

QUANTUM REFLECTION OF X-RAYS IN CALCITE

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Received October 24, 1924

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

CALCITE is usually regarded as a crystal suitable for precision X-ray research, the intensity of the reflections given by it being much nearer those calculated for an ideal crystal than for instance in the case of rock-salt. Calcite should therefore be particularly well-suited for quantitative studies of the type of X-ray reflection which involves a change of frequency and is analogous to the well-known Raman effect in crystals. A strongly exposed Laue photograph showing numerous such reflections by the crystal planes of calcite was reproduced with a letter by Sir C. V. Raman and Dr. P. Nilakantan under date the 18th of August 1940 which was published in the issue of *Nature* dated the 19th October 1940. Attention was there drawn to the appearance in the photograph simultaneously of the quantum reflections of the first, second and third orders by the cleavage planes of calcite, as well as the well-defined character of the quantum reflections. In the present paper, some further observations on the subject are described and additional photographs are reproduced.

The explanation of the appearance of X-ray reflections with altered frequency is, broadly, that the encounter between the X-ray quantum and the crystal lattice results in the infra-red vibrations of the latter being excited, the incident quantum going off with diminished energy in a direction determined by one or other of the different sets of lattice planes in the crystal. The possibility of such a process and the experimental evidence that it actually occurs in the case of the (111) planes of diamond was indicated by Sir C. V. Raman and Dr. P. Nilakantan in an article in *Current Science* for April 1940. In view of the universality of the phenomenon and its great significance in crystal physics, it would appear desirable to present some considerations of an elementary character which may help to elucidate these new ideas.

Regarding a crystal as a pattern in space of atoms, molecules or ions grouped together in an orderly fashion, we notice that the essential feature of it is the repetitive or periodic character of such arrangement. It is this periodicity which gives us the regularly spaced layers of atoms capable of giving monochromatic X-ray reflections of the usual kind when the rays are

incident on them at an appropriate angle. The concept of a crystal as a purely static ordering of atoms is, however, untenable since such static arrangement can be disturbed in a variety of ways, in particular, by the incidence of the radiation itself, as actually happens in the Raman effect with visible light. It is necessary, in fact, to consider the various possible modes of vibration of the regular assemblage of atoms which we call a crystal. For such a vibration to possess a frequency which can be specified with perfect mathematical rigour, the disturbance should be completely periodic both in space and time, in other words, the ions, atoms or molecules should vibrate in identically the same way, with the same frequency, amplitude and phase in all the lattice cells of the crystal. During such a vibration, the crystal does not lose its character as a space-periodic grouping of the atoms, but becomes in addition a time-periodic structure. It is vibrations of this type which are characteristic of the crystalline state and which appear as sharply-defined lines in the Raman spectra.

Applying now the same electrodynamic principles as those by which Laue derived his well-known conditions for the observation of X-ray diffraction in crystals, we see that the secondary radiations from the atoms in a crystal executing monochromatic vibrations automatically divide themselves into three groups, those of the original or undisturbed primary X-ray frequency ν and two others having frequencies $\nu \pm \nu^*$, where ν^* is the frequency of the atomic vibration. Since ν^* is a strictly monochromatic frequency, the radiations from the atoms in the different lattice cells having a frequency $\nu + \nu^*$ or $\nu - \nu^*$ should be capable of interfering with each other and therefore also of giving diffraction patterns having these radiation frequencies in the same way as the radiations of unmodified frequency ν . The situation, it will be noticed, is closely analogous to that arising in the Raman effect. It should be emphasised that such X-ray reflections with altered frequency are possible only when the atoms in all the lattice cells vibrate in identically the same fashion, in other words, with vibrations having the characteristic crystal frequencies. The position is entirely different in regard to the ordinary or elastic vibrations of the lattice. These have a continuous spectrum of frequencies and merely disturb the regularity of the crystal structure. They give rise to a weak X-ray scattering which should be unobservable except when relatively large volumes of the crystal are operative. The introduction of quantum-theoretical ideas in dealing with either type of effect becomes inevitable in view of the change of frequency, exactly as in the case of the Raman effect. The alteration of frequency means an exchange of energy between the X-ray quantum and the crystal, and this can only occur in one direction or in the other, but not in both directions simultaneously. Accordingly,

we would in general, have at low temperatures *only* the reflections of diminished frequency, $\nu - \nu^*$, reflections of increased frequency $\nu + \nu^*$ being however possible at higher temperatures.

