

Development of X-ray Crystallography Research in India

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X-ray crystallography began in India with the successful determination of the structures of naphthalene and anthracene crystals in 1929 by the method of trial and error. The results of these determinations were published in 1930. This beginning however, has an interesting background. C. V. Raman and his students at the Indian Association for the Cultivation of Science in Calcutta were greatly interested in the study of optical anisotropy of molecules from scattering of light. He and Ramanathan extended the optical theory of scattering to X-ray diffraction by liquids and attempts were started in this laboratory by Sogani and others to compare the theory with experimental results. It became clear from these experiments that the shapes of the molecules and the intermolecular forces had profound influence on the diffraction patterns. I found at about the same time that phase changes in the liquid alloys of sodium and potassium could be studied by X-ray diffraction in a way similar to that possible in the case of solid alloys. All these studies led to the idea that the shapes of molecules and the intermolecular forces correspond to some degree in the solid and the liquid states.

C. V. Raman and K. S. Krishnan published at this time their highly interesting work on the magnetic birefringence of liquids which led to a method of measuring also the magnetic anisotropies of molecules. The experimental investigations that followed made it clear that the benzene ring has very strong magnetic as well as optical anisotropy. The direction of the optical anisotropy can be easily deduced theoretically from the idea that the anisotropy originates from the anisotropic polarisation field and that therefore the refrangibility is greater when the electric vector is in the plane of the molecule than when normal to it. From experiments with benzene and other aromatic liquids it was found that the diamagnetic susceptibility is greater numerically for the magnetic field normal to the benzene ring than parallel to it. This is exactly what one should expect theoretically according to quantum mechanical ideas. At about the same time the attempt of W. L. Bragg to explain the optical birefringence of some crystals from their structures by calculating the polarisation

fields was of great interest to us, and I tried to see whether stress-optical effects in alkali halides and amorphous solids could be explained by this method. The attempts proved unsuccessful and it was concluded that there should be changes in the deformations of the atoms due to their displacements and change of crystalline field in the strained state. These changes alter their polarizabilities, and thus may be the cause of the discrepancies.

Since it was clear that knowledge of the magnetic and optical anisotropies of crystals may give a clue to the orientation of the molecules, and as the benzene ring was found to have very marked anisotropy, crystals of the aromatic compounds naphthalene and anthracene were the first to be tried for finding the molecular orientation. Bhagavantam measured the magnetic anisotropies of these two crystals and found that the benzene planes should lie nearer to the bc plane than the ac plane. This is contrary to the structure given by W. H. Bragg in which he puts the molecular plane along ac . The optical anisotropy also corroborated the results of the magnetic measurements. It was therefore felt necessary to re-examine the structure on the basis of X-ray diffraction.

The task of cutting this new ground was taken up by me as crystals fascinate me. The reason for this fascination to my mind is that when I started my research career under Prof. Raman the first problem that he set me was the study of an interesting optical phenomenon in amethyst quartz, namely a phase alternation diffraction pattern produced by twinning in this crystal. The amethyst quartz crystal is a lovely jewel and the pattern seen under the polarising microscope is extremely fascinating.

Trial and error method was therefore applied to find out the structure and it was found that not only the benzene rings are plane but also the rings in both naphthalene and anthracene crystals are coplanar and the molecular planes are inclined not only to the ac planes but also to the c -axis.

While these results were in course of publication in the *Indian Journal of Physics*, J. M. Robertson published a paper on the structures of naphthalene and anthracene in the *Proceedings of the Royal Society*. This was based on the structure given previously by W. H. Bragg but obtained by using much more extensive and accurate measurements than I could think of obtaining at that time in India. So I sat down to compare the relative intensities calculated on the basis of these two structures and compare them with those measured by Robertson and found that the results were clearly in favour of the

structure obtained by me and I sent a note to *Nature* stating these results. I was highly pleased to find this note published with an addendum from Robertson that Bragg and he had also arrived at the same conclusion later and that he fully agreed with my results.

Krishnan and his students calculated the actual anisotropy of the molecules of naphthalene and anthracene from the orientations determined by the X-ray method, and utilized the results for developing a method of finding the molecular orientations in crystals of a large number of aromatic substances.

