INTRODUCTION

The background

Volume 4 of the *Scientific Papers of C V Raman* contains 76 papers on a variety of topics. The first 21 are on a medley of subjects ranging from surface tension to zonal winds—subjects which interested Raman from time to time (from 1905 to 1968!). The second set of 39 papers deals mainly with the colour displayed by objects in nature (mostly minerals) whose visual beauty had a strange fascination for Raman. The last set of 16 papers are again on a mineral for which Raman had a special affection, *the diamond*. As in the introductory essays for the previous volumes, we shall comment on some of the topics touching on historical details where appropriate.

Miscellaneous papers

Surface tension: The experimental work reported in the first paper of this volume was started sometime in 1905. It is a neat piece of research, executing a casual suggestion made by Kelvin in his *Popular Lectures and Addresses* that the surface tension of a liquid can be determined by measuring the curvature of a suspended drop. The young Raman displayed skill and ingenuity in rigging up a spark generator to illuminate the suspended drop to take instantaneous photographs of its shadow, correct for any errors that diffraction of light may introduce, etc.

Viscosity: Raman's phenomenological theory of viscosity is based on the hypothesis that the liquid state is composite in character consisting in part of molecules rigidly attached to each other (as in a solid) and in part of molecules which are relatively mobile (as in the gaseous state). Taking the energies required to separate a pair of molecules of each type and applying the Boltzmann distribution law, Raman derived a simple formula connecting the viscosity of a liquid with that of its vapour. From this he computed the viscosity of liquid benzene at different temperatures. The calculated values agreed with the experimental ones to within 2 parts in a thousand! Staudinger, the pioneer in polymer chemistry later found Raman's model eminently suited to correlate the viscosity of solutions of molecules in various states of polymerization.

Impact: Raman's interest in struck strings led him to investigate the problem of impact where he made some significant advances both in theory and experiment.

While using Hertz's theory, Raman considered all the possible modes of dissipation of energy which could affect the coefficient of restitution when two spheres collide. These were (a) the sound waves and (b) the stresses occurring during impact when they exceed the limits of perfect elastic recovery. His group had shown that the sound waves were generated by the impulses communicated to the atmosphere due to the sudden reversal of the motion of the spheres and the energy thus dissipated is negligible; the dissipation due to imperfect elasticity would also be negligible for small velocities of impact. Therefore Raman argued, the coefficient of restitution at extremely low velocities must tend to unity irrespective of the nature of the material of the balls or their elastic properties. This result was verified by a series of beautiful experiments on balls made of different materials with a wide range of elastic and other properties. Raman also used the idea that part of the translational energy is transformed into elastic wave motion in the substance of the solid to calculate the coefficient of restitution in the case of the sphere and a flat plate. Assuming annular flexural waves to be set up in the plate, the coefficient of restitution was calculated and found to agree well with the experiment.

Many concepts of the manner and mechanism by which a solid breaks down under impact came out of these early researches. When a sphere impacts a plate the stresses in the centre are compressive and the fracture does not start there. The fracture is initiated as a circular crack near the margin and it travels inwards into the plate obliquely at 45° along the surface of maximum shearing stress set up during impact. Raman was also amongst the earliest to use interferometric methods to study the nature of the deformation after breakdown.

The plumage of birds

The striking colours of the plumage of birds fascinated Raman and were the subject of many of his studies. The interest was all the more as the optical characters and distribution of colours were so different in different parts of the same bird, in different specimens and in different species that no single explanation would suffice. Every phenomenon known to the optical scientist—interference, diffraction and scattering of light—had to be invoked. Interference due to thin films on the surface, selective spectral reflection from stratified films, the diffraction of light by discontinuities not small compared to the wavelength of light, the Tyndall effect due to minute air cavities, the anisotropic scattering due to elongated holes and particles, all contribute to these colours. Further the delicate interplay of these physical effects with the chemical colours enhances the spectacular chromatic display seen in birds.

Raman published only one paper on this subject but gave dozens of lectures to large audiences. His favourite title was *Birds, Beetles and Butterflies* but each lecture was unique and usually contained an account of a study he made of a

specific object from his remarkable collection. He was particularly fond of the iridescence displayed by the magnificent tail feathers of the peacock and the gorgeous plumage that covers the head and neck of the Himalayan pheasant. The ubiquitous kingfisher and the plebian parrot were also subjects of his study. Those were days when colour slides were not yet in vogue. For his lectures he did use well mounted museum specimens. At one of these lectures on the commoner garden Indian jay Raman painted word pictures of this bird and its colourful feathers so graphically that the listener could see in his mind's eye the succession of coloured bands of alternating deep indigo blue and light greenish blue, changing dramatically when the bird was in flight; dull and drab when the light is from behind and turning to a brilliant green with almost enamel lustre when lit from the front. The feathers display transient colours after a shower when damp—the blue indigo becoming shimmering green or a dark blue or even a dramatic deep violet depending on the position of the sun and the observer. To Raman birds were beautiful and hence fit subjects for serious study.

