

## LETTERS TO THE EDITORS

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## Raman's Theory of Specific Heat of Crystals

A DESCRIPTIVE article by Dr. W. H. George surveying some recent papers by Sir C. V. Raman and his school<sup>1,2</sup> having appeared in NATURE of May 16, we wish to make a few comments. A detailed criticism of Raman's paper will appear elsewhere.

(1) Raman rejects the result of lattice theory that the vibrational spectrum of a crystal consists of several (three or more) practically continuous branches, and contends instead that it consists of a few discrete vibrations. He bases this assumption on the observation that only a few sharp lines appear in optical absorption and scattering.

Lattice dynamics explains this fact by the optical selection rules: only those mechanical vibrations react with light waves which are in phase in a region of the order of a wave-length. As the wave-lengths concerned are long compared with the lattice constant, this selection rule restricts optical resonance to a practically monochromatic region in each branch of the spectrum. Hence the optical facts provide no argument against lattice dynamics.

(2) Raman<sup>1</sup> calculates the specific heat by superposing a few Einstein functions according to his interpretation of the spectrum. But in the majority of cases treated by his collaborators (Norris, Dayal, Anand, Venkateswaran<sup>2</sup>), these vibrations are not taken from optical data but chosen in such a way as to obtain a fair agreement for the specific heat. These calculations prove therefore only the well-known fact that a few Einstein functions can be fitted to the specific heat data of a solid. Nernst and Lindemann<sup>3</sup> showed in 1911 that even two frequencies in the fixed ratio 1:2 were quite sufficient for many substances. Born<sup>4</sup> has shown further that the higher branches of the vibrational spectrum cover a small frequency interval and can be replaced, for calculations on the specific heat, by a monochromatic vibration. But this is an approximation, and the fundamental fact that a system of  $N \approx 10^{23}$  particles has  $3N$  modes of vibration cannot be explained away.

In the case of rock salt an attempt is made (Venkateswaran<sup>2</sup>) to relate some of the vibrations to peaks in the Raman spectrum; but strangely enough these were considered to be octaves of the required lattice vibrations. The frequencies of sylvine are all taken to be 0.78 of those of rock salt. All these assumptions are quite arbitrary and do not lead to results better than those given by previous calculations (see accompanying table).

(3) Raman's rejection of Debye's theory is based mainly on the alleged better agreement of Raman's formulae with observation. But Debye's formula contains only one frequency and that not arbitrary, but expressible in terms of the elastic constants. It is very likely the best one-constant theory possible and serves remarkably well for monatomic substances. Its deficiencies appear at very low temperatures where particular phenomena are observed (for example, an increase in the value of the Debye parameter for NaCl with falling temperature). These have been satisfactorily explained by the rigorous lattice dynamics<sup>5,6</sup>.

As an example, the experimental specific heat values found for rock salt by Clusius and Perlick<sup>7</sup> are tabulated below, together with the values calculated by Kellermann<sup>8</sup>; the last column is taken from a table calculated by Venkateswaran<sup>2</sup> applying Raman's theory.

T° K.	C <sub>v</sub> (expt.)	C <sub>v</sub> (lat. theory)	C <sub>v</sub> (Raman's theory)
10	0.0326	0.0328	0.036
20	0.310	0.317	0.28
30	1.150	1.154	0.96
40	2.380	2.380	2.04

(4) Raman rejects lattice dynamics because it uses the postulate of the 'cyclic lattice' for the calculation of the vibrations. Raman considers this an arbitrary assumption which leads to wrong results. In fact it is a reasonable method of approximation against which no mathematician has ever raised a doubt. The rigorous solution was known for the monatomic linear lattice, where it leads to the same results; in order to refute Raman's objections the correct solution for a di-atomic linear lattice has been worked out<sup>8</sup>, and again complete agreement with the cyclic method was found. It must further be remembered that most of the well-confirmed results of the quantum theory of electrons in metals (electric conductivity, metal optics, etc.) are based on the cyclic method and can be considered as confirmations of it.

(5) Raman considers the frequencies of a lattice to a first approximation as those of the inner vibration of the single cell; but he suggests that there is an influence of the neighbouring cells which can be taken into account. This is in fact a reasonable and well-known way<sup>4</sup> of approximating to the higher (optical) branches; but it fails completely for the lower (acoustical) branches, and is therefore useless for monatomic lattices (all metals) where there are no higher branches, and, more generally, for substances (like the alkali halides) where it is not possible to consider the atoms in a cell as bound together with stronger forces than those connecting them to the neighbouring cells. It is in these cases that good confirmation is obtained for lattice dynamics in calculating the lattice energy, and elastic, optical, piezo-electric and other constants. All this would have to be abandoned if Raman's ideas were correct.

(6) Raman's theory has been devised to justify his interpretation of the diffuse X-ray scattering. It has been shown<sup>9</sup> that this interpretation is in contradiction with observations and with well-established theory, and that lattice dynamics accounts for the facts more satisfactorily. The diffuse X-ray spots are nothing but photographic images of the quasi-continuous spectrum derived from the lattice theory which Raman attacks.

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<sup>1</sup> Raman, Sir C. V., *Proc. Ind. Acad. Sci.*, A, 14, 459 (1941).

<sup>2</sup> *Proc. Ind. Acad. Sci.*, A, 14, 473-506 (1941).

<sup>3</sup> *Z. Electrochem.*, 17, 817 (1911).

<sup>4</sup> "Atomtheorie des festen Zustandes" (Berlin, 1923).

<sup>5</sup> Blackman, M., *Proc. Roy. Soc.*, A, 159, 416 (1937).

<sup>6</sup> Kellerman, W., *Proc. Roy. Soc.*, A, 178, 17 (1941).

<sup>7</sup> See Keesom, W. H., *Phys. Z.*, 35, 939 (1934).

<sup>8</sup> Born, M., *Proc. Phys. Soc.*, in the press.

<sup>9</sup> Born, M., Lonsdale, K., and Smith, H., *NATURE*, 149, 402 (1942).