

The Diffraction of X-Rays by Liquid Argon

A. EISENSTEIN AND N. S. GINGRICH
University of Missouri, Columbia, Missouri

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The x-ray diffraction pattern of liquid argon has been obtained with crystal-reflected $\text{MoK}\alpha$ radiation. Argon gas under a gauge pressure of 50 lb. per sq. in. was cooled to 90°K in a thin-walled Pyrex glass capillary of 1.7 mm diameter and under these conditions, the argon became liquid. An evacuated camera of 9.53 cm radius was so constructed that the film could be placed outside the vacuum, with entrance and exit windows of aluminum. Exposures of 140 hours were required to give patterns of satisfactory density. Microphotometer records of the films showed three peaks; a very strong peak at $\sin \theta/\lambda = 0.154$, a medium peak at $\sin \theta/\lambda = 0.280$ and a weak peak at $\sin \theta/\lambda = 0.415$. No convincing evidence of another peak could be found beyond this and up to $\sin \theta/\lambda = 1.20$. A Fourier analysis of our diffraction pattern results in an atomic distribution curve [$4\pi r^2\rho(r)$ vs. r] showing approximately 7 atoms at 3.90Å and 5 atoms at about 5.05Å. A third broad peak occurs at over 7Å. This indicates that the distribution of atoms in liquid argon does not follow closely that in crystalline argon, since in the crystal there are 12 nearest neighbors.

INTRODUCTION

THE diffraction of x-rays by liquid argon has been studied by Keesom and de Smedt¹ and their work is of considerable historical interest since it was one of the first investigations of the diffraction of x-rays by liquids. It was probably the first case in which three maxima of intensity were obtained for a liquid. From the positions of these maxima, certain deductions were suggested regarding the structure of liquid argon, but no attempt was made to obtain a complete diffraction pattern. The need for a complete diffraction pattern became evident when the theories of Zernike and Prins² and of Debye and Menke³ were presented. In the present work an attempt has been made to obtain as complete a diffraction pattern of liquid argon as possible, and, from this pattern, to obtain an atomic distribution curve.

EXPERIMENTAL

Since it is essential to use monochromatic x-rays in this work, $\text{MoK}\alpha$ x-rays reflected from a rocksalt crystal were used. A cylindrical brass camera shown in Fig. 1 was constructed so that the distance from the center of the camera to

the film was 9.53 cm. A special liquid-air flask was constructed so that it could be waxed in place as shown in the figure. A thin-walled Pyrex glass capillary 1.7 mm in diameter was sealed to the bottom of the flask and connected to a small glass tube leading out near the top of the flask. Argon gas, 99 percent pure, was passed through concentrated H_2SO_4 and then through P_2O_5 to a line providing for evacuation of the capillary tube and for measuring the argon gas pressure. Argon melts at 83.8°K and boils at

LIQUID ARGON DIFFRACTION CAMERA

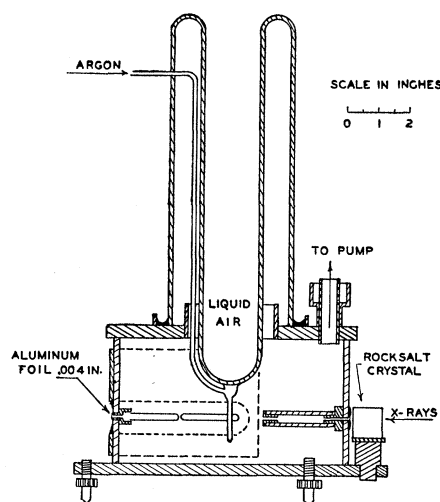


FIG. 1. Diagram of the camera used in obtaining the diffraction pattern of liquid argon.

¹ W. H. Keesom and J. de Smedt, Proc. Amst. Acad. 12, 1 (1923).

² F. Zernike and J. A. Prins, Zeits. f. Physik 41, 184 (1927).

³ P. Debye and H. Menke, Erg. d. tech. Röntgenkunde II (1931).

