

The vibration spectra of crystals—Part II. The case of diamond

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Contents

1. Introduction
2. The eigenvibrations
3. The valence forces
4. Numerical evaluation of the eigenfrequencies
5. Activity in light scattering
6. Activity in infra-red absorption
7. The spectroscopic facts
8. Summary

1. Introduction

Of recent years, there has been a great accession of exact knowledge regarding the spectroscopic behaviour of crystals. Much of this knowledge has been gained by the method of investigation introduced by the present writer in the year 1928, namely, the spectral examination of the scattered radiations from crystals illuminated by monochromatic light. Valuable information has also come to hand from the study of luminescence spectra and of absorption spectra in the visible and ultraviolet regions at low temperatures. Considerable progress has also been made in the study of infra-red absorption by crystals. By working with thin films, and also by using the highest possible resolving powers, the inherent difficulties and imperfections of infra-red spectroscopy as applied to solids have been minimised. Critical investigations by these diverse methods concur in showing that the vibration spectrum of a crystal held at a sufficiently low temperature as observed in the infra-red region of frequency is effectively a *line spectrum*. From the fact that several procedures of experimental study which are wholly different in principle agree in their indications, it is clear that the spectra of

crystals are inherently of this nature and not by virtue of any particular method of observing them.

The earlier theories of the subject which were based on ideas derived from the behaviour of elastic solids identified the atomic vibrations in a crystal with an immense number of "waves" of diverse wavelengths and frequencies assumed to be present in it. This hypothesis led to a conception of the nature of the vibration spectrum of a crystal radically different from that stated above, viz., that it is a *continuous spectrum*, both in the acoustic and in the infra-red ranges of frequency. That such a view gained currency was perhaps not surprising at a time when experimental knowledge of the spectroscopic behaviour of crystals was of a meagre description. It is, however, altogether inconsistent with the facts known at present as the result of recent research, as will be shown in this paper and the others following it.

The case of diamond which we shall proceed to consider in detail is by far the most suitable test for any theory of the spectroscopic behaviour of crystals. For, it is the solid of the simplest structure and composition of which the vibration spectrum is amenable to theoretical calculation as well as to experimental study. Indeed, all the possible different methods of spectroscopic investigation—five in number—which can be applied to the study of a crystal have been successfully employed in the case of diamond. A further special advantage presented by diamond is that its vibration spectrum appears spread out over a wide range of frequency. This makes it possible with only instruments of moderate power to ascertain and establish the true nature of its spectrum unambiguously, while with the aid of more powerful instruments, it is possible to discover and demonstrate the finest details of its spectral behaviour. A further and notable advantage which arises from the high frequencies of atomic vibration in diamond is that the secondary effects due to thermal agitation are unimportant in its case even at ordinary temperatures. Such effects are markedly present in the majority of crystals and disturb the intrinsic simplicity of their spectra.

2. The eigenvibrations

As is well known, the structure of diamond may be described as consisting of two similar Bravais lattices of carbon atoms of the face-centred cubic type interpenetrating each other. Each atom in one of the lattices is linked to four atoms in the other lattice by valence bonds along the four trigonal axes of symmetry of the crystal. The atoms in the two lattices appear in distinct layers in the octahedral as well as in the cubic planes. In the former set of planes, they are alternately nearer and farther apart, while in the cubic planes they are equidistant. This disposition of the layers is a consequence of the quadrivalence of the carbon atoms and is represented in figure 1, for the octahedral planes and in figure 2 for the cubic ones. A_1 and A_2 represent successive layers of carbon atoms belonging to one lattice,

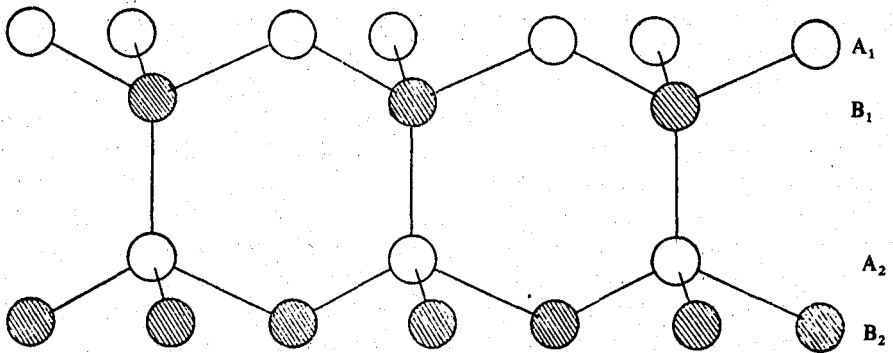


Figure 1. Structure of diamond viewed perpendicular to a trigonal axis.

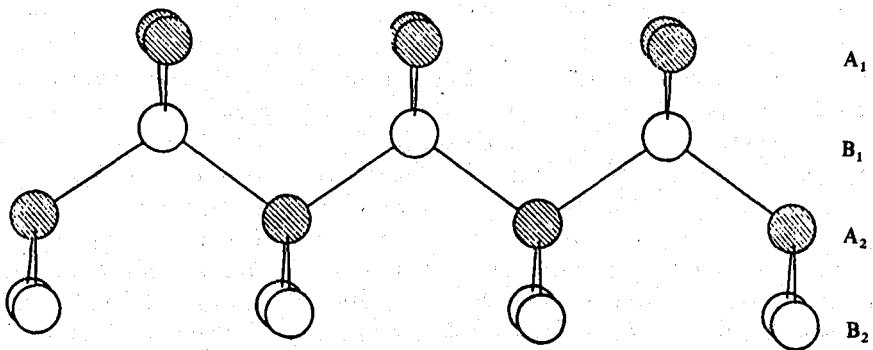


Figure 2. Structure of diamond viewed perpendicular to a cubic axis.

while B_1 and B_2 represent successive layers belonging to the other.

