

# THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

## Part II. The Free Modes of Atomic Vibration

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A WELL-KNOWN theorem in classical dynamics 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 a 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. This identity or opposition of phase is a fundamental property of a normal mode of vibration. In the absence of this phase-relationship, the possible movements of the particles would be infinitely varied and hence incapable of enumeration.

The theory of the specific heats of crystals has, of necessity, to be based on the theorem in classical mechanics stated above and on the principles of the quantum theory and of thermodynamics. It identifies the thermal energy of the crystal with the sum-total of the quanta of vibrational energy of the oscillators of various frequencies constituting the crystal. If these oscillators are correctly identified and enumerated, their total number should come out as equal to the number of degrees of dynamical freedom of the system, *viz.*, thrice the number of atoms comprised in the crystal. This remark serves to remind us that the particles with which we are concerned in the specific heat problem are the atoms. It also emphasises that the vibrational modes enumerated should be normal modes, *viz.*, modes in which the individual atoms all vibrate with the same frequency and in the same or opposite phases. It thus becomes clear that the core of the specific heat problem is the answer to the following question: do the atoms located in the structure of the crystal possess any normal modes of vibration having the stated characters and 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 crystal structure?

The questions raised above can be answered in the following manner. We make use of the fundamental property of a crystal that the 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. Since the modes of free vibration of the structure constitute such a property, we are justified in the inference that a vibration having the stated characters of a normal mode should remain unaltered and continue to be a normal mode following a unit translation. This can 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. When  $n = 1$ , in other words, when the atoms in the crystal occupy the points of a simple Bravais lattice, we have only 21

modes of the second species, besides 3 translations. When  $n = 2$ , we have besides the 3 translations, 3 normal modes of the first species and 42 normal modes of the second species.

When the crystal exhibits a high degree of symmetry, *e.g.*, cubic symmetry, the number of normal modes remains the same, but many of the modes are similar to each other and the number of *distinct* frequencies is thereby greatly reduced. In the particular case of the alkali halides, the 3 normal modes of the first species exhibit a single triply-degenerate frequency, while the remaining 42 modes have only 8 distinct frequencies, *viz.*, two frequencies each with a degeneracy of 4, two frequencies each having a degeneracy of 8, two frequencies each with a degeneracy of 3 and two others each with a degeneracy of 6, thus totalling up to 42 distinct modes of the second species.

The degeneracies listed above arise by reason of the geometric similarity of the various sets of normal modes. The triply degenerate frequency of the first species represents an oscillation of the two sets of non-equivalent atoms along one or another of the three cubic axes. The triply degenerate frequencies of the second species represent vibrations of the two sets of non-equivalent atoms lying in the cubic planes normally to themselves. The sixfold degenerate frequencies similarly represent vibrations of the layers of atoms appearing in the cubic planes tangentially to themselves. Fourfold degeneracy arises when the layers of atoms parallel to the octahedral planes move normally to themselves. Eightfold degeneracy arises when the atoms in the octahedral layers move tangentially to those layers.

The geometry of the various modes of vibration can be readily established. We begin with the case of a simple face-centred cubic lattice, the 24 normal modes of which are listed below, the phases of oscillation alternating in the successive planes.

<i>Description of the modes</i>	<i>Degeneracy</i>
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 octahedral planes .. .. .	8
TOTAL ..	24

The foregoing descriptions can be readily derived by considering the atomic movements in a face-centred cubic lattice for each of the 8 different possibilities regarding their phase-relationships discussed earlier. The directions of atomic movement are those indicated by the symmetry of the crystal.

In the alkali halides, we are concerned with two similar face-centred cubic lattices which interpenetrate each other, their points being occupied respectively by the metal and the halogen atoms. In the cubic planes of the resulting structure, the metal and halogen atoms appear interspersed in the same layers, while in the octahedral planes, they appear in distinct but equidistant layers. Since the phases of oscillation of the metal and halogen atoms may be either the same or the opposite, the 24 modes listed above are doubled up, giving us 48 modes in all. The three translations of each lattice separately are replaced by three translations in which the two lattices move together in the same phase, and by three oscillations respectively along the three cubic axes in which the two lattices move in opposite phases.

	<i>Degeneracy</i>
I. Oscillation of the metal and halogen atoms in opposite phases	3
II. Coupled oscillations of the metal and halogen atoms in the cubic planes:	
(a) Tangential to the planes in opposite phases .. ..	6
(b) Normal to the planes in the same phase .. ..	3
(c) Normal to the planes in opposite phases .. ..	3
(d) Tangential to the planes in the same phase .. ..	6
III. Oscillations of the atoms appearing in the octahedral layers:	
(a) Lighter atoms normal to the planes .. ..	4
(b) Lighter atoms tangential to the planes .. ..	8
(c) Heavier atoms normal to the planes .. ..	4
(d) Heavier atoms tangential to the planes .. ..	8
IV. Translations of both lattices in the same phase .. ..	3
<b>TOTAL</b> ..	<b>48</b>

The nine modes have been listed in the foregoing table, the four vibrations of the cubic layers and the four vibrations of the octahedral layers being arranged amongst themselves in the descending order of their frequencies of vibration as indicated by the dynamical theory to be presented later in the memoir.

#### SUMMARY

It is shown that crystals having the rock-salt structure have nine different frequencies of atomic vibration exhibiting the features of normal modes. One of them is an oscillation of the metal and halogen atoms in opposite phases. Four others are coupled oscillations of the atoms appearing in the cubic layers, while the remaining four are oscillations of the atoms in the octahedral layers. The oscillations in these eight modes alternate in phase from layer to layer and are respectively normal or tangential to those layers.