

LOW-TEMPERATURE STUDIES OF THE RAMAN X-RAY REFLECTIONS IN CRYSTALS

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1. Introduction

EARLY in 1940, Sir C. V. Raman and Dr. P. Nilakantan made the very significant discovery that the (111) planes of the crystal lattice in diamond give a second kind of monochromatic X-ray reflection which is as truly geometric as the usual Bragg reflection, being quite as sharply defined, but having evidently a different origin since it is observable over a wide range of settings of the crystal and obeys a different geometric law. The observed characters of this reflection indicated that it represents the X-ray analogue of the well-known Raman effect observed in the scattering of light. In other words, the X-ray photon falling upon the crystal excites the high frequency or infra-red vibrations of the crystal lattice, the latter deriving their energy from the incident X-rays. The appearance of the X-ray photon of diminished energy as a geometric reflection by the lattice planes is accounted for on the very reasonable assumption that the infra-red vibrations are excited simultaneously in all the lattice cells of the crystal with such phase relations as to give rise to a coherent effect. It follows from these considerations that if the primary X-ray frequency is ν , the reflected X-rays have a frequency $(\nu - \nu^*)$, ν^* being the frequency of the excited infra-red vibrations of the crystal.

It is well known from the Raman effect studies on the scattering of light in crystals that in general, both "Stokes" ($\nu - \nu^*$) and "anti-Stokes" ($\nu + \nu^*$) radiations are observed in the spectra, their absolute intensities being respectively proportional to

$$\frac{1}{e^{h\nu^*/kT}} \text{ and to } \frac{1}{e^{h\nu^*/kT} - 1}$$

and their relative intensity being accordingly $e^{h\nu^*/kT} : 1$. When $h\nu^* \gg kT$, it is evident that only the component of diminished frequency would be present. On the other hand, when $h\nu^* \ll kT$, the two components tend to be of equal intensity. In the case of diamond, the observed facts indicate that the infra-red vibrations excited by the X-rays are the same as those giving the strong Raman line at 1332 cm.^{-1} . Since therefore, $h\nu^*$ is much greater than kT at the ordinary temperature, it

follows that in the case of diamond we are only concerned with X-rays reflected with *diminished* frequency. It follows also, as indicated by the formulæ, that the intensity of the reflection should then be sensibly independent of temperature. This indication of theory was confirmed by Raman and Nilakantan in their earliest experiments by heating the diamond to a few hundred degrees above the room temperature, no marked increase of intensity being then observed. They also suggested as a test of the theory, the study of the effect of cooling down the diamond to liquid air temperature. This test was carried out by them a few months later; the results which were in entire accord with the theory were briefly reported at the time (1940). A more detailed description of the full technique of the investigation appears in a paper by Raman and Nilakantan elsewhere in these *Proceedings*.

It is obviously of great interest to supplement the investigations on diamond by similar researches with other crystals at low temperatures. It is evident that, in general, we would have quantum or Raman X-ray reflections of both *diminished* and *increased frequencies* superposed on each other. The observed intensity of the modified reflection should then be the sum of the two expressions quoted above. In other words, the actual intensity of the quantum reflection would be proportional to

$$\frac{e^{h\nu^*/kT} + 1}{e^{h\nu^*/kT} - 1}$$

At sufficiently low temperatures, this expression reaches the limiting value unity. On the other hand, at sufficiently high temperatures, it asymptotically tends to the value $2kT/h\nu^*$, thus becoming proportional to the absolute temperature. It is evident also that the ratio between the limiting intensity at low temperatures and the values reached at higher temperatures would depend on the frequency of the infra-red vibrations of the crystal excited by the X-rays. The higher this frequency, the more nearly would the intensity tend to remain constant throughout the whole range of temperature. On the other hand, when the frequency ν^* is low, we should have to go down to liquid air temperatures or even lower before the limiting intensity is reached.

It is evident from the foregoing remarks that the study of the quantum or Raman X-ray reflections gives us a method of investigating the infra-red spectrum of crystals from a new point of view, which should obviously prove of great importance. It should also be remarked that the study of the intensity curves of the modified reflections and their comparison with the variation to be expected theoretically from the known infra-red frequencies of the crystal, would furnish an experimental confirmation of the nature of these reflections as quantum or Raman reflections of modified frequency and

indeed enable us to determine by a thermodynamic method the actual changes of frequency occurring in such reflections. To emphasize this aspect of the matter, the present investigation has been carried out with a series of four crystals whose infra-red frequencies are in descending order of magnitude, viz., carborundum, sodium-nitrate, rock-salt and penta-erythritol.

