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ENTROPY MODEL OF CRYSTALS OF HEXAGONAL ICE

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Разработана уточненная энтропийная модель кристаллов гексагонального льда, включающая интерпретацию энтропии заторможенных трансляций и заторможенных колебаний на основе модели Энштейна. Исследована температурная зависимость энтропии в уточненной энтропийной модели кристаллов гексагонального льда. Произведено сравнение предлагаемой модели с полной и модифицированной энтропийными моделями льда.

Изучены сравнительные особенности температурных кривых термодинамической и спектроскопической энтропии для уточненной и известными энтропийными моделями кристаллов льда. Показано, что предлагаемая уточненная энтропийная модель с большей точностью по сравнению с известными моделями описывает температурную зависимость энтропии кристаллов гексагонального льда.

Ключевые слова: тепловые колебания, энтропия, решетка твердого тела, кристаллы, гексагональный лед.

1. Introduction

Studies of the entropy properties of solids are invariably the focus of the natural sciences. At present, the study of these problems has received particular importance in connection with the increased attention of science to the properties of crystalline solids at the nanoscale, since the lattice entropy of a crystal is one of the main basic indicators of its structure. In this regard, the correlation of the spectroscopic entropy of the thermal vibrations of the molecules of a substance with its thermodynamic properties is an urgent task.

In this work, a refined modified entropy model of hexagonal ice crystals is proposed to develop the theory of entropy of solids. Within the framework of this model, an interpretation of the contribution to the entropy of

hindered translations and hindered vibrations based on the Einstein model is proposed. The entropy of ice crystals obtained in the framework of this model is compared with experimental data and the data of known thermodynamic models.

2. Thermodynamic and spectroscopic entropy

Thermal lattice vibrations of solids are interpreted by linear oscillators with lattice vibrations obeying Bose-Einstein statistics [1].

The mode-averaged entropy of linear oscillators in the lattice of the j-th branch of oscillations Sj in the Einstein model is determined by the following formula [1]:

$$S_j = k_B \left[\frac{\eta \omega_j / kT}{e^{\eta \omega_j / kT} - 1} - ln \left(1 - e^{-\eta \omega_j / kT} \right) \right],$$ (1)

where η — Planck constant, k_B — Boltzmann constant, ω_j — Debye frequency of thermal vibrations of the j-th branch, T — absolute temperature.

In the complete thermodynamic model according to formula 1, we calculate the entropy of the optical, librational and intramolecular vibrations of the molecules.

For acoustic vibrations of molecules, the expression for the entropy of vibrations is interpreted in the framework of the Debye model [1]. In the indicated Debye model, the mode-averaged entropy of linear oscillators of the j-th acoustic branch of the molecular vibrations S_j^{ac} is:

$$\begin{aligned} S_j^{ac} =& k_B \left[\frac{4}{3} \left(\frac{T}{\theta_j} \right)^3 \int_0^{\frac{\theta_j}{T}} \frac{x^3}{e^x - 1} dx - ln(1 - e^{-\frac{T}{\theta_j}}) \right] = \\ =& k_B \left[\frac{4}{3} I \left(\frac{T}{\theta_j} \right) - ln(1 - e^{-\frac{T}{\theta_j}}), \right. \end{aligned}$$ (2)

where $\theta_j = \eta \omega_j / k$ — the characteristic temperatures (Debye temperatures) for the j-th branch of oscillations, $I \left(\frac{T}{\theta_j} \right)$ — the Debye integrals.

The expression for the spectroscopic or statistical entropy S_{spectr} calculated from spectroscopic data, within the framework of the full thermodynamic model, will have the following form:

$$S_{spectr} = S_0 + S_{ac} + S_{opt} + S_{libr} + S_{int},$$ (3)

where S_0 — the residual entropy of the lattice of a solid, S_{ac} — the entropy of acoustic vibrations of molecules, S_{opt} — the entropy of optical vibrations of molecules, S_{libr} — the entropy of librational vibrations of molecules, S_{int} — the entropy of intramolecular vibrations. The entropies

S_{ac}, S_{opt}, S_{libr} and S_{int} in formula 3 are summed over all possible branches of vibrations. The hexagonal ice lattice contains three branches for all types of vibrations, namely, optical, acoustic, librational, and intramolecular branches. Moreover, the branches of intermolecular vibrations are summed up over unit cells, and the branches of librational vibrations and intermolecular vibrations over molecules.

