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Intermolecular and Intramolecular Vibrations and Their Contributions into Low-Temperature Thermodynamics

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Abstract

The present paper describes the results of investigations of the dynamic and thermodynamic characteristics of molecular crystal chromium *tris*-acetylacetonate $Cr(C_5H_7O_2)_3$ by means of lattice dynamics and low-temperature calorimetry. Specific heat of $Cr(AA)_3$ crystals is measured according to adiabatic method within the temperature range of 5–320 K. The spectra of intermolecular vibrations at different temperatures are calculated. On this grounds, specific heat is calculated within the range of 5–320 K. Vibrational spectra of the molecule are calculated. The component of specific heat corresponding to intramolecular vibrations is determined. Experimental IR and Raman spectral data are used in calculations along with the literature data on force constants of interatomic interactions and interatomic potential constants. Force constants that are responsible for the low-frequency spectral region of intramolecular vibrations are selected so that the best agreement could be achieved between the calculated and experimental specific heat values within the whole temperature range below 320 K. The calculated specific heat is compared with the experimental one. A good agreement between calculated and experimental characteristics is achieved.

INTRODUCTION

The compound $Cr(AA)_3$ is a typical complex with β-diketones. The compounds of this type crystallize in molecular-type lattices. Highly volatile compounds of this class have a wide range of application [1–5] which determines the necessity to study their properties. In the recent years they became the subject of theoretical investigations [6, 7]. Scientific interest to the investigation of these molecular crystals is connected with the fact that the structure of metal β-diketonates allows to stay within the frames of constant molecular geometry while varying the types of radicals in ligands and thus changing the character of intramolecular vibrations. Besides, it is possible to change molecular mass and volume in a wide range by changing the central atom. This leads to the changes of intermolecular forces and, as a consequence, to the changes of dynamic and thermodynamic characteristics of the complex while the ligands and topology of molecule packing remain unchanged. This model approach is important when studying various aspects of physical chemistry of molecular crystals.

Model description of thermodynamic properties of complicated molecular crystals at the level of quantitative agreement with the experiment remains the problem not solved yet. It is difficult to describe such subjects because rigid properties of molecules is comparable with the rigidity of the carcass formed by these molecules. The energy of external and internal vibration modes of molecules can overlap substantially. This can lead to new effects that should be taken into account to provide correct description of the properties of molecular crystals.

In the present work we report the results of investigation into dynamic and thermodynamic characteristics of the $Cr(AA)_3$ molecular crystal using the lattice dynamics method and low-temperature adiabatic calorimetry.

The goal of this investigation was to study the influence of different regions of the phonon spectrum on dynamic and thermodynamic characteristics of the $Cr(AA)_3$ complex and to compare the quantitative contribution from intermolecular and intramolecular vibrations at different temperatures into thermodynamics.

INTERMOLECULAR VIBRATIONS

Modelling of contributions connected with intermolecular vibrations was performed within the frames of lattice dynamic approach which is usually used for molecular crystals [8]. Within this approach, the molecules of the crystal are considered as rigid ones. Intermolecular interaction is represented in atom-atom approximation by assigning the potentials to describe the interaction between the atoms of different molecules. Dynamic matrix with eigenvalues that determine the phonon spectrum is in this case more complicated than the matrix for ion crystals including translation, rotational and mixed terms. This approach has been already used to describe dynamic and thermodynamic characteristics of metal β-diketonates within the frames of harmonic approximation [7]. In the present paper we use a more complicated technique based on the use of quasi-harmonic approximation. It has been developed recently for molecular crystals for the purpose of investigating the stability of crystal structure within a wide range of pressures and temperatures [9–11]. The newest version of this technique that includes the optimization of both the shape of molecular cell and the positions of mass centres and molecule orientations in the cell is used in the present study to simulate dynamic and thermodynamic characteristics of chromium β-diketonate that are connected with intermolecular vibrations. This version is based on analytical relations given below.

