THE LATTICE DYNAMICS OF ADAMANTANE. II. GROUP- THEORETICAL ANALYSIS OF LATTICE VIBRATIONS IN THE TETRAGONAL PHASE[1]

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The paper gives tables of irreducible representations of the space group D_{2d}^4 and diagrams of the types of symmetry of lattice vibrations for points and directions of high symmetry in the Brillouin zone of the adamantane crystal in the tetragonal phase.

1. Introduction

The group-theoretical analysis of lattice vibrations leads to a classification of dispersion branches in accord with the types of symmetry, and predicts degeneracy of vibrations at the high-symmetry points of the Brillouin zone. Moreover, this analysis gives the polarization vectors of the normal vibrations, and a possibility of block diagonalization of the dynamical matrix. The conclusions obtained from this analysis are very useful when analyzing spectra of Raman scattering, far infrared, and thermal neutron scattering. The information received is all the more valuable that it does not depend on the model of interactions in the crystal.

The method of applying group theory to analysis of lattice vibrations has been described in general and illustrated on the example of β-Sn by Chen [1], and then extended to molecular crystals [2].

The goal of the present work is to present the fullest possible analysis of lattice vibrations for the tetragonal phase of the adamantane crystal, belonging to a non-symmorphic space group.

In the subsequent sections of this work are presented: the principles of the group-theoretical analysis of lattice vibrations, the tables of the irreducible representations of the space group D_{2d}^4 and the way in which they are found, and finally conclusions stemming from vibration analysis for the characteristic points and lines of the Brillouin zone.

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2. *Theoretical principles of lattice vibration analysis*

The equation of motion of molecules in a molecular crystal whose unit cell possesses s molecules can be written in the form of a matrix equation,

$$\omega^2 \boldsymbol{V}(\vec{q}) = \boldsymbol{D}(\vec{q}) \cdot \boldsymbol{V}(\vec{q}) \tag{1}$$

where $\boldsymbol{D}(\vec{q})$ is the dynamical matrix of dimensions $6s \times 6s$, and $\boldsymbol{V}(\vec{q})$ a $6s$-component quantity

$$\boldsymbol{V}(\vec{q}) = [U_1(\vec{q}, 1), \ldots U_3(\vec{q}, s), \theta_1(\vec{q}, 1), \ldots \theta_3(\vec{q}, s)] \tag{2}$$

in which $U_\alpha(\vec{q}, i)$, $\theta_\alpha(\vec{q}, i)$ $(i = 1, \ldots, s)$ are the amplitudes of translational and librational vibrations. The dynamical matrix is invariant with respect to the symmetry operations of the group of the wave vector $G(\vec{q})$ [1]; therefore $6s$ solutions of $V(\vec{q}, j)(j = 1, \ldots, 6s)$ form a reducible representation of the group $G(\vec{q})$. Making use of the formulae derived by Chen, we write the transformation matrices of $\boldsymbol{V}(\vec{q})$ for the case of two molecules in the cell: for symmorphic elements of the wave vector group —

$$A \equiv [a_i|\vec{R}_1]; [\vec{R}_1 = (0, 0, 0)]$$

$$\boldsymbol{S}(A, \vec{q}) = \begin{bmatrix} \lambda_{11} \cdot a & & & \\ & \lambda_{11} \cdot a \cdot \det a & & 0 \\ & & \lambda_{22} \cdot a & \\ & 0 & & \lambda_{22} \cdot a \cdot \det a \end{bmatrix} \tag{3}$$

for non-symmorphic elements of the wave vector group — $A \equiv [a_i|\vec{R}_2]$; $\vec{R}_2 \neq 0$

$$\boldsymbol{S}(A, \vec{q}) = \begin{bmatrix} 0 & & \lambda_{12} \cdot a & \\ & & & \lambda_{12} \cdot a \cdot \det a \\ \lambda_{21} \cdot a & & & \\ & \lambda_{21} \cdot a \cdot \det a & 0 & \end{bmatrix} \tag{4}$$

where

$$\lambda_{ij} = [\exp(i\vec{q} \cdot \vec{R}_a)] \cdot \{\exp[-i\vec{G}(\vec{R}_k - \vec{R}_a)]\}$$

