

Symmetry-Relations and Dynamics of Molecular Crystals in the Long Wave Limit

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Symmetry relations for macroscopic constants are derived. Especially it is shown that the Voigt-symmetry holds for the indices of the elastic constants. This has been doubted several times for lattices of particles with additional degrees of freedom. In the second part a simple model for Br_2 - and J_2 -lattices is discussed. The intermolecular forces are assumed to be van-der-Waals-forces. The influence of the internal degrees of freedom on lattice dynamics is calculated especially for the elastic constants. Further the limiting frequencies for $q \Rightarrow 0$ are given and compared with experimental values.

Introduction

In a former paper general relations for elastic constants of molecular crystals have been derived neglecting the contribution of the intramolecular degrees of freedom to the lattice dynamical properties¹. The method is essentially that used by Born and Huang^{2,3} in obtaining the constants of lattices with basis. The question has been raised whether the Voigt-symmetry of the elastic constants (interchange of the tensor indices) is satisfied or not⁴. This question has been settled for lattices of point ions^{1,5,6}. It has been shown that the Voigt-symmetry can be derived from general invariance relations. The problem has not been settled for lattices of particles with additional degrees of freedom (e.g. rigid molecules) as stated in¹. In the following we give the proof for the Voigt-symmetries of the elastic constants of molecular lattices.

In order to illustrate these relations and to investigate further the influence of the intramolecular motions to the lattice properties, we use

- 1 Ludwig, W.: Springer Tracts in Modern Physics 43, 1–301 (1967).
- 2 Huang, K.: Proc. Roy. Soc. (London) Ser. A 203, 178 (1950).
- 3 Born, M., Huang, K.: Dynamical theory of crystal lattices. Oxford 1954.
- 4 Laval, J.: Compt. Rend. 232, 1947 (1951); 238, 1773 (1954); — Ann. Inst. Henri Poincaré, 1, No. 4, 329 (1964).
- 5 Leibfried, G., Ludwig, W.: Z. Physik 160, 80 (1960).
- 6 Wallace, D. C.: Rev. Mod. Phys. 37, 57 (1965).

the simplest possible model for solid bromine and iodine. These crystals are considered because they have a simple geometrical structure (2 molecules = 4 particles per unit cell) as well as simple intermolecular forces (van der Waals-forces). We can treat these lattices as consisting of point ions with central forces (spring constants) between the ions. By taking the limit of infinite intramolecular spring constant, we obtain a molecular crystal of rigid dumbbell molecules.

Voigt-Symmetry of Elastic Constants

We consider the simplest case, which already shows the problem: a molecular crystal with one rigid molecule per unit cell. This implies, that all the molecules have the same orientation. The equations of motion then read¹:

$$M \ddot{u}_i^m = - \sum_{n,j} \Psi_{i j}^{m n} u_j^n - \sum_{n,j} \Psi_{i j}^{m n} \omega_j^n, \quad (1)$$

$$I_{ik} \ddot{\omega}_k^m = - \sum_{n,j} \Psi_{k j}^{m n} u_j^n - \sum_{n,j} \Psi_{i j}^{m n} \omega_j^n. \quad (2)$$

M and I_{ik} denote mass and tensor moment of inertia, resp. u_j^n is the displacement, ω_j^n is the infinitesimal libration of the molecule n . Mean indices 1 and 2 denote translational or librational motion, resp. Concerning the lower coordinate indices, we use a summation convention. The coupling constants $\Psi_{i j}^{m n}$ obey a number of invariance relations¹:

$$\Psi_{i j}^{m n} = \Psi_{j i}^{n m}; \quad \Psi_{i j}^{m n} = \Psi_{i \beta}^{m+h} \Psi_{j \alpha}^{n+h}; \quad (3a, b)$$

$$\sum_n \Psi_{i j}^{m n} = \sum_m \Psi_{i j}^{m n} = 0; \quad (4)$$

$$\sum_n \{ \Psi_{i j}^{m n} X_k^n - \Psi_{i k}^{m n} X_j^n \} = \sum_n \Psi_{i l}^{m n} \varepsilon_{l k j} \quad (5a)$$

or

$$\sum_n \Psi_{i j}^{m n} X_k^n \varepsilon_{l k j} = \sum_n \Psi_{i l}^{m n}. \quad (5b)$$

X_i^n is the center of mass coordinate of molecule n , ε_{ijk} is the totally antisymmetric tensor of 3rd rank.