A Calcutta University Fellowship for foreign travel enabled me to proceed to London and work at the Royal Institution of Great Britain under Sir William Bragg. The contact with the brilliant group of X-ray crystallographers there assembled was of great benefit to me. J. M. Robertson was engaged in carrying out the structure determinations of aromatic crystals including naphthalene and anthracene by the two-dimensional Fourier synthesis method. In spite of the knowledge of the rough structure already determined in these cases, the labour involved in determining the signs of the terms seemed to be depressing. I also took up the determination of the structure of paradinitrobenzene of which the preliminary structure was not known. The attempt brought me face to face with the labour involved in carrying out a successful Fourier synthesis by fixing the signs by trial. The ambiguity of phases in a Fourier synthesis, as I began to ponder, arises from the fact that theoretically any structure whether physically significant or not, obtained by synthesis with any combination of phases, would give the same distribution of diffracted intensity as is given by the actual crystal. But all except the correct combination can be eliminated because of our knowledge of the chemical nature of the unit cell as containing a definite number of atoms of roughly spherical shape. If we could utilize this knowledge in a mathematical form which enables us to find a priori a consistent set of phases for the structure factors, the problem would be solved. If we regard the electron distributions in the individual atoms to be known from the wave-mechanical pictures of the isolated atoms, the atomic coordinates are the only unknown parameters. The known quantities are the absolute values of the structure factors whose number far exceeds the number of unknown parameters in the cases that interested crystallographers. The problem did not seem to be an impossible one.

About that time a paper by Ott on the determination of the atomic coordinates in graphite attracted my attention. He set up equations whose roots are the coordinates of the atoms in the unit cell. When the

equation is expressed as a polynomial equated to zero, the coefficients of the terms of the equations were shown to be obtainable from the structure factors. The method, however, succeeded in locating the coordinates of the atomic centres in the case of graphite only, because of the high order of symmetry and the small number of unknown parameters involved. In such cases there is no difficulty in locating the atomic centres even without recourse to this method. But this method showed the possibility of setting up equations giving the relationships between the structure factors and the coefficients of terms in the equation whose roots are the atomic coordinates. The number of these coefficients is limited by the number of unknown parameters while the number of equations depends on the number of structure factors measured, which is ordinarily very much larger than the number of unknown coefficients. Thus one can eliminate these coefficients and obtain simple relations between structure factors only. The numerical values of the structure factors being known, their signs can now be found out since these relationships are to be satisfied.

I continued in this line of thinking after returning to India and rejoining the Indian Association for the Cultivation of Science and found out relations that would give the signs of the structure factors in carrying out a Fourier synthesis. The results were published in *Proc. Roy. Soc.* in 1933. After a short stay at the Indian Association for the Cultivation of Science, I joined Dacca University as Reader in Physics and had to devote myself mainly to teaching and to giving some research training to new graduates. So work was restricted mainly to rather routine type of determinations of space groups and to measurements of magnetic anisotropies from which to obtain some preliminary ideas about the structures. Only in the case of anthraquinone a Fourier synthesis was carried out by Dr. S. N. Sen under my direction. Some problems of chemical interest such as an X-ray diffraction study of jute fibres, isomorphism of fluoberyllates and sulphates, and structure of nickel catalysts were carried out. Interest was also taken in the study of isodiffusion lines of diffuse reflections.

In 1943, I returned to the Indian Association for the Cultivation of Science as the Mahendra Lal Sircar Professor and in 1952 I joined the Allahabad University as the Professor of Physics. During these periods, I had the opportunities of building up a research school in X-ray crystallography in India. In structure analysis, J. Dhar made a fairly accurate determination of the structure of diphenyl by the trial and error method quite early. Dr. B. S. Basak determined the structure of phenanthrene by Fourier projection methods, Dr. B. V. R. Murthy

refined the structure of anthraquinone of which the preliminary structure was determined by Sen by two-dimensional Fourier synthesis. The refinement was carried out by a number of successive difference syntheses, the atomic positions being finally fixed by utilizing three-dimensional data. In this determination an innovation was made regarding the evaluation of the anisotropic temperature factor by obtaining it from electron distribution plotted without this correction. This automatically takes into account the effect of overlapping of electron densities of adjacent atoms. Very interesting results were found regarding bond lengths in this compound.

