

The Structures of Liquid Mercury and Liquid Aluminum

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X-ray diffraction intensities from liquid mercury at room temperature and from liquid aluminum at temperatures between 670° and 1000 °C have been measured with both Cu $K\alpha$ and Mo $K\alpha$ radiation. The apparatus employed a focusing geometry, a diffracted-beam monochromator and a scintillation counter. Radial distribution functions and first coordination numbers have been computed: they are in good agreement with previous work for mercury, but they do not confirm the unusual temperature variation reported by Bublik & Buntar for aluminum. It is shown that use of a diffracted-beam monochromator can give rise to peculiar systematic error effects.

Introduction

This paper describes an X-ray diffraction study of liquid mercury at room temperature and of liquid aluminum at temperatures up to 1000 °C. The study of aluminum was undertaken because there is significant disagreement between results published by Gamertsfelder (1941) and by Bublik & Buntar (1958), because the latter results show an unusually large temperature variation of the structure, and because reliable results were needed for a study of liquid iron-aluminum alloys (Black & Cundall, 1965; Cundall, 1963). In order to test the techniques of measurement and analysis, measurements were also made on mercury, for which results have been reported recently by several workers.

There have been large variations in the structures obtained for the same liquids by different experimenters, although Furukawa (1960) has shown that if the primary data are all analysed in the same way the discrepancies are considerably reduced. The artefacts introduced by various techniques of analysis are well understood and the main difficulty now lies in the collection of data free from systematic errors. The first feature of the work described here is the use of both Mo $K\alpha$ and Cu $K\alpha$ radiation. The former permits measurements to be made up to values of μ (where $\mu = 4\pi \sin \theta / \lambda$, θ is the Bragg angle and λ the wavelength) of about 16 \AA^{-1} , which is essential if the absolute scaling of the data is to be investigated adequately. The latter enables the lower range of μ to be studied in more detail, whilst the comparison of data for two wavelengths in approximate ratio 1:2 gives some check on possible sources of systematic error. The second feature of the experimental technique is the use of a diffracted beam monochromator which reduces or removes the corrections for fluorescent and Compton scattering.

Apparatus

The X-ray geometry of the apparatus is illustrated in Fig. 1. For measurements on liquid metals at high temperatures the sample must have a free horizontal surface. A Bragg-Brentano focusing system was used with this horizontal surface, both the X-ray tube and detector rotating on separate arms about an axis in the surface. The monochromator in the diffracted beam eliminated all fluorescent X-rays produced in the specimen but could only reduce the amount of Compton radiation entering the detector. At low angles, the change in wavelength for Compton scattering is too small to be distinguished by any monochromator; at higher angles a lithium fluoride crystal diffracts Compton radiation with reduced efficiency whilst a quartz monochromator can eliminate it completely. The monochromator crystal used for most of this work was a lithium fluoride crystal bent and ground by the method

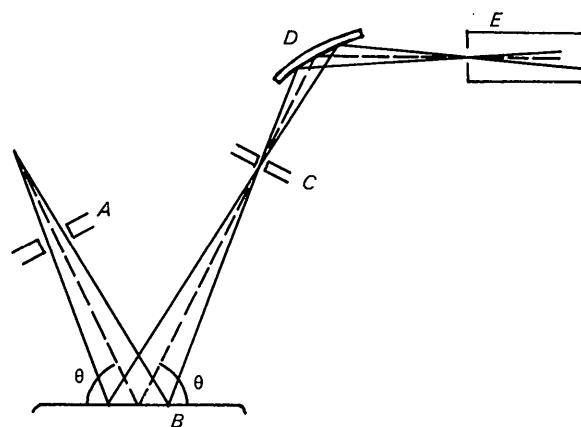


Fig. 1. X-ray geometry of the apparatus. *A*, slit system limiting the divergence of the X-ray beam; *B*, free liquid surface; *C*, scatter slit at primary focus; *D*, bent and ground crystal monochromator; *E*, Scintillation counter;

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described by Priestley (1955) so that Johansson focusing geometry was maintained. In order to correct for Compton radiation reaching the detector, the variation of reflecting power with wavelength at a fixed angular setting had to be known for this crystal: this was deduced from the variation of reflecting power with angle for a fixed wavelength from the same crystal, a deduction which is sufficiently accurate for the small range of wavelengths involved. The detector used was a scintillation counter with pulse height discrimination. The X-ray tube was fed from a stabilized generator (Philips PW 1010) and the X-ray beam intensity was assumed to be constant. The X-ray source was a horizontal line focus, of effective dimensions $1 \text{ cm} \times 0.05 \text{ mm}$ at the viewing angle (3° to the target surface): the divergence of the beam in a plane normal to that of Fig. 1 was limited to 2° by a Soller slit system in the incident beam. The divergence in the plane of Fig. 1 was limited by the slit system at A to $\frac{1}{4}$ or $\frac{1}{2}^\circ$ for low angle measurements and to 2° for measurements at high angles. The maximum value of θ attainable was 72° .

