

## X-RAYS, CRYSTALS AND THE INFRA-RED SPECTRUM

BY

SIR C. V. RAMAN

THE *Proceedings of the Indian Academy of Sciences* for October 1941 is devoted to a symposium of fifteen papers dealing with the interaction between X-rays and crystals which results in an excitation of the infra-red vibrations in the solid and a consequent reflection of the X-rays with change of frequency. This phenomenon was first described in an article in *Current Science* for April 1940 by the present writer and Dr. P. Nilakantan, and was further reported on in the issue of *Current Science* for May 1941. The symposium now published is a comprehensive account of the whole subject and shows that the new facts and ideas put forward in April 1940 were solidly based on reality. The theory given in broad outline in earlier publications is now fully developed and finds striking experimental confirmation in various directions.

The phenomena of the scattering of light in crystals show clearly that the interactions between matter and radiation which involve a change of frequency in the latter can only be successfully interpreted on the basis of quantum mechanics. That a similar situation also arises in regard to X-rays becomes evident when it is recalled that the secondary X-radiation from a vibrating atom in a crystal appears, in part, with a change of frequency. Any coherent vibration of the atoms in a crystal with a specifiable frequency is therefore capable of giving rise to radiations of altered frequency which can interfere with each other and give rise to observable effects. The change of frequency involves an exchange of energy between the crystal and the electromagnetic field, and this can only occur in complete quanta or units of the particular vibration frequency. The interferences which arise may therefore be regarded as due to an inelastic collision of the X-ray photons with the crystal lattice. They appear as geometric reflections of the X-rays by the lattice planes of the crystal, analogous to, but quite distinct from, the reflections of the usual kind involving no change of frequency.

The vibrations possible in a crystal lattice may be classified under two heads. The

first kind are of the macroscopic or elastic type which may be described without specific reference to the atomic architecture of the solid. They present a continuous spectrum of frequencies, and when the limiting wave-length is chosen sufficiently large, their aggregate energy is small, while the energy of a particular frequency of vibration is quite negligible. In these circumstances and in view of the arbitrary wave-length and orientation of the elastic vibrations, their effect on the X-ray propagation is very small, appearing as a diffuse scattering. Of much greater importance from the X-ray point of view are the atomic or infra-red vibrations which involve a time-periodic variation of the fine structure of the solid. These have higher frequencies than the elastic vibrations and appear as monochromatic lines in the infra-red spectrum of the solid. The nature of these vibrations is very fully discussed in the opening paper of the symposium. It is shown that the observed monochromatism of the infra-red vibrations indicates that they take place in a completely ordered fashion, the frequency, amplitude and phase of the vibrations being identical over extended domains in the crystal. The result of such synchronism is that the associated secondary X-radiations have coherent phase-relationships and give rise to X-ray reflections of observable intensity in geometrically specifiable directions. (See Fig. 1.)

The second paper of the symposium is devoted to a mathematical formulation of the theory. The classical and quantum reflections are considered together, as it appears from the theory that they stand in close relation with each other. The secondary radiations from the vibrating atoms in a crystal are analysed, and expressions are derived from the static and dynamic structure factors. In the limiting case when the lattice vibrations are in perfect synchronism in all the cells of the crystal, the intensity problem admits of a complete solution, as the vibration energy of each lattice cell may be then taken as one quantum of the particular frequency. The calculation shows that the quantum X-ray reflections have

an appreciable intensity, smaller than but not negligibly small in comparison with, the intensity of the classical reflections.

