

# THE NORMAL VIBRATIONS IN SOME TYPICAL CUBIC CRYSTALS

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## 1. Introduction

BHAGAVANTAM AND VENKATARAYUDU (1939) investigated the modes of atomic vibration in various crystals, employing group-theoretical methods. The starting point of their work was the proposition that the vibration-pattern repeats itself in every cell of the crystal lattice. On this basis,  $(3p - 3)$  normal modes are possible,  $p$  being the number of non-equivalent atoms in the lattice cell. Crystals consisting of a single Bravais lattice, *e.g.*, various metals, would have no *discrete* frequencies of atomic vibration, while cubic crystals such as rock-salt and diamond containing two non-equivalent atoms in the cell would have only one such frequency representing a triply degenerate mode of vibration. In the introductory paper of this symposium, it has been shown, however, by Sir C. V. Raman that besides the modes considered by Bhagavantam and Venkatarayudu, there are  $21p$  others, and that a super-cell having twice the dimensions and eight times the volume of the unit cell of the crystal lattice is the basis of the repeating pattern of all the modes of atomic vibration except those which may properly be classified as elastic vibrations of the lattice. The complete description of these modes and the determination of their activity or inactivity in light-scattering and infra-red absorption should be possible with the aid of group-theoretical methods as applied to the atoms contained in the super-cell. The classification of the possible modes into 8 different sets characterised by different phase-relations between the successive equivalent atoms along the three axes of the Bravais lattice should considerably simplify this task. The use of the phase-relations and of the geometric description of the modes of vibration to which they lead however enables us to indicate the normal modes for crystals of not too complex a structure by quite elementary methods. Of particular importance are the cases in which the crystal possesses the symmetry of the cubic system, and the number of non-equivalent atoms in its lattice is not large, being only one, two or three.

## 2. Vibrations of Face-Centred Lattices

We shall first consider the case of the face-centred cubic lattice which is of importance in view of the fact that it forms the basis of the structure

of numerous crystals. As is well known, the unit cell of the lattice in this case is a rhombohedron, the six faces of which are parallel to the octahedral planes in the complete cubic crystal. The planes cutting the three axes of the cell at equal angles are also parallel to the faces of the octahedron. The planes which pass through one rhombohedral axis and *internally* bisect the angle between the other two axes are parallel to the dodecahedral faces, while the planes passing through one axis and *externally* bisecting the angle between the other two are parallel to the cube faces. As explained by Sir C. V. Raman in the introductory paper of the symposium, the geometric character of the atomic movements may be described in terms of these planes. The possible modes fall into one or another of the eight sets given by the relations.

$$\alpha = \pm 1, \beta = \pm 1, \gamma = \pm 1,$$

where  $\alpha, \beta, \gamma$  are the amplitude ratios of the vibrations of successive equivalent atoms respectively along the three axes of the super-lattice cell.

The case in which  $\alpha, \beta, \gamma$  are all positive, which we may denote by the symbol (+ + +), represents translations of the cell as a whole. It is thus excluded from the scheme of normal vibrations and goes over to the "elastic spectrum" of the crystal. The four cases represented by the symbols (- + +), (+ - +), (+ + -) and (- - -) of which the meaning should be obvious represent movements in which the *alternate* planes of atoms parallel to the *octahedral* faces oscillate against each other. Each case has three degrees of freedom associated with it, and the total of 12 degrees of freedom accordingly falls into 4 groups, each with three degrees of freedom representing different directions of movement. A *longitudinal* oscillation of the planes, *i.e.*, a movement along the trigonal axis which is their normal, clearly stands on a different footing from *transverse* oscillations of the planes. For the latter, all directions lying in the octahedral planes are clearly equivalent, and we may therefore choose any two orthogonal directions.

The cases (- - +), (+ - -) and (- + -), each with 3 degrees freedom, may be described as movements of the planes of atoms parallel to the *cube* faces. It is then easy to see that the 9 degrees of freedom associated with these modes fall into two distinct groups. In one group, the alternate planes of atoms parallel to the cube faces oscillate *longitudinally*, while in the other group they oscillate *transversely*. We have thus *four* distinct frequencies of vibration of the atoms contained in the super-cell; the degeneracies associated with them, together with the three translations of the super-cell total up to 24 degrees of freedom.

