

Dynamic X-ray reflections in crystals*

1. Introduction

Diamond, by reason of its exceptional properties, has played a notable part in the development of our notions concerning the solid state of matter. For instance, when Einstein put forward his famous theory of specific heats, it was the only known solid exhibiting a marked variation of specific heat with temperature, and one may well believe that it was the behaviour of diamond which inspired Einstein to apply quantum theory to the problem. More recent studies on diamond indeed suggest that the properties of this remarkable substance are the pathway to a correct appreciation of the theory of the solid state. That this remark is applicable to the theory of the propagation of X-rays in crystals and of the attendant phenomena forms the major theme of this address.

Diamond has interested the writer ever since 1930, and numerous investigations with it undertaken at his suggestion have appeared in the earlier volumes of the *Indian Journal of Physics* and subsequent to 1933 in the *Proceedings of the Indian Academy of Sciences*. Early in the year 1940, in connection with certain spectroscopic investigations, a few octahedral cleavage plates of diamond were acquired. These formed the beginnings of a collection that has since grown up very considerably. A powerful X-ray set-up was available at the Institute, and Dr P Nilakantan undertook to obtain some Laue patterns with diamond using a copper target as a source of monochromatic X-radiation. The photographs revealed a phenomenon of such a remarkable character and so clearly incapable of explanation on the basis of familiar X-ray theory that the writer had no hesitation in announcing in *Current Science* of April 1940 the discovery of a new X-ray effect, introducing it in the following words: "The new X-ray phenomenon described and illustrated in the present communication has in its physical nature, something in common with both the Laue and the Compton effects: it is a specular reflection of X-rays by crystals but with a change of frequency explicable only on quantum-mechanical principles." The article went on to suggest that the observed reflections had their origin in the excitation of the eigenvibrations of the diamond structure by the incident X-radiations. It was also pointed out that in view of the known high-frequency of these eigenvibrations, the thermal agitation

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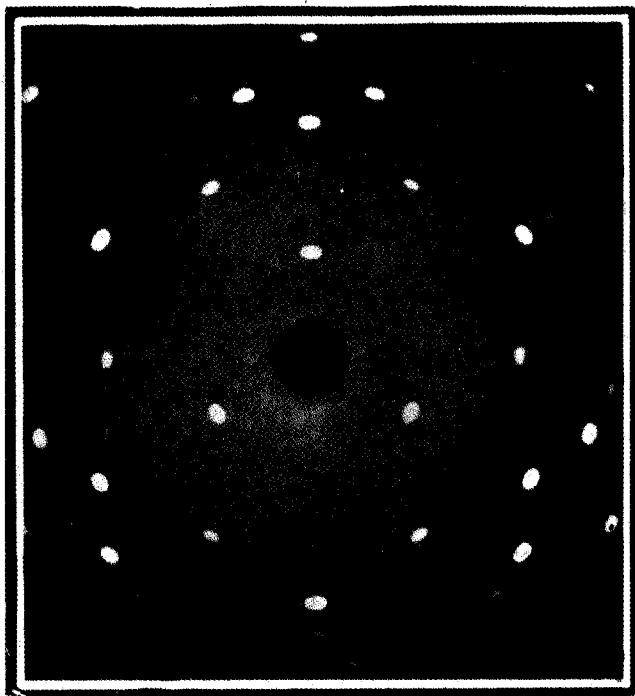


Figure 1. Dynamic X-ray reflections by diamond. CuK_α radiation (after Raman and Nilakantan April 1940).

in the crystal could not be the operative cause of the reflections. Subsequent investigations showed that their intensity was not notably influenced by heating the crystal or cooling it down to liquid-air temperature, thereby confirming the quantum-mechanical nature of the effect. Using fine slits with correspondingly long exposures, the reflections were found to be extremely sharp, thus precluding any explanation of them as due to the thermal X-ray scattering. The appearance of the reflections at various settings of the crystal was explained in the *Current Science* article on the basis of certain considerations regarding the phases of the excited vibrations. These considerations and the formula for the geometric law of the quantum reflection derived therefrom were confirmed with all desirable precision by exact measurements.

