

The vibration spectrum of a crystal lattice

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1. Introduction

It is a fundamental problem in the physics of the solid state to determine the possible modes and frequencies of vibration of the atomic nuclei in a crystal about their positions of equilibrium. The importance of the problem will be evident when we recollect that there is scarcely any physical property of a solid which is not influenced in greater or less measure by the thermal agitation of the atoms, and that the existence of atomic vibrations (excited thermally or otherwise) comes into evidence in a variety of phenomena exhibited by crystals. We may, in particular, mention various optical effects observed with crystals, e.g., the scattering of light with altered frequency, luminescence and absorption spectra at low temperatures, which not only render the existence of atomic vibrations in them obvious, but also enable us to make precise determinations of their vibration frequencies, and even infer their geometric characters.

An appropriate starting point for the inquiry is furnished by the well known result in analytical mechanics that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. In each such mode, the particles of the system execute harmonic vibrations with a common frequency characteristic of the mode, and all pass simultaneously through their positions of equilibrium at some particular phase of the vibration. The question arises for investigation, does the structure of a crystal possess any normal modes of vibration as thus defined, and if so, what are their frequencies? In seeking an answer to this question, it is obviously not permissible to make in advance any arbitrary postulate regarding the nature of the normal vibrations, since this is itself the subject-matter of the investigation. Further, it is essential that we assume the most general type of interaction possible between the atoms in the crystal which is consistent with its known structure and symmetry properties. Indeed, in an investigation intended to deduce results of general application, it is evidently undesirable to make any special postulates regarding the interatomic forces, viz., that they are only

operative as between contiguous atoms or that they are in the nature of central forces whose magnitude varies as some power of the distance. The introduction of arbitrary postulates and assumptions has indeed, as will be shown in this paper, led to misleading results in the past history of the subject.

2. The Lagrangian equations of motion

We denote the displacements of a chosen atom in a particular cell of the crystal structure from its position of equilibrium by the symbols $q_{xrs}, q_{yrs}, q_{zrs}$, these being parallel respectively to the three mutually perpendicular co-ordinate-axes x, y and z . Here r is an index number indicating a particular atom amongst the p atoms in the cell of the crystal structure, while s is an index number indicating the particular cell in which the atom is located. The symbols $q_{x\rho\sigma}, q_{y\rho\sigma}, q_{z\rho\sigma}$ have similar significance, except that ρ and σ which are the atom and cell indices respectively are regarded as unspecified. The masses of the atoms are written as m , or m_p .

The kinetic energy T of the vibrations of the crystal is accordingly given by the summation over all possible values of ρ and σ of the expression

$$\frac{1}{2}m_p[\dot{q}_{x\rho\sigma}^2 + \dot{q}_{y\rho\sigma}^2 + \dot{q}_{z\rho\sigma}^2]. \quad (1)$$

The potential energy V of the displacements of the atoms from their positions of equilibrium is given by the summation of all the terms derived from the expression

$$\frac{1}{2}K_{xrs}^{y\rho\sigma} \cdot q_{xrs} \cdot q_{y\rho\sigma} \quad (2)$$

by making r, s, ρ, σ run over all the possible values, as also by interchanging x, y and z . The dependence of the force-constants jointly on x, r, s and y, ρ, σ is indicated by the indices attached to them. It is evident that

$$K_{xrs}^{y\rho\sigma} = K_{y\rho\sigma}^{xrs} \quad (3)$$

Hence, since each distinct pair of co-ordinates appears twice over in the summation, we may replace the factor $\frac{1}{2}$ by 1 in (2), it being understood that they are written together only once. The factor $\frac{1}{2}$ is however retained for the terms which appear as the squares of the displacements.

The equation of motion which must be satisfied by any particular co-ordinate, e.g., q_{xrs} is

$$\frac{d}{dt} \left(\frac{\partial T}{\partial \dot{q}_{xrs}} \right) + \left(\frac{\partial V}{\partial q_{xrs}} \right) = 0. \quad (4)$$

If we assume that the vibration under consideration is a normal mode for the crystal, the displacement-components of all the atoms must be of the form $q \sin \omega t$ where the q 's are real quantities depending on the atom chosen and the direction

of its displacement, while ω is the same for all atoms in the crystal. On this basis the equation for q_{xrs} becomes

$$(m_r \omega^2 - K_{xrs}^{xrs})q_{xrs} = \sum_{y\rho\sigma} K_{xrs}^{y\rho\sigma} \cdot q_{y\rho\sigma}. \quad (5)$$

The summation indicated on the right-hand side of (5) is to be understood as including the contributions due to all the displacement-components of all the atoms in the crystal with the single exception of the displacement q_{xrs} under consideration which appears on the left-hand side of the equation. There would, of course, be a whole series of equations of this type for the x , y and z displacements of every atom in the crystal, and it is necessary that all these equations are simultaneously satisfied for the given value of ω , for the vibration under consideration to possess the characters of a normal mode.

