

THE LATTICE DYNAMICS OF ADAMANTANE. I. CUBIC PHASE¹

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The paper presents a model of the lattice dynamics of the cubic phase of adamantane. Intermolecular interactions are described by the "6-exp" function with theoretically calculated parameters. Results of computations are compared with the frequency distribution spectrum obtained by Stockmeyer and Stiller from inelastic neutron scattering data. The good agreement received confirms the correctness of the proposed model.

1. Introduction

Recent years have seen development of experimental methods of investigating the dynamics of crystal lattices. At the same time more and more interest is attracted by molecular crystals — in the main, crystals of organic compounds. There thus is a need for looking at these crystals from the theoretical point of view, to see what are the possibilities of calculating the quantities characterizing lattice dynamics accessible from experimental methods. In this field the studies by Hahn and Biem [1, 2] and Cochran and Pawley [3] are fundamental. They dealt with molecular crystals of high symmetry: hexamethylenetetramine (urotropine) [2, 3] and adamantane [2], the latter treating the lattice dynamics of the crystals in a general manner, without assuming any specific form for the potential energy function.

The basic assumption made in the case of molecular crystals is that there is no coupling between internal vibrations of the molecules and lattice vibrations. Assuming the model of a rigid molecule simplifies problems of computation substantially. It should be noted that in the majority of cases this assumption is fulfilled well.

The basic problem, on the other hand, is the choice of a proper function for the crystal's potential energy. A very interesting proposal in this field is provided by the work of Pawley [4], where lattice dynamics were analyzed for two typical molecular crystals, naphthalene and anthracene, with the use of the "atom-atom" potential.

It is presumed here that the adamantane crystal may be treated in like manner. Owing to its very high symmetry, adamantane may be regarded as a model substance in the pro-

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blem of the lattice dynamics of molecular crystals; therefore it is very advisable to consider it closely. This crystal has two polymorphic forms the structures of which are well known.

The goal of this series of papers on the lattice dynamics of adamantane is

1° to perform complete calculations of the lattice dynamics for both polymorphic forms,

2° to analyze lattice vibrations basing on group theory,

3° to calculate some of the physical thermodynamic quantities for both crystalline phases, and

4° to compare the obtained results with experiments.

2. Structure of cubic phase and analysis of lattice vibrations

Adamantane ($C_{10}H_{16}$) has two polymorphic forms, cubic and tetragonal. According to calorimetric experiments [5] the temperature of phase transition is 208.6°K. The crystal structure of both forms had been examined roentgenographically in studies [6, 7].

The structure of the adamantane molecule can be pictured as an octahedron made up of CH_2 groups with a tetrahedron of CH groups built into it. In the cubic phase crystal the molecules are arranged in such a way that all three principal axes of the octahedron are parallel

