SELECTED TOPICS ON DYNAMICS OF CRYSTAL LATTICES

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SUMMARY

page

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FOREWORD

This report contains the detailed description of some of the topics discussed in a course "Dynamics of Crystal Lattices", which was given during the first semester of 1971 at the Instituto de Energia Atômica. The reason for publishing these topics in a compact form is that they can only be found spread in books and specialized articles. Since these topics are also the most relevant for the purpose of setting up a lattice dynamical model, the person faced with such a task is forced to do some search in the literature. It is felt therefore that the publication of these topics in a unified form may be useful, at least to the person getting started in the field.

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INTRODUÇÃO

Êste relatório contém a descrição, com detalhes, de alguns assuntos discutidos no curso "Dinâmica das Redes Cristalinas", que foi ministrado no primeiro semestre de 1971, no Instituto de Energia Atômica.

A razão para publicar êstes assuntos numa forma compacta é que êles só podem ser achados espalhados em livros e artigos especializados. Sendo que êstes assuntos são também os mais importantes para a construção de um modêlo de dinâmica reticular, a pessoa interessada tem que fazer muita pesquisa na literatura. Pensamos, então, que a publicação dêstes assuntos numa forma unificada possa ser útil, pelo menos para a pessoa que vai se iniciar neste campo.

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1. INTRODUCTION

1.1. Purpose of Lattice Dynamics and Historical Notes

The main purpose of lattice dynamics is the study of the vibrational states of the atoms in crystal lattices and the force fields which determine such vibrations. The interest in lattice dynamics research can be motivated on the following arguments.

1) From a quantitative point of view, the collection of data on the interatomic forces in crystals can be compared to the work of crystallographers in collecting structural data for a large number of crystals. In this sense lattice dynamics can be regarded as a "time dependent" crystallography.(1)

2) From a theoretical point of view, the determination of accurate dispersion relations, specially in metals, is important to the theoreticians studying the electron-phonon interaction.(2)

3) From a applied point of view the availability of a lattice dynamical model permits the calculation of scattering laws for neutron moderators. The results of such calculations are commonly employed by reactor designers for the optimization of thermal reactors.(3)

Like other fields of physics, lattice dynamics can be studied from a theoretical and an experimental point of view. Theoretically one can set up a model for the lattice vibrations, based on conveniently postulated force fields. Setting up a model consists of calculating a dynamical matrix for the crystal and involves some knowledge of matrix calculus and of the symmetry properties of the crystal.(4,5) Once the dynamical matrix has been computed, all the vibrational properties as well as many thermodynamic quantities can be calculated. The frequencies of the vibrational modes are the eigenvalues of the dynamical matrix while the eigenvectors are the amplitudes of vibration of the atoms.

Experimentally, lattice dynamics can be studied best by studying the interaction of radiation with crystals. Light (Brillouin scattering), X-rays (thermal diffuse scattering) and neutrons (coherent and incoherent scattering) have been used in these studies. The best method is the method of coherent scattering of thermal neutrons from single crystals, implemented by the triple axis crystal spectrometer.(6) This is the method which has produced the most accurate dispersion relations. Its applicability depends on the availability of single crystals of relatively large size and on the neutron scattering properties of the atoms in the crystal (good coherent scattering cross section, low absorption cross section).

It should be stressed that it is not possible to perform coherent scattering experiments without a preliminary knowledge of the lattice dynamics of the sample to be studied. The reason for this is that the inelastic cross section for a single crystal is very complicated and it would take an exceedingly long time to try to measure this cross section for all the orientations of the crystal. Instead, one can plan the experiment in order to obtain the maximum amount of information with the minimum amount of radiation use. To do this a preliminary knowledge of the eigenvalues and eigenvectors of the dynamical matrix is required. In fact the eigenvalues (frequencies) are needed for planning a measurement at constant momentum exchange with the triple axis spectrometer while the eigenvectors are required to compute the inelastic structure factors, which control the intensity of coherently scattered neutron groups. Historically, the development of lattice dynamics followed the study of propagation of waves in continuous media, a subject which had been thouroughly investigated during the last century.

In 1907 Einstein published a paper in which the specific heat of a solid was calculated considering the solid as an assembly of uncoupled harmonic oscillators. Debye (1912) and Born and von Kármân (1912) introduced more sophisticated models to explain the specific heat of solids at low temperature. The much simpler Debye model, based on a continuum of lattice waves, was very popular for about twenty years. Studies of diffuse X-rays scattering produced later a return to the more sophisticated Born-von Kármân model. This process was to be even more accelerated by the introduction of the technique of coherent inelastic scattering from single crystals. A significant contribution was given by Ewald, who introduced the theta function transformation for the calculation of lattice sums involving Coulomb potentials.Kellermann calculated the lattice dynamics of halkali halides before the advent of digital computers. More recently, the introduction of neutron scattering on one side and the availability of digital computers on the other side have prompted a large number of studies and have permitted the introduction of more sophisticated models. A characteristic example of this sophistication is given by the shell model (Cochran, 1959),(7) which takes into account the polarizability of the ions.

1.2. Interatomic Forces

One of the main purposes of lattice dynamics is the study and determination of interatomic forces in crystals. It is therefore proper to start with a discussion of the character of these forces. It should be noticed that the force constants of lattice dynamics determine the forces which tend to bring an atom back to its equilibrium position, after the atom has been displaced from this equilibrium position. The force constants are therefore only a partial manifestation of the forces which keep the crystal together and are responsible for cohesion.

It is conventional to classify the crystals into four categories, namely:

1) Ionic crystals.

2) Van der Waals crystals.

3) Valency crystals.

4) Metals.

There is a fundamental difference between crystals in group 1 and 2 on one side and crystals in group 3 and 4 on the other side.

Ionic and van der Waals crystals (for example halkali halides and noble gas crystals respectively) are essentially composed of saturated units while valency and metallic crystals are composed of unsaturated units. Saturated units are for example atoms with close shells of electrons. Saturated units are inherently stable and when they are brought together to form the crystal there are not large changes in the wave functions of the atoms. As a consequence perturbation methods can be used for the calculation of the total energy of the crystal as a function of atom separation.

On the contrary, when unsaturated units are brought together there is a large rearrangement of the electronic wave functions and the perturbation method cannot be used.

For the saturated units the total interaction is a sum of two units interactions, so that the potential can be considered as a sum of pairs potentials. For the non saturated units the interaction is instead a many bodies problem.

If a complete description of the forces among atoms were available, one could calculate the equilibrium position, or structure, of the crystal. The case of the halkali halides is the simplest and in this case several calculations have been made to determine theoretically the equilibrium position.What is required is an expression for the total energy of the crystal as a function of the atom separation.

In the case of ionic crystals an important term in the energy is the Coulomb energy. The electrostatic energy per unit cell is given by

$$E_M = \frac{1}{2} \sum_{k} \sum_{k'\ell'}{}' \frac{(ze)^2 q_k q_{k'}}{\left| \underline{r}\binom{0}{k} - \underline{r}\binom{\ell'}{k'} \right|} \tag{1.1}$$

where $\underline{r}\binom{\ell}{k}$ is the vector from the origin to the k-th atom in the ℓ-th cell, q_k is the charge on the k-th ion in units of the minimum ionic charge ze and the second sum does not include the term with $\ell = 0$, $k = k'$. The energy E_M is called Madelung energy. The lattice sum (1.1) converges very slowly and its value can be calculated with the theta function method. This method will be described later in connection with the calculation of Coulomb coefficients. When the sums in (1.1) are performed the result can be put in the forms

$$E_M = - (ze)^2 \frac{\alpha'}{r} = - (ze)^2 \frac{\alpha''}{d} \qquad (1.2)$$

where r is the distance among ions and d is the lattice parameter (for cubic crystals). α' and α'' are known as Madelung constants and their values have been calculated for several structures.

When the lattice parameter decreases the Madelung energy decreases algebraically, as it must be for an attractive term . There are of course contributions to the total energy other than the Madelung term and they are to be taken into account. The simplest way of calculating such contributions is on the basis of the Thomas-Fermi-Dirac statistical model, which replaces the wave function of an atom with an electron density function. The most important contribution to the energy is the kinetic energy of the electrons or zero point kinetic energy. When the ions are brought together to form the crystal, there is some overlap. According to the Pauli principle an element h^3 in phase space can accomodate no more than two electrons, therefore if we try to squeeze the ions by increasing the electron density, states of higher momentum must appear, with consequent increase in the kinetic energy. Quoting from Born and Huang's(4) book: "Pauli's principles is ultimately responsible for the bulk of a lattice". It should be noticed that even in a simple case like the halkali halides, where the forces are well understood, calculations of the equilibrium positions are only approximate.

When a crystal is composed of neutral units the Madelung term disappears while the short range repulsive overlap term remains the same. What provides the attractive term is an effect of dipole interactions, known as the van der Waals force. The van der Waals energy is obtained by considering the second order term in a perturbation calculation of the total attractive energy. The first order term, which corresponds to the static dipole energy, turns out to be less important even in those cases in which a dipole exists on the atoms. The second order term, which predominates, is inversely proportional to the sixth power of the interatomic distance. Therefore, in van der Waals crystals an attractive potential exists, and the energy has the form

$$E_{vdw} = - \frac{2B}{3r^6} \tag{1.3}$$

where the constant B can be calculated but it is a complex function of the states of the atoms and has been calculated using convenient approximations.

For valency crystals and metals it is not possible to use the perturbation method to find a total potential energy. It is possible however to use phenomenological expressions for the potential and to introduce, in the Born-von Kármán formalism, a number of force constants which describe the observed dispersion relations. One of the results of the neutron scattering measurements of dispersion relations in metals has been to establish that long range forces are needed to explain accurately the observed dispersion curves.

2. COHERENT NEUTRON SCATTERING FROM SINGLE CRYSTALS

The mathematical expression for the coherent double differential scattering cross section of neutrons from single crystals will be analyzed to emphasize the importance of the different factors. The derivation of the cross section formula will not be given.

The scattering of thermal neutrons by a nucleus is isotropic at a very high degree of approximation and it is therefore described by one parameter b, the scattering amplitude. The microscopic cross section σ is related to the scattering amplitude by the relation

$$\sigma = 4\pi b^2 \tag{2.1}$$

If we have an assembly of nuclei of the same atomic species but in different spin states or with different atomic weights, we shall also have different scattering amplitudes. The cross section will then be an average cross section $4\pi\langle b^2\rangle$.

This can be written

$$\sigma = 4\pi\langle b^2\rangle = 4\pi\langle b\rangle^2 + 4\pi\left[\langle b^2\rangle - \langle b\rangle^2\right] = \sigma_{coh}+\sigma_{inc} \tag{2.2}$$

The convenience of splitting the cross section into coherent and incoherent terms depends on the following fact. If we have an assembly of N atoms the scattering is given by (assuming the nuclei fixed at their equilibrium position):

$$I = \left|\sum_k e^{2\pi i \underline{Q}.\underline{R}_k}\right|^2 = \sum_{h,k} b_h\, b_k\, e^{2\pi i \underline{Q}.(\underline{R}_h-\underline{R}_k)} \tag{2.3}$$

where R_k are the position vectors of the nuclei and $\underline{Q}$ is the scattering vector. When an average over the scattering amplitudes is made we obtain:

$$I=\left\langle \sum_{h,k} b_h b_k\, e^{2\pi i \underline{Q}.(\underline{R}_h-\underline{R}_k)}\right\rangle = N\left\{\langle b^2\rangle-\langle b\rangle^2\right\}+\langle b\rangle^2 \sum_{h,k} e^{2\pi i \underline{Q}.(\underline{R}_h-\underline{R}_k)} \tag{2.4}$$

Therefore the scattering can be separated into an incoherent component and a component which is coherent and gives interference effects. We are interested presently in the coherent scattering of neutrons by a single crystal and in particular we are interested in the one phonon cross section.

