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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

taken by Ramachandran, Ramanathan and Chandrasekhar respectively. As a result of these studies, it was found that only a small percentage of diamonds was of Type A (Type I) and another small percentage of Type B (Type II) while a large majority of diamonds was of composite nature. The A group diamonds were isotopic, optically perfect, opaque to U.V. and blue luminescent. The group B diamonds were visibly birefringent, transparent to U.V. and non-luminescent.

U.V. AND I.R. ABSORPTION SPECTRA

In addition to the already known facts, Bai, Mani and Ramanathan showed that several selective U.V. absorption bands, some of them quite sharp, appear upon the strong background. The I.R. spectra were studied by Ramanathan and later by Raman himself. In the fundamental region bands at 1332, 1273, 1219, 1176, 1087, 1010, 746 and 624 cm^{-1} with degeneracies 3, 8, 6, 4, 6, 4, 6 and 8 respectively were identified as the 45 modes of atomic vibration of diamond lattice in accordance with Raman's theory of lattice vibrations. Raman suggested that the contrasting behaviour of I.R. absorption and other properties was a result of fundamental difference in lattice structure ; carbon atoms in two Bravais lattices in diamond give rise to tetrahedral, or octahedral structures. Raman's class A are tetrahedral diamonds while class B octahedral. These two, however, are limiting cases. The octahedral diamonds are transparent in 6–13 μ region while the absorption in the 3–6 μ region by all diamonds, according to Raman, is a second order process. The Raman scattering experiments by Krishnan employing Rasetti technique with 2536 Å radiation showed occurrence of the well-known 1332 cm^{-1} line besides additional Raman lines, with frequency shifts 1925, 2175·5, 2245, 2267, 2300·5, 2495, 2518, 1609·5 and 2664·6 cm^{-1}. These lines were identified as octaves or allowed combinations of the eight fundamental frequencies of diamond lattice mentioned above.

THE 4152 Å AND 5032 Å SYSTEMS

Most of the Type A and composite diamonds emit two systems of bands with their principal absorption and emission lines at 4152 Å and 5032 Å respectively. However, not only their absolute intensities but also their relative intensities vary within wide limits. Nayar and later Mani made a detailed study of these emissions and were the first to observe the fine structure associated with them. The principal line is accompanied in the 4152 Å system by a large number of subsidiary lines which are due to lattice vibrations superposed on the main electronic transition. The absorption and excitation spectra are complementary. The 5032 Å system has, however, more continuous background but has similar structure. Ramachandran and Chandrasekhar obtained an emission line in diamond at 7930 Å while Pant found a qualitative inverse relation between photoconductivity and luminescence.

The luminescence was attributed to inherent structure of diamond. If positive and negative tetrahedral structures co-exist interpenetrating each other, blue luminescence arises while if tetrahedral and octahedral structures co-exist, blue and green luminescence arises. Raman completely discarded the impurity origin of luminescence.

IMPURITY ORIGIN OF THE SPECTROSCOPIC PROPERTIES OF DIAMOND

Diamonds are now classified as Type I a, I b,[8] II a and II b.[9] Type I b are mostly synthetic diamonds with I.R. and U.V. absorption supposed to be due to dispersed nitrogen. Type II b are semiconducting diamonds. The I.R. absorption in the 3–6 μ region is a second order process hence exists in all diamonds.[10] U.V. and I.R. absorption (6–13 μ) in Type I, however, was shown to be due to nitrogen impurity.[11] More recent work shows that nitrogen occurs both in dispersed form showing nitrogen e.p.r. and in segregated layer configurations. A critical examination of the nitrogen centres and their role in I.R. and U.V. spectra is given by Sobolev et al.[12] The edge emission spectra and related topics in diamond have been reviewed by Dean[13] who has also given an account of various other new systems observed in emission. The 4152 Å system of Nayar is a Mössbauer type emission with zero-phonon line possibly due to N–Al pair. The 5032 Å system of Nayar and Mani is believed to have a different origin[14] and can be induced in Type I by heat treatment after pile or electron irradiation.[15]

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SOME RESULTS IN NON-LINEAR VIBRATION OF STRETCHED STRINGS

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FOR more than two thousand years, the vibrations of stretched strings fascinated mathematicians, physicists and musicians alike. Pythagoras, Euler, D'Alembert, Helmholtz, Raman and many others made significant contributions to our knowledge of their behaviour. Conceptually simple and elegant, the vibration of a stretched string served as a mathematical model for our understanding of intuitively less tractable notions like electromagnetic waves and atomic wave functions when they were first conceived. The study of vibrations of strings of musical instruments not only marked the beginning of Raman's scientific work, but remained close to his heart throughout his long scientific career. It embodies in a sense his ethos of scientific work, *viz.*, simplicity of experimentation which marked all his work. It is in this spirit that we summarize here some recent results obtained on the non-linear behaviour of strings at the Indian Institute of Science,[1-5] of which he was the head for several years.

RESONANCE RESPONSE OF STRETCHED STRINGS

If a stretched string is driven by a harmonic force $F \cos \omega t$ in the xy plane as shown in Fig. 1, the classical theory tells us that the string would vibrate in the xy plane and its frequency response would be as given by the curve AR..ST of Fig. 2. As a resonance frequency of the string is approached, the amplitude would grow to infinite values but for some amount of damping that is always present.

Actually, experiment reveals something entirely different. It is extremely simple to obtain the frequency response of a string by applying a constant magnetic field in a horizontal direction at right angles to the string and passing an alternating current from an oscillator of variable frequency. A force $F \cos \omega t$ then acts in the vertical or y-direction and the amplitude of the string can be measured with a microscope. If we start a little below a resonance frequency ω_n 'and slowly increase the frequency of the driving force, we find that the amplitude follows the curve AR in the beginning but before approaching the resonance it takes a path like APG....After reaching some point G on this curve, the amplitude suddenly falls down to the point E on the curve ST obtained from the linear theory and then continues on this curve. If the frequency ω of the driving force is decreased now, the amplitude does not retrace the path TEGPA, but follows the path TED'B'PA. At the point D' the amplitude suddenly jumps to the point B' after which the original curve B'PA is retraced.

In addition to the jumps in amplitude exhibited by the frequency response curve, the motion of the string ceases to remain in the plane of the driving force (the xy plane) when a certain critical amplitude is reached. At some point P along the curve the string acquires a component of vibration in the perpendicular plane xz. This z-component of vibration increases continuously along with the y-component. The motion of the string which is planar until this stage becomes gradually a whirling, non-planar motion until the jump occurs at G, after which it becomes planar again. If the frequency of the driving force is decreased, the non-planar motion reappears after the upward jump takes place at D'. Unless the string is heavily damped, the non-planar motion and the jumps near the resonance frequency are always observed, however small the driving force may be. These are typical non-linear features which the classical theory cannot explain even qualitatively.

NON-LINEAR EQUATIONS OF MOTION

Beginning with Carrier, the non-linear equations of motion of a string have been written down to different degrees of generality by several investigators. They differ essentially