

and merging others. Further, we have neglected factors depending on the frequency, which may easily shift a maximum by 10 per cent of its wave-number, and we have chosen a few intensity factors in such a way that the aspect of the spectrum as a whole is correct, without considering detailed agreement. Thus the 'line' 235 cm. which Krishnan finds particularly sharp could be easily accounted for by giving our branch 9 a different amplitude.

If Krishnan would attack our method of approximation and our wholesale simplifications, I should raise no objection apart from asking him to make it better. But his conclusion that "the second-order Raman effect is a discrete one, and is different in its nature from that deduced from the lattice dynamics of Born", shows that he does not understand the theory, which is a straightforward application of quantum mechanics.

I do not intend to continue this discussion.

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¹ *Proc. Roy. Soc., A*, 188, 161 (1947).

Diffraction of Light by High-Frequency Ultrasonic Waves

RECENTLY diffraction patterns have been produced in this laboratory¹ by using ultrasonic waves of frequencies higher than 100 Mc./sec. At such high frequencies, the patterns show some interesting features. Progressive waves of frequency 102.6 Mc./sec. and maintained in water have been employed. When the sound wave is exactly normal to the incident light, the diffraction pattern disappears altogether. On tilting the crystal holder to one side or the other, so that the light rays meet the sound wave-front at an angle of 52', the first-order diffraction line alone on the appropriate side is obtained. This angle agrees closely with the value derived from the equation $\lambda/\lambda^* = 2\mu \sin \theta$, where λ and λ^* are the wave-lengths employed and μ is the refractive index of water. In no position of the sound wave-front has it been possible to get the first-order line on both sides at the same time. The value of the above angle for which the first-order line attains the maximum intensity is quite critical. Even a slight variation of about 2' has been found to reduce its intensity to half. Thus the diffraction effect at such high frequencies ($\lambda^* = 0.00148$ cm.) appears to be very much like reflexion in the Bragg sense.

Contrary to the above results, we have found that patterns at 50 Mc./sec. show the presence of both the first-order lines for normal incidence. For oblique incidence, the first-order line on the appropriate side increases in intensity as the wave-front is tilted and attains a maximum at the corresponding reflexion angle. The first-order line on the opposite side decreases in intensity but does not vanish altogether, showing that the range of reflexion is not so sharp as in the previous case.

Bär², Parthasarathy³ and others have shown that similar phenomena make their appearance, but in a less pronounced manner, at ordinary frequencies such as about 20 Mc./sec. Our investigations show that when 100 Mc./sec. is reached, the well-known features of diffraction are suppressed and the effect simulates reflexion very closely. It may be mentioned here that Nath⁴ had shown that the first order would be dominant over the higher ones in the very high

frequency region. Our observations are in conformity with this view.

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¹ Bhagavantam and Ramachandra Rao, *Nature*, 158, 484 (1946).

² Bär, *Helv. Phys. Acta*, 9, 265 (1936).

³ Parthasarathy, *Proc. Ind. Acad. Sci.*, 3, 594 (1936).

⁴ Nagendranath, *Proc. Ind. Acad. Sci.*, 8, 499 (1938).

Dimensional Changes Accompanying Capillary Condensation

Banks and Barkas¹ have recently directed attention to the mechanical interaction between capillary condensed liquid and the walls of the pores containing it, and they deduce that under certain conditions the pores may collapse when the vapour pressure over the system is lowered. However, when capillary condensation occurs, the liquid condenses on an adsorbed film—not on a bare surface—and it is to be expected that when the vapour pressure is sufficient to cause condensation of liquid, there will always be present an adsorbed film which is *mobile*. A mobile film exerts a pressure² numerically equal to the free-energy lowering per unit surface due to its adsorption, and in a capillary tube this pressure opposes the tension of the condensed liquid. Effects due to the pressure of a surface film have been neglected by Banks and Barkas in their calculations.

The role of the film pressure in this kind of problem may be seen by considering the dimensional changes accompanying adsorption and capillary condensation in a cylindrical cavity with very thin elastic walls. If the cavity is originally *in vacuo*, on adsorption of a vapour the film pressure ϕ stretches the walls of the cylinder. Changes in radius may be examined by considering the forces acting across a plane containing the axis of the cylinder. At equilibrium there is no net force acting over any imaginary plane cutting an isolated system, so that after adsorption the circumferential tension in the wall of the cylinder is equal and opposite to the film pressure ϕ , or $k \frac{(r_1 - r_0)}{r_0} = \phi$, where r_1 , r_0 are the new and original radii and k is related to the elastic constants of the material. (When the expansion is large k may depend on the expansion; for present purposes it is treated as a constant.) Similarly, the cylinder will increase in length until the total longitudinal tension in the walls balances the longitudinal force ($2\pi r_1 \phi$) of the adsorbed film.

When capillary condensation occurs, the wall of the cavity becomes wetted by liquid and the surface pressure increases to $\phi + \gamma \cos \theta$, where γ is the surface tension of the liquid and θ is the contact angle.

(a) *Changes in Radius.* Supposing the radius to remain constant at r_1 , the forces acting over the plane containing the axis of the cylinder would be (i) the

tension in the walls $k \frac{(r_1 - r_0)}{r_0}$, (ii) the film pressure

($\phi + \gamma \cos \theta$), and (iii) the tension in the condensed liquid. This last quantity is $\frac{2\gamma \cos \theta}{r_1} \times 2r_1 \times 1 =$

$4\gamma \cos \theta$ per unit length, and the total expansive force per unit length acting across the plane would be

$$-2k \frac{(r_1 - r_0)}{r_0} + 2(\phi + \gamma \cos \theta) - 4\gamma \cos \theta,$$