R_a is the translation vector related to the given element of the group $G(\vec{q})$, $\boldsymbol{G} = 2\pi \times$(reciprocal lattice vector), and $\boldsymbol{R}_k$ is the vector of the sublattice to which the molecule was transformed due to the symmetry operations of the group $G(\vec{q})$. The set of matrices $\boldsymbol{S}$ obtained in this way form a reducible representation. On the basis of the theorem of character orthogonality we get that the irreducible representation (j) is contained n_j-times in the representation S:

$$n_j = \frac{1}{g} \sum_A \chi^{(j)}(A, \vec{q}) \chi(A, \vec{q}) \tag{5}$$

where g is the order of the group, $\chi^{(j)}(A, \vec{q})$ are the characters of the irreducible representation, and $\chi(A, \vec{q})$ the characters of the reducible representation. Hence, with the use of formula (5) we classify the branches of the dispersion curves.

Since $G(\vec{q})$ is the symmetry group of the crystal and the matrices $\boldsymbol{S}(A, \vec{q})$ form its reducible representation, there must occur the commutation

$$[\boldsymbol{S}(A, \vec{q}), \boldsymbol{D}(\vec{q})] = \boldsymbol{O}. \tag{6}$$

Hence, putting the requirement that the dynamical matrix be commutative with the matrices $\boldsymbol{S}$ we may bring the former to the form appropriate for the considered wave vector. It is also known that commuting matrices are transformed to the diagonal form by means of the same transformation matrix (we denote it $\boldsymbol{M}(\vec{q})$)

$$\begin{aligned} \mathscr{S}(A, \vec{q}) &= \boldsymbol{M}^{+}(\vec{q})\boldsymbol{S}(A, \vec{q})\boldsymbol{M}(\vec{q}) \\ \mathscr{D}(\vec{q}) &= \boldsymbol{M}^{+}(\vec{q})\ \boldsymbol{D}(\vec{q})\boldsymbol{M}(\vec{q}). \end{aligned} \tag{7}$$

In order to find the matrix $\boldsymbol{M}(\vec{q})$, we must construct projection operators according to known formulae [1, 3, 4] and then, making use of the properties of these operators [3], determine the polarization vectors. Polarization vectors obtained thus describe the motion of molecules in the crystal associated with a given vibrational mode.

3. *Tables of the irreducible representation of group* D_{2d}^4

The relatively simplest method of constructing the irreducible representations for non-symmorphic space groups is that of Olbrychski [5] based on the abstract definition of a group.

The group D_{2d}^4 which we are considering possesses eight symmetry elements specified in Table I. The elements on the left-hand side of the table are symmorphic, whereas those on the right are non-symmorphic. The eight rotations of these elements for the point group $G_0 - D_{2d}$.

TABLE I

Elements of the space group $D_{2d}^4 - P\bar{4}2_1c$, $\vec{R}_1 = (0, 0, 0)$ $\vec{R}_2 = (a/2, a/2, c/2)$

Element	Notation according to Seitz [6]	Element	Notation according to Seitz [6]
ε	$\{\bar{x}\, y\, z\|\vec{R}_1\}$	C_2^x	$\{x\, \bar{y}\, \bar{z}\|\vec{R}_2\}$
C_2^z	$\{\bar{x}\, \bar{y}\, z\|\vec{R}_1\}$	C_2^y	$\{\bar{x}\, y\, \bar{z}\|\vec{R}_2\}$
S_4^z	$\{y\, x\, \bar{z}\|\vec{R}_1\}$	$\sigma_v(x+y)$	$\{y\, x\, z\|\vec{R}_2\}$
S_4^{-1}	$\{y\, \bar{x}\, \bar{y}\|\vec{R}_1\}$	$\sigma_v(x-y)$	$\{\bar{y}\, \bar{x}\, z\|\vec{R}_2\}$

Fig. 1 depicts the Brillouin zone for the adamantane crystal. Distinguished are the lines and points (symbols according to Koster [3]) for which the analysis will be made here. The coordinates of the points and the elements of the factor-groups are gathered in Table II.

