The vibrations of the MgO crystal structure and its infra-red absorption spectrum—Part II. Dynamical theory

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1. Introduction

The fundamental property of the atomic structure of a crystal is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence the normal modes of atomic vibration characteristic of the structure of a crystal should satisfy a similar requirement; in other words, they should remain unaltered following such a unit translation. From this, it follows that the atomic modes of vibration satisfy the following rule: in any normal mode, equivalent atoms in the structure have *either* the same amplitude and the same phase, *or* the same amplitude but alternating phases, along the axes of the lattice. In the MgO structure, we have two interpenetrating face-centred cubic lattices of Mg and O atoms respectively. Applying the rule stated, it should be possible to deduce the normal modes of vibration of this structure purely from symmetry considerations. One could also go further and obtain explicit formulae for the frequencies of the normal modes in terms of the interatomic force-constants. We shall, in what follows, carry out the programme here indicated.

2. Vibrations of a face-centred cubic lattice

The three unit translations in a face-centred cubic lattice are parallel to the three edges of the primitive rhombohedral cell of the lattice. These edges are found by joining an atom at a cube corner with the three atoms at the centres of the three adjoining cube faces. The various modes of normal vibration of the lattice given by the rule stated above are found by choosing one or another of the eight possible combinations of the phases of these three atoms relative to the phase of the atom at the cube corner and continuing the scheme to the more distant atoms in the lattice. It is then found that the possible modes of vibration may be described *either* as movements of the cubic planes of atoms in the crystal *or* as

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movements of the octahedral planes of atoms; in either case, the alternation of phase along an axis results in the alternate planes of one or the other species moving in opposite phases. Since we have three sets of cubic planes and four sets of octahedral planes, the movements of these planes normal to themselves would give three and four normal modes respectively, but only two distinct frequencies. We have also to consider the movements of the planes parallel to themselves, and as there are two possible directions of movement in each case, we obtain six and eight such normal modes respectively, but here again only two additional frequencies by reason of the symmetry of the crystal. Thus, in all, we have only four distinct frequencies of vibration. In the foregoing we left out of consideration the case in which the phases of movement of the three atoms at the face-centres and of the atom at the cube corner are the same. This corresponds to a simple translation of the unit rhombohedral cell carrying eight atoms at its corners. The 24 degrees of freedom of movement of these eight atoms are thus distributed as follows amongst the possible movements of the lattice.

Table 1

	Degeneracy
Vibrations of the cubic planes normal to themselves	3
Vibrations of the cubic planes tangential to themselves	6
Vibrations of the octahedral planes normal to themselves	4
Vibrations of the octahedral planes tangential to themselves	8
Translations of the unit cell	3
Total degrees of freedom	24

3. The vibrations of the MgO structure

In the MgO crystal, the Mg and O atoms occupy the points of two similar face-centred cubic lattices interpenetrating each other. These are so disposed that each Mg atom is surrounded by six equidistant O atoms, and each O atom is surrounded by six equivalent Mg atoms. In the cubic planes of the structure the Mg and O atoms appear together, while in the octahedral planes they appear separately but in equidistant planes, each plane of Mg atoms having two planes of O atoms and each plane of O atoms having two planes of Mg atoms situated symmetrically on either side of it. This arrangement has interesting consequences regarding the possible vibrational modes of the structure, as we shall presently see.

   Table 1 would represent equally well the schemes of vibration of the Mg atoms and of the O atoms. Hence, the interactions of these atoms with each other would result in a modification of the frequencies of vibration without altering the

geometry of the modes. Since the cubic planes contain both Mg and O atoms, each of their movements would split into two modes: in one of the two modes, the Mg and O atoms in a cubic plane would oscillate in the same phase and in the other they would oscillate in opposite phases. The situation would be a little different with respect to the atomic layers parallel to the octahedral faces. In view of the disposition of Mg and O atoms in these layers, it is evident that the oscillations of Mg and O layers would occur independently of each other, the Mg planes remaining at rest when the O planes oscillate and vice versa. The three translations of the unit cells would also split into two. The movement of the Mg and O atoms in opposite phases would give a triply degenerate normal mode, while their movement in the same phases would represent a residuum of three translations.

Thus, the structure would have only nine different frequencies of vibration, while the number of normal modes would be 45 which together with the residuum of the three translations would account for the 48 degrees of freedom of movement of 8 atoms of magnesium and 8 atoms of oxygen when added together. The description of the modes of vibration corresponding to each of the nine different frequencies is entered in the second column of table 2, while their respective degeneracies are shown in the third column of the table. These degeneracies are the same as shown in table 1, but they now total up to 48 instead of 24 as in the former table.

