



### **Gems: Objects of Aesthetic Beauty and Scientific Curiosity**

With inexhaustible resources at her disposal and unlimited time to experiment, Nature produces masterpieces of incredible beauty. Among these, a class of crystalline solids, precious stones or gems, occupy a special place. Their intrinsic beauty, enhanced by the skills of the lapidary, has been prized since antiquity. But it is only after the advent of modern science that natural philosophers asked fundamental questions about the unique properties of gems: What is the composition of diamond which makes it brilliant and the hardest terrestrial material? Why do rubies display a dazzling red luminescence when illuminated with blue light? What structural intricacies are at work which create the entrancing flash of colours exhibited by opals with such chromatic purity? Enquiries such as these have marked the beginnings of many a fundamental avenue of research which have led to profound scientific insights and significant technological advances.

With his deep feeling for beauty in Nature and his boundless enthusiasm for optical phenomena, C V Raman did not escape the enchantment of gems. Throughout his scientific career, he often focussed his interests on the many beautiful optical phenomena gems exhibit and, with his discoveries, enriched the science of optics and condensed matter. As illustrative examples of his interest in gems, we discuss here his lifelong preoccupation with diamonds and his fascination for rubies and opals.

Diamond often occurs as a transparent, fully formed, perfect octahedron – one of the five platonic solids. Its symmetry is the highest allowed by the laws of nature for crystalline solids. Newton (*Opticks*, 1704) speculated that diamond is probably “an unctuous substance coagulated”, being intrigued by its large refractive index. But not until Lavoisier (1772) took the extreme measure of actually burning diamonds with focussed sunlight under controlled conditions and examining the end products was it established that diamond – along with graphite and ordinary charcoal – is made of carbon atoms! The internal architecture of diamond was established soon after Max von Laue (1912) conjectured that crystals, with a periodic arrangement of atoms spaced  $\sim 10^{-8}$  cm apart, should diffract X-rays if these were indeed electromagnetic waves with wavelengths of the same order,  $10^{-8}$  cm. After the verification of this conjecture by Friedrich, Knipping and Laue (1912), W H Bragg and W L Bragg (1913) developed their version of X-ray diffraction and deduced the structure of many simple crystals. They showed that diamond consists of carbon atoms bonded to one another, each surrounded by four nearest neighbours forming the corners of a tetrahedron. One labels the carbon atoms at the centers of such tetrahedrons as belonging to one sub-lattice and those at the corners to the second sub-lattice. The symmetry of diamond observed externally reflects the extended internal architecture following this scheme.

The strong covalent bonds between the nearest neighbour carbon atoms, their small masses, and the high crystalline symmetry provide a rational basis for the simple Raman spectrum of diamond. Raman’s younger brother, C Ramaswamy (1930), reported that it consists of a single intense line with a large



Raman shift. Nagendra Nath (1934), one of Raman's students, deduced theoretically the microscopic picture for the Raman line: The two sub-lattices on which the carbon atoms are located vibrate rigidly against each other. During such a vibration, the covalent bonds are compressed and stretched, twisted and bent, resulting in the high frequency and the large intensity of the Raman line.

With his intellectual curiosity fully aroused, Raman meticulously and systematically collected a large number of diamonds, immensely valuable for their scientific interest. He planned and carried out, with the collaboration of his enthusiastic students, a comprehensive program of investigations on a wide range of phenomena and made major contributions to our understanding of the properties of diamond.

With the advent of semiconductor physics, the tetrahedrally coordinated elemental semiconductors, silicon and germanium, and the closely related compound semiconductors, *e.g.*, GaAs, have played a key role in the new age of solid state electronics. With its large energy gap and high thermal conductivity, diamond – the remaining member of the group IV elemental semiconductors – now holds the promise and the potential for a new generation of electronic devices. Significant progress in diamond synthesis has been made in recent years. Diamond is well known as a unique abrasive and as a component of cutting and drilling equipment, thanks to its extraordinary mechanical attributes. Its transparency from the ultraviolet to microwaves (except for a small band of absorption in the near infrared) makes it ideal as an optical window. As a system in which fundamental questions in condensed matter physics can be addressed, diamond, especially isotopically controlled and deliberately doped with controlled concentrations of desired impurities, continues to be an ideal system, offering outstanding scientific opportunities.

