

Spectroscopic investigation of the solid and liquid states

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Amongst the instruments of precision at the disposal of the physicist for the investigation of the structure of matter, the spectroscope occupies the premier position. It may be recalled that our present ideas regarding the structure of atoms and molecules are largely based on the experimental facts revealed by spectroscopy. It is scarcely to be doubted, therefore, that we have similarly to rely on spectroscopic research for an elucidation of the nature of the solid and liquid states of matter. These are not static structures in space, and even a purely geometric description of their build is, therefore, scarcely possible without the use of spectroscopic terminology. When we pass to deeper physical considerations and seek to evaluate the forces which hold together these aggregations of matter, we realise that spectroscopy gives us both the means of investigation and the language to express our results. It follows that a real knowledge of the solid and liquid states—as distinct from purely hypothetical postulates and assumptions—must rest upon a foundation of exact knowledge garnered by experimental spectroscopic research. The symposium of papers now under notice* seeks to provide such a foundation.

When we apply spectroscopy of the visible and the ultra-violet to investigations on solids, three distinct paths of research open out. These are respectively, studies on luminescence, on absorption and on the scattering of light. The case of diamond has been thoroughly investigated in all the three ways by Mr P G N Nayar and the results so far obtained are described in the two opening papers of the symposium. Nayar's work in the main furnishes a striking confirmation of the early work of Bhagavantam on light-scattering in diamond. The studies on luminescence and absorption have yielded new results of great interest. It is shown that the fundamental vibrations of the crystal lattice of diamond form a set of discrete monochromatic frequencies, of which no less than 19 have been recognised and measured. These cover the whole range of frequencies comprised in the so-called "elastic" spectrum of Debye, but their appearance as discrete frequencies with the observed distribution of intensities is a direct contradiction

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of the postulates on which Debye's theory of specific heat is based. Nayar also obtains the remarkable experimental result that the electronic absorption frequencies of diamond form a set of sharply-defined frequencies at low temperatures. Some 25 of these are listed in the paper.

Spectroscopic studies on light-scattering in crystals reveal, in addition to the so-called "internal" frequencies of vibration of the ions or molecules, if any, present in the crystal, other discrete frequencies which are usually much smaller. These appear as sharply-defined lines in the spectrum or else sharpen to such lines when the crystal is cooled down to low temperatures. The observed frequencies lie in the remotest infra-red region, and their appearance and spectral character seem irreconcilable with the ideas either of the Debye theory or of the Born crystal dynamics which demand that the vibrations of crystal lattices form *continuous* spectra. It is *prima facie* evident that these discrete low frequencies are characteristic of the crystalline state and that they play a fundamental role in all branches of crystal physics. Their identification and explanation is thus a matter of prime importance. In a very beautiful investigation from which we reproduce the accompanying illustration (figure 1), Mr T M K Nedungadi shows that a naphthalene crystal exhibits six such frequencies in light-scattering, instead of four as hitherto supposed. When the orientation of the crystal and the state of

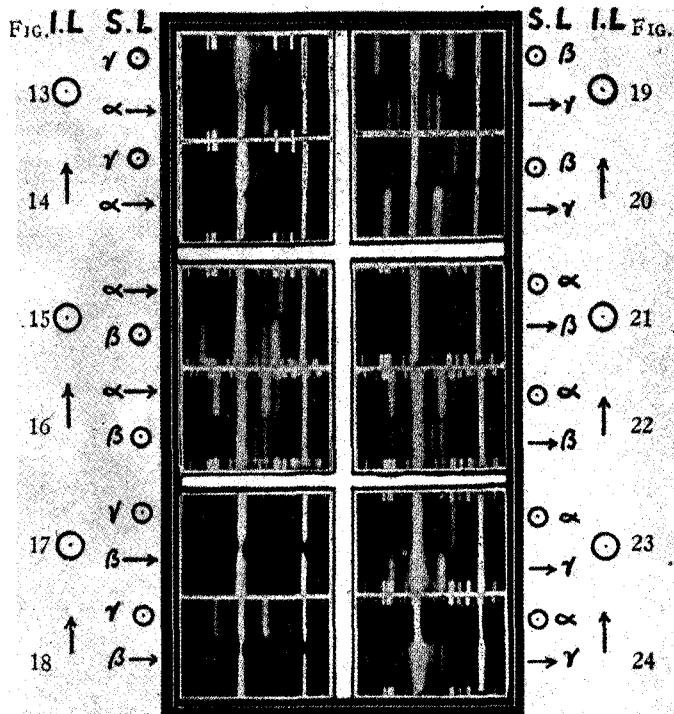


Figure 1. Low-frequency vibrations in a naphthalene crystal.

polarisation of the incident light are varied, the intensities of the lines alter in a remarkable way. It is deduced from these observations that the observed frequencies correspond to the six possible symmetric and antisymmetric rotational oscillations of the two molecules present in the lattice cell.