The liquid sample was held in a cylindrical alumina crucible. For measurements on liquid aluminum this was heated by a resistance element of Kanthal, surrounded by thermal radiation shields of polished molybdenum, and enclosed in a vacuum chamber in which the pressure could be reduced to 10^{-5} mmHg to reduce both contamination and temperature gradients at the liquid surface. At this pressure a mirror-like surface was obtained for liquid aluminum, although small amounts of oxide appeared when melting commenced and then dissolved in the bulk liquid: it was estimated that the quantity dissolved was too small to affect the liquid structure appreciably. The X-ray beams entered and left the enclosure through a Melinex window, 50 microns thick, 2 cm wide, and 27 cm long, curved to subtend an angle of 190° , in the plane of Fig. 1, at the axis of the instrument. This window was shielded from thermal radiation by a thin (5 micron) foil of aluminum which did not have to withstand any pressure and which also served to complete the thermal radiation shield around the specimen. This arrangement of the vacuum window was simpler and gave less X-ray absorption than windows consisting of a single foil of thin metal.

The liquid surface was adjusted to the instrument axis by a screw thread which raised or lowered the whole vacuum furnace; its position was checked with a telescope aligned along the instrument axis.

A chromel-alumel thermocouple in an alumina sheath could be pushed in and out of the liquid surface from above through a vacuum seal: the end of the sheath was only 2 mm in diameter to reduce distortion of the surface by meniscus effects. This thermocouple was the sensing element for a temperature controller. The liquid could be stirred by a retractable stirring rod whilst under vacuum.

The apparatus was aligned, calibrated and tested with the aid of solid aluminum, copper and silicon

specimens. After alignment and testing, angular measurements were shown to be accurate to within $3'$ of arc over the whole angular range.

Correction and scaling of the data

Diffraction data were obtained for liquid mercury at room temperature (about 20°C) with both Cu and Mo radiation, for liquid aluminum at 670°C , 700°C , 800°C , 860°C and 1000°C with Cu radiation, and at 670 – 700°C , 800°C , 900°C and 1000°C with Mo radiation. In all cases the data were collected at angular intervals small compared with the scale of the intensity variations with angle, and at each angle sufficient counts were accumulated to give a statistical error of between 1% and 3% which was always small compared with the systematic errors expected.

The measurements were corrected for background and for effects of polarization of the beam by both the specimen and the monochromator crystal. Corrections were also applied for the Compton radiation, allowance being made for the different absorption coefficients of the modified radiation and for the change in monochromator efficiency with wavelength.

The system departed from an ideal focusing geometry in four different ways as follows:

- (1) X-rays penetrated the specimen surface to a finite depth and could therefore miss the focus slit at C (Fig. 1) after diffraction.
- (2) The liquid surface was flat and not curved to the ideal focusing circle.
- (3) The liquid diffracts at all angles and beams scattered from different depths in the liquid through angles differing from the set value of 2θ can enter the focus slit.
- (4) For a focus slit of finite width some beams falling on the monochromator will not be at the correct angle and will be diffracted by the crystal with reduced efficiency.

These effects are interdependent and a calculation of their combined effect has been made (Cundall, 1963). This shows that the composite correction factor varies with angle by less than 4% for liquid aluminum with Mo $K\alpha$ radiation, and by a negligible amount for liquid mercury, although the variation would be much larger for systems with lower absorption coefficients.

The scaling factor K required to reduce each intensity curve to an absolute scale was obtained:

- (i) By fitting the intensity curve at high values of μ , after correction for incoherent radiation, to the square of the scattering amplitude $f^2(\mu)$.
- (ii) By using the equation of Hultgren, Gingrich & Warren (1935):

$$K = \frac{\int_0^{\mu_{\max}} \mu f^2(\mu) d\mu}{\int_0^{\mu_{\max}} \mu I(\mu) d\mu} \text{ where } I(\mu) \text{ is the intensity;}$$

(iii) By using the equation of Norman (1957) and Krogh-Moe (1956):

$$K = \frac{\int_0^{\mu_{\max}} \mu^2 B(\mu) d\mu - 2\pi Z^2 d / N_0 A}{\int_0^{\mu_{\max}} \mu^2 I(\mu) d\mu}$$

where $B(\mu) = f^2(\mu) + I$ (incoherent) \times efficiency
of monochromator,

Z is the atomic number, A the atomic weight, N_0 Avogadro's number and d the density of the liquid; there should be another term in this equation which depends on the overlap of electron density between atoms but this has been neglected; Mendel (1962) has shown that in the case of liquid benzene where such overlap effects would be expected to be large this term makes only a small contribution for values of $\mu_{\max} \geq 7 \text{ \AA}^{-1}$. The curves for $f(\mu)$ used in this work were those of Freeman (1959) for aluminum with the dispersion corrections of Hönl (1933) and those of James & Brindley (1931) for mercury with the dispersion corrections of Dauben & Templeton (1955).