The equilibrium shape of crystal (external coordinates) is determined, at a given temperature T and stress tensor $\sigma_{\alpha\beta}$, by the equation of state:

$$\sigma_{\alpha\beta} = \frac{1}{V_0}\left(\frac{\partial F_{\text{qh}}}{\partial \eta_{\alpha\beta}}\right) \tag{1}$$

where $\eta_{\alpha\beta}$ is the tensor of finite deformations; free energy of the crystal $F_{\text{qh}} = \Phi + F_{\text{vib}}$ is taken in quasiharmonic approximation. Here Φ is the potential energy of the crystal and F_{vib} is vibrational part of free energy. The derivatives in (1) with respect to $\eta_{\alpha\beta}$ are calculated for the equilibrium configuration; V_0 is the corresponding equilibrium volume.

The change of equilibrium tensor of finite deformations is connected with small changes of the tensor of stress or temperature *via* the following relation:

$$\Delta\eta^{\text{eq}}_{\alpha\beta} = -\frac{1}{V_0}\sum_{\sigma\tau}[C^{\text{is}}_{\alpha\beta\sigma\tau}]^{-1} F^{\text{vib}}_{T,\sigma\tau}\Delta T + \sum_{\sigma\tau}[C^{\text{is}}_{\alpha\beta\sigma\tau}]^{-1}\Delta\sigma_{\sigma\tau} \tag{2}$$

where

$$F^{\text{vib}}_{T,\sigma\tau} = \left(\frac{\partial^2 F_{\text{vib}}}{\partial T \partial \eta_{\sigma\tau}}\right) \tag{3}$$

and $[C^{\text{is}}_{\alpha\beta\sigma\tau}]^{-1}$ is the matrix which is reverse to the matrix of isothermal elastic constants $C^{\text{is}}_{\alpha\beta\sigma\tau}$. Equation (2) is used in our calculations both to describe the changes in the shape of elementary cell with changing temperature and to correct this shape for normal pressure. When describing the change of the elementary cell shape, new parameters are determined from the calculated $\Delta\eta^{\text{eq}}_{\alpha\beta}$ for changing temperature if the initial shape of cell corresponds to normal pressure. If pressure is different from normal one, correction tensor $\Delta\eta^{\text{cor}}_{\alpha\beta}$ is calcualted from equation (2) if the stress tensor for the initial cell shape $\sigma_{\alpha\beta}$ as determined from (1) does not correspond to normal pressure. The change of deformation tensor in (2) is chosen as follows:

$$\Delta\sigma^{\text{cor}}_{\alpha\beta} = p_0\sigma_{\alpha\beta} - \sigma_{\alpha\beta} \tag{4}$$

where $p_0 = 1$ bar, *i. e.* normal pressure. In order to realize the above procedure, it is necessary to calculate isothermal elastic constants. The scheme of this calculation for molecular crystals was discussed earlier [9–11] and is not given herein. In order to optimize internal coordinates, we use the Newton – Rapson method [12] adapted for the case of molecular crystals. Relative coordinates of mass centres and angular variables describing the orientation of all the N

molecules forming the elementary cell are used as $6N - 3$ internal coordinates. In the iteration procedure of the Newton – Rapson method, the difference $\Delta = R_f - R_{in}$ between the initial internal coordinates $R_{\sigma\tau}$ and their improved values R_f at the next step is equal to

$$\Delta = -H^{-1}(R_{in})A(R_{in}) \quad (5)$$

where $H(\mathrm{R}_{in})$ and $A(R_{in})$ are Hessian and vector composed of first derivatives; they are calculated for the initial configuration. In order to calculate these values, we used a simple approximation which is usually used for ion crystals [13]. In order to optimize internal coordinates, this approximation takes account of only the potential part of free energy of the crystal. In this case, the Hessian which is a $(6N - 3)$-dimensional matrix is constructed from dynamic matrix of the molecular crystal at $q = 0$, the matrix being $6N$-dimentional, by deleting three rows and three columns corresponding to the shift of mass centre of one (*e. g.*, the first) molecule of the elementary cell. The representation of the dynamic matrix and the first derivatives in terms of short-range and coulomb intermolecular potentials is well known. It has been presented, for example, in [14].

