

## THE QUANTUM THEORY OF X-RAY REFLECTION

BY

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IN an article in *Current Science* for April 1940 under the title of "A New X-ray Effect", we drew attention to the remarkable features noticeable in a strongly exposed Laue diagram obtained with a cleavage plate of diamond when the X-ray pencil from a copper-target tube passes through the crystal approximately along the trigonal axis. Having convinced ourselves that the features we observed and described lay outside the scope of the classical X-ray optics, we put forward an explanation of the phenomena on novel lines. Basing ourselves on the accepted principles of the quantum theory of radiation, we showed that the lattice planes in a crystal should be capable of giving two kinds of geometric reflection of X-rays; besides the classical or Laue reflections, modified or quantum reflections are also possible which have their origin in the *quantum-mechanical* excitation of the *optical* vibrations of the crystal lattice. The geometric law of the quantum reflection stands in the same relation to the dynamic stratifications of electron density associated with such vibrations of the lattice that the classical reflections have in relation to the static structure amplitudes of the crystal. The investigations we have made during the past twelve months have completely confirmed the views expressed by us in the article referred to. It is our purpose in the present communication to indicate how such confirmation has been reached, and briefly to present the new ideas regarding the dynamics of crystal vibrations of the optical class to which we have been led by our X-ray studies.

The nearest approach to our point of view to be found in the classical literature is a memoir by Laue in the *Annalen Der Physik* for December 1926, in which he subjects the work of Debye, Faxen and Waller on the problem of the scattering of X-rays in crystals to a critical review and treats it afresh on original lines. Laue explicitly restricts himself to those modes of vibration of the crystal lattice which do not involve relative displacements of the atoms in the unit cell, in other words, to the elastic modes of vibration. His most striking result is that the scattering of X-rays occurs

in every case with a change of frequency equal to that of the mechanical vibration of the crystal. He further shows that for elastic vibrations of any specified wave-length and orientation to be effective, the usual Laue conditions must be satisfied with respect to a spacing found by a vectorial combination of the reciprocals of a given lattice spacing and the given wave-length. Laue's investigation thus indicates, in the language of the quantum theory, that the scattering of X-rays by the elastic waves also involves an exchange of momentum and energy between the photon and the crystal. The geometric conditions for such scattering are formally analogous to those for a dynamic reflection. But fundamental differences between the cases of the acoustic and the optical vibrations of the crystal lattice emerge as soon we enter into a closer consideration of the problem.

At a very early stage of our investigations, we considered the question whether the modified reflections observed by us in diamond and other crystals could possibly be explained in terms of the thermal scattering of X-rays by the elastic waves, and came to the conclusion that this was quite impossible. Indeed, Laue himself remarks towards the end of his paper that no noticeable concentrations of intensity in any direction could be expected as the result of X-ray scattering. As some X-ray workers (Lonsdale, Zachariasen) have expressed a different opinion in the recent literature of the subject, it would appear worthwhile to explain why it cannot be correct. The essential feature of the acoustical vibrations of the lattice is that the waves have all possible lengths and orientations, subject to the restriction that the total number of such waves is  $3N$ ,  $N$  being the number of lattice cells in the crystal. This restriction is automatically secured when, following Born, we set out the reciprocals of the wave-vector in a three-dimensional space. The reciprocal points then appear uniformly distributed in the "phase-space". Actually, when the finite resolving-power of the crystal considered as an optical grating is taken into account, these discrete points are "smudged"

out just sufficiently to make the "phase-space" just a uniform continuum within which the terminus of the reciprocal wave-vector must lie. It is obvious that in these circumstances, the scattering of the X-rays cannot give rise to any phenomenon even distantly approaching the character of a geometrical reflection. Further, the intensity of the scattering in any specified direction being proportional to  $N$ , its intensity would be quite negligible in relation to the intensity of the classical reflection which is proportional to  $N^2$ , provided the volume of the irradiated crystal is sufficiently small. In actual experience, however, the modified reflections by the (111) planes in diamond continue to be recorded even when the volume scattering by the crystal is made negligibly small by using a fine X-ray pencil and the edge of a thin plate to obtain the reflection.