The new ideas and principles emerging from the case of diamond naturally suggested a series of investigations with other crystals. The results were published in a series of seven papers in the *Proceedings of the Indian Academy of Sciences* between May and November 1940, and finally in a symposium of fifteen papers under the general title of the "Quantum theory of X-ray reflection" as the October 1941 issue of the *Proceedings*. The subject was then laid aside. It appears

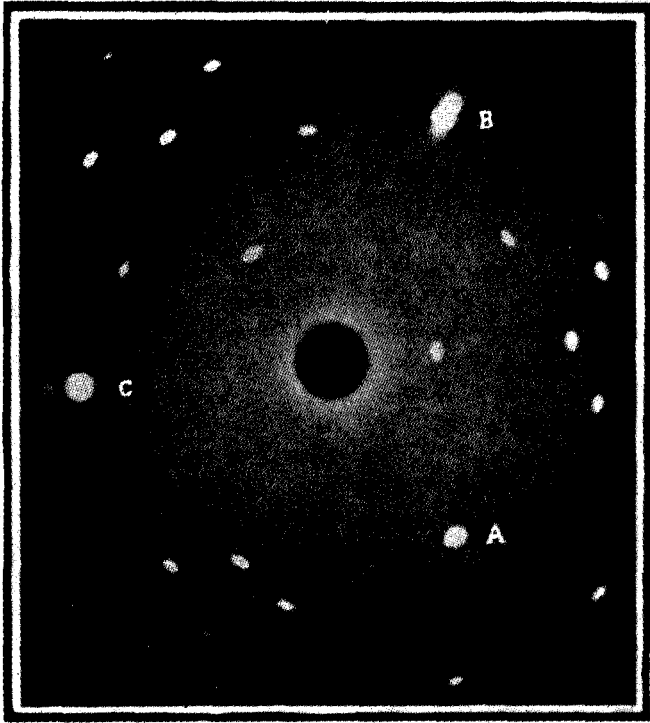


Figure 2. Dynamic X-ray reflections by diamond. CuK_α and K_β radiations (after Raman and Nilakantan, April 1940).

opportune now to return to it, and that some years have elapsed in the interval has not been altogether a disadvantage. For, the studies on several allied topics made at Bangalore during these seven years have cleared the ground for a proper understanding of crystal physics generally and of X-ray physics in particular. Most of the criticisms of the Bangalore publications which were put forward at the time by different writers are seen in the light of the later developments to be without substance or justification.

2. The thermal scattering of X-rays

In considering the phenomena attending the passage of X-rays through a crystal and resulting from the movements of the atoms in it (due to the thermal agitation or other cause), it is desirable in the first instance to fix our attention on such of these movements as can be identified with the elastic vibrations of the solid. There would be an immense number of such movements or normal vibrations possible. Each of these modes extends through the entire volume of the crystal and has a

distinctive frequency and a characteristic pattern of nodal surfaces, the phase of the motion being opposite in every pair of adjacent cells of the pattern. The configuration of the nodal pattern would be determined by several factors, viz., the size of the crystal, its form and the external boundary conditions, the elastic constants and their variation with direction, and it would also be different for each different mode with its particular frequency. It would not be easy—even if it were theoretically possible—to determine the pattern even for a single one of the modes, much less for all of the immense number which need to be considered. We notice, however, that all the factors which are determinative of the nodal pattern are of a *macroscopic* character. Hence, we are justified in inferring that in no case would the nodal pattern bear any particular or specifiable relation to the atomic architecture of the crystal, under which term we refer to the position of the atomic layers and of the individual atoms. The situation here depicted is seen to have important consequences when we proceed to consider the optical aspects of the problem. Fixing our attention on a particular mode of elastic vibration of frequency ν^* , we note that each atom in the track of the X-ray beam can be regarded as a source of secondary radiations of frequency ν , $\nu + \nu^*$, and $\nu - \nu^*$, ν being the frequency of the incident X-radiation. The strength of the radiations of frequencies ($\nu \pm \nu^*$) would be determined by the amplitude of oscillation of the atoms, while the phases of the scattered radiations as received at any point would be determined by the optical paths and *by the phase of the oscillation of the atom*. Since the latter phase is reversed whenever we pass from one side to the other of each nodal surface in the elastic vibration, it follows that the phases of the scattered radiations would be reversed at the same time. Hence, in the final summation over all the atoms in the track of the X-ray beam, the radiations from the atoms included in the successive cells of the nodal pattern would tend to cancel out by interference. Any resultant left over would arise from the varying amplitudes of the vibrations of the atoms and the varying density of their distribution; but since these variations are uncorrelated, the net result would be unpredictable for any particular ν^* and would also be different for each different ν^* .

