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STUDIES OF THE STRUCTURE AND PROPERTIES OF DIAMOND

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SIR C. V. RAMAN's interest in the beauty of the diamond and its remarkable structure and properties was a life-long involvement although in later years it was overshadowed by his love of flowers and his search for an explanation of the origin of their colours and an understanding of the physiology of vision. "Opportunities for observing the luminescence of diamond in an impressive fashion first presented themselves.....in the year 1930 in connection with spectroscopic studies on the scattering of light in crystals.....It was then found that the luminescence spectrum of diamond recorded itself on the spectrograms simultaneously with the scattering of light in the crystal, its leading feature being a band at 4155 Å.U. and its intensity varying enormously from specimen to specimen.....The difficulty of obtaining suitable material discouraged the pursuit of the subject" (Raman, 1944). Later on, noting that "cleavage plates of diamonds of excellent quality and good size could be obtained at very modest prices and that diamond in this form was more suitable for physical investigations than the high-priced brilliants of the jeweller's trade" Sir C. V. Raman acquired a few specimens, which led to a very fruitful series of investigations on the scattering and absorption of light in diamond and its photoluminescence at various temperatures by Dr. P. G. N. Nayar (1941, 1942).

The researches of Dr. Nayar in 1941 and 1942 on the luminescence and absorption spectra of diamonds demonstrated the existence of many more vibrations of the diamond structure with discrete frequencies than the single line with a frequency shift of 1332 cm^{-1} which appears in the Raman spectrum of diamond (Ramaswami, 1930; Bhagavantam, 1930). The main results of the early investigations were summarised by Sir C. V. Raman in his Presidential Address to the Eighth Annual Meeting of the Indian Academy of Sciences at Bangalore in 1942 and published as a supplement to *Current Science* in January 1943.

In 1942, Sir C. V. Raman purchased a representative collection of diamonds mined in Panna in Central India and enlarged his collection of polished cleavage plates. The diamonds in his personal collection in 1944 numbered 310, consisting of crystals in their natural condition, polished cleavage plates and cut brilliants of both Indian and South African origin, a unique collection, probably unparalleled anywhere in a scientist's laboratory or museum Then followed a period of intense activity when almost every student in the Physics Department was working on one aspect or other of the properties of diamond and two symposia on the structure and properties of diamond were published; again unequalled in the scope and range of the aspects studied and the results obtained.

The first symposium on diamond published in 1944 consisted of 17 papers. The first two papers on the crystal symmetry and structure of diamond, and the nature and origin of the luminescence of diamond were by Sir C. V. Raman himself. These were followed by 15 papers by his associates and pupils on the Raman spectrum of diamond, the fluorescence and absorption spectra of diamond in the visible region, the ultraviolet absorption spectrum of diamond, luminescence and birefringent patterns in diamond, the intensity of X-ray reflection by diamond, X-ray topographs of diamond, X-ray reflection and the structure of diamond, ultraviolet transparency patterns in diamond, the lattice spectrum and specific heat of diamond, the mangetic susceptibility of

diamond, the photoconductivity of diamond and the crystal forms of the Panna diamond. Though the papers were by individual workers, one can see the master's hand in each, directing and guiding and finally polishing the text of each paper. His incomparable mastery of the English language, his insistence on perfection in everything one did, his vast and varied knowledge combined with an overpowering kindness and magnanimity, the identification and recognition of merit followed by encouragement and praise, often undeserved, were a continuous source of wonder to all those who had the privilege of working with him.

It was an exhilarating time, a rare experience and privilege to work in the Physics Department of the Indian Institute of Science at that time, to see the pieces falling into place and meaning appear out of the most scattered and disconnected observations, when controlled and guided by the master's hand.

The second symposium on the structure and properties of diamond appeared in 1946. This consisted of 21 papers. The first paper on the crystal forms of diamond and their significance was by Sir C. V. Raman and S. Ramaseshan. The other papers related to the second order Raman spectrum and the temperature variations of the Raman lines, the thermal expansion of diamond, the crystal symmetry of diamond and its X-ray reflections, the nature and origin of laminations in diamond, luminescence of diamond excited by X-radiation, the X-ray topographs of diamond, the cleavage properties of diamond, the Faraday effect in diamond, the absorption spectra in the ultraviolet, visible and infrared, the luminescence, phosphorescence and the thermoluminescence of diamonds and their local patterns and variations and a theory of the crystal forms of diamond.

