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Neutron Diffraction Study of Krypton in the Liquid State*

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The angular distribution of 1.05 Å neutrons scattered by krypton in the liquid state at temperatures of 117°K, 133°K, 153°K, 183°K, and 210°K is reported. By use of a sample cell fabricated from a single aluminum crystal, it was possible to obtain diffraction patterns up to the critical temperature and pressure. The scattering curves were Fourier transformed to obtain the radial atomic distribution function at each temperature. The number of nearest neighbors calculated from these distribution functions ranges from 8.5 at 117°K to 4.0 at 210°K at distances ranging from 4.02 Å to 4.20 Å, respectively. A comparison of radial distribution functions from arbitrarily terminated data shows that the ratio of the last zero-atomic-density position to the first atomic-density-maximum position is a function of the amount of intensity data transformed. It also indicates that the width of the bowl of the effective potential in liquid krypton is in approximate quantitative agreement with that of the Lennard-Jones 12:6 potential.

INTRODUCTION

THE structures of some inert elements in the liquid state have been determined from x-ray and neutron diffraction studies, but the structure of krypton has remained undetermined largely because of its prohibitive absorption of x rays. This material does not strongly absorb neutrons of suitable wavelengths, and hence a study of it by neutron diffraction is a promising means by which to determine its structure. In this way the structure of liquid krypton has been obtained for the first time in the work reported here. The study of argon¹ under 26 conditions of temperature and pressure and that of xenon² under three conditions remain the only extensive x-ray studies yet reported for any of these elements. Helium³ has been studied by neutron diffraction at several temperatures in the liquid state, and neon⁴ and argon^{5,6} have each been investigated at one temperature and pressure by neutron diffraction.

An attempt was made in the present work to use neutron diffraction to determine the structure of liquid krypton at a variety of temperatures and pressures from the lowest obtainable temperature to the critical point using identical techniques and procedures for each temperature so as to facilitate intercomparison.

The structures of a number of other elements in the liquid state have been determined from neutron diffraction studies.⁷ In most, absorption of the neutrons was so small that the absorption correction was considered to be negligible or at least essentially independent of scattering angle for samples approximately one centimeter thick. The relative ease with which neutron diffraction patterns can be corrected, compared with x-ray diffraction patterns, is one of the attractive features of the neutron diffraction technique which in part compensates for the difficulties caused by the lower flux generally available for neutron work. This ease of correction arises from the essentially isotropic nature of neutron scattering from the atomic nucleus. At large angles where interference effects in the coherent scattering from different atoms cannot be detected, the intensity approaches a constant value rather than approaching a rapidly decreasing and sometimes inaccurately known atomic structure factor curve as in

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¹ A. Eisenstein and N. S. Gingrich, *Phys. Rev.* **62**, 261 (1942).

² J. A. Campbell and J. H. Hildebrand, *J. Chem. Phys.* **11**, 334 (1943).

³ D. G. Hurst and D. G. Henshaw, *Phys. Rev.* **100**, 994 (1955).

⁴ D. G. Henshaw, *Phys. Rev.* **111**, 1470 (1958).

⁵ D. G. Henshaw, D. G. Hurst, and N. K. Pope, *Phys. Rev.* **92**, 1229 (1953).

⁶ D. G. Henshaw, *Phys. Rev.* **105**, 976 (1957).

⁷ O. Chamberlain, *Phys. Rev.* **77**, 305 (1950); P. C. Sharrah and G. P. Smith, *J. Chem. Phys.* **21**, 228 (1953); G. H. Vineyard, *J. Chem. Phys.* **22**, 1665 (1954); N. S. Gingrich and LeRoy Heaton, 15th Pittsburgh Diffraction Conference (unpublished).

the case of x rays. This provides relatively higher intensities at large angles of scattering and eliminates dependence upon a knowledge of the exact form of the structure factor of the atom. Corrections for effects such as incoherent scattering, inelastic scattering, and multiple scattering are assumed to be, or have sometimes been calculated to be isotropic.³ With neutrons, in the cases of liquid helium, liquid lithium, and liquid sodium, corrections were made to account for intensity effects due to recoil of the scattering nuclei. In all cases it was assumed that the atomic distribution function could be obtained by Fourier integral transformation of the corrected intensity patterns. Results from this kind of procedure have been reported for helium, nitrogen, oxygen, sulfur, neon, argon, mercury, lead, bismuth, and the alkali metals.