We thus arrive at the conclusion that the scattered radiations from the atoms arising from the elastic vibrations in the solid cannot possibly conspire to build up anything in the nature of a diffraction pattern having a recognizable relationship to the atomic structure of the crystal. That a contrary conclusion has been reached by various writers is evidently due to the erroneous nature of the premises on which they have proceeded to consider the problem. We may remark in this connection that in the case of a finite crystal, it is not permissible to postulate the propagation of plane elastic waves in various directions and to consider the optical results of each such wave *independently*. The proper analysis of the elastic vibration is into a set of normal vibrations, each with its own pattern of nodal surfaces determined by the form of the crystal and other factors as stated above.

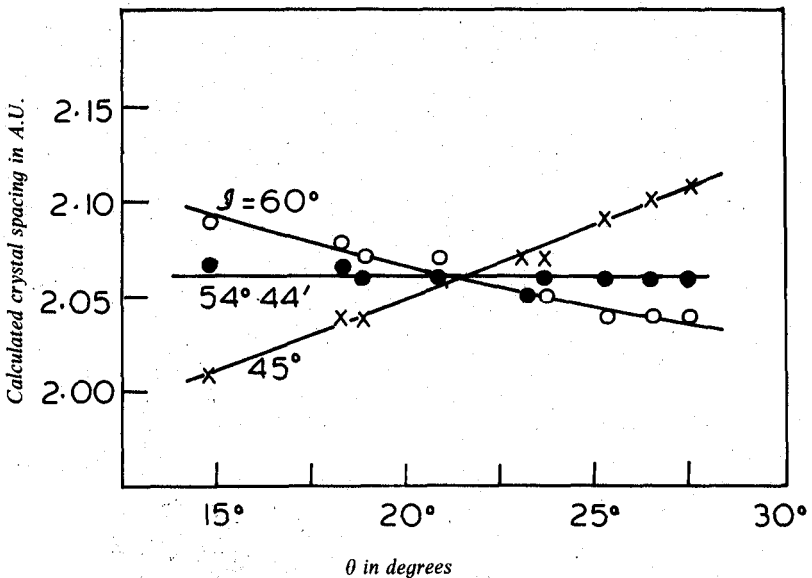


Figure 4. Coincidence of phase waves in diamond with cubic planes (after Raman and Nilakantan, November 1940).

3. The origin of the extra spots

The foregoing remarks make it evident that it is not possible to explain the so-called "diffuse" spots in the Laue pattern of crystals other than diamond on the basis of the elastic vibrations excited in them by thermal agitation or otherwise. This is obvious in the case of diamond by virtue of the observed sharpness or specular character of its extra reflections, but it is equally true for all crystals. In other words, the phenomena exhibited by diamond are exceptional only in the sense that all the properties of diamond are exceptional, viz., they stand out so clearly as to leave little room for being misunderstood. The criticisms of the Bangalore work put forward by various writers who have sought to brush aside the facts observed with diamond on the basis of *ad hoc* explanations or by writing them down as "secondary" phenomena, are thus clearly misconceived.

In the Laue pattern of an octahedral cleavage plate of diamond obtained when the X-ray beam is parallel to a trigonal axis, the extra spots appear symmetrically placed about that axis, and are readily recognized as specular reflections by the (111) spacings of the incident monochromatic radiation, analogous to the ordinary or static X-ray reflections, but obeying a different geometrical law. It follows that the atomic movements in the crystal which give rise to them are related to the structure of the crystal in a precisely definable manner, instead of

