

ATOMIC VIBRATIONS IN CRYSTALS

BY

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THE theory of the specific heat of crystal-line solids is considered from a new standpoint in a symposium of seven papers appearing in the *Proceedings of the Indian Academy of Sciences*, for November 1941. The introductory paper is contributed by the author and is followed by six papers in which the basic ideas there outlined are successfully applied to the explanation of the experimental data for numerous substances of relatively simple composition. The cases of diamond and white phosphorus are considered respectively by Mr. V. B. Anand and Mr. R. Norris. Mr. Dayal has two papers on the specific heat of metals crystallising respectively in the cubic and

hexagonal systems. Dr. C. S. Venkateswaran considers the case of the alkali halides in a specially thorough fashion, while Mr. R. Norris discusses the data for crystalline quartz.

As is well known, Einstein laid the foundations of the quantum theory of specific heats in his classic paper of 1907 in which the specific heat anomaly presented by diamond was explained on the assumption that the atoms in the solid vibrate with a high characteristic frequency. At low temperatures, however, the specific heat of all elementary solids falls off less rapidly than is indicated by the Einstein formula if a single characteristic frequency be assumed.

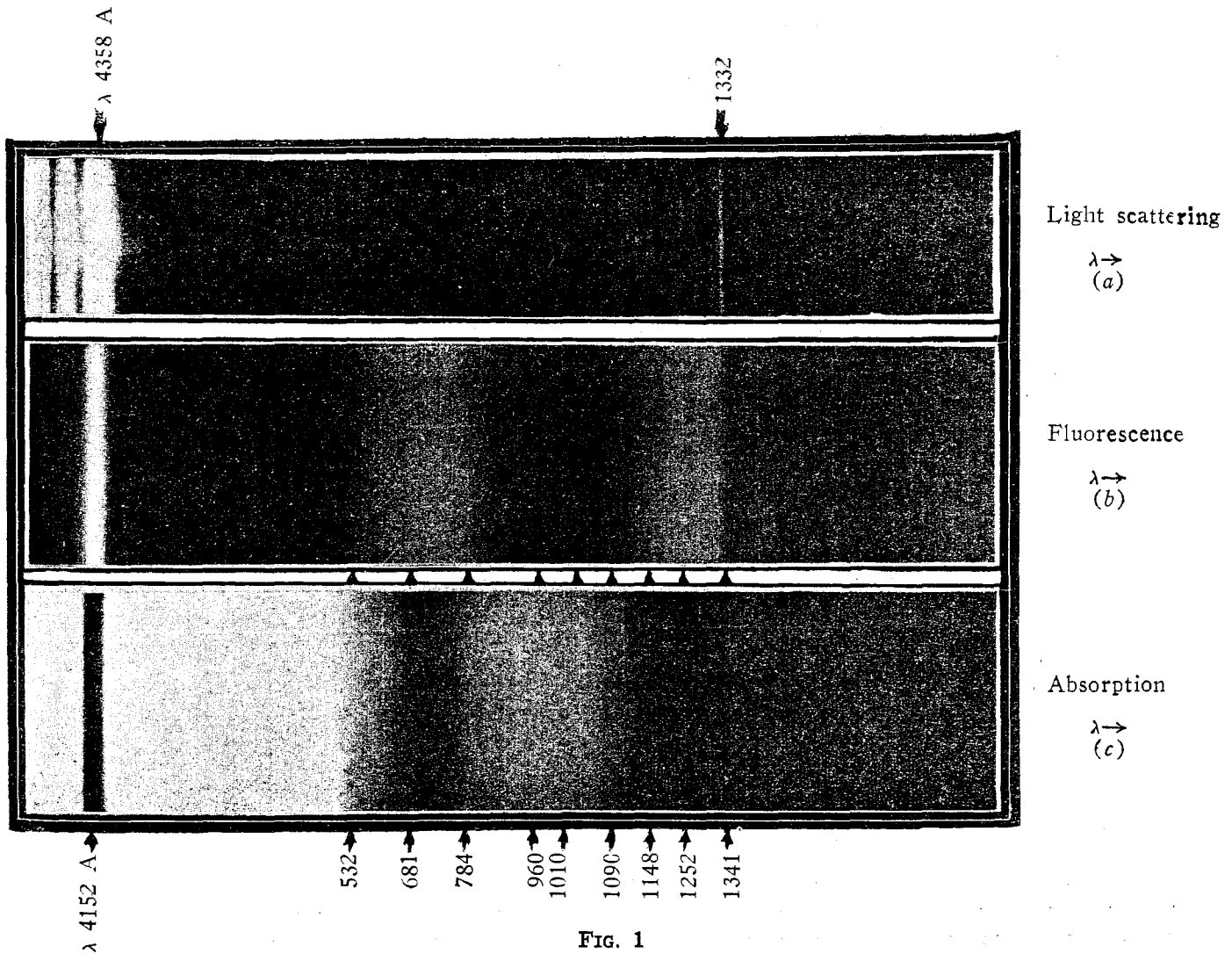


FIG. 1

Lattice Spectrum of Diamond

This was regarded as indicating a failure of the Einstein theory and led to its falling into disfavour. Discussions of the thermal energy data are at present usually based on the alternative theory propounded by Debye which derives its inspiration from the classical mechanics of vibrating elastic solids. Debye disregarded the discrete atomic structure of solids and assumed the atomic vibrations to be identical with the elastic modes of a continuum having various frequencies up to a suitably assumed high limit. An alternative form of the theory developed by Max Born and his school formally takes account of the crystal structure but has as its basis the so-called "postulate of the cyclic lattice". This postulate assumes that the external boundary of the solid determines all the possible modes of atomic movement exactly in the same way as in the classical theory of elastic vibration. The theories of Debye and Born are thus both based on an extrapolation of ideas derived from macroscopic physics into the field