Acta Cryst. (1965). **19**, 1043

Determination of X-ray Scattering Factors with Liquid Specimens*

BY ROY KAPLOW, S. L. STRONG, AND B. L. AVERBACH
Massachusetts Institute of Technology, Cambridge, Massachusetts 02138, *U.S.A.*

(*Received* 21 *December* 1964 *and in revised form* 12 *March* 1965)

Experimental X-ray form factors may be obtained from diffraction experiments on liquid specimens by assuming that the pair distribution function is free of oscillations at distances less than the distance of closest atomic approach. Experimental results for lead, mercury and tin are compared with Thomas–Fermi–Dirac, Hartree–Fock–Slater, Hartree–Fock, and Hartree self consistent field and relativistic calculations in the region $0{\cdot}3 \le \sin\theta/\lambda \le 1{\cdot}1$. The experimental form factors for tin are in excellent agreement with recent calculations and show that the Thomas–Fermi–Dirac approximation is poor for this element. The experimental form factor for mercury rises more steeply than any of the calculations at about $\sin\theta/\lambda = 0{\cdot}4$ and falls more slowly at $\sin\theta/\lambda = 1{\cdot}0$ than any of the theoretical results, with the exception of the Thomas–Fermi–Dirac calculation. The experimental form factor for lead is in good agreement with all the theoretical calculations over most of the same range, but the experimental values also decrease more slowly than the calculated ones at high angles.

The scattering of X-rays by a monoatomic liquid may be written as follows (James, 1954):

$$k\left\{\frac{I(k)}{f(k)^2} - 1\right\} = \int_0^\infty 4\pi r\{\varrho(r) - \varrho_0\} \sin kr dr \qquad (1)$$

or

$$F(k) = \int_0^\infty G(r) \sin kr dr$$

where

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

I = X-ray intensity in electron units, corrected for polarization and Compton modified scattering

f = form factor

r = radial distance

ϱ_0 = mean density

$\varrho(r)$ = atoms/unit volume at distance r from a given atom

$F(k) = k(I/f^2 - 1)$

$G(r) = 4\pi r\{\varrho(r) - \varrho_0\}$.

The radial distribution function, $G(r)$ may be determined from a sine transformation of the intensity function, $F(k)$, starting with theoretical values of the form factors, f. Since the intensity function is sensitive to the shape of f, errors in the latter are carried through the transform process and become apparent in the derived function, $G(r)$.

The relationship between the values of f^2 which are used in the analysis of the data and the true values, $(f^2)^\tau$, may be defined in terms of an error function, $\varepsilon(k)$.

$$f^2 = (f^2)^\tau \left[\frac{1}{1+\varepsilon(k)}\right]. \qquad (2)$$

The experimental intensity function may then be written

$$F(k) = [1 + \varepsilon(k)]F^\tau(k) + k\varepsilon(k). \qquad (3)$$

If $G^\tau(r)$ is the sine transform of the true function, $F^\tau(k)$, and if $H(r)$ is the cosine transform of $[1 + \varepsilon(k)]$, then the transform of the first term in equation (3) will be the convolution of the functions G^τ and H, *i.e.* $\int G^\tau(r)H(r-s)dr$. If the theoretical values have a reasonable shape, $\varepsilon(k)$ will be a slowly varying function and H will be a relatively sharp peak. The convolution will then not differ greatly from G^τ itself. The second term in equation (3) has a more obvious effect. It causes extraneous oscillations which will be confined primarily to the region between $r = 0$ and the nearest neighbor peak, that is, in the region where G^τ should be linear. Therefore, $k\varepsilon(k)$ may be obtained approximately from a transform of those spurious oscillations, and the true scattering factors may then be obtained from equation (2). Generally, the X-ray intensity is measured in arbitrary units, and only the shape of f^2 can be corrected, since any constant multiplying factor will be absorbed into the normalizing constant.

Recent measurements have been made on liquid mercury and lead (Kaplow, Strong & Averbach, 1965) and tin, with Mo $K\alpha$ radiation, and a bent crystal monochromator in the diffracted beam. Oscillations in the transform, $G(r)$, of the type discussed above were encountered. The deviations were maintained through various runs on a given element, were different for the three different elements and were explicable in each case in terms of errors in the theoretical scattering factors.

In Fig. 1 we show the reduced intensity functions, $F(k)$, obtained from the experimental intensity measurements on liquid tin, using TFD† (*International Tables for X-ray Crystallography*, 1962) and SCF (Cromer, Larson & Waber, 1964) theoretical scattering

---

* Work supported by the Office of Naval Research.

† The abbreviations used to specify the type of calculation are: Thomas–Fermi–Dirac, (TFD); Hartree self-consistent field (SCF); Hartree–Fock–Slater (HFS); relativistic Dirac–Slater (RDS); Hartree–Fock (HF); relativistic self-consistent field (RSC); for differences between the approximations, one should consult the referenced papers.

factors, both corrected for dispersion (Dauben & Templeton, 1955; Cromer, 1965). Since $F(k)$ should oscillate about a value of zero, it is apparent that the more recent SCF values are superior. In Fig. 2 we show the oscillations of the transform, $G(r)$, at small values of r, which are due to the slowly varying errors in the reduced intensity functions. The transforms of these oscillations about the best straight lines yield $k\varepsilon(k)$, as discussed above, and the corrected values of $F(k)$ are plotted in Fig. 1. The corrected functions are identical within the thickness of the line used in the plot. The corrected function, and hence the shape of the derived scattering factors, will be the same regardless of the initial values used for f^2, provided there are no high frequency errors in the initial functions. In practice, it may be expedient to by-pass the theoretical values entirely, and begin the analysis with a free-hand curve drawn to fit the data.