By taking slowly varying displacement and libration fields we obtain the long wave elastic limit in the usual way¹ using the stationary solutions

of (2):

$$\rho \ddot{u}_i = \{ \hat{C}_{ij,kl} + \hat{C}_{m,ik} R_{mn} \hat{C}_{n,jl} \} u_{j|kl} = C_{ik,jl} u_{j|kl} \quad (6)$$

with $\rho = M/V_z$ (V_z = volume of unit cell) and

$$\hat{C}_{ij} = -\frac{1}{V_z} \sum_{\mathbf{h}} \Psi_{ij}^{0\mathbf{h}}; \quad \det \hat{C}_{ij} \neq 0; \quad R_{ij} = (\hat{C}^{-1})_{ij}; \quad (7a)$$

$$\hat{C}_{i,jk} = -\frac{1}{V_z} \sum_{\mathbf{h}} \Psi_{ij}^{0\mathbf{h}} X_k^{\mathbf{h}}; \quad (7b)$$

$$\hat{C}_{ij,kl} = -\frac{1}{2V_z} \sum_{\mathbf{h}} \Psi_{ij}^{0\mathbf{h}} X_k^{\mathbf{h}} X_l^{\mathbf{h}}. \quad (7c)$$

Further we introduce

$$\hat{S}_{il,jk} = \frac{1}{V} \sum_{\mathbf{m}\mathbf{n}} \Psi_{ij}^{\mathbf{m}\mathbf{n}} X_l^{\mathbf{m}} X_k^{\mathbf{n}}. \quad (8)$$

By using (3, 4) and neglecting surface contributions to the sum in (7c) it is simple to prove

$$\hat{C}_{ij,kl} = \frac{1}{2} (\hat{S}_{il,jk} + \hat{S}_{ik,jl}). \quad (9)$$

The first step now is the derivation of the symmetry properties of (7) from (3)–(5). Some of them have been given in ¹ already:

$$\hat{C}_{ij} = \hat{C}_{ji}; \quad R_{ji} = R_{ij}; \quad (10a)$$

$$\hat{C}_{i,jk} - \hat{C}_{i,kj} = \hat{C}_{il} \varepsilon_{kj}; \quad (10b)$$

$$\hat{C}_{ij,kl} = \hat{C}_{ji,kl} = \hat{C}_{ij,lk}. \quad (10c)$$

The essential symmetry relation now is related to (8). This has not been realized in ¹. Obviously from definition we have

$$\hat{S}_{il,jk} = \hat{S}_{jk,il}. \quad (11)$$

By multiplying (5) with the center-of-mass-coordinates, we obtain

$$\hat{S}_{il,jk} - \hat{S}_{il,kj} = -\hat{C}_{s,il} \varepsilon_{skj}, \quad (12a)$$

and from this using (11)

$$\hat{S}_{il,jk} - \hat{S}_{il,jk} = -\hat{C}_{s,jk} \varepsilon_{sli}. \quad (12b)$$

Now, from (9) and (11, 12) the essential relation

$$\hat{C}_{ik,ij} - \hat{C}_{ij,lk} = \frac{1}{2} \{ \hat{C}_{s,il} \varepsilon_{skj} + \hat{C}_{s,kj} \varepsilon_{sli} + \hat{C}_{s,jl} \varepsilon_{ski} + \hat{C}_{s,kl} \varepsilon_{slij} \} \quad (13)$$

follows.

