

when either, but not both, of these inequalities is reversed.

The expression for the emergent path length $t(\sigma, \varrho, z, \theta)$ remains unchanged, so that the overall correction factor for both effects now becomes, for N Gaussian points x_i and their corresponding weights w_i , and for a sample (subscript 1) enclosed in a tube (subscript 2):

$$I/I_0^0 = \frac{1}{2}(1 - \sin^2(\theta - \beta) \sin^2 \chi_1)^{-1/2} \cdot \\ \times \sum_{i=1}^N w_i \exp[-\mu_1(\varrho_1 x_i + \varrho_1 + t_1) \\ - \mu_2(\varrho_2 - \varrho_1 + t_2 - t_1)], \quad (3)$$

where

$$z_i = (r_1 x_i + r_2)[1 - \sin^2(\theta - \beta) \sin^2 \chi_1]^{-1/2}.$$

As a bonus, this analysis also produces the absorption correction for a cylindrical sheath (window), sur-

rounding a crystal of conventional size, such as may be encountered in low-temperature studies. It is given by:

$$I/I_0^0 = \exp[-\mu(\varrho_2 - \varrho_1 + \sigma_2 - \sigma_1)] \\ = \exp(-\mu(R_2 - R_1)\{[1 - \sin^2(\theta - \beta) \sin^2 \chi_1]^{-1/2} \\ + [1 - \sin^2(\theta + \beta) \sin^2 \chi_1]^{-1/2}\}) \quad (4)$$

where, in this case, the subscripts 1 and 2 respectively, apply to inner and outer radii.

I am deeply indebted to Dr L. W. Schroeder for many interesting and fruitful discussions.

Reference

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An X-ray Diffraction Investigation of Liquid Mercury

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X-ray diffraction intensities of liquid mercury have been measured at room temperature with Mo $K\alpha$ radiation. Balanced filters in the diffracted beam and a scintillation counter were used for monochromatization. The structure factor agrees well with published data of Halder & Wagner though the experimental procedures differ considerably. The calculated resistivity ($90 \mu\Omega\text{.cm}$) agrees with the experimental value ($94 \mu\Omega\text{.cm}$). The first peak in the reduced radial distribution function is higher and narrower than for other melts indicating that the difference between the structures of liquid mercury and the other melts is probably not due to the presence in liquid mercury of several structures with different nearest neighbour distances.

Introduction

The structure factor $i(k)$ is calculated from the coherent part of the X-ray scattering where $k = 4\pi \sin \theta / \lambda$, 2θ is the angle between the primary beam and the diffracted beam and λ is the wavelength of the radiation used. By Fourier transformation of $k \cdot i(k)$ the term $r \cdot g(r)$ is obtained. $[g(r) + \varrho_0] / \varrho_0$ is the probability of finding an atom at distance r if there is an atom at the origin, and it is normalized to unit probability at large r . ϱ_0 is the average atomic density of the liquid.

A number of diffraction investigations were carried out on liquid mercury. Recent results obtained at room temperature are summarized in Table 1. Most studies were made with Mo $K\alpha$ radiation using a crystal monochromator. They are marked Mo, CM. The markings,

βF and BF indicate approximate monochromatization with β -filters or balanced filters. The position k_1 of the first peak in $i(k)$ is the quantity resulting most directly from the experiment. The published values agree well with each other with few exceptions. Values in brackets were taken from published curves or calculated from other data. In order to get the height of the first peak $i(k_1)$ it is necessary to scale the measured intensities into absolute units. Experimental errors and errors resulting from the scaling are responsible for the fact that the highest value in the table is 50% higher than the lowest one. The disagreement concerning the height of the first peak $r_1 \cdot g(r_1)$ is even greater. Varying results are reported for the positions and amplitudes of further maxima and minima in real and reciprocal space.

In the present work some systematic errors which

may lead to incorrect $i(k)$ are analysed. The electrical resistivity is calculated and conclusions concerning the structure are drawn.