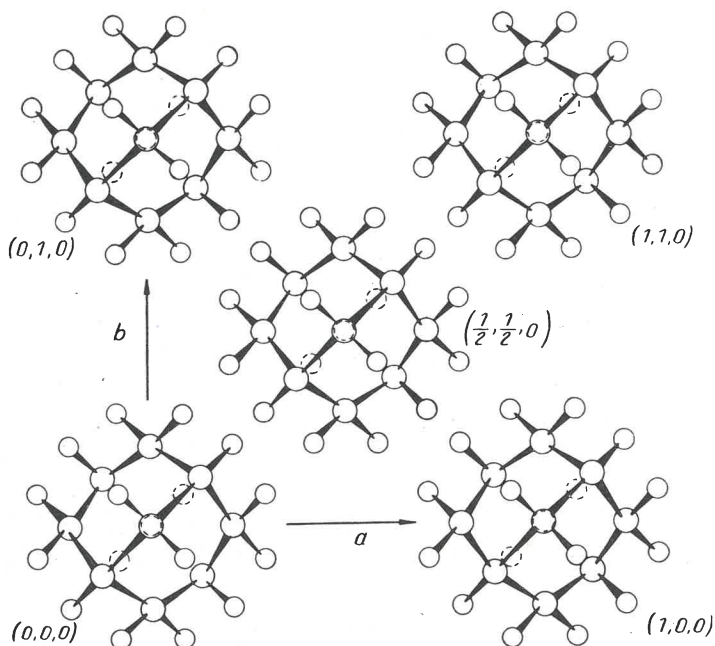


Fig. 1. Structure of cubic phase of adamantane as projected on (001) plane

to the crystallographic axes. Fig. 1 presents the projection of the structure on the (001) plane. The space group of the crystal is $Fm\bar{3}m (O_h^5)$, and there are four molecules in the cubic unit cell of constant $a = 9.43 \text{ \AA}$. The molecules' centers of gravity form a face-centered cubic lattice (f. c. c.). Fig. 2 depicts the Brillouin zone for this type of lattice. The figure

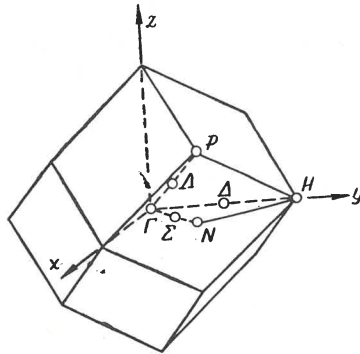
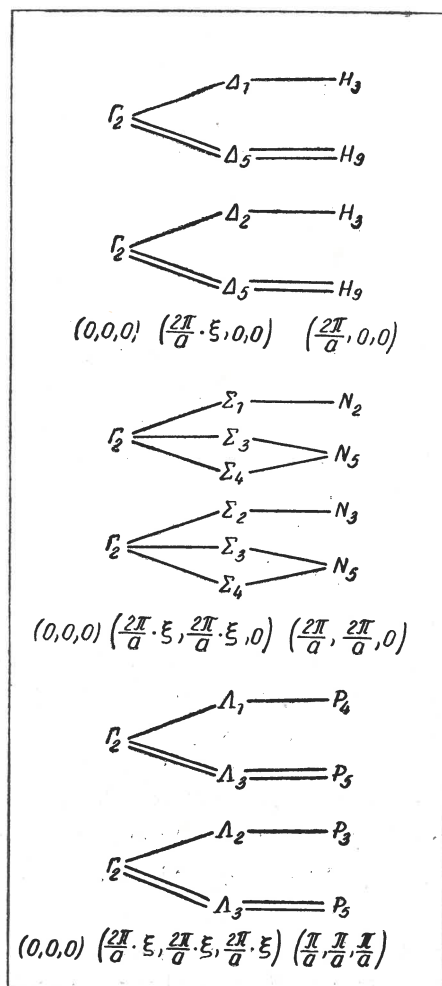
Fig. 2. Brillouin zone for *f.c.c.* lattice

Fig. 3. Diagram of types symmetry of lattice vibrations for high symmetry directions

TABLE I

High symmetry points and directions in the Brillouin zone of the cubic phase of adamantane

Point	\vec{q}	Factor-group
Γ	(0, 0, 0)	O_h
Δ	$\left(\frac{2\pi}{a} \cdot \xi, 0, 0\right)$	C_{4v}
H	$\left(\frac{2\pi}{a}, 0, 0\right)$	D_4
Σ	$\left(\frac{2\pi}{a} \cdot \xi, \frac{2\pi}{a} \cdot \xi, 0\right)$	C_{2v}
N	$\left(\frac{2\pi}{a}, \frac{2\pi}{a}, 0\right)$	D_{2d}
A	$\left(\frac{2\pi}{a} \cdot \xi, \frac{2\pi}{a} \cdot \xi, \frac{2\pi}{a} \cdot \xi\right)$	C_{3v}
P	$\left(\frac{\pi}{a}, \frac{\pi}{a}, \frac{\pi}{a}\right)$	D_3

shows the points (according to Koster symbols [8]) for which the lattice vibration analyses were made. The coordinates of these points and the corresponding group symbols, isomorphic with the given point groups, are given in Table I. As the O_h^5 group is a symmorphic space group, the irreducible representations of the group and corresponding subgroups are obtained directly from the representations of the irreducible point groups [8]. The analysis of lattice vibrations for the points of the Brillouin zone listed in Table I are presented in Fig. 3 in the form of diagrams.

