

The spectroscopic behaviour of rock-salt and the evaluation of its specific heat—Part I. The structure and its free vibrations

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1. Introduction

Sodium chloride, as is well known, crystallises in the cubic system and is therefore optically isotropic. If the material is pure, the crystals are colourless and transparent over a wide range of wavelengths in the spectrum. The absorption is negligible between 0.2μ and 10μ , and is quite small between 10μ and 15μ , but increases rapidly as we proceed further out into the infra-red. The technical possibility of preparing crystals of the material in large sizes from melts and of cutting out prisms from such material has made rock-salt play a highly important role in the development of infra-red spectroscopy. The range of wavelengths covered by recording instruments using NaCl prisms is from 1μ to 15μ .

The simplicity of the composition and structure of rock-salt and the ready availability of the material make its physical properties, including especially its optical and spectroscopic behaviour, matters of very great interest from a theoretical point of view. Quite naturally, therefore, a great volume of literature exists describing the results of experimental studies and also of theoretical discussions concerning these matters. In the present memoir we are concerned with the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths and its relation to the crystal structure and thermal properties of the material. It is, therefore, appropriate that we briefly recall here the major facts which have emerged from the experimental researches on the subject.

Three different methods are available for the study of the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths. The first is that of determining the variation of the reflecting power of rock-salt in the region of great wavelengths. Earlier investigations indicated that the reflecting power is quite small up to about 35μ and that it commences to rise steeply beyond 40μ . It exceeds 80% between 50μ and 55μ , and then drops to 70% at 60μ and to 40% at 70μ . The further diminution at still greater wavelengths is relatively more slow.

The more recent investigations indicate a reflecting power greater than 90% between $50\ \mu$ and $56\ \mu$, and also reveal additional features in the region of lower wavelengths which will be referred to later.

The second method is the study of the absorption of infra-red radiation in its passage through the material. The spectral transmission curve depends very much on the thickness of material traversed. The absorption coefficient which is small at $15\ \mu$ increases more and more steeply with increasing wavelength as we approach the region in which the reflecting power becomes large. In the latter region, the cut-off due to the reflection at the two surfaces of the plate is superposed upon the loss due to absorption. To obtain any sensible transmission in this region, very small thicknesses of the material are needed. Very interesting results were obtained and reported by Czerny (1930). Mentzel (1934) observed that the curve of percentage transmission through a rock-salt plate $24\ \mu$ thick showed an arrest between $34.5\ \mu$ and $35.5\ \mu$, the curve running horizontally between these wavelengths though it goes down steeply with increasing wavelength both above and below this range. Barnes and Czerny (1931) found that the curve of transmission through a plate $8\ \mu$ thick likewise runs horizontally in the wavelength range between $40\ \mu$ and $44\ \mu$. These authors also studied the transmission through evaporated films of NaCl of various thicknesses between $3.6\ \mu$ and $1.35\ \mu$. The percentage transmission exhibited as a graph in their paper shows two downward dips located at $40\ \mu$ and $50\ \mu$ respectively, besides the highly pronounced minimum of transmission around $60\ \mu$. The thinner films showed a further small dip in the transmission curve at about $71\ \mu$. Mentzel in his paper listed $34\ \mu$, $40.5\ \mu$ and $51\ \mu$ as minor maxima of absorption and $61.1\ \mu$ as the major absorption wavelength for NaCl. He also listed $33\ \mu$, $41\ \mu$, $42.5\ \mu$, $47\ \mu$ and $60\ \mu$ as minor absorption peaks and $70.7\ \mu$ as the major absorption wavelength for KCl. The appearance of a whole series of minor absorption peaks is thus evidently a characteristic feature of the spectroscopic behaviour of the alkali halides.

A third and very powerful method for the study of the spectroscopic behaviour of rock-salt was initiated and employed by Rasetti (1931). The transparency of the crystal in the ultra-violet region enables the powerful $2536.5\ \text{\AA}$ radiation emitted by a water-cooled and magnet-controlled mercury arc to be used for illuminating the interior of the solid and for recording the spectrum of the scattered radiation emerging from its interior. Rasetti made the noteworthy discovery that the spectrum thus recorded exhibits a sharp and intense line with a wave-number shift of $235\ \text{cm}^{-1}$ from the exciting radiation. This is the most conspicuous feature observed in the spectrum which commences with a sharp rise in intensity from zero to a large value at the wave-number shift at $360\ \text{cm}^{-1}$ and extends towards smaller frequency-shifts. The drop of intensity beyond the sharply-defined peak of the line at $235\ \text{cm}^{-1}$ to zero in the region of smaller frequency-shifts is also quite steep but is broken by the presence of a feeble band which covers the region of frequency-shifts between $220\ \text{cm}^{-1}$ and $184\ \text{cm}^{-1}$. The upper end of the spectrum exhibits a peak of intensity which is both smaller and not so well defined