The abstract definition of the D_{2d} group is given by the relation between some of its chosen elements:

$$(S_4)^4 = \varepsilon \qquad (S_4 \cdot C_2^x)^2 = \varepsilon$$
$$(C_2^x)^2 = \varepsilon \qquad S_4 \cdot C_2^x = C_2^x \cdot (S_4)^3$$

ε is the identity element. The remaining elements are obtained from the general product

$$(S_4)^p \cdot (C_2^x)^r.$$

Substitution of the elements of the point group D_{2d} by elements of the space group yields

$$\{S_4|0\}^4 = \{\varepsilon|0\}$$

$$\{C_2^x|\vec{R}_2\}^2 = \left\{\varepsilon \left| \begin{bmatrix} 2 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \vec{R}_2 \right.\right\}$$

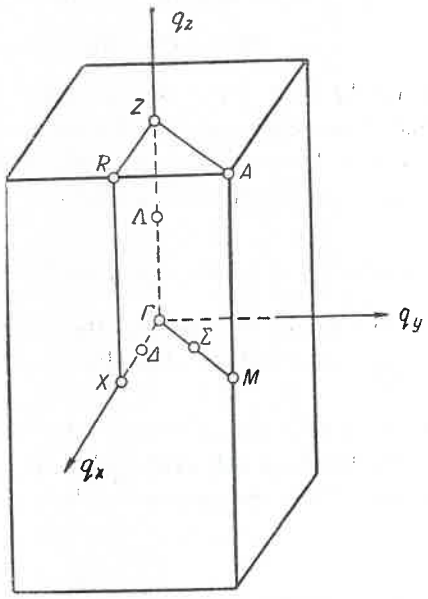

Fig. 1. Brillouin zone for tetragonal phase of adamantane

TABLE II

Point groups $G_0(\vec{q})$ and factor-groups $G(\vec{q})$ for characteristic points and lines in the Brillouin zone

Point	$\vec{q}$	$G_0(\vec{q})$	Elements of factor-group $G(\vec{q})$
Γ	$(0, 0, 0)$	D_{2d}	$\varepsilon, C_2^z, S_4^z, S_4^{-1}$, $\{C_2^x\|\vec{R}_2\}, \{C_2^y\|\vec{R}_2\}$, $\{\sigma_v(x+y)\|\vec{R}_2\}, \{\sigma_v(x-y)\|\vec{R}_2\}$.
Z	$(0, 0, \pi/c)$		
M	$(\pi/a, \pi/a, 0)$		
A	$(\pi/a, \pi/a, \pi/c)$		
X	$(\pi/a, 0, 0)$	D_2	$\varepsilon, C_2^z, \{C_2^x\|\vec{R}_2\}$, $\{C_2^y\|\vec{R}_2\}$.
R	$(\pi/a, 0, \pi/c)$		
Λ	$(0, 0, \pi/c \cdot \xi)$	C_{2v}	$\varepsilon, C_2^z, \{\sigma_v(x+y)\|\vec{R}_2\}$, $\{\sigma_v(x-y)\|\vec{R}_2\}$.
Δ	$(\pi/a \cdot \xi, 0, 0)$	C_2	$\varepsilon, \{C_2^x\|\vec{R}_2\}$
Σ	$(\pi/a \cdot \xi, \pi/a \cdot \xi, 0)$	C_s	$\varepsilon, \{\sigma_v(x+y)\|\vec{R}_2\}$
$\Lambda\Sigma$	$(\pi/a \cdot \xi, \pi/a \cdot \xi, \pi/c \cdot \xi)$		

$$(\{S_4|0\}\{C_2^x|\vec{R}_2\})^2 = \left\{\varepsilon \left| \begin{bmatrix} 1 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \cdot \vec{R}_2 \right.\right\}$$

$$\{S_4|0\}\{C_2^x|\vec{R}_2\} = \left\{\varepsilon \left| \begin{bmatrix} -1 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & -2 \end{bmatrix} \cdot \vec{R}_2 \right.\right\} \{C_2^x|\vec{R}_2\}\{S_4|0\}$$

bearing in mind that S_4 is a symmorphic element. By substituting into the above formula the value $\vec{\boldsymbol{R}}_2 = \left(\frac{a}{2}, \frac{a}{2}, \frac{c}{2}\right)$ and going over to the representation A_i of the wave vector group we obtain four equations for two matrices, A_1 and A_2. Whence we take advantage of a property of the representation of the space group, $d^{\vec{q}\nu}$, *viz.*,

$$A_i = d^{\vec{q}\nu}(\{\varepsilon|\vec{R}_n\}) = \exp i\vec{q}\vec{R}_n \cdot \hat{1}$$

where $\hat{1}$ is the unit matrix. For example, for the point $\Gamma(0, 0, 0)$ we get