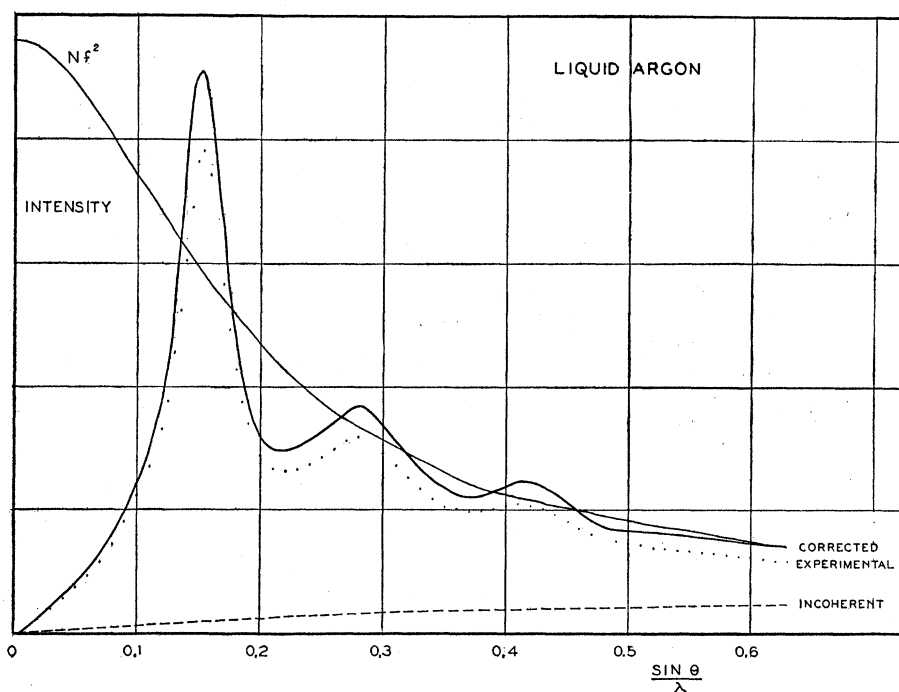


FIG. 2. The experimental and the corrected intensity patterns for liquid argon, taken with monochromatic $\text{MoK}\alpha$ radiation.

87.3°K while oxygen boils at 90°K and nitrogen boils at 77.2°K. Hence liquid nitrogen cannot be used to cool the argon since argon would crystallize at this temperature; nor can liquid oxygen be used since at atmospheric pressure argon would be a gas at this temperature. The procedure adopted consisted of using old liquid air, which was essentially liquid oxygen, and compressing the argon gas to a gauge pressure of 40 to 50 lb./sq. in. The existence of liquid argon in the capillary was verified by measuring the intensity of the x-ray beam leaving the exit window. The inner surface of the liquid-air flask and the outer surface of the capillary were silvered. This thin coating of silver provided a check on the mechanically measured radius since a few weak diffraction lines of silver appeared on the films. The two methods gave values for the radius which checked to within one part in 1000. The camera was evacuated by means of a mercury diffusion pump backed by an oil pump. X-rays were admitted through a small hole covered with 0.004" Al foil and the diffracted x-rays passed through a $\frac{1}{4}$ " milled slot covered with 0.004" Al foil. The film, placed outside the

vacuum, was held in place by a spring brass door. Several exposures were taken with this camera, though only three were good enough to use for the entire pattern. All three patterns checked well with each other over the range of $\sin \theta/\lambda$ reported here. An exposure of 140 hours was required for the best pattern. Because of the construction of this large camera, reliable diffraction patterns could be obtained only as far as about $\sin \theta/\lambda = 0.7$ or 0.75. In order to investigate the large angle scattering more effectively, an essentially similar camera of 5.08 cm radius was constructed. This made possible the investigation of the diffraction pattern as far as $\sin \theta/\lambda = 1.20$.