2. *Crystal Structure and Lattice Spectrum of Calcite*

As is well known, calcite crystallises in the rhombohedral division of the hexagonal system. The distribution of the Ca and CO_3 ions around each other as indicated by the X-ray analysis is very similar to that of the Na and Cl ions in the rock-salt lattice. The calcite lattice may, in fact, be described as a distorted rock-salt structure, the distortion arising from the fact that the oblate CO_3 group replaces the spherically symmetrical Cl ion in it. The Ca and CO_3 ions lie alternately along lines parallel to the trigonal axis of the crystal.

The various modes of vibration with specific frequencies of which the calcite structure is capable may be divided into three groups: (a) internal vibrations of the CO_3 groups, (b) rotational oscillations of the CO_3 groups about axes respectively parallel and perpendicular to the trigonal axis and (c) translatory vibrations of the Ca and CO_3 ions relative to each other. So far as the X-ray problem is concerned, vibrations of the class (a) may be left out of consideration in view of their high frequency and relatively small effect on the structure amplitudes of the crystal planes. We are therefore principally concerned with vibrations of the classes (b) and (c). Here again, except with reference to certain special planes in the crystal, it may be assumed that the vibrations of the class (c), namely, movements of the Ca and CO_3 ions relative to each other are the more important, as they would influence the structure amplitudes of the lattice planes strongly. Such vibrations may be divided into two sub-classes, namely, those in which the movements of the Ca and CO_3 groups are predominately parallel to the trigonal axis, and those in which the movements are perpendicular to it. Vibrations of the first sub-class would influence the lattice planes normal or nearly normal to the trigonal axis, while those of the second sub-class would leave these unaffected. The position would be reversed with regard to crystal planes which are nearly parallel to the trigonal axis.

Raman effect investigations show that calcite has two low-frequency vibrations having wave-number shifts of 156 and 283 respectively. The latter is almost certainly a rotational oscillation of the CO_3 group about a line perpendicular to the triad axis. In the long-wave region of the infra-red spectrum, Liebisch and Rubens observed reflection maxima at 106, 330 and 357 wave-numbers, the second of these appearing only in the ordinary ray. It must be assumed that there are in addition, other modes of vibration which are inactive both in infra-red absorption or reflection and in the Raman effect.

The existing theoretical investigations of the vibrations of the calcite lattice concern themselves with the unit-cell containing two Ca CO_3 groups. It is not yet clear whether these give a really satisfactory explanation of the observed spectroscopic behaviour of calcite.

3. Specular Character of Raman Reflections

Figs. 1*a* and *b* in Plate XXXII reproduce two X-ray diffraction photographs obtained using copper K_{α} radiations and a needle-shaped crystal of calcite bathed by the X-ray pencil. The needle was prepared by dissolving out a cleaved rod of calcite in dilute hydrochloric acid until it was thin enough, thus avoiding all possibility of spurious effects due to distortion of the crystal or formation of disturbed surface layers. The needle is seen as a dark shadow crossing the direct X-ray beam. The Laue and the Raman reflections by the (211) planes of the crystal are seen side by side, the former in two different positions corresponding to the two different settings of the crystal, while the latter appears in the two pictures as a narrow streak in directions making nearly the same angle in both cases ($14^\circ 44'$ and $14^\circ 47'$) with the direction of the incident rays. The dynamic spacing calculated from these angles is practically identical with the known static spacing of the (211) planes of calcite, namely 3.03 A.U.

Figs. 3*a*, *b*, *c* and *d* in Plate XXXIII reproduce a series of four Laue photographs obtained with a thin and perfectly flawless cleavage plate of calcite. The X-rays from a molybdenum target tube run at 45000 peak voltage and 12 milliamperes were employed, the beam emerging from a cylindrical pin-hole 93 millimetres deep and 1.6 millimetres diameter. The plate to film distance was 5 centimetres. In Fig. 3*c*, the X-ray beam was nearly normal to the cleavage face of the crystal, while in Figs. 3*b* and 3*d*, the beam made angles of $7^\circ 14'$ and $5^\circ 16'$ respectively with the normal to the surface. In Fig. 3*a*, the X-ray beam grazed a set of lattice planes within the crystal parallel to an external surface of cleavage. The photographs being well-exposed, they exhibit, besides the usual Laue reflections a great number of quantum reflections by the lattice planes of the crystal which may be readily identified from the angular positions of the spots with reference to the direct X-ray beam.

