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CONSTRUCTION OF EQUATIONS OF THE STATE TO DESCRIBE ISOTHERMAL COMPRESSION OF SOME MOLECULAR CRYSTALS OF NITRO-COMPOUNDS

*Yu. M. Kovalev*¹, yum_kov@mail.ru,

*K. M. Kalinin*¹, mathideas74@gmail.com

¹ South Ural State University, Chelyabinsk, Russian Federation

We propose an approach to construct the equations of state of molecular crystals of nitro compounds. The approach allows to describe isothermal compression, and is based on the division of the Helmholtz free energy into thermal and "cold" parts. It turns out that the "cold" part can be divided into the intramolecular and intermolecular components, while the low-frequency and high-frequency vibrations can be distinguished in the thermal part. We propose to approximate the low-frequency component of the thermal part of the internal energy and the pressure of a molecular crystal by the Debye approximation. In order to describe the intermolecular energy of the Van der Waals interaction, we propose a potential that closes on the heat of sublimation of a molecular crystal. The "cold" part of pressure is determined by the change in intramolecular energy. We assume the "cold" part of pressure to be constant, and use the condition that the pressure is equal to 1 atm. under normal conditions in order to determine this part. This division of the Helmholtz energy allows to obtain explicitly the expressions for all thermodynamic values in the equations of state. In this paper, we assume the linear dependence of the Gruneisen coefficient on the volume. The use of a more complex relationship is not necessary, since we consider the isothermal compression, and the thermal component makes an insignificant contribution to the total pressure. We use the obtained dependences of thermodynamic values on temperature and volume in order to find the coefficients related to the known experimental data. A comparative analysis of the calculated and experimental values of the specific volumes of the molecular crystal of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as a function of pressure shows their coincidence with an accuracy of 1%.

Keywords: equation of state; molecular crystal; isothermal compression; Helmholtz energy; characteristic Debye temperature; Gruneisen equation; Debye approximation.

Introduction

At present, the balance between detonation power and sensitivity to external influences is a fundamental principle in the development of next-generation high-explosives. This approach led to the creation of new inert explosives (IE). For example, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was created. An interesting feature of TATB is extensive intermolecular hydrogen bonds leading to the formation of graphite crystalline structures. Moreover, TATB is especially attractive due to the fact that its resistance to external influences is combined with high density, high detonation pressure, and high detonation speed [1, 2]. Despite the fact that TATB was synthesized in 1988, TATB turned out to be less studied than its more sensitive and stronger equivalents, for example, hexogen and

octogen. This is due to the fact that TATB crystals have triclinic symmetry [3–5], which complicates the determination of material properties due to internal anisotropy.

The introduction of new methods for registering high-speed processes, as well as the development of computer technology, led to the fact that mathematical modelling is a competent method to study physical processes, which allows to obtain reliable information. As a result, there is an increase in the requirements for mathematical models of the equations of state describing the thermodynamic properties of substances. Indeed, the reliability and accuracy of calculations of high-speed processes in condensed substances are determined primarily by the inadequacy of the equations of state of the environment.

At present, quantum-mechanical methods to calculate the equations of state are actively developed [6–8]. The main difficulty in the implementation of the methods is the need to choose an adequate mathematical model of interparticle interaction. The constant increase in the speed of computing technology allows to complicate the mathematical equations of state. However, the results of calculations must be compared with experimental data [9]. Despite the progress achieved in the development of the equations of state, these equations can be used to study a limited number of problems, for example, to study the isothermal compression of solids, including molecular crystals. However, these equations can not be used to solve dynamic problems that consider high-speed processes and require to calculate the thermodynamic state of the medium at each time layer and at each space point.

