both of classical and of quantum theory. From the classical point of view it is the Doppler effect for the reflexion of X-rays by waves of atomic vibrations; in quantum language it is the transfer of energy from a photon to an acoustical quantum, or vice versa. This frequency shift has long been acknowledged by the thermal theory. Since the frequency changes are much too small to be observed, they are not of practical significance except in so far as they are intimately connected with the incoherence of the scattered rays, which is an essential feature of the phenomenon.

Raman also gives the impression (which is not refuted by Preston) that his theory is a "quantum" theory and that the thermal theory is a "classical" one. The exact opposite is the case. As Preston remarks, Raman's presentation is obscure, but it is clear enough that at no stage (except when he introduces the effect of temperature change) does Raman make use of quantum mechanisms at all. He does not attempt, for example, to calculate the intensity with the help of transition probabilities. The thermal theory, on the other hand, although originally presented, nineteen years ago, in a semi-classical form, has since been given a strictly quantum-mechanical basis. The facts are that Raman's "excited vibrations" must exist (either from a classical or a quantum point of view), but that their contribution to the scattering is extremely small as compared with the effect of the thermal vibrations.

All the experiments described by Raman and his colleagues are in entire accordance with the thermal theory, but experiments on metals and on the "forbidden" reflexions of diamond, which he did not attempt, definitely prove that his theory cannot account for the facts. We have outlined some of our arguments in the following communications (written before we had read Mr. Preston's account) and have elaborated them in papers to be published elsewhere.

M. B.

K. L. and H. S.

Sir C. V. Raman's theory of the extra spots on Laue photographs having now been published in detail, I wish to deal with the theoretical aspect, as I believe it is now possible to show exactly where Raman's statements are incorrect.

(1) Raman assumes that the extra spots are due not to the acoustical (low-frequency) branch of the vibrational spectrum but to *monochromatic infra-red vibrations.*

This assumption contradicts the results of lattice dynamics, which show that the elastic spectrum consists of different branches, each of N vibrations (N number of unit cells), uniformly distributed in reciprocal space (co-ordinates: components of wave vector q). In order to justify this contradiction, Raman points out that lattice theory uses the method of the 'cyclic lattice' (replacing the boundary conditions by the postulate of periodicity in a parallel-epiped of N cells), a method which he says is not proved but arbitrarily invented to simplify the mathematical treatment. As a matter of fact, it is not proved, apart from a simple example (chain of equal particles) and a limiting case (continuous medium). These cases show, however, that the cyclic method is not arbitrary, but mathematically reasonable; and it is also well confirmed by its applications (for example, conductivity of metals). As Raman attacks the validity of the method, in particular for the optical branches, I have rigorously solved the problem of a finite di-atomic one-dimensional lattice (chain of two alternating particles); the result is, of course, uniform distribution of the frequencies in both branches and the same law for their dependence on wave number as given by the cyclic method.

The intensity of X-ray scattering of all branches will be incoherent and proportional to N. Raman's contention that the scattering due to an excited infra-red vibration will be coherent and proportional to N^2 has no theoretical justification whatever.

(2) Bisheshwar Dayal attempts to support Raman's assumption of monochromatic infra-red vibrations by calculations about the *specific heat* of metals, which he contends cannot be represented by a Debye function but needs additional terms of the Einstein type. This suggestion is not new; it was given in my book "Dynamik der Kristallgitter", published in 1915 (formula 200, p. 77), where I showed that the optical branches of the lattice oscillations are narrow bands which for the calculation of specific heat can be approximately replaced by one frequency. It is clear that no support for Raman's hypothesis can be obtained from a formula previously derived from lattice dynamics.

(3) Raman considers the *sharpness of the lines* observed in the optical Raman spectrum of crystals as a proof of the monochromatic character of the infra-red vibrations. It is not. Lattice theory explains it as a consequence of the optical selection rule: emission of light waves will not occur for every case of resonance, since the electric moments of the different cells of the crystal are in general out of phase; it is restricted to long waves for which the phases in a large group of cells are equal, and this corresponds to an extremely small region of the reciprocal space near the point $q = 0$. To each 'optical branch' of frequency there belongs only one sharp 'optical resonance'. (I regret if the term 'optical branch' has led to this misunderstanding; but the facts are clearly stated in several publications.)

