Atomic Distribution in Liquid and Solid Neon and Solid Argon by Neutron Diffraction

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The angular distribution of 1.06_4 A neutrons scattered from liquid neon at 26.0 ± 1.5°K and 1.7 atmospheres and that from solid neon and solid argon at 4.2°K were measured over the angular range 5° to 64°. The transmission cross section of liquid neon was also measured and is 2.7 ± 0.3 barns for 1.06_4 A neutrons.

The scattering pattern and corresponding distribution function $4\pi r^2[\rho(r)-\rho_0]$ for liquid neon are similar in form to those of other measured inert gases. A study of the distribution function gives 2.45 A, 3.17 A and 8.8 for the nearest distance of approach of two atoms, the most probable separation of, and the number of neighbors under, the first shell of atoms, respectively. It is concluded that the effective potential in the liquid has a broader bowl than that of the Lennard-Jones 12:6 and other similar potentials.

The lattice parameters a_0 for the f.c.c. structures of solid neon and solid argon are 4.42_9 A and 5.25_6 A, respectively. The Debye temperature for solid neon corresponding to the intensity of the diffraction maxima is 73°K. The results suggest that the density change during the solid-liquid transformation cannot be accounted for by either a uniform depletion of atoms from, or a uniform dilation of, a basic structure.

INTRODUCTION

KNOWLEDGE of the atomic distribution in liquids and solids is important for the theory of condensed systems. Information about the condensed inert gases is desired as these systems are the most amenable to theoretical explanation. The atomic distributions in liquid helium and liquid argon have been measured both by neutrons[1–3] and by x-rays.[4–6]

In the present work the angular distributions of 1.06_4 A neutrons were measured for liquid neon at 26.0 ±1.5°K and 1.7 atmospheres, and for solid neon and solid argon at 4.2°K. The measured liquid scattering pattern has been transformed to the radial distribution function. The scattering from solid neon and solid argon at 4.2°K has been interpreted in terms of the known f.c.c. structures. The change in the number of nearest neighbors in neon is discussed in relation to the change in density during the solid-liquid transformation, and the distribution function is compared with that expected from an accepted two-particle potential for neon.

APPARATUS

The measurements of the angular distribution of scattered neutrons were made by using one of the Chalk River neutron spectrometers[7] with the arm recording in the parallel rocking position. For these measurements the spectrometer has been modified. In the present arrangement of the spectrometer, a 2-in.×2-in. beam of neutrons from the reactor is monochromated by reflection from an aluminum single crystal cut in the Fankuchen manner so as to reflect a 2-in.×1-in. beam. Collimation is by Soller slits located after the monochromating crystal and before the arm counter. The beam is monitored by a "thin" flat BF_3 counter interposed between the monochromating crystal and the Sollar slits. Using 1.06_4 A neutrons, the scattered intensities were measured at about 210 equally spaced points in the angular range 5° to 64°. At each of these points, the total number of counts was recorded for a preset number of neutrons incident upon the specimen. The specimens of liquid and solid were formed and held in a 1-in. diameter aluminum cassette mounted on the base of the liquid helium chamber of the cryostat.[1] For these measurements the liquid helium chamber had been lengthened so as to hold about six liters of liquid helium. The arrangement of the cassette of the cryostat used to hold the liquid specimens is shown in Fig. 1. The base of the cryostat has been modified so that the cassette may be maintained at any temperature in the range 1.2°K to 400°K. The temperature controller consists of a former on which is wound a heater winding and a copper resistance winding used as a temperature-sensitive element. This former is suspended from the bottom plate of the helium chamber by means of a $\frac{3}{4}$-in. diameter, 0.010-in. thick stainless steel tube. The

