

the form of an orange amorphous precipitate. Further, the complex was suspended in alcohol and decomposed with carbon dioxide, then the alcoholic solution was concentrated to a faintly coloured syrupy solution. The latter solution was gradually poured into dry acetone; thus a white ashless powder was obtained. It melted between 190° and 200° (decomp.), and characterized by giving a white precipitate with barium hydroxide, a bluish precipitate with Fehling's solution, and a yellow colour with concentrated sulphuric acid. Hydrolysis of the saponin with hydrochloric acid gave a water-insoluble precipitate which crystallized from acetone in the form of a brownish semi-crystalline product. It was further purified by extraction (Soxhlet) with light petroleum, then crystallized from dioxan in white plates, m.p. 184°. The crystalline product gave the colour reactions of sapogenins, and appeared to be a mixture of sapogenins from which a pure compound, m.p. 198°, was isolated and assigned the formula  $C_{27}H_{42}O_3$ , comprising a free hydroxyl group and two inactive oxygen atoms. There is also evidence that it belongs to the sarsasapogenin group of sapogenins, and identity of its structure is now the subject of a detailed study.

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<sup>1</sup>J. de Pharm. et. de Chim., 20, 183 (1919).

## Dynamics of Real Crystals

IN his well-known theory of the specific heat of solids, Einstein made the fundamental assumption that all the atoms in a crystal are capable of vibrating independently of one another with the same frequency. It was not meant as an exact description: the intention was to get a sufficiently good approximation without unessential intricacies. His theory has been recalled here at the outset because we find that his approximation is only an extreme form of the hypothesis to be formulated at the end of this note.

In their theory of the vibrations of solids, Born and Kármán introduced the so-called "cyclic lattice hypothesis", which is the basis of the whole theory of crystal dynamics developed by Born and his collaborators. Sir C. V. Raman has recently questioned the correctness of the hypothesis and has suggested that it is dynamically unsound; it need scarcely be said that if the hypothesis is unjustified from the mathematical point of view it must be given up. Even if the exact theory of the lattice vibrations based on certain extreme idealizations be worked out, it will not serve to describe the vibrations of a real crystal unless it conforms to experiment. The exact and complete solution of the problem of the vibrations of a linear diatomic lattice under internal forces was obtained here some time last year, and has been given independently by Born. Born's work, however, contains some mathematical errors, for his enumeration does not include the obvious translation of the lattice as a whole, or that vibration which, when the number of atoms is only two, corresponds to their mutual vibration.

The cyclic lattice method originally proposed by Born affords the solution that the vibrations take

place as those of the infinite lattice the wave-lengths of which are sub-multiples of the dimensions of the finite lattice. In his recent paper he appears to suggest that the cyclic lattice method is justified because the frequency-range given by it is the same as that given by the exact theory. This is not the point of dispute. What had to be shown is that there are vibrations of the finite lattice to which we can ascribe wave-lengths, and that they are of the order  $L/N + o(1/N)$ .

There are certain features of the cyclic lattice solution which are misleading, such as the degeneracy of over-vibration, and secondly, the existence of progressive wave solutions. It can be shown that over-vibration of a finite lattice is non-degeneracy, and progressive wave solutions are impossible. The exact theory shows that there will be the so-called optical and acoustic branches. However, for displacement ( $a$ ) of the first atom, the maximum displacement of any atom will be  $O(a)$  in acoustical vibrations, while the maximum amplitude will be  $O(Na)$  in optical vibrations. The magnitude of the maximum amplitude falls off far more readily in the case of the optical branch than in the other. The important point is that whereas the acoustical vibrations depend on the nature of the boundary, it would require a very perfect crystal with perfect boundary conditions for all the atoms in an optical vibration to vibrate in the same phase, though not with the same amplitude. In the exact solution, infinitesimal displacements in not negligible regions have to form as nodal bridges. These considerations force us to draw a distinction between vibrations in perfect crystals and in real crystals.

The following is a working hypothesis to describe the vibrations taking place in a real crystal:

(1) There will be two types of vibrations, one of high frequency and the other of low frequency. These types must not be confused with the optical and acoustical branches introduced by Born.

(2) Almost all the vibrations will be of the high-frequency type, that is, the number of vibrations will be  $O(3N)$ .

(3) A high-frequency vibration can appear anywhere in the crystal, being limited only by a closed surface which we term the 'vibrational volume', outside which the disturbance caused will be negligible. The dimensions of the vibrational volume depend only on the nature of the crystal forces and crystalline symmetry, for the high-frequency spectrum will be a monochromatic one with a small number of frequencies.

These assumptions include Einstein's hypothesis in an extreme form when the vibrational volume is the atomic volume itself and over-vibration is a high-frequency one. The ideas contained in (2) and (4) have been stressed by Sir C. V. Raman in his publications.

In contrast with the difficulties of the idealized theories, and the lack of satisfactory correspondence with experimental results, the above hypothesis would seem to account for many of the results, especially the numerous Raman lines in crystals, the infra-red bands, the specific heat and the thermal conductivity of crystals.

Details of this work will appear elsewhere.

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<sup>1</sup> Proc. Roy. Soc., A, July 1942.