The double differential cross section can be written in the following form(8)

$$\frac{d^2\sigma}{d\Omega dE}(E_o,E,\Phi) = \frac{d^2\sigma}{d\Omega dE}(\underline{Q},\omega) = \frac{k'}{k}\left| F\ (\underline{Q},\omega)\right|^2 \tag{2.5}$$

where E_o, E are the incident and final energy of the neutron, Φ is the scattering angle, $\underline{Q}$ is the momentum transfer and ω the energy transfer (in frequency units).

It is possible to expand $|F(\underline{Q},\omega)|^2$ in series of the displacement of the atoms from their equilibrium positions. This is the so called phonon expansion. The first and second terms in the expansion are

$$\left| F(\underline{Q},\omega)\right|^2 = \frac{(2\pi)^3 N}{V}\left|F_o(\underline{Q})\right|^2 \delta(\underline{Q}-\underline{\tau})\delta(\omega) +$$

$$+ \sum_j \int d^3\underline{q}\ \left|g_j(\underline{Q})\right|^2 \delta(\underline{Q}-\underline{q}-\underline{\tau})\delta(\omega\pm\omega_j)\begin{Bmatrix} N_j \\ N_j+1 \end{Bmatrix} + \ldots \tag{2.6}$$

The first term is the zero phonon or elastic scattering term, with

$$F_o(\underline{Q}) = \sum_k b_k\ e^{2\pi i\underline{Q}\cdot\underline{r}_k}\ e^{-W_k} \tag{2.7}$$

In (2.6) and (2.7) N is the number of unit cells in the crystal, V is the volume of the unit cell, r_k are the basic vectors (position vectors of the atoms inside the unit cell), W_k the Debye Waller factors.

The second term in (2.6) is the one-phonon term.The sum over j is a sum over different branches of the dispersion relation, while the integral is extended to all reciprocal space.

In the one phonon term we recognize an inelastic structure factor $|g_j(\underline{Q})|^2$ and a statistical factor $\left\{\begin{matrix} N_j \\ N_j+1 \end{matrix}\right\}$.

We use N_j for energy gain processes (upscattering) and N_j+1 for energy loss processes (downscattering), with:

$$N_j = \frac{1}{e^{\hbar\omega_j/K_B T} - 1} \tag{2.8}$$

The inelastic structure factor is given by

$$g_j(\underline{Q}) = \sum_k \frac{b_k(\underline{Q}\cdot\underline{C}_k(\underline{q},j))}{\sqrt{2NM_k\omega_j}} \; e^{2\pi i\, \underline{\tau}\cdot\underline{r}_k} \; e^{-W_k} \tag{2.9}$$

Here $\underline{C}_k$ $(\underline{q},j)$ is the polarization vector for the atom k in the mode characterized by the wave vector $\underline{q}$ and the branch index j, $\underline{\tau}$ is a reciprocal lattice vector, M_k the mass of the atom k. The sum is performed over the atoms in the unit cell. The delta functions in (2.6) correspond to the kinematics of the one phonon scattering. Accordingly, one phonon scattering takes place when the conservation conditions:

$$E - E_o = \pm \hbar\omega_j \tag{2.10}$$

$$\underline{k} - \underline{k}_o = \underline{q} + \underline{\tau}$$

are satisfied. The intensity of the process is controlled by the inelastic structure factor.

It is important to become familiar with the geometry of the one phonon processes in reciprocal space. The frequencies and the polarization vectors are periodic functions of $\underline{q}$, the periodicity zone being the Brillouin zone. An example of Brillouin zone for the case of the face centered cubic lattice is given in fig.1, where the irreducible part is also shown shaded.

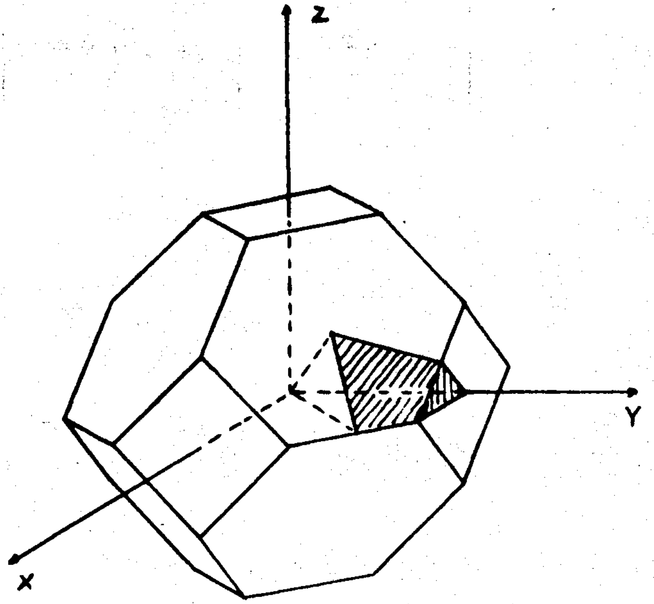

Figure 1

The inelastic structure factor is not a periodic function of $\underline{Q}$. When divided by $|\underline{Q}|^2$ the structure factor is usually periodic but with a periodicity larger than the Brillouin zone.

Let us now consider a plane in reciprocal space of an f. c. c. lattice, say the (001) plane and let us mark the boundaries of the Brillouin zones.

The wavevectors $\underline{k}_o$ and $\underline{k}$ are shown. For elastic scattering $|\underline{k}_o| = |\underline{k}|$ and the condition $\underline{k}_o - \underline{k} = \underline{\tau}$ is equivalent to the Bragg condition $\lambda = 2\, d \sin \theta_B$, with $\theta_B = \phi/2$, ϕ being the scattering angle. For X-rays $|\underline{k}_o| = |\underline{k}|$ for all practical purposes and therefore the scattering surface, or the locus of the endpoints of the vectors $\underline{k}$ is the Ewald sphere. The situation is different for neutrons, as it can be seen in fig. 3.

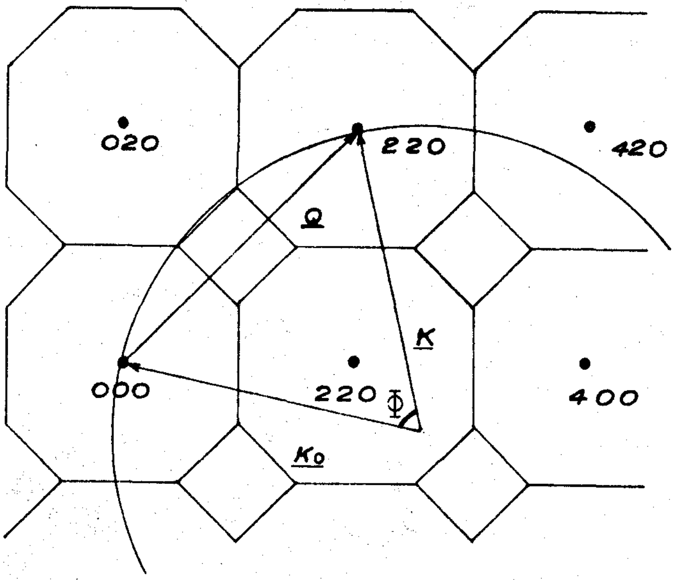

Figure 2

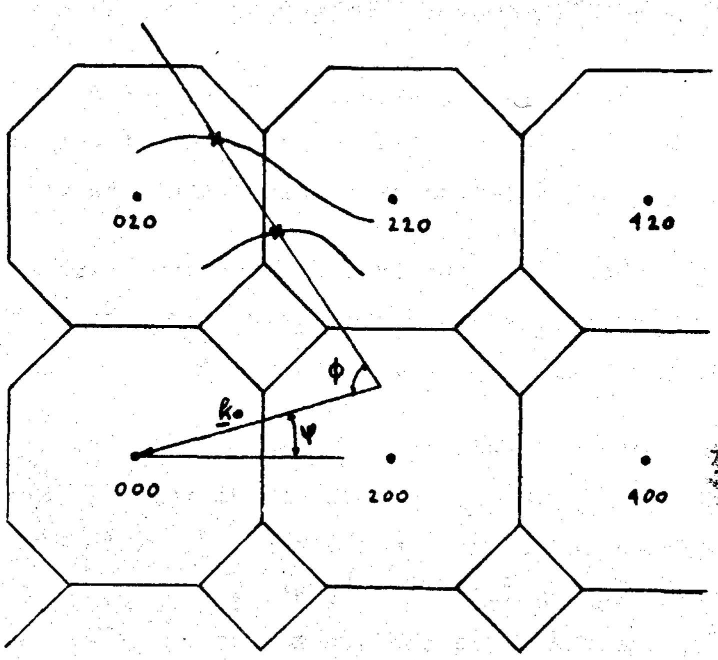

Figure 3

Let us define the vector $\underline{k}_o$, in the plane of the reciprocal lattice, and the angle Φ. This defines the direction of the vector $\underline{k}$. Then as we move along the direction of $\underline{k}$ we find different frequencies (for each branch). At a certain point the energy and momentum conditions (2.10) will be satisfied for a frequency ω_j. At this point there will be a peak in the one phonon cross section. If we change the scattering angle each branch will contribute a new point and there will be scattering surfaces which are not spheres anymore like in the elastic scattering case. If we change the angle ψ (orientation of the crystal with respect to the incident monochromatic neutron beam) we obtain a new family of scattering surfaces. One way of measuring dispersion relations in then to measure the energy distribution of neutrons scattered at fixed angle. This type of measurement, which can be performed with a time of flight spectrometer, is not the best because data are obtained mainly outside the symmetry directions in the crystal. The triple axis crystal spectrometer allows data to be obtained along symmetry directions only and it has proved to be the best instrument for measurements of dispersion relations.

A suitable sample for dispersion relation measurements should have the following characteristics:

1) Relatively simple structure (few atoms per unit cell).
2) Relatively large size (of the order of 10 cm^3).
3) Small neutron capture cross section and large coherent scattering cross section.
4) The crystal should be as perfect as possible.

3. EQUATIONS OF MOTION OF A VIBRATING LATTICE

Let us define a perfect crystal. The unit cell of the crystal is defined by three non-coplanar vectors $\underline{a}_1$, $\underline{a}_2$, $\underline{a}_3$. The unit cell contains n atoms, whose positions are defined by the basic vectors $\underline{r}(1)$, $\underline{r}(2)$, $\underline{r}(3)$, ..., $\underline{r}(n)$.

The position of an atom inside the crystal is defined by a vector

$$\underline{r}\binom{\ell}{k} = \ell_1\, \underline{a}_1 + \ell_2\, \underline{a}_2 + \ell_3\, \underline{a}_3 + \underline{r}(k) \tag{3.1}$$

where $\ell \equiv (\ell_1, \ell_2, \ell_3)$ is the cellular index.