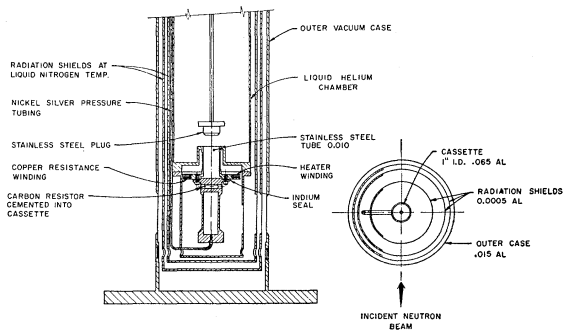

FIG. 1. The arrangement of the scattering chamber for forming and holding the specimen of liquid neon. The thermal contact between the liquid helium and the cassette is broken by inserting the stainless steel plug and applying power to the heater winding, which causes vapor to form in the stainless steel tube. The temperature of the cassette is automatically controlled by maintaining the resistance of the copper resistor or carbon resistor at a preset value with an electronic regulator.

[1] D. G. Hurst and D. G. Henshaw, Phys. Rev. **100**, 994 (1955).
[2] D. G. Henshaw (to be published).
[3] D. G. Henshaw, Phys. Rev. **105**, 976 (1957).
[4] C. F. A. Beaumont and J. Reekie, Proc. Roy. Soc. (London) **A228**, 363 (1955).
[5] Gordon, Shaw, and Daunt, Phys. Rev. **96**, 1444 (1954).
[6] N. S. Gingrich, Revs. Modern Phys. **15**, 19 (1943).
[7] Henshaw, Hurst, and Pope, Phys. Rev. **92**, 1229 (1953).

cassette is bolted to the former and the vacuum seal is made with indium. A carbon resistor cemented into the top of the cassette is also used as a temperature-sensitive element. The cassette may be evacuated or filled with fluid through a $\frac{1}{8}$-in. diameter nickel silver tube brazed into the base of the cassette. The tube passes between the liquid helium chamber and the inner radiation shield and is insulated from the liquid helium chamber by asbestos. The other end of the tube is soldered to a fitting in the top cover plate of the cryostat and is then connected to a valve, neon cylinder, and vacuum system arrangement. With the stainless steel plug removed, the liquid helium is in contact with the top of the cassette. The thermal contact between the liquid helium and the top of the cassette is broken by inserting the stainless steel plug into the stainless steel tube. With the plug inserted and power supplied to the heater winding, vapor forms in the stainless steel tube which reduces the heat transfer between the solid and the liquid. With the present arrangement it is possible to maintain a temperature of 30°K, with a power of 0.2 watt supplied to the heater winding.

The temperature of the cassette is maintained and controlled by a temperature regulator based on the design of Dauphinee.[8] Using this device, the power supplied to the heater winding is automatically adjusted to maintain the resistance of either the copper or carbon resistor used as temperature-sensitive elements at a predetermined setting. It is possible to maintain temperature in the range 30°K to better than ±0.5°K.

The arrangement of the scattering chamber of the cryostat used for obtaining the diffraction patterns of the solid is shown in Fig. 2. The arrangement is similar to that of Fig. 1 except that the temperature controller is replaced by a base plate. The cassette was sealed to the bottom plate with indium and a $\frac{5}{8}$-in. diameter extension protrudes into the liquid helium for a distance of 10 in. in order to insure good thermal contact between the cassette and the liquid helium. In this arrangement the nickel silver pressure tube is also insulated from the liquid helium chamber. The temperature of the cassette is measured and recorded by measuring the resistance of the carbon resistor used as a temperature-sensitive element.

LIQUID NEON

The transmission of the 1.06$_4$-A neutrons through a flat 0.995-in. liquid neon specimen was measured with the neon at 27±1°K and at a pressure of 35 psi gauge. The transmission is 0.78. Using a value[9] of 1.20 grams/cc for the density of liquid neon, the calculated transmission cross section for the specimen of liquid neon is 2.7±0.3 barns for 1.06$_4$ A neutrons. This value is close to the published value of the scattering cross section, 2.4 barns,[10] and indicates that the absorption cross section for 1.06$_4$ A neutrons is <0.6 barn.