as the line at 235 cm^{-1} and covers the region of frequency-shifts between 360 cm^{-1} and 340 cm^{-1} . Clearly separated from both of these principal features in the spectrum and approximately midway between them appears a group of four maxima of intensity located respectively at the frequency-shifts of 314 cm^{-1} , 300 cm^{-1} , 280 cm^{-1} and 258 cm^{-1} . These are clearly separated from each other in the spectrum as well as in its microphotometer record.

It is proposed in this memoir to consider the spectroscopic behaviour of rock-salt in its fundamental aspects and also in relation to its activity in infra-red absorption and reflection and its activity in the scattering of light with change of frequency. A satisfactory explanation is given for the facts established by experimental study in both of these fields of research. The thermal energy content of rock-salt and the variation of its specific heat with temperature also receive a quantitatively satisfactory explanation in terms of the spectroscopic properties of the crystal.

2. The structure of rock-salt

All crystals may be described as assemblages of two kinds of particles differing in their nature and properties, being respectively the heavy positively charged nuclei and the light negatively charged electrons. These two types of particles by reason of their mutual interactions hold each other in place and form a regularly arranged grouping in space. The massive nuclei are located at specific points in the structure but are capable of executing oscillatory movements about those positions. On the other hand, since the mass of the electrons is very small, they are appropriately described as forming a cloud which envelops the nuclei and fills up the volume of the solid. The attraction of a nucleus on the electrons in its immediate vicinity results in a closer association between them. As a consequence, the field due to each positive charge is more or less completely cancelled out at a distance from it. Part of the electronic cloud however remains subject to the influence of more than one nucleus and this plays a highly important role in holding the crystal together as a coherent solid. The physical properties of the crystal and especially its spectroscopic behaviour in the lower ranges of frequency are largely determined by it.

The numbers of Na and Cl nuclei in rock-salt are equal and their dispositions in the structure are very similar. The usual description of the structure is that it consists of two interpenetrating face-centred cubic lattices, the points of which are occupied respectively by Na and Cl nuclei. Each Na nucleus appears surrounded by six Cl nuclei and each Cl nucleus by six Na nuclei, the distance between the nearest neighbours being one-half of the edge-length of the cubic cell as measured from one Na nucleus to the next or from each Cl nucleus to the next. In the atomic layers parallel to the cubic faces of the crystal, the Na and the Cl nuclei appear interspersed in such manner that each Na nucleus has four Cl nuclei as its

immediate neighbours, while each Cl-nucleus has four Na nuclei similarly situated with respect to it. On the other hand, in the atomic layers which are equally inclined to all the cubic axes, in other words are parallel to the faces of the octahedron, the Na nuclei and Cl nuclei do not appear together but are located in separate but equidistant layers. The distance a between neighbouring Na and Cl nuclei is also the spacing of successive atomic layers parallel to the cubic faces, while the separation of each Na layer from either of the two Cl layers adjacent to it in the octahedral planes is $a/\sqrt{3}$.

The structure of rock-salt may also be described as arising from the juxtaposition of two rhombohedral lattices displaced with respect to each other, the points of the two lattices being occupied respectively by Na and by Cl nuclei. Eight nuclei occupying the corners of a rhombohedron delineate the cells of each lattice. Six of them are located at the face-centres of a cube while the remaining two are located at opposite cube-corners.