As a result of the Born-Oppenheimer approximation one can introduce an effective potential energy for the nuclei (this potential energy contains the kinetic energy of the electrons) and treat the system as a classical vibrating system of point masses. The potential energy, developed in powers of atomic displacements, is:

$$\Phi=\Phi_o + \sum_{\ell k\alpha} \Phi_\alpha\binom{\ell}{k} u_\alpha\binom{\ell}{k} + \frac{1}{2} \sum_{\substack{\ell k\alpha \\ \ell' k' \beta}} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'}\, u_\alpha\binom{\ell}{k}\, u_\beta\binom{\ell'}{k'} + \dots \tag{3.2}$$

$u_\alpha\binom{\ell}{k}$ is the α-component of the displacement from equilibrium of the atom in $\underline{r}\binom{\ell}{k}$. Φ_o is the static potential energy, while

$$\Phi_\alpha\binom{\ell}{k} = \left.\frac{\partial\Phi}{\partial u_\alpha\binom{\ell}{k}}\right|_o$$

$$\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = \left.\frac{\partial^2\Phi}{\partial u_\alpha\binom{\ell}{k}\,\partial u_\beta\binom{\ell'}{k'}}\right|_o \tag{3.3}$$

$\Phi_\alpha\binom{\ell}{k}$ is the negative of the force acting on atom (ℓ,k) at the equilibrium position and therefore it vanishes. The physical significance of the force constant $\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'}$ is the α - component of the force acting on the atom (ℓ,k) when the atom in (ℓ',k') is moved a unit distance in the direction β.

Because of the translational periodicity of the lattice, the coefficients $\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'}$ depend only on the difference of the indexes ℓ, ℓ'. Therefore:

$$\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = \Phi_{\alpha\beta}\binom{\ell-\ell'}{k\ k'} \qquad (3.4)$$

Also, the coefficients are symmetric:

$$\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = \Phi_{\beta\alpha}\binom{\ell'\ell}{k'k} \qquad (3.5)$$

Some relations among the force constants can be derived from the invariance of the potential and its derivatives under rigid translations and rotations. So, for example, if we consider a translation, formally we have:

$$\Phi = \Phi_o + \frac{1}{2}\sum_{\substack{\alpha\beta\\ \ell\ell'\\ kk'}} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'}\, v_\alpha\, v_\beta = \Phi_o \qquad (3.6)$$

$$\frac{\partial\Phi}{\partial u_\alpha\binom{\ell}{k}} = \left.\frac{\partial\Phi}{\partial u_\alpha\binom{\ell}{k}}\right|_o + \sum_{\ell'k'\beta} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} v_\beta = \left.\frac{\partial\Phi}{\partial u_\alpha\binom{\ell}{k}}\right|_o$$

The sums must be zero for any value of $\underline{v}$. This requires that:

$$\sum_{\substack{\ell\ell'\\ kk'}} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = 0 \qquad\qquad \sum_{\ell'k'} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = 0 \qquad (3.7)$$

The last relation is useful in practice to determine the coefficients with $\ell = \ell'$, $k = k'$. For example

$$\Phi_{\alpha\beta}\binom{\ell\ell}{kk} = \Phi_{\alpha\beta}\binom{o}{kk} = -\sum_{\ell' k'}{}' \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} \tag{3.8}$$

Other relations among the force constants are obtained by the invariance of the potential with respect to rigid rotations.

We consider now the classical equations of motion for the lattice. They are:

$$m_k \ddot{u}_\alpha\binom{\ell}{k} = -\frac{\partial\Phi}{\partial u_\alpha\binom{\ell}{k}} = -\sum_{\beta\ell' k'} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} u_\beta\binom{\ell'}{k'} \tag{3.9}$$

It is customary to introduce the reduced displacement

$$v_\alpha\binom{\ell}{k} = \sqrt{m_k}\; u_\alpha\binom{\ell}{k} \tag{3.10}$$

and the reduced force constant

$$D_{\alpha\beta}\binom{\ell\ell'}{kk'} = \frac{1}{\sqrt{m_k m_{k'}}} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} \tag{3.11}$$

The advantage of this transformation is to simplify eq.(3.9) as :

$$\ddot{v}_\alpha\binom{\ell}{k} = -\sum_{\beta\ell' k'} D_{\alpha\beta}\binom{\ell\ell'}{kk'} v_\beta\binom{\ell'}{k'} \tag{3.12}$$

If we take a solution of the form

$$v_\alpha\binom{\ell}{k} = C_\alpha(k)\; e^{2\pi i \underline{q}.\underline{r}\binom{\ell}{k}}\; e^{i\omega t} \tag{3.13}$$

by substitution in (3.12) we obtain

$$-\omega^2 C_\alpha(k) e^{2\pi i \underline{q}.\underline{r}\binom{\ell}{k}} = -\sum_{\beta\ell' k'} D_{\alpha\beta}\binom{\ell\ell'}{kk'} C_\beta(k') e^{2\pi i \underline{q}.\underline{r}\binom{\ell'}{k'}}$$

or $$\omega^2\, C_\alpha(k) = \sum_{\beta k'} D_{\alpha\beta}(\underline{q}|kk')\, C_\beta(k') \qquad (3.14)$$

where we have introduced the dynamical matrix:

$$D_{\alpha\beta}(\underline{q}|kk') = \sum_{\ell} D_{\alpha\beta}\binom{\ell}{kk'} e^{2\pi i \underline{q}\left[\underline{r}\binom{\ell}{k} - \underline{r}\binom{0}{k'}\right]} =$$

$$= \frac{1}{\sqrt{m_k m_{k'}}} \sum_{\ell} \Phi_{\alpha\beta}\binom{\ell}{kk'} e^{2\pi i \underline{q}\cdot\left[\underline{r}\binom{\ell}{k} - \underline{r}\binom{0}{k'}\right]} \qquad (3.15)$$

Equations (3.14) can be solved when the determinant of the matrix of the coefficients is zero:

$$\left| D_{\alpha\beta}(\underline{q}|kk') - \omega^2\, \delta_{\alpha\beta}\, \delta_{kk'} \right| = 0 \qquad (3.16)$$

or in matrix form

$$\left| D(\underline{q}|kk') - \omega^2 I \right| = 0 \qquad (3.17)$$

where I is a unit matrix of order 3n.

The solutions of equation (3.16) are the branches of the dispersion relation. There are 3n of such branches. It is easy to see that if we increase $\underline{q}$ by a reciprocal lattice vector $\underline{\tau}$ we have (remember that $\underline{\tau} = h_1\underline{b}_1 + h_2\underline{b}_2 + h_3\underline{b}_3$)

$$D_{\alpha\beta}(\underline{q}+\underline{\tau}\; kk') = \sum_{\ell} D_{\alpha\beta}\binom{\ell}{kk'} e^{2\pi i(\underline{q}+\underline{\tau})\cdot\left[\underline{r}\binom{\ell}{k} - \underline{r}\binom{0}{k'}\right]} =$$

$$= \sum_{\ell} D_{\alpha\beta}\binom{\ell}{kk'} e^{2\pi i \underline{q}\cdot\left[\underline{r}\binom{\ell}{k} - \underline{r}\binom{0}{k'}\right]} e^{2\pi i \underline{\tau}\cdot\underline{r}\binom{\ell}{k}} e^{-2\pi i \underline{\tau}\cdot\underline{r}\binom{0}{k'}} =$$

$$= e^{2\pi i \underline{\tau}\cdot\left[\underline{r}(k) - \underline{r}(k')\right]} \sum_{\ell} D_{\alpha\beta}\binom{\ell}{kk'} e^{2\pi i \underline{q}\cdot\left[\underline{r}\binom{\ell}{k} - \underline{r}\binom{0}{k'}\right]} e^{2\pi i \underline{\tau}\cdot\underline{r}(\ell)} =$$

$$= e^{2\pi i \underline{\tau}\cdot\left[\underline{r}(k) - \underline{r}(k')\right]}\, D_{\alpha\beta}(\underline{q}|kk')$$

where we have used the definition of reciprocal lattice vectors $\underline{a}_i \circ \underline{b}_j = \delta_{ij}$. Therefore changing $\underline{q}$ by a reciprocal lattice vector we only multiply the dynamical matrix by a phase factor. The eigenvalues are therefore unchanged. In view of this property we can limit the dynamical matrix and the dispersion relation to a Wigner-Seitz cell in reciprocal space, namely the Brillouin zone.

One property of the dynamical matrix is that

$$D_{\alpha\beta}(\underline{q}|kk') = D^*_{\beta\alpha}(\underline{q}|k'k) \tag{3.18}$$

another property is that

$$D_{\alpha\beta}(-\underline{q}|kk') = D^*_{\alpha\beta}(\underline{q}|kk') \tag{3.19}$$

It can be shown that the frequencies of three branches of the dispersion relations vanish for $\underline{q} = 0$. These branches are called acoustic branches while the others are called optical branches.

Finally we want to say something about the reduction of the coefficients in the force constant matrices. $\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'}$ is a 3 x 3 matrix which has therefore nine coefficients. Often the crystal symmetry allows to reduce the number of these coefficients. The argument goes as follows. Suppose that T is a transformation of the crystal in it self, in the sense that it transforms the vector $\underline{r}\binom{\ell}{k}$ into $\underline{r}\binom{L}{K}$. Then

$$\Phi\binom{LL'}{KK'} = T\Phi\binom{\ell\ell'}{kk'}\tilde{T} \tag{3.20}$$

If T is such a transformation that it does not change the position of the atoms in (ℓ,k) and (ℓ',k'), then:

$$\Phi\binom{\ell\ell'}{kk'} = T\,\Phi\binom{\ell\ell'}{kk'}\tilde{T} \tag{3.21}$$

This is a useful relation which allows to reduce the number of components of a force constant matrix.

4. SHORT RANGE FORCES

4.1. Tensorial, Axially Symmetric and Central Forces

Let us consider the harmonic interaction between two atoms. This interaction is described by a force constant matrix of the form

$$\Phi = \begin{vmatrix} \Phi_{11} & \Phi_{12} & \Phi_{13} \\ \Phi_{21} & \Phi_{22} & \Phi_{23} \\ \Phi_{31} & \Phi_{32} & \Phi_{33} \end{vmatrix} \tag{4.1}$$

This is the form for general tensorial forces. The matrix Φ can be referred to a system in which one principal axis, say the x-axis, coincides with the line joining the two atoms. If, in such a system, the matrix has the form

$$\Phi = \begin{vmatrix} A & 0 & 0 \\ 0 & B & 0 \\ 0 & 0 & B \end{vmatrix} \tag{4.2}$$

the forces are said to be axially simmetric.(9)

A particular case of axially symmetric forces is the case of central forces. In such a case the total potential is a sum of central potentials of the form $\Phi(r)$. In such case

$$A = - \frac{d^2\Phi}{dr^2}\bigg|_{r=r_o} \qquad B = - \frac{1}{r_o}\frac{d\Phi}{dr}\bigg|_{r=r_o} \tag{4.3}$$

where r_o is the equilibrium distance between the two atoms.

Proof. In the case of central forces, where the total potential Φ_T is a sum of pair potentials $\Phi(r)$, the force constants are given by

$$\Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = \frac{\partial^2\Phi_T}{\partial u_\alpha\binom{\ell}{k}\partial u_\beta\binom{\ell'}{k'}} = \frac{\partial^2\Phi_T}{\partial r_\alpha\binom{\ell}{k}\partial r_\beta\binom{\ell'}{k'}} =$$

$$= \frac{\partial^2}{\partial r_\alpha\binom{\ell}{k}\partial r_\beta\binom{\ell'}{k'}}\,\frac{1}{2}\sum_{\substack{\ell\ell'\\kk'}}{}' \Phi\left(\left|\underline{r}\binom{\ell\ell'}{kk'}\right|\right)\Big|_o = -\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\Big[\Phi(\underline{r})\Big]_{\underline{r}\binom{\ell\ell'}{kk'}}$$

Here x_α indicates the α - component of the vector $\underline{r}$.

Consider now the atoms at $(0,0,0)$ and $(r_o,0,0)$, interacting with the potential $\Phi(r)$, with $r = \sqrt{x^2+y^2+z^2}$.