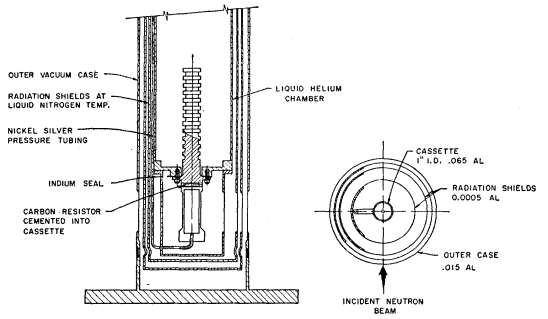

FIG. 2. The arrangement of the scattering chamber of the cryostat for forming and holding the specimens of solid neon and argon. The extension of the cassette insures good thermal contact between the cassette and the liquid helium. The carbon resistor is used as a temperature-sensitive element.

The background was measured with the cassette evacuated and at liquid helium temperature. Except at angles below 10° the background was essentially constant between the lines associated with the f.c.c. structure of the aluminum of the cassette. Below 10°, the background rose continuously and became very large for angles less than 3°. In applying a correction for background to the measured curves, allowance was made for attenuation of the background through the specimens using the measured transmission cross section for liquid neon.

The angular distribution of 1.06$_4$-A neutrons scattered by liquid neon at 26±1.5°K and 1.7 atmospheres is shown in Fig. 3. The scattered intensities are corrected for background, counter resolution in the region of the main diffraction peak and for multiple scattering of the neutrons solely in the liquid neon. No correction has been applied for those neutrons multiply scattered in both the neon and the walls of the cassette as this was estimated and found to be small. The statistical error of the measurements may be estimated from the scatter of the points. The curve consists in low scattering at small angles, a peak at 23.5°, and an oscillation about a nearly uniform scattering at large angles. The large scatter of the points in the region of 31° and 45° is owing to the background lines of the aluminum cassette. The curve has been dotted in this region. The fact that the scattering at small angles is low may be taken (see below) as evidence that the isothermal compressibility of the liquid is small and that the incoherent scattering which could arise from isotope incoherence is also small.

The measured angular distribution of the scattered neutrons has been transformed to the radial distribution function $4\pi r^2[\rho(r)-\rho_0]$ by using the formula commonly

[8] T. M. Dauphinee, Can. J. Phys. **31**, 577 (1953).

[9] No allowance has been made for the change in density with pressure or temperature. These changes have been estimated and found to be small and therefore have been neglected. The effects of these corrections would increase the liquid density and thus give a lower value for the total cross section.

[10] S. P. Harris, Phys. Rev. **80**, 20 (1950).

