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(1) Diamond and Its Mysteries

The lapidaries of yore knew of the perfect octahedral cleavage of diamond and used this knowledge to advantage. Can laws governing cleavage in crystals be formulated? The energy of cleavage (i.e. the energy required to rupture the bonds connecting atoms on either side of a plane) must be a minimum; and its variation with direction must also be large if the cleavage is to run true. A study of the fractured diamonds in the Raman Collection lent statistical support to these two criteria¹.

Some of the most beautiful objects in nature are single crystals of diamonds from Panna (India) with their exquisite curved faces and delicate tracery of edges. The shapes that crystals take are usually determined by the growth rate of their faces. However, measurements and calculations show that in these Indian diamonds, the surface energy controls the external morphology². Could the curved forms be caused by abrasion (which is connected with surface energy)? If so, how can the faces still remain so lustrous?

A thin film of oil invariably forms on diamond surface. Half a century ago, Raman was convinced that unsatisfied dangling bonds on the surface attracted the hydrocarbons. By cleaving a diamond in vacuum and studying the reflection characteristics, an idea of the rate of growth of the film was obtained. Diamond

surfaces and their dangling bonds are still worthy of study using modern techniques.

Diamond is said to belong to the highest holohedral centro-symmetric class; and yet many specimens exhibit hemihedry (acentricity). An extensive examination of Indian diamonds by Raman and myself established that a majority of these were acentric. Many optical and spectroscopic properties of diamond were explained by Raman as due to the mixing of centric and acentric structures (which he felt arose due to an intrinsic property of the carbon atom). [Raman C V, *Proc Indian Acad Sci*, 24A (1946) 1]. It is now known that these effects are probably due to impurities (B, N, etc) which lower the holohedral symmetry at the microscopic level. Can these trace impurities alter the macroscopic symmetry and hence the crystal form itself?

Most diamond plates exhibit strain birefringence. This reduces the measured Faraday rotation, making it difficult to derive the true magneto-optic constant. Using the concept of the Poincaré representation of polarized light, a neat method was developed to calculate the real rotation³.

(2) Studies on Optics and on the Effect of Pressure on Physical Properties

The revival of the Poincaré sphere concept played a crucial role in the

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development of optics in India at that time (G N Ramachandran, V Chandrasekharan, S Pancharatnam). New theorems were discovered in magneto-optics, novel designs of optical instruments ensued and new techniques of measuring photo-elastic constants were evolved. Classical papers on the Generalised Theory of Interference, written much before the discovery of lasers, led to the understanding of partial coherence and partial polarization⁴.

A series of discoveries on the effect of pressure on physical properties followed: (a) uniaxial stress, like a magnetic field, splits the dispersion frequency; (b) natural birefringence and its dispersion with wavelength are also caused by the splitting of the dispersion frequency by the anisotropic distribution of the ions⁵; (c) metals exhibit photo-elasticity and the major contribution to this effect is by the free electron motion in an anisotropic lattice; (d) stress profoundly affects optical rotation and it can even induce optical activity in a certain class of non-optically active crystals⁶; (e) pressure can induce liquid crystallinity⁷; and (f) even a solid-solid transformation can show a critical point (SmS isostructural transition Cr Pt 825°C 10.5 kbar)⁸.

(3) Optical and X-ray Effects

The wavelength of X-rays is more than a thousand times shorter than that of light. Can effects seen in optics be observed in the X-ray region and vice-versa? (a) "Optical activity" in the X-ray region was detected in cinnabar and quartz (0.1-1% of that in the visible region and in the same direction)⁹. (b) The Faraday effect in X-rays was not observed. (c) "Optical activity" was predicted for polarized neutrons transmitted along the axis of

helimagnetic structures like didymium and holmium and experimentally verified in Brookhaven a few years later¹⁰. (d) The violation of Friedel's law and the Borrmann effect are important X-ray effects arising because of multiple reflections in absorbing crystals. Both these could be observed in light in multilayer films (each layer consisting of unequal transparent and absorbing material)¹¹. Optical Borrmann effect could not be detected (in twinned iridescent KClO_3). The best success in this direction was achieved when my student, Rajaram Nityananda (quite independent of me), predicted that the Borrmann effect must be observable in a class of absorbing liquid crystals. This was experimentally verified by the Raman Research Institute Liquid Crystal Group.