Next to diamonds, rubies have long commanded universal fascination. Again, the chemical composition and internal architecture are simple. It consists of two 'molecules' of  $\text{Al}_2\text{O}_3$ , with the  $\text{O}_3$  forming equilateral triangles and two Al's poised symmetrically above and below their centers. There are two  $\text{Al}_2\text{O}_3$ 's in each building block (unit cell) of the crystal and the entire structure has an axial (three-fold) symmetry normal to the oxygen planes – the so-called optic axis. When free of impurities, the crystals are called sapphire or corundum, a highly prized gemstone in its own right. Verneuil (1904) made sapphire crystals in the laboratory and today crystals many centimeters in diameter and 10–15 cm long are routinely grown in the laboratory for scientific and technological applications. The substitution of a fraction of  $\text{Al}^{3+}$  in sapphire with  $\text{Cr}^{3+}$  results in ruby. In the crystalline environment in which  $\text{Cr}^{3+}$  ions find themselves, their electronic energy levels are reorganized. As a consequence, ruby crystals have strong and broad absorption bands centered  $\sim 25,000\text{ cm}^{-1}$  and  $18,000\text{ cm}^{-1}$  causing the characteristic pink or red colour of ruby. When illuminated with strong radiation in these bands, the excited electrons relax into two metastable (long lived) states and finally make optical transitions to the ground states emitting two sharp lines in the red, the  $R_1$  line at  $14403\text{ cm}^{-1}$  and the  $R_2$  line at  $14431\text{ cm}^{-1}$ . The phenomenon of the red luminescence thus generated has been studied comprehensively and the





relevant electronic levels have been delineated in great detail. The  $R_1$  and  $R_2$  lines are pressure sensitive and their spectral positions as a function of hydrostatic stresses have been calibrated to well over 50 GPa (1 Pa =  $10^{-5}$  bar). It serves as a 'barometer' in much of high pressure research based on the diamond anvil cell in which hydrostatic pressures well over 100 GPa can be generated. Here we have a magnificent example of two celebrated gems known since antiquity playing a central role at the frontiers of modern science and technology! It is equally remarkable that one of the first solid state masers utilized the ground state of  $\text{Cr}^{3+}$  in ruby placed in a magnetic field; it played a crucial role in the discovery of the 3K radiation by Wilson and Penzias (1965). And to crown it all, the first laser was experimentally realized by Maiman (1960) by achieving the characteristic stimulated emission at the  $R_1$  transition. Raman was strongly attracted to the scientific opportunities in the study of ruby and encouraged his students and collaborators to investigate the photoluminescence and inelastic light scattering (Raman and Brillouin) of this remarkable gemstone.

When Raman founded the Raman Research Institute where he worked during the last decades of his life (1948 to 1970), he took immense pleasure and great care in planning and creating an outstanding mineralogical museum. The selection of the specimens was largely motivated by the many scientific projects he wished to pursue. Raman and Jayaraman (1953) made several comprehensive studies on iridescent opals. To quote them: "In the finest specimens, the play of colour takes the form of localised internal reflections exhibiting hues of extraordinary brilliance and saturation which vary from place to place in a surprising manner with the angle of incidence of the light". On the basis of the spectroscopic examination of the iridescence and structural studies exploiting optical microscopy and X-ray diffraction, they conjectured that iridescent opal is a stratified medium with alternating layers of two distinct crystalline modifications of silica. With the much more powerful tool of electron microscopy, Sanders and coworkers (1968) in Australia – one of the prime locations for outstanding specimens of opals – were able to show that opals actually consist of close packed aggregates of silica spheres immersed in a transparent matrix of a different refractive index. The size of the spheres, their uniformity and packings conspire to make the system a 'scaled-up' version of a crystal. In a manner not unlike X-ray diffraction, visible light is now 'Bragg reflected', producing the marvellous display of colours with its spectral purity. There is current interest in 'colloidal crystals' made of polystyrene spheres immersed in a suitable liquid; they are model systems in which fascinating scientific issues can be addressed with optical techniques. By creating iridescent opals, Nature has anticipated us in this context perhaps millions of years ago.

Raman's passion for science and his intense feeling for aesthetic beauty were inseparable; his work on gems bears eloquent testimony to this aspect of his scientific personality.

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