$$(A_1)^4 = \hat{1} \quad (A_1 \cdot A_2)^2 = \hat{1}$$

$$(A_2)^2 = \hat{1} \quad A_1 \cdot A_2 = A_2 \cdot (A_1)^3.$$

Solving this set of equations we get the representations for the elements $\{S_4|0\}$ and $\{C_2^x|\vec{R}_2\}$, and using the formula

$$d^{\vec{q}\nu}(\{a_1|\vec{R}_1\})d^{\vec{q}\nu}(\{a_2|\vec{R}_2\}) = \exp i(a_1^{-1}\vec{q} - \vec{q}) \cdot \vec{R}_2 \cdot d^{\vec{q}\nu}(\{a_1|\vec{R}_1\}\{a_2|\vec{R}_2\})$$

we also find the representations for all other elements of group. Tables III to X give the irreducible representations for the wave vector groups listed in Table II.

TABLE III

Irreducible representations of group $G(\vec{q})$ at points Γ (0,0,0) and A (π/a, π/a, π/c)

Γ	A	ε	C_2^z	S_4	S_4^{-1}	$\{C_2^x\|\vec{R}_2\}$	$\{C_2^y\|\vec{R}_2\}$	$\frac{1}{4}\{\sigma_v(x+y)\|\vec{R}_2\}$	$\{\sigma_v(x-y)\|\vec{R}_2\}$
Γ_1	A_1	1	1	1	1	1	1	1	1
Γ_2	A_2	1	1	1	1	−1	−1	−1	−1
Γ_3	A_3	1	1	−1	−1	1	1	−1	−1
Γ_4	A_4	1	1	−1	−1	−1	−1	1	1
Γ_5	A_5	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$	$\begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}$	$\begin{bmatrix} i & 0 \\ 0 & -i \end{bmatrix}$	$\begin{bmatrix} 0 & i \\ -i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 0 & -1 \\ -1 & 0 \end{bmatrix}$

$\vec{R}_2 = (a/2, a/2, c/2)$

TABLE IV

Irreducible representations of group $G(\vec{q})$ at points Z $(0, 0, \pi/c)$ and M $(\pi/a, \pi/a, 0)$

Z	M	ε	C_2^z	S_4	S_4^{-1}	$\{C_2^x\|\vec{R}_2\}$	$\{C_2^y\|\vec{R}_2\}$	$\{\sigma_v(x+y)\|\vec{R}_2\}$	$\{\sigma_v(x-y)\|\vec{R}_2\}$
Z_1	M_1	1	-1	i	$-i$	i	$-i$	1	-1
Z_2	M_2	1	-1	i	$-i$	$-i$	i	-1	1
Z_3	M_3	1	-1	$-i$	i	i	$-i$	-1	1
Z_4	M_4	1	-1	$-i$	i	$-i$	i	1	-1
Z_5	M_5	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & -1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

$R_2 = (a/2, a/2, c/2)$.

TABLE V

Irreducible representations of group $G(\vec{q})$ at point X $(\pi/a, 0, 0)$

X	ε	C_2^z	$\{C_2^x\|\vec{R}_2\}$	$\{C_2^y\|\vec{R}_2\}$
X_1	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$	$\begin{bmatrix}i & 0\\0 & -i\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$

TABLE VI

Irreducible representations of group $G(\vec{q})$ at point $R(\pi/a, 0, \pi/c)$

R	ε	C_2^z	$\{C_2^x\|\vec{R}_2\}$	$\{C_2^y\|\vec{R}_2\}$
R_1	$\begin{bmatrix}1 & 0\\0 & 1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$	$\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$	$\begin{bmatrix}0 & 1\\-1 & 0\end{bmatrix}$

TABLE VII

Irreducible representations of group $G(\vec{q})$ at point $\Lambda(0, 0, \pi/c \cdot \xi)$

Λ	ε	C_2^z	$\sigma_v(x+y)\|\vec{R}_2$	$\sigma_v(x-y)\|\vec{R}_2$
Λ_1	1	1	ω	ω
Λ_2	1	1	$-\omega$	$-\omega$
Λ_3	1	-1	ω	$-\omega$
Λ_4	1	-1	$-\omega$	ω

$\omega = \exp[i(\pi/2) \cdot \xi]$

TABLE VIII

Irreducible representations of group $G(\vec{q})$ at point $\Delta(\pi/a \cdot \xi, 0, 0)$