S. N. Srivastava has carried out the Fourier synthesis of anthrone. A very remarkable phenomenon has been observed in this crystal. The chemical formula with one oxygen on one side and two hydrogen atoms on the other side is not regularly repeated in the same order, but oxygens and hydrogens are arranged in a random way on either side of the molecule, although the carbon structure maintains complete regularity as is expected in a crystal. Srivastava is continuing his studies on this statistical structure. Dr. S. C. Chakraborty and U. C. Sinha have carried out the analysis of benzalazine by two-dimensional Fourier synthesis and refined the structure by difference synthesis. Dr. B. S. Basak and M. G. Basak have carried out the analysis of 1, 2-cyclopentenophenanthrene by two-dimensional synthesis and refinement by difference synthesis. The atomic positions were finally fixed by utilizing three-dimensional data.

A very interesting type of sharp extra reflections was observed in the case of phloroglucine dihydrate crystal. These reflections were studied in very great detail in order to find out the type of lattice defect producing them. Another interesting piece of work that was carried out during this period is the development of a new method of studying monochromatized low-angle scattering in which the direct beam is avoided by placing the monochromator crystal after the scatterer.

Dr. R. K. Sen developed the photographic method of studying the intensities of diffuse reflections. He was thus able to extend the applicability of the X-ray diffraction method of determining elastic constants to crystals of symmetry lower than are possible by the Geiger counter method and also where large single crystals are not available. The corrections that are necessary for this method have been systematized and the accuracy of the method has been tested against the counter method as well as by means of a crystal whose elastic constants are known. Thus he and Dr. S. C. Chakravorty determined all the elastic constants of the rhombohedral class in which benzil crystallizes.

Dr. S. C. Chakravorty and Dr. R. C. Srivastava have determined also the elastic constants of pentaerithritol which belongs to a tetragonal class. An attempt has also been made to distinguish between the classical and the atomistic theories of elasticities in these cases but the differences are too small even for the photographic method. S. K. Joshi in Allahabad is engaged in studying the elastic spectrum from the distribution of the intensities of diffuse reflections and trying to obtain in this way the vibration spectra of the crystal lattice.

Structure of glasses of various kinds have been studied by Dr. B. K. Banerjee. He has made extensive studies of the nature of alkali halides and colouring materials dissolved in the glasses. The mechanism of devitrification and the natures of glass surfaces and glass fibres were also studied. Dr. G. B. Mitra evolved a method of classifying coal by X-ray diffraction. He also systematized the method of testing the efficiency of coal-washing by X-ray diffraction of the samples. Mineral contents and particle sizes of the minerals of several coal samples have been studied by him by means of X-ray diffraction. At Kharagpur he and his students are studying the thermal expansion of crystals and the relations between lattice defects and particle sizes. He has also developed a micro-wave analog for the calculation of structure factors for use in crystal structure analysis.

After independence, there has been a great impetus to scientific research in India and a very large number of active research centres have developed. In X-ray crystallography also a number of other centres that have grown up are showing great promise.

I wish to make particular mention of a developing school in Madras under G. Ramachandran at the Physics Department of the Madras University, and another at Bangalore at the Indian Institute of Sciences under R. S. Krishnan and S. Ramaseshan.

G. Ramachandran and his students have been engaged in finding the structure of collagen and chitin by a combination of optical and X-ray methods. Ramaseshan, with a number of collaborators, has been carrying on an extensive series of investigations in structure analysis both organic and inorganic. The inorganic series covers potassium permanganate, cupric complexes with varying amounts of water of crystallization, and barium complexes. The organic series includes 3-3' dibromobenzophenone, 4 bromo-diaminobenzophenone, 4 bromo-dicarboxylbenzophenone and nitrobromofluorene. R. S. Krishnan has been engaged in designing new types of analogue computers useful for crystallographic work.