2. Experimental Arrangements

The X-ray camera used for taking the Laue photographs at low temperatures is constructed essentially on the principles developed by Nilakantan and is illustrated in Fig. 1. The crystal C is mounted in a cavity at the end of a copper rod R fixed to the bottom of the inner tube of a cylindrical metal

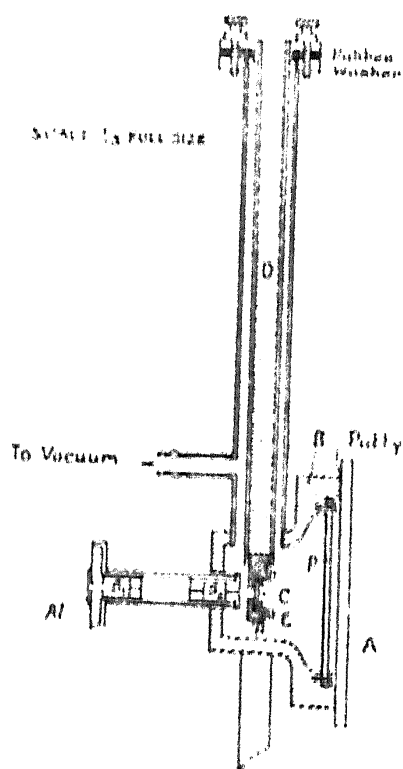


FIG. 1
Low-temperature high-vacuum
X-ray camera

Dewar flask D and carefully pressed into metallic contact by thin copper foils and a screw ring E. $S_1 - S_2$ is the lead-slit system which is fixed to the camera B in such a way that the narrow beam of X-rays emerging from it passes through the centre of the crystal, and falls on the photographic film. The film adapter P is screwed on to the flange-end of the camera and an aluminium flat A is fixed at the end by pressing it home with high-vacuum putty. The lead slit S_1 is rendered vacuum tight by a thin aluminium foil. A high vacuum is maintained in the camera throughout the exposure by means of an oil diffusion pump. One fill of the tube D with liquid air lasts for half an hour; but during the exposure, the level is made up every fifteen minutes. The exposure is started only half an hour after the crystal is cooled down to the liquid air temperature, thus ensuring the crystal being at that temperature from the start of

the exposure. In photographing the spectra, an intensifying screen is not used, as it was found that the latter becomes a serious source of error in the measurement of the intensities of spots. The X-ray generator is a demountable Coolidge tube with a Mo-anticathode and operated at 45 K.V. and a fairly steady milliamperage of 25 m.A. Laue photographs exhibiting the Raman reflections are taken at the room temperature for the same time of exposure under identical experimental conditions. Their relative intensities are measured microphotometrically making use of a density-log. intensity curve and for the same mode of development as that employed for the other

films obtained for the molybdenum radiations. In the case of rock-salt, photographs were also taken for the temperature of solid carbon dioxide and the relative intensities obtained microphotometrically were checked up by those got by an alternative method of varying the time of exposure till the intensities of the spots at the two temperatures are equal. If t_1 and t_2 are the times of exposure at the two temperatures T_1 and T_2 , the ratio of intensities $I_1/I_2 = (t_2/t_1)^n$, where n is the Schwarzschild constant which is found experimentally to be nearly unity for the X-ray film and the radiations used. Considering the limitations of the experimental method, the possible error in the values will be as high as 10%. The photographs with carborundum were also obtained at 600°T and 900°T using for the purpose an electrical heater of nichrome wire, and their intensities were compared with that obtained at the room temperature for the same setting of the crystal.

3. The Experimental Results and their Significance

Figs. 2 *a-h* in the accompanying Plate illustrate the Laue patterns obtained with carborundum, rock-salt, sodium nitrate and penta-erythritol. It will be noticed that in every case the reflections persist at the liquid air temperature. The corresponding Laue reflections exhibit an enhanced intensity which is the greater when the diminution of intensity of the Raman reflections is most marked. This clearly indicates that the temperature dependence of the intensity of the Bragg or the Laue reflections can only be correctly explained when their relation to the Raman reflections from the same crystal planes is taken into account.