Experimental Procedures

Neutrons of wavelength $\lambda = 1.05$ Å were selected from a beam of neutrons from the CP-5 reactor operated at 2×10^6 watts by reflection from the (111) planes of a copper single crystal. The krypton sample under study filled a cylindrical volume of 0.660-inch diameter and 1.5-inch height in a cell fabricated from a single crystal of aluminum. The walls of the cell were 0.220 inch thick in the region upon which the monochromatic neutrons were incident. The hermetically sealed sample cell was filled with high-purity krypton by passing it as a gas through a small-diameter pressure tube to the cell where it liquefied. When the cell had been filled, as indicated by the cessation of condensation and by the increase in diffracted neutrons registered by the detector counter, the pressure was rapidly decreased by use of a vacuum pump and the krypton was allowed to boil to reach equilibrium between the liquid and vapor states. A vacuum-tight valve was then closed and no krypton was added to or removed from the system until the entire series of runs had been completed. The filled cell, contained in an evacuated cryostat cooled with liquid nitrogen, was mounted over the center of the diffractometer table, and incident and scattered neutron beams passed into and from the cryostat through thin aluminum windows. A 10-watt heater wound on an aluminum cylinder was provided between the sample cell and the liquid nitrogen reservoir, and a copper-constantan thermocouple imbedded in the cylinder served as the sensing element of an electronic temperature control unit. By passing a current through the heater, the temperature of the sample was controlled to within 0.05 K° for periods up to 175 hours. In order to reach some of the higher temperatures without large loss of coolant, alcohol was frozen in the bottom of the liquid nitrogen reservoir to provide a longer and poorer heat conductor across which a high thermal gradient could exist.

The incident beam of monochromatic neutrons was monitored with a fission counter, and the number of

scattered neutrons for a preset number of monitor counts was counted with a BF_3 detector. Automatic operation gave a chart record of the number of scattered neutrons per preset number of monitor neutrons as a function of scattering angle up to about 100 degrees with approximately nine readings per degree. With this experimental arrangement, neutron diffraction patterns were obtained for 17 different values of temperature and pressure along the vapor-pressure curve and five of these points were selected for very careful study. The results for these five points are presented here.

Although the triple point of krypton is 104°K , it was not possible to maintain the sample in the liquid state at temperatures below 117°K . This is likely due to the temperature difference across the three inches of krypton being about 1.8 K° while the difference between boiling and freezing at a mean temperature of 117°K is about 3 K°. Any attempt to lower the temperature below 117°K resulted in formation of crystals in the sample as indicated by the diffraction pattern.

Correction for scattering from material other than the sample was made by taking runs with the empty cell under identical conditions and subtracting this empty-cell intensity from the loaded-cell intensity at each scattering angle. This background correction was almost entirely lacking in prominences, since it was primarily due to the single-crystal sample cell. The small value of the mass absorption coefficient makes this simple correction allowable and eliminates any appreciable angular variation of absorption correction.

Experimental Results

Figure 1 shows the observed intensity curves of liquid krypton at temperatures of 117°K , 133°K , 153°K , 183°K , and 210°K . These patterns have been corrected for background, empty cell, and incoherent scattering. After correction the counting rate at the main peak of krypton at 117°K was about 5800 counts per minute giving nearly 6000 counts per intensity point. All data were obtained with the CP-5 reactor operating at 2×10^6 watts. In each pattern the data began at approximately $(\sin\theta)/\lambda = 0.056$ Å⁻¹, and from this point to the origin the intensity curve is drawn as an estimate of the unobserved intensity.

As can be seen in Fig. 1, a gradual change in the diffraction pattern takes place as the temperature is increased. The most striking change is the decrease in intensity of all of the diffraction prominences. The first prominence decreases from a maximum value of 5800 counts per minute at 117°K to about 3000 counts per minute at 210°K . Four diffraction maxima can easily be observed at 117°K , but as the temperature is increased the last maximum decreases until it can no longer be observed at a temperature of 183°K .

A change which is much less pronounced than the intensity change is the change in position of the first

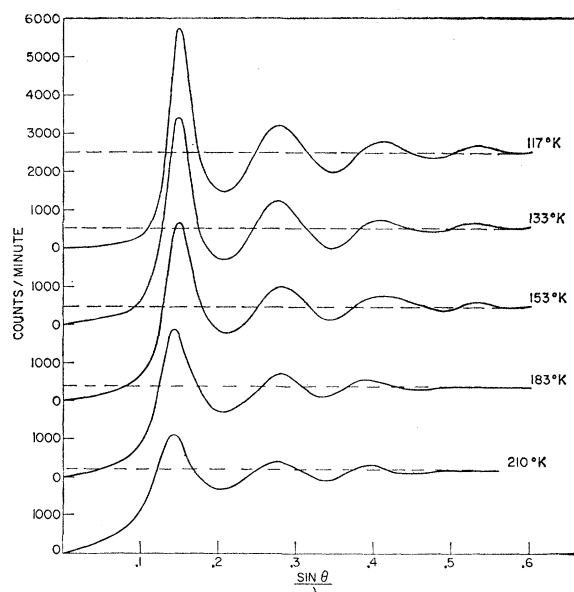


Fig. 1. Neutron diffraction patterns of liquid krypton ($\lambda = 1.05 \text{ \AA}$).