Experimental procedure

High purity mercury, not previously treated (Waseda, Iida, Suzuki, & Takeuchi, 1969; Waseda, Suzuki, 1970), has been studied. The liquid was in a crucible of pure copper which was amalgamated inside and so wetted. A sufficiently flat surface was thus obtained, for surface ripples resulting from vibrations were essentially smaller than with mercury in an unwetted crucible. The sample was kept in a chamber through which He(5N6) was flowing, Mo $K\alpha$ radiation was used and because of the Hg L -fluorescence radiation, balanced filters for monochromatization were placed between the sample and the receiving slit. The angle between the primary beam and the sample surface was fixed at 5.3° and the intensity measured in the region of the first peak in steps of $\frac{1}{6}^\circ$ in 2θ . For higher angles steps of $\frac{1}{4}^\circ$ were made.

Correction and scaling of the data

The intensity resulting from the balanced filter procedure was corrected in the usual way for polarization and absorption. The resulting intensity $I(k)$ was then normalized by calculating $X(k) = I(k) / [f(k)^2 + B(k) \cdot C(k)]$ (Ruppersberg & Seemann, 1965), where $f(k)$ is the scattering factor and $C(k)$ the Compton intensity per atom including dispersion and relativistic corrections. The Compton shift leads to the additional absorption correction $B(k)$ (Ergun, Bayer & van Buren, 1967). $X(k)$ should oscillate around a horizontal line, the ordinate of which represents the normalization factor. Any other behaviour of $X(k)$ indicates that large errors are present.

The best values of $X(k)$ result from the f -values calculated by Cromer & Waber (1965) and Doyle & Turner (1967). Poorer results are obtained with values from Cromer & Waber (1968) (+3% deviation from the horizontal line at $k = 15 \text{ \AA}^{-1}$) and from Thomas & Umeda (1957) which are cited by Sagel (1958) (-3%

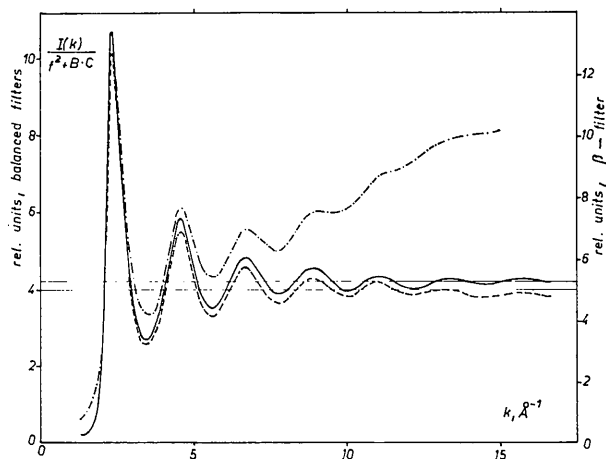


Fig. 1. Monochromatization with different filters.
 ----- Zr-Y, spectral window from 0.6888 to 0.7276 \AA ,
 ————— Zr-Sr, spectral window from 0.6888 to 0.7697 \AA ,
 - · - · - · Zr β -filter (ordinate scale on the right).

deviation). Analogous conclusions were drawn from a study of liquid indium (Ruppersberg & Winterberg, 1971). The choice of the filter pair affects $B(k)$ considerably. With Zr-Y as filters and assuming a sharp Compton profile, the Compton scattering from $K\alpha_2$ should be cut off at 9.6 \AA^{-1} and that from $K\alpha_1$ should vanish beyond 11.0 \AA^{-1} . The dashed curve in Fig. 1 was calculated with $B=1$. At the k -values mentioned no discontinuities appear; furthermore, it can be shown that at the highest k -values Compton scattering from the characteristic spectrum is still present. This behaviour is due to the angle dependent Compton profile for which, as far as we know, correction cannot be made. Therefore, we finally used Zr-Sr as filter pair and the curve obtained oscillates in a perfect manner around a horizontal line. If in the calculation the Compton scattering is not taken into account ($B=0$) at $k = 15 \text{ \AA}^{-1}$ a +10% deviation from the horizontal line results and a deviation of -2% is obtained if the absorption correction is neglected ($B=1$). The higher position of the full curve in Fig. 1 is due to the additional coherent contribution of the bremsstrahlung be-