We have

$$A = -\frac{\partial^2\Phi}{\partial x^2}\Big|_o = -\frac{\partial}{\partial x}\left(\frac{d\Phi}{dr}\frac{\partial r}{\partial x}\right)\Big|_o = -\left[\frac{d^2\Phi}{dr^2}\left(\frac{\partial r}{\partial x}\right)^2 + \frac{d\Phi}{dr}\frac{\partial^2 r}{\partial x^2}\right]_o$$

$$\frac{\partial r}{\partial x} = \frac{x}{r} \qquad \frac{\partial^2 r}{\partial x^2} = \frac{1}{r} - \frac{x^2}{r^3} \qquad \frac{\partial r}{\partial x}\Big|_o = 1 \qquad \frac{\partial^2 r}{\partial x^2} = 0$$

Therefore

$$A = -\frac{d^2\Phi}{dr^2}\Big|_{r=r_o}$$

Similarly

$$B = -\frac{\partial^2\Phi}{\partial y^2}\Big|_o = -\left[\frac{d^2\Phi}{dr^2}\left(\frac{\partial r}{\partial y}\right)^2 + \frac{d\Phi}{dr}\frac{\partial^2 r}{\partial y^2}\right]_o$$

$$\frac{\partial r}{\partial y} = \frac{y}{r} \qquad \frac{\partial^2 r}{\partial y^2} = \frac{1}{r} - \frac{y^2}{r^3} \qquad \frac{\partial r}{\partial y}\Big|_o = 0 \qquad \frac{\partial^2 r}{\partial y^2} = \frac{1}{r_o}$$

Therefore

$$B = -\frac{1}{r_o}\frac{d\Phi}{dr}\bigg|_{r=r_o}$$

4.2. Example of Calculation of the Dynamical Matrix

Having developed the formal theory of lattice vibrations, we now give an example of how to calculate the dynamical matrix for a simple crystal.

We consider a crystal of argon, which has a face centered cubic lattice. We shall calculate the dynamical matrix in the hypothesis of central forces extending to the second neighbours.

As it is well known a simple face centered cubic structure can be described by a non cubic cell which contains only one atom (the cubic cell contains four). It is convenient to choose the cell with minimum number of atoms. Accordingly, the dynamical matrix for argon will be a three by three matrix and we can ignore the basic indexes k, k'.

Fig. 4 shows the f.c.c. lattice and the non cubic unit cell.

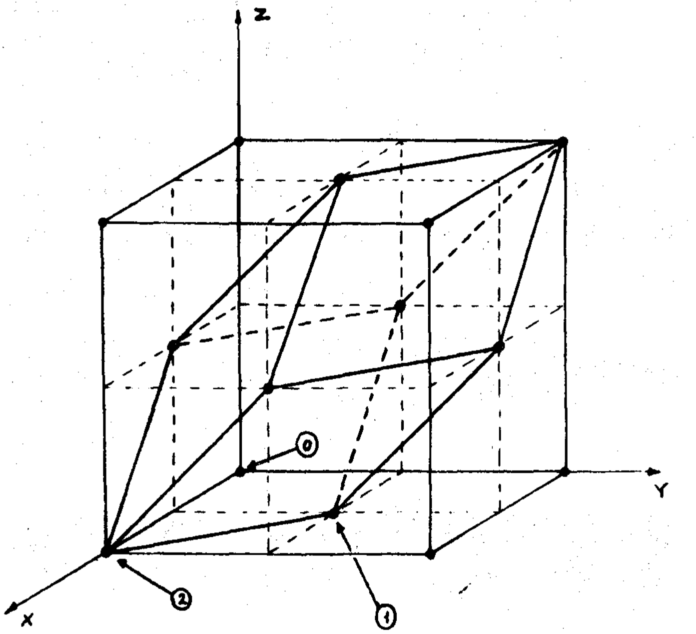

Figure 4

We consider the atom at the center of the system of coordinates in Fig. 4 (labeled 0). This atom is surrounded by a shell of twelve first neigbours (like atom 1) and a shell of six second neighbours (like atom 2). The coordinates of the first and second neighbours are as follows

First neighbours		Second neighbours
$(a/2, a/2, 0)$	$(-a/2, 0, a/2)$	$(a, 0, 0)$
$(a/2, -a/2, 0)$	$(-a/2, 0, -a/2)$	$(-a, 0, 0)$
$(-a/2, a/2, 0)$	$(0, a/2, a/2)$	$(0, a, 0)$
$(-a/2, -a/2, 0)$	$(0, a/2, -a/2)$	$(0, -a, 0)$
$(a/2, 0, a/2)$	$(0, -a/2, a/2)$	$(0, 0, a)$
$(a/2, 0, -a/2)$	$(0, -a/2, -a/2)$	$(0, 0, -a)$

We can introduce the force constant matrices and use the crystal symmetry to simplify the form of the matrices themselves.

Let us first consider the interaction between atom 0 and atom 1. This interaction can in general be described by the matrix

$$\Phi^{(0,1)} = \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} \tag{4.4}$$

This is a general tensorial form. We observe now that the vector (a/2, a/2, 0), connecting the two atoms, is left unchanged by a reflection in the plane xy. This symmetry operation of the crystal structure is represented by the matrix

$$T_{(z=0)} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \tag{4.5}$$

Therefore we can apply the relation (3.21)

$$T_{(z=0)}\Phi^{(0,1)}\tilde{T}_{(z=0)} = \Phi^{(0,1)} \qquad (4.6)$$

obtaining

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} = \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ -A_{31} & -A_{32} & -A_{33} \end{vmatrix} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} =$$

$$= \begin{vmatrix} A_{11} & A_{12} & -A_{13} \\ A_{21} & A_{22} & -A_{23} \\ -A_{31} & -A_{32} & A_{33} \end{vmatrix} = \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix}$$

It follows from this that $A_{13}= A_{23}= A_{31}= A_{32}= 0$ and therefore the symmetry argument allows to simplify the matrix as

$$\Phi^{(0,1)} = \begin{vmatrix} A_{11} & A_{12} & 0 \\ A_{21} & A_{22} & 0 \\ 0 & 0 & A_{33} \end{vmatrix}$$

A second symmetry operation of the crystal which leaves invariant the vector (a/2, a/2, 0) is the reflection in the plane $x = y$, described by the matrix

$$T_{(x=y)} = \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

From the equation

$$T_{(x=y)}\,\Phi^{(0,1)}\,\tilde{T}_{(x=y)} = \Phi^{(0,1)} \qquad (4.7)$$

we obtain similary

$$\begin{vmatrix} A_{11} & A_{12} & 0 \\ A_{21} & A_{22} & 0 \\ 0 & 0 & A_{33} \end{vmatrix} = \begin{vmatrix} A_{22} & A_{21} & 0 \\ A_{12} & A_{11} & 0 \\ 0 & 0 & A_{33} \end{vmatrix}$$

from which $A_{11} = A_{22}$ and $A_{12} = A_{21}$. Therefore the matrix can be written

$$\Phi^{(0,1)} = \begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \delta \end{vmatrix} \tag{4.8}$$

involving only three coefficients.

We can rotate the system of axes 45^o about the z-axis so that the x-axis will be along the direction connecting the two atoms. The rotation is performed by the matrix

$$T_{(45)} = \begin{vmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ -\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

When this rotation is applied to the matrix $\Phi^{(0,1)}$ we obtain

$$\begin{vmatrix} \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ -\frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \delta \end{vmatrix} \begin{vmatrix} \frac{\sqrt{2}}{2} & -\frac{\sqrt{2}}{2} & 0 \\ \frac{\sqrt{2}}{2} & \frac{\sqrt{2}}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix} = \begin{vmatrix} \alpha+\beta & 0 & 0 \\ 0 & \alpha-\beta & 0 \\ 0 & 0 & \delta \end{vmatrix} \tag{4.9}$$

If we assume the forces to be axially symmetric we must have $\alpha-\beta=\delta$. If in addition the forces derive from a central potential $\Phi(r)$ we have

$$\alpha+\beta = - \left.\frac{d^2\Phi}{dr^2}\right|_{r=a/\sqrt{2}} \qquad \alpha-\beta=\delta= - \frac{\sqrt{2}}{a}\left.\frac{d\Phi}{dr}\right|_{r=a/\sqrt{2}} \tag{4.10}$$

For the computation of the coefficients of the dynamical matrix we shall use the axially symmetric form.

We shall now turn to the matrix $\Phi^{(0,2)}$ describing the harmonic interaction between the atoms in (0,0,0) and (2,0,0). The general form of this matrix is

$$\Phi^{(0,2)} = \begin{vmatrix} B_{11} & B_{12} & B_{13} \\ B_{21} & B_{22} & B_{23} \\ B_{31} & B_{32} & B_{33} \end{vmatrix} \tag{4.11}$$

The vector joining the two atoms is left unchanged by the symmetry operation $T_{z=0}$ which, as in the previous case, leads to the form

$$\Phi^{(0,2)} = \begin{vmatrix} B_{11} & B_{12} & 0 \\ B_{21} & B_{22} & 0 \\ 0 & 0 & B_{33} \end{vmatrix} \tag{4.12}$$

The vector (2,0,0) is also invariant under a reflection in the plane y = 0, described by the matrix

$$T_{y=0} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \tag{4.13}$$

and under a rotation of 90^o about the x-axis, described by the matrix:

$$T_{90} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix} \tag{4.14}$$

Application of (4.13) to $\Phi^{(0,2)}$ leads to

$$\begin{vmatrix} B_{11} & B_{12} & 0 \\ B_{21} & B_{22} & 0 \\ 0 & 0 & B_{33} \end{vmatrix} = \begin{vmatrix} B_{11} & B_{21} & 0 \\ B_{12} & B_{22} & 0 \\ 0 & 0 & B_{33} \end{vmatrix}$$

from which $B_{12} = B_{21} = 0$.

Application of (4.14) to $\Phi^{(0,2)}$ leads to

$$\begin{vmatrix} B_{11} & 0 & 0 \\ 0 & B_{22} & 0 \\ 0 & 0 & B_{33} \end{vmatrix} = \begin{vmatrix} B_{11} & 0 & 0 \\ 0 & B_{33} & 0 \\ 0 & 0 & B_{22} \end{vmatrix}$$

from which $B_{22} = B_{33}$. It follows that the matrix $\Phi^{(0,2)}$ is naturally axially symmetric and has the form

$$\Phi^{(0,2)} = \begin{vmatrix} \delta & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{vmatrix}$$

In the case of central forces we would have

$$\delta = - \left.\frac{d^2\Phi}{dr^2}\right|_{r=a} \qquad \gamma = - \frac{1}{a}\left.\frac{d\Phi}{dr}\right|_{r=a} \tag{4.15}$$

Having determined the simplest forms for the two force constant matrices, we can now calculate the dynamical matrix

$$D_{\alpha\beta}(\underline{q}) = \sum_{\ell} \Phi_{\alpha\beta}(\ell)\, e^{2\pi i \underline{q}\cdot\left[\underline{r}(\ell)-r(o)\right]} \tag{4.16}$$

It can be seen that this form, as compared to the general form given previously, does not contain the basic indices k or k'. For the calculation of the matrix it is convenient to make a tabulation of force constant matrices and of vectors $\underline{r}(\ell) - \underline{r}(0)$ for all the eighteen (twelve first and six second neighbours) atoms involved. The matrices can be obtained from $\Phi^{(0,1)}$ and $\Phi^{(0,2)}$ by application of symmetry operations.