3. Calculations

A. Potential energy of crystal

It is now assumed that the potential energy of a molecular crystal is additive and may be written as the sum of interactions between the individual pairs of atoms,

$$V = \sum_{mn} V_{mn}, \quad (1)$$

where m and n are indices of the two types of atoms. The potential V_{mn} of the interaction between atoms m and n usually written in the form of the so-called "6-exp" function,

$$V_{mn} = -A_{mn} \sum_{p,s} r_{p,s}^{-6} + B_{mn} \sum_{p,s} \exp(-\alpha_{mn} \cdot r_{p,s}), \quad (2)$$

where $r_{p,s}$ is the distance between the atoms. The parameters A_{mn} , B_{mn} and α_{mn} are found semiempirically [9,10], while a check of the correctness of this determination is conformity with such physical quantities of the crystals as heat of sublimation and unit cell parameters.

A very interesting attempt of describing the potential energy of a molecular crystal is given in the paper by Poltev and Sukhorukov [11]. The potential energy V is treated as the sum of potentials of various kinds of interaction:

$$V = \sum_{mn} (E_{mn} + H_{mn} + I_{mn} + F_{mn}). \quad (3)$$

Here, E_{mn} is the energy of electrostatic interactions between the atoms m and n , H_{mn} is the energy of interactions determined by induction effects, I_{mn} is the energy of dispersion interactions (van der Waals interactions), F_{mn} is the energy of repulsion due to overlapping of electron shells of the atoms m and n .

It happens that the first two terms contribute very little to the total energy of the crystal in the case of hydrocarbons (about three per cent) [11]. We assume, therefore, that the potential energy of a crystal of hydrocarbon is satisfactorily described by the latter two terms of Eq. (3). Hence,

$$V = \sum_{mn} (I_{mn} + F_{mn}), \quad (4)$$

what in the "6-exp" function form is written as

$$V = \sum_{mn} [-A'_{mn} \sum_{p,s} r_{p,s}^{-6} + B'_{mn} \sum_{p,s} \exp(-\alpha'_{mn} \cdot r_{p,s})]. \quad (5)$$

The parameters A'_{mn} , B'_{mn} and α'_{mn} are not fitted as in the case of formula (2), but calculated theoretically. In order to find the constant of dispersion interactions use is made of the approximate London formula

$$A'_{mn} = \frac{3}{2} \cdot \frac{a_m \cdot a_n \cdot J_m \cdot J_n}{J_m + J_n} \quad (6)$$

where a_m and a_n are the atomic polarizabilities, and J_m and J_n are the ionization potentials of the atoms in the given configuration. The parameter α'_{mn} is found from the graph of the dependence of α'_{mn} on atomic number, which was obtained on the basis of scattering data for noble gas atoms [12].

Using the condition

$$\frac{\partial [I_{mn} + F_{mn}]}{\partial r_{p,s}} = 0 \quad (7)$$

determining the minimum of function (5), we get parameter B'_{mn} .

The parameters obtained in this way for crystals of hydrocarbons are given in Table II.

TABLE II

Parameters of the "6-exp" function

mn	A'_{mn} [erg. Å ⁻⁶]	B'_{mn} [erg]	α'_{mn} [Å ⁻¹]
H...H	2.88×10^{-12}	7.65×10^{-10}	4.54
C...H	8.85×10^{-12}	75.51×10^{-10}	4.56
C...C	27.2×10^{-12}	903.89×10^{-10}	4.58

B. Dynamical matrix

The equations of motion of the k -th particle in the l -th elementary cell are in the harmonic approximation the following:

$$\begin{aligned} m\ddot{u}_x(lk) &= - \sum_{l',k',i} \Phi_{xi}(lk, l'k') u_i(l'k') \\ I_\alpha \ddot{u}_\alpha(lk) &= - \sum_{l',k',i} \Phi_{\alpha i}(lk, l'k') u_i(l'k') \end{aligned} \quad (8)$$

where $u_i(lk)$ is one of the six components of the molecule's displacement vector, m is the mass of the molecule, and I_α is its moment of inertia along the x -axis. The force constants in Eq. (8) are defined in the expression for the crystal's potential energy,

$$\Phi_{ij}(lk, l'k') = \frac{\partial^2 V}{\partial u_i(lk) \partial u_j(l'k')} \quad (9)$$