of atomistics. Such an extrapolation, besides being theoretically indefensible, leads to results which stand definitely contradicted by the experimental facts in many fields of inquiry. It is sufficient here to mention one example, namely the results of spectroscopic study of the scattering of light in crystals. Such studies show clearly the correctness of the original hypothesis of Einstein, namely that the atomic vibrations in crystals have *monochromatic frequencies*. Numerous sharply defined lines are recorded in the spectrum of monochromatic light diffused by transparent crystals, the frequency shifts observed being both greater and smaller than the so-called "limiting frequency" calculated from the elastic data (see Fig. 1).

The proper approach to the problem of atomic vibrations in crystals is evidently *not* from the macroscopic point of view, but from atomistic considerations which take as their starting point the known periodic space-grouping of the ultimate particles in the solid. What are the departures from the static grouping in space which are dynamically possible and what are their frequencies? In seeking an answer to these questions, we are justified, in view of the very fine scale of the atomic structure, in ignoring the existence of an external boundary and considering the solid to be of unlimited extension. On this assumption, it

follows that the possible vibration patterns must be simply related to the architecture of the crystal. Any departure from the static grouping of the atoms will repeat itself with perfect periodicity in time only if it be also perfectly recurrent in space, in other words, only if the vibrations occur in identically the same fashion throughout the solid. The unit "cells" of the dynamic pattern must thus be either identical with the lattice cells of the crystal or else must embrace an integral number of such cells, thereby forming a superlattice. In other words, the atoms throughout the crystal occupying equivalent positions in the lattice or superlattice cells should oscillate in the same way. Such an oscillation would have a perfectly defined frequency, and the number of such frequencies would be determined by the number of atoms contained in each lattice cell or superlattice cell as the case may be. The larger the cell of the superlattice, the more completely would such an analysis (carried out in detail by the methods of the group theory) represent all the possible modes of atomic vibration in the crystal.

