THE SPECIFIC HEATS OF THE ALKALI HALIDES AND THEIR SPECTROSCOPIC BEHAVIOUR

Part III. The Interatomic Forces

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WE shall now consider the problem of evaluating the frequency of each of the nine normal modes of vibration of the atoms described in Part II of this memoir. These frequencies are determined by the masses of the atoms, the geometric characters of the vibration and especially by the forces of interaction between the atoms brought into play by reason of their displacements. The evaluation of these forces is indeed the essence of the problem.

We may begin by recalling the characteristic features of the crystal structure of the alkali halides. Each metal atom has six halogen atoms as its immediate neighbours. These are situated on either side of it on the three cubic axes and at the same distance in each case. Likewise, each halogen atom has six metal atoms as its immediate neighbours, also located on the three cubic axes in the same manner. This grouping of the metal and halogen atoms around each other with cubic symmetry determines the architecture of the crystal, and the forces which result in such grouping would necessarily play the leading role in determining the physical properties of the solid.

As has been remarked above, the forces which determine the frequencies of atomic vibration arise by reason of their displacements from their positions of equilibrium. Since the atoms are held together in the crystal by their mutual interactions, what we are really concerned with are their *relative* displacements. We are justified in assuming that the forces which determine the frequencies of vibration of the structure would be principally those due to the displacements relative to each other of the metal and halogen atoms held together in the structure in the manner described above. Considering a particular pair of metal and halogen atoms, it is evident from considerations of symmetry that if a metal atom is displaced with respect to the adjacent halogen atom *along* the cubic axis on which they both lie,

the restoring force would also be along the same axis and that there would be no transverse components. As a first approximation this restoring force may be taken to be proportional to the relative displacement, and if the distance between the two atoms is denoted by d (which is half the lattice spacings in the crystal) and the same is increased or diminished by $\triangle$, the restoring force may be written as $\alpha\triangle$, where α is the force-constant involved.

Likewise, considering a relative displacement $\triangle$ of the two atoms *transverse* to the cubic axes on which they both lie, considerations of symmetry indicate that the restoring force would be parallel to the displacement and hence transverse to the cubic axis, and that there would be no components along the two other perpendicular cubic axes. We may denote the restoring force in this case by $\beta\triangle$, β being the force-constant now involved which would obviously be different from α. We may describe α as the longitudinal force-constant and β as the transverse force-constant. If we assume the metal and halogen atoms to be held together by chemical bonds along the lines joining them, α would be the force-constant for a stretching of the bonds and β the force-constant arising from a change of the bond-angles. It is evident that if a cube of the crystal is subjected to a hydro-static compression, only the bond-lengths would be altered by the stress and not the bond-angles. If, on the other hand, the cube is subject to a shearing stress, in other words, to tractive forces parallel to its faces, the bond-lengths would remain unaltered but the bond-angles would alter. Thus, in terms of atomic interactions, α is related to the macroscopic stresses arising in a cubic compression, while also in terms of atomic interactions, β is related to the macroscopic forces arising in a pure shear. We shall later make use of this correspondence in seeking to find appropriate values for the force-constants α and β.

The considerations set forth suggest that it should be possible by making use of only the two force-constants α and β and giving them appropriately chosen values, to derive a reasonably satisfactory picture of the dynamics of the atomic vibrations in the alkali halides and hence also of the spectroscopic and thermal behaviour of these crystals. Indeed, it will appear later that this anticipation is justified. However, it would not be correct completely to ignore the interactions arising from the relative displacements of the atoms in the crystal other than the nearest neighbours. Actually, besides the six nearest neighbours situated on the cubic axes, each metal atom has eight halogen atoms located at the corners of the cube of edge length $2d$ at the centre of which it is itself located. Likewise, each halogen atom has eight metal atoms situated in a similar manner with respect to it.

The distance between each such pair of metal and halogen atoms is $d\sqrt{3}$, and since this is substantially greater than the distance between adjacent metal and halogen atoms in the crystal, we may assume that the forces arising from their relative displacements would be much less important. There is, however, no difficulty in formally taking them into account in writing down the equations of motion. We may conveniently resolve the relative displacements along each of the three cubic axes, and likewise also resolve the restoring forces along these three axes. Considerations of symmetry indicate that *two* force-constants suffice in all cases to express the ratios of the forces to the displacements. One of them which we shall denote by γ is the ratio of the force to the displacement when they are both parallel to the same cubic axis. The other force-constant relates to the cases in which the force and the displacement are respectively along two mutually perpendicular cubic axes. Since this force-constant does not actually appear in the equations of motion for any of the nine modes of vibrations with which we are concerned, we shall not trouble to give it a symbol.

Each metal atom in the crystal has also twelve metal atoms as its near neighbours and likewise, each halogen atom has twelve halogen atoms as its neighbours. The line joining each atom with the other similar atoms is of length $d\sqrt{2}$ and is equally inclined to two of the cubic axes and perpendicular to the third. If we proceed on the basis of symmetry considerations alone, it follows that three additional force-constants would be required to express the interaction of the metal atoms with each other and likewise three other constants in the case of the halogen atoms. A considerable simplification however becomes possible when we remark that the distance between the interacting atoms is substantially greater than their common diameter. Hence, the restoring force due to a relative displacement may be expected to be sensible only when this is along their line of join and negligible for a transverse displacement. It follows that the force-constants for a displacement along one of the three cubic axes may be neglected and those which refer to movements along the two other axes would be sensibly equal. Accordingly, only one force-constant which we shall denote by ϕ would be required to express the interactions between the metal atoms, and likewise only one constant which we shall denote by ψ to express those between the halogen atoms.

SUMMARY

It is shown that the restoring forces which arise by reason of the relative displacements of the atoms in the alkali halides during a normal

vibration may be expressed by five force-constants which are designated by α, β, γ, ϕ and ψ. The first two are the principal ones and correspond respectively to a stretching of the bonds between adjacent metal and halogen atoms and to a change of the bond-angles. γ is the operative force-constant for relative displacements of metal and halogen atoms separated from each other by a distance $d\sqrt{3}$. ϕ and ψ are the force-constants for the relative displacements of like atoms situated at a distance $d\sqrt{2}$ from each other, ϕ being the constant for the metal atoms and ψ the constant for the halogens.