The calorimetric entropy of S_{cal} is determined from experimental data on measuring the temperature dependence of the heat capacity of ice C_{cal} in the calorimeter as follows:

$$S_{cal} = \int_0^T \frac{C_{cal}}{t} dt. \tag{4}$$

The integration in formula 4 is performed with a step in t (integrand temperature) of 10 K, in the range from 0 K to the current temperature T in accordance with the available experimental data on heat capacity.

3. Entropy of hexagonal ice crystals

Physical characteristics and constants for crystals of hexagonal ice I_h, as a symmetry group, coordination number, number of molecules per unit cell, H_2O molecule mass, etc., were taken from [2–4]. The calorimetric data on the specific heat in the temperature range 20–273 K were taken from [5]; for 10 K, from [6]; for 3 K, the upper limit for the specific heat obtained by the authors for the interval 0–4 K in [7] was used. The residual entropy for hexagonal ice crystals is 0.805 cal/(mol*K) or $3.493*10^{-5} eV/K$ [4].

The values of the characteristic frequencies of thermal vibrations (inhibited translations), librational (inhibited) molecular vibrations, and intramolecular vibrations were taken from [8]. The author thoroughly studied the IR absorption spectra of ice crystals in the range of inhibited translations of 50-360 cm^{-1}. The maxima were established, which the authors attributed to longitudinal LA and transverse TA acoustic vibrations of 164 and 65 cm-1, respectively. Also, maxima were found that correspond to longitudinal LO and transverse TO optical vibrations of 190 and 229 cm^{-1}.

In this article, based on the above characteristic frequencies, a complete and refined modified entropy model of ice crystals is constructed. The temperature curve of calorimetric entropy is derived by formula 4 (Fig. 1). The entropy curve was separately plotted in the temperature range from 0 to 30 K (Fig. 2), since there the behavior of thermodynamic quantities near absolute zero differs significantly from the behavior at high temperatures. The complete entropy model of ice is constructed on the basis of formulas 1–3 by summing over all branches of vibrations with characteristic frequencies

of acoustic vibrations of 164, 164, 65 cm^{-1} (Debye model), optical vibrations of 190, 229, 229 cm^{-1} (here and further Einstein's model), librational vibrations of 840, 840, 840 cm^{-1} and intramolecular vibrations of 3220, 1650, 3220 cm^{-1} (symmetric valence, deformation and valence antisymmetric absorption bands).

Within the framework of the full entropy model, the spectroscopic entropy Sspectr of ice crystals was calculated (Fig. 1). It can be seen from the figure that the entropy in the complete entropy model describes the Ucal calorimetric curve well only at temperatures below 200 K, and above this threshold it is significantly lower than the experimental data. The pair linear correlation coefficient calculated in this work and the average deviation error of these curves, calculated by formula 5, are 0.9985 and 4.1% in the temperature range 0–270 K, and 0.9993 and 5.1% in the range 0–30 K.
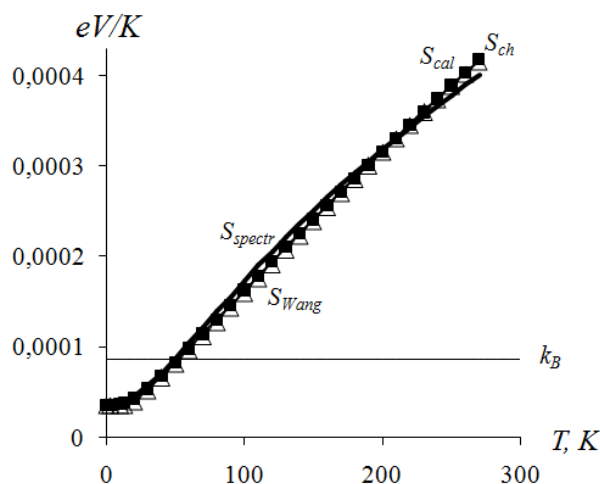