Development of mathematical models for constructing semi-empirical equations of state [10] can help to solve this problem. In this case, we use theoretical considerations in order to determine the form of the functional dependence of one of the thermodynamic potentials for the semi-empirical equation of state. At the same time, the coefficients of the thermodynamic potential should be determined on the basis of the results of thermodynamic experiments. Recently, quite a large number of publications, both experimental and theoretical, are devoted to the study of various aspects of the behavior of molecular crystals: the study of isothermal compression, the construction of dependencies describing the behavior of the frequencies of normal vibrations on pressure, shock adiabats, etc. Nevertheless, the theory of constructing mathematical models of semi-empirical equations of state of molecular crystals is constantly developed and far from its completion [9–12]. Let us give two possible reasons. On the one hand, the theoretical determination of the thermodynamic properties of molecular crystals, including solid explosives, is complicated by the fact that a considerable computational resource is required even for the simplest models describing the interparticle interactions and the vibrational motion of molecules forming a molecular crystal of nitro compounds. On the other hand, experimental work is limited by the possibility of explosive transformations at high pressures.

As a rule, in order to construct mathematical models of semi-empirical equations of state of molecular crystals, the pressure and internal energy are divided into two components: thermal and "cold" [9–13]. In the equations of state, the thermal component is determined by the kinetic energy of the atoms forming the crystal molecules, and the cold component is determined by the change in the potential energy of the interparticle interaction, both within the molecule and between molecules, depending on the volume of the molecular crystal. It is necessary to use known experimental data in order to verify the reliability of the constructed equations of state by independent verification of the

thermal and "cold" components of pressure and internal energy. In order to verify the thermal component of pressure and internal energy, we can use experimental data on the dependence of the heat capacity and isobaric coefficient of volume expansion of a molecular crystal on temperature, and for the "cold" one – the isothermal compressibility data.

The objectives of the paper are as follows.

1. Construct the equations of state of a molecular crystal in order to describe the isothermal compression of TATB.

2. Verify the obtained dependence of pressure on the relative specific volume. To this end, we use experimental data on the isothermal compression of 1,3,5-2,4,6-trinitrobenzene crystals (TATB) [4].

1. Equations of State of Molecular Crystals of Nitro Compounds

Depending on the set of experimental data, the construction of a semi-empirical equation of state of a molecular crystal begins with the choice of the thermodynamic potential. In this paper, we choose the Helmholtz free energy as such a thermodynamic potential, since the Helmholtz free energy is most simply and naturally associated with the model of the structure of substance [14–16], and is automatically divided into thermal and "cold" components:

$$F = U + E_0 + kT \sum_{\alpha} \ln \left(1 - \exp \left(-\frac{h\omega_{\alpha}}{kT} \right) \right), \quad E_0 = \frac{1}{2} \sum_{\alpha} h\omega_{\alpha}. \quad (1)$$

Here U , T , h , k , ω_{α} , and E_0 are the energy of interparticle interaction between atoms of a crystal, body temperature, Planck constant, Boltzmann constant, frequencies of normal vibrations, and energy of zero vibrations, respectively. In formula (1), the sum is taken over the frequencies of vibrations of both the molecules forming the crystal structure, and the atoms forming the molecules. We determine the expression for the Helmholtz free energy function $F(V, T)$, differentiate the given thermodynamic potential by volume and temperature, and find all forms to determine both measured and calculated thermodynamic characteristics [17].

In the equation for the Helmholtz free energy $F(V, T)$ (1), the energy of interparticle interaction between the atoms of a molecular crystal can be divided into the following two components: the intramolecular U_M , which determines the energy of the interaction of atoms inside the molecule, and the intermolecular (elastic) U_C , which determines the energy of non-valence interactions of atoms between molecules. The elastic energy U_C depends on the geometry of the molecular crystal, i.e. on the spatial arrangement of the molecules and the volume of the unit cell. The intramolecular energy U_M is the energy of formation of a molecule and depends exclusively on the structure of the molecule.

