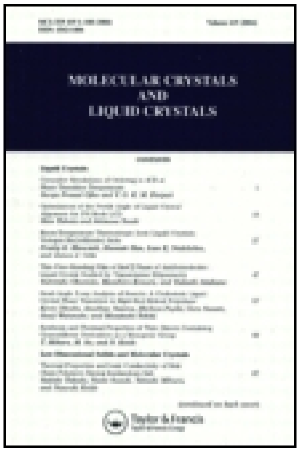

Molecular Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl15

Dependence of the Lattice Energy of Molecular Crystals on the Unit Cell Volume Calculated by the Atom-Atom Potential Method and Thermodyanamic Data

A. I. Kitaigorodsky [a] & K. V. Mirskaya [a]

[a] Institute of Elemento-Organic Compounds, Academy of Sciences of the U.S.S.R., Moscow

Version of record first published: 21 Mar 2007.

To cite this article: A. I. Kitaigorodsky & K. V. Mirskaya (1969): Dependence of the Lattice Energy of Molecular Crystals on the Unit Cell Volume Calculated by the Atom-Atom Potential Method and Thermodyanamic Data, Molecular Crystals, 6:3-4, 339-350

To link to this article: http://dx.doi.org/10.1080/15421407008083471

Molecular Crystals and Liquid Crystals. 1970. Vol. 6, pp. 339–350

Printed in Great Britain

Dependence of the Lattice Energy of Molecular Crystals on the Unit Cell Volume Calculated by the Atom-Atom Potential Method and Thermodynamic Data

A. I. KITAIGORODSKY and K. V. MIRSKAYA

Institute of Elemento-Organic Compounds,
Academy of Sciences of the U.S.S.R.,
Moscow

Received August 7, 1969

Abstract—The lattice energy (U) of naphthalene and anthracene crystals as a function of the unit cell volume (v) has been calculated by the atom-atom potential method. The experimental thermal expansion tensor has been used in this calculation. The first and the second derivatives of the lattice energy with respect to the unit cell volume have been obtained from the curve $U(v)$. Methods of comparison of these values with experimental data on the crystal internal energy and its volume derivatives and also ways of calculating the vibrational part of the crystal internal energy have been discussed. It has been shown that vibrational corrections to the lattice energy and its volume derivatives are small.

1. Atom-Atom Potentials

Recently it has been shown[1-7] that in principle an atom-atom approximation can be used for calculating the energy of interaction of molecules in a crystal. Based on experimental data for several hydrocarbon crystals, we have obtained the interatomic potential curves for C-C, C-H and H-H[3,5] that give good agreement between theoretical and experimental magnitudes of the lattice energies, unit cell dimensions at low temperatures and molecular orientations in crystals[8,9]. They also proved rather successful for calculating the spectra of intermolecular vibrations in benzene[10], naphthalene and anthracene[11-13] crystals.

2. Lattice Energy as a Function of the Unit Cell Volume

The purpose of this paper is to consider the comparison of the lattice energy calculated by the atom-atom potential method with thermodynamic data. Since the problem is dealt with for the first time we shall discuss the comparison with the experimental data in a scalar aspect. If, as discussed in previous papers,[3,8,9] the energy surface of a crystal has been obtained we can imagine any thermodynamic process as the movement of a point on the surface from the bottom of the energy well (absolute zero of temperatures) along a certain curve U $(a, b, c, \alpha, \beta, \gamma)$. Since we have in mind only the comparison with scalar thermodynamic values it is sufficient to represent this curve as $U(v)$. It is convenient to compare with isobaric data not only $U(v)$, that is the change in the lattice energy in the process of thermal expansion, but also the first and second derivatives of the lattice energy with respect to the unit cell volume, $(\partial U/\partial v)$ and $(\partial^2 U/\partial v^2)$. According to the agreement between theoretical and experimental $U(v)$ curves and their derivatives we can judge more clearly the atom-atom approximation in predicting different thermodynamic values.

3. The Lattice and the Internal Energies

The values of the lattice energy and its derivatives cannot be separated from the thermodynamic measurements. In order to compare the $U(v)$ curve calculated by the atom-atom potential method with thermodynamic data a model of a solid has to be used.

