

XRay Diffraction Study of Liquid Sodium

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respect may be explained by the very great difference in magnitude of regions or groups in which noticeable orderliness or molecular arrangement occurs.

4. The depression and greater width of the depressed curve peak of the liquid crystal, and the discussion of areas are in harmony with the conclusion that a small temperature gradient produces a preferred orientation of the liquid crystal "swarms" or groups with their longitudinal axis perpendicular to the direction of the maximum temperature gradient. One hesitates to adopt this conclusion without reservation, for a detectable turning moment caused by the scattering of the elastic waves with such a small gradient seems surprising. The experiments were so carefully performed, however, that one may emphasize the striking agreement of this interpretation with the results of the numerous experiments reported in Fig. 1. Something certainly occurs that is, in our experiments, equivalent to this interpretation. At any rate these experiments may be regarded as adding confirmatory evidence to that from magnetic and electric studies, in emphasizing the relatively large size of these liquid crystal swarms.

5. The range of temperature in the liquid crystalline experiments would, with greater

refinement, be of importance. The temperatures for the present observations varied from 122°C to 130°C without any noticeable effect on the location of the peak of the intensity diffraction curve or its magnitude. This does not mean that there can be no gradual alteration in structure in the liquid crystalline state, but only that it is small.

6. The size of the liquid crystalline groups must be quite large, as already stated. In the transparent liquid one has no definite measure of the size of the cybotactic groups. Experience in computation of diffraction intensity curves of liquids by using a density function leads one to expect that the size of the striking regularity in liquid groups of para-azoxyanisole would not need to be over 30Å in its longer dimension with a gradual fading of regularity with distance. Thus one would anticipate no noticeable optical scattering. The large liquid crystal group is not merely an orderly aggregate of the small liquid groups for there is a definite change in structure. But the much larger aggregation of closely similar groups is a prominent characteristic of the change of phase.

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X-Ray Diffraction Study of Liquid Sodium

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The x-ray scattering curve for liquid sodium is obtained photographically with Mo $K\alpha$ radiation, monochromatized by reflection from rocksalt. By a Fourier analysis of the corrected scattering curve, one obtains directly the radial distribution of atoms about any atom in the liquid.

The distribution curve shows a first concentration at about 4.0Å, followed by a dip at 5.0Å, and a second concentration at about 7Å. The significance of the curve as giving a picture of a simple monatomic liquid is discussed.

INTRODUCTION

IT has been shown^{1,2} that from a Fourier analysis of the x-ray scattering curve of a liquid, one gets directly the radial distribution of atoms surrounding any average atom. It is of

considerable interest to apply the method to a monatomic liquid, and get directly and uniquely a picture of this simplest type of liquid. Debye and Menke have successfully applied the method to liquid mercury. While mercury is an excellent example of a simple liquid, it is not however well suited to x-ray study, since the absorption co-

¹ Zernike and Prins, *Zeits. f. Physik* **41**, 184 (1927).

² Debye and Menke, *Erg. d. tech. Röntgenkunde*, II.

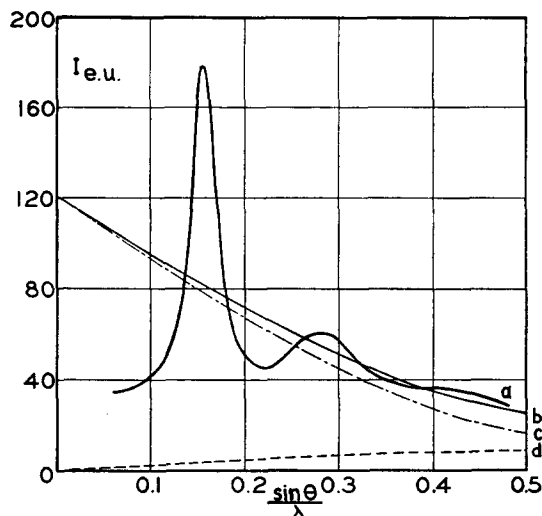


FIG. 1. (a) Corrected experimental intensity curve for liquid sodium in electron units per atom. (b) Total independent scattering per atom. (c) Independent unmodified scattering per atom. (d) Modified scattering per atom.

efficient for mercury is so large that the final intensity curve depends markedly upon the absorption correction. A better material for a quantitative x-ray study is liquid sodium. Using Mo $K\alpha$ radiation the absorption correction can be made practically negligible.

EXPERIMENTAL

The liquid sodium was contained in an evacuated thin-walled Pyrex tube³ of diameter 2.0 mm, and maintained at a temperature of 103° by a heating coil. A test run showed that the scattering by the Pyrex tube was negligible compared to that of the sodium. The sample was at the center of a cylindrical camera of radius 8.61 cm. The radiation used was Mo $K\alpha$ monochromatized by reflection from a rocksalt crystal. At 35 kv and 20 ma exposures were of the order of 24 hours. The microphotometer record of the pattern was changed to an intensity curve in the usual way. The correction for absorption in the sample was negligible. Correcting for polarization, one obtains the final intensity curve in electron units on an arbitrary scale, Fig. 1a.

APPLICATION OF FOURIER METHOD

For a material containing only one kind of atom, the average density of surrounding atoms

³ The technique of preparing the sample is described in Randall, *The Diffraction of X-Rays and Electrons by Amorphous Solids, Liquids and Gases*, p. 129.