For the detailed development of these ideas, the reader may be referred to the papers appearing in the symposium. The thermal energy content of most crystals at ordinary temperatures depends almost exclusively on the modes of vibration which may be found by considering dynamic repetition patterns in which the space unit is the smallest which is fully representative of the structure and symmetry of the crystal. Even so, there would usually be several Einstein frequencies requiring consideration. In some cases, *e.g.*, diamond, phosphorus, alkali halides and quartz, these frequencies and the weights to be attached to them may be ascertained from the spectroscopic data and the known crystal structure. In other cases, *e.g.*, the metals, the specific heat data have themselves to be utilized to supplement the information furnished by considerations of crystal structure.

The principal lattice frequencies represent the movements of the atoms within the unit cell relatively to each other. They necessarily include the internal vibrations of any ions or molecules present in the lattice, as also the frequencies of their hindered translations and rotations. The superlattice vibrations which appear in the theory may be pictured as representing the oscillations

of neighbouring lattice cells or groups of lattice cells against each other. Such oscillations are necessarily of lower frequency and of lower statistical weight than the principal lattice frequencies. The contribution which they make to the specific heat would be sensible only at low temperatures, except in the case of crystals of very simple composition where they may have to be taken into consideration even at ordinary temperatures. The superlattice oscillations are the nearest analogue in the present theory to the elastic vibrations of macroscopic physics, but differ from them in being

precisely related to the crystal structure and in possessing specifiable frequencies. That the existence of such vibrations is a physical fact and not a mere hypothesis is evident from the spectroscopic data for various actual crystals, e.g., diamond (see Fig. 1).

The most significant point which emerges from the symposium is that the experimental facts in several cases which refused obstinately to fit into the Debye and Born theories find a natural explanation in the new theory without the aid of any special hypotheses.

RADIO RECEPTION DURING THE MAGNETIC STORM AND IONOSPHERIC DISTURBANCE FROM 17th SEPTEMBER TO 20th SEPTEMBER 1941

BY

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SHORT WAVE radio services were very badly affected during the period 17th to 20th September 1941, due to a magnetic storm of severe intensity lasting for several hours and three sudden but short fadeouts of the Dellinger type. As published radio data from India on this subject is rather scanty and as such information may be useful for correlating world-wide conditions, it is proposed to present here the conditions of radio reception as reported by the various Receiving Centres of A.I.R. distributed throughout India, together with the results of pulse observations made at the main Receiving Centre at Todapur near Delhi.

The times of occurrence of the disturbances as far as can be estimated from radio observations are given below:—

- (a) September 17, 1941: Sudden complete fadeout 1400^h–1425^h I.S.T.
- (b) September 18, 1941: Sudden fadeout (partial) 0750^h–0819^h I.S.T.
- (c) September 20, 1941: Sudden fadeout (partial) 0800^h–0850^h I.S.T.
- (d) September 19, 1941: Magnetic storm effect—practically the whole day and night and up to 10 a.m. I.S.T. on the morning of 20th September 1941.

The times given for the commencement of the fadeouts (a), (b) and (c) are those noted at the Receiving Centre at Todapur

and differ by a few minutes from those mentioned by the other A.I.R. Receiving Centres, which is mainly due to the sudden and unexpected nature of the phenomenon. The timings given for the end of the fadeouts are very approximate because of the varying duration of the fadeout on different frequencies.

The first three fadeouts can be easily identified as of the Dellinger type on account of the following characteristics:—

- (i) The fadeouts occurred during daylight hours.
- (ii) The commencement of the fadeouts was very sudden.
- (iii) When conditions were returning to normal, stations working in the 16, and 19 metre bands were received before those working in the 25 and 31 metre bands.
- (iv) Medium wave stations were not affected.

In addition to the above-mentioned fadeouts there was a severe ionospheric disturbance due to a magnetic storm of great intensity which occurred on September 18th and 19th.¹ The following particulars have been very kindly supplied by the Director of the Colaba Observatory, Bombay:—

¹ M. R. Rangaswami and A. S. Chaubal, *Curr. Sci.*, 1941, 10, 432.