A detailed calculation procedure was as follows. The characteristics of the elementary cell and positions of molecules in it at T =300 K were taken as initial parameters. The shape of the cell and the positions of molecules were optimized for normal pressure at a given temperature according to the technique described above. The parameters thus obtained were used as initial ones to obtain structural parameters at lower temperatures. Further on, the procedure was repeated with temperature decreased stepwise till T = 5 K. The density of phonon states was calculated in all the temperature points using $5 \times 5 \times 5$ points of the Brillouin zone. In order to describe the interaction between the atoms of different molecules, Buckingham potential was used, as earlier in [7]. The parameters of this potential for the interaction between light atoms were taken from [15] while for the interaction of chromium with oxygen they were taken from [16]. As a result of these calculations, intermolecular vibraional spectra at different temperatures within the range of 5–310 K have been obtained. Figure 1 shows spectral density of vibrational modes at 5 and 310 K.

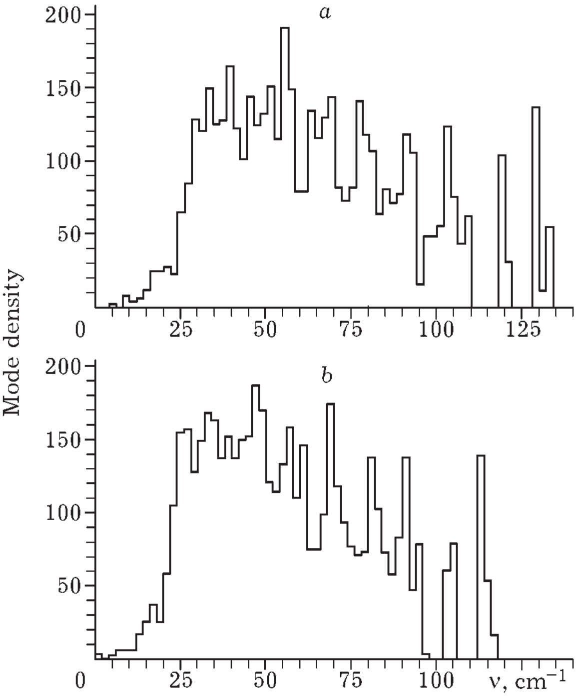

Fig. 1. Spectral density of intermolecular vibration modes of $\mathrm{Cr(AA)_3}$ at temperatures, K: 5 (*a*) and 310 (*b*).

INTRAMOLECULAR VIBRATIONS

In order to calculate vibration spectrum of chromium acetylacetonate molecule, we obtained numerical solution of the Schroedinger equation in harmonic approximation [17]:

$$\left[-\frac{\hbar^2}{2}\sum_{ij}\tau_{ij}\frac{\partial^2}{\partial q_i \partial q_j} + \frac{1}{2}\sum_{ij}u_{ij}q_i q_j\right]\Psi = E\Psi$$

Here $\hbar$ is Planck's constant, q_i are vibrational coordinates, τ_{ij} are cinematic coefficients, u_{ij} are force constants. We found 123 frequencies corresponding to internal vibrations of the $\mathrm{Cr(AA)_3}$ molecule.

Here initial parameters were the force constants of interatomic interactions and the characteristics of atom positions in the molecule. Well known force constants [17, 18] that provide good agreement of the calculated vibration spectra with experimental ones were used for valence bonds and angles. They were not varied further on. We varied mainly force constants connected with non-planar coordinates, which

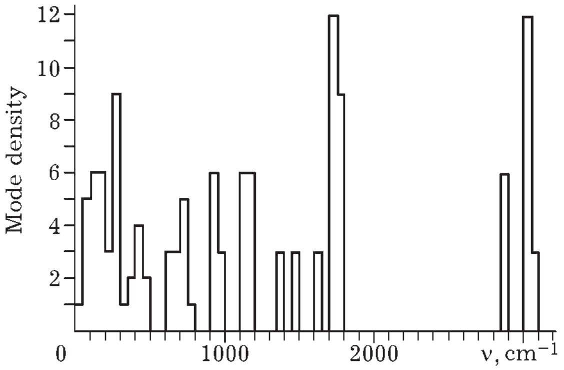

Fig. 2. Mode number per 50 cm^{-1} as a function of frequency for intramolecular vibrations of $Cr(AA)_3$.

were unknown for the compound under investigation. We used the spectroscopic data on isostructural compounds of this class [19, 20], as well as IR and Raman spectroscopic data obtained in the present work for $Cr(AA)_3$. It is necessary to stress that complications arise when choosing force constants responsible for the low-frequency spectral region. These complications are due to the absence of any information concerning the characteristic behaviour of frequency spectrum in this region and mode density within the frequency range under consideration. However, this spectral region substantially determines the behaviour of thermodynamic characteristics at temperatures below 320 K. In the present work we varied the corresponding force constants in order to achieve better agreement of the functional behaviour of specific heat $C_{CM}(T)$, calculated on the basis of frequency spectrum of intramolecular vibrations, with the component of specific heat $C_{EM}(T)$ obtained experimentally (see below). The result of the calculations for the frequencies of intramolecular vibrations is presented in Fig. 2 as the dependence of mode number on frequency.