In part I of this series of papers, we have already derived the nine possible eigenvibrations of diamond, and they may be readily visualised with the help of a model of its structure. Figures 1 and 2 above are also helpful in this connection. The principal oscillation of the structure is the one in which the atoms of each lattice move together in the same phase against the atoms in the other lattice moving together in the opposite phase. It is a triply degenerate oscillation, and hence the direction of motion may be either normal or tangential to the atomic planes in either of the two figures, viz., up and down the printed page or horizontally across it. The other eight possible movements arise from the three pairs of possible alternatives; the oscillations may be of the octahedral or of the cubic planes of atoms; the oscillations may be normal or tangential to these planes; the oscillations may be symmetric, or antisymmetric, adjacent layers of the structure belonging to the two lattices moving in the same phase in the symmetric modes, and in opposite phases in the antisymmetric ones. Thus, for

instance, in the tangential symmetric oscillation of the octahedral planes, the layers A_1 and B_1 in figure 1 move together horizontally across the page against the layers A_2 and B_2 moving together in the opposite direction. Similarly, in the tangential antisymmetric oscillation of the cubic planes, the layers A_1 and B_2 in figure 2 move together horizontally across the page against the layers B_1 and A_2 moving together in the opposite direction.

3. The valence forces

The forces coming into play when the atoms in diamond oscillate are principally of two kinds, viz., those due to changes of bond-lengths and those due to changes of bond-angles. The forces of the first kind are predominantly of greater strength, and this fact taken together with the geometry of the modes enables us readily to arrange them in a descending sequence of frequency as shown in table 1. We shall, to begin with, consider only the forces due to the changes of bond-lengths. It is immediately evident that they are absent in the tangential symmetric oscillation of the octahedral planes, as also in the tangential antisymmetric oscillation of the cubic planes described in the preceding paragraph. These two modes have therefore the lowest frequencies and are accordingly placed at the bottom of the table. On the other hand, the tangential antisymmetric oscillation of the octahedral planes, and the tangential symmetric oscillation of the cubic planes both involve large variations of bond-length. By reference to figures 1 and 2, it is seen that the changes of bond-length in each case are exactly the same as in the analogous movements of the two lattices against each other in mode I. Accordingly, these three modes have the highest frequency and are placed at the top of the table. The four modes in which the atomic layers move normally to themselves remain to be considered. It is readily seen that the symmetric and antisymmetric normal vibrations of the cubic planes would have identical frequencies owing to the disposition of the valence bonds and of the atoms in equidistant layers. On the other hand, the symmetric and antisymmetric normal oscillations of the octahedral planes are obviously different. A simple calculation based on the inclination of the valence bonds to the direction of movement shows that the symmetric oscillation would have a higher frequency than the antisymmetrical, while the normal oscillation of the cubic planes would have an intermediate frequency.

In the final ordering of the modes, we have also to consider the forces due to the variations of the bond-angles. These differ notably in the modes VIII and IX in which bond-length variations are totally absent, as also in the modes I, II and III in which they are of equal magnitude, and hence enable us to arrange them in the proper sequence of frequency. The tangential symmetric oscillation of the octahedral planes (mode IX) obviously involves variations of fewer bond-angles than the tangential antisymmetric oscillation of the cubic planes (mode VIII). It

Table 1

Descending order of frequency	Degeneracy	Description of mode
I	3	Oscillation of the two lattices
II	8	Tangential antisymmetric oscillation of the octahedral planes
III	6	Tangential symmetric oscillation of the cubic planes
IV	4	Normal symmetric oscillation of the octahedral planes
V*	3	Normal antisymmetric oscillation of the cubic planes*
VI*	3	Normal symmetric oscillation of the cubic planes*
VII	4	Normal antisymmetric oscillation of the octahedral planes
VIII	6	Tangential antisymmetric oscillation of the cubic planes
IX	8	Tangential symmetric oscillation of the octahedral planes

*Note—Modes V and VI have the same frequency.

therefore now appears at the bottom of the table, with the latter immediately above it. The principal lattice oscillation (mode I) involves variations of all six bond-angles and is therefore placed at the top of the table, followed in order by the tangential antisymmetric oscillation of the octahedral planes (mode II) and the tangential symmetric oscillation of cubic planes (mode III) in which only three bond-angles and one bond-angle respectively vary sensibly. The nine eigenvibrations as thus finally arranged are shown in table 1.

4. Numerical evaluation of the eigenfrequencies

The descending sequence of frequency shown in table 1 is sufficient to enable the modes of vibration manifesting themselves in the spectrum of diamond to be individually identified. It is possible, however, to go further and make a numerical estimate of the frequency of each of the modes, thereby confirming the assignment of the observed spectral frequencies to the different modes and placing their identification on a secure basis. We shall proceed to show how this may be done.

In any eigenvibration, equivalent atoms have the same amplitude of motion, and since the masses of the two sets of equivalent atoms in diamond are the same, it follows that the atomic displacements are also the same. It is sufficient therefore to find the forces acting on any one atom in a given mode of vibration to ascertain