Colours exhibited by minerals

In the new Institute he built for himself to work in peace after he formally retired, he started by arranging his magnificent now famous, collection of minerals; specimens he had gathered from all over the world for the extraordinary optical phenomena they exhibited—(limestones, marbles, alabaster, gypsums, tourmalines, agates, quartzites, jades, amethysts, fluorites, micas and serpentines, iolites, malachites, lapis lazuli and feldspars).

Feldspars were truly intriguing—labradorite, a special variety, displayed, brilliant colours; another group, moonstones, found use in jewellery because of the beautiful optical effect called *schiller*. He continuously leaned on his old experiences with scattering of light in liquids. For example he compared the blue schiller from the best moonstones he had with the blue opalescence in binary liquid mixtures as the critical temperature is approached; or the spectacular blue colour exhibited by many labradorites with the blue opalescence when water is added to methanol containing benzene in solution (when benzene tends to separate). He concluded that although in a common macroscopic sense these substances, moonstones and labradorites, were monocrystals they had optical heterogeneities in them.

To begin with, the basic facilities had not yet been established at his Institute. There was as yet no electric power and so he had to revert to the use of his old trusted technique of using a beam of sunlight (the technique he had used to discover the Raman Effect) to explore and understand the optics of these substances. He felt that the passage of light through the mineral and its diffusion would reveal the existence and nature of optical heterogeneities, i.e., the local variations in composition and refractive index. These optical inhomogeneities

could be embedded in a matrix. But there were a large number of possibilities. The inhomogeneities could be cavities or crystallites or just variations of composition. They could be isotropic or birefringent, oriented randomly or with a preferred direction; they could show periodicities in one, two or three dimensions. The medium itself could be amorphous or crystalline, polycrystalline or a mono-crystal, isotropic or birefringent. All these variations Raman wanted to probe with just a beam of light. He knew that it would be best to generalise the Raman–Nath theory considering not only the phase corrugations due to these random optical inhomogeneities but also the states of polarisation. But being pragmatic Raman (with Viswanathan) developed a theory based on simpler models. The character of the diffused light, its spectral nature, its intensity, and state of polarisation, and its distribution in different directions and the variation with setting of the crystal and the direction of the passage of light furnished him with the data needed to infer the nature and distribution of the local heterogeneities.

He studied a variety of minerals, iridescent potassium chlorate, iridescent shells, feldspars, moonstones, fiery opals, iridescent agates, iridescent calcite, iridescent quartz, jadeite, cryptocrystalline quartz, polycrystalline gypsum (and also a variety of natural and synthetic fibres). It is remarkable how much detailed information he could extract from this simple means of sending a beam of sunlight through the mineral. Many of his conclusions were right but some wrong as well. For example, Raman (with Jayaraman) deduced that in opal the fiery colour was due to isotropic inhomogeneities with a refractive index lower than that of the surrounding medium but segregated periodically. Later electron microscopic studies showed that they were isotropic and of lower refractive index and also periodically distributed in the lattice but were really submicroscopic air bubbles!

He was amongst the earliest to worry about the existence of periodic compositional segregation in minerals which he felt was much more common than usually supposed. This phenomenon underlies the modulated structures which are widely studied today.

Pearls: A special word about the pearl; the gemstone which does not need the services of a lapidiary to enhance its natural beauty. The precise understanding of the optics behind its loveliness was a matter of more than ordinary interest to Raman. He (with Krishnamurti) discovered that light falling normally on the rear surface does not travel through the pearl but around it (as does sound in a whispering gallery—a subject in which he had done much research), following the lamination of its structure. The beauty of the pearl is to be found in this effect, together with the superposition of the chromatic diffusion halo and also the reflected light.