Δ	ε	$\{C_2^x\|\vec{R}_2\}$
Δ_1	1	ω
Δ_2	1	$-\omega$

$\omega = \exp[i(\pi/2) \cdot \xi]$

TABLE IX

Irreducible representations of group $G(\vec{q})$ at point Σ

Σ	ε	$\{\sigma_v(x+y)\|\vec{R}_2\}$
Σ_1	1	ω^2
Σ_2	1	$-\omega^2$

$\omega = \exp[i(\pi/2)\cdot\xi]$

TABLE X

Irreducible representations of group $G(\vec{q})$ at points $\Lambda\Sigma$

$\Lambda\Sigma$	ε	$\{\sigma_v(X+y)\|\vec{R}_2\}$
$\Lambda\Sigma_1$	1	ω^3
$\Lambda\Sigma_2$	1	$-\omega^3$

$\omega = \exp[i(\pi/2)\cdot\xi]$

4. Results of lattice vibrations analysis

Benefitting from Eqs (3), (4) and (5) we classify the lattice vibrations of adamantane at the center of the Brillouin zone. At this point there are twelve vibration modes:

$$\Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+4\Gamma_5$$

where the Γ_5 model vibrations are doubly degenerate. Using the method of projection operators we find the polarization vectors of the individual modes:

$$\vec{e}(\Gamma_1) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4x_6-4x_{12} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -4x_6+4x_{12} \end{bmatrix}, \text{ and after normalization: } \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{bmatrix}$$

The Γ_1 mode is therefore a librational vibration, for the vector $\vec{e}[\Gamma_1]$ possesses components of librational vibrations only: x_6 of the first molecule and x_{12} of the second molecule. The

polarization vector of the Γ_2 mode has the form

$$\vec{e}(\Gamma_2) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4x_6+4x_{12} \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4x_6+4x_{12} \end{bmatrix} \rightarrow \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \end{bmatrix}$$

which indicates that this is a librational vibration.
The polarization vector of the Γ_3 mode,

$$\vec{e}(\Gamma_3) = \begin{bmatrix} 0 \\ 0 \\ 4x_3-4x_9 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -4x_3+4x_9 \\ 0 \\ 0 \\ 0 \end{bmatrix} \rightarrow \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

shows that these are translational vibrations. As the molecules move in opposite direction these will be optical translational vibrations. Vibrations of the Γ_4 mode are acoustic translational, as is evidenced by the form of the polarization vector,

$$\vec{e}(\Gamma_4) = \begin{bmatrix} 0 \\ 0 \\ 4x_3+4x_9 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4x_3+4x_9 \\ 0 \\ 0 \\ 0 \end{bmatrix} \rightarrow \frac{1}{\sqrt{2}} \begin{bmatrix} 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \end{bmatrix}.$$

The polarization vectors of degenerate vibrations are presented in Table XI. Since there are four vibrations of mode Γ_5, the vectors $e_1(\Gamma_5)$ and $e_2(\Gamma_5)$ obtained by the ordinary method of projection operators are a superposition of four different vectors. Table XI

TABLE XI

Polarization vectors of four vibrations of mode Γ_5

	Translational modes		Librational modes	
	$\Gamma_5^{(1)}$	$\Gamma_5^{(2)}$	$\Gamma_5^{(3)}$	$\Gamma_5^{(4)}$
$\vec{e}_1$	$2x_1+2ix_2$	$2ix_7+2x_8$	0	0
	$-2ix_1+2x_2$	$2x_7-2ix_8$	0	0
	0	0	0	0
	0	0	$2x_4-2ix_5$	$2ix_{10}-2ix_{11}$
	0	0	$2ix_4+2x_5$	$-2x_{10}-2ix_{11}$
	0	0	0	0
	$2x_7+2ix_8$	$2ix_1+2x_2$	0	0
	$-2ix_7+2x_8$	$2x_1-2ix_2$	0	0
	0	0	0	0
	0	0	$2x_{10}-2ix_{11}$	$2ix_4-2x_5$
	0	0	$2ix_{10}+2x_{11}$	$-2x_4-2ix_5$
	0	0	0	0
$\vec{e}_2$	$-2ix_7+2x_8$	$2x_1-2ix_2$	0	0
	$2x_7+2ix_8$	$2ix_1+2x_2$	0	0
	0	0	0	0
	0	0	$-2ix_{10}-2x_{11}$	$2x_4+2ix_5$
	0	0	$-2x_{10}+2ix_{11}$	$-2ix_4+2x_5$
	0	0	0	0
	$-2ix_1+2x_2$	$2x_7-2ix_8$	0	0
	$2x_1+2ix_2$	$2ix_7+2x_8$	0	0
	0	0	0	0
	0	0	$-2x_4-2ix_5$	$2x_{10}+2ix_{11}$
	0	0	$-2ix_4+2x_5$	$-2ix_{10}+2x_{11}$
	0	0	0	0

presents the vectors after their separation into two translational and two librational vibrations each.

