The Effect of Pressure on the Intensity of X-Rays Scattered from Nitrogen at Small Angles

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It is found that at small angles the scattering from a "permanent" gas diminishes due to intermolecular interference. The scattering curves at various pressures closely resemble those of a liquid or solid. It is concluded that this is due to the closeness of the scattering centers rather than to any preferred orientation of molecular groups since it is unlikely that such groups would be present in a gas so far from the liquid state.

IF the molecules of a gas are assumed to scatter independently, so that the scattering from n molecules is n times that from a single molecule, then on the basis of the classical theory Raman[1] and Compton[1] have shown that the distribution of intensity of x-rays scattered by a monatomic gas should be given by

$$S = 1 + (Z-1)f^2/Z^2,\qquad(1)$$

where S is the scattering per electron in terms of the Thomson value and f the atomic structure factor of the atom. If account be taken of the fact that the various electrons in the atom have different probability distributions[2,3] and also that part of the scattered radiation is reduced in intensity due to the Compton effect then, as has been pointed out by Woo,[4] Eq. (1) becomes

$$S = \frac{f^2}{Z} + \frac{1 - \left(\sum_{j=1}^{Z} E_{jj}{}^2\right)\Big/Z}{(1 + \alpha \text{ vers } \phi)^3}\qquad(2)$$

where ϕ is the angle of scattering, $\alpha = h/mc\lambda$ and E_{jj} is the contribution to f due to the jth electron so that $f = \sum E_{jj}$. Eq. (2) is in agreement with that obtained by Wentzel[5] for the total scattering from an atom on the basis of wave mechanics. The more exact result of Waller and Hartree[6] in which account is taken of the Pauli exclusion principle differs from Eq. (2) by the addition of a small negative term in the numerator of the second half of this equation, which, for the range of angles to be considered in this paper, is completely negligible.[7] Eq. (2) may easily be ex-

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[1] C. V. Raman, Ind. J. Phys. **3**, 357 (1928); A. H. Compton, Phys. Rev. **35**, 925 (1930).

[2] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931).

[3] G. Herzog, Zeits. f. Physik **69**, 207 (1931).

[4] Y. H. Woo, Phys. Rev. **41**, 21 (1932).

[5] G. Wentzel, Zeits. f. Physik **43**, 1, 779 (1927).

[6] I. Waller, Phil. Mag. **4**, 1228 (1927); Nature **120**, 155 (1927); Naturwiss. **15**, 969 (1927); Zeits. f. Physik **41**, 213 (1928); I. Waller and D. R. Hartree, Proc. Roy. Soc. **A124**, 119 (1929).

[7] Cf. G. G. Harvey, P. S. Williams and G. E. M. Jauncey, Phys. Rev. **46**, 365 (1934).

tended to the case of a polyatomic gas[8] by using a result due to Debye[9] and gives

$$S = \left\{ \sum_i \sum_j f_i f_j \frac{\sin ks_{ij}}{ks_{ij}} + \sum_i \frac{Z_i - (\sum E_{ij}^2)_i}{(1 + \alpha \text{ vers } \phi)^3} \right\} \Big/ \sum Z_i, \quad (3)$$

where s_{ij} is the distance between the ith and jth atoms in a molecule (assumed constant) and $k = 4\pi (\sin \phi/2)/\lambda$. For the particular case of a diatomic gas consisting of two like atoms Eq. (3) gives

$$S = \left(1 + \frac{\sin ks}{ks}\right)\frac{f^2}{Z} + \frac{1 - (\sum E_{ij}^2)/Z}{(1 + \alpha \text{ vers } \phi)^3}. \quad (4)$$