3. The free vibrations of the structure

The atomic nuclei being enormously more massive than the electrons, it is permissible, when we seek to find and enumerate the normal modes of vibrations of the nuclei about their positions of equilibrium in the structure, to regard the electrons as being in the nature of massless elastic springs holding the nuclei in their places. Since the crystal also consists of an enormous number of similar and similarly situated structural units each containing its quota of atomic nuclei which is the same for all the structural units, we may justifiably adopt the following procedure in dealing with the problem. We proceed on the basis of the theorem in the classical mechanics which states that the small vibrations of a system of connected particles about their positions of equilibrium are a summation of a set of normal modes in each of which all the particles of the system vibrate in the same or opposite phases, while the total number of normal modes is the same as the number of degrees of dynamical freedom of the system of particles. It follows that the vibrations of the atomic nuclei should satisfy the following two requirements: in any normal mode, the nuclei should all vibrate in the same or opposite phases; a normal mode should remain a normal mode following a unit translation of the crystal along any one of the three axes of the crystal structure. Taking these two principles together, it follows as a necessary consequence that following a unit translation of the crystal, the atomic nuclei in the structural unit would retain the same amplitudes of vibration while their phases would either *all* remain unaltered or else would *all* be reversed. Thus, we have two species of normal modes satisfying the requirements for each of the three axes of the structure, and since these possibilities are independent, we have $2 \times 2 \times 2$ or 8 species of normal modes in all.

We may readily apply these results to the case of a simple rhombohedral lattice at whose points only one kind of nucleus is located. Each of the 8 species of

normal modes corresponds to a different disposition of the phases of vibration of the 8 nuclei situated at the corners of the cell. As each nucleus has three degrees of dynamical freedom, we have 24 available degrees of freedom. The nature of the 24 different possible movements allowed by these degrees of freedom can be readily ascertained by considering the different combinations of the phases of vibrations of the nuclei located at the points of the rhombohedral lattice. Three of them are movements of all the nuclei in the same phase, in other words, simple translations of the whole group of nuclei. Nine of them represent movements in which the nuclei lying in the same cubic plane move in the same phase while those in the adjoining cubic planes move in the opposite phase. The remaining twelve represent movements in which the nuclei lying in the same octahedral plane move in the same phase while those lying in the adjacent octahedral plane move in the opposite phase. These two groups may be further sub-divided by considering the directions of movement indicated by the cubic symmetry of the whole structure. Thus the 24 possible movements may be listed as below, it being noted that the oscillations of the nuclei located in the successive planes (cubic or octahedral as the case may be) are in opposite phases.

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

Thus, the 24 degrees of dynamical freedom of the group of 8 nuclei located at the corners of the rhombohedral cell are duly accounted for, 3 of them as simple translations and the remaining 21 as normal modes which fall into four groups with degeneracies 3, 6, 4 and 8 respectively, arising by reason of the cubic symmetry of the structure.

In the rock-salt structure we are concerned with two sets of nuclei (Na and Cl respectively) occupying the points of two similar rhombohedral lattices. Hence the foregoing description would apply to each of them. The phases of oscillation of the Na and Cl nuclei in each of the 24 modes may be either the same or opposite. Hence, we have 48 normal modes in all, corresponding to the 48 degrees of dynamic freedom of a group of 16 nuclei, 8 of Na and 8 of Cl. 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 of the two lattices moving in opposite phases, the movement of the Na nuclei being balanced by the movement of the Cl nuclei in the contrary direction. Besides these, we have *four modes* which are coupled oscillations of the Na and Cl nuclei, two being normal and two tangential to the cubic planes with the Na and the Cl nuclei in those planes moving

respectively in the same or in the opposite phases with respect to each other; also *four modes* in which the *Na nuclei alone* or the *Cl nuclei alone* present in the octahedral planes oscillate respectively normal and tangential to those planes.

4. The normal modes of vibration

The nine normal modes of vibration and the three residual translations are listed below as a table:

	Degeneracy
I. Oscillation of the Na and Cl lattices in opposite phases	3
II. Coupled oscillations of the Na and Cl nuclei 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 nuclei appearing in the octahedral layers:	
(a) Na nuclei normal to the planes	4
(b) Na nuclei tangential to the planes	8
(c) Cl nuclei normal to the planes	4
(d) Cl nuclei tangential to the planes	8
IV. Translations of both lattices in the same phase	3
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Total	48
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The nine modes have been numbered and shown in the table in a particular order for reasons which will presently be explained. Figures 1, 2 and 3 in the text below illustrate the character of the oscillations in each case, the numbering of the figures following the same order as in the table. The hatched circles represent the Na nuclei and the open circles the Cl nuclei. Figures 1 and 2 represent the structure viewed along, a cubic axis; the cubic layers depicted are assumed to be horizontal, and the arrows represent the movements of the nuclei. Figure 3 is a view of the structure in a direction which is the intersection of an octahedral plane with a diagonal plane of the cube. It exhibits the Na and the Cl nuclei as appearing in distinct layers parallel to the faces of the octahedron.