The modes have been shown in the first column of table 2 in the order of the magnitude of their respective frequencies suggested by the approximate formulae

Table 2

Sl. No.	Description of mode	Degeneracy
I	Oscillation of the Mg and O atoms in opposite phases	3
II	Tangential oscillations of the cubic planes, Mg and O atoms having opposite phases	6
III	Normal oscillations of the cubic planes, Mg and O atoms having same phases	3
IV	Normal oscillations of the octahedral planes of O atoms	4
V	Tangential oscillations of the octahedral planes of O atoms	8
VI	Normal oscillations of the octahedral planes of Mg atoms	4
VII	Tangential oscillations of the octahedral planes of Mg atoms	8
VIII	Normal oscillations of the cubic planes, Mg and O atoms having opposite phases	3
IX	Tangential oscillations of the cubic planes, Mg and O atoms having same phases	6
X	Translations	3
	Total degrees of freedom	48

of the dynamical theory to be given presently. But this arrangement is subject to revision on the basis of a more accurate evaluation of those frequencies. It will be noticed that at the top of the table listed as mode I appears the triply degenerate oscillation of the Mg and O atoms in the structure moving against each other in opposition of phase. It will also be noticed that next to it in the descending order of frequency appear the tangential and normal modes of oscillation of the cubic layers of atoms. These are listed in the table as modes II and III, while two other modes of oscillation of the cubic layers in which the phases of movement of the Mg and O atoms are different appear at the bottom of the table as VIII and IX respectively. The oscillations of the octahedral layers of atoms appear in an intermediate position as IV, V, VI and VII respectively.

4. Dynamical theory: First approximation

The normal modes of atomic vibration in a crystal remain unaltered when a unit translation is given to the structure along any one of its three axes. Accordingly, it is sufficient to write down and solve the equations of motion of the atoms contained in any one unit cell of the structure. The features of the vibration deduced therefrom would equally well describe the possible atomic movements in the other cells of the structure. In the present problem, therefore, we have only to frame the equations of motion of a magnesium atom and of an adjoining oxygen atom in the structure for each of the possible modes of vibration deduced from the geometry of the structure. Their solution would give us the frequencies of those modes of vibration.

The forces acting on an atom which determine its movements are those arising from the displacements of other atoms in the crystal by reason of their mutual interactions. We shall proceed on the assumption that the interactions between any two atoms are determined by their *relative* displacements measured from the positions they occupy when at rest in the crystal. The forces of interaction may be expected to be greatest between atoms which are near neighbours and to diminish rapidly in respect of those atoms which are further and further removed from each other.

The nearest neighbours of each magnesium atom in the MgO structure are six oxygen atoms. These are situated in pairs, one on either side along the x, y and z axes of the structure. Likewise, each oxygen atom has six magnesium atoms as its nearest neighbours arranged in a similar fashion. We shall, in the first instance, proceed to work out the dynamics of the vibrations taking into account only the interactions between each magnesium atom and its six neighbouring oxygen atoms and vice versa. It is clear that two force-constants which we shall denote as α and β respectively would suffice to specify these interactions. The constant α refers to the interaction between an Mg atom and an O atom arising from their relative displacement *along* the direction of the cubic axis on which

they both lie. The force resulting from such displacement would be parallel to the direction of the displacement. The constant β refers to the interaction arising from a relative displacement *transverse* to the line joining the two atoms and parallel to one of the other two cubic axes. In this case as well, the resulting force would be parallel to the direction of such displacement.

We denote by m_1 and m_2 the masses of the Mg and O atoms respectively. ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2 are the displacements of the Mg and O atoms under consideration respectively along the x, y and z axes. The forces acting on these atoms are found by multiplying the displacements of the interacting atoms relatively to each of them by the appropriate force-constants and adding them up. The equations are then solved by writing

$$\xi_1 = x_1 \sin \omega t, \qquad \eta_1 = y_1 \sin \omega t, \quad \text{etc.,}$$

and eliminating the quantities x_1, y_1, etc., which represent amplitudes. An expression is then obtained which gives ω^2 in terms of α, β and the masses m_1 and m_2. We shall consider in turn the different modes of vibration indicated by table 1 as possible for a face-centred cubic lattice.

The first case we shall consider is that in which the Mg atoms and O atoms oscillate as groups along the x-axis. The equations of motion are then

$$m_1 \frac{d^2 \xi_1}{dt^2} = - K_0(\xi_1 - \xi_2)$$

and

$$m_2 \frac{d^2 \xi_2}{dt^2} = - K_0(\xi_2 - \xi_1),$$

where K_0 is an abbreviation for $(2\alpha + 4\beta)$. Proceeding as already indicated, we obtain a quadratic equation for ω_1^2, the solutions of which are

$$\omega_1^2 = \frac{K_0}{\mu}, \quad \omega_{10}^2 = 0, \tag{1}$$

where μ is the reduced mass given by the formula $1/\mu = 1/m_1 + 1/m_2$. The first solution represents mode I in table 2 above, while the zero frequency represents the translations appearing at the foot of that table.