Fig. 1. The temperature dependence of the entropy of hexagonal ice crystals in the range 0-270 K according to S_{cal} calorimetric data (square black markers), Sspectr spectroscopic entropy (thick line) calculated from spectroscopic data, SWang entropy (white triangles) and Sch (thin line), calculated in modified and refined modified models, respectively. kB - the value of the Boltzmann constant. The curves are calculated according to formulas 1-4 and are presented per one molecule

At a hexagonal ice temperature of 273 K, the total contribution of acoustic vibrations to Sspectr is 57.7%, the contribution of optical vibrations is 29.5%, and the contribution of librational vibrations is 4.1%. The contribution of residual entropy in this case is 8.7%. At the same temperature, the S_{spectr}/S_{cal} ratio is 95.9%. The entropy of intramolecular

Sint vibrations can be neglected, since even at 270 K their entropy is much lower than S$_{spectr}$.
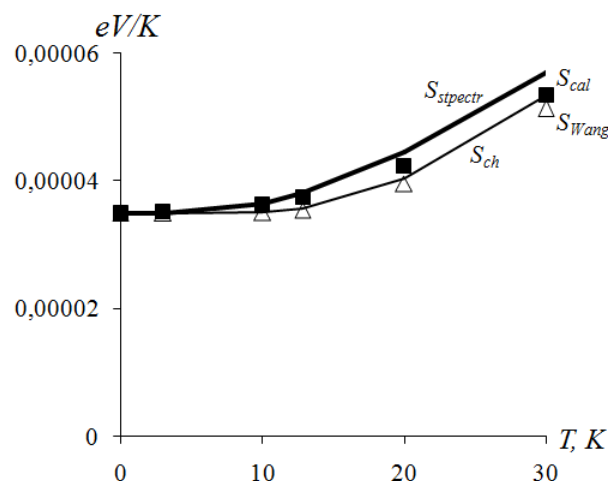

Fig. 2. Temperature dependence of the entropy of hexagonal ice crystals in the range of 0-30 K according to S_{cal} calorimetric data (square black markers), S$_{spectr}$ spectroscopic entropy (thick line) calculated from spectroscopic data, SWang entropy (white triangles) and Sch (thin line), calculated in modified and refined modified models, respectively. The curves are calculated according to formulas 1-4 and are presented per one molecule

Due to the large number of branches of vibrations of molecules in the structure of any substance, the entropy models built on the basis of harmonic oscillators, such as the full and modified entropy models, accumulate an error with each term. Accurate calculation of thermodynamic characteristics is possible only at the quantum physical level, taking into account the anharmonicity of molecular vibrations. Such a calculation is very complicated and possible only for any specific conditions (specific temperature, etc.). In addition, it is based on numerical methods and is also approximate.

To describe the temperature dependence of entropy in physicochemical studies, it is necessary to have an analytical expression for the value of entropy in order to calculate the heat capacity at any temperature as accurately as possible. The calorimetric curve gives the values of entropy only at the reference points at which measurements were made. At the same time, it is practically impossible to obtain the corresponding characteristic vibration frequencies by regression analysis of the calorimetric curve due to the essentially nonlinear nature of the temperature dependence of the heat

capacity. In addition, ice samples may contain impurities and defects that affect the absolute value of entropy.

Therefore, Einstein's thermodynamic models with a much smaller number of characteristic frequencies are used as an analytical dependence of the ice entropy on temperature, compared with the full model. The characteristic frequencies of the thermodynamic model and the corresponding wave vectors are selected near the maxima of the IR absorption spectra, while these maxima are very blurred. In accordance with studies of the infrared absorption spectrum of ice, the range of wave vectors at the maxima of the infrared absorption spectrum of hexagonal ice for acoustic vibrations is $60–164$ cm^{-1}, for optical vibrations is $190–229$ cm^{-1}, for libration vibrations are $500–840$ cm^{-1} [2].