diffraction maximum. This is a gradual change but can be observed easily because of the wide range of temperature over which the study was performed. It moves from a position of $(\sin\theta)/\lambda = 0.148 \text{ \AA}^{-1}$ at 117°K to $(\sin\theta)/\lambda = 0.141 \text{ \AA}^{-1}$ at 210°K which corresponds to a net change of 0.007 \AA^{-1} .

Analysis of Diffraction Patterns

The experimental patterns were analyzed to determine the atomic distributions as in previous analyses,⁷ using the method worked out by Zernike and Prins⁸ and Debye and Menke.⁹ The form of the equation used is:

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^{S_m} s i(s) \sin(rs) ds, \quad (1)$$

where r is distance from any atom-center in the liquid, $\rho(r)$ is the actual density of atoms at distance r from the origin atom, ρ_0 is the average density of atoms, $s = 4\pi(\sin\theta)/\lambda$, and $i(s)$ is a function of the corrected experimental intensity. For neutron patterns,

$$i(s) = [I(s) - k]/(k - c),$$

where $I(s)$ is the observed intensity corrected for effects for which corrections are known, k is the constant intensity at large angles where interference effects can no longer be observed, and c is a factor which is introduced for the purpose of allowing for effects which are independent of angle but which cannot be easily calculated. Assuming that $I(s)$, k , and c have been found, it is then a matter of straightforward calculation

to determine $4\pi r^2 \rho(r)$, the radial atomic distribution function, and this was done with the Argonne National Laboratory computer GEORGE.

In all of these determinations it is recognized that the correctness of the results is limited by the precision of the experimental data and the validity of the corrections and the analyses. One source of uncertainty arises from the fact that in Eq. (1), the upper limit of the integral should be infinity, but for obvious practical reasons, it must be some finite value, which is designated S_m . In practice, scattering was observed to as large an angle as possible and successive runs were made in an attempt to establish the upper limit of s beyond which no reproducible fluctuations of intensity could be observed. Beyond this point $I(s) = k$ and $i(s) = 0$. To determine the constant c , the experimental intensity was measured to the smallest angle of scattering that could be obtained without interference from the incident beam, and the curve was extended arbitrarily to zero angle. The intensity at zero angle was taken to be the constant c which represents angularly independent intensity such as that from incoherent scattering. Since this constant was not assigned with assurance of its correctness, in a number of cases several values were tried in an attempt to learn how sensitive the radial distributions were to the choice of c . In all cases tried, changing c did affect the shapes of the distribution curves, but, for changes in c that appeared reasonably possible, alterations in the resulting curves were not severe.

The assignment of k is more straightforward. However, it is often difficult to determine from the last weak observable oscillations of intensity exactly where the intensity is to be considered to have reached a constant value. A guide to the choice of this curve-fitting is available in the criterion that

$$\int_0^{S_m} s^2 i(s) ds = -2\pi^2 \rho_0,$$

and in all cases this condition was used to help in finding satisfactory fittings.

Atomic Distributions

Figure 2 shows the atomic distributions for liquid krypton at all temperatures for which the analysis was carried out, and Table I lists data for each temperature which were taken from the curves of Figs. 1 and 2. These five atomic distribution curves are similar in their general features, all showing that the nearest neighbors are not discrete or permanent. The number of nearest neighbors, measured similarly and rounded off to the nearest one-half atom, varies between 8.5 and 4.0. The differences are primarily due to the change in density as the temperature changes. The position of the first peak in general shows a slight shift to higher r values for the higher temperatures. It is also seen in

⁸ F. Zernike and J. Prins, *Z. Physik* **41**, 184 (1927).

⁹ P. Debye and H. Menke, *Ergeb. d. Tech. Röntgenk.*, Vol. II (1931).