$\underline{r}(\ell)-\underline{r}(0)$	$\Phi_{\alpha\beta}(\ell)$	Phase factor in (4.16)
(a,0,0)	$\begin{vmatrix} \delta & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{vmatrix}$	$e^{2\pi i q_x a}$
(-a,0,0)	$\begin{vmatrix} \delta & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \gamma \end{vmatrix}$	$e^{-2\pi i q_x a}$
(0,a,0)	$\begin{vmatrix} \gamma & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \gamma \end{vmatrix}$	$e^{2\pi i q_y a}$
(0,-a,0)	$\begin{vmatrix} \gamma & 0 & 0 \\ 0 & \delta & 0 \\ 0 & 0 & \gamma \end{vmatrix}$	$e^{-2\pi i q_y a}$
(0,0,a)	$\begin{vmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \delta \end{vmatrix}$	$e^{2\pi i q_z a}$
(0,0,-a)	$\begin{vmatrix} \gamma & 0 & 0 \\ 0 & \gamma & 0 \\ 0 & 0 & \delta \end{vmatrix}$	$e^{-2\pi i q_z a}$
$(a/\sqrt{2},a/\sqrt{2},0)$	$\begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \alpha-\beta \end{vmatrix}$	$e^{\pi i a(q_x+q_y)}$

$\underline{r}(\ell)-\underline{r}(0)$	$\Phi_{\alpha\beta}(\ell)$	Phase factor in (4.16)
$(-a/\sqrt{2},-a/\sqrt{2},0)$	$\begin{vmatrix} \alpha & \beta & 0 \\ \beta & \alpha & 0 \\ 0 & 0 & \alpha-\beta \end{vmatrix}$	$e^{-\pi i a(q_x+q_y)}$
$(a/\sqrt{2},-a/\sqrt{2},0)$	$\begin{vmatrix} \alpha & -\beta & 0 \\ -\beta & \alpha & 0 \\ 0 & 0 & \alpha-\beta \end{vmatrix}$	$e^{\pi i a(q_x-q_y)}$
$(-a/\sqrt{2},a/\sqrt{2},0)$	$\begin{vmatrix} \alpha & -\beta & 0 \\ -\beta & \alpha & 0 \\ 0 & 0 & \alpha-\beta \end{vmatrix}$	$e^{-\pi i a(q_x-q_y)}$
$(a/\sqrt{2},0,a/\sqrt{2})$	$\begin{vmatrix} \alpha & 0 & \beta \\ 0 & \alpha-\beta & 0 \\ \beta & 0 & \alpha \end{vmatrix}$	$e^{\pi i a(q_x+q_z)}$
$(-a/\sqrt{2},0,-a/\sqrt{2})$	$\begin{vmatrix} \alpha & 0 & \beta \\ 0 & \alpha-\beta & 0 \\ \beta & 0 & \alpha \end{vmatrix}$	$e^{-\pi i a(q_x+q_z)}$
$(a/\sqrt{2},0,-a/\sqrt{2})$	$\begin{vmatrix} \alpha & 0 & -\beta \\ 0 & \alpha-\beta & 0 \\ -\beta & 0 & \alpha \end{vmatrix}$	$e^{\pi i a(q_x-q_z)}$
$(-a/\sqrt{2},0,a/\sqrt{2})$	$\begin{vmatrix} \alpha & 0 & -\beta \\ 0 & \alpha-\beta & 0 \\ -\beta & 0 & \alpha \end{vmatrix}$	$e^{-\pi i a(q_x-q_z)}$

$\underline{r}(\ell)-\underline{r}(0)$	$\Phi_{\alpha\beta}(\ell)$	Phase factor in (4.16)
$(0,a/\sqrt{2},a/\sqrt{2})$	$\begin{vmatrix} \alpha-\beta & 0 & 0 \\ 0 & \alpha & \beta \\ 0 & \beta & \alpha \end{vmatrix}$	$e^{\pi ia(q_y+q_z)}$
$(0,-a/\sqrt{2},-a/\sqrt{2})$	$\begin{vmatrix} \alpha-\beta & 0 & 0 \\ 0 & \alpha & \beta \\ 0 & \beta & \alpha \end{vmatrix}$	$e^{-\pi ia(q_y+q_z)}$
$(0,a/\sqrt{2},-a/\sqrt{2})$	$\begin{vmatrix} \alpha-\beta & 0 & 0 \\ 0 & \alpha & -\beta \\ 0 & -\beta & \alpha \end{vmatrix}$	$e^{\pi ia(q_y-q_z)}$
$(0,-a/\sqrt{2},a/\sqrt{2}$	$\begin{vmatrix} \alpha-\beta & 0 & 0 \\ 0 & \alpha & -\beta \\ 0 & -\beta & \alpha \end{vmatrix}$	$e^{-\pi ia(q_y-q_z)}$
$(0,0,0)$	$-\begin{vmatrix} 2\delta+4\gamma+12\alpha-4\beta & 0 & 0 \\ 0 & 2\delta+4\gamma+12\alpha-4\beta & 0 \\ 0 & 0 & 2\delta+4\gamma+12\alpha-4\beta \end{vmatrix}$	1

In computing the force constant matrices to be used in the sum (4.16) we should not forget the term with $\ell=0$. In general this term is obtained from the invariance relation

$$\sum_{\ell' k'} \Phi_{\alpha\beta}\binom{\ell\ell'}{kk'} = 0 \qquad (4.17)$$

which leads to the last term in the previous listing of matrices.

At this point it is possible to use (4.16) and compute the dynamical matrix. After changing from exponential to trigonometric form and using the symbols:

$$\begin{aligned} C_x &= \cos 2\pi a q_x \\ C_{x+y} &= \cos \pi a(q_x+q_y) \qquad (4.18) \\ C_{x-y} &= \cos \pi a(q_x-q_y) \end{aligned}$$

we obtain the following expressions for the coefficients of the dynamical matrix:

$$\begin{aligned}
D_{11}(\underline{q}) &= \Big\{ 2\delta(C_x-1)+2\gamma(C_y+C_z-2)+2\alpha(C_{x+y}+C_{x-y}+C_{x+z}+C_{x-z}+C_{y+z}+C_{y-z}-6)- \\
&\qquad -2\beta(C_{y+z}+C_{y-z}-2)\Big\}/m \\
D_{22}(\underline{q}) &= \Big\{ 2\delta(C_y-1)+2\gamma(C_x+C_z-2)+2\alpha(C_{x+y}+C_{x-y}+C_{x+z}+C_{x-z}+C_{y+z}+C_{y-z}-6)- \\
&\qquad -2\beta(C_{x+z}+C_{x-z}-2)\Big\}/m \\
D_{33}(\underline{q}) &= \Big\{ 2\delta(C_z-1)+2\gamma(C_x+C_y-2)+2\alpha(C_{x+y}+C_{x-y}+C_{x+z}+C_{x-z}+C_{y+z}+C_{y-z}-6)- \\
&\qquad -2\beta(C_{y+z}+C_{y-z}-2)\Big\}/m \\
D_{12}(\underline{q}) &= 2\beta(C_{x+y}-C_{x-y})/m \\
D_{13}(\underline{q}) &= 2\beta(C_{x+z}-C_{x-z})/m \qquad (4.19) \\
D_{23}(\underline{q}) &= 2\beta(C_{y+z}-C_{y-z})/m \\
D_{\alpha\beta}(\underline{q}) &= D_{\beta\alpha}(\underline{q})
\end{aligned}$$

We have therefore expressed the dynamical matrix as a function of four parameters or force constants $\alpha,\beta,\delta,\gamma$. The problem is now to determine these parameters. Some help can be obtained from the knowledge of the elastic constants. In the case of a cubic crystal there are three independent elastic constants, c_{11}, c_{12} and c_{44}. These constants can be related to the force constants.

This requires the use of the method of the long waves, which will be presented later. In the case of argon the elastic constants are not very well known, for the difficulty of obtaining a single crystal. On the contrary the central interaction potential is better known. One can therefore assume a Lennard-Jones type potential

$$\Phi(r) = -\frac{c}{r^6} + \frac{b}{r^{12}} \qquad (4.20)$$

with $c = 1.03 \times 10^{-58}$ erg cm^6 and $b = 1.62 \times 10^{-103}$ erg cm^{12}. The data are from R. A. Buckingham$^{(10)}$.

Using (4.20), (4.10) and (4.15) with a = 5.43 Å we obtain:

$\alpha = -\ 358$ dyn/cm $\qquad \beta = -\ 352$ dyn/cm

$\delta = 44.1$ dyn/cm $\qquad \gamma = -\ 7.15$ dyn/cm

5. ELECTROSTATIC FORCES IN LATTICE DYNAMICS

5.1. The Ewald Transformation

When Coulomb forces are present in crystals we are faced with the calculation of rather special lattice sums. These sums are very slowly convergent and a special technique, introduced by Ewald, has to be employed for their computation.

A typical function that one may have to calculate is the following:

$$F(\underline{r}) = \sum_{\ell} \frac{e^{2\pi i \underline{q}.r(\ell)}}{|\underline{r}-\underline{r}(\ell)|} \qquad (5.1)$$

This function and its second derivatives with respect to the components of $\underline{r}$ is encountered in crystal physics whenever an electrostatic field is present. It we tried to compute $F(\underline{r})$ directly from (5.1) we would not get the correct result because of the slow convergence. The Ewald method consists of separating the sum (5.1) into two sums. The first sum is over direct vectors, like (5.1), while the second sum is over reciprocal vectors. The splitting in two terms depends on a parameter and the result is rather insensitive to the choice of this parameter, even when the two sums are truncated to a finite number of terms. This is so because the two sums converge rapidly. Basically, then, the Ewald transformation allows to write

$$F(\underline{r}) = \sum_{\ell} F_{\ell}^{(D)}(\underline{r}) + \sum_{h} F_{h}^{(R)}(\underline{r}) \qquad (5.2)$$

$F_{\ell}^{(D)}(\underline{r})$ is a function of the direct vectors $\underline{r}(\ell)$, while $F_{h}^{(R)}(\underline{r})$ is a function of the reciprocal lattice vectors $\underline{b}(h)$. The two sums converge rapidly. Usually a very accurate value of $F(\underline{r})$ can be obtained using (5.2) and a few hundreds reciprocal and direct vectors.