Substitution of the plane wave equation into Eq. (8) yields

$$\begin{aligned} m\omega^2(\vec{q}) U_x(k, \vec{q}) &= \sum_{k',i} U_i(k', \vec{q}) \cdot M_{xi}(k, k', \vec{q}) \\ I_\alpha \omega^2(\vec{q}) U_\alpha(k, \vec{q}) &= \sum_{k',i} U_i(k', \vec{q}) \cdot M_{\alpha i}(k, k', \vec{q}) \end{aligned} \quad (10)$$

where

$$M_{xi}(k, k', \vec{q}) = \sum_{l'} \Phi_{xi}(lk, l'k') \exp i\vec{q} \cdot [\vec{r}(lk) - \vec{r}(l'k')] \quad (11)$$

is an element of the dynamical matrix.

The tensors of the force constants $\Phi(lk, l'k')$ were calculated in the reference frame of the crystal axes. The program for the computer in the "ODRA-ALGOL" language was written with use being made on the formula²

$$\frac{\partial^2 V}{\partial u_i(lk) \partial u_j(l'k')} = \sum_{mn, ps} \left[\left(\frac{\partial V}{\partial r_{ps}} \right) \left(\frac{\partial^2 r_{ps}}{\partial u_i(lk) \partial u_j(l'k')} \right) + \left(\frac{\partial^2 V}{\partial r_{ps}^2} \right) \left(\frac{\partial r_{ps}}{\partial u_i(lk)} \right) \left(\frac{\partial r_{ps}}{\partial u_j(l'k')} \right) \right]. \quad (12)$$

The derivatives of the atomic spacings (r) with respect to molecule displacements are for the translation-translation force constants as follows:

$$\begin{aligned} \left(\frac{\partial r}{\partial u_i(lk)} \right) \left(\frac{\partial r}{\partial u_j(l'k')} \right) &= - \frac{1}{r^2} \cdot r_i \cdot r_j \\ \left(\frac{\partial^2 r}{\partial u_i(lk) \partial u_j(l'k')} \right) &= - \frac{1}{r^3} (\delta_{ij} \cdot r^2 - r_i r_j) \end{aligned}$$

² Calculations were performed on the ODRA 1204 computer at the Computation Center of the Institute of Physics of the Jagellonian University.

$i, j = 1, 2, 3$. Here, r_i and r_j are the components of the interatomic distance vector, and δ_{ij} is the Kronecker delta function.

In the case of libration-libration force constants the formulae become more involved [13], and the time of computation longer several times.

The partial derivatives for libration-libration couplings are:

$$\left(\frac{\partial r}{\partial u_i(lk)} \right) \left(\frac{\partial r}{\partial u_j(l'k')} \right) = -\frac{1}{r^2} \cdot r_a \cdot r_b \cdot P$$

$$\left(\frac{\partial^2 r}{\partial u_i(lk) \partial u_j(l'k')} \right) = -\frac{1}{r^3} (\delta_{ab} r^2 - r_a r_b) \cdot P$$

where

$$P = A_{ac}(lk) A_{bd}(l'k') \cdot \delta_{cie} \cdot \delta_{djf} \cdot \sigma_e(lk) \cdot \sigma_f(l'k')$$

for $a, b, c, d, e, f = 1, 2, 3$ and $i, j = 4, 5, 6$. A_{ac} is the direction cosine between the a -axis of the crystal and the c -axis of the molecule, $\sigma_e(lk)$ is the coordinate of an atom in the molecule (lk) in the reference frame of the molecule, and δ_{cie} is the antisymmetric Levi-Civita tensor.

Formulae for the derivatives in the case of transition-libration ($i = 1, 2, 3; j = 4, 5, 6$) and libration-translation ($i = 4, 5, 6; j = 1, 2, 3$) can be readily derived now.

For the cubic phase of adamantane the tensors of force constants between the $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$ molecules and the $(0, 0, 0)$ and $(1, 0, 0)$ molecules were computed. Force constants for the remaining pairs of molecules were obtained from the $\Phi(\frac{1}{2}, \frac{1}{2}, 0)$ and $\Phi(1, 0, 0)$ tensors by means of relevant relationships stemming from crystal symmetry. The symmetries of the individual tensors and general formulae for the dynamic matrix elements are given in Ref. [2].