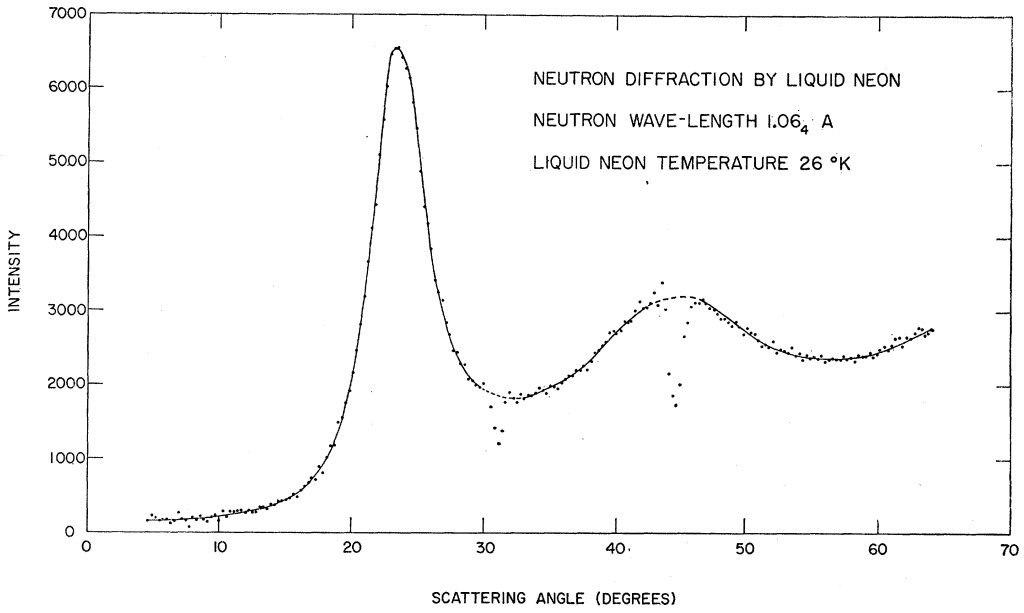

FIG. 3. The angular distribution of 1.06$_4$ A neutrons scattered by liquid neon at 26±1.5°K and 1.7 atmospheres corrected for background, counter resolution, and multiple scattering. The curve has been dotted in the region of 31° and 45° where the scatter of the points is large because of the intense background lines of the aluminum cassette.

applied to neutron scattering, which may be written[2] as

$$4\pi r^2[\rho(r)-\rho_0]=\frac{2r}{\pi}\int_0^\infty si(s)\sin(rs)ds,$$

where r=distance from an atom chosen as center, $\rho(r)$=atomic density at a distance r, ρ_0=mean atomic density of the liquid, $s=(4\pi/\lambda)\sin(\varphi/2)$, λ=neutron wavelength, φ=angle of scattering, and $i(s)=(I_s-I_\infty)/[I_\infty(1-\Delta)]$. I_s=intensity of total scattering for the value s of the variable, I_∞=value of I_s for $s=\infty$, and Δ=ratio of the incoherent scattering to total scattering. The incoherent scattering has been assumed to be isotropic.

The radial distribution function $4\pi r^2[\rho(r)-\rho_0]$ was calculated[11] in steps of 0.1 A for spacing in the range $0\leq r\leq 20.0$ A. The transform was calculated for $\Delta=0$ and normalized so that $\rho(r)\to 0$ for $r\to 0$ by choosing I_∞ such that $-2\pi^2\rho_0=\int_0^{s_{\max}} s^2 i(s)ds$, where $s_{\max}$ corresponds to the last measured value of s. The result of the calculation is shown in Fig. 4. For small spacings, the function $4\pi r^2[\rho(r)-\rho_0]$ oscillates about $-4\pi r^2\rho_0$, rising rapidly at 2.45 to a maximum at 3.17 A. Beyond 2.45 A, the curve oscillates about zero with an amplitude which decreases with increasing radius. The amplitude falls from a value of 6.0 atoms/A at 3.17 A to 1.15 atoms/A at 13.8 A, thus showing that the degree of order in the liquid decreases rapidly with increasing separation. The small oscillations for $r<2.45$ A are certainly spurious[12] and arise from the finite range of s over which the measurements could be made and from experimental error. These oscillations presumably extend to larger spacing and probably cause the irregularities in the curve in the region of 4 A, 8 A, and 18 A.

In liquids of monatomic gases, $4\pi r\rho(r)$ should equal zero for spacings out to the nearest distance of approach of two atoms in the liquid. For the curve shown in Fig. 5, the average value of $4\pi r\rho(r)$ lies slightly below zero for spacing out to 2.45 A. Analysis of the neutron diffraction data for liquid argon[2] showed that the average value of $4\pi r\rho(r)$ could be made equal to zero for spacings out to 3 A by choosing Δ to correspond to the level of the incoherent scattering. Transforms have therefore been calculated for several values of Δ corresponding to different levels of the assumed incoherent scattering. The average value of $4\pi r\rho(r)$ became zero for small negative values of Δ. In view of the uncertainty in the knowledge of the liquid density, and in view of the large oscillations in the diffraction curve at the last measured value of s, it is not known whether the use of a negative value of Δ is realistic, and the transform using $\Delta=0$ has been taken as best representing the density distribution in the liquid. The value $\Delta=0$ implies that the incoherent scattering is small, in agreement with the conclusion drawn from the inspection of the liquid diffraction pattern.