The elastic constants $C_{ik,jl}$ are defined by (6), but because only the symmetric part in k, l enters (6), we have

$$\frac{1}{2}(C_{ik,jl} + C_{il,jk}) = A_{ij,kl} \quad (14a)$$

with

$$A_{ij,kl} = \hat{C}_{ij,kl} + \frac{1}{2}\{\hat{C}_{m,ik}R_{mn}\hat{C}_{n,jl} + \hat{C}_{m,il}R_{mn}\hat{C}_{n,jk}\}. \quad (14b)$$

Formally these expressions are identical with the corresponding expressions for the elastic constants in point ion lattices with basis. For these one can show that both the contributions in (14b) already have the correct and necessary symmetries which allow for a solution of (14a) with respect to the elastic constants $C_{ik,jl}$. It is obvious from (10b) and (14) that in the case of molecular lattices neither the first nor the second part in (14b) has the correct symmetries. But now we are able to show that the sum of both, i.e. $A_{ij,kl}$ has the correct symmetries, which essentially means, that the parts with incorrect symmetries in both the contributions of (14b) just cancel out. From (14b) it follows immediately

$$A_{ij,kl} = A_{ji,kl} = A_{ij,lk}, \quad (15a)$$

if (10a) and (10c) are taken into account. For $A_{kl,ij}$ we obtain with (13) and (10b)

$$\begin{aligned} A_{kl,ij} = & A_{ij,kl} + \frac{1}{2}\{\varepsilon_{mik}(\hat{C}_{m,jl} - \hat{C}_{m,lj}) + \varepsilon_{sjk}(\hat{C}_{s,il} - \hat{C}_{s,li})\} \\ & + \frac{1}{2}\{\varepsilon_{mik}\hat{C}_{ms}\varepsilon_{s,jl} + \varepsilon_{mil}\hat{C}_{ms}\varepsilon_{s,jk}\}. \end{aligned}$$

Using (10b) again for the differences in the first curly brackets, we get expressions which just cancel the expressions in the second curly brackets, so that

$$A_{kl,ij} = A_{ij,kl}. \quad (15b)$$

(15a) and (15b) are necessary and sufficient for solving (14a); the solution is given by

$$C_{ik,jl} = A_{ij,kl} + A_{kj,il} - A_{ki,jl}. \quad (16)$$

By (16) the elastic constants are related to the microscopic force-constants of molecular lattices when Eqs. (7) and (14b) are taken into account.

Model Calculations for Br₂ and J₂

The simplest molecular lattices seem to be solid Br₂- and J₂-crystals. This statement is related to the geometrical structure (Fig. 1) as well as to the molecular interaction. The latter should be essentially determined

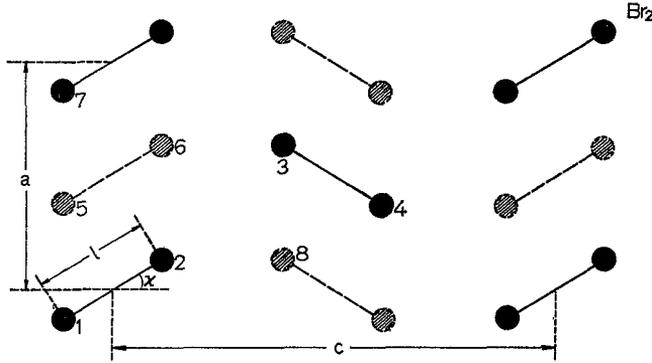


Fig. 1. Br_2 -lattice. The hatched particles belong to planes at distance $b/2$ below or above the drawing plane. In the J_2 -lattice, the distance between particles 2 and 3 is relatively smaller compared to the distance between 1 and 2

by the van-der-Waals-interaction between two molecules μ and ν

$$\phi_{\mu\nu} = -\frac{I_\mu I_\nu}{4(I_\mu + I_\nu)} \alpha_{ij}^{(\mu)} \alpha_{kl}^{(\nu)} \frac{(\delta_{ik} - 3n_i n_k)(\delta_{jl} - 3n_j n_l)}{(R_{\mu\nu})^6}. \quad (17)$$