Methods (2) and (3) use a greater range of the experimental intensity curve. In Table 1 are given values of K obtained by methods (2) and (3) for various values of μ ; method (1) gave values which agreed with and showed the same trend as those of method (3). There is no good theoretical justification for method (2) and since it gives values of K consistently higher than those of (1) or (3) its results have not been used. The decrease of K with increasing μ for all methods must be due to some systematic error which varies with angle. The existence of such an error was revealed independently by other measurements. When the slits at A (Fig. 1) were changed to give a different angular divergence the ratio of intensities obtained did not have the value given from the ratio of the divergences and this ratio was a function of the angle at which it was measured. This angular variation was largest for the larger divergences and became almost negligibly small (less than 3%) when the ratio of two small divergences ($\frac{1}{2}^\circ$ to $\frac{1}{4}^\circ$) was taken. It was assumed that the values for the smallest divergence were not in error and experimental values taken with larger divergences were corrected by an interpolated angular variation factor derived from measurements at a few angles of the ratio between intensities for the large and the smallest divergences. It was found that this correction converted $i(\mu)$ where

$$i(\mu) = \frac{I(\mu)}{f^2(\mu)} - 1$$

from a curve which departed monotonically from zero above $\mu = 6.0 \text{ \AA}^{-1}$ into a curve showing only oscillations about zero. The right hand section of Table 1 shows values of K obtained after correction of the intensity curve used for this divergence ratio factor. After this detailed investigation of one curve, all other experimental curves were scaled by method (3), using the criterion that $i(\mu)$ have a zero mean value at high μ to adjust the divergence ratio correction.

Nothing has been assumed in the above procedure about the cause of this effect. Extensive measurements on its variation with λ , with absorption coefficient of the specimen and with various aberrations deliberately introduced into the system are described elsewhere (Cundall, 1963). The following explanation, although only qualitative, is consistent with all of these measurements. The angular and linear distribution of intensity in the diffracted beam coming through the focus slit varies with diffraction angle because of factors (1) to (3) above: hence different areas of the monochromator crystal play a different relative role in determining the final intensity, and if the monochromator is not uniform and is not bent to a perfect arc the divergence ratio will be a function of diffraction angle. Such an effect would obviously depend on the area of crystal used, which increases with beam divergence, and on the linear width of the beam, which increases as absorption in the specimen decreases. It follows that measurements with a diffracted beam monochromator can impose a systematic and spurious variation with angle on the data unless extremely small divergences, which lead to extremely small intensities, are used. In unfavourable cases (low absorption, high divergence) the variation can lead to a 20% error.

An angular variation of K with μ has been found before. Workers using Cu $K\alpha$ only would not expect to see this because μ_{\max} is about 7.5 \AA^{-1} and the effect is hidden by structural ripples in the diffraction curve. Krebs, Haucke & Wegard (1958), using Mo $K\alpha$, found that K increased with μ_{\max} and attributed the effect to bending in the arm holding the monochromator in the diffracted beam. They did not report investigation of the effect of angular divergence, or changes in absorption, and they finally abandoned the Bragg-Brentano geometry. Elasticity calculations and the calibration measurements on solid specimens show that bending of the arm cannot be the cause in the present work. Levy, Agron & Danford (1959) working with a monochromatized incident beam found a variation in divergence ratio with angle for a sample of low absorption and they also changed their geometry from the Bragg-Brentano system without explaining the effect quantitatively.

Table 1. *Absolute scaling factor K*

| μ_{\max} | Before divergence ratio correction | | | | | After divergence ratio correction | | | | | | |
|--------------|------------------------------------|------|------|------|------|-----------------------------------|------|------|------|------|------|------|
| | 6 | 8 | 10 | 12 | 14 | 15 | 6 | 8 | 10 | 12 | 14 | 15 |
| Method 2 | 1.72 | 1.63 | 1.58 | 1.55 | 1.52 | 1.51 | 1.61 | 1.55 | 1.53 | 1.51 | 1.51 | 1.51 |
| Method 3 | 1.47 | 1.45 | 1.43 | 1.42 | 1.40 | 1.39 | 1.37 | 1.38 | 1.39 | 1.39 | 1.39 | 1.39 |

Values of μ in \AA^{-1} . All values of K on the same scale.