The last and most accurate entropy model of hexagonal ice crystals is the modified model described in [9] and based on the Einstein model and the frequencies of hindered vibrations of 65, 229, 229 cm^{-1}and hindered vibrations of $540, 540, 540$ cm^{-1}. The entropy values in the framework of this SWang model are presented in Fig. 1 and 2 white triangles. The pair linear correlation coefficient and the average deviation error, calculated according to formula 5, of the SWang and S_{cal} curves are 0.99996 and 1.0% in the temperature range $0–270$ K, and in the range $0–30$ K $— 0.9906$ and 5.4%, respectively.

$$Q = \frac{1}{\bar{S}_{cal}} \sqrt{\sum_{i=1}^{m} \frac{\left(S_{ch}\left(i\right) - S_{cal}(i)\right)^2}{(m-2)}}, \qquad (5)$$

where Q — the average deviation error (variation) of the Sch and S_{cal} curves, $\bar{S}_{cal}$ — the average value of the calorimetric entropy, m - the number of points on the temperature curve.

The paired linear correlation coefficient r is calculated by the following formula:

$$r = \frac{cov(S_{ch}, S_{cal})}{\sigma_{ch}\sigma_{cal}}, \qquad (6)$$

where cov(Sch,S_{cal}) — the covariance of the temperature curves Sch, S_{cal} and σ_{cal} — the standard deviation of the corresponding temperature curves Sch and S_{cal} [10].

The average error of the deviation of the curves over the entire temperature range is 4 times less than the error in the full entropy model. Moreover, in the range of 0-30 K, the deviation error of the curves in the modified model is 0.3% larger than in the full model. This discrepancy in

the entropy curves in the modified model is partially removed by taking into account the Lawrence broadening effect, which significantly complicates the calculations and leads to the loss of the analytical form of equation [9] due to non-table integrals.

We propose a refined entropy model of hexagonal ice crystals with characteristic frequencies of hindered vibrations of 62, 229, 229 cm^{-1} and hindered vibrations of 571, 571, 571 cm^{-1}. The calculation of entropy along the branches of oscillations is carried out in the Einstein model. The temperature curve in this Sch model is shown in Fig. 1 and 2 thin line.

A comparison of the curves shows that this model better describes the experimental data. The paired linear correlation coefficient of the curve in this Sch model and the S_{cal} experimental curve and the average deviation error of these curves are 0.99997 and 0.7% in the temperature range 0-270 K, and in the range 0-30 K - 0.9926 and 3.7%, respectively. In this model, in the range of 0-270 K, the correlation coefficients are higher, and the deviation errors of the Sch and S_{cal} curves are lower than for the full and modified models. Compared with the modified model, the deviation error decreases by 1.4 times, and compared with the full model by almost 6 times. In the range of 0-30 K, the same situation is compared with the full and modified models - the deviation error is 1.4 times less.

Thus, using the refined modified thermodynamic model, we can analyze the temperature dependence of the entropy of hexagonal ice crystals.

4. Conclusion

A refined entropy model with characteristic frequencies (wave vectors) of 62, 229, 229, 571, 571, 571 cm^{-1}, which describes the temperature dependence of the entropy of hexagonal ice crystals, is proposed.

The temperature curves of the entropy of hexagonal ice crystals for the complete, modified, and refined entropy models were constructed and compared with experimental calorimetric curves. The average errors of the deviation of the temperature curves of entropy in the refined entropy model in comparison with the modified and full models are 1.4 and 5.9 times lower, respectively.

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Summary
Cheredov V. N.　Entropy model of crystals of hexagonal ice

A refined entropy model of hexagonal ice crystals is developed, including an interpretation of the entropy of hindered translations and hindered vibrations on the basis of the Einstein model. The temperature dependence of the entropy in the refined entropy model of hexagonal ice crystals is studied. A comparison of the proposed model with the complete and modified entropy models of ice is made.

Comparative features of the temperature curves of thermodynamic and spectroscopic entropy for the refined entropy model of ice crystals, modified

and known, were studied. It is shown that the proposed refined entropy model describes the temperature dependence of the entropy of hexagonal ice crystals with greater accuracy in comparison with known models.

Keywords: thermal vibrations, entropy, lattice of a solid, crystals, hexagonal ice.

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