In deriving (17) the same approximations as for atomic van-der-Waals-interactions have been used. I_μ is the ionization energy of the molecule,

$$\alpha_{ij}^{(\mu)} = \frac{2Q_\mu^2}{I_\mu} \langle 0 | x_{\mu i} x_{\mu j} | 0 \rangle \quad (18a)$$

its polarizability tensor, where $|0\rangle$ denotes the ground state of the molecule. $R_{\mu\nu}$ is the distance between the centers-of-mass and $\mathbf{n} = \mathbf{R}_{\mu\nu}/R_{\mu\nu}$. In the case of a lattice with equal dumbbell molecules the polarizability can be written as

$$\alpha_{ij}^{(\mu)} = \alpha_\perp \delta_{ij} - (\alpha_\perp - \alpha_\parallel) m_i^{(\mu)} m_j^{(\mu)}; \quad (18b)$$

$m_i^{(\mu)}$ is the unit vector in the direction of the dumbbell axis, α_\parallel the main polarizability in this direction, and α_\perp the polarizability perpendicular to the dumbbell axis.

For the repulsive interaction we may use an angle-dependent power law, e.g. an expansion with respect to spherical harmonics for the relative orientation. For simplicity we have assumed the same angle-dependence as given by (17) and (18a), which is in accordance with the geometrical shape of the molecules; we used the repulsive power 12.

Table 1

	α_{\perp} (\AA^3)	α_{\parallel} (\AA^3)	I (eV)	a (\AA)	b (\AA)	c (\AA)	l (\AA)	χ ($^{\circ}$)
Br ₂	4.65	11.2	13	4.48	6.67	8.72	2.27	31.31
J ₂	7.2	15.93	9.7	4.774	7.250	9.772	2.70	32.71

The polarizabilities of Br₂ and J₂ have not been measured. With a relation given by Silberstein⁷ they can be obtained approximately from those of HBr and HJ. The values are given in Table 1. The only parameter we are left with is the repulsion constant, which can be taken from the equilibrium conditions (four conditions, three for the lattice constants, one for the orientation of the rigid dumbbells). We have determined this parameter by the equilibrium condition for the lattice constants a and c . Then the other conditions are not satisfied, or the other parameters are about 30% in error, resp. Nevertheless, we used this procedure to have a simple model.

From the potential thus given we can obtain the force-constants by taking the corresponding derivatives with respect to translations (of the center-of-mass) and infinitesimal rotation angles. We then have the interaction in a lattice of rigid molecules.

Our aim is to investigate the contribution of the intramolecular motions to the elastic constants and to show that the Voigt-symmetries hold for rigid-molecular lattices as well as for non-rigid-molecular lattices. To include the intramolecular motions we replace the interactions by those between the single constituents of the lattice. We put the force constants between seventh and higher neighbors equal to zero. The intramolecular constant f_1 is taken from the eigenfrequency of the free molecule*, the other ones are chosen in such a way that the interaction discussed above is described by the effective spring constants. The rigid molecules can be obtained in the limit $f_1 \Rightarrow \infty$. The set of force-constants used is given in Table 2 (see Fig. 1 for the meaning).

The calculation of the elastic constants is then straight-forward using the method described in⁸ e.g. for four atoms per unit cell. From this procedure it is obvious that the Voigt-symmetry of the elastic constants holds. Then taking the limit $f_1 \Rightarrow \infty$ one can see immediately that the

* It seems that the force constants f_1 in the solid state are different from those of the free molecule.