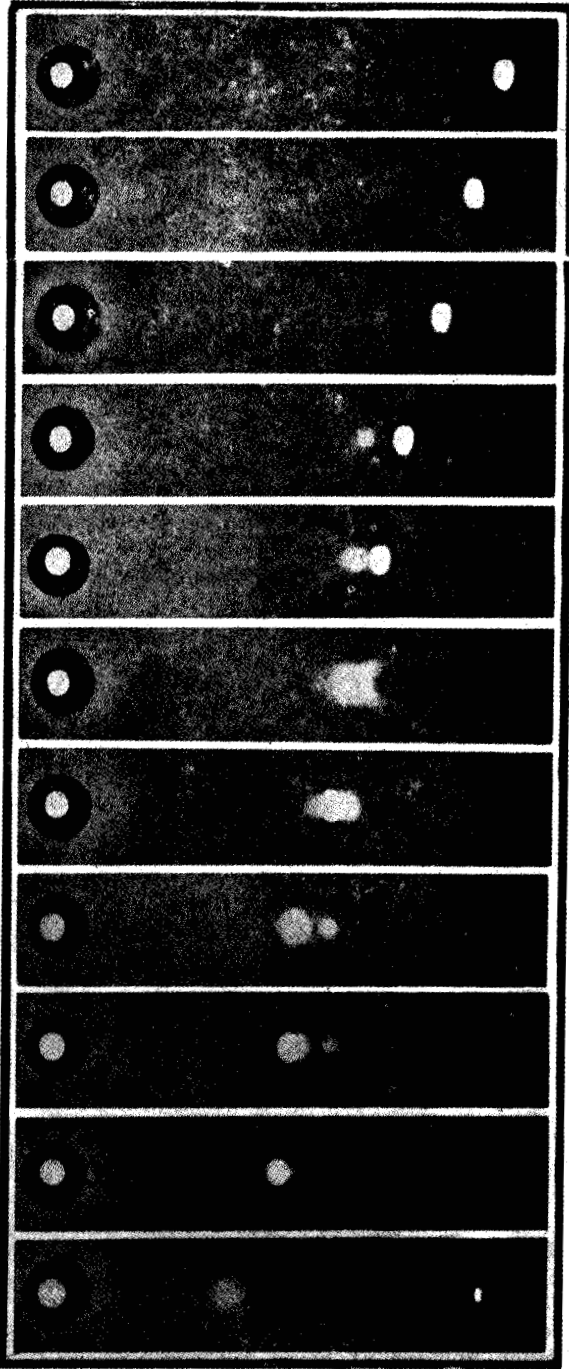


Figure 3. Sequence of changes in (111) reflections by diamond with alteration of crystal setting (after Raman and Nilakantan, November 1940).

being entirely uncorrelated with them as in the case of the elastic vibrations. As we have seen, the incapacity of the elastic modes of vibration to give rise to such effects arises from the fact that they are determined by *macroscopic* factors, including especially the existence of an external boundary and the conditions there subsisting. Even in the purely conceptual case of an infinite crystal where the elastic disturbances can be considered as waves, different wavelengths and directions of propagation can co-exist, thereby precluding the possibility of giving rise to sharply defined "extra" spots. For the same reason, therefore, the atomic movements in diamond which give the observed reflections cannot be described as waves whose wavelengths and directions are arbitrary in the same manner as those of elastic waves in an infinite solid. Indeed, the analysis of the positions of the reflections by the (111) planes of diamond as actually observed for various settings shows that the planes of constant phase in the atomic movements are severely restricted in their orientation, being in fact exactly parallel to the (100) planes in the crystal. Which of the three sets of these planes is effective, or whether all of them come into operation depends on the particular setting of the crystal with respect to the incident X-ray beam.



Figure 5. Dynamic reflections by sodium nitrate at 225° C (after Raman and Nilakantan, May 1940).

Thus, alike from theoretical considerations and from the experimental facts, and as in the case of diamond, so also for all other crystals, it is clear that the origin of the "extra" spots has to be sought in types of atomic movement which are precisely related to the structure of the crystal, and which unlike the familiar waves of elastic theory, are uninfluenced by the presence of an external boundary, and whose planes of constant phase are restricted to certain specified orientations. By a simple process of exclusion, we are forced to the conclusion that these movements are the eigenvibrations of the crystal structure which manifest themselves in spectroscopic studies with crystals, and further, that such eigenvibrations possess characters wholly different from the vibrations pictured in the classical theory of elasticity.

4. The eigenvibrations of crystal structure

Our argument thus leads us to recognize the fundamental relationship between the physics of X-ray propagation in crystals and the physics of their spectroscopic behaviour. It also shows that the older views which sought to force the spectroscopic picture of crystal behaviour into a pattern similar to that of its elastic vibrations are fundamentally erroneous. Indeed, the X-ray phenomena observed with diamond compel us to make a fresh approach to the theory and of their relationship to the spectroscopic phenomena. Such an approach has been made in the introductory paper of a symposium on "The dynamics of crystal lattices", published by the *Indian Academy of Sciences* as its *Proceedings* for November 1943. More recently, the spectroscopic consequences of the new theory have been worked out and the results compared with the experimental facts in numerous cases, viz., diamond, magnesium oxide, the alkali halides, etc. The results have been published as a symposium of the eigenvibrations of crystal structures of nineteen papers on "The vibration spectra of crystals" forming the *Proceedings of the Indian Academy of Sciences* for December 1947. The theory is so successful in explaining the facts of observation, including such as are wholly unintelligible on the basis of the older theories, as to leave no room for doubt regarding the essential correctness of the new approach.