This extensive and wide-ranging study of the physical properties of diamond involved the development of a number of new techniques of observation and measurement. Those deserving special mention are the mapping of the ultraviolet transparency and X-ray reflection intensity patterns developed respectively by Rendall and Ramachandran. Sir C. V. Raman showed that the luminescence of diamond was not as originally thought due to impurity atoms present in it but is physical in origin and fundamentally connected with the crystal structure of the diamond itself and is an inherent property of the diamond. He explained the discrete frequencies associated with the 4152 ÅU and 5032 ÅU lines appearing in fluorescence and absorption spectra by a new theory of the dynamics of the crystal lattice. He described for the first time the crystal forms of the Panna diamond and showed that,

Diamonds with tetrahedral symmetry of structure are in general blue luminescent;

Diamonds with octahedral symmetry are non-luminescent; and

Diamonds in which the tetrahedral and octahedral types of structure are intimately mixed exhibit the greenish-yellow type of luminescence. The idea that the luminescence of diamond is associated with the interpenetration of different crystal structures and the inhomogeneity resulting therefrom was furnished by X-ray studies. The non-uniformity of structure of a plate of diamond was made manifest by the luminescence patterns, ultraviolet transparency patterns, structural birefringence patterns and later by the X-ray topographs. To use his own words, "All these patterns have an eventually similar origin, *viz.*, the interpenetrative or lamellar twinning of the different possible crystal structures in diamond. The interpenetration of the positive and negative tetrahedral structures gives rise to blue luminescence without any structural birefringence, the diamond remaining ultraviolet opaque. The interpenetration of the tetrahedral and octahedral structures gives rise to the yellow luminescence accompanied by a banded structural birefringence and an imperfect ultraviolet transparency. The lamellar twinning of the two possible octahedral structures gives diamond which is both non-luminescent and ultraviolet transparent but with a characteristic finely streaky birefringence."

Writing after a visit to Panna, Sir C. V. Raman drew attention to "the remarkable beauty of the Panna crystals with their exquisitely perfect geometric forms, their smooth lustrous surfaces and the sharpness of the edges which divide the curved faces into distinct sections". We in our admiration and awe used to compare them to him, and his work, to quote his own words on Prof. S. Chandrasekhar, "bears witness to his energy, the strength and range of his scientific interests and his powers of investigation and exposition".

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SPECTROSCOPIC STUDIES ON DIAMOND BY RAMAN AND HIS GROUP

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Introduction

SIX years after the publication of the historical paper on two types of diamonds by Robertson, Fox and Martin,[1] a short note on "A New X-Ray Effect" in *Current Science* by Professor Raman[2] heralded an era of extensive researches on diamond by him and his group. These studies lasted over two decades till Raman's fascination for the physics of colour and vision became his more dominant interest. The researches have been published in various issues of the *Proceedings of the Indian Academy of Sciences* including two symposia,[3,4] several memoirs of the Raman Research Institute[5] and a comprehensive article.[6] Occasionally, a few papers have appeared elsewhere[7] also.

The new dynamic X-ray reflection was shown by Type I diamonds only and was suggested to be a consequence of excitation of the high frequency infrared optical mode by X-ray photon. If diamond structure has full holohedral symmetry (Oh), this mode ($\nu = 1332\ cm^{-1}$) should be Raman-active and I.R.-inactive. However, Type I diamonds absorb in the fundamental region (6 to 13 μ) though Type II do not. There are, besides, several contrasting properties of the two types, *e.g.*, U.V. absorption, luminescence, birefringence, photoconductivity, etc. Thus, Type I diamonds absorb below 3000 Å, while Type II are transparent upto 2250 Å. Similarly, Type I show fluorescence while Type II are non-luminescent. The Bangalore group studied and correlated the diverse properties by studying a large number of diamonds of various origins (over 300) in the collection of Prof. Raman.

Diamond Patterns

Besides spectroscopic studies in the conventional way, luminescence patterns under near U.V. excitation, U.V. transparency patterns and birefringence patterns of hundreds of diamonds were photographed by Rendall, Bai, Jayaraman and Ramachandran. Besides, X-ray topographs, infrared transparency patterns and phosphorescence patterns were also