First of all, let us suppose that the crystal part of the internal energy can be represented as a sum of

$$E\,(v, T) = U(v) + E_{\text{vib}}\,(v, T),$$

where $E_{\text{vib}}\,(v, T)$ is the energy of intermolecular vibrations Since the zero point energy of intermolecular vibrations is negligible in most of molecular crystals we can assume that $E_0 = U_0$. Furthermore, it is clear that $(\partial E/\partial v)_T$ and $(\partial^2 E/\partial v^2)_T$ should not differ greatly from $(\partial U/\partial v)$ and $(\partial^2 U/\partial v^2)$ because the harmonic approximation should be valid, at least roughly. From these general physical considerations it is also clear that the corresponding derivatives of E and U should coincide better the lower the temperature (volume) is.

4. Results of the Calculation of the Lattice Energy as a Function of Volume for Naphthalene and Anthracene Crystals

The above comparison of $U(v)$ with thermodynamic data has been made for naphthalene $C_{10}H_8$ and anthracene $C_{14}H_{10}$ crystals. The direct result of the calculation by the atom-atom potential method is the curve $U(v)$. A given point can be connected with the temperature either by calculating the free energy (see below) or by measuring the expansion tensor. We have used the experimental $v(T)$ curves in our tables below.

The values of the unit cell volume per one molecule at several temperatures, as measured by Ryzhenkov and Kozhin,[14] are given in Table 1 for a naphthalene crystal. Also listed in the same table are the values of the lattice energy at these temperatures calculated by the atom-atom potential method (the radius of summation is 15 Å) and ΔU values counted from the value of the lattice energy at 78 °K.‡ At each temperature point, that is for

TABLE 1 The Lattice Energy and its Volume Derivatives for a Naphthalene Crystal

T (°K)	v (cm³/mole)	U (kcal/mole)	ΔU (cal/mole)	$\partial U/\partial v$ (cal/cm³)	$\partial^2 U/\partial v^2$ (cal/cm⁶)
78	103.1	−17.75	0	50	23
123	104.0	−17.69	59	71	21
173	104.7	−17.64	109	85	20
293	108.3	−17.22	532	149	17
323	109.7	−16.98	767	173	17

---

‡ Certainly it would be more convenient to calculate $(U - U_0)$. But reliable experimental data for temperatures lower than liquid nitrogen are lacking.

every set of cell dimensions a, b, c, β, the lattice energy corresponding to the best molecular orientation in the crystal has been found.[9] In the last two columns of the Table we list the derivatives $(\partial U/\partial v)$ and $(\partial^2 U/\partial v^2)$. The estimation of these derivatives from the $U(v)$ curve has been made by the method of finite

TABLE 2 The Lattice Energy and its Volume Derivatives for an Anthra-cene Crystal

T (°K)	v (cm^3/mole)	U (kcal/mole)	ΔU (cal/mole)	$\partial U/\partial v$ (cal/cm^3)	$\partial^2 U/\partial v^2$ (cal/cm^6)
100	138.3	−23.16	0	42	28
150	138.6	−23.15	14	50	26
200	139.4	−23.11	58	68	22
250	140.9	−22.96	200	98	15
300	142.8	−22.76	404	122	12
350	144.9	−22.48	687	144	10
400	147.2	−22.11	1054	166	7

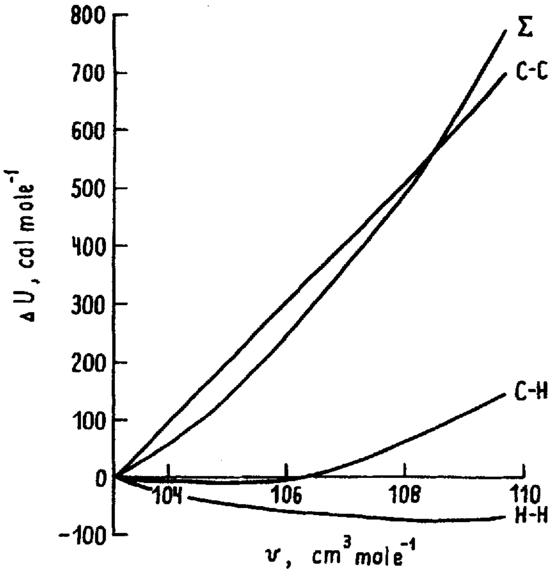

Figure 1. Contributions of C-C, C-H and H-H interactions to the change in the lattice energy in the process of thermal expansion for a naphthalene crystal.

differences followed by a smoothing of the resulting curve. The precision of this estimation is about 5%.