Though the Raman reflections as recorded in the photographs do not appear so sharply defined as the Laue spots, it should not be supposed that this is due primarily to any inherent diffuseness in the reflections. This is clearly indicated by Figs. 1 *a* and *b* where their linear width as recorded on the plates appears actually less than that of the more strongly exposed Laue reflections. As explained by Mr. Rama Pisharoty in the July 1941 issue of

these *Proceedings*, very striking differences in the appearance of the Laue and the Raman reflections arise as the result of several factors, namely (a) the finite lateral extension of the X-ray beam, its angular divergence and the variation of its intensity within the cross-section of the beam; (b) the difference in the nature of the reflection, *viz.*, white and monochromatic respectively, as also the difference in their relative intensities and the geometric laws which they obey, and (c) the finite thickness of the crystal employed. The X-ray beam employed in obtaining Laue photographs has usually a considerable angular divergence, being in the present experiments nearly 2 degrees of angle. Fig. 4 in the text illustrates the effect of the arrangement employed to restrict the divergence of the beam on the distribution of intensity inside it.

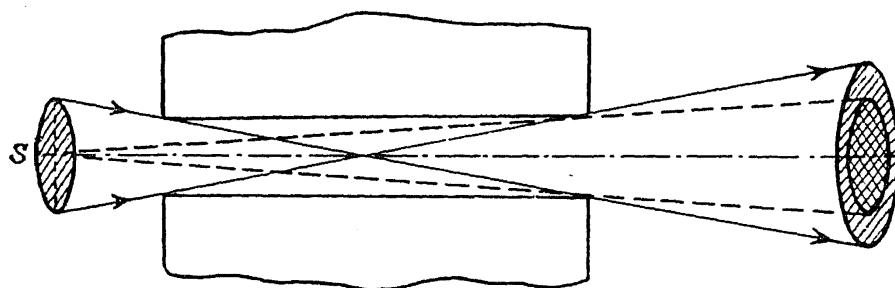


FIG. 4. Cross-Section of X-Ray Beam

It is evident from the figure that there would be an intense central part in the emerging beam having a diameter slightly larger than that of the pin-hole and a less intense peripheral part; these we may designate as the umbra and penumbra respectively. The reflection of the intense central cone of rays would naturally be the first to be recorded, while the reflection of the penumbral rays would follow later. Accordingly, unless the exposures are sufficiently prolonged, a certain lack of sharpness in the boundary of the reflection is inevitable. A similar lack of definition at the edges would also result from the finite thickness of the plate, as illustrated in Fig. 5. This again would be much more obvious in recording a weak reflection photographically than a strong one.

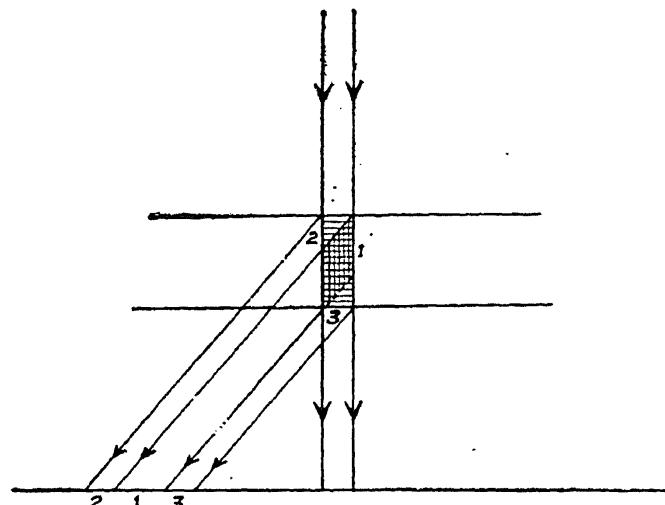


FIG. 5. Reflection from a Plate of Finite Thickness

It should not, however, be inferred from the foregoing remarks that the Raman reflections of calcite are geometrically as sharp as those of the (111) planes in diamond. Indeed, it is obvious that there is a great difference in the behaviour of various crystals in this respect. The reflections of calcite, for instance, are definitely superior in definition to those of sodium nitrate which has a very similar crystal structure. It is evident that one of the factors which make for sharpness of the reflections is the rigidity of the bindings in the crystal. This is indicated by the fact that the frequencies of the similar modes of lattice vibrations are much higher for calcite than for sodium nitrate.