					Degeneracy
(1) Translations	..	..	..	..	3
(2) The octahedral planes vibrate longitudinally	..			..	4
(3) The octahedral planes vibrate transversely	..			..	8
(4) The cubic planes vibrate longitudinally..	..			..	3
(5) The cubic planes vibrate transversely	..	..		..	6
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TOTAL					.. 24

### 3. *The Zincblende Lattice*

In this crystal, the zinc and sulphur atoms form face-centred cubic lattices which interpenetrate each other, their relative displacement along the trigonal axis being one-fourth of the length of the body-diagonal. We have  $24 \times 2$  or 48 degrees of freedom in all. There are four layers of atoms (alternately Zn and S) in the super-cell parallel to the octahedral and cubic planes. From the general considerations set out by Sir C. V. Raman in the introductory paper of the symposium, it follows that the oscillations of the structure are obtained by doubling up the modes derived above for a face-centred lattice, one set representing movements of the adjacent zinc and sulphur atoms in the same phases, while in the other set they are in opposite phases. We may, in fact, immediately write down the modes with *nine* distinct frequencies arising in this way, the degeneracies associated with them together with the three translations of the super-cell totalling to 48 degrees of freedom.

					Degeneracy
(1) Translations	..	..	..	..	3
(2) Oscillation of the zinc and sulphur lattices against each other					3
(3) Oscillation of the octahedral planes of atoms normally with the phases		+	+	- -	4
(4) Same as (3) but with the phases	..	+	- -	+ +	4
(5) Oscillation of the octahedral planes of atoms transversely with the phases		+	+	- -	8
(6) Same as (5) but with the phases		+	- -	+ +	8
(7) Oscillations of the cubic planes of atoms normally with the phases		+	+	- -	3
(8) Same as (7) but with the phases	..	+	- -	+ +	3
(9) Oscillation of the cubic planes tangentially with the phases		+	+	- -	6
(10) Same as (9) but with the phases	..	+	- -	+ +	6
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TOTAL					.. 48

4. *The Diamond Lattice*

The case is clearly similar to that of the zincblende lattice except that we have now two similar atoms instead of two dissimilar ones. There are four similar layers of carbon atoms in the super-cell parallel to the octahedral planes and also parallel to the cubic planes. The spacing of the layers parallel to the octahedral planes is alternately greater and smaller, and hence the similarity of the two atoms leaves unaffected the distinctness of the frequencies of the modes in which the layers closer to each other move respectively with the same or opposite phases. On the other hand, the four layers of atoms present in the cubic planes are equidistant, and the question therefore arises whether the movements of these planes fall into two distinct sets or merge into one. An examination of a model of a crystal shows however that in respect of oscillations in a direction *normal* to the cubic planes, all the four successive layers are symmetrically and identically circumstanced. Hence, the modes in diamond analogous to those listed as (7) and (8) for the case of zincblende have identical frequencies. On the other hand, the situation is different for oscillations *transverse* to the cubic planes. *Alternate* pairs of atoms in the planes parallel to the cubic faces appear laterally displaced with respect to each other. Hence, the modes of oscillation in which the closely adjacent layers of carbon atoms move transversely with the same or the opposite phases are quite distinct and their frequencies are different. We have accordingly the following scheme of normal vibrations for diamond, giving *eight* distinct frequencies.

		Degeneracy
(1) Translations .. .. .	3	3
(2) Oscillation of the two interpenetrating lattices against each other .. .. .	3	3
(3) Oscillation of the octahedral planes of atoms normally with the phases	+ + - -	4
(4) Same as (3) with the phases .. ..	+ - - +	4
(5) Oscillation of the octahedral planes of atoms transversely with the phases	+ + - -	8
(6) Same as (5) with the phases .. ..	+ - - +	8
(7) Oscillation of the cubic planes of atoms normally with the phases	or + - - +	6
(8) Oscillation of the cubic planes of atoms transversely with the phases .. ..	+ + - -	6
(9) Same as (8) with the phases	+ - - +	6
	TOTAL ..	48

5. The Rock-Salt Lattice

Here, the sodium and chlorine ions form face-centred lattices which interpenetrate in such a manner that in the octahedral planes, the two sets of ions appear separately in alternate and equidistant layers, while in the cubic planes, they also appear in equidistant layers, but interspersed. The five sets of possibilities for the case of a face-centred lattice therefore get doubled up as in the case of zincblende, but the description of the modes would be different owing to the altered nature of the atomic arrangements. It is evident that the layers of sodium ions lying in the octahedral planes can oscillate against each other independently of the chlorine ions, and *vice versa*. On the other hand, in the cubic planes, the oscillations of the two sets of ions are necessarily coupled with each other. We have thus the following scheme for the rock-salt lattice giving *nine* distinct frequencies.