SPECIFIC HEAT

Chromium *tris*-acetylacetonate $Cr(C_5H_7O_2)_3$ sample for experimental studies of specific heat was prepared according to the standard procedure [21]. Final purification of the sample was performed by double sublimation in vacuum gradient furnace. Visually, $Cr(AA)_3$ is a violet crystal powder with a mean crystallite size of 0.3–0.5 mm. The sample was characterized by means of chemical analysis, IR and Raman spectroscopy, derivatography and X-ray phase analysis. According to the results of the latter, the compound is single-phase and the structure of the crystals thus prepared corresponds to the structure of $Cr(AA)_3$ determined in [22].

Specific heat $C_p(T)$ of the $Cr(AA)_3$ sample was measured according to the adiabatic method in 107 points of 5–320 K temperature range using a calorimetric set-up characterized in [23, 24]. Square mean deviation of experimental points from the smoothed curve is 0.87 % within the temperature range of 5–14 K, 0.11 % within 14–105 K and 0.03 % within 105–320 K. Experimental $C_p(T)$ dependence is shown in Fig. 3.

On the basis of the calculated spectrum of intermolecular vibrations at different temperatures, the corresponding specific heat at constant volume $C_{VL}(T)$ and constant pressure $C_{pL}(T)$ was calculated (see Fig. 3). Specific heat $C_{CM}(T)$ connected with intramolecular vibrations involving 123 vibration modes was calculated within the temperature range of 5–320 K. It is shown in Fig. 3. Figure 3 shows also experimentally obtained specific heat of this component C which was determined as the difference $C_p(T) - C_{pL}(T)$.

It should be noted that the intermolecular component of specific heat is weakly changed within a broad temperature range of 50–320 K because here it has already achieved the Dulong – Petit law region. This is connected with the fact that intermolecular vibration spectrum is low-frequency. A definite error of the calculation of this component in the frames

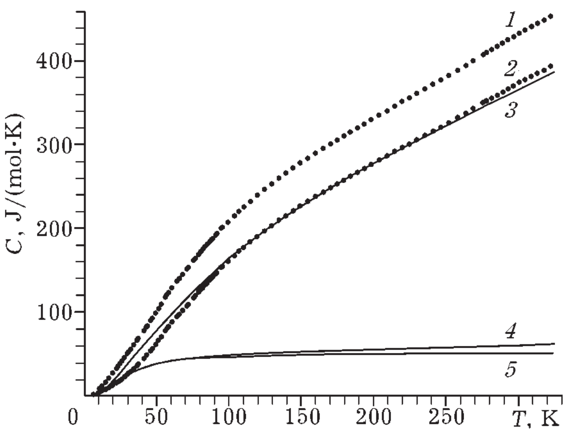

Fig. 3. Contributions from inter- and intramolecular vibrations into the specific heat of $Cr(AA)_3$: *1* – $C_p(T)$, experimental; *2* – $C_p(T) - C_{CM}(T)$, *3* – $C_{CM}(T)$, calculated; *4* – $C_{pL}(T)$, calculated; *5* – $C_{VL}(T)$, calculated.

of the model used by us would not cause any noticeable changes in the mentioned temperature range of 50–320 K. This gives us the possibility to compare the calculated intramolecular component $C_{\mathrm{CM}}(T)$ with the component $C_{\mathrm{EM}}(T)$ obtained by subtracting intermolecular component from the experimental value.