The films so obtained were microphotometered and the intensity pattern is shown in Fig. 2. The experimental curve is shown with dots. There are three distinct peaks located at $\sin \theta/\lambda = 0.154$, 0.280 and 0.415. No unambiguous and reproducible evidence of a fourth peak could be found. Some indication of a very weak fourth peak appeared on a weak film, but on those films best suited for showing this peak, no definite evidence for its existence could be obtained. Certainly, if

there is one, it must be very much weaker than the third peak. The experimental intensity pattern was corrected and fitted to the f^2 curve in the usual manner,⁴ with the resultant curve as shown in Fig. 2. The fully corrected and fitted curve was then analyzed⁵ to give the atomic distribution curve, which is shown in Fig. 3.

DISCUSSION OF RESULTS

The positions of the intensity peaks obtained in this work can be compared with the early work of Keesom and de Smedt.¹ This comparison can best be made by referring to Table I which lists the peak positions they obtained with Mo filtered and with Cu filtered radiation. Our first peak position happens to fall between their two values, but there is considerable discrepancy in the other two peak positions. Our peak positions were checked on several films and it is believed that of the values listed here, the first peak position is correct to within less than one percent and, because of the uncertainty in locating the highest point on a broad peak, the other two to within possibly two percent.

The atomic distribution curve (Fig. 3) shows a concentration of approximately 7 atoms at 3.90Å as the nearest neighbors. The second concentration of about 5 atoms is at 5.05Å and the third concentration occurs at somewhat over 7.0Å. It is interesting to compare this liquid structure with the crystalline structure of argon. For ready reference, lines whose heights are proportional to the number of neighbors in the crystal are drawn under the atomic distribution curve for the liquid. There are twelve nearest neighbors at 3.84Å, six neighbors at 5.43Å,

TABLE I. Positions of peaks in experimental curves.

		1	2	3
Keesom and deSmedt				
Mo $K\alpha$	$\sin \theta/\lambda$	0.159	0.235	0.371
Cu $K\alpha$	$\sin \theta/\lambda$	0.151	0.269	—
Present work				
Mo $K\alpha$	$\sin \theta/\lambda$	0.154	0.280	0.415

⁴ F. H. Trimble and N. S. Gingrich, Phys. Rev. **53**, 278 (1938).

⁵ B. E. Warren and N. S. Gingrich, Phys. Rev. **46**, 368 (1934).

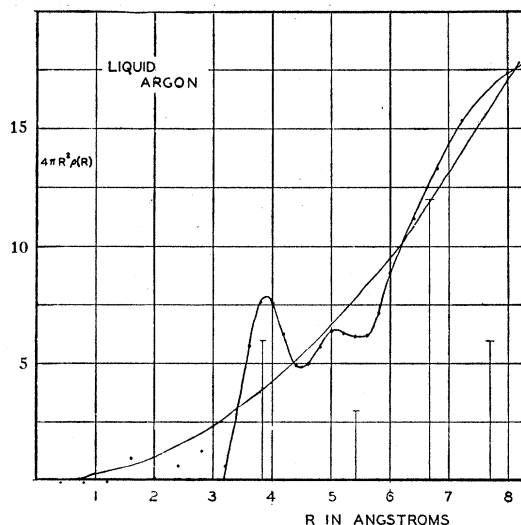


FIG. 3. The atomic distribution in liquid argon. The vertical lines represent the idealized distribution in crystalline argon.

twenty-four at 6.64Å and so on. The difference in the number of nearest neighbors in the liquid and in the crystal appears to be real. From past experience in this sort of work, it seems that the position of, and the area under, the first peak are relatively unaffected by inaccuracies in the analysis, but that the shape of the first peak is apt to be affected by inaccuracies. Hence we believe this conclusion is based on reasonably good evidence. Similar structural changes have been obtained in the work of Gamertsfelder⁶ in the cases of indium and cadmium. Coulson and Rushbrooke⁷ have suggested the possibility of structural change on melting in those substances for which there is a large change in density. Argon experiences a decrease of about 11 percent in density in going from the crystal to the liquid phase so that such a change in structure might be expected in this case.

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⁶ C. Gamertsfelder, Phys. Rev. **57**, 1055A (1940).

⁷ C. A. Coulson and G. S. Rushbrooke, Phys. Rev. **56**, 1216 (1939).