	Degeneracy
(1) Translations .. .. .	3
(2) Oscillation of the sodium and chlorine lattices against each other .. .. .	3
(3) Oscillation of the sodium layers against each other normally to the octahedral planes .. .. .	4
(4) Oscillation of the chlorine layers against each other normally to the octahedral planes .. .. .	4
(5) Same as (3) but transversely .. .. .	8
(6) Same as (4) but transversely .. .. .	8
(7) (a) } Coupled oscillation of the sodium and chlorine ions normally to the	3
(7) (b) } cubic planes .. .. .	3
(8) (a) } Coupled oscillation of the sodium and chlorine ions tangentially to the	6
(8) (b) } cubic planes .. .. .	6
TOTAL ..	48

6. The Fluorspar Lattice

The fluorite structure differs from that of zincblende and diamond in having *three* interpenetrating face-centred lattices instead of two, all the eight places within the cubic cell being occupied by the F ions instead of four being empty as in the diamond structure. We have in all  $24 \times 3$  or 72 degrees of freedom, and the modes of vibration may be derived from those of a face-centred lattice by considering the three possible alternatives; (a) the Ca and the two F ions are all in the same phase of vibration; (b) the Ca ion is one phase and the two F ions in the opposite phase; and (c) the two F

ions move in opposite phases, the Ca ions being at rest. In the octahedral planes, the Ca and F ions appear in distinct layers at unequal intervals, each Ca layer having two F layers disposed symmetrically on either side. On the other hand, in the cubic planes, the atoms appear in equidistant layers, the Ca ion and the F ions jointly occupying the alternate layers. We have accordingly the following scheme of normal modes for the fluorite lattice, giving us fourteen distinct frequencies of vibration.

							Degeneracy
(1) Translations	..	..	..	..	..	..	3
(2) Oscillation of the Ca lattice jointly against the two F lattices	..	..	..	..	..	..	3
(3) Oscillation of the two F lattices against each other, the Ca lattice being at rest	..	..	..	..	..	..	3
(4) Oscillation of the octahedral planes normally against each other with the phases		+	+	+	-	-	-
		F	Ca	F	F	Ca	F
(5) Same as (4) with the phases	..	-	+	-	+	-	+
		F	Ca	F	F	Ca	F
(6) Same as (4) with the phases	..	+		-	-		+
		F		F	F		F
(7) Same as (4) but transversely	..			..			8
(8) Same as (5) but transversely	..			..			8
(9) Same as (6) but transversely	..			..			8
(10) Oscillation of the cubic planes normally with the phases		+	+	-	-		
		Ca	F <sub>2</sub>	Ca	F <sub>2</sub>		3
(11) Same as (10) with the phases	..	+	-	-	+		
		Ca	F <sub>2</sub>	Ca	F <sub>2</sub>		3
(12) Same as (10) with the phases	..	-	+	+	-		
		F	F	F	F		3
(13) Same as (10) but transversely	..			..			6
(14) Same as (11) but transversely	..			..			6
(15) Same as (12) but transversely	..			..			6
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						TOTAL	.. 72

### 7. The Vibrations of Body-Centred Lattices

The unit rhombohedral cell in this case has its faces parallel to *three* of the dodecahedral planes of the cubic crystal, while the planes which pass through one rhombohedral axis and internally bisect the angle between the other two are also *three other* dodecahedral planes orthogonal to the first set. It follows that all the six cases (+ + -), (+ - +), (- + +),

(+ - -), (- + -) and (- - +), each of which is associated with 3 degrees of freedom, represent movements of the planes of atoms lying in the dodecahedral planes alternately in opposite phases. There are 6 such planes, and allowing three orthogonal directions of movement in each case, a total of 18 degrees of freedom is accounted for. The three orthogonal directions of movement of the atoms lying in a dodecahedral plane are evidently (1) normal to it and parallel to a face-diagonal; (2) tangential to it and parallel to a cube-edge and (3) tangential to it and parallel to a face-diagonal, and these represent distinct cases. The case (+ + +) represents translations of the super-cell, while the case (- - -) represents an oscillation of all the atoms located at the cube-corners moving in the same phase against all the atoms located at the body-centres moving together in the opposite phase.