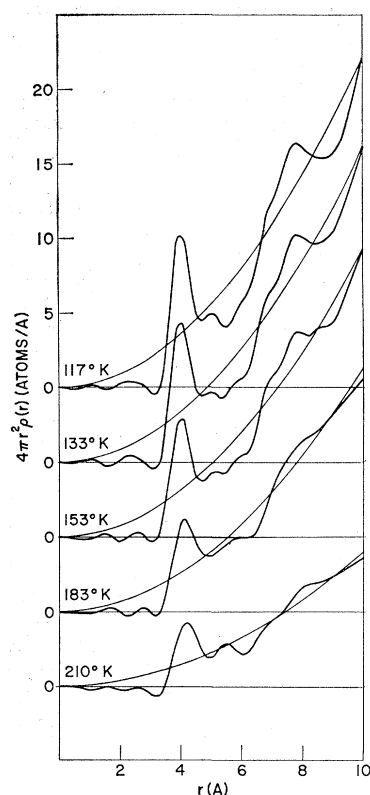


FIG. 2. Atomic distributions of liquid krypton.

Table I that the nearest neighbor distance changes from 4.02 Å to 4.20 Å as the temperature is increased from 117°K to 210°K. This shift is compatible with but less than the shift found in the study of argon by Eisenstein and Gingrich.¹ It is of interest to note that the value of 4.02 Å found here at the lowest temperature is in agreement with the value quoted by Clark¹⁰ as the atomic diameter of krypton. Ricci¹¹ has compared the radial distribution function obtained here with the work of Henshaw for helium, neon, and argon, making use of the principle of corresponding states, and has

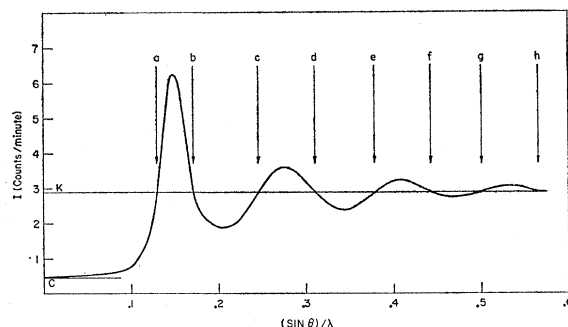


FIG. 3. Intensity vs $(\sin\theta)/\lambda$ for liquid krypton at $T=117^\circ\text{K}$ and $P=0.8$ atmosphere, showing arbitrary terminations ($\lambda=1.05$ Å).

¹⁰ George L. Clark, *Applied X Rays* (McGraw-Hill Book Company, Inc., New York, 1955), p. 503.

¹¹ F. P. Ricci, *Nuovo cimento* **16**, 532 (1960).

found good agreement between the atomic distribution functions of the three heavier elements.

In addition to the two major concentrations of atoms at about four and eight angstroms, respectively, a small ripple pervades the entire curve and a subsidiary peak is prominent at approximately five angstroms. Because of the existence of the ripple over the entire curve and because of the existence of such a concentration of atoms between the first and second nearest neighbor groups is open to question, the validity of the small peak is in serious doubt. A subsidiary peak of this general type has been reported for many liquids. Eisenstein and Gingrich¹ have reported such a peak at certain temperatures for liquid argon, and the work of Campbell and Hildebrand² shows a similar peak in each radial distribution for xenon. However, Henshaw reported no such peak for neon⁴ or argon.⁶ While an extensive investigation into the origin of the subsidiary peak in this work was inconclusive, it indicated that termination of the $si(s)$ integral was probably a major contributing factor to this peak.

Even if all of the experimental data were known with unlimited certainty to the greatest value of $(\sin\theta)/\lambda$ for

TABLE I. Some parameters of liquid krypton.

Temperature	Density (atoms/Å ³)	First intensity peak $(\sin\theta)/\lambda$	Nearest neighbor distance (Å)	Number of nearest neighbors
117°K	0.0176	0.148	4.02	8.5
133°K	0.0166	0.147	4.04	8.0
153°K	0.0154	0.146	4.08	7.0
183°K	0.0130	0.143	4.10	6.5
210°K	0.0075	0.141	4.20	4.0

which measurements were made, there still remains the finite termination feature of the analysis which can introduce spurious details in the radial distribution function. Because of this possibility of spurious effects, the best determined and most intense diffraction pattern was subjected to a series of exploratory procedures to provide information in this connection. In one test, the intensity curve was arbitrarily terminated at eight points, giving corresponding distributions that show progressive changes in their detail. Figure 3 shows the intensity curve with the eight termination points marked by arrows, and Fig. 4 shows the radial distributions which resulted from transformation of the intensity data out to each termination point. This series of curves indicates that the observation of such a peak depends on having a strong diffraction pattern of about three prominences. Where fewer data are transformed the subsidiary peak appears to be hidden under the large peak representing the second nearest neighbor atoms. The slope on the small r side of the peak that represents the number of nearest neighbors is one important feature that changes. The ratio of the last value of r , $r(0)$, for which the distribution function