The main result of the new theory is that, whereas on the older theories the vibrations both in the acoustic and optical ranges of frequency yield continuous spectra, they appear in the new theory as a set of modes with sharply-defined monochromatic frequencies $(24p-3)$ in number, there being p atoms in the unit cell of the crystal lattice. In $(3p-3)$ of these modes, the vibrations have the same amplitude and phase in adjacent cells of the lattice, while in the remaining $21p$ modes, the amplitude is the same while the phase alternates in successive cells along one, two or all three of the axes of the lattice. The actual number of discrete frequencies would be much less than $(24p-3)$, if the crystal belongs to the higher symmetry classes. In the case of diamond, for instance, the $(3p-3)$ frequencies

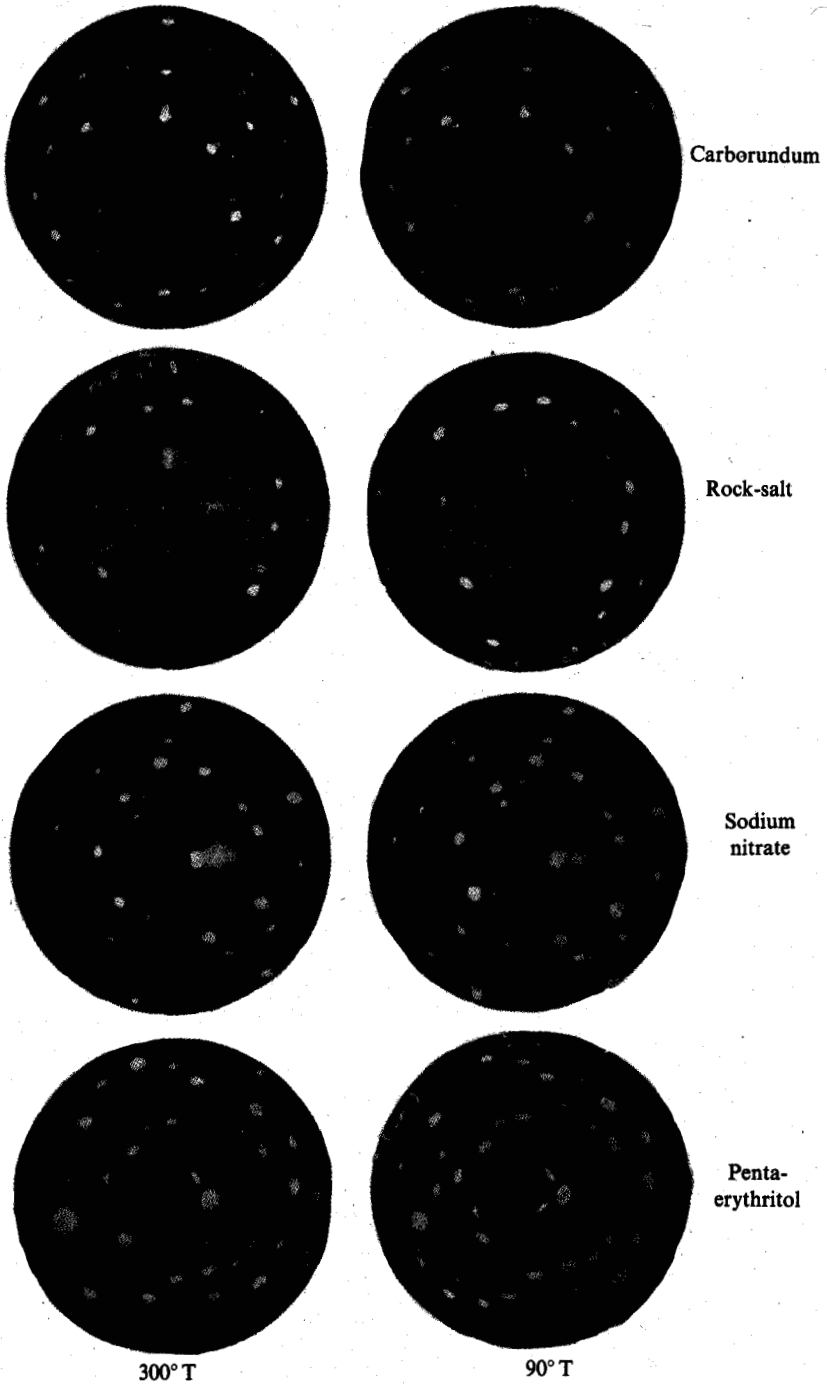