The next case is that of the tangential oscillation of the cubic layers of atoms which are parallel to the yz plane along the y-axis. The alternate layers oscillate in opposite phases. The equations of motion are:

$$m_1 \frac{d^2 \eta_1}{dt^2} = - K_0 \eta_1 + 2\alpha \eta_2$$

and

$$m_2 \frac{d^2 \eta_2}{dt^2} = 2\alpha \eta_1 - K_0 \eta_2.$$

The solutions of these equations are:

$$\omega_{2,9}^2 = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{K_0^2}{4\mu^2} - \frac{(K_0^2 - 4\alpha^2)}{m_1 m_2}\right]^{1/2}. \tag{2}$$

The alternative signs appearing in formula (2) give the frequencies of vibration ω_2 and ω_9 respectively. The higher frequency ω_2 refers to the case in which the Mg and O atoms appearing in the same yz planes move in opposite phases. The lower frequency ω_9 represents the case in which the Mg and O atoms appearing in the same yz planes move in the same phase. ω_2 and ω_9 refer respectively to the modes listed as II and IX in table 2. From formula (2) it is evident that

$$\omega_9^2 = \omega_1^2 - \omega_2^2.$$

The third case we shall consider is that in which the cubic layers of atoms in the crystal lying in the yz planes oscillate normally to themselves along the x-axis, the alternate layers being in opposite phases. The equations of motion are:

$$m_1 \frac{d^2\xi_1}{dt^2} = -K_0\xi_1 - (K_0 - 8\beta)\xi_2$$

and

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K_0 - 8\beta)\xi_1 - K_0\xi_2.$$

The solutions of these equations are:

$$\omega_{3,8}^2 = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{\frac{1}{4}K_0^2}{\mu^2} - \frac{32\alpha\beta}{m_1 m_2}\right]^{1/2}. \tag{3}$$

The alternative signs appearing in the formula give the two frequencies of vibration ω_3 and ω_8. The higher frequency ω_3 represents the case in which the Mg and O atoms which appear in any yz plane oscillate in the same phase, while the Mg and O atoms adjacent to each other in adjoining yz layers vibrate in opposite phases. The lower frequency ω_8 refers to the case in which the Mg and O atoms which appear in the same yz planes move in opposite phases, while the Mg and O atoms which are nearest to each other in adjacent yz layers oscillate in the same phase. ω_3 and ω_8 refer respectively to the modes listed as III and VIII respectively in table 2. From the formula (3), it is evident that

$$\omega_8^2 = \omega_1^2 - \omega_3^2.$$

We have next to consider the oscillations of the octahedral layers of atoms normally or tangentially to themselves. The Mg and O atoms are located in separate octahedral layers which alternate and are equidistant from each other. Hence, when two layers of Mg atoms oscillate in opposite phases, the layer of oxygen atoms midway between them remains at rest, and vice versa. A single equation of motion determines the frequency of oscillation for the magnesium atoms, while another such equation yields the frequency for the oxygen atoms. It

is also evident that when the interactions only with the nearest neighbours are considered, the frequency for oscillations normal and tangential to the octahedral planes would not be different. We obtain

$$\omega_{4,5}^2 = \frac{K_0}{m_2},\tag{4}$$

for the modes listed as IV and V in table 2 and

$$\omega_{6,7}^2 = \frac{K_0}{m_1},.\tag{5}$$

for the modes listed as VI and VII in table 2.

5. Dynamical theory: Second approximation

In the foregoing, we took into account only the interactions between the atoms which are nearest to each other. This enables a first approximation to be obtained in a simple manner for the frequencies of vibration and permits of their being arranged, at least provisionally, in an ordered sequence. There is no difficulty, however, in taking the interactions with more distant neighbours into account and finding more exact formulae. Besides the six neighbouring oxygen atoms, each magnesium atom has twelve magnesium atoms as next nearest neighbours located on the face-diagonals. It has also eight oxygen atoms as more distant neighbours located on the body-diagonals. Likewise, each oxygen atom has twelve oxygen atoms as next nearest neighbours and eight magnesium atoms as more distant neighbours. The movements of these neighbours relatively to the atom under consideration and the interactions arising therefrom have to be taken into consideration in framing its equations of motion and deducing therefrom the frequencies of its vibration. We shall consider in succession the various modes of vibration listed in table 2.