4. Geometry and Intensity of Raman Reflections

As already mentioned above, the particular crystal planes which give the quantum reflections are in most cases readily identified. For this purpose, we measure the angular distance of the spots from the direction of the central beam and hence calculate the dynamic spacing responsible for the reflection; this is then compared with the known list of the static spacings of the crystal giving an appreciable intensity of reflection. The disagreements are never large. If there be any doubt, this can be resolved by analysing the Laue diagram and identifying the planes giving associated Laue reflections. A fairly complete analysis of all the Raman reflections seen in Fig. 3 *c* which refers to the case in which the crystal is set with its cleavage face normal to the X-ray beam is exhibited geometrically in Fig. 6.

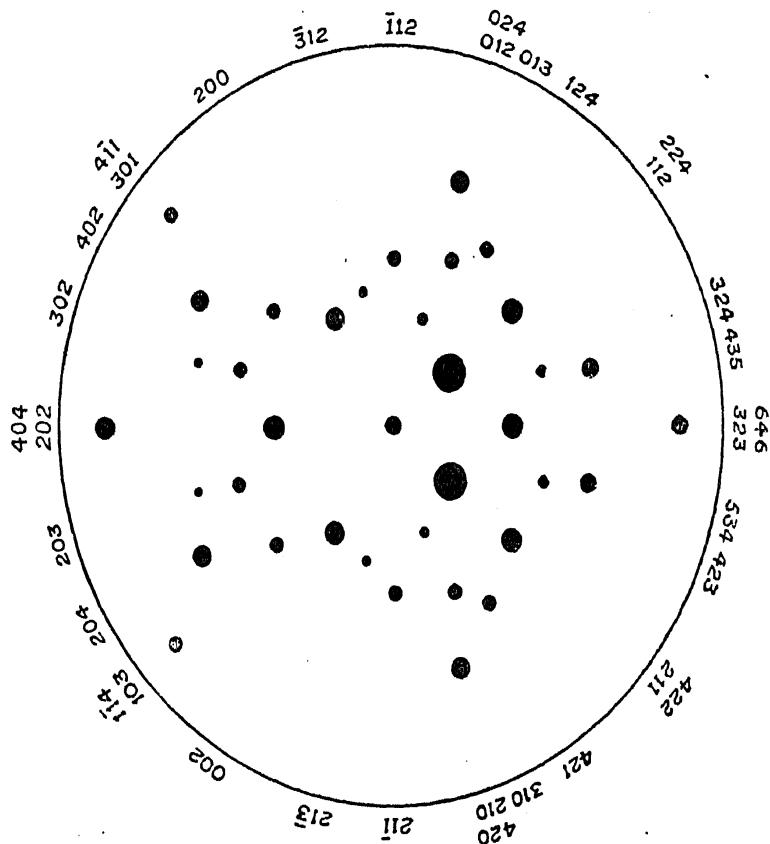


FIG. 6. Raman Reflections in Calcite Crystal

Comparing Fig. 3 *c* with Figs. 3 *b* and 3 *d*, it will be seen that though the Laue patterns themselves are completely different, the Raman reflection patterns show only changes of intensity and no noticeable changes in the position of the spots.

Table I gives a detailed list of all the crystal spacings in calcite which have been identified from the Laue photographs as giving quantum reflections. The table has been put in to emphasise the fact that numerous crystal planes give these reflections and that within the rather restricted range of

TABLE I
Raman Reflections in Calcite

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A.U.	Static spacing in A.U.	Intensity estimate
112	3° 2'	10° 18'	2.99	3.03	10
	9° 52'	3° 27'	3.04	3.03	10
	14° 39'	-1° 14'	3.06	3.03	3
224	9° 52'	19° 8'	1.52	1.52	2
	14° 39'	12° 11'	1.53	1.52	6
336	18° 50'	12° 28'	1.01	1.01	4
	19° 25'	11° 53'	1.01	1.01	..
200	12° 19'	6° 53'	2.12	2.09	5
	13° 3'	6° 9'	2.12	..	5
	7° 8'	12° 8'	2.12	..	5
	6° 16'	13° 7'	2.11	..	4
400	18° 59'	20° 36'	1.05	1.045	6
	17° 29'	21° 52'	1.05	..	4
012	10° 27'	7° 24'	2.29	2.28	2
	10° 14'	6° 24'	2.32	..	2
	11° 23'	6° 45'	2.25	..	0.5
	10° 58'	7° 2'	2.27
024	16° 26'	19° 20'	1.15	1.14	4
	16° 13'	19° 57'	1.14	..	4
	17° 54'	18° 30'	1.14	..	5
	17° 50'	18° 26'	1.14	..	5
112	14° 54'	10° 18'	1.62	1.60	2
	13° 58'	11° 8'	1.63	1.60	3
	15° 17'	9° 43'	1.64	..	2
	15° 11'	10° 1'	1.62	..	2
	14° 40'	10° 38'	1.62	..	2
	15° 34'	9° 26'	1.64	..	2
323	12° 49'	8° 41'	1.90	1.91	10
	19° 3'	..	1.94	..	4
202	12° 37'	8° 41'	1.92	1.93	4
	17° 53'	..	1.97

TABLE I (contd.)

