table 2). It can be explained by significant decrease in frequencies of the vibrational spectrum at $Fe(C_5HF_6O_2)_3$ that is connected with the presence of heavy fluorine atoms on the molecule periphery (in ligands).

Deviations of the experimental heat capacity values for all metal β-diketonates from the values obtained from eq 2 in viewed intervals of temperatures (see Table 2) are presented in the Figure 4.

After α and Θ were determined for all objects, it is possible to use eq 4 to present heat capacity data without referring to logarithmic coordinates. Heat capacity curves are presented in the Figure 5 for metal β-diketonates under study in the coordinates $(3RC_P^{-1} - 1)$ versus $(\Theta^{\alpha}T^{-\alpha})$. As it can be seen

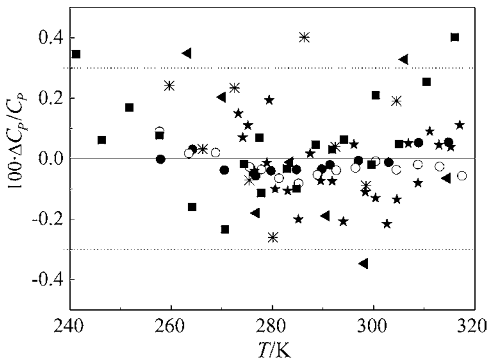

Figure 4. Fractional deviations $\Delta C_p = C_p(\text{exptl}) - C_p(\text{calcd})$ of the experimental heat capacity C_p(exptl) of metal tris-β-diketonates from the values C_p(calcd) obtained from eq 2 in the temperature range of (T_1 to T_2) K (see Table 2). ○, $Cr(C_5H_7O_2)_3$; ●, $Al(C_5H_7O_2)_3$; left-pointing triangle, $Fe(C_5H_7O_2)_3$; ∗, $Ir(C_5H_7O_2)_3$; ★, $Fe(C_5F_6HO_2)_3$; ■, $Fe(C_{11}H_{19}O_2)_3$; and dashed line, uncertainty of eq 2.

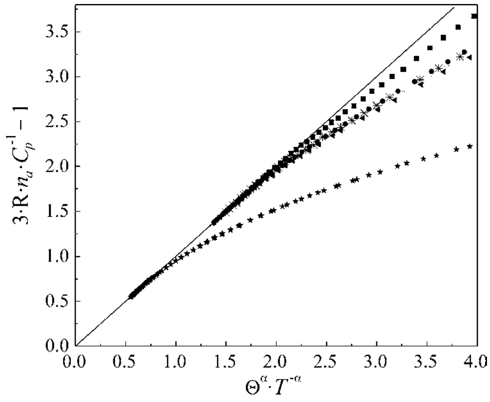

Figure 5. Description of the experimental heat capacity of metal tris-β-diketonates according to eq 4. ■, $Fe(C_{11}H_{19}O_2)_3$; ∗, $Ir(C_5H_7O_2)_3$; ●, $Al(C_5H_7O_2)_3$; ○, $Cr(C_5H_7O_2)_3$; left-pointing triangle, $Fe(C_5H_7O_2)_3$; ★, $Fe(C_5F_6HO_2)_3$; and line, eq 4.

from the image curves, $C_p(T)$ for all objects asymptotically forms a straight line at a high temperature range at small argument values. The straight line is described by eq 4, and that can be characterized as universal behavior. Four isoligand substances ($Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, $Ir(C_5H_7O_2)_3$) at a high temperature range have similar behavior to that of $C_p(T)$ that is comparable with the experimental spread. On the other hand, compounds with other ligands have extremely different behaviors. It can be assumed that heat capacity behavior similar to the row containing $Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, and $Ir(C_5H_7O_2)_3$ will be observed for other isoligand rows of metal tris-β-diketonates. At this point, the approach of $C_p(T)$ curves can be expected when increasing the temperature.

Using the representation described earlier together with the correlation between heat capacity at a temperature of 298.15 K and the effective molecule volume that we have detected, it is possible to depict heat capacity behavior of β-diketonates in a rather wide range of temperatures. For example, when we measure during the experiment the temperature of one of the compounds from an isoligand group of β-diketonates, we assume that it is possible to forecast with high precision and confidence the behavior of the temperature heat capacity dependence for other compounds from this group.

4. Discussion

Molecular crystals $Al(C_5H_7O_2)_3$, $Cr(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, and $Ir(C_5H_7O_2)_3$ have the same ligands. As it was shown earlier, these compounds do have the same $C_p(T)$ behavior in wide range of temperatures. The similarity of the ligand structure defines similar vibration frequencies that are responsible for the range of high frequencies, because of the fact that the highest frequencies in the vibrational spectrum of the crystal are generated by the atom vibrations in the ligand.[36] The listed peculiarities of the structure in the isoligand row determine the similarity of the high frequency part of their spectrum and affect the observed heat capacity behavior of these compounds (Figure 5).

Heat capacity divergence for zeolites at low temperatures, observed in the work,[21] is related to the difference in structure in long-range ordering. An analogous behavior is observed in our case as the long-range ordering is determined by different energies of intermolecular interactions. Intermolecular interactions in the compounds under study are in their nature connected with van der Waals attraction determined by the electron density distribution in the molecule size and by the dynamics of this density depending on the temperature. The latter one depends not only on the molecule structure but also on the mass of atoms. van der Waals interaction forms the crystal structure from molecules, assuming the effective distance between molecules, through this determination of the effective molecule volume in a molecular crystal. Thus, the observed volume correlation with heat capacity (see eq 1) mostly tracks the changes in intermolecular interactions in the range of compounds under consideration. This behavior is also justified by the fact that at low temperatures long-wavelength vibrational modes are filled, the frequency spectrum of which is significantly affected by weak intermolecular interaction.[36]

We assume that the regularities of the examined behavior of thermodynamic and structural characteristics will be observed for all rows of metal β-diketonates that are united into isoligand groups. The usage of an empirical eq 1 as well as universal $C_p(T)$ behavior, that was observed in the framework of the isoligand group, allows us to forecast the behavior of thermodynamic characteristics of metal β-diketonate class compounds, for which there are no experimental data obtained.

5. Conclusion

A correlation between the heat capacity and the effective molecule volume was detected for metal tris-β-diketonates. This correlation reflects the intensity of intermolecular interactions. It was shown that universal heat capacity behavior is observed for metal β-diketonates with identical ligands in the wide range of temperatures. The explanation of the detected regularities in the isoligand row is linked to the identical structural organization in short-range ordering, which in its turn determines the coincidence of the objects' vibrational spectra in the high frequencies range. A simple equation was put forward that allowed us, in the framework of detected regularities, to describe the behavior of heat capacity in compounds under study in a wide range of temperatures. The results obtained can be used to calculate thermodynamic characteristics of unstudied objects for which the structural data are known. The detected regularities present a general character because of the fact that revealed features that initiate such behavior are connected with identical structure organization in other classes of molecular crystals.

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