In Fig. 5 the density rises from zero at 2.45 A, which represents the nearest distance of approach of two atoms in the liquid, while the first maximum occurs at 3.17 A. The arrow at 3.13 A represents the spacing between nearest neighbors in the solid at 4.2°K. The number of neighbors has been deduced from the atomic distribution function assuming a peak symmetrical in $4\pi r\rho(r)$, about the maximum in $4\pi r\rho(r)$. The number is 8.8 and is

[11] The Fourier transforms were calculated by Dr. N. K. Pope using the Datatron of the Computation Center, Division of Physics at the Chalk River Laboratories.

[12] Similar oscillations in the distribution function for liquid argon[3] have been eliminated using an analytic extrapolation for the $i(s)$ function obtained from the Born-Green theory of liquids. N. K. Pope, Report of the Second Informal Symposium on Melting, Diffusion and Related Topics, Ottawa, October 21–27, 1957 (unpublished).

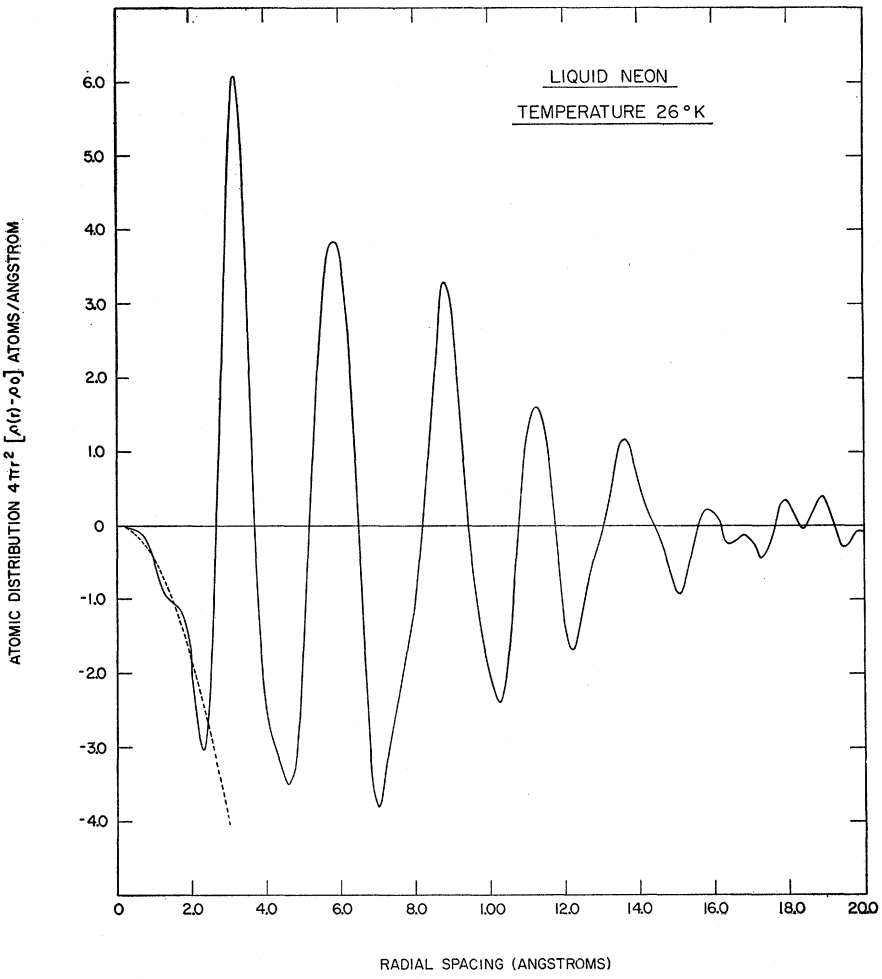

FIG. 4. The radial distribution function $4\pi r^2[\rho(r)-\rho_0]$ calculated from the measured diffraction pattern of Fig. 3. Beyond 2.45 A, the curve shows a series of smooth oscillations which decrease monotonically with increasing radial spacing. The dotted curve represents $-4\pi r^2\rho_0$, the negative of the mean atomic density.

similar to that found for argon[3] and helium[2] for temperatures and pressures near their freezing points.