In Fig. 3, the intensities of the Raman reflections at the different temperatures as compared with that given at the liquid air temperature by the

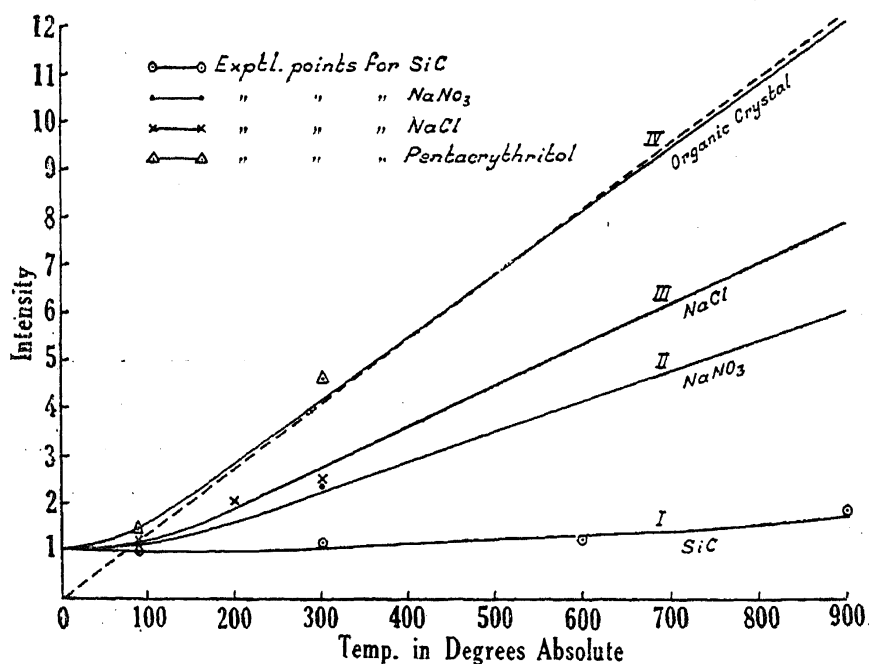


FIG. 3

Intensity of Quantum Reflections as a Function of Temperature

theory taken as the standard, are plotted along side the theoretical curves of intensities obtained in accordance with the equation given earlier and with appropriate frequencies chosen for each case (see Table I).

TABLE I

Crystal	T ⁰	90	200	300	600	900
	kT × 10 ⁻¹⁵	12.3	27.4	41.1	82.2	123
Carborundum ν* = 800 cm. ⁻¹	$\frac{h\nu^*}{kT}$	12.9	5.8	3.9	1.94	1.3
	Intensity (Theo.)	1	1.006	1.042	1.34	1.77
	Intensity (Exp.)	1	..	1.1	1.3	1.82
Rock-salt ν* = 160 cm. ⁻¹	$\frac{h\nu^*}{kT}$	2.58	1.161	.774	.387	.258
	Intensity (Theo.)	1.163	1.9	2.72	5.3	7.9
	Intensity (Exp.)	1.163	1.93	2.43
Sodium nitrate ν* = 200 cm. ⁻¹	$\frac{h\nu^*}{kT}$	1.65	.74	.5	.23	.165
	Intensity (Theo.)	1.073	1.588	2.209	4.125	6.128
	Intensity (Exp.)	1.073	..	2.36
Penta-erythritol ν* < 100 cm. ⁻¹	$\frac{h\nu^*}{kT}$	1.65	.74	.5	.23	.165
	Intensity (Theo.)	1.48	2.82	4.08	8.14	12.1
	Intensity (Exp.)	1.48	..	4.59

Carborundum.—The carborundum crystal used in the investigation is a clear plate of nearly 1 mm. thick and the Laue photograph shows that it belongs to the hexagonal type. The X-rays were incident nearly normal to the cleavage face. The Raman reflection appears in close proximity to the Laue reflection as a *round* spot which is fairly intense. The reflection shows only a small increase of intensity as the temperature is raised from 90° T to 900° T. This suggests that the infra-red frequency active in the Raman reflection of X-rays is relatively high. According to Schaefer and Thomas (1923), the hexagonal type of carborundum crystal shows only one strong sharp infra-red

reflection at $12\ \mu$ ($830\ \text{cm.}^{-1}$) which they assume as the fundamental frequency for SiC. Accordingly, Curve 1 in Fig. 3 is drawn assuming that the Raman frequency associated with the modified spot is nearly $800\ \text{cm.}^{-1}$. It will be noticed that the experimental points all fall in the neighbourhood of this curve, indicating that the frequency change involved in the reflection is the same as the characteristic infra-red frequency.