Eqs. (2) and (4) have been well verified[10] for angles of scattering of 10° and larger and for moderate pressures. It will be seen that for $\phi \rightarrow 0$ Eq. (3) predicts $S \rightarrow \sum Z_i$. As has been said, the above equations are all based on the assumption that the molecules of the gas scatter independently. But at small angles of scattering this can no longer be true. On the basis of a statistical-thermodynamical treatment Einstein and Smoluchowski[11] have shown that the scattering of ordinary light by a fluid can be accounted for by the accidental fluctuations of density in the fluid. This result rests essentially on the fact that for optical wave-lengths the fluid may be treated as continuous and the fluctuations of density within a cube of edge considerably smaller than $\lambda/(\sin \phi/2)$ may be treated as completely independent. This in general will not be true for x-ray wave-lengths. It will, however, be true even for x-rays provided that ϕ is taken small enough. If we take as a rough estimate for the minimum size of cube, for which the optical theory is valid, one, fifty molecules thick, then at a pressure of 100 atmospheres the optical theory for a gas should also hold for x-rays out to angles of about 6′ for

Mo $K\alpha$ radiation and although the theory would not be strictly valid beyond this it should be at least qualitatively true out to about a degree or more. A more complete treatment, applicable to the x-ray case, has been given by Raman and Ramanathan[12] in which account is taken of the fact that a fluid cannot be treated as a continuum for x-ray scattering except at very small angles. This theory predicts a peak in the scattering curve at an angle ϕ_0 given by

$$\lambda = 2\lambda_0 \sin \phi_0/2 \quad (5)$$

where λ_0 is the "mean distance between molecules" in the fluid, and at smaller angles a rapid decrease in intensity approaching the value given by the ordinary optical theory. The intensity distribution given by Raman and Ramanathan is

$$I = \text{const. } \exp\left\{ -\frac{N}{16RT\beta} \cdot \lambda_0^3 \cdot \left(1 - \frac{\lambda_1^3}{\lambda_0^3}\right)^2 \right\}, \quad (6)$$

where R and N are, respectively, the gas constant and Avogadro constant for a gram molecule, β the isothermal compressibility and λ_1 is given by

$$\lambda = 2\lambda_1 \sin \phi/2. \quad (7)$$

As explicitly pointed out by Raman and Ramanathan Eq. (6) of course takes no account of the structure of the individual molecules but only an average structure of the fluid as a whole. Its principal accomplishment is to account for the main diffraction peak observed in liquids and amorphous solids and the very small scattering at angles less than the position of this peak. It should also be applicable to a gas of very high density. On the assumption of the closest packing of spheres[13] $\lambda_0 = 2^{1/6} (M/N\rho)^{1/3} = 1.33 (M/\rho)^{1/3} = 37.5 \, p^{-1/3}$ where M is the molecular weight, ρ the density, p the pressure in atmospheres, and λ_0 is measured in A. Thus at atmospheric pressure the peak should occur at $(\sin \phi/2)/\lambda = 0.0133$ or, for Mo $K\alpha$ radiation, $\phi_0 = 1° \, 10'$ and at a pressure of 100 atmospheres $\phi_0 = 5°$. At high pressures the decrease in intensity due to intermolecular interference should thus be easily observable.

[8] Y. H. Woo, Proc. Nat. Acad. Sci. 17, 467, 470 (1931); Phys. Rev. 39, 555 (1932); also reference 4.

[9] P. Debye, Ann. d. Physik 46, 809 (1915); Phys. Zeits. 41, 419 (1930).

[10] e.g. E. O. Wollan, Phys. Rev. 37, 862 (1931); Proc. Nat. Acad. Sci. 17, 475 (1931); Rev. Mod. Phys. 4, 205 (1932); G. Herzog, Zeits. f. Physik 69, 207 (1931); 70, 583 and 590 (1931); P. Debye, L. Bewilogua and F. Ehrhardt, Phys. Zeits. 30, 84 (1930); L. Bewilogua, Phys. Zeits. 32, 265 (1931); R. W. James, Phys. Zeits. 33, 737 (1932); W. Van der Grinten, Phys. Zeits. 34, 609 (1933).

[11] von Smoluchowski, Ann. d. Physik 25, 205 (1908); A. Einstein, Ann. d. Physik 33, 1275 (1910). Cf. Fowler, Statistical Mechanics, pp. 143 and 515.

[12] C. V. Raman and K. R. Ramanathan, Proc. Ind. Assoc. Cultiv. Sci. 8, 127 (1923).

[13] Jeans, Dynamical Theory of Gases, 4th Edition, p. 330.