A transform of the function $i(\mu)$ should give the radial distribution function (r.d.f.) of the system. A transform of a curve of $i(\mu)$ made without correction for this divergence ratio effect showed ripples which were obviously spurious and which masked some of the main r.d.f. features: these ripples did not appear when a corrected $i(\mu)$ curve was used.

Computations and results

The r.d.f. for each specimen was computed from the equation:

$$4\pi r^2[\varrho(r) - \varrho(0)] = 2(r/\pi) \int_0^{\mu_0} \mu i(\mu) \sin \mu r d\mu$$

where $\varrho(0)$ is the mean atomic density and $\varrho(r)$ the atomic density at a distance r from a selected atom centre. Values of $\varrho(0)$ were calculated from measurements of the density of liquid aluminum made by Gebhardt, Becker & Dorner (1953) and confirmed by Cundall (1963). The computer program allowed the cut-off value μ_0 to be varied so that the production of spurious ripples in the r.d.f. could be investigated. It also allowed an exponential damping factor to be applied to $i(\mu)$. A similar program allowed electronic distribution functions to be calculated, but results of these calculations show little that is not shown by the atomic r.d.f. and they will not be discussed here (see Cundall 1963).

The termination of $i(\mu)$ at a finite value of μ_{\max} gives rise to ripples of frequency $2\pi/\mu_{\max}$ in the trans-

form. Similarly, errors in the shape of $i(\mu)$ at position μ cause spurious ripples of frequency $2\pi/\mu$ to appear, and also broaden the main peaks slightly (Waser & Schomaker, 1953; Finbak, 1949). In the present results the transformed curves all showed spurious ripples. In Fig. 2 results for liquid aluminum at 800 °C are shown; the function plotted is $4\pi r^2[\varrho(r) - \varrho(0)]$, as this shows more detail than the direct r.d.f., $4\pi r^2\varrho(r)$. It can be seen that superimposed on the main curve are ripples, the frequency and position of which are different for the different values of μ_0 and which persist in the region $r < 2 \text{ \AA}$ where they can have no physical significance. Application of an exponential damping factor, $\exp(-0.009 \mu^2)$, reduces the ripples and broadens the main peak slightly. It is easy to select from the several calculated curves of Fig. 2 the main features which are not artefacts and a mean curve can be drawn which represents the liquid structure fairly accurately; the variations in Fig. 2 are a rough guide to its accuracy.

From such mean r.d.f.'s the positions of the main maxima in atomic density were found and also the numbers of atoms in the first coordination shell. Different workers have measured this first coordination number in different ways so that their results are not comparable. The ways that have been used are as follows.

A. The area of the first peak in the curve $4\pi r^2\varrho(r)$ is found, where the trailing edge is made symmetrical with the leading edge (*A*, Fig. 3).

B. Method (1) is used except that the trailing edge is drawn as a straight line.

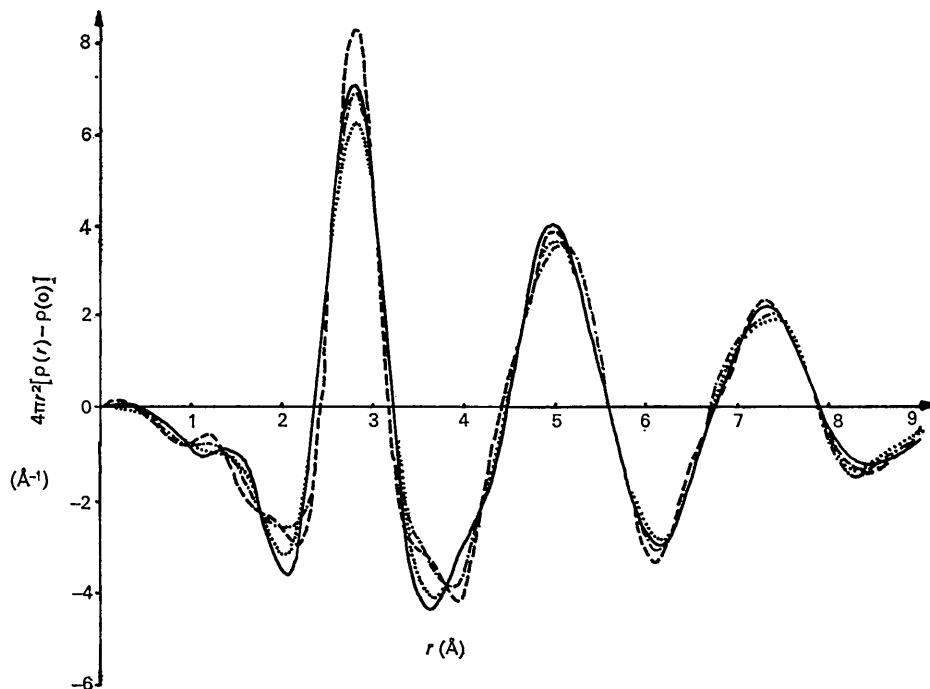


Fig. 2. The curve $4\pi r^2 [\varrho(r) - \varrho(0)]$ against r for aluminum at 800 °C with Mo $K\alpha$ radiation.