Figure 6. Quantum X-ray reflections by crystals at 30° C (left) and -180° C (right) (after C S Venkateswaran, September 1941).

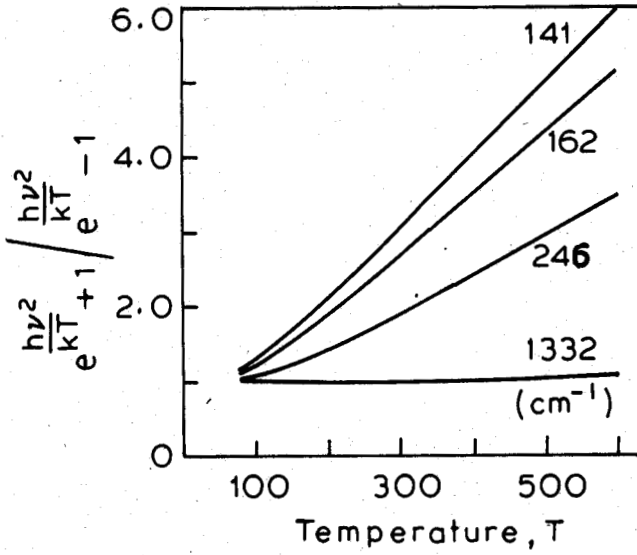


Figure 7. Temperature factor of quantum reflection, theoretical (after Raman, September 1941).

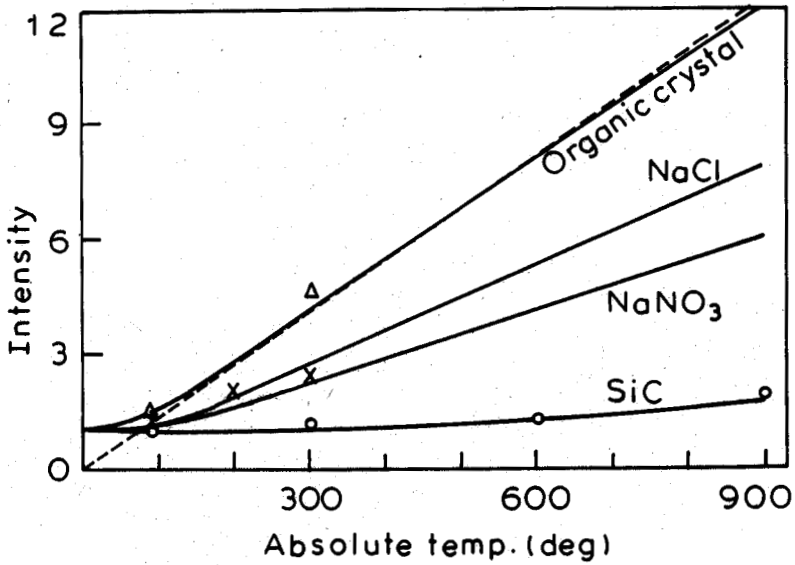


Figure 8. Temperature factor of quantum reflection, experimental (after C S Venkateswaran, September 1941).

reduce to only one, where the $21p$ frequency reduce to seven in number. The vibrations and their respective frequencies may be regarded as characteristic properties of the dynamic unit of the crystal structure which is a super-cell with twice the dimensions and eight times the volume of the unit cell of the lattice. It may be remarked that the 3 excluded degrees of freedom form the residue which goes over into the spectrum of the elastic vibrations of the crystal.