Generally speaking, the dynamical matrix for the cubic phase of adamantane is a Hermitian matrix of sixth order. For each value of wave vector it was resolved by the method given in Ref. [14], *i. e.* by forming each time a real matrix of 12-th order.

4. Dispersion curves and frequency distribution functions

Computations for the adamantane crystal were made for two temperatures, 298°K and 209°K. The values of the lattice constant at 209°K were calculated with the use of the known value of expansion coefficient 4.4×10^{-4} degree⁻¹ [15]. At each temperature the dispersion curves were calculated for three directions of the Brillouin zone, *viz.*, [100], [110] and [111]. In Figs 4-9, representing the dispersion curves, the vibrational modes resulting from an analysis based on group theory are indicated.

Unfortunately, there are no data in the literature on the values of the frequency of three-fold degenerate optical vibration at $\vec{q} = 0$. The performed lattice-dynamical calculations with the assumed model of interactions in the crystal may be compared with experiment only for the frequency distribution function. Figures 10 and 11 depict the functions $g(\omega)$ obtained experimentally and *via* calculations in the form of a histogram. The theoretical $g(\omega)$ functions were calculated from 4000 points of the Brillouin zone.

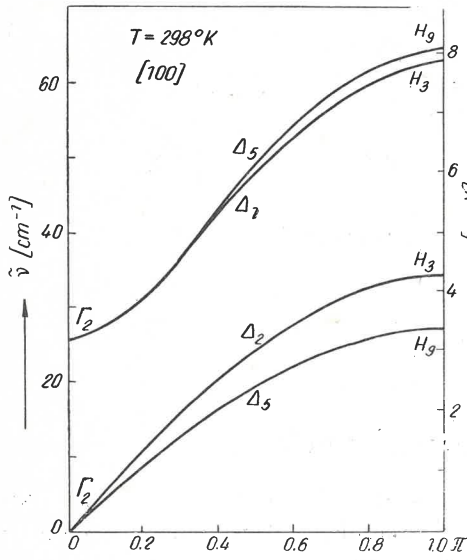


Fig. 4

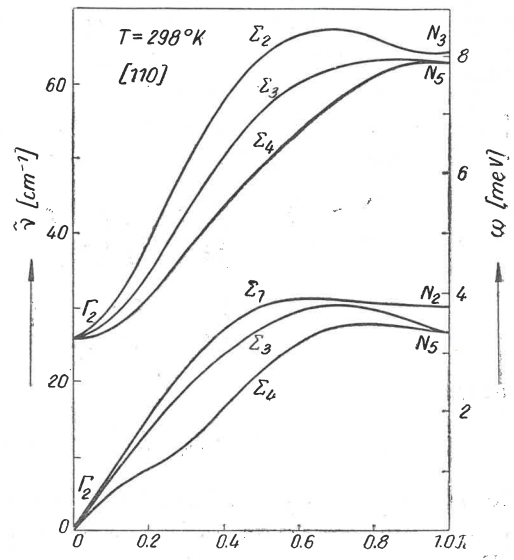


Fig. 5

Fig. 4. Dispersion curves for (100) direction at 298°K
 Fig. 5. Dispersion curves for (110) direction at 298°K