Divide all frequencies of normal vibrations of atoms in a crystal into the low-frequency (deformation) and high-frequency (intramolecular) [18, 19]. Here low-frequency vibrations include six vibrations of the molecule as a whole (three vibrations of the center of mass, and three Euler angles), as well as vibrations inside the molecule depending on the crystal field, for example, torsional vibrations of nitro groups and amino groups. High-frequency vibrations inside the molecule have larger order than low-frequency ones. Therefore, we can divide the vibrational component of the Helmholtz free energy into low-frequency and high-frequency ones. Note that the frequencies of the deformation vibrations are

determined by the change in the energy U_C , i.e. the energy of non-valent interactions between molecules. Consequently, only low-frequency vibrations depend on the volume. The papers [13, 20] successfully use the possibility of frequency division in molecular crystals in order to calculate the temperature at the shock wave front for a number of organic nitro compounds, while the paper [21] experimentally confirm this possibility in the case of nitromethane.

Let us use the Debye approach to describe the low-frequency component of the Helmholtz free energy $F(V, T)$. Then we can rewrite the vibrational component of the free energy in expression (1) as follows:

$$F = U_C + U_M + E_0 + 3MRT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\frac{\theta_D}{T}} \xi \ln(1 - \exp(-\xi)) d\xi + RT \sum_{i=M+1}^{3N} \ln \left(1 - \exp \left(-\frac{\theta_i}{T} \right) \right). \quad (2)$$

Here R , M , N , $3N - M$, θ_D , θ_i are the universal gas constant divided by the molecular mass of the substance μ , the number of low-frequency vibrations, the number of atoms in a molecule, the number of high-frequency vibrations, the characteristic Debye temperature, the characteristic temperatures of high-frequency vibrations, respectively.

Integrate by parts the fourth term in the expression for the free energy $F(V, T)$ defined by equality (2), use the Debye function $D(x)$ [22],

$$D(x) = \frac{3}{x^3} \int_0^x \xi^3 \frac{d\xi}{\exp \xi - 1},$$

and obtain the following equality:

$$F = U_C + U_M + E_0 + MRT \left(\ln(1 - \exp(-x_D)) - \frac{D(x_D)}{3} \right) + RT \sum_{i=M+1}^{3N} \ln \left(1 - \exp \left(-\frac{\theta_i}{T} \right) \right), \quad (3)$$

where $x_D = \frac{\theta_D}{T}$.

We use expression (3) for the free energy $F(V, T)$ in order to obtain the expressions for the pressure P and the entropy S . To this end, we differentiate the free Helmholtz energy by volume and temperature, respectively:

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = - \frac{\partial U_C}{\partial V} - \frac{\partial U_M}{\partial V} - \frac{dE_0}{dV} - MRTD(x_D) \frac{d(\ln \theta_D)}{d(\ln V)} \frac{1}{V}, \quad (4)$$

$$S = - \left\{ MR \left[\ln(1 - \exp(-x_D)) - \frac{D(x_D)}{3} \right] - MRD(x_D) + R \sum_{i=M+1}^{3N} \ln(1 - \exp(-x_i)) - R \sum_{i=M+1}^{3N} \frac{x_i}{\exp(x_i) - 1} \right\}. \quad (5)$$

In expression (5), we introduced characteristic temperatures for high-frequency vibrations $x_i = \frac{\theta_i}{T}$. In order to obtain the formula, we used the following feature of the Debye function:

$$D(x) = \frac{x}{\exp(x) - 1} - \frac{x}{3}D'(x),$$

where the prime denotes differentiation by the characteristic temperature x .

Equations (3) and (5) allow to determine the expressions for the total energy E and the heat capacity at a constant volume C_V :

$$E = F + TS = U_C + U_M + E_0 + MRTD(x_D) + RT \sum_{i=M+1}^{3N} \frac{x_i}{\exp(x_i) - 1}, \quad (6)$$

$$C_V = C_{VD} + C_{VM} = MR \left(4D(x_D) - \frac{3x_D}{\exp(x_D) - 1} \right) + R \sum_{i=M+1}^{3N} \frac{x_i^2 \exp(x_i)}{(\exp(x_i) - 1)^2}. \quad (7)$$

Here C_{VD} and C_{VM} are the components of heat capacity at a constant volume that depend on low-frequency and high-frequency (intramolecular) vibrations of the molecule, respectively. C_{VD} is determined in the Debye approximation, and C_{VM} is called intramolecular.