5. The frequencies of the normal modes

It would obviously be useful if the nine modes of vibration described and pictured above can be arranged in descending order of frequency, as this would greatly

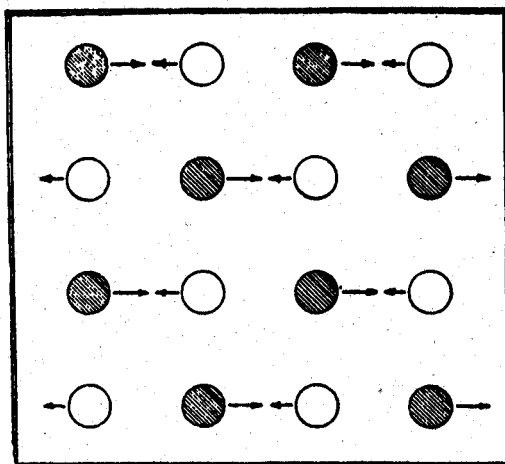


Figure 1. Oscillation of the Na and the Cl lattices in opposite phases.

facilitate the comparison with the spectroscopic data and a definitive determination of their frequencies.

The mode illustrated in figure 1 evidently stands apart in a category by itself. This oscillation repeats itself from cell to cell, whereas in all the other eight modes the phase of vibration alternates from layer to layer. It may therefore be safely presumed that figure 1 represents the mode of highest frequency. The coupled oscillations of the Na and Cl nuclei in the cubic planes have been listed and pictured in the order of figures 2(a), (b), (c) and (d). This would clearly also represent their arrangement in descending order of frequency. For, the movement in figure 2(a) most closely resembles that in figure 1 and the movement in figure 2(b) rather less closely, while the movements in figures 2(c) and 2(d) are clearly of a different nature. Indeed, figure 2(d) closely resembles a transverse oscillation of the cubic layers as a whole and hence should have the lowest frequency of the four modes and indeed also of all the nine modes.

Since the masses of the Na nuclei are much smaller than those of the Cl nuclei, it is evident that the modes depicted in figures 3(a) and 3(b) would both have higher frequencies than the modes shown in figures 3(c) and 3(d). The mode shown as figure 3(a) would evidently have a higher frequency than the mode shown as figure 3(b), since the Na layers approach each other normally in one case and move tangentially to each other in the other case. Likewise, the frequency of mode III(c) would be higher than that of mode III(d). But the differences between the normal and tangential modes in either case would not be very large for the reason that the six nearest neighbours of each oscillating nucleus are situated symmetrically around it and hence its interactions with them would be the same in both cases.

