

RAMAN SPECTRA OF CRYSTALS AND THEIR INTERPRETATION*

ITS universal applicability, simplicity of technique, precision of results obtained and ease of interpretation make the Raman effect a powerful tool for the study of the structure of matter. The information yielded by Raman spectra has been of great value in the investigations of relatively simple molecules as well as of the more complicated polyatomic ones. Its utility in the investigations of the physico-chemical problems set by the crystalline state of matter is equally great. Although numerous papers have appeared on the Raman spectra of crystals since the discovery of the effect, very little progress was made till 1943 in using Raman effect data for the elucidation of the physical properties of solids. This state of affairs may be attributed to the fact that the physics of the solid state was dominated for many years by theories which had their birth before the discovery of the Raman effect. The reference here is to the well-known theories of solid behaviour originally put forward about the same time by Debye and by Max Born.

It is a significant fact that, subject to some noteworthy qualifications and exceptions, the modes of atomic vibration appearing in the Raman spectra of crystals are represented by sharp lines irrespective of the nature of the substance, or of the frequency of the vibrations. Basing himself on this and similar optical effects observed in crystals, e.g., luminescence and absorption spectra at low temperatures, Sir C. V. Raman (1943) formulated a new theory of lattice dynamics. The new theory leads among other things to the most important result, namely the vibration spectrum of a crystal consists essentially of a finite number of discrete frequencies. On the basis of the Raman theory, crystal lattice has in general $(24p-3)$ modes of normal vibration (excluding simple translations) in $(3p-3)$ of which all the units in the structure have the same phases, while in the remainder equivalent atoms in neighbouring cells along one, two or all three primitive translations vibrate with opposite phases. The experimental confirmation of this prediction became a matter of fundamental importance for the progress of crystal physics. As the available data on the Raman spectra of crystals were insufficient, it became necessary to carry out a series of investigations using an improved experimental technique to give a decisive answer to the following issues raised by the new lattice dynamics: (1) Are the vibrations in crystals which manifest themselves in the Raman spectrum, waves extending through the volume of the crystal, or are they the vibrations of the atoms in the individual cells of the lattice? (2) Is the complete vibration spectrum of the crystal in the infra-red region a continuous diffuse spectrum, or is it a discrete spectrum exhibiting a finite set of monochromatic frequencies?

It has been the practice generally to use the $\lambda 4046$ and $\lambda 4358$ radiations of the mercury arc as exciter in the studies on the Raman spectra of crystals. The Raman lines excited by these radiations fall in the very region where the weak fluorescence exhibited by many crystals appear and where the spectrum of the mercury arc itself shows a weak continuum. Consequently feeble Raman lines may not be detected as they will appear overpowered by the continuum. In view of these difficulties, the technique of using the $\lambda 4046$ and $\lambda 4358$ radiations for the study of the Raman effect in crystals appeared to have already been pushed to the limit of its utility during recent years. It became clear that some radical improvement in the technique of study had to be effected in order to get further useful information about the Raman spectra of crystals. This was achieved by the so-called ultra-violet technique described below.

As is well-known, it is essential to employ a monochromatic light source which is very intense for recording the extremely feeble Raman scattering in crystals. It is also of great importance that there should be no continuous spectrum accompanying the same. This is secured by using the $\lambda 2533.5$ mercury resonance radiation from a water-cooled magnet-controlled quartz arc. The enormously increased scattering power of the resonance radiation arising from its exceptional intensity as compared with the other mercury radiations and from the λ^{-4} law has made it an ideal source for Raman effect studies in the case of crystals that are transparent to the ultra-violet and do not get coloured by prolonged exposure to this radiation. The $\lambda 2533.5$ radiation from the light scattered by the medium is effectively suppressed before its entry into the spectrograph by absorption in a column of mercury vapour, as otherwise the photographic plate would be fogged. This makes it possible to record faint Raman lines with small frequency shifts on a clear background.

Using the improved experimental technique for exciting the Raman spectra, many crystals have been studied by Dr. R. S. Krishnan during the last five years and a rich harvest of results obtained in every one of the cases investigated. The results obtained in the case of diamond, rocksalt, potassium bromide, ammonium chloride and ammonium bromide afford a direct experimental verification of the predictions of the new theory of crystal dynamics. In all these cases, the second order Raman spectra exhibit a series of sharply defined frequency shifts. The numerical evaluation of the eigen frequencies for the above crystals on the basis of the new lattice dynamics leads to results in good agreement with observational data. Their activities in light-scattering and in infra-red absorption are also in accordance with the theoretical predictions.

From the experimental facts presented herein on the Raman spectra of crystals, it is clear that the parts of the vibration spectrum in the lower and upper ranges of frequency differ radically in their behaviour. The first part is totally inactive in light scattering,

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