

The dynamics of the fluorite structure and its infra-red behaviour—Part II. The free modes of vibration

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A consideration of the possible free modes of vibration of the atoms in a crystal about their positions of equilibrium is, of necessity, the starting point in the theory of its specific heats and also for an understanding of its spectroscopic behaviour. We are concerned to discover the nature of the movements of the massive positively charged nuclei about the locations in which they are held in the crystal by the clouds of the mobile negative charges which surrounds and encompass them. A practicable approach to the problem is that based on the principles of the classical mechanics.

A well known theorem states 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. The number of normal modes is equal to the number of degrees of dynamical freedom of the system, and in each such mode, the particles of the system execute harmonic vibrations with common frequency characteristic of the mode and their phases are all the same or opposite, in other words, they all pass simultaneously through their positions of equilibrium. It should be emphasised that this identity or opposition of phase is a fundamental feature of the normal modes. In the absence of such a phase-relationship, the possible movements of the particles would be infinitely varied and hence incapable of enumeration.

We have thus to answer the following questions. Do the atoms located in the structure of the crystal possess any normal modes of vibration having the stated characters? If so, what is the number of such modes and how is their number related to the number of atoms comprised in each unit cell of the structure? To find the answer to these questions, we make use of the fundamental property of a crystal that its structure comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Since each atom comes into coincidence with an equivalent atom in the next cell, all physical properties of the crystal determined by the atomic locations and the atomic interactions should also remain unaltered. It follows as a necessary consequence of this

situation that a vibration having the characters of a normal mode should continue to be a normal mode following a unit translation. This can evidently happen in two ways. Equivalent atoms brought into coincidence can have identical amplitudes and phases of vibration. Alternatively, their amplitudes can be the same but all the phases are reversed. (In the latter case, the original phases are regained after a half-period and hence the normal mode is effectively unaltered.)

The two alternative possibilities indicated above arise in respect of a unit translation along each of the three axes of the lattice. Since these are independent of each other, we have $2 \times 2 \times 2 = 8$ different possibilities in all. In each of these 8 possibilities, the amplitudes of vibration of the atoms in the cells adjoining a particular cell are the same as those of the equivalent atoms in that cell. Hence, if there are n atoms in each unit cell of the structure, their $3n$ equations of motion involving their interactions with the surrounding atoms which are assumed to be proportional to their relative displacements contain only $3n$ displacement co-ordinates. Hence the equations of motion can be completely solved, the solutions obtained giving us the frequencies and the ratios of the atomic displacements along each of the co-ordinate axes.

Considering all the eight possibilities referred to above, we have $8 \times 3n = 24n$ distinct solutions or normal modes of vibration. In $3n$ of these modes, the vibrations of equivalent atoms have the same phase in the adjoining cells, while in the remaining $21n$ modes, they appear with alternating phases along one or two or all three axes of the lattice. By the nature of the case, however, 3 out of the $3n$ modes have a zero frequency, in other words, represent simple translations. Hence we have only $(3n - 3)$ normal modes properly so-called of the first species and $21n$ normal modes of the second species.

The fluorite structure can be described as the result of the interpenetration of three similar rhombohedral (= face-centred cubic) lattices, one of calcium atoms and two of fluorine atoms. Hence, in what has been stated above, we have $n = 3$, and the number of normal modes of vibration of the first species is, therefore, 6 and of the second species is 63. The number of distinct frequencies of vibration would however be far smaller, by reason of the cubic symmetry of the entire structure and consequent degeneracy of the modes of vibration. The actual number of such frequencies and the modes of vibration exhibiting them can be readily derived in the following manner. We begin by considering the possible modes of vibration of each of the three lattices of atoms with which we are concerned. The eight possible alternatives regarding the relative phases of the atomic vibration in any one lattice give rise to 24 possible types of movement listed in a table on next page.