Full line: without temperature factor, $\mu_{\max} = 7.2 \text{ \AA}^{-1}$.

Dashed line: without temperature factor, $\mu_{\max} = 11.4 \text{ \AA}^{-1}$.

Dotted line: with temperature factor $\exp(-0.009 \mu^2)$, $\mu_{\max} = 7.2 \text{ \AA}^{-1}$.

Chain dotted line: with temperature factor, $\mu_{\max} = 11.4 \text{ \AA}^{-1}$.

C. The trailing edge of the first peak in the curve $r\rho(r)$ is made symmetrical with the leading edge; the curve is then transformed to $4\pi r^2\rho(r)$ and the area found (Furukawa, 1962).

D. A perpendicular is dropped from the first minimum on the curve $4\pi r^2\rho(r)$ to the axis and the area under the peak to be left of this is found.

In this work all four methods have been used so that the results can be compared with one another and with those of other workers.

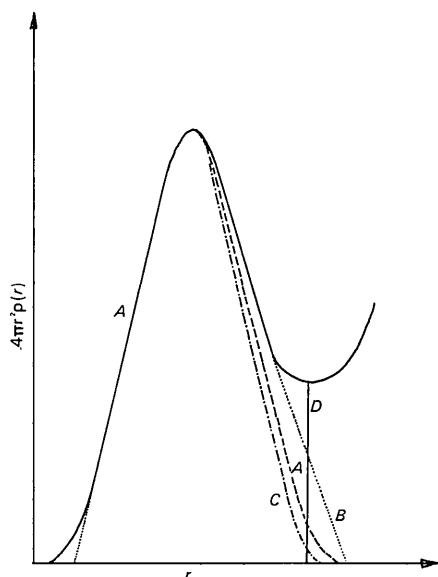


Fig. 3. Part of the radial distribution function depicting different methods of defining the coordination number.

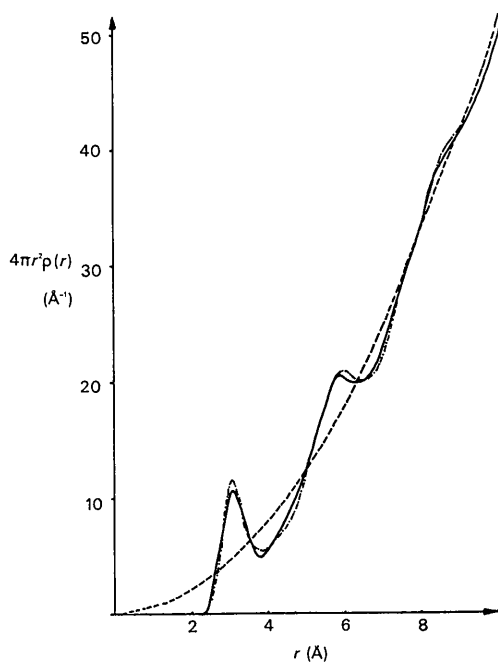


Fig. 4. R.D.F. for mercury at room temperature with two different radiations. Full line: Cu $K\alpha$ radiation. Chain dotted line: Mo $K\alpha$ radiation. Dashed line: $4\pi r^2\rho(0)$.

Fig. 4 shows the curves of $4\pi r^2\rho(r)$ for mercury at room temperature. It can be seen that there are differences between results obtaining with Mo $K\alpha$ and Cu $K\alpha$ radiation. In Fig. 5 the functions $i(\mu)$ from which the transform curves were derived are shown, together with the statistical error in the measurements and the possible variations in $i(\mu)$ due to the spread of published values of $f(\mu)$. The latter are quite large and although they do not contribute to the differences between the $i(\mu)$ curves, since the same f curve was used for both (except for dispersion corrections), they might account for the difference in the transforms because of the larger range of μ used in the Mo results.

In Table 2 the results of the present work on mercury are presented together with results of previous workers. It can be seen that there is good agreement with values for the radii of coordination peaks but that large differences occur in values of the coordination number. It is difficult to evaluate these because they are at least partly due to the different methods of calculation employed. The errors are estimated from computations made from curves affected by spurious ripples. The difference in results by method A for the Mo $K\alpha$ and Cu $K\alpha$ results is surprisingly high and shows that this parameter can be sensitive to quite small differences in the data.