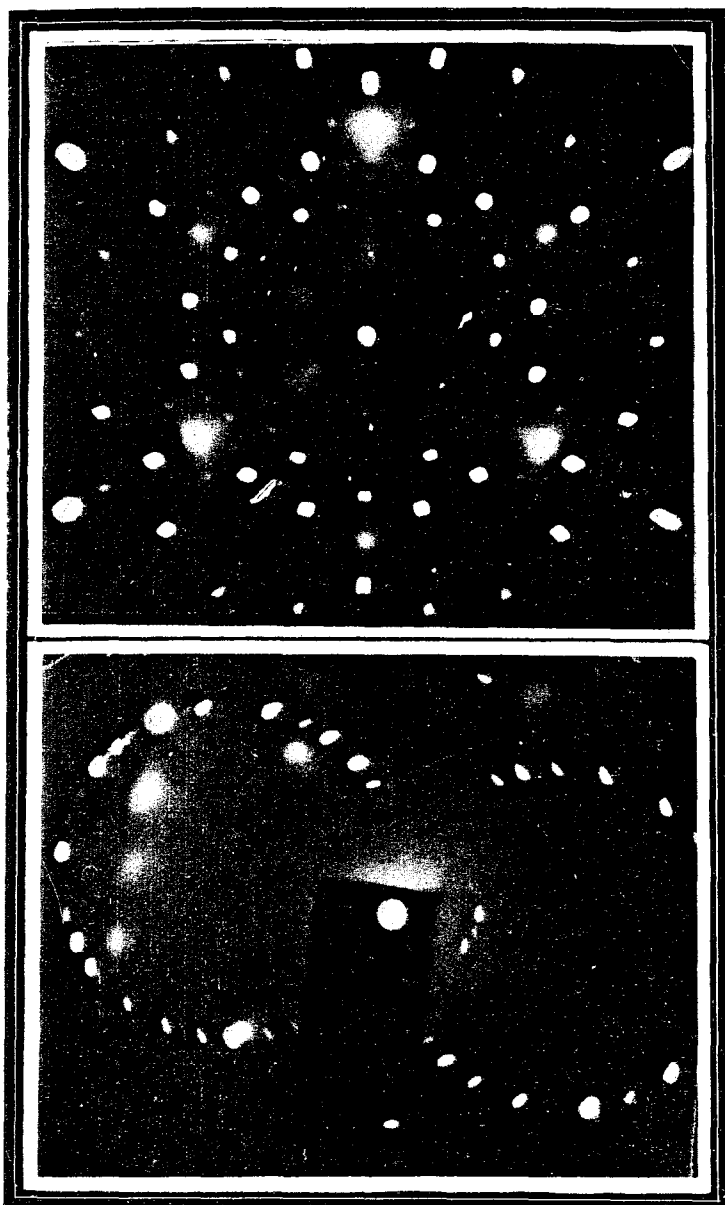


FIG. 1

Quantum X-ray Reflections in Benzil Crystals

The third paper in the symposium presents the experimental evidence in a particular case, *viz.*, that of diamond, quantitatively confirming the theory. Particularly noteworthy are the photographs of the (111) quantum reflections of diamond taken with a very fine beam of X-rays and very prolonged exposures and reproduced as Fig. 6 in Plate XVIII accompanying the paper. The reflections appear as exceedingly fine lines in the record, indeed as sharp as they

would be if they were true geometric or specular reflections without any angular spread. These two photographs alone would be sufficient to show that the various alternative theories of the phenomenon which have been recently put forward in the X-ray literature are untenable. All these theories indicate a broad or diffuse scattering, instead of a sharply defined geometric reflection as is actually observed in the case of diamond.

Of the remaining twelve papers in the symposium, no fewer than six are contributed by Dr. C. S. Venkateswaran. Particularly valuable are his studies of the intensity of the quantum X-ray reflections at liquid air temperatures by a series of crystals, *viz.*, carborundum, rock-salt, sodium nitrate and penta-erythritol. The experimental data are in complete accord with the theoretical formulæ and indicate that such X-ray studies with crystals open a new avenue of approach to infra-red spectroscopy. The case of metals dealt with by Mr. Bisheswar Dayal in another paper in the symposium is an instance where such an approach might prove of great importance.