Table 1. Structure factors of liquid mercury

| Reference | Radiation | k_1 | $i(k_1)$ | r_1 | $r_1 \cdot g(r_1)$ |
|------------------------------------|---------------|--------|----------|--------|--------------------|
| Wagner, Ocken & Joshi (1965) | Mo, CM | 2.27 | 1.50 | 3.05 | (0.21) |
| Kaplow, Strong & Averbach (1965) | Mo, CM | 2.33 | 1.47 | (3.01) | (0.26) |
| Black & Cundall (1965) | Mo, CM | 2.30 | (1.08) | (3.04) | (0.18) |
| | Cu, CM | 2.30 | (1.18) | (3.05) | (0.15) |
| Ocken & Wagner (1966) | Mo, CM | (2.31) | (1.52) | 3.02 | (0.24) |
| Rivlin, Waghorne & Williams (1966) | Cu, CM | 2.31 | (1.63) | (3.05) | (0.23) |
| Halder, Metzger & Wagner (1966) | Mo, CM | 2.29 | (1.48) | 3.02 | (0.26) |
| | Mo, CM | (2.30) | (1.54) | (3.04) | (0.24) |
| Halder & Wagner (1967) | Mo, CM | 2.29 | (1.52) | 3.02 | (0.27) |
| Halder & Wagner (1968) | Mo, CM | 2.29 | (1.52) | 3.02 | (0.27) |
| Caputi, Rodriguez & Pings (1968) | Ag, βF | (2.38) | (1.17) | 2.99 | (0.18) |
| Waseda & Suzuki (1970) | Mo, βF | 2.32 | (1.44) | (3.05) | (0.23) |
| This work (1972) | Mo, βF | 2.31 | 1.55 | 3.00 | 0.28 |

tween 0.7276 and 0.7697 Å. The larger spectral width leads to a widening of the curve in k -space. These errors were graphically corrected. The third curve in Fig. 1 results when only a β -filter is used and normalization is not possible.

The resulting $k \cdot i(k)$ is shown dashed in Fig. 2. By transformation, $r \cdot g(r)$ is obtained. This curve shows some small ripples. Such subsidiary features have long been the object of speculation and some controversy, and distribution functions calculated from the configuration data for a computer-simulated model of a dense fluid of Lennard-Jones disks show similar additional structure (Fehder, 1970). To see whether the ripples are of any significance, $r \cdot g(r)$ was smoothed and transformed back. The resulting curve is shown, together with the original one, in Fig. 2. The difference is within the experimental error.

Discussion

The structure factor obtained is very similar to the one published by Halder & Wagner (1967, 1968) though the experimental procedures differ considerably, (see Table 1 and Fig. 2). Our first peak is 2% higher and somewhat broadened at higher k -values. The correc-

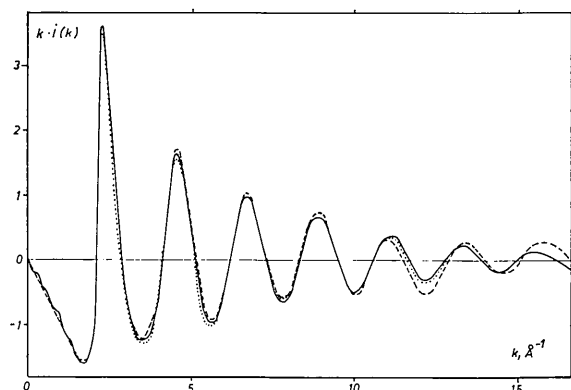


Fig. 2. $k \cdot i(k)$ from the experiment (----) and corrected (—). Results from Halder *et al.* (1967): ·····.

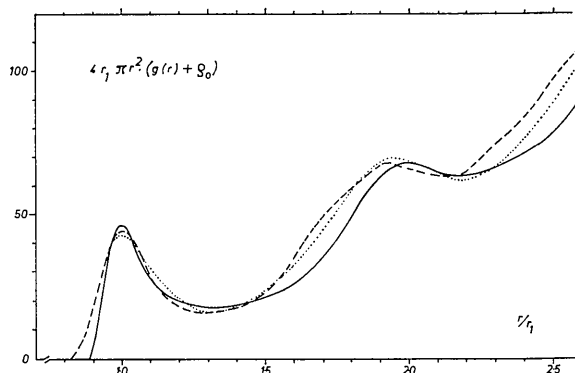


Fig. 3. Reduced radial distribution functions of Hg (—), Al (----) and Pb (·····).

tion for the spectral width has not changed this significantly. The positions of the further maxima and minima are practically identical. It is thus shown that the features of the structure factor of a liquid can be reproduced to within an error of a few %. The calculation of the electrical resistivity using the pseudopotential of Evans, Greenwood, Lloyd & Ziman (1969) yields 90 $\mu\Omega\cdot\text{cm}$ in good agreement with experiment (94 $\mu\Omega\cdot\text{cm}$).