Similar data for anthracene crystal are shown in Table 2. The thermal expansion tensor of anthracene has been measured by Ryzhenkov, Kozhin and Miasnicova.[15] ΔU values are counted here from the lattice energy at 100 °K.

Figures 1 and 2 show C-C, C-H and H-H contributions to the $\Delta U(v)$ curve. We can see clearly that the curve is determined mainly by the interactions of carbon atoms.

5. Determination of the Internal Energy Volume Derivatives from Thermodynamic Data

The internal energy volume derivatives needed for comparing $U(v)$ with experiment can be determined from the thermodynamic

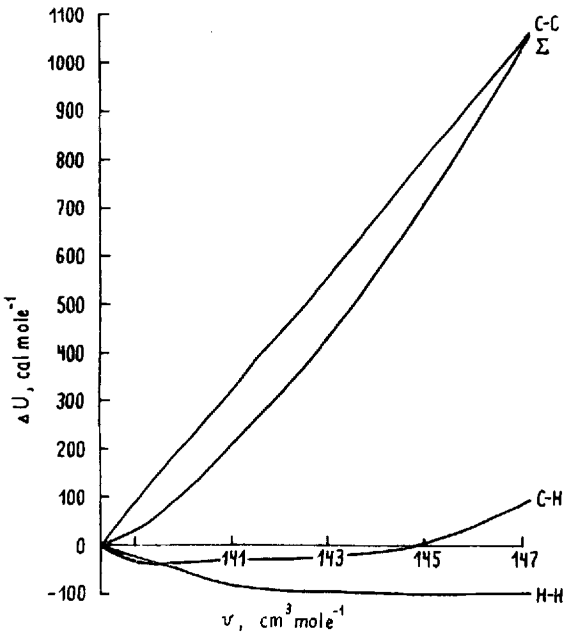

Figure 2. Contributions of C-C, C-H and H-H interactions to the change in the lattice energy in the process of thermal expansion for an anthracene crystal.

measurements of the difference of specific heat capacities, $(c_p - c_v)$. Indeed, if the atmospheric pressure is neglected in comparison with $(\partial E/\partial v)_T$, which is quite justifiable,[16] we obtain from the known expression $(c_p - c_v) = (\partial E/\partial v)_T(\partial v/\partial T)_p$ the derivative

$$(\partial E/\partial v)_T = (c_p - c_v)/\alpha v, \qquad (1)$$

where α is the volume thermal expansion coefficient. By integrating and differentiating expression (1), which it is convenient to perform graphically, we obtain $\Delta_v E$, the change in the internal energy due to the change in volume in the process of thermal expansion and the second derivative $(\partial^2 E/\partial v^2)_T$, respectively.

The experimental values $(c_p - c_v)$ as a function of temperature have been taken from the paper by Afanassieva and Koreshkov.[17] Tables 3 and 4 give the values we are interested in.

TABLE 3 The Internal Energy and its Volume Derivatives for a Naphthalene Crystal

T (°K)	$\Delta_v E$ (cal/mole)	$(\partial E/\partial v)_T$ (cal/cm^3)	$(\partial^2 E/\partial v^2)_T$ (cal/cm^6)
78	0	33	26
123	42	54	22
173	91	66	20
293	479	132	17
323	664	152	15

TABLE 4 The Internal Energy and its Volume Derivatives for an Anthracene Crystal

T (°K)	$\Delta_v E$ (cal/mole)	$(\partial E/\partial v)_T$ (cal/cm^3)	$(\partial^2 E/\partial v^2)_T$ (cal/cm^6)
100	0	5	23
150	3	11	29
200	25	38	38
250	125	82	18
300	320	106	9

The three quantities of interest are compared in Figs. 3 and 4. The main result of this comparison is encouraging since the experimental and theoretical curves are quite similar. Nevertheless the discrepancy is not negligible. The question is whether