The considerations stated are sufficient to show that the observed effects are not due to X-ray "scattering". It is worthwhile, however, to go rather more deeply into the matter. The believers in the "scattering" theory place their reliance on the fact that the expression for its intensity contains a factor proportional to the square of the wave-length of the elastic waves. This factor undoubtedly becomes important when the elastic wave-lengths are great. But it is just at this stage that the scattering coincides in direction with a classical reflection and is therefore wholly unobservable. When the crystal setting is altered even by a degree of arc, the numerical factor ceases to be important, and instead of a "peak" the theory indicates only a "hump" in the scattering intensity curve which becomes rapidly less pronounced as the crystal is moved away from the correct setting for a monochromatic reflection. The actual experimental observations with the (111) reflections of diamond reveal a very different state of affairs. As can be seen from Fig. 1, the modified reflections persist with undiminished sharpness over a wide range of settings of the crystal.

A crucial test of the whole question is furnished by our low-temperature experiments with diamond. As already mentioned, a change of frequency, in other words, a transition between the different energy levels in the crystal is involved in either case. On the "scattering" theory, we are dealing with elastic waves of relatively

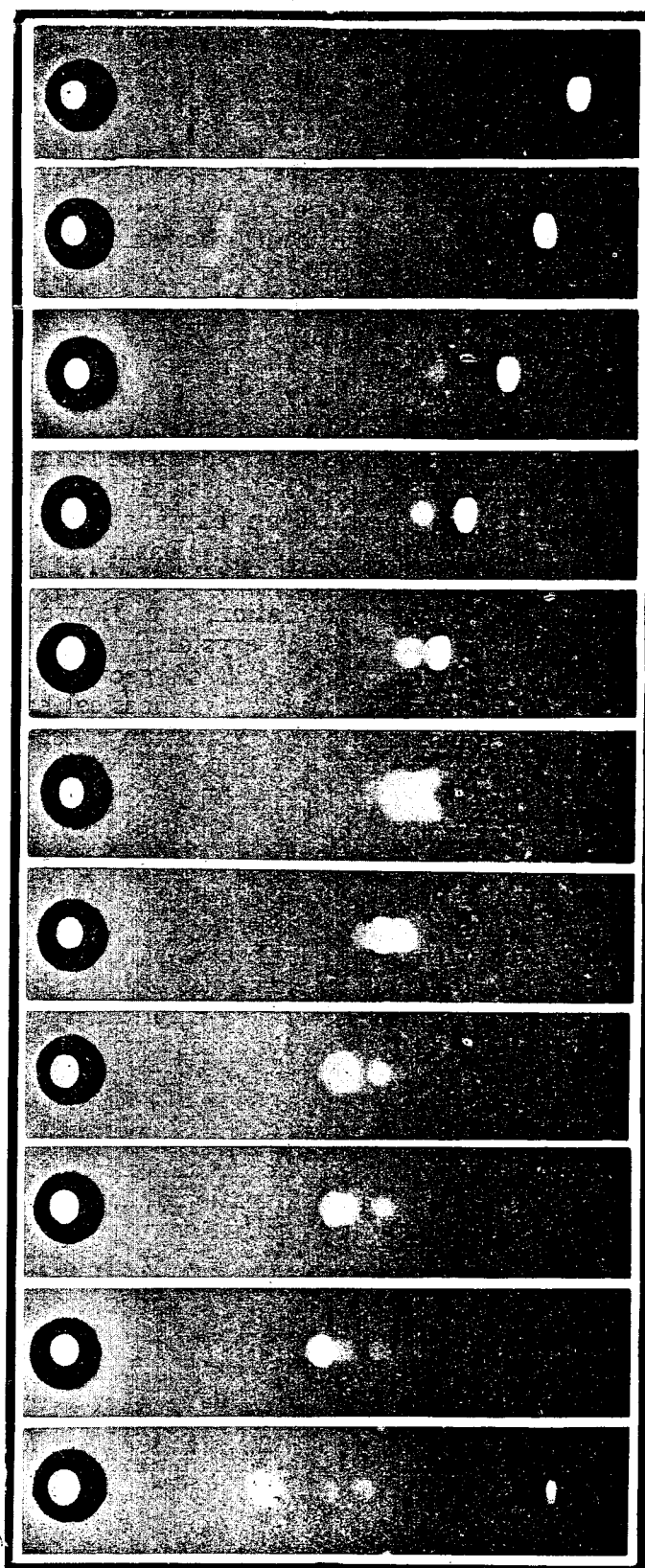


FIG. 1. The Modified Reflection by the (111) planes of a diamond crystal at various settings with copper  $K\alpha$  and  $K\beta$  X-rays

great wave-length and low frequency. Indeed, the nearer the direction of scattering is to that of the classical reflection, the longer would be the effective wave-length and the lower the frequency of the