In Fig. 6 the r.d.f. curves for liquid aluminum at three temperatures are shown for both Cu and Mo radiation. For clarity, results taken at temperatures intermediate to those shown are omitted. They could be accurately predicted by interpolation (Cundall, 1963). The chief effect of the temperature rise is to reduce the amplitude of the density fluctuations. The positions of the peaks are only slightly changed but their breadths increase and the coordination numbers decrease. The results for the two radiations give peak positions at slightly different distances, despite agreement in the position of the first peak in the corresponding $i(\mu)$ curves, whilst the Cu $K\alpha$ results give consistently higher values for the first coordination number. Numerical data showing the main features of the curves are given in Table 3 together with the data of other workers.

The cause of the differences between results for the two radiations is not understood; errors in the f factors are one possible source. The results for Mo $K\alpha$ should be less affected by scaling and termination errors so that the interpolated 'ideal' r.d.f. should be more accurate: the coordination numbers for Mo decrease systematically with temperature where those for Cu vary irregularly. However, the absorption is lower for Mo $K\alpha$ and so systematic errors which depend on penetration of the beam into the specimen might be larger than for Cu $K\alpha$. The results for Mo are probably more accurate but the discrepancy shows that the data may not be free from systematic errors which change when λ changes.

Two previous results are listed in Table 3. Those of Gamertsfelder (1941) were obtained from photographic measurements. A crystal monochromatized beam of

Mo $K\alpha$ X-rays was directed onto a liquid wire of aluminum of 1.7 mm diameter contained in its own oxide skin. A cylindrical film of 9 cm radius was used. Bublik & Buntar (1958) made measurements on films of aluminum a few hundred Å thick by electron diffraction. Their results differed considerably from those of Gamertsfelder and they found that the r.f.d. peaks varied appreciably in position as temperature increased from

670° to 850°C. They also found two peaks on the intensity curves which have not been detected in our measurements, whilst Gamertsfelder found a different extra peak at low angles: the positions of these are given in brackets in Table 3. Apart from this last feature, the results of the present work are in agreement with those of Gamertsfelder, but do not agree with those of Bublik & Buntar.

Table 2. Summary of results for liquid mercury

| Reference | Peaks in $I(\mu)$ curve, $\sin \theta/\lambda$ (Å ⁻¹) | | | Peaks in $4\pi r^2 \rho(r)$ | | First coordination | |
|---------------------------------|---|-------|-------|-----------------------------|---------|-------------------------|-------------|
| | 1 | 2 | 3 | r_0 Å | r_1 Å | Coord. No. (Coord. No.) | Method* |
| Debye & Menke (1930) | 0.163 | 0.358 | 0.520 | — | — | — | — |
| Boyd & Wakeham (1939) | 0.135 } 0.214 } | 0.360 | 0.550 | — | — | — | — |
| Campbell & Hildebrand (1943) | 0.100 } 0.191 } | 0.37 | 0.52 | 3.0 | — | 6.7, 5.8 | B and C |
| Gamertsfelder & Gingrich (1943) | 0.118 } 0.184 } | 0.37 | 0.52 | — | — | — | — |
| Hendus (1947) | 0.182 | 0.360 | 0.521 | 3.0 (3.47) | — | 6+4 | A |
| Smallman & Frost (1956) | 0.188 | 0.36 | 0.53 | 3.1 | — | 8.2 | E |
| Jennings (1950) | 0.185 | 0.361 | 0.530 | 3.11 | — | 8.6 | B |
| Vineyard (1954) | — | — | — | 3.10 | 6.0 | 8.3 | E |
| Lukesh <i>et al.</i> (1955) | 0.191 | — | — | 3.0 | — | — | — |
| Pfannenschmid (1960) | 0.182 | 0.358 | — | 3.05 | 6.05 | 7.5 | A |
| Kim <i>et al.</i> (1961) | — | — | — | 3.1-3.2 | — | 8 | E |
| Present work | | | | | | | |
| Mo $K\alpha$ | 0.183 | 0.356 | 0.521 | 3.06 | 6.0 | 7.9 8.0 7.4 | A B D |
| Cu $K\alpha$ | 0.183 | 0.357 | 0.527 | 3.07 | 6.0 | 9.5 8.4 7.9 | A B D |

* A Straight line
C Perpendicular
E Not given
B Symmetrical $4\pi r^2 \rho(r)$
D Symmetrical $4\pi r \rho(r)$