RESULTS AND DISCUSSION

Figure 1 shows that the edge of intermolecular vibration spectrum changes from 115 to 135 cm^{-1} when temperature increases from 5 to 310 K. Two localized bands separated by about 15 cm^{-1} are observed near the edge of the spectrum. When temperature is changed, these bands shift and can be observed at any frequency within the mentioned range. Intramolecular vibrations (see Fig. 2) within the frequency range of 500–3000 cm^{-1} exhibit frequency-localized peaks. Below 500 cm^{-1} high mode density is observed until the range of 50–40 cm^{-1}. Against the background of continuous spectrum, characteristic peaks with large mode density are observed in this range. Separate peaks at ~ 150, 270 and 450 cm^{-1} are clearly seen. The position of these peaks is not changed with temperature. The comparison of intermolecular and intramolecular spectra shown in Figs. 1 and 2 shows that they overlap within the frequency range of 50–140 cm^{-1}. In simple or not very complex crystals the inter- and intramolecular spectra are observed at different frequencies and usually do not touch each other. The data presented here show that when temperature is changed within 5–320 K, the peaks located near the boundary of intermolecular vibration spectrum are shifted and can coincide with the peaks of intramolecular vibrations that get into the region of overlapping. The equal frequencies of peaks with large mode densities related to different types of vibrations (inter- and intramolecular ones) can lead to their interaction.

Vibration modes in the vicinity of the edge of intramolecular spectrum (~ 3100 cm^{-1}) have practically no impact on specific heat since their contribution at 320 K is only 0.04 %. The contributions from all the modes with frequencies above 1200 cm^{-1} are comparable with the experimental error of $C_p(T)$ determination. The contributions from modes above 600 cm^{-1} are also small (about 1 %). Substantial effect on the behaviour of specific heat was found to be produced by vibration modes with frequencies below 500–600 cm^{-1}. Our data suggest that intramolecular vibrations have a decisive effect on the behaviour of low-temperature thermodynamic characteristics. For example, the contribution from intermolecular vibrations into total specific heat $C_p(T)$ at $T = 320$ K is about 85 %. The terms $C_{\mathrm{CM}}(T)$ and $C_{p\mathrm{L}}(T)$ become equal only at a low temperature of ~ 55 K. This behaviour is explained by the presence of high mode density below ~ 200 cm^{-1} in the intramolecular vibration spectrum.

The calculated $C_{\mathrm{CM}}(T)$ and experimental $C_{\mathrm{EM}}(T)$ specific heat values well coincide within the range of 80–320 K. The deviation in the vicinity of room temperatures can be explained by non-harmonic vibrations in the low-frequency region of the spectrum of intramolecular vibrations. Deviation below 80 K is quite noticeable. We could not exclude this difference by selecting force constants responsible for low-frequency spectral region. One can describe $C(T)$ for temperatures below 80 K if another set of force constants is used that changes substantially the vibration modes below 200 cm^{-1}. In our opinion, the reason of this may be the changes in the structure of molecules or crystals leading to the dependence of force constants on temperature.

The presence of overlapping in the spectra of inter- and intramolecular vibrations and the possibility of the interaction of vibration modes of different types can result in the occurrence of some phase transition. If we do not take such processes into account we are unable to describe specific heat within the whole temperature range using only one set of force constants. The authors of [25] who investigated specific heat, magnetic susceptibility, ESR and optical absorption spectra at different temperatures assumed the existence of a structural phase transition in $\mathrm{Cr(AA)_3}$ at 60 K which was connected with the dynamics of methyl groups $\mathrm{CH_3}$. In the case under consideration, the difference between $C_{\mathrm{CM}}(T)$ and $C_{\mathrm{EM}}(T)$ at temperatures below 80 K can also be considered as the evidence of structural change in Cr(AA)$_3$. The frequencies of methyl group torsion vibrations are close to those related to the overlapping parts of inter- and intramolecular vibration spectra. This increases the probability of the participation of interaction of vibration modes of different types in phase transition mechanism discovered in [25].

In general, we believe that at temperatures above 80 K a good agreement between calculated and experimental thermodynamic characteristics has been achieved. The deviation is comparable with experimental error. The results obtained can be used to calculate thermodynamic characteristics for isostructural compounds including β-diketonates. The choise of force constants with the help of experimental specific heat is a method surely having advantage since it takes correct account of mode density in separate spectral regions (especially in the most low-frequency region) which cannot be achieved using spectroscopic data. The technique used to bring calculated dynamic and thermodynamic characteristics into agreement with experimental ones can be applied to the studies of other complicated molecular crystals.