The 24 degrees of freedom of the atoms contained in the super-cell have accordingly to be grouped in the following manner, giving *four distinct* frequencies.

	Degeneracy
(1) Translations .. .. .	3
(2) Oscillations of the alternate dodecahedral planes against each other normally to themselves along a face-diagonal of the cube .. .. .	6
(3) Oscillations of the alternate dodecahedral planes against each other tangentially to themselves along a cube edge ..	6
(4) Oscillations of the alternate dodecahedral planes against each other tangentially along a face-diagonal of the cube ..	6
(5) Oscillations of the body-centre atoms against the cube-corner atoms in any three orthogonal directions .. ..	3
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TOTAL ..	24

### 8. *The Cæsium Chloride Lattice*

This structure consists of two simple cubic lattices interpenetrating each other in such manner that the Cs ions are located at the body-centres of the cubic lattice formed by the Cl ions and *vice versa*. As a preliminary to the discussion of this case, therefore, we have to write down the modes of vibration for a simple cubic lattice.

The following scheme of modes for a simple cubic lattice is almost self-explanatory in view of the preceding detailed consideration of the face-centred and body-centred lattices.

	Degeneracy
(1) Translations .. .. .	3
(2) Cubic planes vibrating alternately in opposite phases, normally .. .. .	3
(3) Same as (2) but tangentially .. .. .	6
(4) Dodecahedral planes vibrating alternately in opposite phases tangentially along a cube axis .. .. .	3
(5) Dodecahedral planes vibrating alternately in opposite phases along the two dodecahedral axes in the perpendicular plane .. .. .	6
(6) Octahedral planes vibrating alternately in opposite phases in three orthogonal directions .. .. .	3
<b>TOTAL</b> ..	<b>24</b>

The introduction of a second interpenetrating lattice will result in all these six possibilities being doubled up, corresponding respectively to the cases in which the two adjacent non-equivalent atoms vibrate in the same phase or in opposite phases. It may be remarked that in the cubic planes the Cs and the Cl ions appear alternately in distinct and equidistant layers. Accordingly, we have the following scheme of normal vibrations for the CsCl lattice.

	Degeneracy
(1) Translations .. .. .	3
(2) The Cs and the Cl lattices vibrate against each other along any 3 orthogonal directions .. .. .	3
(3) The Cs ions in the cubic planes vibrate against each other with alternate planes in opposite phases, normally ..	3
(4) Same as (3) but tangentially .. .. .	6
(5) Movement of the chlorine layers in the alternate cubic planes against each other, normally .. .. .	3
(6) Same as (5) but tangentially .. .. .	6
(7) } Coupled oscillations of the Cs and Cl ions in the dodeca-	
} hedral planes with alternate planes .. .. .	3 }
(8) } vibrating normally in opposite phases.. .. .	3 }
(9) } Same as (7) but tangentially .. .. .	6 }
(10) }	6 }
(11) Alternate Cs layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions .. .. .	3
(12) Similar motion as above of the chlorine layers .. .. .	3
<b>TOTAL</b> ..	<b>48</b>

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*Summary*

The normal modes of vibration of the simple cubic, body-centred and face-centred lattices as well as of the zincblende, diamond, rock-salt, flourspar and caesium chloride lattices have been derived by simple geometric methods on the basis of the fundamental ideas set out by Sir C. V. Raman in the introductory paper of the symposium. It is shown that the lattices mentioned have 5, 4, 4, 9, 8, 9, 14 and 11 distinct frequencies respectively.

REFERENCES

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| See also S. Bhagavantam                | .. <i>Ibid.</i> , 1941, <b>13</b> , 547.               |
| Sir C. V. Raman                        | .. <i>Ibid.</i> , 1943, <b>18</b> , 237.               |
| See also Sir C. V. Raman               | .. <i>Ibid.</i> , 1941, <b>14</b> , 459.               |