The development of a zinc-amalgam lamp giving monochromatic radiations of high intensity free from disturbing satellites has enabled Dr. C S Venkateswaran to carry out spectro-interferometric investigations of great value on the scattering of light in gases, liquids and solids. The perfection of his experimental technique and the thoroughness of the research has enabled results to be obtained which are trustworthy, besides being of fundamental importance. The work has also been

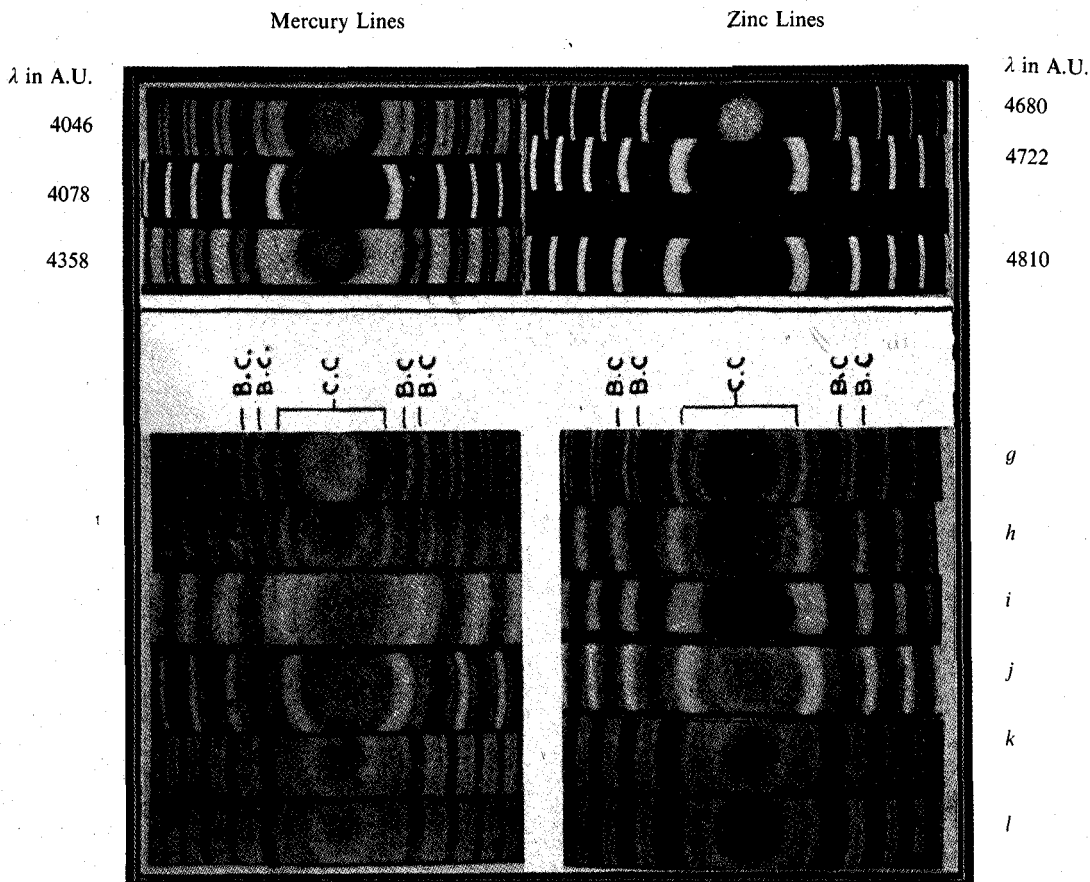


Figure 2. Interferometer Patterns of Light Scattering of Liquids.

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|-------------------------------|------------------------|--------------------------------------|
| a. Water (30°) | e. Ethyl alcohol (25°) | i. Ethyl ether (30°) |
| b. Cyclohexane (30°) | f. Ethyl alcohol (65°) | j. Tetralin (30°) |
| c. Carbon tetrachloride (25°) | g. Acetone (28°) | k. <i>iso</i> -Butyric acid (25°) |
| d. Benzene (28°) | h. Acetone (54°) | l. <i>iso</i> -Butyric acid (154°C.) |

effectively followed up by Mrs K Sunanda Bai. Seven out of the fifteen papers in the symposium are devoted to the work of these authors. We reproduce in figure 2 an illustration from one of Venkateswaran's papers.

The work of Venkateswaran and Sunanda Bai shows clearly that the conclusions reached earlier by experimenters as well as theorists in this field need radical revision. The picture of the liquid state which now emerges presents little or no resemblance to that of a crystalline solid, the analogy being rather with the amorphous or glassy state. The more viscous the liquid or the lower its temperature, the more nearly does it approximate in its behaviour to a glassy solid. This statement, in fact, covers the experimental situation as revealed by the studies on the positions and intensities of the lines in the interferometer patterns, as well as their states of polarisation.

The so-called "internal" vibrations of the molecules which become manifest in light-scattering also receive attention in the paper of Nedungadi on naphthalene mentioned above. They form the principal theme of three studies with organic liquids contributed to the symposium by Venkateswaran and Pandya. Nedungadi's work shows clearly that the selection rules for these internal vibrations are determined primarily by the symmetry of the crystal in which the molecules are imbedded and only secondarily by the symmetry of the molecules themselves. It is also evident from the investigations that even in the liquid state, the vibrations of an individual molecule are strongly influenced by those of its neighbours.

Limitations of space permit only a brief mention of B S Satyanarayana's paper on the relation between fluorescence and light-scattering in uranyl salts. This is a preliminary report of a very promising investigation.