We want now to find the explicit expression for the identity (5.2). We start by using the integral representation:

$$\frac{1}{|\underline{r}-\underline{r}(\ell)|} = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-|\underline{r}-\underline{r}(\ell)|^{2}\rho^{2}} d\rho \qquad (5.3)$$

Using (5.3), (5.1) becomes:

$$F(\underline{r}) = \sum_{\ell} \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} e^{-|\underline{r}-\underline{r}(\ell)|^{2}\rho^{2}+2\pi i\underline{q}.\underline{r}(\ell)} d\rho =$$

$$= \int_{0}^{\infty} d\rho \, \frac{2}{\sqrt{\pi}} \left\{ \sum_{\ell} e^{-|\underline{r}-\underline{r}(\ell)|^{2}\rho^{2}-2\pi i\underline{q}.\left[\underline{r}-\underline{r}(\ell)\right]} \right\} e^{2\pi i\underline{q}.\underline{r}} \qquad (5.4)$$

Consider the expression in the curly brackets in (5.4). This is of the form $\sum_{\ell} f(\underline{r}-\underline{r}(\ell))$, where f is a general function, and therefore is a periodic function with the periodicity of the lattice. The function in curly brackets, which we call $S(\underline{r})$ can therefore be expanded in Fourier series.

$$S(\underline{r}) = \sum_{h} g(h)\, e^{2\pi i \underline{b}(h)\cdot\underline{r}} \tag{5.5}$$

$\underline{b}(h)$ are the reciprocal lattice vectors and the coefficients g(h) are given by (V_a is the volume of the unit cell):

$$g(h) = \frac{1}{V_a}\int_{\text{cell}} S(\underline{r})\, e^{-2\pi i \underline{b}(h)\cdot\underline{r}}\, d\underline{r} =$$

$$= \frac{1}{V_a}\int_{\text{cell}} \sum_{\ell} e^{-|\underline{r}-\underline{r}(\ell)|^2\rho^2 - 2\pi i \underline{q}\cdot[\underline{r}-\underline{r}(\ell)] - 2\pi i \underline{b}(h)\cdot\underline{r}}\, d\underline{r}$$

We make the change of variable $\underline{x} = \underline{r} - \underline{r}(\ell)$

$$g(h) = \frac{1}{V_a}\sum_{\ell}\int_{-\ell\text{cell}} e^{-|\underline{x}|^2\rho^2 - 2\pi i \underline{q}\cdot\underline{x} - 2\pi i \underline{b}(h)\cdot[\underline{x}+\underline{r}(\ell)]}\, d\underline{x} =$$

$$\frac{1}{V_a}\sum_{\ell}\int_{-\ell\text{cell}} e^{-|\underline{x}|^2\rho^2 - 2\pi i (\underline{q}+\underline{b}(h)\cdot\underline{x}}\, d\underline{x} \tag{5.6}$$

In writing (5.6) we have used the fact that $e^{2\pi i \underline{b}(h)\cdot\underline{r}(\ell)}$ is equal to unity and the fact that the change of variable changes the limits of integration too.

The sum in (5.6) is equivalent to an integration over all space. This integral can be avaluated in spherical coordinates, taking for polar axis the direction $\underline{q}+\underline{b}(h)$.

$$g(h) = \frac{1}{V_a}\int_{\text{all space}} e^{-|\underline{x}|^2\rho^2-2\pi i(\underline{q}+\underline{b}(h))\cdot\underline{x}}\, d\underline{x} =$$

$$= \frac{1}{V_a}\int_0^{\infty} dR \int_0^{\pi} d\theta \int_0^{2\pi} d\phi R^2 \sin\theta\; e^{-R^2\rho^2-2\pi i|\underline{q}+\underline{b}(h)|R\cos\theta} =$$

$$= \frac{\pi^{3/2}}{V_a}\frac{1}{\rho^3}\, e^{-\frac{\pi^2}{\rho^2}|\underline{q}+\underline{b}(h)|^2} \qquad (5.7)$$

Replacing this expression of g(h) into (5.5) we obtain

$$S(\underline{r}) = \frac{\pi^{3/2}}{V_a}\frac{1}{\rho^3}\sum_h e^{-\frac{\pi^2}{\rho^2}|\underline{q}+\underline{b}(h)|^2+2\pi i\underline{b}(h)\cdot\underline{r}} =$$

$$= \sum_{\ell} e^{-|\underline{r}-\underline{r}(\ell)|^2\rho^2-2\pi i q\cdot[\underline{r}-\underline{r}(\ell)]} \qquad (5.8)$$

This identity is the Ewald transformation, also known as theta function transformation. The sum over the indices h converges rapidly for small values of ρ, while the sum over the indices ℓ converges rapidly for large values of ρ. Since the function $S(\underline{r})$ appears as an integrand from zero to infinity in (5.4), we can split the integral into two parts and use the two alternative expressions for $S(\underline{r})$. We therefore introduce a splitting parameter R_E and compute $F(\underline{r})$ in the following way:

$$F(\underline{r}) = \sum_{\ell}\frac{e^{2\pi i\underline{q}\cdot\underline{r}(\ell)}}{|\underline{r}-\underline{r}(\ell)|} = \frac{2\pi}{V_a}\sum_h\int_0^{R_E}\frac{1}{\rho^3}\, e^{-\frac{\pi^2}{\rho^2}|\underline{q}+\underline{b}(h)|^2+2\pi i(\underline{q}+\underline{b}(h))\cdot\underline{r}}\, d\rho +$$

$$+ \frac{2}{\sqrt{\pi}}\sum_{\ell}\int_{R_E}^{\infty} e^{-|\underline{r}-\underline{r}(\ell)|^2\rho^2+2\pi i\underline{q}\cdot\underline{r}(\ell)}\, d\rho \qquad (5.9)$$

This is the expression for $F(\underline{r})$ in the form of Eq.(5.2).

If we now look at the parts dependent on ρ in the two integrals, we see that they are

$$I_1 = \int_0^{R_E} \frac{1}{\rho^3} e^{-\frac{\pi^2}{\rho^2}|\underline{q}+\underline{b}(h)|^2} d\rho \qquad (5.10)$$

and

$$I_2 = \int_{R_E}^{\infty} e^{-|\underline{r}-\underline{r}(\ell)|^2\rho^2} d\rho \qquad (5.11)$$

The integral I_2 can be expressed in terms of the error function

$$\mathrm{erf}(t) = \frac{2}{\sqrt{\pi}} \int_0^t e^{-x^2} dx \qquad (5.12)$$

with the result

$$I_2 = \frac{\sqrt{\pi}}{2|\underline{r}-\underline{r}(\ell)|} (1- \mathrm{erf}(R_E|\underline{r}-\underline{r}(\ell)|)) \qquad (5.13)$$

The integral I_1 can be easily calculated with the results

$$I_1 = \frac{1}{2\pi^2|\underline{q}+\underline{b}(h)|^2} e^{-\frac{\pi^2}{R_E^2}|\underline{q}+\underline{b}(h)|^2} \qquad (5.14.a)$$

Introducing the two functions:

$$G(x) = \frac{e^{-x}}{x} \qquad \text{and} \qquad H(x) = \frac{1-\mathrm{erf}(x)}{x} \qquad (5.14.b)$$

equation (5.9) can be written:

$$\sum_{\ell} \frac{e^{2\pi i \underline{q}\cdot\underline{r}(\ell)}}{|\underline{r}-\underline{r}\ (\ell)|} = \frac{\pi}{V_a R_E^2} \sum_{h} G\left(\frac{\pi^2}{R_E^2}|\underline{q}+\underline{b}(h)|^2\right) e^{2\pi i(\underline{q}+\underline{b}(h))\cdot\underline{r}} +$$

$$+ R_E \sum_{\ell} H(R_E|\underline{r}-\underline{r}(\ell)|)\ e^{2\pi i \underline{q}\cdot\underline{r}(\ell)} \qquad (5.15)$$

It is interesting to not that, as far as $\underline{q}$ is different from zero, there are not divergent terms in the second member of (5.15), even when $|\underline{r}-\underline{r}(\ell)|$ vanishes. The only divergent term is the term with $h = 0$ in the sum over reciprocal vectors when $\underline{q}$ vanishes.

5.2. The Electrostatic Coefficients

When part of the interaction among atoms in a crystal is of electrostatic nature, a contribution to the dynamical matrix is given by the Coulomb field. If e_k, $e_{k'}$ are the charges on the ions k, k' separated by a vector $\underline{r}(\ell)+\underline{r}(k)-\underline{r}(k')$, the force constant of electrostatic origin among the two ions can be written

$$\Phi_{\alpha\beta}\binom{\ell}{kk'} = e_k e_{k'} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left[\frac{1}{|\underline{r}(\ell)-\underline{r}|}\right]^{\,o}_{\underline{r}'(kk')} \qquad (5.16)$$

where x_α, x_β are the cartesian components of the vector $\underline{r}$.

It is convenient to write the Coulomb coefficients of the dynamical matrix in the following way:

$$C_{\alpha\beta}(\underline{q}|kk') =$$

$$= -e^{2\pi i \underline{q}\cdot[\underline{r}(k)-\underline{r}(k')]}\, e_k e_{k'} \sum_{\ell} e^{2\pi i \underline{q}\cdot\underline{r}(\ell)} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left[\frac{1}{|\underline{r}(\ell)-\underline{r}|}\right]_{\underline{r}\binom{o}{k'k}} +$$

$$+ e_k \delta_{kk'} \sum_{\ell''k''} e_{k''} \frac{\partial^2}{\partial x_\alpha \partial x_\beta} \left[\frac{1}{|\underline{r}(\ell'')-\underline{r}|}\right]_{\underline{r}\binom{o}{k''k}} \qquad (5.17)$$

This form requires some explanation. The first term is the conventional form of the dynamical matrix, but it can be seen that it contains a divergent term for $\ell = 0$, $k = k'$. For $k \neq k'$ the second term vanishes because of the Kronecker $\delta_{kk'}$. For $\ell = 0$, $k = k'$, one term in the second sum (the term with $\ell'' = 0$, $k'' = k$) cancels the divergent part in the first sum and what is left is simply the force constant $\Phi_{\alpha\beta}\binom{o}{kk}$ which satisfies the general invariance relation:

$$\sum_{\ell k'} \Phi_{\alpha\beta}\binom{\ell}{kk'} = 0 \qquad (5.18)$$

In conclusion we can say that the form (5.17) is convenient insofar it automatically satisfies the invariance relation (5.18).

In (5.17) we can now introduce the Ewald transformation (5.15). This requires taking the derivatives of the functions G and H introduced previously. The final result, after applying the Ewald transformation, can be put in the following form:

$$C_{\alpha\beta}(\underline{q}|kk') = - e_k e_{k'}\, C^{o}_{\alpha\beta}(\underline{q}|kk') + e_k \delta_{kk'} \sum_{k''} e_{k''} C^{o}_{\alpha\beta}(kk'') \qquad (5.19)$$

where

$$C^{o}_{\alpha\beta}(\underline{q}|kk') = \sum_{\ell}{}' S^{R}_{\alpha\beta}\left(\underline{q}\middle|\begin{matrix}\ell\\ kk'\end{matrix}\right) + \sum_{h} Q^{R}_{\alpha\beta}\left(\underline{q}\middle|\begin{matrix}h\\ kk'\end{matrix}\right) + (1-\delta_{kk'}) S^{R}_{\alpha\beta}\left(\underline{q}\middle|\begin{matrix}o\\ kk'\end{matrix}\right) \qquad (5.20.a)$$

$$C^{o}_{\alpha\beta}(kk') = \sum_{\ell}{}' S^{R}_{\alpha\beta}\left(0\middle|\begin{matrix}\ell\\ kk'\end{matrix}\right) + \sum_{h}{}' Q^{R}_{\alpha\beta}\left(0\middle|\begin{matrix}h\\ kk'\end{matrix}\right) + (1-\delta_{kk'}) S^{R}_{\alpha\beta}\left(0\middle|\begin{matrix}o\\ kk'\end{matrix}\right) \qquad (5.20.b)$$

The dash sign on the sums indicates that the term with $\ell = 0$ or $h = 0$ must not be included. Notice that in (5.20.b) the sum over h does not include the term with $h = 0$.