(4) Anomalous Scattering of X-rays and Neutrons

My incursions into anomalous scattering of X-rays also came through the interest in the optics of absorbing crystals. Friedel's law violation arises due to an inherent phase change by the absorbing atom (f'). Bijvoet, in his classic paper of 1949, suggested that this can be used not only to determine the absolute configuration of structures but also to phase reflections. In his second classic of 1951 on strychnine sulphate-selenate, he suggested that by combining the isomorphous and his anomalous techniques, the phase problem can be solved without ambiguity. When there is an isomorphous replacement, the scattering power of the replaced atom changes. Since near the absorption edge the scattering power also changes (by f'), the thought occurred to me (1952) that a change in incident wavelength will achieve what isomorphous replacement does with the advantage that the "isomorphism" is

perfect⁹. Hence by comparing the effects of f'' and f' at many wavelengths, one can solve the phase problem completely. The consequent details were worked out. This idea seems to have found a revival with the coming of the intense tunable synchrotron sources^{11,12}.

The suggestion of using neutron anomalous scattering for phasing very large structures made in 1965 has also had a fair success. Here again, one has to wait for an improvement in the neutron source intensity for the method to be universally applied¹¹.

The f'' and f' effects are really methods of labelling absorbing atoms. Hence, anomalous scattering techniques have been suggested for solving many crystallographic problems: polarization vectors; static displacement; and modulated structures. Our method of determining partial structure factors of binary liquids is regularly used for liquid alloys. It has also been applied by us to electron scattering, to explain the resistivity anomaly in caesium liquid at high pressures wherein some atoms have suffered "electron collapse"¹².

(5) Are Ions Compressible?

From among the possible coordination polyhedra, the Platonic solid—the icosahedron—was omitted by Linus Pauling (probably because of its pentagonal symmetry). Since there was no *a priori* reason for this omission, a systematic study was made of the coordination in compounds with highly polarizable ions. The oxygen coordination around Ba ion varied in different crystals from 6 to 12 and it was pleasing to find that in $\text{Ba}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$, the polyhedron is actually a perfect icosahedron¹³.

These studies provoked the question: Can an ion be considered to be "soft", characterized by (i) a radius and (ii) a compressibility? When this was worked out using the Born theories, an important result followed. These two characteristic parameters of an ion can be used for that ion in *any* other crystal. The success of such an approach has been much beyond expectation¹⁴. Amongst other things, it explains the crystal structures of the 20 alkali halides, a problem that remained unsolved for several decades; one can calculate the lattice spacings, crystal structures, compressibilities and thermal expansions of a series of simple and complex crystals, as also the values of the temperatures and pressures at which they transform. It gives a plausible explanation for the semiconductor-metal transition of SmS , SmSe and SmTe ¹⁵; it estimates the interionic distances in ionic melts.

(6) Applied Research

An interdisciplinary group gathered round me, and we made excursions into many fields of applied materials research. Some problems tackled with fair success were: the development and manufacture of FRP radomes to protect weather radar stations from cyclones; large sweep FRP fan blades for thermal power stations; big microwave dishes, porous FRP tubes for desalination; filament winding machines; high strength organic fibres for reinforcements; high silica fibres for insulation; electrocomposites for self-lubricating bearings and wear resistant surfaces; metal forming machines for spark erosion and electrochemical milling; stress measurement, stress relief, stress corrosion cracking, etc. [Valluri S R & Rajagopalan S R, *Bull Mater Sci*, 5 (1983) 373-80]. I shall not discuss the interplay of

basic and applied research which made this exercise truly worthwhile.

Much of the work described cursorily in this account was done along with my gifted students and colleagues, many of whom in later years have distinguished themselves. To K Venkatesan, M A Viswamitra, N V Mani, H Manohar, A K Singh, S R Rajagopalan, N Balasubramanian, G R Ranganath, Rajaram Nityananda, T G Ramesh, Ramesh Narayan, R V Ramani, A V Ramani, Indira Rajagopalan and many others I record my grateful thanks for the privilege of being associated with them.

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