7 Silberstein, L.: Phil. Mag. 3, 33, 92, 215, 521 (1927).

8 Leibfried, G.: Handbuch der Physik, VII/1, S. 104. Berlin-Göttingen-Heidelberg: Springer 1955.

Table 2. Force constants between atoms (see Fig. 1)

	2-1 f_1	2-3 f_2	2-7 f_3	2-5 f_4	2-6 f_5	2-8 f_6	
Br ₂	24.6	0.271	0.213	0.077	0.072	-0.017	$\cdot 10^4$
J ₂	17.2	0.235	0.269	0.032	0.041	-0.014	dyn · cm ⁻¹

Table 3

	Br ₂		J ₂		
	$f_1 = 24.6 \cdot 10^4$	$f_1 = \infty$	$f_1 = 17.2 \cdot 10^4$	$f_1 = \infty$	
c_{11}	0.528	0.683	0.475	0.546	$\cdot 10^{11}$ dyn/cm ²
c_{22}	0.460	0.456	0.213	0.211	
c_{33}	0.570	0.519	0.547	0.479	
c_{12}	0.067	0.148	0.059	0.063	
c_{13}	0.552	0.551	0.483	0.490	
c_{23}	0.035	0.056	0.026	0.006	
c_{44}	0.084	0.084	0.088	0.088	
c_{55}	0.420	0.461	0.361	0.338	
c_{66}	0.153	0.153	0.077	0.077	
$1/\kappa$	0.320	0.352	0.263	0.262	

Voigt-symmetry is not changed by taking the limit. This, of course, only verifies the statements of (15) and (16) for our simple example.

The explicit expressions for the elastic constants are very lengthy and cannot be given here. The numerical values of the constants are given in Table 3. Though the intramolecular force constant is about 75 to 90 times larger than the others, the table shows that the influence of the intramolecular motions cannot be neglected in every case. It depends on the stresses applied whether the spring in the molecule is forced strongly compared to the springs between different molecules.

A comparison with experimental data can be given only for the compressibility of $J_2; 1/\kappa = 0.756 \cdot 10^{11}$ dyn · cm⁻². This value is about thrice the value of Table 3. The reasons for this can be found in the intermolecular potential. If, in an atomic van-der-Waals-lattice the constants are calculated with the van-der-Waals-parameters taken from gas data, the constants are wrong by a factor of about two⁸. The values can be improved by taking other parameters in the repulsive part of the interaction. Further, anharmonicities should not be neglected. But all these changes would not be sufficient to shift the values by a factor of three.

Table 4

	Br ₂		J ₂			
	$f_1 = 24.6 \cdot 10^4$	$f_1 = \infty$	$f_1 = 17.2 \cdot 10^4$	$f_1 = \infty$		
c_{11}	1.805	2.064	1.404	1.640	$\cdot 10^{11}$ dyn/cm ²	
c_{22}	1.372	1.366	0.636	0.633		
c_{33}	1.844	1.556	1.616	1.438		
c_{12}	0.393	0.443	0.180	0.187		
c_{13}	1.712	1.651	1.438	1.470		
c_{23}	0.107	0.168	-0.006	0.017		
c_{44}	0.246	0.246	0.267	0.267		
c_{55}	1.247	1.145	1.181	1.014		
c_{66}	0.459	0.459	0.232	0.232		
$1/\kappa$	1.049	1.057	0.764	0.784		exp: 0.756

Table 5

	O_1	O_3	L_4	L_3	L_2	L_1	I_1	I_2	
Br ₂	1.06	1.13	0.62	0.70	1.25	1.44	6.11	6.16	$\cdot 10^{13}$ sec ⁻¹
$f_1 = \infty$					1.21	1.39			
J ₂	0.78	0.84	0.27	0.35	1.00	1.11	4.07	4.11	
$f_1 = \infty$					1.00	1.11			

The vibration frequency of the free molecule is $6.09 \cdot 10^{13}$ sec⁻¹ for Br₂, $4.04 \cdot 10^{13}$ sec⁻¹ for J₂.