vibrations. Transitions between such low frequency levels are necessarily determined with all desirable accuracy by the classical dynamics. In other words, the intensity of the X-ray scattering should diminish in proportion to the absolute temperature. The case of diamond is specially suitable for such a test, because in respect of elastic waves of the length effective at small angles of scattering,  $h\nu^* \ll kT$ , while for the optical vibrations  $h\nu^* \gg kT$ . The necessary experimental tests have been tried out by us and fully confirm the prediction published in May 1940. They show that the modified reflections by the (111) planes in diamond appear with sensibly unaltered intensity when the crystal is cooled down to liquid air temperature, and that is the case, irrespective of the crystal setting employed. The observations clearly indicate that  $h\nu^* \gg kT$ , in other words, that the modified reflections are due to the optical vibrations of the lattice, and not the acoustic ones. They also demonstrate that the modified reflection is a quantum-mechanical effect.

ments of the lattice cells, the optical vibrations represent all the remaining degrees of freedom of atomic movement, and are best regarded as oscillations of the interpenetrating lattices in the crystal with respect to one another. In all actual crystals, the number of such possible vibrations is comparable with and indeed in many crystals very much greater than the number of the acoustic degrees of freedom. As is very clearly shown by spectroscopic studies of light scattering in crystals, these optical vibrations may often be of quite low frequency and are therefore powerfully excited by the thermal agitation of the crystal. Even considered from the purely classical point of view, therefore, the optical vibrations of the lattice must play an extremely important part in X-ray optics. There is ample evidence that this is actually the case and that the modified reflection of X-rays is directly associated with such optical vibrations. To mention only one instance, we may refer to our published results on the special behaviour of the classical and modified reflections by the

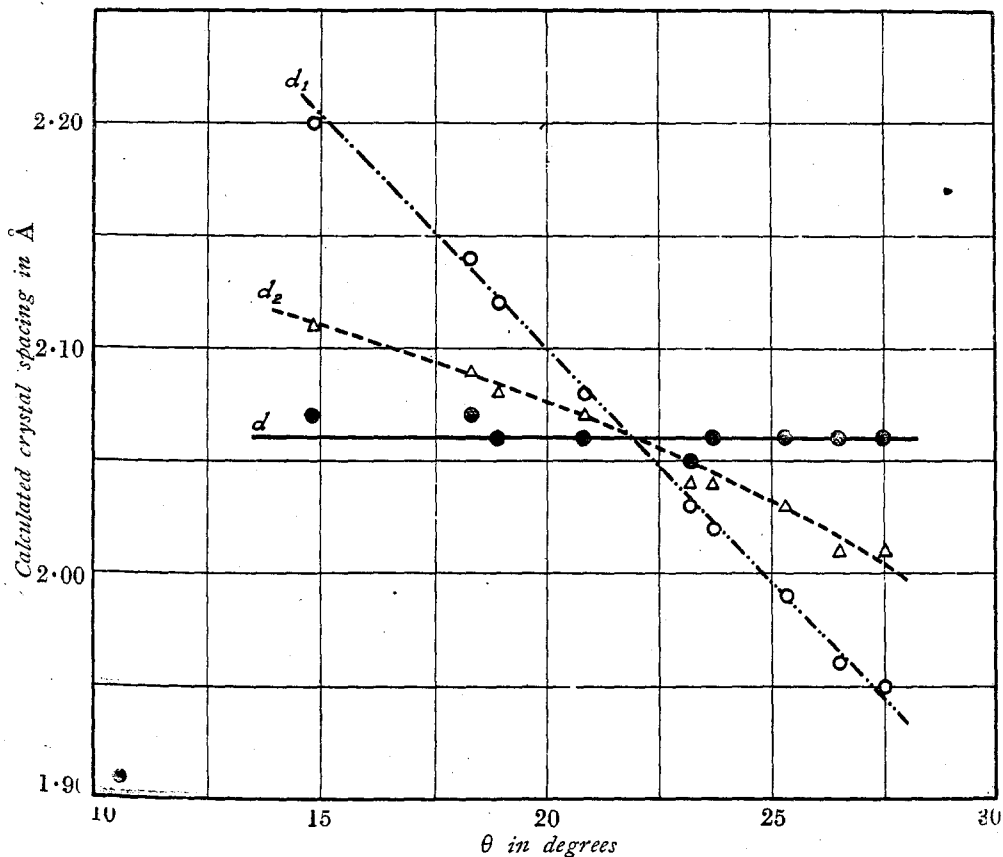


FIG. 2

Showing the failure of the Faxen formula for the (111) reflections by diamond

While the elastic vibrations of the lattice correspond to the three translatory move-

coupled to each other, they are necessarily in coherent phase-relationship with

(210) planes in sodium nitrate and their relation to the thermal excitation of the rotational oscillations of the NO<sub>3</sub> ions in the crystal.