Debye[14] has treated the subject of intermolecular interference from a different point of view. His calculation is based on the assumption that the gas consists of rigid spherical molecules of radius a. Thus the closest distance of approach of two molecules is $2a$, the radius of the sphere of influence. Debye assumes that for distances greater than $2a$ the distribution of matter is of uniform density and calculates the scattering from such a distribution. The result for a monatomic gas, written in terms of S, is

$$S_{coh.} = [1 - (\Omega/V)\phi(2ka)]f^2/Z, \qquad (8)$$

where

$$\phi(u) = (3/u^3)(\sin u - u \cos u) \qquad (9)$$

and

$$\Omega/V = (4\pi N/3)(2a)^3, \qquad (10)$$

where N is the number of molecules in the volume V. For a diatomic gas

$$S_{coh.} = \left[1 + \frac{\sin kl}{kl} - 2\frac{\Omega}{V}\left(\frac{\sin kl/2}{kl/2}\right)^2 \phi(2ka)\right]\frac{f^2}{Z}, \qquad (11)$$

where l is the interatomic distance and a is again the effective radius of the *molecule*. These equations are only supposed to be valid for small values of Ω/V.

The method of Zernicke and Prins[15] which takes account of the actual distribution of density in the scattering substance has met with considerable success in explaining the scattering curves obtained with liquids.[16] Warren has extended this to the case of glasses[17] and found that here too the results are very satisfactory. Quite recently Gingrich and Warren[18] have applied the method to a study of the scattering from a fluid at various densities and have again found very good agreement.

The present investigation was undertaken to see just how large the effect of intermolecular interference is in the case of a gas and to study its dependence on pressure.
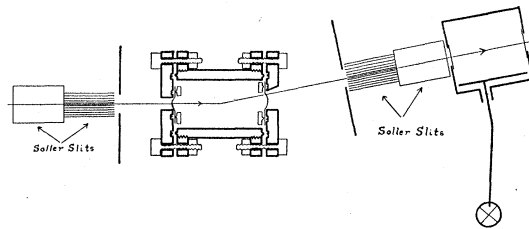
[14] P. Debye, J. Math. and Phys. **4**, 133 (1925); Phys. Zeits. **28**, 135 (1927).
[15] F. Zernicke and J. A. Prins, Zeits. f. Physik **41**, 184 (1927).
[16] B. E. Warren, Phys. Rev. **44**, 969 (1933).
[17] B. E. Warren, Phys. Rev. **45**, 657 (1934).
[18] N. S. Gingrich and B. E. Warren, Phys. Rev. **46**, 248 (1934). The writer is indebted to Dr. Gingrich and Professor Warren for a copy of this paper previous to its publication.

FIG. 1. Scattering cell and slit system.

EXPERIMENTAL

The first essential in such an investigation is a scattering cell which will withstand the pressures involved and yet transmit an appreciable portion of the radiation. A modification of the high pressure ionization chamber described by Williams[19] was used. A cross section of the cell is shown in Fig. 1; for details of construction reference may be made to the paper of Williams. The primary and scattered beams of x-rays were collimated by means of crossed Soller slits, giving a maximum angular divergence in any direction of less than one degree. An ordinary molybdenum target water-cooled tube was used together with a ZrO_2 filter. The ionization currents in a chamber filled with krypton were measured with a Compton electrometer operating at sensitivities of from 15,000 to 20,000 mm/volt. At best the currents were excessively weak, a ten centimeter deflection requiring from 7 to 15 minutes at various pressures. The procedure consisted in measuring the scattering with the cell filled with nitrogen at a given pressure and then again with the cell empty. In the latter case sufficient aluminum was placed in the primary beam so that the absorption of the gas-filled cell was the same as that of the cell plus aluminum. This background reading consists of scattering from the cell windows, scattering from the slits, and natural drift of the electrometer due to alpha-particles and radioactive contamination of the laboratory. The background was always a large portion of the total measured effect, sometimes as much as eighty percent. A run consisted of measurements every half degree throughout the available range of angles, taking one or two readings at each setting and going back and forth over this range until at least five or six values were obtained for each angle. This procedure was followed so as to eliminate any change in deflection with time, al-