The functions $S^{R}_{\alpha\beta}\left(\underline{q}\middle|{}^{\ell}_{kk'}\right)$ and $Q^{R}_{\alpha\beta}\left(\underline{q}\middle|{}^{h}_{kk'}\right)$ are defined as

$$S^{R}_{\alpha\beta}\left(\underline{q}\middle|{}^{\ell}_{kk'}\right) = R^{2}\left\{\left[RH''(t) - \frac{H'(t)}{\left|\underline{r}\binom{\ell}{kk'}\right|}\right]\frac{x_{\alpha}\binom{\ell}{kk'}x_{\beta}\binom{\ell}{kk'}}{\left|\underline{r}\binom{\ell}{kk'}\right|^{2}} + H'(t)\frac{\delta_{\alpha\beta}}{\left|\underline{r}\binom{\ell}{kk'}\right|}\right\} e^{2\pi i\underline{q}\cdot\underline{r}\binom{\ell}{kk'}} \qquad (5.21.a)$$

and

$$Q^{R}_{\alpha\beta}\left(\underline{q}\middle|{}^{h}_{kk'}\right) = -\frac{4\pi^{3}}{V_{a}R^{2}}\, G\left(\frac{\pi^{2}}{R^{2}}\left|\underline{q}+\underline{b}(h)\right|^{2}\right)\left(q_{\alpha}+b_{\alpha}(h)\right) \cdot \left(q_{\beta}+b_{\beta}(h)\right)e^{2\pi i\underline{b}(h)\cdot\overset{o}{\underline{r}}(k'k)} \qquad (5.21.b)$$

In equations (5.20.a), (5.20.b), (5.21.a), (5.21.b) R is the Ewald splitting parameter, $t = R\left|\underline{r}\binom{\ell}{k'k}\right|$, V_{a} is the volume of the unit cell and the functions H and G have the same definition as in (5.14.b).

Notice that the first and second derivative of H with respect to the argument are required.

5.3. Rigid Ion Model

In an ionic crystal there are two types of forces among ions. The electrostatic forces give rise to the coefficients of the dynamical matrix previously defined. In addition, a part of the dynamical matrix, which we indicate by $R_{\alpha\beta}(\underline{q}|kk')$ is due to short range repulsive forces. The total dynamical matrix is given by

$$D_{\alpha\beta}(\underline{q}|kk') = C_{\alpha\beta}(\underline{q}|kk')+R_{\alpha\beta}(\underline{q}|kk') \qquad (5.22)$$

The rigid ion model was first used by Kellermann(11) to compute the vibrational frequencies of sodium chloride.

5.4. Shell Model

The shell model assumes that the ions are polarizable. Accordingly, the model describes each ion as composed of a central core (the nucleus and some internal electron shells) and a shell of electrons. If each atom in the crystal is splitted into core and shell, the number of units within the unit cell is doubled. The different units (cores or shells) interact among each others through the following forces:

a) Electrostatic forces among cores and shells.

b) Electrostatic forces among cores and cores.

c) Electrostatic forces among shells and shells.

d) Short range interaction forces among shells.

In addition an elastic restoring force between core and shell of the same ion is usually postulated. This force is of course very directly related to the polarizability of the ion.

We shall not derive here the equations for the shell model. A good reference for this work is the article "Lattice dynamics of alkali halide crystals", by A.D.B.Woods, W. Cochran, and B.N. Brockhouse.(12) We shall only given an idea of how the equations are derived. Suppose for example that we have a crystal with two atoms per unit cell. Then in the rigid ion formulation the dynamical matrix would be a 6 x 6 matrix. The equations of motion would be

$$m_k\omega^2U_\alpha(k) = \sum_{\beta k'} D_{\alpha\beta}(\underline{q}|kk')U_\beta(k') \qquad (5.23)$$

m_k being the mass of ion k and $\underline{U}(k)$ its polarization vector.

If we use a supermatrix notation we can drop the indices α, β and write (5.23) as:

$$\begin{aligned} m_1\omega^2\underline{U}(1) &= D(\underline{q}|11)\underline{U}(1)+D(\underline{q}|12)\underline{U}(2) \\ m_2\omega^2\underline{U}(2) &= D(\underline{q}|21)\underline{U}(1)+D(\underline{q}|22)\underline{U}(2) \end{aligned} \qquad (5.24)$$

When we turn to a shell model, we have four units (two cores and two shells) and the system of equations of motion would be:

$$\begin{aligned} m_1\omega^2\underline{U}(1) &= D'(\underline{q}|11)\underline{U}(1)+D'(\underline{q}|12)\underline{U}(2)+D'(\underline{q}|13)\underline{U}(3)+D'(\underline{q}|14)\underline{U}(4) \\ m_2\omega^2\underline{U}(2) &= D'(\underline{q}|21)\underline{U}(1)+D'(\underline{q}|22)\underline{U}(2)+D'(\underline{q}|23)\underline{U}(3)+D'(\underline{q}|24)\underline{U}(4) \\ m_3\omega^2\underline{U}(3) &= D'(\underline{q}|31)\underline{U}(1)+D'(\underline{q}|32)\underline{U}(2)+D'(\underline{q}|33)\underline{U}(3)+D'(\underline{q}|34)\underline{U}(4) \\ m_4\omega^2\underline{U}(4) &= D'(\underline{q}|41)\underline{U}(1)+D'(\underline{q}|42)\underline{U}(2)+D'(\underline{q}|43)\underline{U}(3)+D'(\underline{q}|44)\underline{U}(4) \end{aligned} \qquad (5.25)$$

Here the indices 1 and 2 refer to the cores, the indices 3 and 4 refer to the shells and the coefficients $D'(\underline{q}|kk')$ can be obtained as convenient combinations of the coefficients $D(\underline{q}|kk')$, involving of course the charges on cores and shells as well as the restoring force among core and shells of the same ion. The next step consists of setting $m_3 = m_4 = 0$ in (5.25) (the mass of the shells is zero). It is then possible to solve the last two equations of (5.25) for U_3 and U_4 and substitute the values obtained into the first two equations. After this is done we obtain a system of equations formally similar to (5.24). The dynamical matrix for the shell model will be a 6 x 6 matrix, as in the case of the rigid ion model, but of course the coefficients will be different. It is always convenient, when setting up a shell model, to set up first the corresponding rigid ion model. The change to shell model can then be made at the level of equations of motion, using the coefficients of the dynamical matrix previously derived.

The shell model has been very effective in the interpretation of the dispersion relations of many ionic and partially ionic crystals.

Proof of Equations (5.19), (5.20), (5.21)

Start from the Ewald transformation (5.15) and derive twice with respect to x_α x_β.

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta} \sum_\ell \frac{e^{2\pi i \underline{q}\cdot\underline{r}(\ell)}}{|\underline{r}(\ell)-\underline{r}|} = \sum_h Q^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{h}{\underline{r}}\right) + \sum_\ell S^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{\ell}{\underline{r}}\right)$$

where

$$S^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{\ell}{\underline{r}}\right)=R^2\left\{\left[RH''(t)-\frac{H'(t)}{|\underline{r}-\underline{r}(\ell)|}\right]\frac{x_\alpha\ x_\beta}{|\underline{r}-\underline{r}(\ell)|^2}+\frac{H'(t)}{|\underline{r}-\underline{r}(\ell)|}\ \delta_{\alpha\beta}\right\}e^{2\pi i\underline{q}\cdot\underline{r}(\ell)}$$

$$Q^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{h}{\underline{r}}\right)= -\frac{4\pi^3}{V_a R^2}G\left(\frac{\pi^2}{R^2}|\underline{q}+\underline{b}(h)|^2\right)(q_\alpha+b_\alpha(h))(q_\beta+b_\beta(h))e^{2\pi i(\underline{q}+\underline{b}(h))\cdot\underline{r}}$$

Introducing the above expressions into (5.17) we obtain:

$$C_{\alpha\beta}(\underline{q}|kk')=e^{2\pi i\underline{q}\cdot|\underline{r}(k)-\underline{r}(k')|}\,e_k e_{k'}\left\{\sum_h Q^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{h}{\underline{r}}\right)+\sum_\ell{}' S^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{\ell}{\underline{r}}\right)+S^R_{\alpha\beta}\left(\underline{q}\middle|\genfrac{}{}{0pt}{}{o}{\underline{r}}\right)\right\}_{\underline{r}\left(\genfrac{}{}{0pt}{}{o}{kk'}\right)} +$$

$$+\ e_k\delta_{kk'}\sum_{k''}e_{k''}\left\{\sum_h{}' Q^R_{\alpha\beta}\left(o\middle|\genfrac{}{}{0pt}{}{h}{\underline{r}}\right)+Q^R_{\alpha\beta}\left(o\middle|\genfrac{}{}{0pt}{}{o}{\underline{r}}\right)+\sum_\ell{}' S^R_{\alpha\beta}\left(o\middle|\genfrac{}{}{0pt}{}{\ell}{\underline{r}}\right)+S^R_{\alpha\beta}\left(o\middle|\genfrac{}{}{0pt}{}{o}{\underline{r}}\right)\right\}_{\underline{r}\left(\genfrac{}{}{0pt}{}{o}{k''k}\right)}$$

The term $Q^R_{\alpha\beta}\left(o\middle|{o \atop \underline{r}}\right)$ does not depend on $\underline{r}$. Therefore the contribution to the second sum is $Q^R_{\alpha\beta}\left(o\middle|{o \atop \underline{r}}\right) \sum_{k''} e_{k''}$ which is zero because of charge neutrality. Therefore the term can be dropped. Also note that the term $S^R_{\alpha\beta}\left(\underline{q}\middle|{o \atop \underline{r}}\right)$ for $k = k'$ cancels the term $S^R_{\alpha\beta}\left(o\middle|{o \atop \underline{r}}\right)$ for $k'' = k$. Therefore we can write:

$$C_{\alpha\beta}(\underline{q}|kk') = e^{2\pi i\underline{q}.\left[\underline{r}(k)-\underline{r}(k')\right]}\, e_k e_{k'} \left\{ \sum_h Q^R_{\alpha\beta}\left(\underline{q}\middle|{h \atop \underline{r}}\right) + \right.$$

$$\left. + \sum_{\ell}{}' S^R_{\alpha\beta}\left(\underline{q}\middle|{\ell \atop \underline{r}}\right) + (1-\delta_{kk'}) S^R_{\alpha\beta}\left(\underline{q}\middle|{o \atop \underline{r}}\right) \right\}_{\underline{r}\left({o \atop kk'}\right)} + e_k \delta_{kk'} \sum_{k''} e_{k''} \left\{ \sum_h{}' Q^R_{\alpha\beta}\left(o\middle|{h \atop \underline{r}}\right) + \right.$$

$$\left. + \sum_{\ell}{}' S^R_{\alpha\beta}\left(o\middle|{\ell \atop \underline{r}}\right) + (1-\delta_{kk''}) S^R_{\alpha\beta}\left(o\middle|{o \atop \underline{r}}\right) \right\}_{\underline{r}\left({o \atop k''k}\right)}$$

It is now easy to recognize that this expression is equivalent to eq. (5.19), with the definitions (5.20) and (5.21).

6. CONNECTION WITH THE ELASTIC CONSTANTS

6.1. The Method of Long Waves

The method of long waves is used to derive relationships between the microscopic force constants in a crystal and the macroscopic elastic constants.(13) The idea behind the method is that when the wave vector tends to zero the equations of motion of a vibrating lattice must tend to the equations of motion of an elastic continuum whose properties are described by the elastic constants.