5. Excitation of the eigenvibrations

It is possible to excite the eigenvibrations of a crystal in various ways, the most obvious and universal method being that of thermal agitation which is always effective, provided the temperature is sufficiently high. We have also various optical methods in which the evidence of excitation is furnished by spectroscopic study, e.g., observations of the spectrum of the scattered light, of the absorption in the infra-red, and also in favourable cases of the absorption in the visible spectrum, and of the luminescence spectrum at low temperatures. The monochromatic character of the vibration frequencies comes directly into evidence in all such cases, irrespective of the particular method of excitation adopted, showing thereby that it is a characteristic property of crystal structure and not a consequence of the particular method of excitation employed. The activity of the individual modes may, however, differ in respect of the different methods of excitation. For instance, in the cases of light-scattering and of infra-red absorption, they are complementary and mutually exclusive in respect of the fundamental frequencies in the case of crystals possessing a centre of symmetry. This feature disappears when we consider the overtones and summations of the fundamental frequencies where anharmonicity, mechanical or optical, comes into play. The appearance of overtones and summations with appreciable intensities in the optical methods of excitation indicates that the vibrations excited are highly localised, and that in consequence, the vibration amplitudes are comparable with the interatomic distances. If, on the other hand, the excitation extends over a large volume in the crystal, the energy of a quantum of the particular frequency distributed over such volume would result in the amplitudes being infinitesimal and hence incapable of giving rise to overtones or summations with appreciable intensities. On the other hand, in the excitation which results in dynamic X-ray reflections, we must picture the vibration as occurring in the same phase or with slowly varying phases over an extended volume of the crystal, since otherwise no observable reflection could result. The larger the volume in which the excitation occurs, the more sharply defined would the resulting reflections be. The extreme sharpness of the dynamic reflections in the case of diamond where the bonding between each lattice cell and the next is strong is readily understood on the basis, while the diffuseness of the "extra" spots in weak crystals, such as for instance organic compounds, is also intelligible as a consequence of the weakness

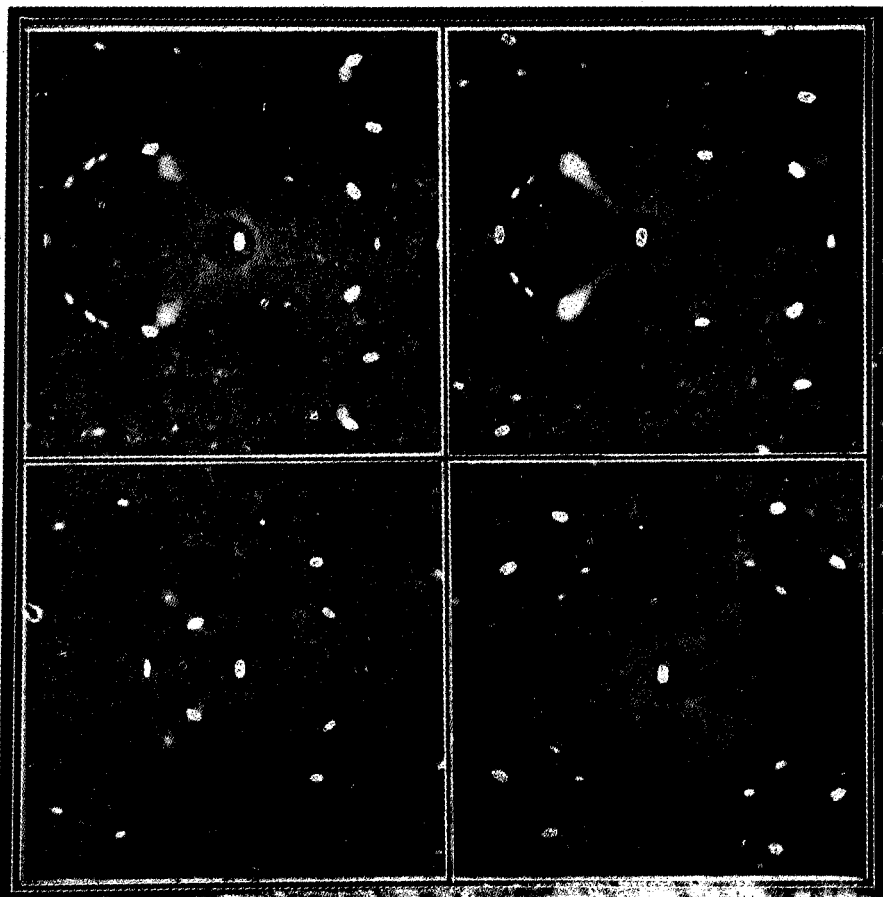


Figure 9. Dynamic X-ray reflections by hexamethyl tetramine (after C S Venkateswaran, October 1941).

of the binding between the successive cells of the structure. It should be remarked that the restriction in the volume of excitation would result in an increase of the amplitude of vibration, and this would exactly set off the decrease in the number of lattice cells which co-operate to give a dynamic reflection. The amplitude of vibration, would also be dependent on the masses and binding forces involved. Hence, it is quite possible for crystals which give only "diffuse" spots nevertheless to exhibit them with notable intensities.