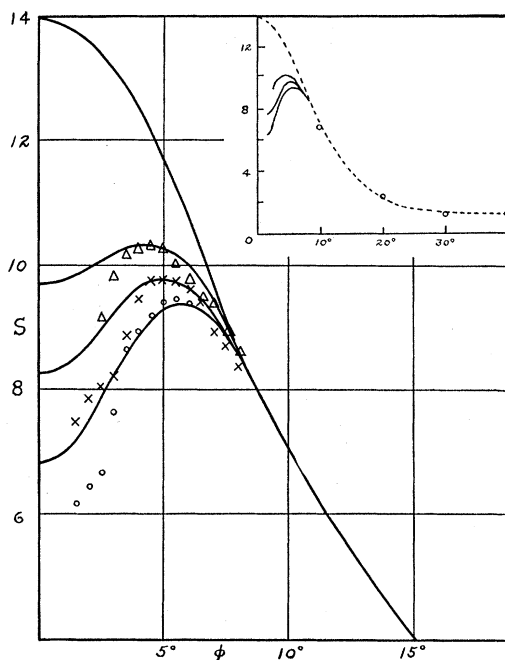[19] J. H. Williams, Rev. Sci. Inst. **3**, 586 (1932).

Fig. 2. Solid curves: Scattering according to Debye's theory for 0, 60, 80, and 100 atmospheres, respectively. Experimental points: triangles, 60 atmospheres; crosses, 80 atmospheres; circles, 100 atmospheres. Inset shows complete curve out to 40°. Dotted curve, scattering from free atom; solid curves, experimental results at 60, 80 and 100 atmospheres. Circles, Wollan's data (see reference 22).

though no readings were considered of any value unless the electrometer remained very steady throughout the entire run of from twenty to thirty hours. The input to the x-ray tube was always very constant. To keep the background intensity as low as possible the thickness of the windows (celluloid) of the scattering cell was so chosen at each pressure used as to be just great enough to withstand that pressure without breaking, an extra 100 pounds usually causing it to burst; the scattering from the cell windows always constituted the largest part of the background except at the smallest angles. Measurements were made at pressures corresponding to 60, 80 and 100 atmospheres at 0°C. The deviations from Boyle's law in this range are about one percent[20] so that the pressures may be taken as proportional to the densities of the gas. Fig. 2 shows the results obtained. Since absolute measurements could not be made the ordinates of the experimental curves were adjusted so as to

give the best fit with the theoretical ones in the vicinity of the peak and this in general gave a good fit at larger angles where the effect of intermolecular interference rapidly diminishes in importance. The theoretical curves are calculated from Eq. (11) for 0, 60, 80 and 100 atmospheres with the addition of the small term $1 - (\sum E_{ij}^2)/Z$ to take account of the incoherent scattering. The value of l was taken to be 1.09A.[21a] The value of $2a$ used, 3.56A, was taken from data on the equation of state for nitrogen.[21b] Although the absolute values of the theoretical curves depend on the value of a used the positions of the peaks are practically independent of this, at least for small variations. It is thus satisfactory to find that the peak positions as measured experimentally are practically identical with the theoretical positions. The inset in Fig. 2 perhaps gives a more comprehensive view of the results. The solid curves represent the experimental values while the dotted curve is the theoretical scattering from a free atom. The points at 10°, 20°, 30° and 40° are taken from the data of Wollan.[22]

It is of course true that the density distribution assumed by Debye is only a rough approximation and it would be more correct to apply the method of Zernicke and Prins, as has been done by Gingrich and Warren.[18] This has not been attempted for two reasons. First, the experimental data are not as reliable as might be desired, not only because of the weak intensity but also due to uncertainty in applying corrections to the measured values. For example, the calculation of the effective scattering volume depends on the assumption that the x-ray beam is of uniform intensity throughout. Although the scattering volume changes by a maximum amount of thirteen percent between 1° 10′ and 8° the effect of lack of uniformity of the beam would not be negligible. The second reason for not applying the method of Zernicke and Prins is because at small angles the effect of statistical fluctuations begins to be appreciable, as mentioned above. This would cause the scattered intensity to drop off more rapidly with decreasing angle, as is in fact

[20] I.C.T. 3, page 17.

