Scattering of Light in Crystals

SINCE its discovery[1], early in 1928, the scattering of light with altered frequency has been investigated in many crystals, and much valuable information has been accumulated. The significance of the results and their relation to theories of the solid state are clearly matters of great interest.

The outstanding result of the experimental studies is that the atomic vibration spectrum of crystals in the infra-red region reveals itself in light-scattering as a set of discrete frequencies, the approach to monochromatism being the more complete the more perfect the crystal, and the lower the temperature at which it is studied. It is particularly significant that this feature obtains not only in respect of the so-called internal vibrations of the ions or molecules comprised in the crystal, but also in respect of their translatory and rotatory oscillations which are characteristic of the crystalline state. As a typical case, calcite may be mentioned. Dr. R. S. Krishnan has recorded extremely intense spectra with this crystal employing the 2537 A. radiations of a water-cooled, magnet-controlled quartz mercury arc as the exciter and giving prolonged exposures. Besides the internal vibrations of the CO_3'' ions and their translational and rotational oscillations, octaves and combinations of these frequencies are also found recorded in the spectrum. All of them appear as sharp lines, *but not a trace of continuous spectrum is noticeable on the plates.*

Comparative studies with various substances in the molten and solid states make it clear that every mode of infra-red vibration which gives rise to appreciable variations of optical polarizability in the volume elements of a crystal also manifests itself as a frequency-shift. Hence, as in the cases of gases and liquids, we are entitled to infer that the spectrum of light-scattering in a crystal is a faithful map of the fundamental infra-red vibration spectrum, excepting only the modes for which the symmetry excludes any variation of optical polarizability.

Recently, by a straightforward dynamical investigation[2], I have shown that the fundamental vibration spectrum of a crystal containing p sets of non-equivalent atoms consists of the $(3p-3)$ modes which repeat themselves in adjacent cells of the Bravais lattice, and in addition $21p$ other modes in which the phase alternates in successive cells. The prediction confidently made that these $21p$ modes should also manifest themselves in light-scattering has been strikingly confirmed by Dr. R. S. Krishnan[3] in the case of diamond.

It is clearly impossible to reconcile the facts stated above with the theories of the solid state which assume, or claim to show, that the atomic vibration spectrum of a crystal in the infra-red region is a continuous one. To effect any such reconciliation, it would be necessary to invent a mechanism which could transform the assumed continuous spectrum of frequencies into a discrete line spectrum by a process of exclusion. One such mechanism which has often been suggested is that the phases of the infra-red vibration are perfectly coherent over the whole volume of the crystal, in consequence of which all the scattered radiations disappear by optical interference except those arising from the so-called limiting modes of vibration, $(3p-3)$ in number, the phase wave-lengths of which are comparable with the length of the light waves and satisfy the Bragg condition for reflexion. To this suggestion, however, there is a fatal objection, namely, that $21p$ other modes which have much smaller phase wave-lengths not satisfying this condition are also observed in light-scattering, while the infinitely numerous others which are also assumed to exist in the aforesaid theories fail to manifest themselves. A further objection is that, in actual crystals, the assumed coherence of phase can scarcely be expected to extend over sufficiently great volumes for optical interference to be effective. For the latter reason, the continuous spectrum assumed to exist in such theories should manifest itself fully in light-scattering or at least give an observable indication of its existence. Since this is not the case, we can only infer that the postulated continuum does not exist in the infra-red region of frequency. We are, of course, here not discussing the low-frequency or elastic solid vibrations in which the discrete atomic structure is not explicitly involved.

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[1] Raman, C. V., *Ind. J. Physics* (1928).
[2] Raman, C. V., *Proc. Ind. Acad. Sci.*, A, **18**, 237 (1943).
[3] Krishnan, R. S., *Proc. Ind. Acad. Sci.*, A, **19**, 216 (1944).