(4) Raman's proof that *the acoustical branch cannot produce sharp spots* is, shortly, the following: The scattering is proportional to the mean square of the amplitude of vibration, $\overline{\xi^2}$. On the other hand, the mean potential energy of an oscillator of angular frequency ω, $\frac{1}{2}\omega^2\overline{\xi^2}$, is equal to half the mean total energy $\frac{1}{2}kT$, ($\hbar\omega << kT$), hence $\overline{\xi^2} = kT/\omega^2$. Raman replaces ω by $2\pi c/\lambda$, where λ is the wavelength of the elastic wave, c the velocity of sound. Thus he obtains the scattering of the acoustical branch proportional to $kT\lambda^2$, which is a smooth function and cannot give rise to spots.

The fallacy of this argument lies in the assumption that c is a constant. It is not. In fact, the relation between λ and ω is involved. ω is a periodic function of the components of the wave vector q (length $q = 1/\lambda$). Consider as illustration the oscillations of a set of parallel equidistant planes in the lattice (spacing a) which will be roughly the same as that of a chain of equidistant mass points (linear lattice); it is well known that the frequency in this case is $\omega = \omega_0 |\sin(\pi a/\lambda)| = \omega_0 |\sin(\pi q/b)|$, where $b = 1/a$ is the lattice constant of the reciprocal lattice. The dynamical theory of the scattering leads to the same result as de Broglie's quantum condition: the intensity is enhanced if the difference of the momentum vectors for the incident and reflected photon is equal to the momentum of the acoustical quantum, or $2Q\sin\delta = q$, where $Q = 1/\Lambda$ is the wave number of the X-ray. (As the left-hand term may have any

value, q cannot be restricted to the domain $0 \leqslant q \leqslant b/2$, or $2a \leqslant \lambda \leqslant \infty$, for which $\omega(q)$ assumes all possible values.) Taking for the mean square amplitude Raman's approximate expression kT/ω^2, the 'scattering power' is proportional to

$$S(q) = \frac{kT}{\omega_0^2 \sin^2(\pi q/b)},$$

and the intensity for the direction δ is $S(2Q \sin \delta)$. $S(q)$ is a periodic distribution in the 'reciprocal space' q; it has sharp peaks (infinities) at the points of the reciprocal lattice $q = 0, b, 2b, 3b, \ldots$. These correspond to the Bragg reflexions; for $2Q \sin \delta = nb$ is the same as $2a \sin \delta = n\Lambda$.

If all possible sets of reflecting planes are simultaneously considered, the formulæ are more involved, but the principal features unaltered : the scattering power $S(\mathbf{q})$ is a function of the three components of the wave vector $\mathbf{q}$, and the scattered intensity due to the vibrations is $S(\mathbf{Q}' - \mathbf{Q})$, where $\mathbf{Q}$ and $\mathbf{Q}'$ are the wave vectors of the incident and scattered beam (of practically equal length). $S(\mathbf{q})$ consists of additive terms each corresponding to one branch of the vibrational spectrum, and these have peaks (infinities) for the acoustical branches in the points of the reciprocal lattices (which correspond to the Laue spots); but the terms for the optical branches are quite smooth functions, as for these $\omega(\mathbf{q})$ does not approach zero.

Hence the correct theory attributes the observed extra spots to the acoustical vibrations—just contrary to Raman—and this is well confirmed by experiments of Lonsdale and Smith on various metals.

The optical branches may give broad but relatively weak intensity maxima halfway between Laue spots because $\omega(\mathbf{q})$ has minima there (in the linear case for $q = \frac{1}{2} b, \frac{3}{2} b, \frac{5}{2} b, \ldots$).