[21a] R. S. Mulliken, Rev. Mod. Phys. 4, 82 (1932).
[21b] Cf. Jeans, Dynamical Theory of Gases, p. 139 or Fowler, Statistical Mechanics, p. 234.
[22] E. O. Wollan, Proc. Nat. Acad. Sci. 17, 475 (1931).

observed. As a matter of fact this experiment was first undertaken in the hope of detecting a rapid decrease in scattering at very small angles, due to statistical fluctuations. A system of Soller slits was constructed giving a maximum angular divergence of less than 15' and it was possible to come within 30' of the primary beam and yet not have the direct radiation enter the ionization chamber, but the scattered radiation was collected throughout such a small solid angle that measurement was hopeless and the experiment had to be revised.

CONCLUSION

The present experiment has shown that the effect of intermolecular interference is not negligible even in the case of a gas under moderate pressures. The scattering curves are very similar to those obtained for liquids and solids, the principal difference being that the main diffraction peak occurs at a smaller angle due to the greater mean molecular distance. We would thus conclude with Warren,[17] and with Gingrich and Warren[18] that such a decrease in scattering at small angles is due merely to the fact that there are a large number of scattering centers within a small space, rather than to any preferred grouping of the molecules, since the existence of such groups would be very unlikely in a gas so far from the liquid state.

In conclusion the author wishes to express his appreciation to Professor Arthur H. Compton for his interest in the work and the use of the Ryerson Physical Laboratory as well as for numerous suggestions and discussions during its progress.

An X-Ray Study of a Long X-Cut Quartz Crystal Vibrating Under the Transverse Piezoelectric Effect*

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The sixth order reflection from the (110) set of planes of a long X-cut quartz crystal of the $K\alpha$ radiation of Mo was photographed for the following conditions: (1) with the crystal non-oscillating, (2) with the crystal oscillating at its fundamental frequency under the transverse piezoelectric effect, and (3) with the crystal oscillating at its second harmonic frequency. From the microphotometer analysis of these lines it is shown that no increase in width of the lines reflected from the crystal oscillating at its fundamental frequency over the width of the lines reflected from the non-oscillating crystal is observed. This fact shows that there is no elastic deformation of the spacing of the (110) set of planes greater than 1.45×10^{-5} per unit dimension. This value is the limit of the sensitivity of the spectrograph and microphotometer used. However, an appreciable increase in intensity in the lines reflected from the crystal oscillating at its fundamental frequency over the lines reflected from the non-oscillating crystal is shown. A microphotometer analysis of Laue spots obtained by passing a rectangular beam of x-rays through the middle of the crystal when it was oscillating at its fundamental frequency confirms the prediction made by the authors in an article recently published in this journal. The results seem to indicate that any increase in intensity of the reflected x-rays from any portion of a quartz crystal produced by piezoelectric oscillations of the crystal is due almost entirely to a reduction of secondary extinction.

INTRODUCTION

SINCE Fox and Carr[1] reported a decided increase in the intensity of Laue spots obtained from a quartz crystal oscillating piezoelectrically along the direction of thickness of the plates caused by the longitudinal effect,[2] a number of investigators have conducted experiments with plates oscillating under this "thickness vibration" or more properly longitudinal effect; however, the authors are the only ones who have experimented with a long crystal vibrating under the transverse effect.[3, 4] From the interferometer experiments of Osterberg[5, 6] we now know that the strains in the plates

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[1] Fox and Carr, Phys. Rev. **37**, 1622 (1931).

[2] The terminology here used is taken from *Piezoelectric Terminology* by W. G. Cady, Inst. Radio Eng. **18**, No. 12 (1930).

[3] Colby and Harris, Phys. Rev. **42**, 733 (1932).

[4] Colby and Harris, Phys. Rev. **43**, 562 (1933).

[5] Osterberg, Phys. Rev. **43**, 819 (1933).

[6] Osterberg, Rev. Sci. Inst. **5**, 183 (1934).