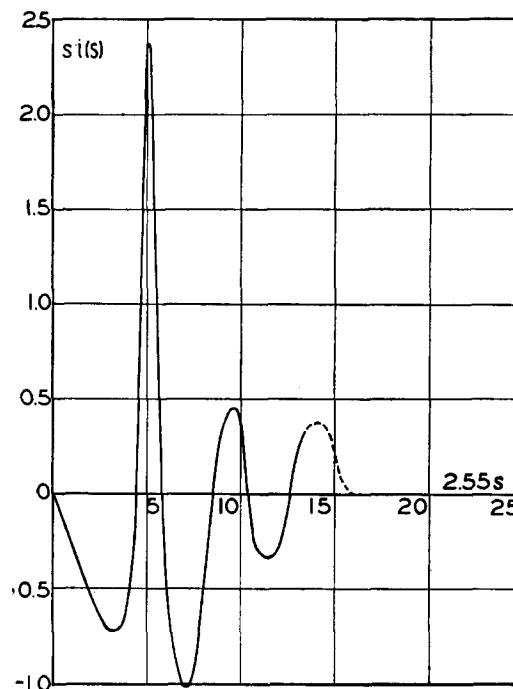


FIG. 2. The curve $si(s)$ for liquid sodium. The scale of abscissae $2.55s$ is chosen so that successive harmonics on the analyzer correspond to 0.4Å intervals.

is given by the relation

$$4\pi r^2 \rho(r) = 4\pi r^2 \rho_0 + \left(\frac{2r}{\pi}\right) \int_0^\infty si(s) \sin rs ds \quad (1)$$

where

$4\pi r^2 \rho(r) dr$ is the number of atoms between distances r and $r+dr$

ρ_0 = average density of sample in atoms per unit volume

$s = 4\pi \sin \theta / \lambda$

$i(s) = (I/N - f^2)/f^2$

I/N = unmodified intensity per atom in electron units

f = atomic scattering factor.

Curve 1c gives the independent unmodified scattering per atom f_{Na}^2 , and curve 1d the modified scattering per sodium atom.⁴ The total independent scattering per atom is given by curve 1b. At large values of $\sin \theta / \lambda$ the scattering curve of any material approaches independent scattering, and curve 1a is therefore drawn to such a scale that it approaches curve 1b at large values of

⁴ From tables of f and Σf^2 Compton and Allison, *X-Rays in Theory and Experiment*.

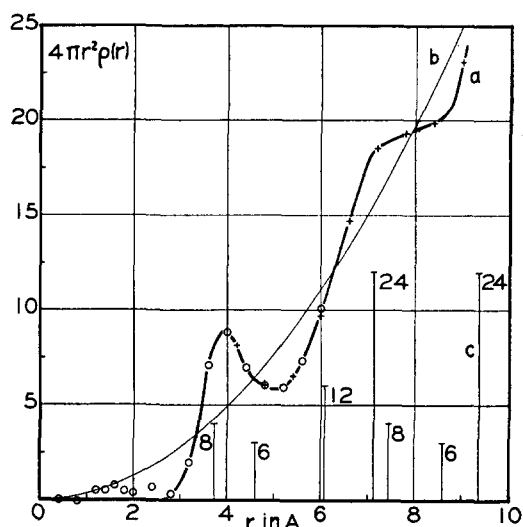


FIG. 3. (a) Radial distribution curve for liquid sodium $4\pi r^2 \rho(r)$. (b) Average density curve $4\pi r^2 \rho_0$. (c) Distribution of neighbors in crystalline sodium.

$\sin \theta/\lambda$. This serves to put the experimental curve upon an absolute basis, electron units per atom. Subtracting b from a, and dividing through by c, gives the quantity $i(s)$ in absolute units. On the experimental intensity curve, the outer part of the third peak is somewhat indefinite, and accordingly the outer part of the third peak on the $si(s)$ curve, Fig. 2, is arbitrarily rounded off. The integration involved in Eq. (1) is then carried out on a Coradi harmonic analyzer. By plotting the curve $si(s)$ to several different scales of abscissae, a large number of points are obtained upon the final distribution curve.

DISCUSSION OF RESULTS

The resulting radial density curve $4\pi r^2 \rho(r)$ is shown in Fig. 3 plotted against r . The area under the curve in any region gives the number of atoms in that range of distances. The first concentration of neighboring atoms comes at about 4.0A. Beyond this point there is a slight dip, and then a second concentration at about 7A. At larger

distance the density curve approaches curve b, the uniform density $4\pi r^2 \rho_0$.

The resulting density curve is conveniently interpreted in terms of a box full of ball bearings continuously shaken. About any one ball bearing we will never expect to find another closer than the diameter of the balls. At about this distance we will expect to find the centers of several balls, since at any instant there will be a number of balls in approximate contact with the one under consideration. At a somewhat larger distance the number of centers must drop a little, since the balls already considered, prevent others from coming into the immediate vicinity of the first ball.

For purpose of comparison, the number of neighbors and their distances in crystalline sodium are also given in Fig. 3. It is very evident that the density curve of the liquid is essentially a smoothed out distribution curve for the crystalline phase. That this must approximately be the case, follows directly from the fact that the density of the liquid is not very different from that of the crystal.

The density curve of Fig. 3 represents the "structure" of liquid sodium as specifically as this quantity can be represented. It should perhaps be emphasized that this curve is obtained directly from the experimental x-ray curve, without making any *a priori* assumptions as to the atomic arrangement in the liquid. It is evident that there is such a thing as a "structure" in a liquid, a structure which has to do with the average distribution of neighboring atoms about any one atom. There appears to be no necessity for postulating a crystalline type of structure⁵ in the liquid, to explain a distribution curve such as Fig. 3.

⁵ By a *crystalline structure* one means an array of atoms in which some unit of structure repeats itself identically at regular intervals in three dimensions. In using terms such as "structure" it is necessary to state precisely whether *crystalline structure* is meant, or whether the term is being used in a more general sense.