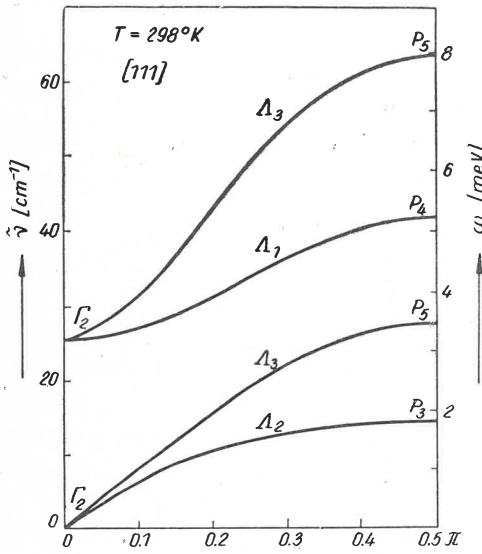


Fig. 6

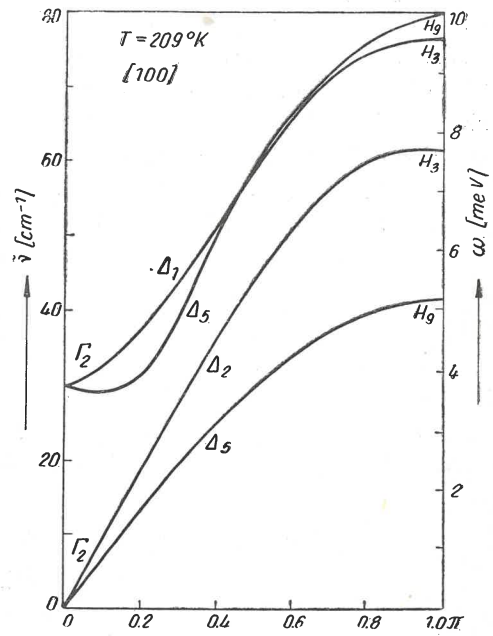


Fig. 7

Fig. 6. Dispersion curves for (111) direction at 298°K
 Fig. 7. Dispersion curves for (100) direction at 209°K

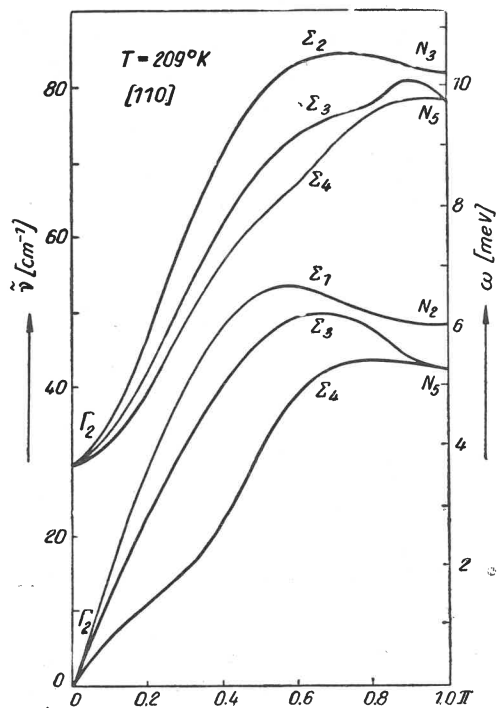


Fig. 8

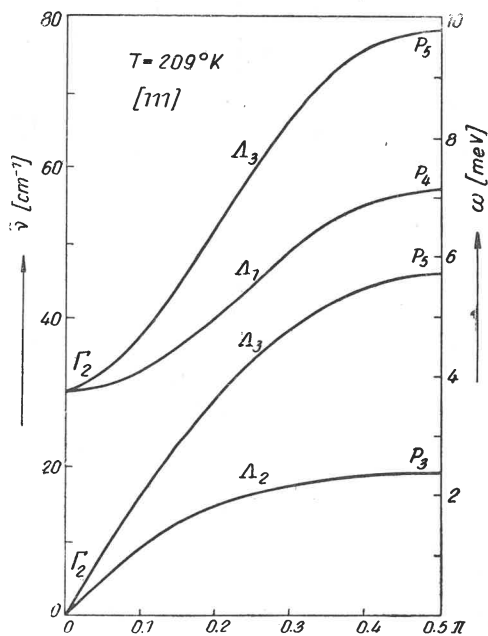
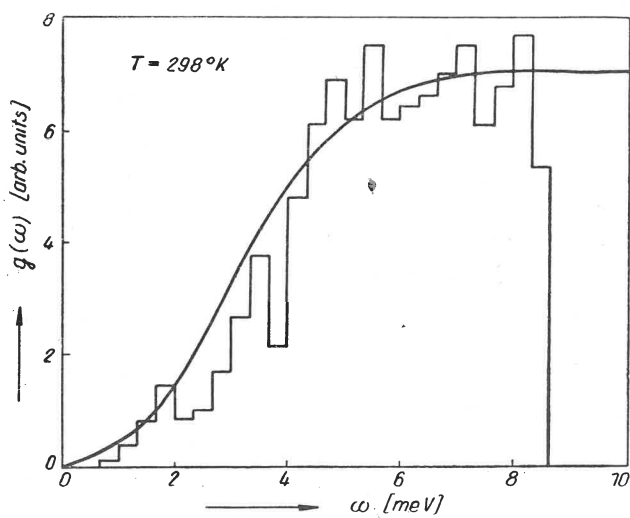