The diamond

Soon after the discovery of the Raman Effect, C. Ramaswamy, Raman's younger brother, asked him to suggest a research problem which he could pursue. Seeing

the diamond ring that the newly wed Ramaswamy sported on his finger, Raman suggested the study of *the. modified scattering* in diamond. Ramaswamy discovered the famous 1332 cm^{-1} Raman line of diamond. This was followed by the work of Bhagavantam, one of Raman's star pupils recording the Raman spectrum of a 140 carat diamond that was borrowed from the Maharaja of Dharbhanga. Bhagavantam graphically describes how he spent two days and two nights in the dark spectroscopy room in trepidation praying that nothing untoward should happen to the precious gem. He confirmed Ramaswamy's discovery and also recorded the complex luminescence spectrum around 4152 Å. Raman must have had this in mind when he relates how he was "reduced to the expedient of borrowing diamond rings from wealthy friends who, though willing to oblige, were slightly apprehensive about the fate of their property". Raman later visited another of his wealthy friends when he was "graciously permitted by His Highness the Maharaja of Panna to examine his famous garland of fifty two large (Panna) diamonds of exquisite beauty, all in their natural uncut state as crystals ranging from 25 carats to 2 carats strung into the form of an exquisite necklace". He then wrote: "With their perfect geometric forms and their smooth lustrous beauty they look absolutely fresh from nature's crucible, although actually taken from sedimentary formations a thousand million years old. The strongly marked curvature of the crystal faces and the smoothly rounded edges are a surprising feature of these crystals". These diamonds as seen now, according to Raman, are exactly in the same state as they were when first formed. The love affair with diamond had begun.

Obtaining the material in the form suitable for study was his first obstacle. He discovered that flat pieces of diamond of excellent quality, not too expensive could be purchased in useful sizes from many jewellers in India. The diamond auctioneers in remote corners of India were very accommodating. They had never seen such a colourful personality, that too a scientist, sitting crosslegged in their midst. Contrary to all their usual custom they obligingly permitted him to examine each specimen under a microscope, a fluoroscope and a strain viewer (which he carried with him) and permitted him to form his own "lots" wondering why anyone should mix such expensive stones with such utterly worthless ones! Raman purchased hundreds of representative specimens, euhedral crystals, cut gems, or plates. They were bought for their beauty of form, colour, fluorescence or birefringence.

The results of the X-ray analysis of the crystal structure of diamond by W H Bragg and W L Bragg (1913) were regarded as demonstrating that diamond possesses the highest holohedral cubic symmetry. This was in conflict with the view of all the earlier crystallographers. Raman had in his personal library the works of some of the recognised authorities on mineralogy from all over the world—Groth, Liebisch, Hintze, Dana, Lewis, Miers etc. It was his custom to read these regularly—particularly those with painted illustrations. Without exception diamond was assigned to the ditessaral polar class i.e. the hemihedral tetrahedral class of the cubic system. The assignment was based on the fact that

although crystals of diamond exhibiting octahedral symmetry of form were seen in numbers, specimens showing only the tetrahedral symmetry were also forthcoming. It was the view of these crystallographers that the highest symmetry when observed was the result of supplementary twinning of positive and negative tetrahedral forms. The manifestation of grooves in many octahedral crystals was a clear proof of this. Raman was, of course, familiar with Van der Veens work that diamond does not exhibit any pyroelectric properties, which was considered irreconcilable with the assignment of tetrahedral symmetry.

Much controversy had taken place upon the question whether diamond is actually octahedral or tetrahedral. Raman was very troubled by all this. In the twenties when he represented India at the bicentenary celebrations of the Academy of Sciences of the U.S.S.R. he discussed this with many Russian crystallographers as also Sir Henry Miers, the reputed British mineralogist (who represented the United Kingdom and the Royal Society) at these celebrations. Miers reiterated the statement he had made in his book "The problem is now regarded as decided in favour of the tetrahedrite class". Raman paid much credence to the conclusions of the older scholars and felt that the evidence they had gathered after careful study must not so easily be brushed aside. He also believed that while the structure as determined by X-rays was essentially right, the symmetry itself was open to question because of the basic ambiguity of X-ray methods in symmetry determination.

In 1934 many things happened. Nagendra Nath at Raman's instance studied the dynamics of the diamond lattice and published a series of papers in which he showed that the fundamental frequency of the diamond structure ($1332 \, cm^{-1}$ frequency) is a triply degenerate oscillation of the two face-centred cubic lattices of carbon atoms with respect to each other. In the same year the celebrated article of G. Placzek *Rayleigh–Streuung und Raman Effekt* appeared. In this he discussed the relation between the symmetry class of a crystal and the activity of its vibration in infrared absorption and the Raman Effect. He showed that for groups which contain a centre of symmetry the selection rules for the two are complementary; but for groups that do not have a centre of symmetry there is a possibility that the same vibration may appear both in Raman Effect and in infrared absorption. In the case of the triply degenerate vibration in a crystal having octahedral symmetry it can manifest itself *only* in the infra-red absorption *or* in scattering of light but *not in both*. On the other hand, in a crystal with tetrahedral symmetry, such a vibration must appear *both* in infra-red absorption and Raman Effect or *can appear in neither*.