Another possibility is to take the potential in the form (17), but to determine the van-der-Waals-parameter [the factor in the expression (17)] by fitting it to the experimental compressibility. In the simplest way of fitting this would mean to change the intermolecular spring constants f_2 - f_6 by a factor of three (one parameter is fitted). The resulting elastic constants are given in Table 4.

A further comparison with experimental data is possible if we use optical data related to the eigenfrequencies in the limit of infinite wave length. We use the force-constants which have been taken for the elastic constants given in Table 4. In the limit $q=0$ only the highest libration frequencies (L_1, L_2) are coupled to the internal vibrations of the molecules (I_1, I_2). The expressions are given in the Appendix, whereas the numerical values can be found in Table 5. Fig. 2 gives the eigenvectors of the vibration states.

In our model the mode O_2 is unstable. This is directly related to the fact, that the equilibrium condition for the lattice constant b is not satisfied. A slight improvement of the repulsive part of the potential

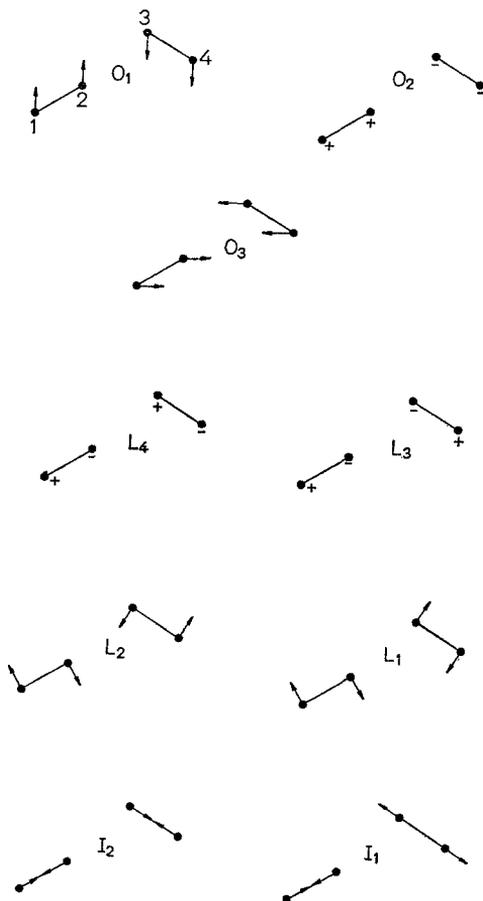


Fig. 2. Eigenvectors for the vibrations in the long wave limit $q=0$. Only the displacements for the molecules in one unit cell (molecules 1-2 and 3-4 of Fig. 1) are shown. +, - indicate motions perpendicular to the drawing plane. The states L_1 , L_2 , I_1 or L_2 , I_2 , resp. are weakly coupled. Therefore the displacements do not have exactly the "ideal" direction indicated in the figure

would change f_6 to a positive value, which makes the mode stable. In any case, this mode should have the lowest frequency (apart from the translational modes with $q=0$).

Some of the frequencies can be compared with experimental data^{9,10}. The optical frequencies (O_1 , O_3) have been measured at 77 °K. The

⁹ Wagner, V.: Phys. Letters 22, 58 (1960); - Z. Physik 224, 353 (1969) and private communication.

¹⁰ Walmley, S. H., Anderson, A.: Mol. Phys. 7, 411 (1963).

values are 0.92 and $1.40 \cdot 10^{13} \text{ sec}^{-1}$ for Br_2 , 0.77 and $1.22 \cdot 10^{13} \text{ sec}^{-1}$ for J_2 , resp. They are in a qualitative agreement with the values in Table 5. The agreement is better for the O_1 -mode than for the O_3 -mode, which again is related to the force-constant f_6 (see Appendix). A positive sign for f_6 would give a much better agreement.