Fig. 9

Fig. 8. Dispersion curves for (110) direction at 209°K

Fig. 9. Dispersion curves for (111) direction at 209°K

Fig. 10. $g(\omega)$ function: histogram — calculations for 298°K; continuous line — experiment [16] for 293°K

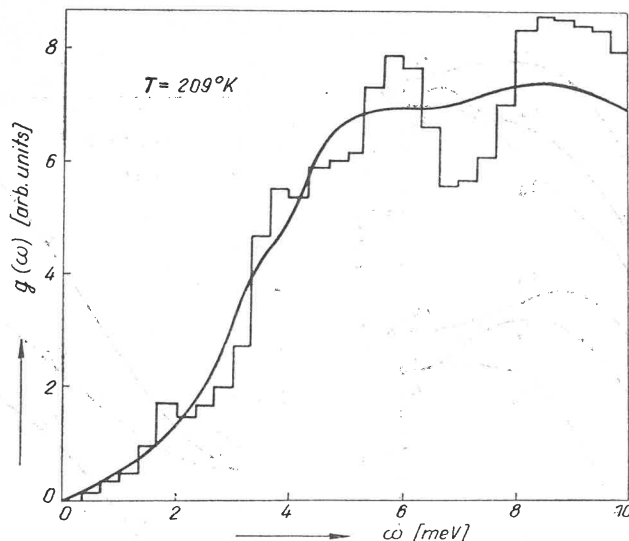


Fig. 11. $g(\omega)$ function: histogram — calculations for 209°K; continuous line — experiment [16] for 253°K

Measurements were made by the method of incoherent inelastic neutron scattering by Stockmeyer and Stiller [16]. For the comparison use was made of the measured $g(\omega)$ functions for a neutron scattering angle of 60° at temperatures of 293°K and 253°K [16].

5. Discussion and conclusions

The lattice dynamics of adamantane was the subject of considerations in three papers [2, 16, 17]. In our discussion we shall limit ourselves to experimental studies [16, 17], where the authors propounded a model of lattice dynamics fitted to the observed frequency distribution functions.

In the model proposed here, on the other hand, a concrete type of interaction between the molecules of adamantane is assumed, and the parameters of the function of the crystal's potential energy are treated as characteristic quantities for the given pair of atoms. This model does not make use of any selectable parameter. The comparison between the computed frequency distribution functions with those found experimentally (Figs 10 and 11) allow us to state that the proposed general model of the lattice dynamics of adamantane is accurate. Moreover, it describes the effect of temperature on the frequency distribution spectrum well. The found values of the frequencies of three-fold degenerate optical vibration at $\vec{q} = 0$ are rather low, 26 cm^{-1} (298°K) and 29.5 cm^{-1} (209°K), and are compatible with the librational frequencies of the adamantane molecule estimated in Ref. [17].

However, the value of 26 cm^{-1} can be compared with the frequency calculated according to the formula

$$\tilde{\nu} = \sqrt{\frac{k \cdot T}{4\pi^2 \cdot I \cdot \Theta^2 \cdot c^2}}$$

if the amplitude Θ of the molecule's thermal vibrations is known. According to Ref. [6] this value is equal to 8 degrees. The frequency of librational vibration calculated according to the above formula equals 29 cm^{-1} and agrees well with the expected frequency of 26 cm^{-1} .

In conclusion, it is possible to establish that

1° in the adamantane crystal the dispersion interactions and those due to overlapping of the atomic electronic shells are decisive, and

2° the harmonic approximation is valid, despite large amplitudes of oscillations (usually, an increase in amplitude causes enhanced anharmonicity of vibrations).

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