We introduce the Gruneisen coefficient by the formula

$$\gamma_D(V) = -\frac{d(\ln \theta_D)}{d(\ln V)},$$

and write expression (4) as follows:

$$P = -\frac{\partial U_C}{\partial V} - \frac{\partial U_M}{\partial V} - \frac{dE_0}{dV} + \frac{MRT\gamma_D(V)D(x_D)}{V}. \quad (8)$$

Based on the definition of the energy of zero vibrations and taking into account the division of frequencies, we obtain expressions for the functions E_0 and $\frac{dE_0}{dV}$:

$$E_0 = \frac{1}{2} \sum_{\alpha} h\omega_{\alpha} = \frac{3}{8}MR\theta_D(V) + \frac{1}{2}R \sum_{i=M+1}^{3N} \theta_i, \quad \frac{dE_0}{dV} = -\frac{3}{8} \frac{MR\gamma_D(V)\theta_D(V)}{V}. \quad (9)$$

Taking into account equality (9), differentiate expression (3) by volume V and obtain the expression for pressure P :

$$P = \frac{MRT\gamma_D(V)}{V}(D(x_D)) + P_C, \quad P_C = -\frac{\partial U_C}{\partial V} - \frac{\partial U_M}{\partial V} + \frac{3}{8}MRT\gamma_D(V)x_D/V, \quad (10)$$

where expression (10) defines the cold component of pressure. The papers [18, 19] give a detailed description of the approaches to determine the number of low-frequency vibrations M .

2. Mathematical Model of the Elastic Component of the Equation of State of High-Molecular Structural Materials

In order to construct a mathematical model of the elastic component of the equation of state of molecular crystals, it is necessary to choose the form of potential of nonvalent interactions between atoms of different molecules that form a molecular crystal, to calculate the energy of the crystal lattice, and to compare the energy with the heat of sublimation. In practice, the scheme of atomic potentials [14] is a good tool to calculate the energy of the lattice of organic molecular crystals. In the scheme, the potentials can be represented by the analytical expressions of the Buckingham (6-exp) or Lennard-Jones (6-12) type, where arbitrary parameters of the expressions are determined experimentally and, possibly, taking into account the electrostatic interactions. The paper [23] shows that the energy of electrostatic interactions can be up to 30% of the energy of the lattice of molecular crystals of nitro compounds.

The papers [6–8] show that detalization of calculations of interparticle interactions leads to enormous expenditure of computer time. In the A.I. Kitaygorodskiy model, an approximation of the energy of non-valent intermolecular interactions by a set of potentials leads to the appearance of a large number of constants, which sometimes can not be adequately determined from the available experimental data.

Consequently, it is necessary to choose some effective potential of elastic interaction having the following properties. First, the potential takes into account the features obtained as a result of detailed calculations of the energy of elastic interactions of molecular crystals of nitro compounds. Second, the potential can be used to solve problems of mathematical physics. Therefore, in accordance with the ideas of the work [15] and taking into account the recommendation of the work [23], the energy of elastic interactions can be expressed as follows:

$$U_C = \frac{3A}{b\rho_0} \exp \left[b \left(1 - x^{\frac{1}{3}} \right) \right] - \frac{C}{2\rho_0} x^{-2} - \frac{3D}{\rho_0} x^{-\frac{1}{3}}, \quad (11)$$

where $x = \rho_0/\rho$ is a dimensionless volume; A , b , C , D are constants to be defined. In equality (11), the second term describes the energy of Van der Waals, and the third term describes the energy of electrostatic interaction. Due to the fact that the second and third terms describe the energy of attraction [23], the terms are presented with a minus sign. Therefore, it is necessary to modify the potential of elastic interactions (11). Taking into account that the expressions describing the energy of attraction have an extremum at a point, we replace the sum of the second and third terms with one function as follows:

$$U_C = \frac{3A}{b\rho_0} \exp \left[b \left(1 - x^{\frac{1}{3}} \right) \right] - \frac{C}{n\rho_0} x^{-n}. \quad (12)$$

Potentials of elastic interactions (11) and (12) differ in that the exponent is not fixed in the expression describing the energy of attraction, and must be determined from experimental data [1, 2]. In order to determine the constants of expression (12), it is necessary to choose four parameters from an experiment, and close the equations of state to the parameters at a temperature of $T = 0$ K or $T = 293$ K.