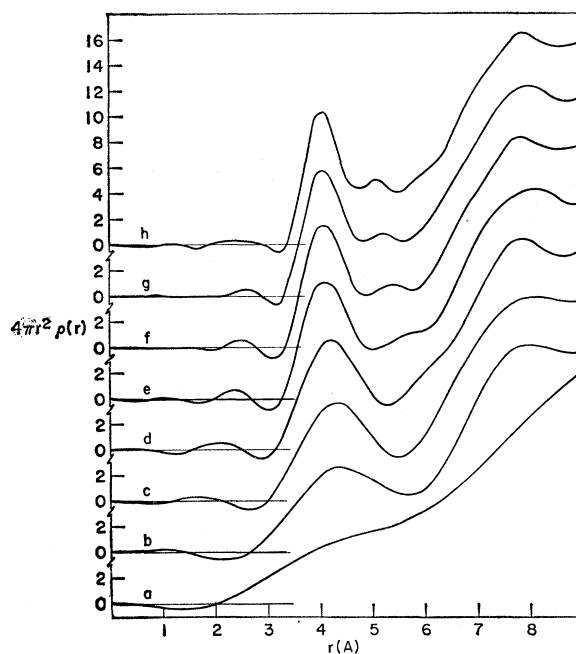
TABLE II. $r(0)$ and $r(\max)$ for distributions from terminated data.

Distribution	S_m	$r(0)$ (Å)	$r(\max)$ (Å)	$r(0)/r(\max)$
<i>b</i>	0.170	2.62	4.46	0.590
<i>c</i>	0.246	3.00	4.30	0.697
<i>d</i>	0.310	3.12	4.20	0.742
<i>e</i>	0.378	3.28	4.14	0.792
<i>f</i>	0.440	3.30	4.08	0.809
<i>g</i>	0.504	3.34	4.05	0.824
<i>h</i>	0.580	3.38	4.02	0.841

equals zero, to the $r(\max)$ of the maximum height of the first peak for each distribution from terminated data is given in Table II and is seen to increase as the amount of the intensity curve transformed is increased. The value obtained for $r(0)/r(\max)$ when all of the intensity curve is used in the transformation is 0.84, which is somewhat less than the 0.891 predicted by the Lennard-Jones 12:6 potential and would seem at first to indicate a potential bowl of greater width than that of the Lennard-Jones 12:6 potential. However, when the manner in which the $r(0)/r(\max)$ ratio increases with increasing S_m is considered, it must be concluded that only if the intensity measurements could be carried out to infinitely large values of s could an $r(0)/r(\max)$ ratio be obtained which would be truly indicative of the potential bowl width. Since in practice it is never possible to measure the $i(s)$ function to very large values of s , the $r(0)/r(\max)$ ratio must be recognized as indicating a maximum value for the width of the potential bowl with the actual value being somewhat less than the ratio indicates. A plot of this ratio as a function of termination position indicates that extrapolation of $i(s)$ to termination beyond presently available experimental limitations would lead to a $r(0)/r(\max)$ ratio between 0.88 and 0.91. Allowing for possible error in this type of analysis, either value is in reasonable agreement with the 0.891 value predicted by the 12:6 Lennard-Jones function. This tends to indicate that, although present results are probably good as far as they go, a certain amount of information remains beyond the limit of present experimental

TABLE III. Coordination numbers resulting from terminated data.

Distribution	Coordination number
<i>b</i>	12.0
<i>c</i>	11.5
<i>d</i>	11.0
<i>e</i>	10.0
<i>f</i>	9.5
<i>g</i>	9.0
<i>h</i>	8.5

FIG. 4. Radial distributions from terminated data for liquid krypton at $T=117^\circ\text{K}$ and $P=0.8$ atmosphere.

observation. A second important feature of the series of radial distributions from terminated data is the change in coordination number as a function of termination. The coordination number corresponding to the area of the first peak of each of the curves in Fig. 4 is given in Table III. Rounded off to the nearest half atom, the number decreases from 12 to 8.5 as the diffraction data are increased. This also illustrates the necessity of careful measurement of the intensity to the greatest possible value of $(\sin\theta)/\lambda$. A third feature noted in this series of curves is the change in position of the first peak with termination. It appears from this that at least part of the peak shift at higher temperatures mentioned above and shown in Table I may be due to the diffraction data having been terminated earlier in the higher-temperature patterns.

It seems apparent that premature termination of experimental data can cause invalid conclusions to be drawn concerning the interatomic potential, the value of the coordination number, and the nearest neighbor distance, as well as causing spurious ripples to appear on the radial distribution curve.

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