Miller Indices	Glancing angle θ	Glancing angle ϕ	Dynamic spacing in A.U.	Static spacing in A.U.	Intensity estimate
235	19° 34'	15° 38'	1.17	1.18	3
	19° 1'	16° 5'	1.17
556	20° 40'	19° 38'	1.02	1.03	6
	20° 50'	19° 48'	1.02
512	16° 59'	22° 43'	1.04	1.04	2
	17° 29'	22° 7'	1.04
411	22° 54'	20° 24'	0.96	0.96	1
	23° 13'	20° 9'	0.96
446	20° 57'	18° 31'	1.05	1.06	2
	21° 26'	17° 58'	1.05
435	18° 17'	15° 25'	1.23	1.23	..
	18° 21'	15° 17'	1.23	..	4
302	12° 15'	15° 11'	1.50	1.47	..
	12° 0'	15° 32'	1.49	..	1
301	13° 58'	12° 54'	1.53	1.52	5
	14° 4'	12° 42'	1.53	..	4

settings of the crystal employed, the dynamic spacings do not diverge noticeably from the static values. Only in a few cases, however, are the settings sufficiently varied to enable any conclusions to be drawn about the value of the phase-wave inclination, ϑ , to the crystal planes under study. In the case of the (112) planes, for instance, there is a distinct progressive change of the dynamic spacing with alteration of the crystal setting, indicating that ϑ is definitely smaller than 90°. A more detailed investigation, however, would be necessary to settle this matter definitely.

A careful study of the Laue patterns shows that the Raman reflections do not always lie on the same radial line as the corresponding Laue reflections. A distinct lateral shift or azimuth effect is detectable in a number of cases. The streaks due to the white radiations are also in certain cases not radial. Only when the plane of incidence coincides with a crystallographic plane of symmetry that it can be definitely said that there is no lateral shift or azimuth effect. Usually, however, the Laue and Raman reflections are too near each other and the size of the spots too large to arrive at any definite conclusions. The fact that the azimuth effect is observable at least in certain cases indicates that the phase waves in calcite, as in diamond, have an orientation and an azimuth standing in definite relation to the crystal structure.

It may also be mentioned in passing that a careful analysis of the four Laue patterns reproduced as Fig. 3 revealed the presence of a few diffuse spots in each case whose origin could not be definitely identified.

The intensities shown in the last column of Table I are of course, only relative, and vary with the setting. They are, however, of some interest in relation to the question as to the relative intensity of the Bragg and Raman reflections by the individual planes. Theory indicates that there is not necessarily a proportionality between the static and dynamic structure amplitudes of a set of lattice planes, the latter depending on the particular modes of vibration responsible for the dynamic reflection. While broadly it may be said that the planes which give strong Bragg reflections, *e.g.*, the cleavage planes, also give strong Raman reflections, there are evidently exceptions to this rule. In particular, the (556) planes which are nearly normal to the trigonal axis of calcite give Raman reflections which are remarkably strong considering their relatively small static structure amplitude. It should be remarked in this connection that several of the possible lattice vibrations in calcite involve movements of the Ca and CO_3 ions along the trigonal axis, and hence should give marked variations of the structure amplitudes of planes normal to it. A fuller study of this point would obviously be of great interest.

Figs. 2*a* and *b* in Plate XXXII illustrate the effect of rising temperature on the relative intensity of the classical and quantum reflections in calcite. The two types of reflection exhibit a reciprocity of behaviour, a marked diminution of intensity in the classical reflection with rise of temperature being accompanied by a marked increase of intensity of the quantum reflections. It is noteworthy that the (210) planes of calcite do not exhibit the exceptional behaviour observed with the same planes in sodium nitrate crystals.

5. Summary

The paper presents the results of a preliminary study of the X-ray reflections of the second kind observed in calcite. Numerous planes in this crystal exhibit such reflections, the dynamic spacings in most cases varying but little with the setting of the crystal. Observations are recorded concerning the sharpness of the reflections, their intensity and the influence of temperature on the same. The results are considered in the light of the quantum theory of X-ray reflection.