Rock-salt.—The Laue photographs of a thin plate of rock-salt are obtained for 90° , 194° and 300° T with X-rays nearly normal to the 100 plane. A lowering of the temperature is accompanied by a change of intensity of the modified reflections which approximately fits in with a frequency of $160\ \text{cm.}^{-1}$ for the active infra-red vibration as shown by Curve 3 in Fig. 3. Rock-salt has only one rest-strahlen frequency at $52\ \mu$ ($192\ \text{cm.}^{-1}$) and its Raman spectrum obtained by Fermi and Rasetti (1931) shows two fairly intense lines at 160 and 350 and at least two other weak diffuse maxima between 200 and $300\ \text{cm.}^{-1}$. In a separate paper, the vibrations of the sodium chloride lattice are analysed and the X-ray active mode of vibration is indicated. The results of the present investigation show that the frequency of this vibration is in the neighbourhood of $160\ \text{cm.}^{-1}$. In addition to a diminution of intensity, a slight sharpening of the Raman reflections is also noticeable at the liquid air temperature. This observation is of great theoretical significance, but the exact extent of sharpening can be ascertained only by using a linear slit and the reflection method for photographing it.

Sodium nitrate.—The Laue patterns reproduced in Figs. 2 *e* and *f* show the strong Raman reflections from the 211 plane of a crystal of sodium nitrate very near the Bragg setting in addition to other weak reflections. The relative intensities of this spot at 90° and 300° T plotted in Curve 2, Fig. 3 show agreement with a vibrational frequency of nearly $200\ \text{cm.}^{-1}$. The Raman spectrum of sodium nitrate yields two intense lattice frequencies at 98 and $185\ \text{cm.}^{-1}$ (Nisi, 1932; Nedungadi, 1938) and thus the latter is to be taken as the active vibration in the modified reflection of X-rays by the 211 plane. Raman and Nilakantan (1940) observed that if the temperature is raised to 280° C., the modified reflection of X-rays from the 210 plane gains rapidly in intensity with a corresponding fall in intensity of the Laue reflections. This observation taken in conjunction with the results obtained here suggests that the active frequency for these two planes may be different. The temperature studies of intensity of the modified reflection from various crystal planes thus affords a method of determining the mode of vibration which varies the structure amplitude of any plane to the maximum extent.

Penta-erythritol.—This crystal is chosen as the representative of organic crystals of which the lattice is molecular and the units are held together by

weak van der Waals forces. The intensity of the modified reflection is considerably diminished at 90° T and is nearly one-third of that at 300° T, being thus nearly proportional to the absolute temperature. In view of this marked diminution of intensity at the liquid air temperature, it is not surprising that Lonsdale, 1940 (see Preston, *Nature*, 1941) failed to observe the same in organic crystals especially as the pattern obtained by her at the lower temperature is masked by the intense halo of liquid air. From the measurements of relative intensities made up to 90° T, it is not possible to obtain even the roughest estimate of the infra-red frequency in this case. We could however, conclude that this frequency should be less than 100 cm.^{-1} as shown by Curve 4 in Fig. 3. The dotted curve by its side shows what the rate of fall would be if it were proportional to the absolute temperature. This conclusion regarding the Raman-active lattice vibration in modified X-ray reflection by organic crystals is in agreement with the experimental observation in the Raman effect that a large variety of these crystals yield discrete lattice oscillations with a frequency range of 25–120 cm.^{-1} (Venkateswaran, 1938).

General Remarks. The present investigation thus clearly demonstrates that the determination of the rate of change of intensity of the modified X-ray reflection with temperature provides a new method of obtaining the infra-red spectrum of crystals. The frequency of vibration could be estimated fairly accurately by measurements made at the room temperature and at liquid air temperature if it falls in the region 250–500 cm.^{-1} . For frequencies below 250 cm.^{-1} , temperatures lower than 90° T will have to be employed to obtain the same degree of accuracy. The method promises to be particularly suitable for crystals for which the methods of light scattering and the infra-red absorption or reflection are not applicable.

In conclusion the author wishes to express his heartfelt thanks to Sir C. V. Raman, F.R.S., for his suggestions and keen interest in the work.

Summary

The Raman reflections of X-rays by carborundum, rock-salt, sodium nitrate and penta-erythritol are obtained at liquid air temperature with a specially designed vacuum X-ray camera and their intensities are compared with those at room temperature. For rock-salt an intermediate temperature of solid carbon dioxide and for carborundum two higher temperatures namely 600° and 900° T have also been employed. From the relative intensities of these reflections at various temperatures, the infra-red frequency active in the particular reflection is ascertained in each case making use of the following formula

Intensity $\propto \frac{e^{h\nu^*/kT} + 1}{e^{h\nu^*/kT} - 1}$. These frequencies are about 800 cm.⁻¹ for rock-salt, 160 cm.⁻¹ for sodium nitrate and 100 cm.⁻¹ for penta-erythritol. They coincide with one or other frequencies observed in the Raman effect or in the infra-red spectrum of the respective crystal. This new X-ray effect thus provides a novel method of evaluating the infra-red frequencies of crystals and is specially applicable to substances for which the methods of light scattering and infra-red spectroscopy are inapplicable.

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