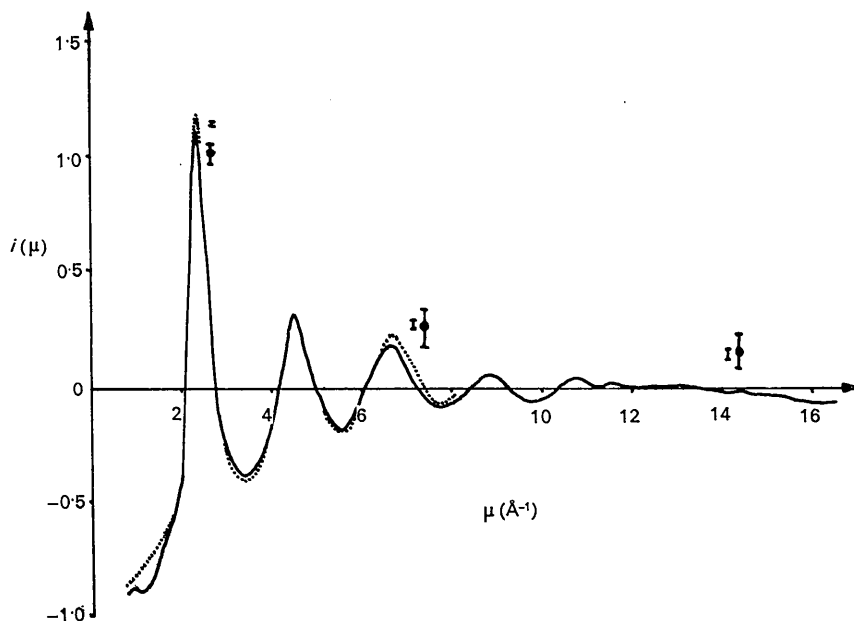


Fig. 5. The curve $i(\mu)$ obtained for mercury at room temperature. — Mo $K\alpha$, Cu $K\alpha$ radiation. Vertical bars are probable statistical errors. Vertical bars with dots give the possible error due to the spread in the published values of $f(\mu)$.

Discussion

The results obtained from liquid mercury are comparable in accuracy with the best recent results for this liquid, and the values for r_0 and the first coordination number are within the range of those found by other workers.

The results for aluminum are more comprehensive, and accurate than those of previous workers. They establish accurate values for r_0 and show that this distance varies by less than 0.03 Å in the temperature range 670°C–1000°C. The coordination number has

been shown to decrease with temperature in this range, although values of this number are subject to large errors. This parameter is not uniquely defined and differences in its value between results for Cu $K\alpha$ and Mo $K\alpha$ radiation show that it may be sensitive to small systematic errors.

For mercury it appears that the coordination number is appreciably less than the value of 10.8 suggested by Furukawa (1960) for his theory of simple liquids, and this value is probably too high also for aluminum.

No previous workers have reported attempts to obtain results for radiations with very different wave-

Table 3. Summary of results for liquid aluminum

The figure in brackets after each number is the estimated error in units of the last significant figure of the result as quoted.

| | Present work | | | | | | Gamertsfelder (1941) | Bublik & Buntar (1958) | | |
|--|-----------------------------------|-----------------------|-----------------------|-----------------------|------------------------|------------------------|----------------------|------------------------|-------|-------|
| | Mo $K\alpha$ 670–700°C | Cu $K\alpha$ 670°C | Mo $K\alpha$ 800°C | Cu $K\alpha$ 800°C | Mo $K\alpha$ 1000°C | Cu $K\alpha$ 1000°C | | 700°C | 670°C | 850°C |
| $\mu(\text{\AA}^{-1})$ for first peak in $I(\mu)$ | 2.66(3) | 2.66(3) | 2.64(3) | 2.64(3) | 2.64(3) | 2.64(3) | (1.26) | 2.76 (3.20) | 2.64 | |
| $\mu(\text{\AA}^{-1})$ for second peak in $I(\mu)$ | 4.78(8) | 4.70(8) | 4.80(8) | 4.75(8) | 4.84(8) | 4.82(8) | 4.52 | 4.56 (5.30) | 4.14 | |
| Width $\Delta(\mu)$ of first peak at 0.75 peak intensity | 0.43(4) | 0.31(4) | 0.49(5) | 0.40(5) | 0.52(5) | 0.47(4) | | | | |
| Ratios of { 1st peak: 1st dip | 5.5(1) | 5.4(2) | 4.9(1) | 4.7(1) | 4.3(1) | 4.3(1) | | | | |
| intensity { 2nd peak: 1st dip | 1.71(5) | 1.67(6) | 1.61(5) | 1.60(6) | 1.45(5) | 1.18(4) | | | | |
| $r_0(\text{\AA})$ for first peak in $4\pi r^2 \rho(r)$ | 2.84(3) | 2.94(3) | 2.83(3) | 2.93(3) | 2.82(3) | 2.91(3) | 2.96 | 2.7 | 2.98 | |
| $r_1(\text{\AA})$ for second peak in $4\pi r^2 \rho(r)$ | 5.35(20) | 5.63(20) | 5.25(20) | 5.55(20) | 5.6(2) | 5.6(2) | 5.2 | 4.2 | — | |
| Coordination numbers for first peak | Straight edge | 9.7(7) | 11.1(8) | 9.2(7) | 10.7(8) | 8.7(7) | 11.2(8) | | | |
| | Symmetrical on $4\pi r^2 \rho(r)$ | 8.7(5) | 10.8(8) | 8.7(5) | 10.8(8) | 8.3(5) | 9.4(8) | 10.6 | | |
| | Symmetrical on $4\pi r \rho(r)$ | 9.9(5) | 10.8(8) | 9.3(5) | 10.1(8) | 8.7(5) | 10.9(8) | | | |
| | Perpendicular | 10.2(8) | 11.3(10) | 9.7(8) | 11.2(10) | 9.0(8) | 11.9(10) | | | |
| | Not described | — | — | — | — | — | — | | 11.4 | 9 |