In the radial distribution function $4\pi r^2[g(r) + \rho_0]$, the nearest neighbour distance $r_1 = 3.01$ Å has the same value as for solid rhombohedral mercury. The reduced density (Ruppersberg, 1967, 1969) has a value of $r_1^3 \cdot \rho_0 = 1.12$. Liquid mercury is, within this definition, less densely packed than most other liquid metals for which a reduced density of about 1.2 is found. This agrees with the thermodynamic considerations of Hultgren & Orr (1967). Fig. 3 shows the reduced radial distribution functions of Hg, Al and Pb. The Hg curve does not simply lie a factor 1.12:1.2 below the others. This indicates that the lower density is not due to additional, arbitrarily distributed vacancies. The curve differs in a characteristic manner from the others in that the rises to the first and second peaks are much steeper and that the first peak of Hg is comparatively narrow. If several structures with different nearest neighbour distances were present, as is stated, *e.g.* by Rivlin, Waghorne & Williams (1966), Waghorne, Rivlin & Williams (1967) and Richter & Breitling (1967), the contrary ought to be the case. For several melts the width of the symmetrical portion of the first peak $\langle u_1^2 \rangle^{1/2}$ has come out exactly the same size as in the solid state at the melting point (Ruppersberg, 1967, 1970). It would be of interest to investigate whether $\langle u_1^2 \rangle$ in solid Hg is as small as in liquid Hg, *i.e.* whether the relation between lattice dynamics and atomic distribution in the liquid state also exists for mercury.

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A Highly Efficient Neutron Diffraction Technique: Use of White Radiation*

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A technique, using a white-radiation neutron beam, has been developed that dramatically increases both counting precision and data-collection rates over conventional monochromatic beam techniques. The theoretical equation of scattering and practical equations for incident flux, absorption correction, and extinction correction are presented. Using a NaCl crystal, the incident flux was found to correspond to a Maxwellian distribution. Using a 5 MW research reactor, 2286 data points were collected in a period of one week from a 2 mm³, α -oxalic acid dihydrate crystal. Refinement based on all observed intensities produced parameters that were in excellent agreement with literature values. Of the 680 observations with $I > 3\sigma_I$, the weighted R value = 0.102.

Introduction

A major limitation in single-crystal neutron diffraction studies is the relatively low flux of the neutron beams employed. To obtain adequate counting rates, large single crystals are usually required. These crystals are often difficult to obtain and can exhibit appreciable secondary extinction effects. In particular, hydrogen-containing compounds must be deuterated to avoid the strong effective absorption resulting from hydrogen incoherent scattering.

Present inefficient methods contribute greatly to the low flux of the neutron beam. The conventional monochromatic beam technique is poor in this sense. Monochromatic crystals are never totally efficient diffractors and they 'see' only a very small effective source at the reactor core, due to the small mosaic spread of the crystal. The time-of-flight (TOF) technique does not provide an improvement over monochromatic beams,

due to the necessarily low efficiency of Fermi choppers. Alternate methods using Fourier choppers (Collwell, Miller & Whittemore, 1968) or correlation choppers (Gompf, Reichardt, Glaser & Beckurts, 1968) are being tested experimentally. These choppers are $\approx 25\%$ efficient, and a large increase in incident flux can be expected. However, sophisticated electronics are required, and results to date are not impressive.

The Laue diffraction method can be used to greatly increase the incident flux, and, consequently, smaller crystals can be studied at faster data rates. The large increase in flux results from several factors. First, the inefficiency of a crystal monochromator (or chopper) is eliminated. Second, the effective source of the incident beam can be much larger than that 'seen' by a monochromating crystal. Finally, the neutron-path length from the reactor core to the sample crystal can be a minimum since secondary equipment (such as a monochromator or chopper) is eliminated. The diffracted intensity is also enhanced by two other effects. First, each integrated intensity can be measured with a single-peak height measurement (Lowde, 1956) due

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