Continuing our analysis of vibrations along the $\Gamma-\Lambda-Z$ line we shall classify the dispersion branches at the points $(0, 0, \pi/c \cdot \xi)$: As follows from Table VII, there are only non-degenerate vibrations at these points. From formula (5) we get

$$2\Lambda_1+2\Lambda_2+4\Lambda_3+4\Lambda_4.$$

We shall give here by way of illustration the polarization vectors for the Λ_1 and Λ_2 modes:

$$\vec{e}(\Lambda_1^{(1)}) = \begin{bmatrix} 0 \\ 0 \\ 2x_3+2x_9 \cdot \omega \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2x_3 \cdot \omega+2x_9 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad \vec{e}(\Lambda_1^{(2)}) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2x_6-2x_{12} \cdot \omega \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -2x_6 \cdot \omega+2x_{12} \end{bmatrix}$$

acoustic vibration, longitudinal wave (LA)

librational vibration, longitudinal wave (LO)

$$\vec{e}(\Lambda_2^{(1)}) = \begin{bmatrix} 0 \\ 0 \\ 2x_3-2x_9 \cdot \omega \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ -2x_3 \cdot \omega+2x_9 \\ 0 \\ 0 \\ 0 \end{bmatrix} \qquad \vec{e}(\Lambda_2^{(2)}) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2x_6+2x_{12} \cdot \omega \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 2x_6 \cdot \omega+2x_{12} \end{bmatrix}$$

optical translational vibration, longitudinal wave (LO)

librational vibration, longitudinal wave (LO)

The polarization vectors of vibrations at Λ points depend on the value of wave vector through the factor $\omega = \exp\left(i\frac{\pi}{2}\xi\right)$. If we compare vibration polarizations at the Γ point and Λ points we see that $\Gamma_1 \to \Lambda_1^{(2)}$, $\Gamma_2 \to \Lambda_2^{(2)}$, $\Gamma_3 \to \Lambda_2^{(1)}$ and $\Gamma_4 \to \Lambda_1^{(1)}$. In turn, each Γ_5 vibration splits up into two vibrations, Λ_3 and Λ_4.

At the point $Z(0, 0, \pi/c)$ there are lattice vibrations of the following types:

$$2Z_1+2Z_2+2Z_3+2Z_4+2Z_5$$

The Z_5 vibrations are doubly degenerate (Table IV). After finding the polarization vectors of vibrations at point Z and comparing them with the vectors for points Γ and Λ we get the correlation diagram shown in Fig. 2. It seems to be interesting that the non-degenerate vibrations at the center of the Brillouin zone become degenerated at its surface, unlike that

