

The eigenvibrations of crystal structures*

1. Introduction

As is well known, the atomic architecture of a crystal may be described as a three-dimensionally periodic distribution of matter in space on a very fine scale. The regularity of such arrangement is, however, liable to be disturbed in various ways and especially by the thermal agitation in the crystal or by the incidence of radiations on it, and the atoms then vibrate about their respective positions of equilibrium. A knowledge of the modes and frequencies of the vibrations thus arising is of the greatest possible importance for the theory of the solid state. For, it enables us to evaluate the strength of the interatomic forces and thus to obtain a quantitative physical picture of the structure of the crystal, supplementing the geometric description furnished by X-ray analysis. Further, such knowledge is the basis for a development of the theory of the physical properties of crystals, including especially all those which depend on or are influenced by the temperature of observation.

The volume of papers under review is intended to furnish a definitive answer to the problem of ascertaining the modes and frequencies of vibration of the atoms in a crystal in relation to their geometric distribution in space and the forces holding them together as a rigid structure. Of the 19 papers forming the symposium, 9 describe new experimental results obtained from investigations specially designed to throw light on this fundamental problem. These experimental papers are richly illustrated, no fewer than 65 separate spectrograms and 35 microphotometer records besides numerous diagrams being reproduced to aid the reader's understanding and appreciation of the results of the researches. The introductory paper of the symposium furnishes the necessary theoretical background, while the remaining nine papers are devoted to the consideration of the consequences of the theory in particular cases and their comparison with the facts of experiment. Before entering into a discussion of the theoretical aspects of the subject, it appears desirable to present the reader with a review of the experimental situation as it emerges from the symposium.

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2. The scattering of light in crystals

Many investigations on the vibration spectra of crystals have been made during the past twenty years by the method first employed in 1928 by the present writer, viz., illuminating the crystal by monochromatic light and recording the spectrum of the scattered radiations emerging from it. While much empirical knowledge of value has accumulated as the result of such studies, they left untouched the fundamental problem of ascertaining what the *complete* vibration spectrum of any crystal is and of how it is related to the structure of the crystal. Investigations designed to resolve this problem were undertaken at Bangalore a few years ago by Dr R S Krishnan. Numerous crystals have been studied with the utmost possible thoroughness and a rich harvest of results obtained in every one of the cases investigated, viz., calcite, quartz, barytes, gypsum, fluorspar, corundum, topaz, diamond, rock-salt, sylvine, ammonium chloride, ammonium bromide. We shall presently proceed to take note of such of these studies as are now reported on. As an example of the results which previously found publication, we may mention the case of calcite, with which no fewer than 16 frequency shifts were recorded by R S Krishnan as against a maximum of 7 by earlier workers. The following facts observed with this crystal may be regarded as typical of those noticed with inorganic crystals generally. (a) The frequency shifts recorded with small or moderate exposures represent the *first-order* spectrum, namely, the fundamental eigenfrequencies of atomic vibration in the crystal which are active in light scattering. (b) In strongly exposed spectrograms, frequency shifts are recorded with appreciable intensity which represent the vibration-spectra of higher orders, viz., the overtones and summationals of the eigenfrequencies, including those not recorded as fundamentals. (c) The frequency shifts of all orders are recorded as

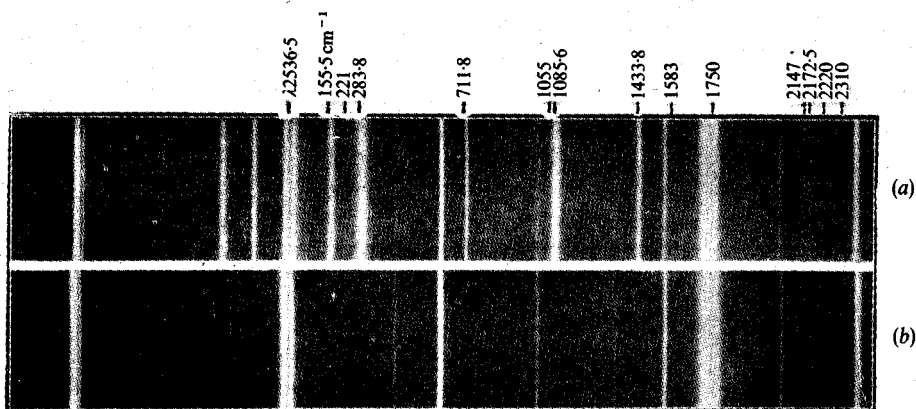


Figure 1. (a) Raman spectrum of calcite. (b) Mercury spectrum (after Dr R S Krishnan).

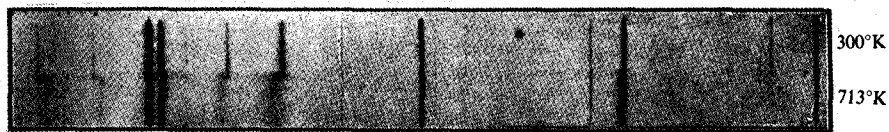


Figure 2. Variation with temperature of the Raman spectrum of calcite (after P K Narayanaswamy).

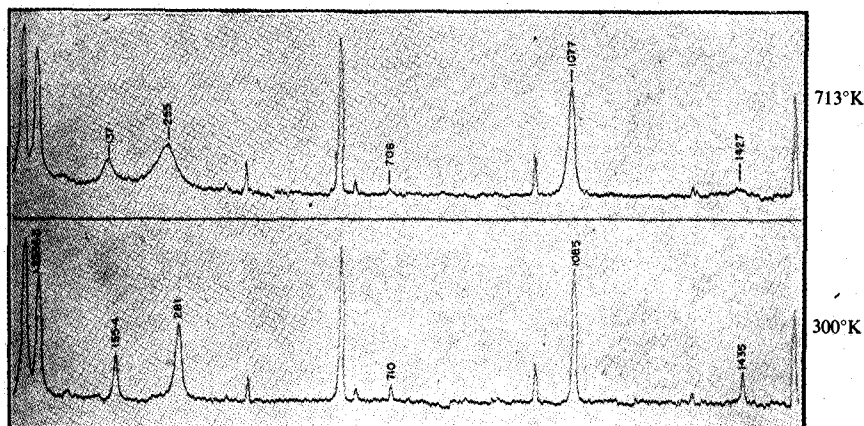


Figure 3. Microphotometer records of the Raman spectrum of calcite at two different temperatures (after P K Narayanaswamy).

sharply defined lines on a clear field, the apparent spectral width of such lines in many cases being no greater than that of the mercury arc lines registered on the plates with comparable intensities. (d) When the crystal is heated, the spectral lines broaden and shift towards the position of the exciting radiation and their peak intensities diminish notably. (e) Vice-versa, if the crystal is cooled to liquid-air temperature, the spectral lines sharpen and shift away from the exciting radiations while their peak intensities increase. But these effects are by no means so conspicuous as those of the opposite kind noticed on heating (see figures 1, 2 and 3).

3. The cases of corundum and topaz

These are two well known crystals found in nature, while the former can also be prepared synthetically. Corundum is of much simpler composition and structure than topaz, and is a crystal of the trigonal class, while topaz is orthorhombic. These differences are reflected in the degree of complexity of their vibration spectra, 7 frequency shifts being recorded by Dr R S Krishnan with corundum