(5) Raman claims that the extra spots are due to a peculiar *new type of quantum effect*. His theory, as now made known, is however completely classical, whereas the so-called 'thermal' theory based on lattice dynamics (which Raman rejects) is developed strictly on quantum principles. The only point where Raman introduces a quantum consideration is in respect of the temperature dependence of scattering produced by his monochromatic infra-red vibrations. With the help of strange reasoning he obtains a formula which is in fact (apart from a factor of 2) identical with the formula for the energy of an oscillator with zero-point energy, according to Planck. Now this quantity determines the intensity also in the theory based on lattice dynamics.

Venkateswaran tried to confirm Raman's assumption by deriving the characteristic frequency in the Planck formula from the observed temperature effect of the extra spots, and to compare it with other determinations of infra-red vibrations (Raman effect). These observations had to be made on extra spots well separated from the corresponding Laue spots and would therefore in any case refer to oscillations of relatively high frequency. All the experiments showed was that for carborundum the oscillations were of higher frequency than those for a soft organic crystal, a result which the theory of lattice dynamics undoubtedly predicts, because of the differences in the quasi-elastic forces in the two substances.

(6) In order to explain the *specific intensity of extra spots* corresponding to different Laue spots, Raman introduces special assumptions about the directions of his monochromatic waves. Lattice dynamics provides the explanation without any assumption,

by expressing the scattering power $S(\mathbf{q})$ as a function of the quasi-elastic forces between the atoms. These can be approximately expressed in terms of the elastic constants (Zachariasen, Jahn, Sarginson). Jahn has shown that the elastic anisotropy of cubic crystals leads to a characteristic anisotropic distribution of $S(\mathbf{q})$ around each point of the reciprocal lattice ; Lonsdale and Smith have used Jahn's formula very successfully for representing their observations.

The extra spots are not, as Raman assumes, in contradiction to lattice dynamics, but provide a powerful method of checking it in every detail.

University of Edinburgh.   Max Born.

Prof. Born and Miss Sarginson[1] have pointed out that according to the quantum mechanical calculations of Ott (1935) and also from the point of view of Placzek's quasi-classical theory, the excitation by the X-ray energy of characteristic crystal vibrations (analogous to the Raman effect in light scattering) would only be expected to give X-ray interference effects entirely secondary in importance to those of the thermal vibrations. Ott[2] suggested, however, that in regions where a Bragg reflexion would normally be forbidden, the Raman effect might possibly give an observable reflexion, and questioned whether the 222 reflexion from diamond might not be such an instance.

This suggestion has recently been revived by Sir C. V. Raman[3] (who does not, however, either admit the secondary importance of the excited vibrations or refer to Ott's paper) and has been worked out in quantitative detail by P. Rama Pisharoty[4], on the basis of an excited 1,332 cm.$^{-1}$ oscillation *normal to one set of (111) planes only*. This procedure we believe to be incorrect and misleading, since such oscillations, if excited at all, will certainly take place with equal probability normal to all the {111} planes. However, Pisharoty makes the following predictions for a perfect diamond set for reflexion at the Bragg angle appropriate to each plane in turn :

(1) There is no 222 Bragg reflexion, but that there is a 222 extra reflexion (which he alternately calls a modified, quantum or Raman reflexion), the intensity of which is roughly equal to that of the 111 extra reflexion.

(2) There is no 220 extra reflexion, or alternatively, that if there is, it will be *very* much weaker than the 111 extra reflexion. He reports that Dr. Nilakantan has failed to find such a reflexion in spite of many trials.

(3) There is no 200 Bragg reflexion, but that there is a 200 extra reflexion. The intensity of this extra reflexion he estimates to be about one third of the 222 intensity, but in so doing he has neglected to allow for the difference in Bragg angle. Actually, his theory would make them nearly equal.

We have investigated these reflexions with the greatest care, and have fully established the following experimental facts :

(1) The 'forbidden' 222 reflexion is in every respect similar to a Bragg reflexion and has none of the peculiar characteristics of an 'extra' reflexion. It appears sharply at the appropriate Bragg angle (for our D(2) diamond its intensity was about 0·04 of that of the 111 Bragg reflexion), and when the angle of setting is varied it disappears completely even when the exposure given is several times as long as that required to record the 111 extra reflex-