SOLID NEON

The angular distribution of 1.06$_4$-A neutrons scattered by solid neon at 4.2°K and at atmospheric pressure is shown in Fig. 6. The solid neon was formed in the cassette by cooling it to liquid helium temperatures, admitting neon gas at a pressure of 250 psi gauge, and allowing it to freeze in the cassette. The freezing process was followed by recording the temperature of the cassette as a function of time. The cassette was valved off when the temperature of the cassette fell to 4.2°K. The scattered intensities are corrected for background and for multiple scattering. No correction has been applied for neutrons scattered in both the neon and the walls of the cassette as this correction was estimated and found to be small. The diffraction pattern consists in lines superimposed upon a diffuse background which increases with increasing angle. The fact that the small-angle scattering is low is again taken as evidence in support of the hypothesis that the incoherent scattering which could arise from isotope incoherence is small.

To deduce the lattice parameters corresponding to the face-centered cubic structure, it is necessary to determine whether the solid formed in the cassette was a powder since large-crystal formation could cause the position of the diffracted lines to be in error by the resolution of the instrument. In order to show that the solid formed was a powder, the crystal-structure scattering intensities are plotted semilogarithmically *versus* $\sin^2\theta$ in Fig. 7. The Debye-Waller temperature factor for a given substance causes the crystal-structure scattering intensities to vary exponentially with $\sin^2\theta$ and thus for a powder specimen, the plot of the crystal-structure scattering intensities should be linear in the semilogarithmic plot of Fig. 7. Within the accuracy of the measurements a straight line best represents the variation, thus showing that the solid formed can be considered a powder. The slope of the line corresponds to a Debye temperature of 73°K. In determining the intensities under the diffraction peaks, no allowance was made for the structure in the thermal diffuse

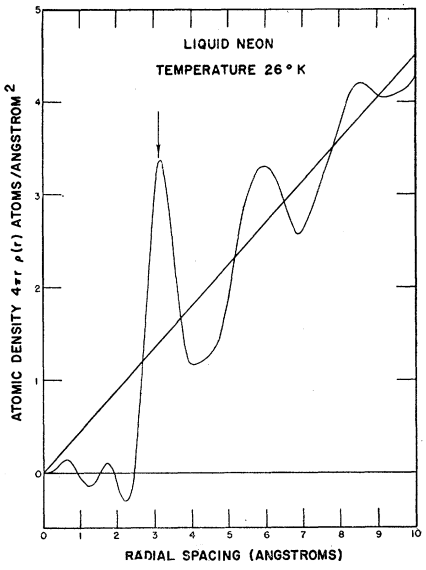

FIG. 5. The atomic distribution function $4\pi r\rho(r)$ corresponding to the curve of Fig. 4. The arrow at 3.13 A represents the measured spacing between two atoms in the solid at 4.2°K. The nearest distance of approach of two atoms in the liquid is 2.45 A, while the number of neighbors around each atom in the liquid is 8.8.

scattering[13] which results in sharp peaks in the immediate vicinity of each *hkl* reflection. Because of this effect, some errors could be expected in the determination of the Debye temperature.

Seven diffraction lines were observed in the pattern for solid neon. The positions of the observed lines together with the calculated *d* spacing are listed in Table I. On the basis of a face-centered cubic structure the lattice parameter a_0 has been deduced for each of the line positions on the basis of the assigned values of *hkl*. The average value of a_0 is 4.42_9 A, while the maximum deviation of a measured *d* spacing from the mean is 0.019 A. The calculated density of the solid at 4.2°K, using the above lattice parameter, is 1.54 gram/cc, while the separation between nearest neighbors is 3.13_2 A.