An oscillation of the interpenetrating lattices in the crystal with reference to one another alters the structure amplitudes of the unit cells without appreciably displacing them from their positions in the ordered arrangement of the crystal. Such oscillation is therefore capable of giving rise to geometric reflections by the crystal planes with an intensity proportional to N<sup>2</sup> and to the square of the periodic variation of structure amplitude produced by such oscillation. Since the atomic vibrations in the different cells are of identical frequency and are mechanically

each other. It is readily shown that for a modified reflection to be observable in any specified direction, the usual Laue condition must be satisfied by the dynamic spacing obtained by a vectorial combination of the reciprocals of the crystal spacing and of the phase wave-length of the optical oscillations in the crystal. To find the directions in which the modified reflections appear, we proceed to set out the reciprocal wave-vectors for the particular optical vibration in a three-dimensional diagram.\* It is at this point that the fundamental difference between the acoustical and optical modes of the vibration of the lattice emerges. As we have already seen, such a diagram for the elastic waves is effectively a continuum which is everywhere of uniform density. If this were also true for the diagram in the optical case, there would be no possibility of explaining the actually observed reflections. We are obliged therefore to conclude that *the Born diagram correctly represents only the acoustic "phase-space" and has no application or significance with respect to the optical "phase-space"*.

ing the oscillations of the lattice is purely geometrical in spirit and is essentially only a refinement of the well-known Rayleigh-Jeans method, and its physical content must therefore be the same. In other words, its validity is restricted to the enumeration of the acoustic vibrations. The optical vibrations of the lattice, on the other hand, may be regarded as analogous to the specific vibrations of a molecule of giant size, and there is no logical reason that one can discover for assuming that the reciprocal phase wave-lengths for the oscillations of such a molecule when represented geometrically should fill space with uniform density. On the contrary, it is reasonable to assume that the possible orientations of the phase-waves are of a highly restricted character and have a specific relation to the symmetry characters of the crystal and of the particular mode of vibration involved. Accepting this idea, we realise immediately that intense and highly localised modified X-ray reflections become possible when oscillations with such a character are excited.

A convincing proof of the correctness of

the ideas above set forward is furnished by a quantitative study of the (111) modified reflections of diamond for various orientations of the crystal, the plane of incidence coinciding with a plane of symmetry. A full account of the work will appear shortly in the *Proceedings of the Indian Academy of Sciences*. It will be sufficient here to refer to the results shown graphically in Figs. 2 and 3. In Fig. 2, the actually observed angular positions of the reflections are represented against the crystal spacings as calculated from three different formulæ.