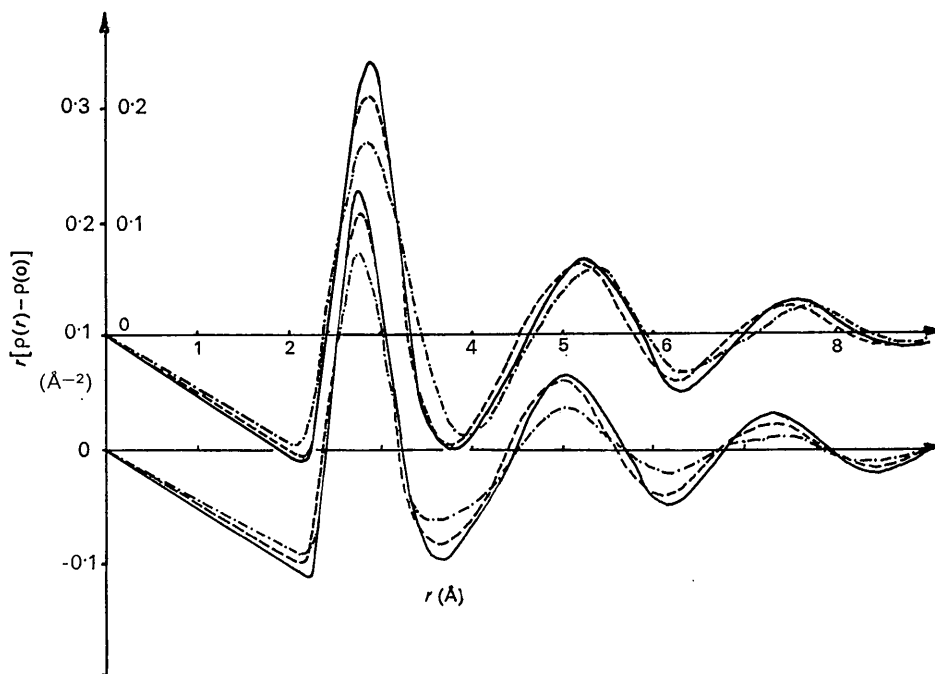


Fig. 6. Curves $r[\rho(r) - \rho(0)]$ for liquid aluminum at different temperatures. Bottom curves Mo $K\alpha$ radiation, top curves Cu $K\alpha$ radiation. Full line: 670°C. Dashed line: 800°C. Chain dotted line: 1000°C.

lengths for the same apparatus and specimens. The agreement of such results is a check on systematic error effects. In the present work it is clear that there are uncorrected errors which give rise to appreciable uncertainties in coordination numbers, although the general shapes of the r.d.f.'s and their variation with temperature are in good agreement.

The use of a diffracted beam monochromator can introduce systematic errors as serious as those it is intended to remove. In general, for materials of low absorption and where small angular divergences cannot be used it should be avoided, whereas for materials where absorption is high and where fluorescent effects are large it is probably preferable.

Attempts to work with small angular divergence can increase the time required to obtain sufficient statistical accuracy in counting. For measurements on liquids at high temperatures evaporation of the specimen is bound to cause a deposit on furnace windows which introduces into the X-ray beams an absorption which varies with time. This was checked in the present work by repeating measurements on one particular angle at regular intervals, and for the longer runs significant correction factors had to be applied. This effect would make it impossible to perform a whole scan with the substantial reduction in beam intensity which might be required if all measurements were made at small angular divergence.

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