One of the intramolecular frequencies is found to be 5.65 for Br_2 and $3.38 \cdot 10^{13} \text{ sec}^{-1}$ for J_2 . These values are smaller than those of the free molecules. This cannot be explained by a change in the van-der-Waals-interaction, because the coupling of the internal vibrations (I_1, I_2) to the libration modes (L_1, L_2) is not very strong (Table 5). This can be seen from a comparison of the values with $f_1 < \infty$ and $f_1 = \infty$ in Table 5. For J_2 the difference occurs only in the third decimal. The behavior of Br_2 and J_2 in this respect is related to the fact that $f_2 > f_3$ for Br_2 and $f_2 < f_3$ for J_2 in our model (Table 2).

To explain the difference between experimental and theoretical values of the internal frequencies we have to assume different internal springs (f_1) in solid and free state. This seems to be not very surprising. Further anharmonic effects may not be neglected. An indication for this statement can be found in the strong temperature dependence of the modes⁹.

The qualitative behavior is quite well described by our model. By fitting one parameter to the compressibility of J_2 , we can even explain the frequencies of Br_2 when the same procedure is used. The complete dispersion curves and an improvement of the model will be given in another paper.

Appendix

Force-Constant Tensors

See Fig. 1 for the numeration of the atoms. Central forces are assumed.

$$\begin{aligned}
 2-1: & \begin{Bmatrix} \beta_1 & 0 & \delta_1 \\ 0 & 0 & 0 \\ \delta_1 & 0 & \alpha_1 \end{Bmatrix}; & 2-3: & \begin{Bmatrix} \beta_2 & 0 & \delta_2 \\ 0 & 0 & 0 \\ \delta_2 & 0 & \alpha_2 \end{Bmatrix} \\
 2-7: & \begin{Bmatrix} \alpha_3 & 0 & \delta_3 \\ 0 & 0 & 0 \\ \delta_3 & 0 & \beta_3 \end{Bmatrix}; & 2-5: & \begin{Bmatrix} \gamma_4 & \varepsilon_4 & \zeta_4 \\ \varepsilon_4 & \alpha_4 & \delta_4 \\ \zeta_4 & \delta_4 & \beta_4 \end{Bmatrix} \\
 2-6: & \begin{Bmatrix} \beta_5 & \delta_5 & 0 \\ \delta_5 & \alpha_5 & 0 \\ 0 & 0 & 0 \end{Bmatrix}; & 2-8: & \begin{Bmatrix} 0 & 0 & 0 \\ 0 & \alpha_6 & \delta_6 \\ 0 & \delta_6 & \beta_6 \end{Bmatrix}.
 \end{aligned}$$

The values of these force-constants can be calculated from the spring constants (Table 2), if the lattice constants of Table 1 are used.

Limiting frequencies for infinite wave length.

$$\begin{aligned}
 O_1: M\omega^2 &= -4\beta_2 & A &= -\beta_1 - 2\beta_2 - \alpha_3 - 2\gamma_4 \\
 O_2: &= -4\alpha_6 & C &= -\alpha_1 - \beta_3 - 2\beta_4 \\
 O_3: &= -4\alpha_2 - 4\beta_6 & B &= -\delta_1 - \delta_3 - 2\zeta_4 \\
 L_4: &= -4\alpha_4 - 4\alpha_6 & D &= -\beta_1 - \alpha_3 - 2\gamma_4 \\
 L_3: &= -4\alpha_4 & F &= -\alpha_1 - 2\alpha_2 - \beta_3 - 2\beta_4 - 2\beta_6 \\
 L_2: &= D + F - \sqrt{(D-F)^2 + 4B^2} \\
 L_1: &= A + C - \sqrt{(A-C)^2 + 4B^2} \\
 I_1: &= A + C + \sqrt{(A-C)^2 + 4B^2} \\
 I_2: &= D + F + \sqrt{(D-F)^2 + 4B^2}.
 \end{aligned}$$

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