CONCLUSION

A complex investigation of the molecular crystal of chromium *tris*-acetylacetonate which is a typical representative of metal β-diketonates is reported. Overlapping of inter- and intramolecular vibration modes is observed. The contribution from intramolecular vibrations into specific heat of chromium *tris*-acetylacetonate is found to be decisive. The analysis of the data obtained points that this behaviour is the common property of metal β-diketonates.

A technique of the determination of force constants responsible for the low-frequency spectral region is proposed. It can be considered as a supplement to spectroscopic methods because the application of the latter within this spectral region is streitened, since the density of vibration modes at different frequencies within this spectral region is a poorly defined parameter. The necessity to use two different sets of force constants when describing the experimental specific heat above and below 80 K indicates that a phase transition occurs. This confirms the conclusions made by the authors of [25] concerning structural changes that occur at low temperature in the compound under investigation.

The approach proposed in the present study can be applied to the investigation of the properties of various solids with complex crystal structure.

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REFERENCES

1 G. A. Razuvayev, B. G. Gribov, B. A. Domrachev *et al.*, Metalloorganicheskiye soyedineniya v elektronike, Nauka, Moscow, 1972.
2 Pat. 2043325 UK, 1959.
3 I. K. Igumenov, Yu. V. Chumachenko and S. V. Zemskov, Problemy khimii i primeneniya β-diketonatov metallov, Nauka, Moscow, 1982, p. 100.
4 I. J. Junichi, *Cryst. Growth*, 115 (1991) 762.
5 Pat. 5096737, IBM US, 1992.
6 E. A. Mazurenko, A. I. Gerasimchuk and G. N. Bublik, *Ukr. khim. zhkurn.*, 57 (1991) 1011.
7 R. V. Belosludov, I. K. Igumenov, V. R. Belosludov and V. P. Shpakov, *Mol. Physics*, 82 (1994) 51.
8 G. Venkataraman and V. C. Sahni, *Rev. Mod. Phys.*, 42 (1970) 409.
9 V. P. Shpakov, J. S. Tse, V. R. Belosludov and R. V. Belosludov, *J. Phys. Condens. Matter*, 9 (1997) 5853.
10 V. P. Shpakov, J. S. Tse, C. A. Tulk *et al.*, *Chem. Phys. Lett.*, 282 (1998)107.
11 V. R. Belosludov, V. P. Shpakov, J. S. Tse and B. Kvamme, *Khimiya v interesakh ustoychivogo razvitiya*, 6 (1998) 75.
12 P. E. Gill, W. Mirray and M. H. Wright, Practical Optimization, Acad. Press, London, 1981.
13 G. M. Watson, P. Tschaufeser, A. Wall *et al.*, in C. R. A. Catlow (Ed.), Computer Modeling in Inorganic Crystallography, Acad. Press, San Diego, 1997, p. 55.
14 G. Nielson and S. A. Rice, *J. Chem. Phys.*, 80 (1984) 4456.
15 A. I. Kitayigorodsky and K. V. Mirskaya, *Kristallografiya*, 6 (1969) 507.
16 P. A. Stabnikov, I. K. Igumenov, V. R. Belosludov *et al.*, *Izv. SO AN SSSR. Ser. khim. nauk*, 1 (1985) 37.
17 M. V. Volkenstein, L. A. Gribov, M. A. Elyashevich and B. I. Stepanov, Kolebaniya molekul, Nauka, Moscow, 1972.
18 E. N. Yurchenko, Sovremennaya kolebatelnaya spektroskopiya neorganicheskikh soyedineniy, Nauka, Novosibirsk, 1990.
19 Yu. S. Yezhov, S. A. Komarov and V. G. Sevastyanov, *Zhurn. strukt. khimii*, 39 (1998) 633.
20 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, J. Wiley & Sons Publ., 1991.
21 W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, 5 (1951) 130.
22 B. Morosin, *Acta Cryst.*, 19 (1965) 131.
23 V. N. Naumov and V. V. Nogteva, *PTE*, 5 (1985) 86.
24 G. I. Frolova, L. E. Reznik and I. E. Paukov, *J. Chem. Thermodynamics*, 21 (1989) 25.
25 V. N. Naumov, G. I. Frolova, V. V. Nogteva *et al.*, *Chemistry for Sustainable Development*, 8, 1–2 (2000).