INTRODUCTION

Background

Volume V of the *Scientific Papers* represents the work done by C V Raman mainly on various aspects of crystal dynamics. The first set of papers relate to the experimental discovery of thermal diffuse X-ray reflections as also temperature independent diffuse reflections. Raman thought the latter were due to the interaction of X-rays with optical phonons and there was much dispute about this interpretation. The next set of papers are on his theory of the dynamics of crystal lattices which was also the subject of a raging controversy. He then published a large number of papers using his crystal dynamics to calculate the vibrational spectra and the specific heats of crystals. These papers are also included in this volume, as also the four papers in which he and K S Viswanathan developed a generalised theory of elasticity.

Raman's quest for the interaction between optical phonons and matter ended in 1928 but by then he was already looking further. In the lecture *A New Radiation* (1928) he said "If a quantum of radiation can be absorbed in part and scattered in part in the optical region of the spectrum, should not a similar phenomenon occur in X-ray scattering? The type of scattering discovered by Professor Compton may possibly be one of the numerous types of scattering with modified frequencies; some with a line spectrum and some in the nature of continuous radiation."

His foresight was borne out a decade later when he investigated the interaction of X-rays with crystal vibrations. It was known that the possible vibrations in a crystal fall into two broad types. The acoustic spectrum was made up of elastic waves which traverse the crystal in all directions ranging in frequency from zero to a certain upper limiting value as postulated in Debye's very successful theory of specific heats at low temperatures. The second type consisted of "optical" vibrations of the crystal which could also give rise to well-defined spectral lines in infra-red absorption or in the Raman Effect.

Diffuse X-ray reflections

The effect of thermal vibrations on the intensity of X-ray reflections had been considered by many scientists as it was of immediate significance in the determination of crystal structures by X-ray methods. When X-rays fall on an

atom occupying a fixed position in a crystal it would emit in all directions secondary radiations having the same frequency as the primary X-rays falling upon it. In a crystal these secondary radiations cancel in most directions except specific discrete cases in which they reinforce to give sharp (Laue–Bragg) "reflections". An oscillation of the atom about its position of equilibrium would result in a periodic variation of the phase of the secondary radiation and according to Max von Laue's analysis in 1926 the secondary radiation itself would have components with frequencies increased and diminished respectively by the oscillation frequency of the atom. As pointed out by Debye and Waller the effect of these vibrations is to decrease the intensity of the X-ray reflections.

Raman pictured these vibrations as periodic pulsations of the electron density equivalent to superposing a dynamic stratification on each static stratification. The phase of oscillation of the atoms varies from one unit cell to the next. A progressive change in the phase of the atomic pulsation in a direction parallel to the particular set of planes is then equivalent to a tilt of the wave-front of the dynamic pulsations away from the static crystal planes. The Bragg condition for the particular spacing (of the periodic pulsation) must be satisfied so that one can get a reflection from the tilted dynamic sets of planes. One notices that this new type of reflection is in a direction which is displaced from the usual geometric position.

Raman had thus shown that X-ray reflections from the static and dynamic planes are separable by the simple device of tilting the crystal away from the correct glancing angle for the X-ray wavelength employed, (a procedure now called exploring the reciprocal space). There should therefore be a measurable intensity of X-rays diffracted in a direction other than the Bragg maximum.

Raman and Nilakantan looked for the existence of such dynamic reflections and observed them in various crystals. In diamond they observed two types of diffuse reflections – one temperature-dependent and the other temperature-independent. These "reflections" from the dynamical periodicity induced by thermal and other waves in the crystal structure are by their nature diffuse i.e. less sharp than the conventional Bragg reflections. The discovery of the non-Bragg reflection probably made for the first time in Raman's laboratory in 1939 was confirmed by the work of several other laboratories.

Raman derived the correct formulae for the directions of these non-lattice reflections. In working out the theory of the dynamical reflections, Raman emphasized the change of frequency occurring when X-rays interact with the thermal waves, stating that if the X-ray reflections could be analysed by a spectroscope of sufficiently high resolving power, one would find components with the frequency greater and less than that of the X-rays by an amount equal to the frequency of the waves in the crystal. At that time, the diffraction of neutrons had not yet been demonstrated and he was probably one of the few to emphasize the change of frequency and the change of direction of scattering. In fact, it is just the combination of these two measurements that gave the diffraction of slow

neutrons by lattice vibrations and other excitations the fundamental role it now enjoys in exploring condensed matter. Raman's formula showed that in the case of acoustical waves regular geometric reflections would clearly be visible only for small tilts away from the Bragg angle. However the temperature-independent reflections from diamond were sharper and were persistent over much larger angles. Raman and Nilakantan attributed them to the excitation of optical vibrations of the crystal lattice by the X-ray photon and termed the phenomenon "quantum reflection". Strangely enough, Raman was well aware that impurities in crystals under certain circumstances can also give rise to such reflections. Unfortunately, he had intuitively ruled out the possibility of any impurities in diamond. Because of this he was drawn into a long controversy with the distinguished crystallographer Kathleen Lonsdale about these diffuse reflections from diamond which she believed were due to imperfections of various kinds. Years later it was established without doubt that nitrogen and other atoms are present in diamond as substitutional impurities. The extra diffuse spots that Raman and Nilakantan observed were in fact associated with platelets of nitrogen impurities!