In the modes listed as (2), (3), (4) and (5), the oscillations alternate in phase as we proceed from layer to layer. The directions in which the layers of atoms oscillate, viz., normal or tangential as the case may be, are fixed by the symmetry of the structure. The symmetry also determines the degeneracies shown against the

Description of the modes	Degeneracy
1. Simple translations	3
2. Oscillations normal to the cubic planes	3
3. Oscillations tangential to the cubic planes	6
4. Oscillations normal to the octahedral planes	4
5. Oscillations tangential to the cubic planes	8
Total	24

respective modes. The free modes of vibration of the fluorite structure would evidently be superpositions of the movements or oscillations of the three lattices, these being geometrically similar but with amplitudes and phases relative to each other which are dynamically permissible. Taking first the simple translations of the three lattices, one of them reduces to a simple translation of all the three lattices together, and the other two give us the modes of oscillation pictured in figures 1 and 2 below respectively, each of which is three-fold degenerate. In the oscillation pictured in figure 1 the calcium atoms all move together in phase, while the fluorine atoms move together in the opposite phase. In the oscillation pictured in figure 2, the calcium atoms remain at rest, but the fluorine atoms oscillate with the two lattices in opposite phases.

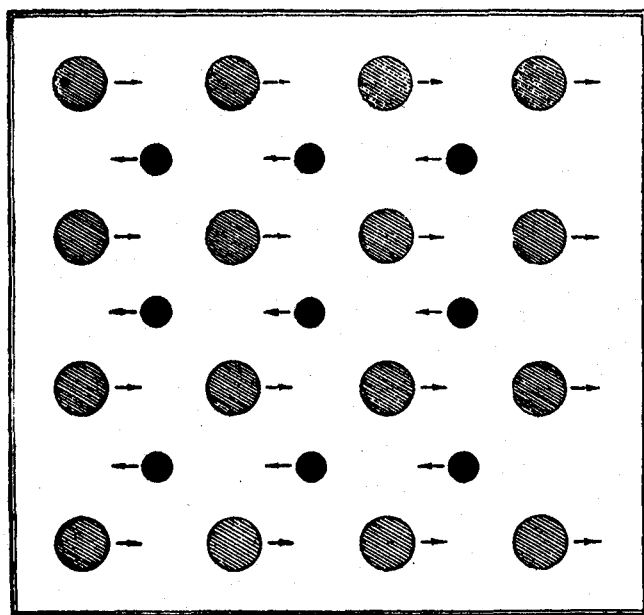


Figure 1. Oscillation of the calciums against the fluorines.

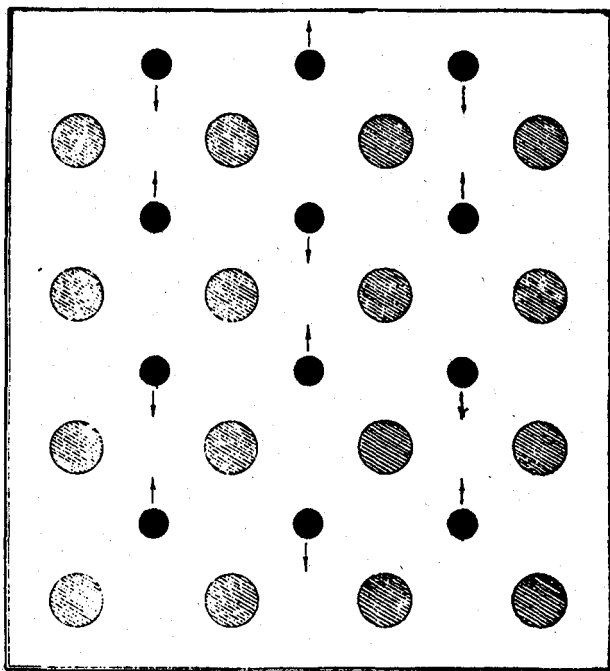


Figure 2. Oscillations of the fluorine atoms with the two lattices in opposite phases.

Likewise, the mode of oscillation of the cubic layers of atoms normal to themselves listed as (2) in the table resolves itself into three modes. In one of them, adjoining layers of fluorine and calcium atoms move in opposite phases. In another, they would move in the same phase. In the third mode, the calcium atoms would remain at rest and the layers of fluorine atoms would oscillate against each other. These three modes of vibration are shown diagrammatically in figures 3(a), (b) and (c) respectively. Each of these modes would have a degeneracy of 3. The corresponding modes of oscillation tangential to the cubic layers are shown diagrammatically in figures 3(d), (e) and (f). Each of them would have a degeneracy of 6.