Differentiate expression (12) by specific volume V and obtain the following form of the expression of the elastic pressure P_C conditioned by the energy of elastic interactions $U_C(x)$:

$$P_C = Ax^{-\frac{2}{3}} \exp \left[b \left(1 - x^{\frac{1}{3}} \right) \right] - Cx^{-(n+1)}. \quad (13)$$

In order to obtain the relationship between the coefficients in the expressions for the elastic components of the internal energy (12) and pressure (13), with the properties of crystals that are more understandable from the point of view of physics, we make a number of transformations. By definition, the isothermal compressibility β_T is related to the isothermal speed of sound as follows:

$$\frac{1}{\beta_T} = \frac{c_T^2}{V} = -V \left(\frac{\partial P}{\partial V} \right)_T. \quad (14)$$

Substitute expression (10) in the right-hand side of equality (14) and obtain

$$\begin{aligned} \frac{1}{\beta_T} &= -V \frac{\partial}{\partial V} \left\{ MRT \gamma_D(V) \left[\frac{3}{8} x_D + D(x_D) \right] / V + P_C \right\}_T = \\ &= MRT [\gamma_D^2(V) + \gamma_D(V)] \left[\frac{3}{8} x_D + D(x_D) \right] / V - V \frac{\partial P_C}{\partial V} - MRT \gamma_D^2(V) D_C(x_D) / V - \\ &\quad - MRT \gamma_D'(V) \left[\frac{3}{8} x_D + D(x_D) \right], \end{aligned} \quad (15)$$

where γ_D' is the derivative with respect to V of the Gruneisen coefficient

$$D_C(x_D) = \left(4D(x_D) - \frac{3x_D}{\exp(x_D) - 1} \right), \quad \frac{\partial x_D}{\partial V} = -\frac{x_D}{V} \gamma_D(V).$$

In order to obtain equality (15), we take into account that the change in the intramolecular energy U_M under the action of the crystal field is small compared with the energy of the molecule formation [14]. Therefore, further, we can assume that the derivative of the intramolecular energy U_M with respect to the volume is constant and is determined from the condition that the pressure is equal to 1 atm. under normal conditions.

In the case of small compression, the papers [24, 25] show that the dependence of the Gruneisen coefficient on the specific volume can be described by the following expression:

$$\gamma_D = \gamma_D^0 \left(\frac{V}{V_0} \right), \quad (16)$$

which is widely used to process experimental data. Here γ_D^0 is the value of the Gruneisen coefficient under normal conditions $V = V_0$, $T = T_0$. In order to use expression (14) for the Gruneisen coefficient γ_D , it is necessary to determine its value γ_D^0 corresponding to the initial specific volume V_0 . To this end, the paper [19] obtain an analogue of the Gruneisen equation for molecular crystals in the following form:

$$\alpha C_T^2 = \gamma_D(V) C_{VD}, \quad (17)$$

where the values of the isobaric coefficient of volume expansion α and isothermal velocity of sound C_T are chosen from the experiment, and the heat capacity is determined at a constant volume C_{VD} of equation (7) at the initial values of the specific volume and temperature.

Substitute the expression for the Gruneisen coefficient (16) in equality (15). We obtain the expression for isothermal compressibility in the following form:

$$\begin{aligned} \frac{1}{\beta_T} &= -V \frac{\partial}{\partial V} \left\{ MRT\gamma_D(V) \left[\frac{3}{8}x_D + D(x_D) \right] /V + P_C \right\}_T = \\ &= MRT\gamma_D^2(V) \left[\frac{3}{8}x_D + D(x_D) - D_C(x_D) \right] /V - V \frac{\partial P_C}{\partial V}. \end{aligned} \quad (18)$$