TABLE I. Measured *d* spacings and calculated lattice parameter for solid neon.

Position number	Measured spacing (A)	*hkl*	Calculated lattice parameter a_0 assuming f.c.c. structure (A)
1	2.55_5	111	4.42_6
2	2.21_9	200	4.43_7
3	1.56_4	220	4.42_3
4	1.33_8	311	4.43_9
5	1.27_9	222	4.42_9
6	1.10_7	400	4.43_8
7	1.01_2	331	4.41_0
		Average $a_0=4.42_9$ A	

SOLID ARGON

The angular distribution of 1.06_4-A neutrons scattered by solid argon at 4.2°K and at atmospheric pressure has also been measured. The solid argon was formed in the cassette by first forming liquid argon in the cassette and then cooling the assembly rapidly to 4.2°K by filling the helium chamber of the cryostat with liquid helium. The

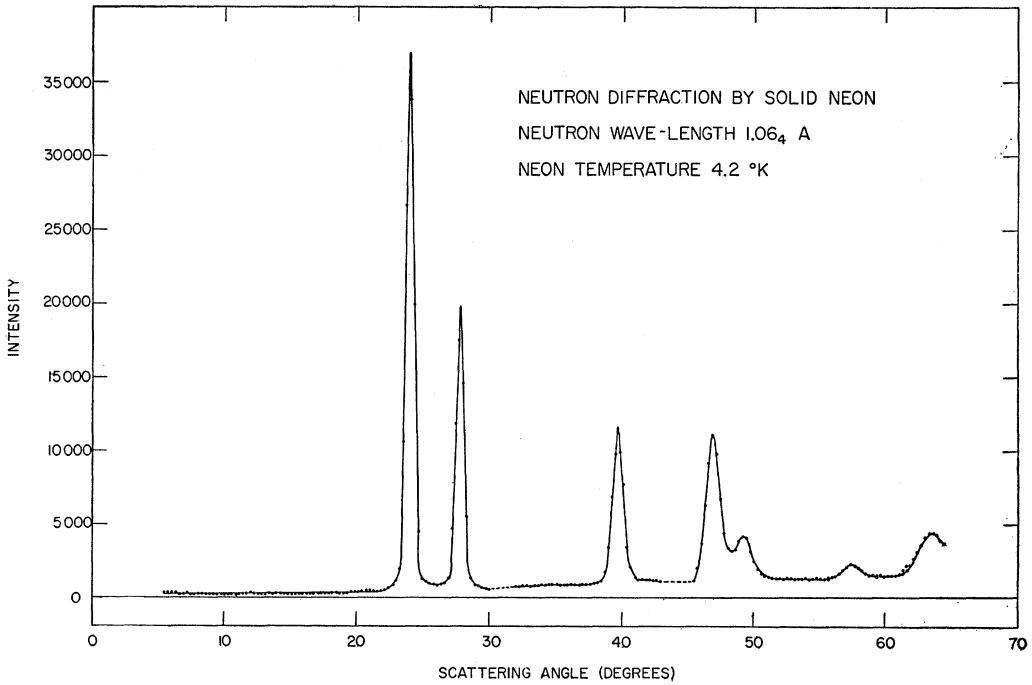

FIG. 6. The angular distribution of 1.06_4 A neutrons scattered from solid neon at 4.2°K corrected for background and multiple scattering. The curve has been dotted in the region of 32° and 45° where the accuracy of the measurements is low owing to the large background lines from the aluminum cassette. The position of the lines has been fitted to the known f.c.c. structure in which $a_0=4.42_9$ A.

[13] B. E. Warren, Acta Cryst. **6**, 803 (1953).

resultant pattern consists in lines superimposed upon a large incoherent background.