It is strange that the discovery of the Raman Effect was due to his intuitive belief that the weak fluorescence which his group observed in light scattering was not due to impurities. But the same intuition seems to have played him false in the case of diamond when he was older by twenty years.

Interest in crystal dynamics

In 1939, using the Raman Effect, Raman and Nedungadi discovered what is now called the "soft mode process" for crystal transformations. In the same year he and Nilakantan also discovered two types of diffuse scattering, one of which he thought was due to the excitation of an optical phonon. These two discoveries made him look for better experimental methods of determining the vibrational spectra of crystals. He was also interested in formulating methods of enumerating these vibrations and computing their frequencies, at least in the case of simple crystal structures like rock-salt, diamond, etc. It was at this stage that he returned to the remarkable photograph of the Raman spectrum of NaCl published by Fermi and Rasetti in 1931. They illuminated a 5 cm-thick NaCl crystal with the 2536.5 Å resonant radiation from a magnet-controlled water-cooled quartz mercury arc. To prevent the complete fogging of the photographic plate which would have resulted from long exposures with intense illumination, Rasetti had introduced a filter of mercury vapour which absorbed the resonance radiation producing a clear photograph in which the spectral lines could have been seen as close as fifty wavenumbers from the incident line. The actual spectrum recorded was the second order Raman spectrum of NaCl (the first order being forbidden by symmetry). It was described by them as follows: "The effect is however very

different from the usual Raman effect observed in crystals. It consists of a continuous spectrum over which were superposed a few apparently randomly distributed maxima and minima." Raman discerned in these "randomly distributed maxima and minima" nine "lines" which was exactly the number of vibrations of the NaCl lattice expected on the basis of his theory.

So impressed was Raman with the Rasetti technique that he urged his associates to set up this arrangement immediately in his laboratory and if possible improve upon it by using higher dispersion spectrographs. The second order Raman spectra of NaCl and diamond were recorded by R S Krishnan and in his skilful hands it became perhaps the best method for studying the vibration spectra of crystals till it was overshadowed by the use of lasers.

Reformulation of crystal dynamics and its achievements

Raman formulated his crystal dynamics starting from the classic work of Lord Rayleigh. In a normal mode of a connected system of particles, they all vibrate with the same frequency and can have either the same or opposite phases. Raman then introduced the basic principle of crystal architecture: that the crystal consists of sets of equivalent atoms ordered in such a manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set. He deduced that in a normal mode of a crystal, equivalent atoms in it, all have the same amplitude of vibrations, their phases being either the same or else opposite in successive cells of the lattice along each of the three axes. This is equivalent to saying that atomic vibrations repeat themselves exactly in a space pattern of which the unit has twice the dimensions in each direction and therefore eight times the volume of a unit cell of the crystal lattice. If, therefore, each unit cell contains p atoms then these cells contain $8p$ atoms and these have $24p$ modes of vibration or $(24p - 3)$ normal modes if one excludes the three translations. Hence according to Raman the fundamental result emerges that a crystal containing p interpenetrating (Bravais) lattices of atoms has only $(24p - 3)$ characteristic modes of vibration each of which is characterized by a specific frequency. In $3p - 3$ of these modes equivalent atoms have the same phases of oscillation in adjacent cells and in the $21p$ other modes the amplitudes are the same, while the phases alternate in adjacent cells (along one, two or three axes of the lattice).

Raman next proceeded to give a physical picture of the $21p$ modes in cubic crystals. For example, in the case of rock-salt these modes are oscillations of the alternate planes of equivalent atoms in a crystal relative to each other, the planes being either the octahedral planes or the cubic planes. The degeneracies were then calculated and the modes enumerated to be nine for NaCl, eleven for CsCl, and eight for diamond etc. The description of each mode was given. The numbers in

almost every case corresponded to the numbers of the peaks observed in the second order Raman spectra of these crystals. He then proceeded to calculate the frequencies of these $24p - 3$ modes for many crystals in terms of force constants. The agreement between calculated frequencies and the experimentally observed ones was very good. He then calculated the specific heats of these crystals assuming the frequency spectrum to consist of $24p - 3$ discrete frequencies and using them as simple Einstein oscillators, with an appropriate Debye term added. Again the agreement between theory and experiment was rather good.

The large number of papers on the Raman spectra and infrared spectra of a number of crystals had valuable experimental data and good fits with theory and one would have thought that all these indicated a success of his ideas. Indeed, if these papers had been presented as a simple and physical approximation capturing the essential features of optical modes, they would have been regarded as a significant contribution in the field. But to Raman, the successes of his approach meant that the entire body of lattice dynamics as formulated by Born and von Karman and developed by Born and his students was completely wrong. He launched a scathing criticism of their ideas on fundamental grounds. This period was marked by bitter controversy, basic errors, and much wasted time and effort on his part, and can only be described as a tragic failure.