Let us estimate the contributions of individual terms that form the isothermal compressibility. Under normal conditions $T = 293$ K and $V_0 = 0.5162$ cm³/g, it turns out that the contribution of the first term in equation (18) is three orders of magnitude less than the contribution of the second term. Therefore, further, the first term in equation (18) can be ignored. We turn from isothermal compressibility to isothermal speed of sound, and obtain

$$\frac{c_T^2}{V_0} = -V_0 \frac{dP_C}{dV}. \quad (19)$$

Substitute expression (12) for cold pressure in the right-hand side of equality (19), for $x = 1$ we obtain

$$\begin{aligned} -V_0 \frac{\partial P_y}{\partial V} &= -\frac{\partial P_y}{\partial V} = \frac{2}{3}Ax^{-5/3} \exp[b(1 - x^{1/3})] + \frac{1}{3}Abx^{-4/3} \exp[b(1 - x^{1/3})] - \\ &- C(n+1)x^{-(n+2)} = \frac{2}{3}A + \frac{1}{3}Ab - C(n+1). \end{aligned} \quad (20)$$

Note that the elastic component of the internal energy has a minimum for $x = 1$. Therefore, the value of the elastic component of pressure is zero for $x = 1$. Also, as follows from expression (13), the coefficients A and C are equal. We use equations (19) and (20) to determine the coefficient A by the speed of sound C_T for $x = 1$ and $T = 293$ K:

$$A = 3c_T^2\rho_0/(b - 3n - 1).$$

In this case, the expressions for the elastic component of the internal energy and the elastic component of pressure take the following form:

$$U_C = \frac{3c_T^2}{bn(b - 3n - 1)} \left[3n \exp \left(b \left(1 - x^{\frac{1}{3}} \right) \right) - bx^{-n} \right], \quad (21)$$

$$P_C = \frac{3c_T^2\rho_0}{(b - 3n - 1)} \left[x^{-2/3} \exp \left(b \left(1 - x^{\frac{1}{3}} \right) \right) - x^{-(n+1)} \right]. \quad (22)$$

3. Equations of State of Molecular Crystals of Nitro Compounds to Describe Isothermal Compression

In order to describe the behavior of molecular crystals of nitro compounds under isothermal compression, it suffices to construct one equation of state, which determines the dependence of the pressure P on the density ρ or specific volume V . We use the condition that the pressure is equal to 1 atm. under normal conditions in order to normalize equation (10) with the help of the derivative of the intramolecular energy with respect to the volume. As a result, we obtain the following equality:

$$P = MRT_0\gamma_D^0\rho_0(D(x_D) - D(x_D^0)) + P_C + \frac{3}{8}MR\gamma_D^0\rho_0(\theta_D - \theta_D^0) + P_0. \quad (23)$$

Here, the values with zero index correspond to the values of the parameters under normal conditions. Let us estimate the contributions of individual terms in equality (23). It turns out that the value of the elastic pressure P_C is three orders of magnitude greater than the values of the other terms. Consequently, equality (23) can be simplified and represented as follows:

$$P \approx \frac{3c_T^2 \rho_0}{(b - 3n - 1)} \left[x^{-\frac{2}{3}} \exp \left(b \left(1 - x^{\frac{1}{3}} \right) \right) - x^{-(n+1)} \right]. \quad (24)$$

Here the parameters c_T , b , n are determined from the experimental data of the work [4]: 2975 m/s, 14.5, and 3.1, respectively. Table 1 shows the experimental values of pressure, relative density x_{EX} , the experimental error, the lower and upper limits of the relative density in accordance with the error presented in [4], as well as the relative density x_c calculated by equation of state (24).