Eight diffraction lines were observed in the pattern for solid argon. The measured spacings corresponding to the positions of the diffracted lines are listed in Table II. The lattice parameter a_0 has been deduced for each of the measured line positions on the basis of the assigned values of *hkl* corresponding to the face-centered cubic structure. The average value of a_0 is 5.25_6 A, while the maximum deviation of a measured line position from the mean is 0.01 A. The density of the solid at 4.2°K calculated from the measured lattice parameter is 1.83 grams/cc, while the separation between nearest neighbors is 3.71_7 A.

The value of the lattice parameter reported here is smaller than the value of 5.31±0.01 A extrapolated from higher temperature x-ray measurements.[14] Thus

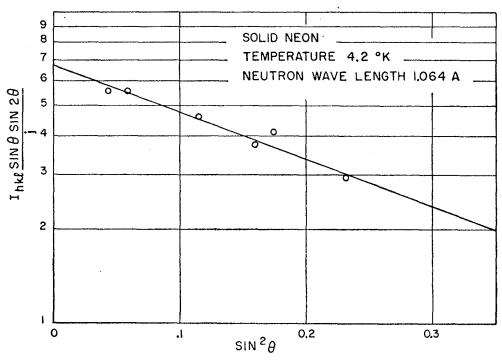

FIG. 7. The crystal-structure scattering intensities plotted as a function of $\sin^2\theta$ for the diffracted lines of Fig. 6. The points fall on a straight line showing that the solid formed was a powder. The slope of the line corresponds to a Debye temperature of 73°K.

the neutron measurements give a higher value for the calculated density at 4.2°K, which implies a larger value for the expansivity of solid argon at low temperature than deduced from the x-ray measurements.

DISCUSSION

The most probable separation of, and number of neighbors under, the first shell of atoms is 3.13 A and 12, and 3.17 A and 8.8 for the solid and liquid neon, respectively. On the basis of a uniform dilation of a basic structure, the change in density calculated from the change in separation is 4% while on the basis of a uniform depletion of atoms from a basic structure, the change in density calculated from the change in the number of nearest neighbors is 27%. The actual change in density is estimated to be ~10%. Thus these results imply that the change in density during the solid-liquid transformation cannot be accounted for either by a uniform depletion of atoms from, or by a uniform dilation of, a basic structure. This is in agreement with the interpretation of the measurements of liquid argon[3] and liquid helium.[2]

A knowledge of the effective interatomic potential together with the atomic distribution function allows all the thermodynamic properties of a liquid to be calculated. The positions where the density rises from zero (density cutoff) and the maximum in the atomic distribution function have been previously compared[3] with that expected from known two-particle potentials for argon. On the basis of the Lennard-Jones 12:6 potential, the expected ratio should be 0.89. The actual measured ratio for liquid argon[2] was 0.79. It was concluded from this that the bowl of the effective potential in the liquid argon is wider than that of the Lennard-Jones 12:6 potential and other similar potentials. The ratio of these spacings in liquid neon is 0.77, which is within experimental error the same as measured for liquid argon. On the basis of the similarity of neon and argon, these results then indicate that the form of the effective potential in liquid neon has a broader bowl than that given by the Lennard-Jones 12:6 and other similar potentials.

TABLE II. Measured *d* spacings and calculated lattice parameter for solid argon.

Position number	Measured spacing (A)	*hkl*	Calculated lattice parameter a_0 assuming f.c.c. structure (A)
1	3.03_3	111	5.25_3
2	2.62_3	200	5.24_6
3	1.86_1	220	5.26_1
4	1.58_7	311	5.26_1
5	1.52_1	222	5.26_7
6	1.31_4	400	5.25_6
7	1.20_4	331	2.25_0
8	1.07_3	422	5.25_2
		Average $a_0=5.25_6$ A	

ACKNOWLEDGMENTS

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[14] E. R. Dobbs *et al.*, Nature **178**, 483 (1956).