An important result indicated by the quantum theory of X-ray reflection is that in particular cases, the classical reflections may vanish while the quantum reflections persist, or *vice versa*. In a remarkable paper appearing in the symposium, Mr. Rama Pisharoty calculates the intensities of the (222) and (662) quantum reflections by diamond and shows that they are in agreement with the intensities as actually observed, thereby indicating that these so-called "forbidden" reflections which should not appear on the classical theory are in reality quantum reflections. Another remarkable case of the kind is furnished by the ratio of the intensities of the (111) and (222) reflections by the lattice planes in rock-salt. The theoretical calculations by Dr. Venkateswaran indicate, in striking agreement with observation, that this ratio is far smaller for the quantum reflections than for the classical reflections.

Four of the papers in the symposium deal with the case of organic crystals, *e.g.*, naphthalene, benzophenone, hexamethylenetetramine and benzil. Fig. 1 above is

reproduced from the plate accompanying Mr. R. V. Subramanyam's paper on benzil. In the case of aromatic compounds, the infra-red vibrations with which we are principally concerned are those of relatively low frequency involving rotational or translational movements of the aromatic rings. It is evident that the crystal planes parallel to the aromatic rings would be strongly affected by such movements and would

therefore give intense quantum reflections, while the lattice planes parallel to the rings would be unaffected by such movements and would therefore fail to give the quantum reflections. This indication of theory is strikingly confirmed by observation. Indeed in the case of benzil, the intense quantum reflections observed immediately indicate the number, orientation and azimuth of the benzil molecules present in each lattice cell.

## CAMOUFLAGE PAINTS

BY

S. S. BHATNAGAR AND N. N. SEN GUPTA

(Laboratories of the Director of Scientific and Industrial Research, Calcutta)

SINCE the World War of 1914-18 the word camouflage, originally a French word, has been adopted throughout the world to denote a particular type of military deception in which paints and artists play the major role. In the unrestricted sense the word may be applied to any device which is calculated to mislead the enemy. Such general camouflage has been practised by belligerent nations throughout history. The Wooden Horse of Troy, the Moving Forest in Shakespeare's Macbeth and the incalculable Shivaji's escape in a basket of sweetmeat under the very nose of Aurangzeb are some of the popular examples of camouflage in the general sense. Napoleon is known to have made extensive use of camouflage in his campaigns, and it will be readily understood that in war, in which everything is considered to be fair, military deception must occur to generals and soldiers alike as almost a first principle.

As in all great things, man learnt the broad principles of this art of military camouflage from nature. She is the effortless master camoufleur who resorts to camouflage in order to preserve her species. Examples of nature's camouflage extend from the tropical vegetation, through the desert sand, to the bare winter twigs of the temperate zone and the snows of the Polar regions, and these are too many and well known to mention. The principle followed by nature is to produce species which in colour and form are more or less indistinguishable from their surroundings in order to avoid easy

detection by enemies. Much of the military camouflage follows exactly the same principle. Gun positions, machine gun emplacements, observation posts, aerodromes, industrial buildings and large installations have to elude detection by the searching eye of the enemy from the air, and the means is camouflage which renders them indistinguishable from the general surroundings. Ships have to mislead submarine commanders as to their exact course, and "dazzle painting"—a form of camouflage in paints—was one of the devices adopted during the last Great War. Even the colours of the field uniforms are a form of camouflage.

Camouflage as an established military and naval practice originated during the Great War of 1914-18. The French gave the lead and the British and the other belligerent nations followed and developed the principle and practice rapidly in all possible spheres. As the aerial eye became ubiquitous and the aerial attack the most potent form of warfare, the necessity for reasonably effective camouflage became one of the fundamental concerns of Governments and fighting forces.

In this article it is proposed to deal with the technical aspects of camouflage paints which are being used in colossal quantities in all belligerent countries. Extensive demands have arisen in this country and paint manufacturers in India are being required to supply large quantities at short notice. These demands are likely to increase as the war situation develops in the Middle and