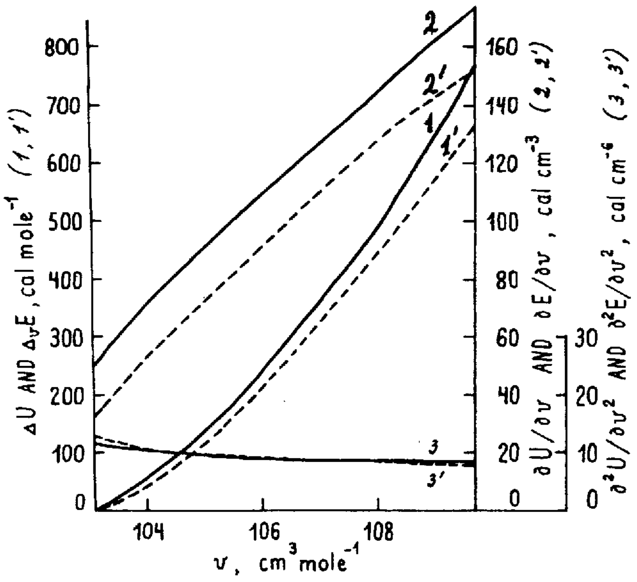

Figure 3. Comparison of the lattice energy and its volume derivatives calculated by the atom-atom potential method with the internal energy and its derivatives obtained from the experimental data for a naphthalene crystal. 1 – ΔU, 1' – $\Delta_v E$, 2 – $(\partial U/\partial v)$, 2' – $(\partial E/\partial v)_T$, 3 – $(\partial^2 U/\partial v^2)$, 3' – $(\partial^2 E/\partial v^2)_T$.

the reason for this discrepancy is an unsatisfactory choice of the potentials or the fact that the vibrational part of the energy has not been taken into consideration. However, the fact that the $U(v)$ curve lies above the $\Delta_v E(v)$ curve can only be connected with an inexact choice of the potential curves. The correction of the potential curves must be performed in accordance with these results.

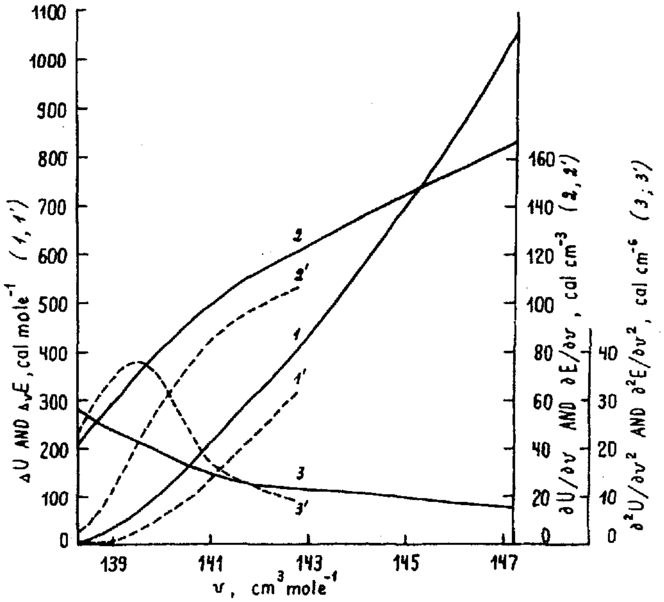

Figure 4. Comparison of the lattice energy and its volume derivatives with the internal energy and the corresponding derivatives for an anthracene crystal. The designations are the same as in Fig. 3.

6. Methods of Estimation of the Vibrational Part of the Crystal Internal Energy

Let us assume that we have succeeded in finding the exact atom-atom potentials. Then the differences of the ordinates of the curves in Figs. 3 and 4 are equal to $\Delta_v E_{\text{vib}}$, $(\partial E_{\text{vib}}/\partial v)_T$ and $(\partial^2 E_{\text{vib}}/\partial v^2)_T$. There are the following possibilities for an independent estimation of these values:

1. A dynamic (and consequently thermodynamic) problem can be solved quite strictly on the basis of the atom-atom potentials.

2. The vibrational spectrum of a crystal and then the crystal parts of the thermodynamic functions can be calculated in the quasiharmonic approximation.