The oscillation of the octahedral layers normal to themselves listed as (4) in the table would likewise divide up into three modes. In one of them, the three adjacent layers containing the calcium and fluorine atoms would move together in the same phase, the phase of all the three together reversing from one set of three layers to the next set. In another mode, the fluorine layers would move together in one phase and the calcium layers intermediate between them in the opposite phase. This movement again would reverse its phase in the next adjacent set of layers. In the third mode, the fluorine layers alone would oscillate in

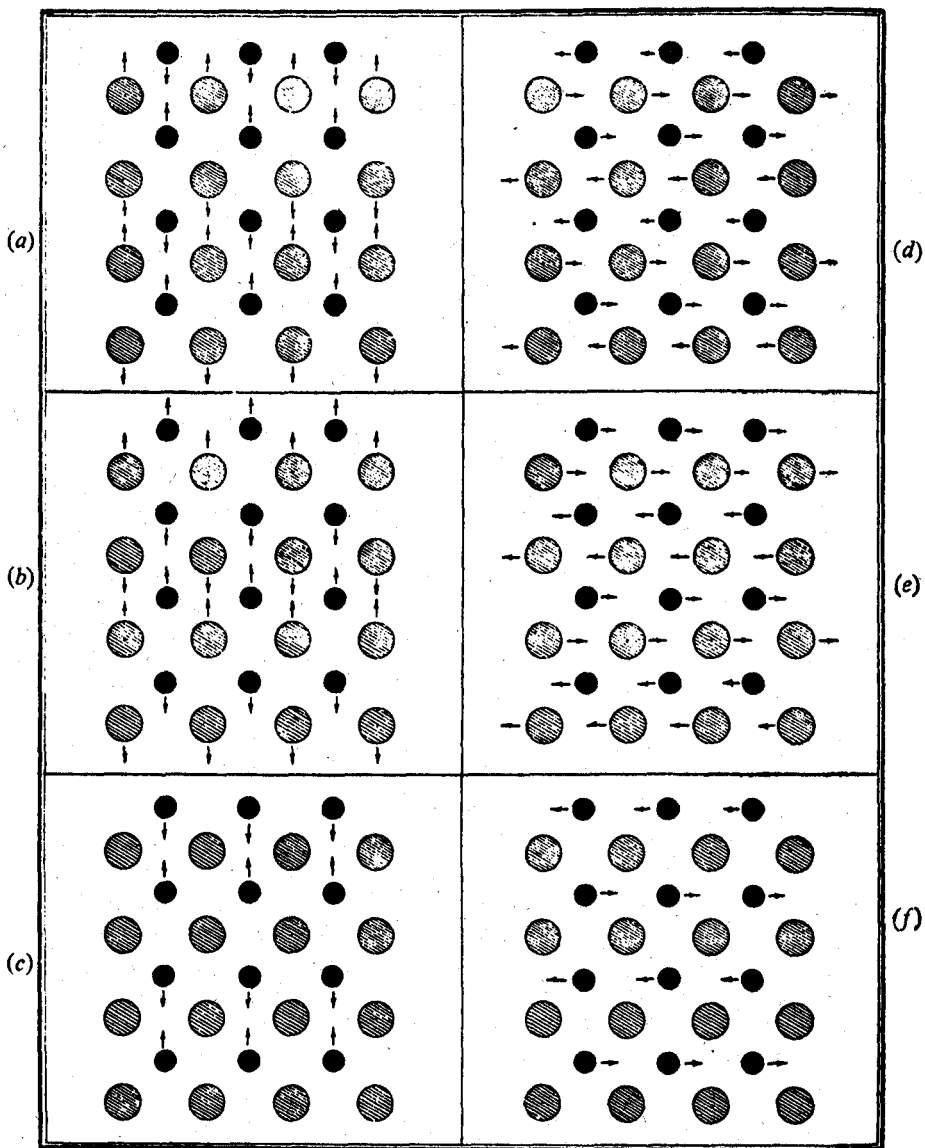


Figure 3. (a), (b), (c), (d), (e) and (f): Oscillations of the cubic layers of atoms.