3. The solution of the equations

The clue to the discovery of the normal modes of vibration is furnished by the basic principle of crystal architecture which may be stated as follows: *A crystal consists of sets of equivalent atoms ordered in such manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set.* From this it follows that the force-constant which connects the displacements of any pair of atoms in the crystal is the same as that which connects the displacements of any other pair of atoms, provided that the two pairs of atoms can be simultaneously brought into coincidence by simple translations of the crystal lattice parallel to its axes.

Consider now the equation of motion analogous to (5) for the r th atom in a different cell, say s' . In writing it down, it is convenient to choose a running cell-index σ' different from the σ appearing in (5), but so related to it that the translations of the crystal lattice which would bring s' into coincidence with s would also bring σ' into coincidence with σ . We have then

$$(m_r \omega^2 - K_{xrs'}^{xrs'})q_{xrs'} = \sum_{y\rho\sigma'} K_{xrs'}^{y\rho\sigma'} \cdot q_{y\rho\sigma'}. \quad (6)$$

Now the relation between s , σ and s' , σ' assumed above, taken in conjunction with the physical structure of the crystal, gives us at once the relations

$$K_{xrs}^{xrs} = K_{xrs'}^{xrs'}, \quad (7)$$

$$K_{xrs}^{y\rho\sigma} = K_{xrs'}^{y\rho\sigma'}, \quad (8)$$

between the force-constants appearing in (5) and (6). This identity of the force-constants appearing on both sides of the equations of motion of equivalent atoms suggests that their displacements in a normal mode of vibration are also related to each other in a simple way. Algebraically, it is evident that if there exists

between them a general relationship of the form

$$\frac{q_{xrs}}{q_{xrs'}} = \frac{q_{y\rho\sigma}}{q_{y\rho\sigma'}}, \quad (9)$$

it follows therefrom that when equation (5) is satisfied, equation (6) will also simultaneously be satisfied, and indeed also the similar equations for *all* the equivalent atoms of index r in the crystal. Further, if the general relations indicated in (9) subsist, they are sufficient to ensure that when the equations of motion of an atom of *any* chosen index number in a particular cell are satisfied, the equations of all the other equivalent atoms of the same index number in every other cell of the crystal lattice are also simultaneously satisfied; the latter is a necessary condition for the vibration to be a normal mode.

4. Nature of the normal modes

We shall now consider more closely the significance of the relations stated in (9). They may be written in the form

$$\frac{q_{y\rho\sigma}}{q_{xrs}} = \frac{q_{y\rho\sigma'}}{q_{xrs'}}. \quad (10)$$

Stated in words, the meaning of (10) is that the vibrations of the equivalent atoms in the crystal are quantitatively related to the vibrations of the other atoms forming their respective environments in an identical fashion. *Prima facie*, this is what we should expect, since equivalence of geometric position in the crystalline array of atoms necessarily involves an equivalence in the strength of the forces holding the atoms together as indicated in equations (7) and (8), and hence should result also in equivalence in respect of dynamic behaviour in a normal vibration. To make the meaning of such equivalence clearer, we may return to equation (9) and take a case in which the cells s and s' occupy contiguous positions along one of the axes of the Bravais lattice. It follows that σ and σ' would similarly occupy contiguous positions along a parallel axis. Equation (9) thus signifies that the ratio of the corresponding displacements of *any pair* of contiguous equivalent atoms in the crystal lattice is a constant characteristic of the particular axis and of the particular normal mode under consideration.

We may apply the same arguments to cells contiguous to each other respectively along the second and third axes of the Bravais lattice. The three characteristic constants thus obtained need not necessarily be the same, and we therefore denote them by α , β , γ respectively. Since the atomic displacements are real quantities and their phases in a normal mode are all either the same or opposite, the constant ratios α , β , γ must be assumed to be *real* quantities which may be either positive or negative. If, starting from a particular cell, we move out