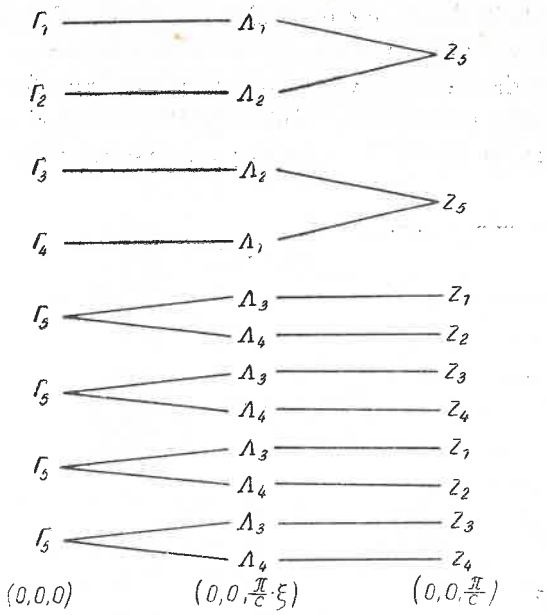

Fig. 2. Symmetry types of lattice vibrations for [001] direction

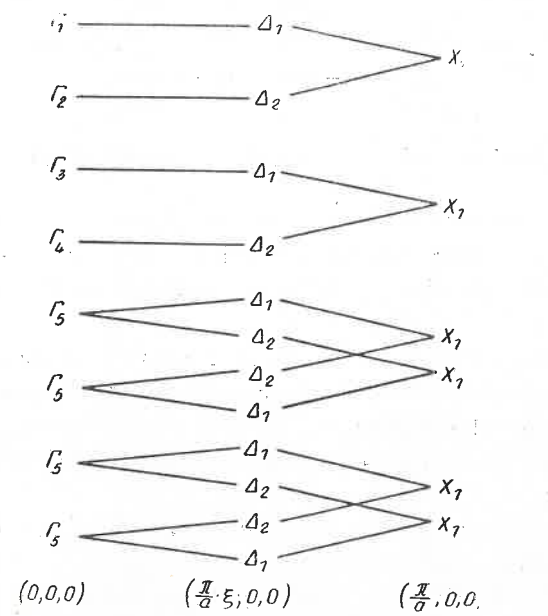

Fig. 3. Symmetry types of lattice vibrations for [100] direction

of Γ_5 modes which become split at the surface. One might also suppose, looking at this diagram, that Z_5 vibrations will play an important role in the frequency distribution function.

An analysis for the $\Gamma-\Delta-X$ line enables us to get the diagram presented in Fig. 3.

At the point $X(\pi/a, 0, 0)$ there are only doubly degenerate vibrations, and the vibrations $X_1^{(1)}$, $X_1^{(5)}$ and $X_1^{(6)}$ have a librational character while the remaining a translational character.

In order to find the modes of vibrations and the diagram for the $\Gamma-\Sigma-M$ line we make use of the so-called compatibility relations [7]. Such relations appear in the case when two lines of symmetry intersect at the symmetry center or when the intersection line of two

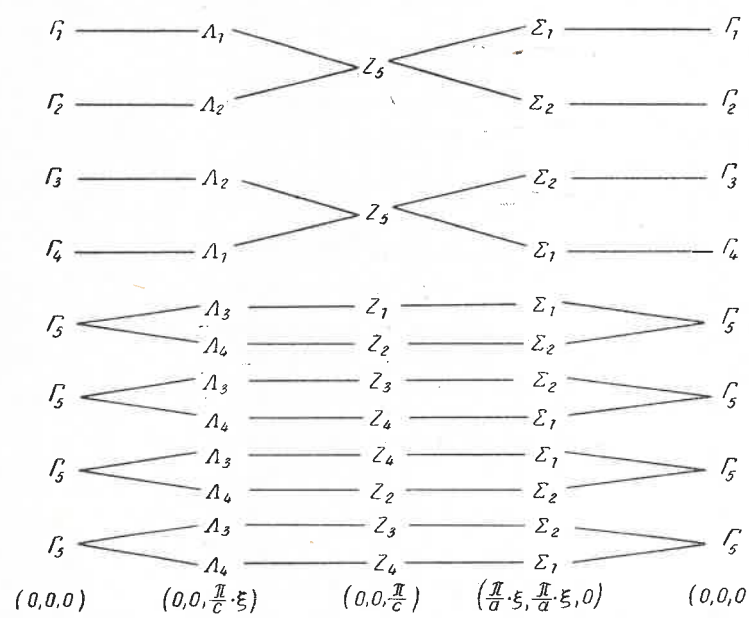

Fig. 4. Compatibility relation between symmetry types for [001] and [110] directions

symmetry planes is at the same time a symmetry line. In the adamantane crystal we encounter the latter case. Compatibility relations occur between the $\Gamma-\Delta-Z$ line and $\Gamma-\Sigma-M$ line. Using the method described in [7] we get these relations in the form of the diagram shown in Fig. 4.

Apart of degeneracy predicted by group-theoretical methods there may also occur accidental degeneracies, consisting in the intersection of dispersion curves. We exclude from our considerations those degeneracies which stem from the assumed model of interactions in the crystal. On the basis of rules given by Herring [8] we may state that for tetragonal adamantane:

1) dispersion curves may intersect along the $\Gamma-\Delta-Z$ line only if they belong to different representations, and

2) along the $\Gamma-\Delta-X$ line accidental degeneracy may happen for vibrations belonging to the same or different representations.

Group-theoretical analysis of lattice vibrations gives a number of results which, however, cannot be directly compared with experiments. A comparison is possible only when information from the group-theoretical analysis is associated with dispersion curve computations. The next paper on the adamantane crystal will be devoted to precisely this problem.

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