The lattice dynamics controversy

Raman deduced that a crystal having N cells (with p particles in each cell) has only $(24p - 3)$ modes. His critics pointed out that this is in direct conflict with Lagrange's theorem which states that a dynamical system composed of Np particles has $3Np - 3$ normal modes. Since N is large for real crystals, theory predicts that the phonon spectrum must be continuous, in conflict with Raman's assertion that it is discrete; and further $(24p - 3)$ is a very small number compared to the actual number of degrees of freedom of a crystal. Of course, it should be mentioned that in fitting the specific heats of solids, Raman used the correct total number of degrees of freedom, which means that he regarded his modes as highly degenerate.

Raman's perceptive student K S Viswanathan, starting from the conventional lattice dynamics, proved that the group velocities of the lattice waves vanish for these special modes, which correspond to the limiting (zone centre or zone boundary) optical modes. Since the density of states in the frequency spectrum is inversely proportional to the group velocity of the waves, these (Raman) modes correspond to singularities which are particular cases of those classified in general by van Hove a few years later. From the conventional lattice dynamics it can be shown that these frequencies should appear as maxima in the Raman spectra of crystals and in this way the theory is consistent with Raman's observations. It was pointed out correctly that even if the group velocity vanishes for this handful of

$(24\,p - 3)$ modes, it does not mean that the other modes do not exist, nor does it mean that the frequency spectrum is discrete.

Raman rejected the notion used by Born and von Karman that normal modes could be described in terms of travelling waves. To him the Born cyclic postulate was an artificial device without any physical meaning. This particular criticism of Raman seemed a valid one and therefore many theoretical physicists looked into it. For example, Peierls proved that the normal modes in a crystal with boundaries are by no means identical to those of a cyclic crystal (with no boundaries) but the frequency spectra of the two are practically identical if the ratio of the number of atoms on the surface to those in the bulk is small. Thus except in special situations where surface effects are likely to be important the mathematically simpler (though artificial) picture given by the cyclic postulate is a very good approximation. It is of some interest that Peierls published this paper in an Indian journal.

Since Raman started from the correct definition of the normal mode given by Rayleigh, at what stage did the theory take a wrong turn? It is in his second assertion that in a normal mode in a crystal, equivalent atoms in adjacent cells must vibrate with the same amplitude with the same or opposite phases. This is reminiscent of the famous Bloch condition in solid state physics which is only valid for travelling waves! Raman inappropriately imposed this condition on a standing wave situation which completely restricted his attention to 8 cells. Although this proved important in explaining and calculating the frequencies at the "zone centres" and "zone boundaries" and explained some important features observed in the second order Raman spectra of crystals, the nature of the complete lattice spectrum was missed.

This volume also contains papers on a new view of the theory of elasticity in which the symmetries of the stress and strain tensors and the number of independent elastic constants differed from the standard view. These papers naturally proved controversial as well.

The controversies in perspective

This volume contains many papers based on ideas which were hotly disputed even in Raman's time and are recognized to be incorrect today. It is probably natural that a scientist who relies on his powerful intuition (as Raman did) would sometimes be led into errors. The experimental proof of the spin of the photon has already been mentioned in Volume I and the intrinsic tetrahedral symmetry of diamond in Volume IV. In this volume, we have his view that the excitation of optical phonons was the cause of the temperature-independent diffuse X-ray reflection in diamond. In all these cases, it is fair to say that the state of knowledge at that time left genuine room for doubt. It is true that in his later years, Raman was prone to ignore or dismiss evidence which contradicted his point of view.

His work on the foundations of lattice dynamics stands apart from the three instances given so far. Firstly, it concerned a subject in which he was an acknowledged master – waves and vibrations. One sees a combination of many factors which shaped his strong, unyielding and ultimately incorrect objections to Born's theory of lattice dynamics. To start with, the artificial looking cyclic postulate must have put Raman off. Elaborate calculations (not fully carried out till the advent of computers a decade or more later) were needed to predict the simplest of optical and thermal properties from the Born theory. Lacking the notion of singularities in the spectrum, again not to come for a decade, the sharp features seen in the Raman scattering found no explanation. In this situation it is natural that Raman sought an alternative, and once it turned out to match the experiments, he was blind to its theoretical flaws. By the time the crucial evidence in favour of the Born theory had accumulated, his attitude had hardened and even his close associates and students could not get through to him on this subject. More than any of the other errors mentioned earlier, it was his stand on lattice dynamics which genuinely diminished his stature as a scientist in later years. While this controversy (and others to a lesser extent) caused a great deal of pain to those around him at that time, they fit into a pattern which is not at all unusual in the history of science. The same qualities (intuition and persistence in Raman's case) which are responsible for a scientist's great successes can also let him down on other occasions. It is essential for the biographer, historian or even the student of science to be well aware of this side of Raman and hence these papers have been reprinted here in full to give a complete picture of the man. But in the long run, there is no doubt that Raman's towering contributions to so many areas of physics – exemplified by the other volumes of his collected papers – will outweigh by far the errors of interpretation and judgement we have just discussed.

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