We shall first derive the equations of motion of an elastic continuum. The deformation tensor is defined as

$$\xi_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}\right) \tag{6.1}$$

where u_α is the component of the displacement vector of a point of the continuum originally at position $\underline{r}$. The condition of stress at any point is described by the stress tensor $p_{\alpha\beta}$. The stress tensor and the deformation tensor are related by the elastic tensor:

$$p_{\alpha\beta} = \sum_{\gamma\delta} \varepsilon_{\alpha\gamma\beta\delta}\, \xi_{\gamma\delta} \tag{6.2}$$

The force per unit volume on an element of the continuum is given by the divergence of the stress tensor. Therefore the equation of motion for an element of the continuum is (ρ being the density):

$$\rho \ddot{u}_\alpha = (\text{div } p)_\alpha = \sum_\beta \frac{\partial p_{\alpha\beta}}{\partial x_\beta} \tag{6.3}$$

and taking into account (6.1) and (6.2):

$$\rho \ddot{u}_\alpha = \sum_{\beta\gamma\delta} c_{\alpha\gamma\beta\delta} \frac{\partial^2 u_\beta}{\partial x_\gamma \partial x_\delta} \tag{6.4}$$

By replacing into (6.4) a solution of the type $u_\alpha = U_\alpha e^{i\omega t}\, e^{2\pi i \underline{q}\cdot\underline{r}}$ we obtain the relation

$$\rho\omega^2\, U_\alpha = 4\pi^2 \sum_{\beta\gamma\delta} c_{\alpha\gamma\beta\delta} q_\gamma q_\delta U_\beta \tag{6.5}$$

Instead of the elastic tensor (whose indices vary from 1 to 3), it is common to use the elastic constants c_{ik}, whose indices vary from 1 to 6. The transformation from elastic tensor components to elastic constants is made by replacing pairs of indices in the elastic tensor by Voigt indices, according to:

$$\begin{array}{cccccc} 11 & 22 & 33 & 23,32 & 13,31 & 12,21 \\ \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ 1 & 2 & 3 & 4 & 5 & 6 \end{array} \qquad (6.6)$$

For example c_{1321} would be the elastic constant c_{56}.

It is convenient to introduce the symetric matrix $\overset{*}{D}_{\alpha\beta}(\underline{q})$ defined in terms of the elastic constants, by the relation:

$$\begin{vmatrix} \overset{*}{D}_{11}(\underline{q}) \\ \overset{*}{D}_{22}(\underline{q}) \\ \overset{*}{D}_{33}(\underline{q}) \\ \overset{*}{D}_{23}(\underline{q}) \\ \overset{*}{D}_{13}(\underline{q}) \\ \overset{*}{D}_{12}(\underline{q}) \end{vmatrix} = \begin{vmatrix} c_{11} & c_{66} & c_{55} & c_{56} & c_{15} & c_{16} \\ c_{66} & c_{22} & c_{44} & c_{24} & c_{46} & c_{26} \\ c_{55} & c_{44} & c_{33} & c_{34} & c_{35} & c_{45} \\ c_{56} & c_{24} & c_{34} & \frac{1}{2}(c_{23}+c_{44}) & \frac{1}{2}(c_{45}+c_{36}) & \frac{1}{2}(c_{25}+c_{46}) \\ c_{15} & c_{46} & c_{35} & \frac{1}{2}(c_{45}+c_{36}) & \frac{1}{2}(c_{55}+c_{13}) & \frac{1}{2}(c_{14}+c_{56}) \\ c_{16} & c_{26} & c_{45} & \frac{1}{2}(c_{25}+c_{46}) & \frac{1}{2}(c_{14}+c_{56}) & \frac{1}{2}(c_{12}+c_{66}) \end{vmatrix} \begin{vmatrix} q_1^2 \\ q_2^2 \\ q_3^2 \\ 2q_2q_3 \\ 2q_1q_3 \\ 2q_1q_2 \end{vmatrix} \qquad (6.7)$$

In terms of $\overset{*}{D}_{\alpha\beta}(\underline{q})$ equation (6.5) can be written

$$\rho\omega^2 U_\alpha = 4\pi^2 \sum_\beta \overset{*}{D}_{\alpha\beta}(\underline{q}) U_\beta \qquad (6.8)$$

Equation (6.8) allows to determine the propagation of sound waves in a continuous medium of which the elastic constants are known.

For any wave vector $\underline{q}$ the frequencies are determined by the solutions of the determinantal equation:

$$\left\| D^*_{\alpha\beta}(\underline{q}) - \frac{\rho}{4\pi^2} \omega^2 \delta_{\alpha\beta} \right\| = 0 \qquad (6.9)$$

Equation (6.7), (6.8), (6.9) are important to determine for example the velocities and polarization of the three acoustic waves propagating in any direction in a crystal.

We now consider the limit for $\underline{q} = 0$ of the lattice dynamical equations of motion, to be later identified with (6.8).

To simplify the argument we consider the case of a Bravais crystal, with no basic indices involved.

The equations of motion in matrix form are as follows:

$$\omega^2 \underline{V} = D(\underline{q})\underline{V} \qquad (6.10)$$

where we have indicated with $\underline{V}$ the polarization vector.

We expand in series of the components of $\underline{q}$ the quantities ω, $\underline{V}$ and $D(\underline{q})$, truncating the expansion at the second order:

$$\begin{aligned} \underline{V} &= \underline{V}^{(0)} + \underline{V}^{(1)} + \underline{V}^{(2)} \\ \omega &= \omega^{(1)} + \omega^{(2)} \\ D(\underline{q}) &= D^{(0)} + D^{(1)}(\underline{q}) + D^{(2)}(\underline{q}) \end{aligned} \qquad (6.11)$$

Notice that ω starts with the first order term (this would be true even in a structure with more than one atom per unit cell) because we are considering acoustical branches. When (6.11) are replaced in (6.10) we obtain the zero, first and second order equations

$$D^{(0)}\underline{V}^{(0)} = 0 \tag{6.12}$$

$$D^{(0)}\underline{V}^{(1)}+D^{(1)}(\underline{q})\,\underline{V}^{(0)} = 0 \tag{6.13}$$

$$\omega^{(1)^2}\underline{V}^{(0)} = D^{(0)}\underline{V}^{(2)}+D^{(1)}(\underline{q})\underline{V}^{(1)}+D^{(2)}(\underline{q})\underline{V}^{(0)} \tag{6.14}$$

It can be seen that $\underline{V}^{(0)} = \sqrt{m}\,\underline{U}$, where m is the mass and $\underline{U}$ is any constant vector, satisfies eq.(6.12). In fact

$$D^{(0)}\sqrt{m}\,\underline{U} = \frac{1}{m}\sum_{\ell}\Phi(\ell)\sqrt{m}\,\underline{U} = \frac{1}{\sqrt{m}}\left\{\sum_{\ell}\Phi(\ell)\right\}\underline{U} = 0$$

for the translational invariance condition.

When the solution $\underline{V}^{(0)}$ is replaced into (6.13) we can solve for $\underline{V}^{(1)}$ as a function of $\underline{U}$. The solution will be

$$\underline{V}^{(1)} = -\,D^{(0)^{-1}}D^{(1)}(\underline{q})\,\sqrt{m}\,\underline{U} = \Gamma\,\underline{U} \tag{6.15}$$

When $\underline{V}^{(0)}$ and $\underline{V}^{(1)}$ are substituted into (6.14) we obtain

$$D^{(0)}\underline{V}^{(2)} = \left\{\omega^{(1)^2}\sqrt{m} - D^{(1)}(\underline{q})\Gamma - D^{(2)}(\underline{q})\sqrt{m}\right\}\underline{U} \tag{6.16}$$

We observe now that in (6.16) the homogeneous equation admits a solution other than zero (the solution $\sqrt{m}\,\underline{U}$). The condition for solubility of the inhomogeneous equation is then that the scalar product of the vector on the right side of (6.16) and the particular solution vector be zero. The condition of solubility finally is:

$$\omega^{(1)^2} m \underline{U} = \sqrt{m} \left\{ D^{(1)}(\underline{q})\Gamma + D^{(2)}(\underline{q})\sqrt{m} \right\} \underline{U} \tag{6.17}$$

Equation (6.17) can be formally identified with equation (6.8), providing the desired expressions for the elastic constants as a function of the force constants. In the more general case in which basic indices are present (more than one atom per unit cell) the first member of (6.17) would contain $\sum_k m_k$, which is the total mass in the unit cell. When this mass is divided by the volume of the unit cell we obtain the density of the crystal, to be identified with ρ in equation (6.8).

From a practical point of view, we observe that it is not convenient to use the symbolic form (6.17). This is especially true in the case of a complex structure, in which the form of the matrix Γ is more complicated. Instead, it is more convenient to start from the actual dynamical matrix, calculate $D^{(0)}$, $D^{(1)}(\underline{q})$ and $D^{(2)}(\underline{q})$ and perform the steps (6.15), (6.16) and (6.17), up to the identification with the continuum equations, with the actual matrices.

6.2. Example of Derivation of the Elastic Constants

The above arguments will be illustrated by an example, the derivation of the elastic constants for the crystal of argon, starting from the lattice dynamical matrix previously obtained.

First of all we notice that for a cubic crystal there are only three independent elastic constants, namely c_{11}, c_{12} and c_{44}. Beside this, several symmetry relations hold, so that for a cubic crystal equation (6.7) can be written:

$$\left|\begin{array}{c} D^*_{11}(\underline{q}) \\ D^*_{22}(\underline{q}) \\ D^*_{33}(\underline{q}) \\ D^*_{23}(\underline{q}) \\ D^*_{13}(\underline{q}) \\ D^*_{12}(\underline{q}) \end{array}\right| = \left|\begin{array}{cccccc} c_{11} & c_{44} & c_{44} & 0 & 0 & 0 \\ c_{44} & c_{11} & c_{44} & 0 & 0 & 0 \\ c_{44} & c_{44} & c_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{2}(c_{12}+c_{44}) & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{2}(c_{12}+c_{44}) & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{2}(c_{12}+c_{44}) \end{array}\right| \left|\begin{array}{c} q_1^2 \\ q_2^2 \\ q_3^2 \\ 2q_2q_3 \\ 2q_1q_3 \\ 2q_1q_2 \end{array}\right| \qquad (6.18)$$

We then expand the dynamical matrix derived previously in powers of the component of $\underline{q}$. The result is:

$$D^{(0)} = 0$$

$$D^{(1)}(\underline{q}) = 0$$

$$D^{(2)}(\underline{q}) = -\frac{4\pi^2 a^2}{m}\left|\begin{array}{ccc} A & \beta q_1q_2 & \beta q_1q_3 \\ \beta q_1q_2 & B & \beta q_2q_3 \\ \beta q_1q_3 & \beta q_2q_3 & C \end{array}\right|$$

with

$$A = (\delta+\alpha)q_1^2 + (\gamma+\alpha-\frac{\beta}{2})q_2^2 + (\gamma+\alpha-\frac{\beta}{2})q_3^2$$

$$B = (\gamma+\alpha-\frac{\beta}{2})q_1^2 + (\delta+\alpha)q_2^2 + (\gamma+\alpha-\frac{\beta}{2})q_3^2$$

$$C = (\gamma+\alpha-\frac{\beta}{2})q_1^2 + (\gamma+\alpha-\frac{\beta}{2})q_2^2 + (\delta+\alpha)q_3^2$$

Because $D^{(0)}$ and $D^{(1)}(\underline{q})$ are zero, we can use immediately equation (6.17) obtaining

$$\omega^{(1)^2}\underline{U} = D^{(2)}(\underline{q})\ \underline{U} \qquad (6.19)$$

which can be compared with the matrix form of (6.8):

$$\rho\omega^2\underline{U} = 4\pi^2 D^*(\underline{q})\underline{U} \qquad (6.20)$$

Noting that for the f.c.c. lattice the density ρ is equal to $4m/a^3$, we obtain, using (6.18):

$$c_{11} = -\frac{4(\delta+\alpha)}{a}$$

$$c_{12} = \frac{-6\beta + 4\gamma + 4\alpha}{a}$$

$$c_{44} = \frac{4\gamma + 4\alpha - 2\beta}{a}$$

which are the desired expressions for the elastic constants as functions of the force constants.

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