3. Further, the quasiharmonic ($\theta = \theta(v)$) Debye approximation

can be used for the crystal parts of the thermodynamic functions. There are four ways of calculating the $\theta(v)$ curve. Firstly, there is a possibility of passing from the average square of frequencies of the intermolecular vibrational spectrum, $\overline{\omega^2}$, to the characteristic temperature, θ,[18] $\overline{\omega^2}$ being calculated with the help of the atom-atom potentials. In this case temperature can be introduced by calculating the $\partial\overline{\omega^2}/\partial\epsilon_i$ tensor, (a). Secondly, we can follow the same procedure but use the experimental curve $v(T)$,[19] (b). Thirdly, the $\theta(v)$ curve can be chosen in an " optimal "[20] way directly from the thermodynamic data, (c). And lastly, (d), if the curve $(\partial U/\partial v)$ has been calculated by means of the atom-atom potentials and the value of θ is known from the thermodynamic data at least for one temperature point the $\theta(v)$ curve can be calculated from the equation of state of a crystal, which in the Debye form is

$$(\partial U/\partial v) = -6R(T/\theta)D(\theta/T)(\partial\theta/\partial v)$$

(the atmospheric pressure has been neglected in comparison with $(\partial U/\partial v)$).

In cases 1, 2 and 3(a) the thermodynamics of a crystal is calculated successively by the atom-atom potential method without using any data from experiment. Problem I is too complicated. The possibilities of the second case are being investigated at our laboratory. In cases 3 (b), (c), (d) the experimental data on the thermal expansion of a crystal are to be used for comparing the theoretical and experimental values of the energy.

We have tried the last three methods of case 3 for a naphthalene crystal. The respective $\theta(v)$ curves are shown in Fig. 5 and designated (b), (c), (d). In case (d), we have taken as initial $\theta = 138°$ at 78°K obtained[21] from calorimetric and spectral data.[22] The calculations have shown that the slope of the $\theta(v)$ curve depends but slightly on our choice of the initial θ.

From the known equation,

$$(\partial E_{\text{vib}}/\partial v)_T = 6RD'(\theta/T)(\partial\theta/\partial v), \qquad (2)$$

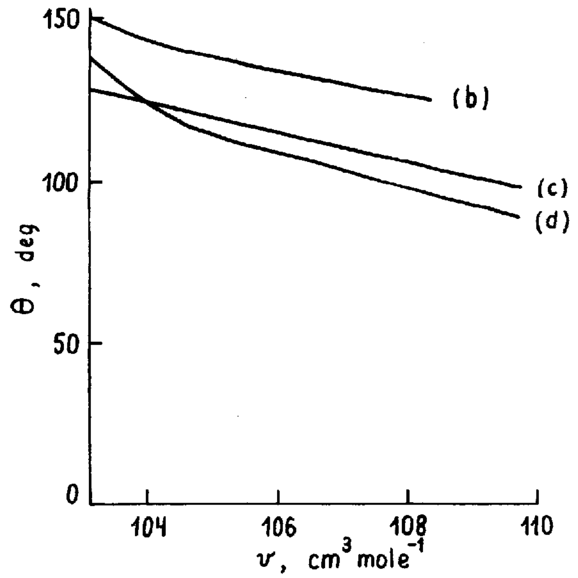

Figure 5. The dependence of the characteristic temperature (θ) on the unit cell volume (v) for a naphthalene crystal. $\theta(v)$ has been obtained as follows: (b) from the $\overline{\omega^2}$, (c) from the thermodynamic data, (d) from the equation of state.

it follows that all these $\theta(v)$ curves give values $(\partial E_{\text{vib}}/\partial v)_T$ and $\Delta_v E_{\text{vib}} = \int(\partial E_{\text{vib}}/\partial v)_T\,dv$ having an opposite sign than those which we obtain with the present choice of the potentials upon subtraction of the curves $(\partial E/\partial v)_T$ and $(\partial U/\partial v)$, $\Delta_v E$ and ΔU in Fig. 3. Indeed, each of the three $\theta(v)$ curves can be expressed by the formula $\theta = \theta_0 - a(v - v_0)$, where " a " is a positive constant. From equation (2) we then obtain $(\partial E_{\text{vib}}/\partial v)_T = -6aRD'(\theta/T)$. Since $D'(\theta/T)$ is negative, $(\partial E_{\text{vib}}/\partial v)_T$ and $\int(\partial E_{\text{vib}}/\partial v)_T\,dv$ will be positive. Therefore, it is not worthwhile to analyse every $\theta(v)$ curve separately, but bearing in mind the possibility for improving the potential curves it is reasonable to consider the order of magnitude of the quantities $\Delta_v E_{\text{vib}}$, $(\partial E_{\text{vib}}/\partial v)_T$ and $(\partial^2 E_{\text{vib}}/\partial v^2)_T$.