6. Influence of temperature

In many cases, and especially where the binding forces are weak or the atomic masses are large and hence the eigenfrequencies are low, the eigenvibrations would be excited by thermal agitation, and hence such thermally excited eigenvibrations would have to be considered in respect of the X-ray phenomena as well. The theoretical position is somewhat analogous to that arising in the case of the excitation by optical methods, viz., the scattering of light, where we are concerned with both positive and negative shifts of frequency in the spectrum of the diffused light. Instead of the ground state, the thermally excited state of eigenvibration would be the starting point for their excitation by the incident X-radiation, and hence it can occur in either direction, viz., further excitation or a de-excitation. The dynamic reflections arising in either way would appear superposed in the finally observed result, and the net consequence to be theoretically expected would be an increase in the intensity of the reflection with rising temperature, besides subsidiary effects such as increase in diffuseness. The magnitude of the increase in intensity would depend on the frequencies of the eigenvibrations which are effective in giving the observed reflection, and the proportionate increase would be the smaller, the higher the frequency or frequencies under consideration. *Per contra*, the intensity would diminish when the temperature is lowered, but since the quantum-mechanical excitation would persist in every case, the reflection would not disappear even at the lowest

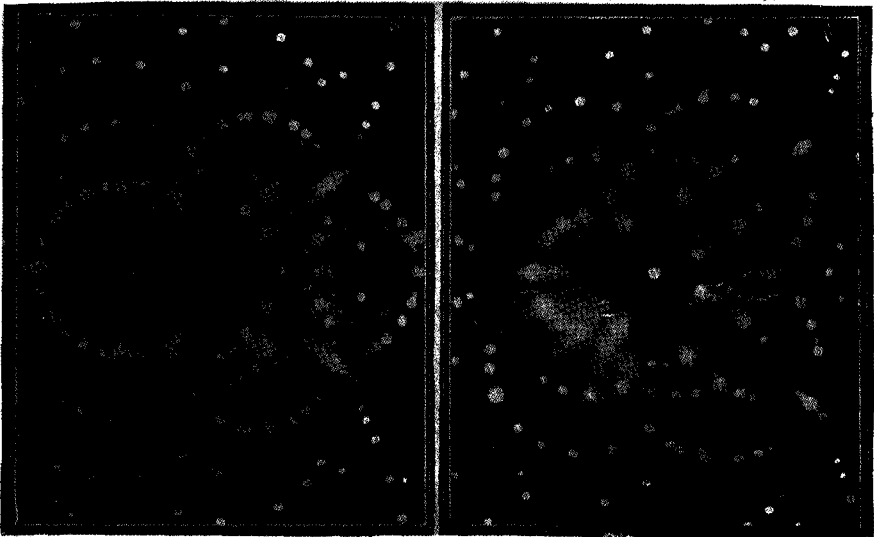


Figure 10. Dynamic X-ray reflections by calcite for different settings (after Nilakantan and Nayar, October 1941).

temperatures but would on the other hand persist. The intensity at low temperatures would be relatively the largest in the case where the eigenvibrations involved would have relatively the highest frequencies. There is no reason to expect any notable dependence of the magnitude of the temperature variation on the setting of the crystal at which the dynamic X-ray reflections are recorded.

7. Dependence on crystal structure

It will be evident from what has been stated above that the pattern of dynamic X-ray reflections by a crystal would be largely determined by the number and nature of its eigenvibrations and their frequencies, and also on the manner in which these eigenvibrations influence the structure-amplitudes of the various crystal planes. Each individual case would have to be considered on its merits as in the case of static X-ray reflections, but general considerations regarding the nature of the oscillations possible in ionic, molecular or layer lattices would enable us to predict or at least understand the general nature of the dynamic X-ray patterns to be expected in these respective cases. But it would take us beyond the scope of the present article to enter into these details.

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