Again in 1934, Robertson, Fox and Martin showed that diamonds are not identical in their behaviour in infra-red absorption—one group which represents the majority of cases showing strong absorption in the 1300–$1350 \, cm^{-1}$ region which is wholly absent in a second and rarer variety.

When his collection of diamonds had expanded Raman decided to examine (along with a student) a large number of diamonds in their natural form—

obtained from various sources—many of them from India. There was no doubt whatsoever that many of these exquisite clear, water white crystals displayed the symmetry of the tetrahedral class. To Raman it appeared that the view of the earlier crystallographers in assigning the hemihedral or lower symmetry to diamond was justified and it was vindicated by the infra-red asborption data and the selection rules so far as the common variety of diamond was concerned. He was also certain that the rarer variety *must* be credited with the full holohedral symmetry. Here was the enigma. It was quite confusing.

Raman was convinced that the intensive study of diamond itself would surely not only provide the answer but could be of import to physics and chemistry. He felt history had a way of repeating itself. For, did not diamond exhibit in a striking fashion many phenomena which are scarcely noticeable in other solids under ordinary circumstances? The variation of specific heat with temperature was known as an experimental fact in the case of diamond at least 50 years before it was recognised as a universal property of the solid state. Weber's data published in 1875 formed the basis of Einstein's epoch-making paper introducing the quantum theory of specific heat.

So experimental activity was mounted at a rate never before undertaken in India and results and techniques began to pour out.

Even if it is conceded that diamond has tetrahedral symmetry, the two variant subclasses, the positive and negative tetrahedral structures, would be identical in respect to energy of formation. It is therefore possible to have both of these in the same structure but this cannot give a crystal which has a centre of symmetry at a microscopic level.

To explain the existence of diamond with octahedral symmetry Raman was obliged to give symmetry properties to the atom itself—that the carbon atom *itself* had a tetrahedral symmetry (as distinct from the symmetry of its bonds). If the structure had either positive tetrahedral carbon atoms or negative ones *only* and they were all oriented in the same direction, a diamond structure with positive or negative tetrahedral symmetry will result giving two tetrahedral forms of diamond. A positive tetrahedral carbon atom can combine with a negative one in two ways to get a centre of symmetry between the two atoms—with their apices pointing to each other or away from each other—giving two more forms of octahedral diamond structure. He then considered the effect of these four types intermingling in the same crystal, the strains they would generate, their imperfections as seen in X-ray topography, their infra-red absorption, the fluorescence they would exhibit under ultraviolet light and X-rays, the ultraviolet absorption and many other properties. He tested these in his diamond plates—and the correlations were striking. He could look at the birefringence patterns of a plate and predict the patterns they would show in regard to other properties. It was almost uncanny. Raman therefore thought he was right. It is now believed that all this was based on a wrong premise and the accepted explanation of these variations is that they are caused by impurities.

The possible role of impurities had in fact been suggested to Raman but it went against his intuition and he rejected it.

It is interesting how intuition played a vital role in his earlier important discoveries. The discovery of the Raman Effect owed much to his intuitive belief, dating from 1923, that the "weak fluorescence" that he and his students observed in light scattering was not due to impurities but originated from the molecules that constituted the liquid. It must have been this unshakable conviction that made him drive his student collaborators into purifying and repurifying scores of liquids to look for specific characteristics in the scattered light which would distinguish it from the molecular scattering or fluorescence due to impurities. However, the same intuition seems to have played him false in the case of diamond. Unable to purify his diamonds, he studied hundreds of specimens. All the while he was unwilling to believe that the "prince of crystalline solids" could be flawed by major impurities. Years later it was established that many of the phenomena he and his students discovered arose due to impurities (like nitrogen) in the diamond lattice. It is ironic that the symmetry changes induced by these are similar to those Raman proposed to explain the observed phenomena and which he considered intrinsic to the carbon atom.

We have pointed out that Raman's vision of intrinsic tetrahedral symmetry in diamond did not prove correct. But the number of new ideas and techniques which came out of the extensive studies of this crystal is truly remarkable. The use of X-ray topography for the study of crystal imperfection was discovered independently in Raman's laboratory. The application of the Jamin effect (now called ellipsometry) for the study of thin surface films was introduced. The cleavage properties and energies and hardness anisotropy of crystal surfaces were studied and ideas such as dangling bonds discussed. The fluorescence and phosphorescence of crystals was studied and a whole range of optical effects such as second order Raman scattering, Brillouin scattering, photoelastic properties of solids, and many others were systematically investigated, many for the first time. It would be no exaggeration that a whole school of crystal physics grew and flourished in that period with its roots in Raman's fascination for the diamond. Even though the tetrahedral symmetry that Raman sought proved elusive, the tools and results of his quest came to be of lasting value to the physics of solids.

S RAMASESHAN