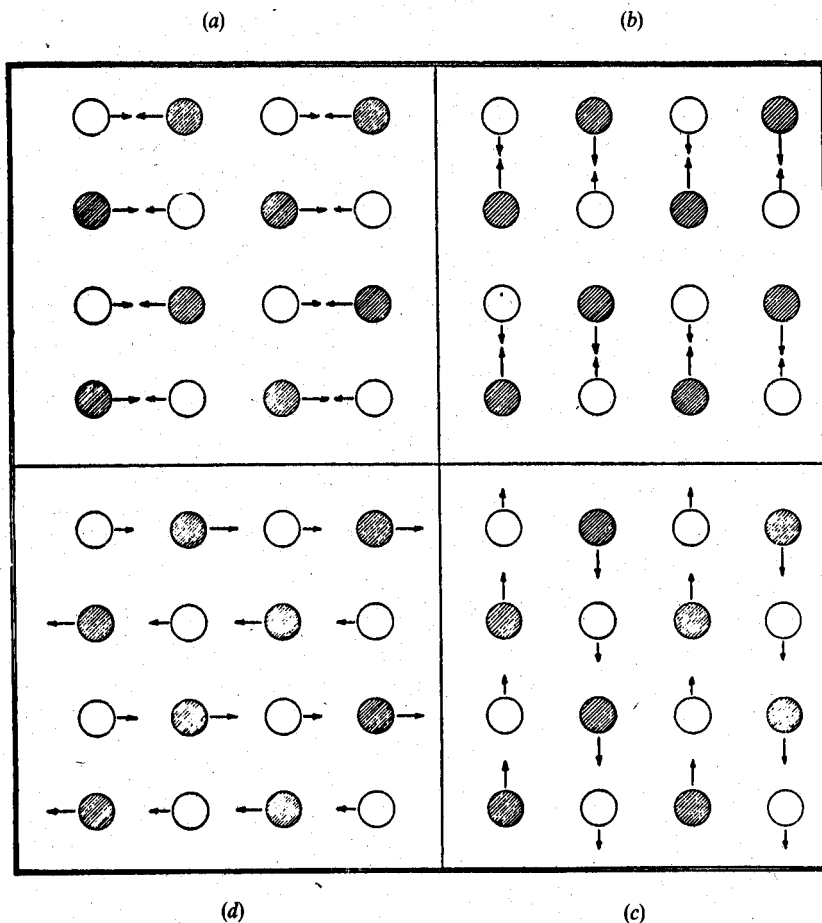


Figure 2. (a), (b), (c) and (d): Coupled oscillations of the Na and Cl nuclei in the cubic layers.

6. Approximate evaluation of the frequencies

We may go a little further and make a rough computation of the frequencies of all the nine modes on the basis of a simplified picture of the internuclear forces which are operative in a vibration. We notice that in figure 1 the movements are along a cubic axis of the crystal and represent an approach of a Na nucleus to the Cl nucleus which is its nearest neighbour on one side and a recession from the Cl nucleus on the other side. (We may interchange the Na and the Cl nuclei in this description.) The forces brought into play would be principally those resisting

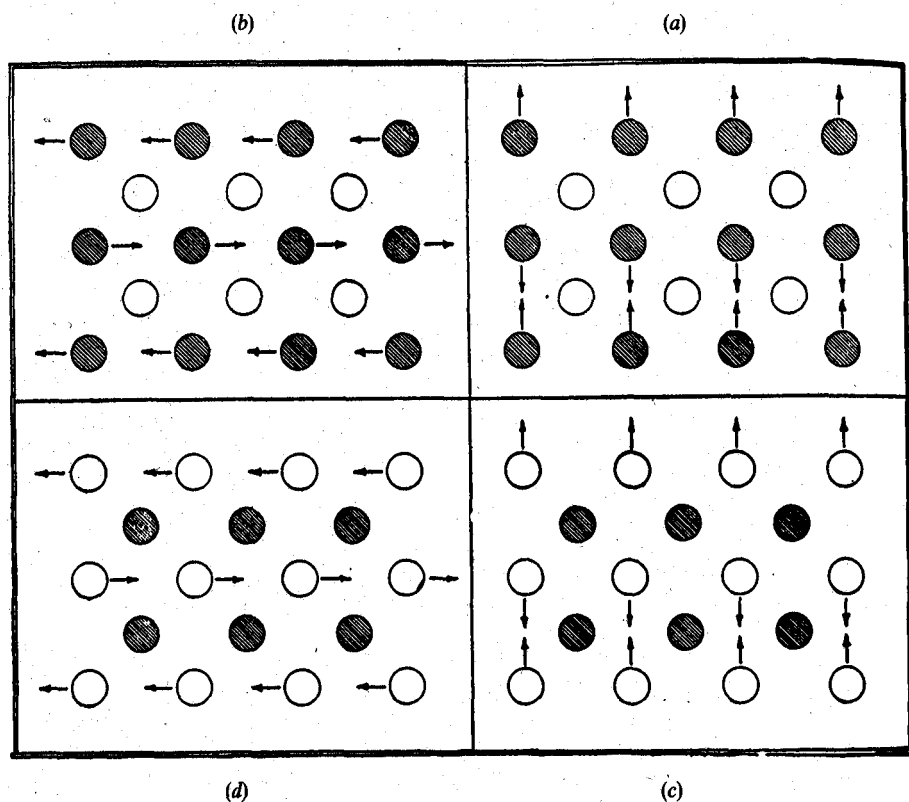


Figure 3. (a), (b), (c) and (d): Oscillations of the Na and the Cl nuclei in the octahedral layers.

such approach or recession. Of lesser importance would be those resisting the transverse displacement of each Na nucleus with respect to the four other Cl nuclei which are also its nearest neighbours on the perpendicular cubic axes. We shall assume these forces to be respectively proportional to the relative displacements, the constants of proportionality being α and β respectively. We neglect all other interactions. Such neglect is fully justified as regards interactions with more distant nuclei of the same species, since they move with the same amplitudes and phases. Writing down the equations of motion of two adjoining nuclei (Na and Cl respectively) and solving them, we find that the circular frequency of the vibrational mode I is given by

$$\omega_1^2 = (2\alpha + 4\beta)(1/m_1 + 1/m_2),$$

where m_1 and m_2 are respectively the masses of the Na and Cl nuclei.