The calculations show that $(\partial E_{\text{vib}}/\partial v)_T$ changes but slightly in the whole temperature interval and its average value is near

15 cal/cm^3. It is seen from Fig. 3 that if we considered it necessary to change the potentials relying on the values of $(\partial E_{\text{vib}}/\partial v)_T$, these corrections at least for higher temperatures would not exceed 10–20%. Differentiating $(\partial E_{\text{vib}}/\partial v)_T$ with respect to "v" we obtain $(\partial^2 E_{\text{vib}}/\partial v^2)_T = 6a^2R(I/T)D''(\theta/T)$. The second derivative $D''(\theta/T)$ is positive and so the vibrational correction to $(\partial^2 U/\partial v^2)$ is positive too, but what seems to us essential is that it is quite small. This correction hardly exceeds 5–10% of the value we are interested in.

Our general conclusion is that an exact estimation of the vibrational parts of the lattice energy and its derivatives is hardly possible at present. These values are very sensitive to the choice of the $\theta(v)$ curve and since the curve itself is determined on the basis of a number of assumptions, the calculation can only yield an estimate of the order of magnitude. However, the use of the atom-atom potential method for the calculation of a number of thermodynamic quantities need not wait for precise methods of estimating the vibrational components because, as the main result of this work shows (see Figs. 3 and 4), the vibrational corrections to the lattice energy and its volume derivatives are slight. Of course, the general validity of this conclusion is to be shown by calculations for other crystals.

REFERENCES

1. Kitaigorodsky, A. I. and Mirskaya, K. V., *Kristallografia* **6**, 507 (1961).
2. Yamasaki, K., *J. Phys. Soc. Japan*, **17**, 1262 (1962).
3. Kitaigorodsky, A. I. and Mirskaya, K. V., *Kristallografia* **9**, 174 (1964).
4. Kimel, S., Ron, A. and Hornig, D. F., *J. Chem. Phys.* **40**, 3351 (1964).
5. Kitaigorodsky, A. I., *J. Chimie. Phys.* **63**, 9 (1966).
6. Williams, D. E., *J. Chem. Phys.* **45**, 3770 (1966); **47**, 4680 (1967).
7. Giglio, E., Liquori, A. M., *Acta Cryst.* **22**, 437 (1967).
8. Kitaigorodsky, A. I., Mirskaya, K. V. and Tovbis, A. B., *Kristallografia* **13**, 225 (1968).
9. Mirskaya, K. V. and Kozlova, I. E., *Kristallografia* **14**, 412 (1969).
10. Oliver, D. A., Ph.D. Thesis, London University (1967).
11. Pawley, G. S., *Phys. Stat. Sol.* **20**, 347 (1967).
12. Weulersse, P., *Compt. Rend. Acad. Sci. Paris* **264B**, 327 (1967).
13. Kitaigorodsky, A. I. and Muhtarov, E. I., *Kristallografia* **14**, 784 (1969).

14. Ryzhenkov, A. P. and Kozhin, V. M., *Kristallografia* **12**, 1079 (1967).
15. Ryzhenkov, A. P., Kozhin, V. M. and Miasnikova, R. M., *Kristallografia* **13**, 1028 (1968).
16. Born, M. and Hyang, K., *Dynamical Theory of Crystal Lattices*, Oxford University Press (1954).
17. Afanassieva, G. K. and Koreshkov, B. D., Transactions of the Pedagogical Institute, Kolomna, USSR (1970).
18. Leibfried, G. and Ludwig, W., Theory of Anharmonic Effects in Crystals, Academic Press Inc., New York–London (1961).
19. Kitaigorodsky, A. I. and Muhtarov, E. I., *Fiz. Tverd. Tela* **10**, 3474 (1968).
20. Kitaigorodsky, A. I. and Koreshkov, B. D., *Fiz. Tverd. Tela,* in press.
21. Koreshkov, B. D., Dissertation, Moscow (1968).
22. Kitaigorodsky, A. I., *Kristallografia* **7**, 195 (1962).