Mode I.—In addition to the force-constants α and β already introduced, we have to consider a third force-constant γ, which expresses the interactions between the magnesium atoms and the oxygen atoms located along the body-diagonals of the cubic structure. It is readily shown that the frequencies are given by

$$\omega_1^2 = \frac{K}{\mu} \quad \text{or} \quad \omega_{10} = 0,\tag{6}$$

where K is an abbreviation for $(2\alpha + 4\beta + 8\gamma)$.

Modes II and IX.—In these modes, we have now to consider also the interactions of each Mg atom with the twelve Mg atoms in its neighbourhood.

Likewise, we have to take into account the interaction of each O atom with its twelve neighbouring O atoms. The forces and displacements with which we are concerned in these interactions are parallel to each other and to one or another of the three cubic axes. Four of the atoms are located in each of the three cubic planes containing the atom under consideration. It emerges that in four cases out of the twelve, the force and the displacement are both perpendicular to the cubic plane in which the interacting atoms are situated, while in the remaining eight cases, they are both parallel to that plane. We have accordingly to introduce two new force-constants θ_1 and ϕ_1 for the interactions between the magnesium atoms, and likewise two other force-constants θ_2 and ϕ_2 for the interactions between the oxygen atoms. The equations of motion then take the form

$$m_1 \frac{d^2\eta_1}{dt^2} = -(K + 8\theta_1 + 8\phi_1)\eta_1 + (K - 4\beta - 16\gamma)\eta_2$$

and

$$m_2 \frac{d^2\eta_2}{dt^2} = (K - 4\beta - 16\gamma)\eta_1 - (K + 8\theta_2 + 8\phi_2)\eta_2.$$

Substituting

$$\eta_1 = y_1 \sin \omega t \quad \text{and} \quad \eta_2 = y_2 \sin \omega t$$

and eliminating y_1 and y_2, we obtain a quadratic equation which enables $\omega^2_{2,9}$ to be expressed in terms of the force-constants and the masses m_1 and m_2.

Modes III and VIII.—Only five out of the seven force-constants already introduced appear in the equations of these two modes.

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 16\phi_1)\xi_1 - (K - 8\beta)\xi_2$$

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K - 8\beta)\xi_1 - (K + 16\phi_2)\xi_2.$$

Substituting

$$\xi_1 = x_1 \sin \omega t \quad \text{and} \quad \xi_2 = x_2 \sin \omega t,$$

and eliminating x_1 and x_2, we obtain a quadratic equation which gives $\omega^2_{3,8}$ in terms of the force-constants and the masses m_1 and m_2.

Modes IV, V, VI and VII.—We have now to introduce two additional force-constants ψ_1 and ψ_2, which represent interactions in which the force and the displacement are mutually perpendicular, the displacement being along one cubic axis and the force along another cubic axis, while the interacting atoms lie in the plane defined by the two axes. ψ_1 refers to the case in which the interacting

atoms are both of magnesium, while ψ_2 refers to the case in which they are both oxygen atoms. These force-constants appear in considering the movements of the octahedral layers either normally or tangentially to themselves, by reason of the simultaneous movements along all the three cubic axes or along two cubic axes which need to be taken into account in these cases. The equations of motion for normal and tangential movements of a magnesium atom respectively are:

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 4\theta_1 + 8\phi_1 + 8\psi_1)\xi_1$$

and

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 4\theta_1 + 8\phi_1 - 4\psi_1)\xi_1.$$

The frequencies are therefore respectively:

$$\omega_6^2 = \frac{(K + 4\theta_1 + 8\phi_1 + 8\psi_1)}{m_1}$$

and

$$\omega_7^2 = \frac{(K + 4\theta_1 + 8\phi_1 - 4\psi_1)}{m_1}. \tag{7}$$

The equations of motion for normal and tangential oscillations of an oxygen atom are respectively

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K + 4\theta_2 + 8\phi_2 + 8\psi_2)\xi_2$$

and

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K + 4\theta_2 + 8\phi_2 - 4\psi_2)\xi_2.$$

The frequencies are therefore respectively

$$\omega_4^2 = \frac{(K + 4\theta_2 + 8\phi_2 + 8\psi_2)}{m_2}$$

and

$$\omega_5^2 = \frac{(K + 4\theta_2 + 8\phi_2 - 4\psi_2)}{m_2}. \tag{8}$$

6. Summary

The fundamental property of a normal vibration indicated by the classical dynamics, viz., that the particles in the system oscillate with the same frequency and in the same or opposite phases, considered in relation to the three-

dimensionally periodic structure of a crystal, enables the possible modes of atomic vibration in a crystal to be uniquely characterised and enumerated. The simplicity and high symmetry of the structure of MgO enables this procedure to be carried further and the modes of normal vibration to be completely described and explicit formulae obtained from their frequencies. It emerges that the structure of MgO has nine distinct frequencies of vibration. Expressions have been derived for these frequencies of these modes, both in the first and in the second approximation.