Considering only the interactions between each Na nucleus and the surrounding six Cl nuclei, and vice versa, the equations of motion may be written down and solved for the two modes represented in figures 2(a) and 2(d). The circular frequencies of these modes may be found on evaluating the two roots of the equation which is obtained as the solution, viz.,

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 16\beta(\alpha + \beta)/m_1 m_2 = 0.$$

Likewise, on the same basis, the equations of motion for the two modes represented by figures 2(b) and 2(c) may be written down and solved. Their circular frequencies may be found from the two roots of the equation

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 32\alpha\beta/m_1 m_2 = 0.$$

It will be noticed from these equations that the frequencies of the two coupled oscillations in each case are related to the frequency ω_I of mode I by the simple relations

$$\omega_{II} a^2 + \omega_{II} d^2 = \omega_I^2$$

and

$$\omega_{II} b^2 + \omega_{II} c^2 = \omega_I^2.$$

It is evident also from these relations that mode I has the highest frequency of all the five modes considered. They can all be computed if the values of α and β are known. Alternatively, if the frequency of mode I is known and some reasonable assumption is made for the ratio α/β , as for example that $\alpha = 2\beta$, the frequencies of the four other coupled oscillations of the Na and Cl nuclei can be found from that of the mode of highest frequency.

Assuming that the frequency of mode I expressed in wave-numbers is 180 cm^{-1} and that $\alpha = 2\beta$, we find the following values for the frequencies of the four other modes also in wave-numbers:

Frequency of mode I (assumed)	180 cm^{-1}
Frequency of mode II(a) (calculated)	158 cm^{-1}
Frequency of mode II(b) (calculated)	140 cm^{-1}
Frequency of mode II(c) (calculated)	113 cm^{-1}
Frequency of mode II(d) (calculated)	87 cm^{-1}

Thus, the descending sequence of frequency in which these five modes were arranged in the table and numbered in the figures is seen to be correct. It should be remarked however that the calculations ignored the interactions between each nucleus and the others of the same species present in the adjacent layers and moving with the same amplitude but in an opposite phase. As these nuclei are however situated further from it than the nuclei whose interactions have been considered, the calculations of frequency cannot be seriously in error. But they can only be considered only as approximations.

Considering now the four modes pictured as figures 3(a), (b), (c) and (d) it is obvious that their frequencies would be very simply related to that of mode I, provided that we take into account only the interactions between each Na nucleus and the six Cl nuclei around it, and vice versa. The relevant formulae are:

$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_1$$

for the modes III(a) and III(b) and

$$\omega_{\text{III}}^2 = (2\alpha + 4\beta)/m_2$$

for modes III(c) and III(d). If we take the frequency of mode I as 180 cm^{-1} in wave-numbers, that of modes III(a) and III(b) come out as 140 cm^{-1} and that of modes III(c) and III(d) as 113 cm^{-1} . This procedure for deducing the frequencies results in the modes of vibration tangential and normal to the octahedral planes having the same value. This is a consequence of our having neglected the interactions between the nuclei of the same kind which are in relative movement and hence would influence the frequencies of the vibration. As will be seen from figures 3(a), (b), (c) and (d), the adjacent layers of similar nuclei slide past each other in the tangential modes, while they alternately approach and recede from each other in the normal modes. The interactions between the moving layers would, in these circumstances, not be negligible. Their influence on the frequencies of vibration would evidently be greater in the normal modes than in the tangential ones, thereby making the frequencies in these cases different. It is also evident that the frequencies of 140 cm^{-1} and 113 cm^{-1} as computed and shown above would be slightly smaller than the correct values for the tangential modes, and definitely less than the correct values for the normal modes. Each moving nucleus comes under the influence of six nuclei of the same kind and six nuclei of the other kind in its movement, the distances between the interacting nuclei being $2a/\sqrt{3}$ and a respectively. In these circumstances, an increase of say 10% in the frequencies of the tangential modes and say 20% in the frequencies of the normal modes may be hazarded as a rough estimate of an alteration in the calculated frequencies produced by taking the interactions between like nuclei also into account.

7. Summary

The nine normal modes of free vibration of the rock-salt structure have been deduced theoretically and fully described. They have been arranged in descending order of frequency and an approximate estimate of their frequencies is also given. The mode of highest frequency is that in which the Na and Cl lattices oscillate in opposite phases.

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