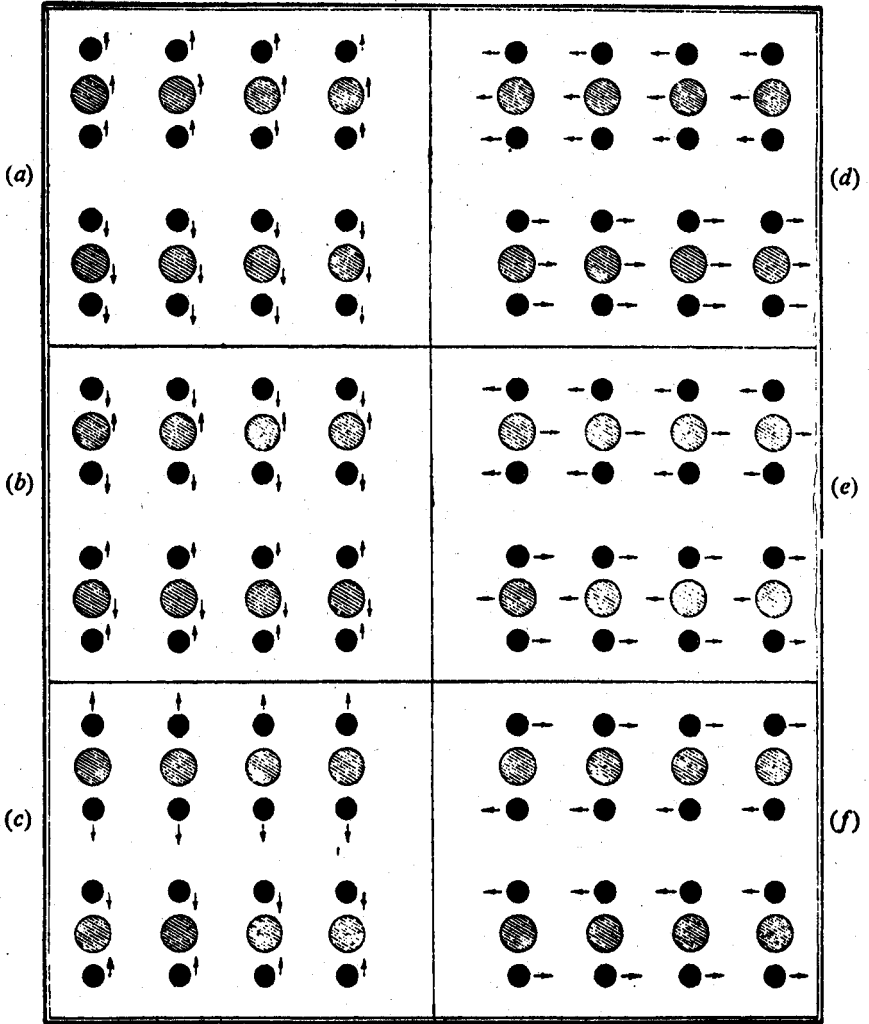


Figure 4. (a), (b), (c), (d), (e) and (f): Oscillations of the octahedral layers of atoms.

opposite phases, the intermediate calcium layer remaining at rest. This movement again would reverse in phase as we pass from one set of three layers to the next. Each of these three modes would have a degeneracy of 4. They are represented in figures 4(a), (b) and (c) respectively. The three corresponding tangential modes are represented in figures 4(d), (e) and (f). They have each a degeneracy of 8. The degeneracies of all the fourteen normal modes when summed up give 69 to which, on adding the three omitted translations, we obtain 72 as the total.

Summary

It is shown that the fluoride structure has 14 different frequencies of vibration corresponding to the same number of normal modes with degeneracies of 3, 3, 3, 6, 3, 6, 3, 6, 4, 8, 4, 8, 4, 8, 4 and 8, besides three translations, making up a total of 72 degrees of freedom. The normal modes have been described and represented diagrammatically.