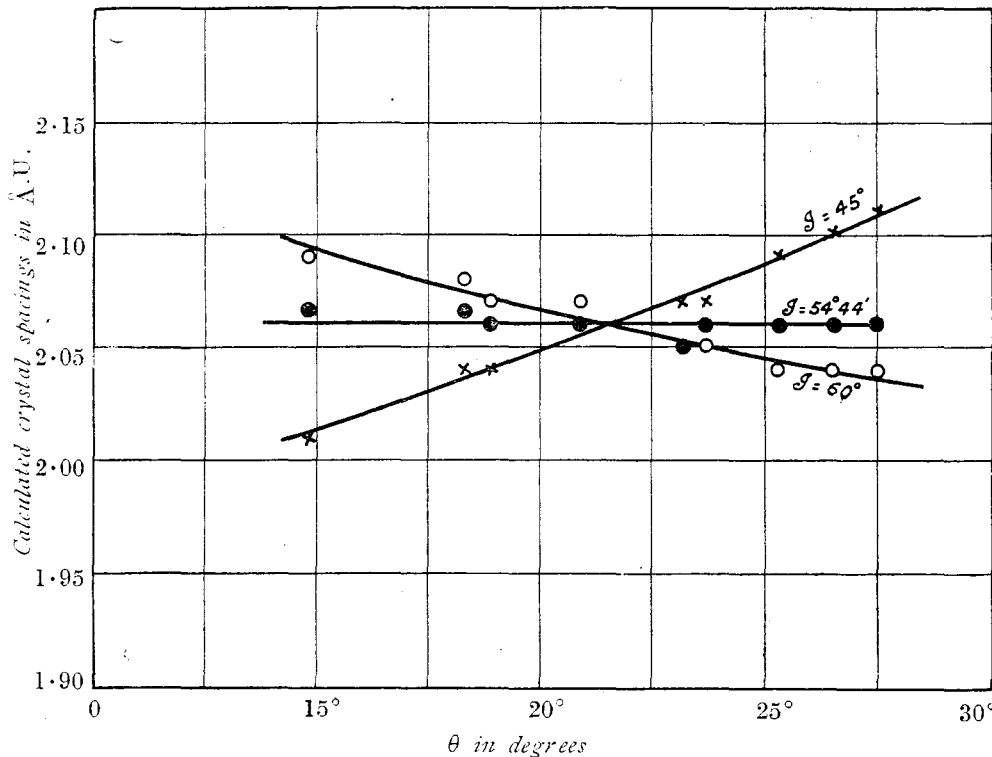


FIG. 3

Determination of the Inclination of Phase-Waves to the (111) Crystal Spacings in Diamond

The conclusion stated above cannot be regarded as in any way incredible or even surprising. The Born method of enumerat-

The graph marked  $d_1$  assumes that the phase-waves are normal to the static crystal-spacing. The graph marked  $d_2$  is a curved

line which represents the crystal spacing calculated from the Faxen formula. The graph marked *d* is calculated on the assumption that the phase-waves, are inclined to the (111) planes at a constant angle of  $54^{\circ} 44'$  which is half the tetrahedral valence angle, in other words parallel to the (100) planes transverse to the plane of incidence. It will be seen from the figure that the third graph is a horizontal straight line and gives a constant spacing very close to the actual one, namely 2.055 A.U.

In order to exhibit how closely the observed inclination of the phase-waves may be determined from the observed data, Fig. 2 shows the crystal spacing worked out for three different values of the angle, namely  $45^{\circ}$ ,  $54^{\circ} 44'$  and  $60^{\circ}$ . It is evident that if the

graph is to be a horizontal line, the angle cannot differ from half the tetrahedral valence angle by more than  $1^{\circ}$  either way. It is thus clear that the Faxen formula is wholly irrelevant to the present problem and that the modified reflections arise from the fact that the phase-waves of the optical vibration have a precisely determined orientation and azimuth with reference to the crystal planes. Further striking confirmation of these conclusions is afforded by the observations of fainter reflections by the phase-waves parallel to the two other (100) planes inclined to the plane of incidence, and by the effect of inclining the plane of incidence to the plane of symmetry. Into these details we need not here enter.

## THE SULPHUR POSITION IN INDIA

BY

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IT is not necessary to enumerate the numerous uses of sulphur. Sulphur and sulphuric acid are indispensable to any country not only for the production of war-time requirements, but also for the needs of all important industries even during peacetime.

It is well known that all sulphur used in India and Burma is imported. Essential supplies cannot be obtained from within the Empire. The quantities in tons of sulphur imported during recent years and the sources from which the supplies were obtained are shown in the following table:

It is obvious from the table that the principal importing countries before the outbreak of war were Italy, Japan, Java and the United States of America.

The rapidity with which the European conflagration is spreading and the threats of war from our eastern neighbours have brought the sulphur problem in India to the forefront and both the Government and the public outside have studied the subject with more than usual enthusiasm and concern. In the second meeting of the Board of Scientific and Industrial Research held in Simla on the 12th and 13th June 1940,

	1933-34	1934-35	1935-36	1936-37	1937-38 (Excluding Burma)
British Empire .. .. .	69	89	29	55	145
Germany .. .. .	1,604	492	2,108	918	177
Italy .. .. .	12,258	10,680	9,226	9,472	18,363
Java .. .. .	2,091	2,448	1,643	1,837	991
Japan .. .. .	4,856	5,945	12,376	11,742	9,221
U.S.A. .. .. .	1,286	541	591	1,729	380
Other countries .. .. .	10	53	25	1,780	131
Total all countries .. .. .	22,174	20,221	27,993	27,539	29,408

Note.—The estimated value of the 29,408 tons imported in 1937-38 was Rs. 25,95,206 or approximately Rs. 90 per ton. The present price is approximately Rs. 150 per ton.