Table 1

Comparison of experimental and calculated values of relative density

Pressure, GPa	x_{EX}	Error, %	Lower limit	Upper limit	x_c
0.56	0.9608	0.27	0.9581	0.9635	0.9715
0.85	0.9498	0.32	0.9466	0.953	0.9592
1.2	0.9397	0.42	0.9355	0.9439	0.946
1.66	0.927	0.43	0.9227	0.9313	0.9308
1.95	0.9148	0.44	0.9104	0.9192	0.9221
2.42	0.9054	0.51	0.9003	0.9105	0.9094
3.29	0.8834	0.58	0.8776	0.8892	0.8891
4.95	0.858	0.71	0.8509	0.8651	0.8581
8.18	0.8134	0.96	0.8038	0.823	0.8148
8.53	0.8045	0.99	0.7946	0.8144	0.811
9.53	0.7943	1.1	0.7833	0.8053	0.8006
10.17	0.7869	1.2	0.7749	0.7989	0.7945
11.64	0.7707	1.26	0.7581	0.7833	0.7816
13.22	0.7579	1.52	0.7427	0.7731	0.7691

Conclusion

Based on the results of the presented work, we conclude the following.

1. Analysis of the data given in Table 1 shows that the experimental and calculated values of the relative density are in good agreement with each other within the experimental error.

2. Equations of state for describing the isothermal compression of molecular crystals of nitro compounds (24) are based on a minimum set of experimental data. Nevertheless, the equations allow to describe the experiment rather accurately.

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Yurii M. Kovalev, DSc (Math), Full Professor, Head of the Department of Computational Mechanics, South Ural State University (Chelyabinsk, Russian Federation), kovalevym@susu.ru.

Konstantin M. Kalinin, Student, Department of Computational Mechanics, South Ural State University (Chelyabinsk, Russian Federation), mathideas74@gmail.com.

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ПОСТРОЕНИЕ УРАВНЕНИЙ СОСТОЯНИЯ ДЛЯ ОПИСАНИЯ ИЗОТЕРМИЧЕСКОГО СЖАТИЯ НЕКОТОРЫХ МОЛЕКУЛЯРНЫХ КРИСТАЛЛОВ НИТРОСОЕДИНЕНИЙ

Ю. М. Ковалев, К. М. Калинин

В настоящей работе был предложен подход к построению уравнений состояния молекулярных кристаллов нитросоединений, позволяющий описывать изотермическое сжатие. Данный подход основан на разделении свободной энергии Гельмгольца на тепловую и «холодную» составляющие. Оказалось, что «холодную» часть свободной энергии можно разделить на внутримолекулярную и межмолекулярную, а в тепловой части выделить низкочастотные и высокочастотные колебания. Низкочастотную компоненту тепловой части внутренней энергии и давления молекулярного кристалла было предложено аппроксимировать приближением Дебая. Для описания межмолекулярной энергии взаимодействия Ван-дер-Ваальса был предложен вид потенциала, замыкающийся на теплоту сублимации молекулярного кристалла. Компонента «холодной» составляющей давления, определяемая изменением внутримолекулярной энергии, полагалась постоянной величиной и определялась из условий равенства давления 1 атм. при нормальных условиях. Данное разделение энергии Гельмгольца позволило получить в явном виде выражения для всех термодинамических величин, входящих в уравнения состояния. Для коэффициента Грюнайзена в настоящей работе была принята линейная зависимость от объема. Применение более сложной зависимости оказалось не целесообразным в связи с тем, что рассматривается изотермическое сжатие и тепловая составляющая вносит незначительный вклад в суммарное давление. Определенные в работе зависимости термодинамических величин от температуры и объема были использованы для нахождения коэффициентов, завязанных на известные экспериментальные данные. Проведение сравнительного анализа расчетных и экспериментальных значений удельных объемов молекулярного кристалла 1,3,5-триамино-2,4,6-тринитробензола (ТАТБ) в зависимости от давления показало их совпадение с точностью до 1%.

Ключевые слова: уравнение состояния; молекулярный кристалл; изотермическое сжатие; энергия Гельмгольца; характеристическая температура Дебая; уравнение Грюнайзена; приближение Дебая.

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Ковалев Юрий Михайлович, доктор физико-математических наук, профессор, заведующий кафедрой вычислительной механики, Южно-Уральский государственный университет (г. Челябинск, Российская Федерация), yut_kov@mail.ru.

Калинин Константин Михайлович, студент, кафедра вычислительной механики, Южно-Уральский государственный университет (г. Челябинск, Российская Федерация), mathideas74@gmail.com.

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