In Figs. 3, 4 and 5 we show experimental shapes for f^2 obtained from measurements of liquid lead, mercury and tin. The experimental results have been fit arbitrarily to the TFD values at $\sin\theta/\lambda=0{\cdot}6$. Experimental values are not shown for the low angle region where the ratio I/f^2 is small or rapidly varying and the corrections less precise. Also shown on the same figures are values given by TFD, HFS (Hanson, Herman, Lea & Skillman, 1964) and (for mercury) RSC (Ibers, 1958) calculations. The HFS and RSC values have also been fit to the TFD at $\sin\theta/\lambda=0{\cdot}6$. The figures are adequate for exhibiting the shapes qualitatively, and a few general characteristics may be noted. (1) The theoretical mercury values exhibit negative deviations at low angles. (2) The TFD tin values show negative deviations at both low and high angles. (3) There is generally good correspondence between the experiments and the HFS tin values, and the HFS and TFD lead values. The percentage deviations of the theoretical values from the experimental shape are tabulated in Table 1. Included, in addition to those shown in the figures, are the deviations for SCF (CLW) and RDS (Cromer & Waber, 1965) calculations for all three elements and for an Sn^{2+} HF calculation (Freeman & Watson, 1965). Although the numbers in the table have been carried to a tenth per cent, it is doubtful that deviations less than one per cent are significant.

It is interesting to note, from the table of deviations, that the various calculations for each element have quite similar shapes with the exception of the tin and mercury TFD values. These correspondences exist in spite of the fact that the absolute values of the scattering powers (at $\sin\theta/\lambda=0{\cdot}6$) differ by as much as 5%. One may note further that the HF calculation is in very good agreement with the experimental shape for tin, except for the value at $\sin\theta/\lambda=0{\cdot}3$, where the effect of the ionization, which produces a positive deviation at this angle, becomes noticeable. The SCF, HFS, RDS and TFD values agree with the experimental shape for

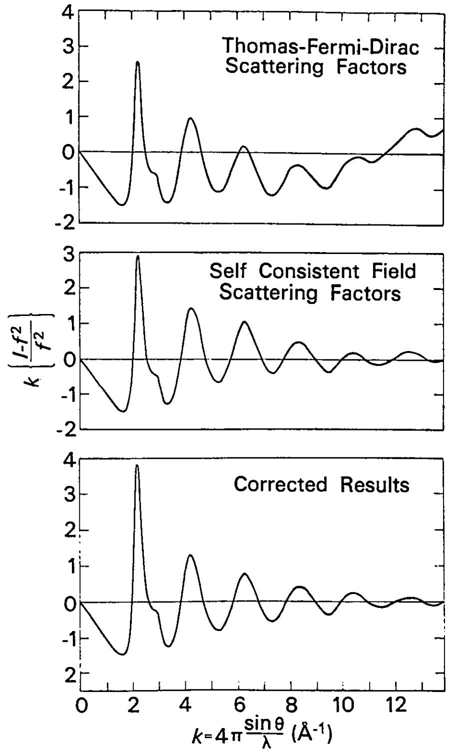

Fig. 1. Experimental and corrected reduced intensity functions for tin.

Table 1. *Percentage deviations in shapes of dispersion-corrected* theoretical* f^2 *values when fit to experimental values at* $\sin\theta/\lambda=0{\cdot}6$

	Mercury					Lead				Tin				
$\sin\theta/\lambda$	TFD	RSC	SCF	HFS	RDS	TFD	HFS	SCF	RDS	TFD	HFS	SCF	HF^{+2}	RDS
0·3	−4·7	−6·4	−5·6	−4·7	−5·7	+0·3 %	0·0 %	0·0 %	−1·1 %	−3·2 %	+2·2 %	+1·0 %	+3·1 %	+1·6 %
0·4	−2·2	−3·4	−3·2	−2·5	−3·0	+1·0	+1·0	−0·6	−0·3	−3·2	+0·3	−1·4	−0·3	+0·1
0·5	−0·9	−1·6	−1·7	−1·4	−1·5	−0·7	−1·0	−1·2	−1·2	−1·2	−0·2	−1·6	−0·9	−0·1
0·6	0	0	0	0	0	0	0	0	0	0	0	0	0	0
0·7	+0·6	+0·7	+0·9	+1·1	+0·8	−1·6	−1·3	−0·8	−1·0	−2·1	−0·7	+0·2	−0·5	−0·2
0·8	+1·6	+1·4	+1·4	+1·9	+1·7	−1·4	−0·8	−0·6	−0·7	−5·3	−0·8	+1·0	0·0	−0·6
0·9	+2·4	+1·1	+0·8	+1·8	+1·7	−0·7	−0·4	−0·7	−0·4	−9·2	−0·1	+1·3	0·0	−0·7
1·0	+2·0	−0·8	−1·9	−0·5	−0·4	−1·1	−2·2	−2·5	−2·0	−13·0	−0·8	+1·1	+0·4	−0·2
1·1	+0·8	−3·8	−5·4	−4·1	−3·5	−3·7	−6·2	−8·0	−7·5	−15·2	−1·4	−0·4	0·0	−1·0

* Mo $K\alpha$ radiation dispersion corrections from Dauben & Templeton (1965).

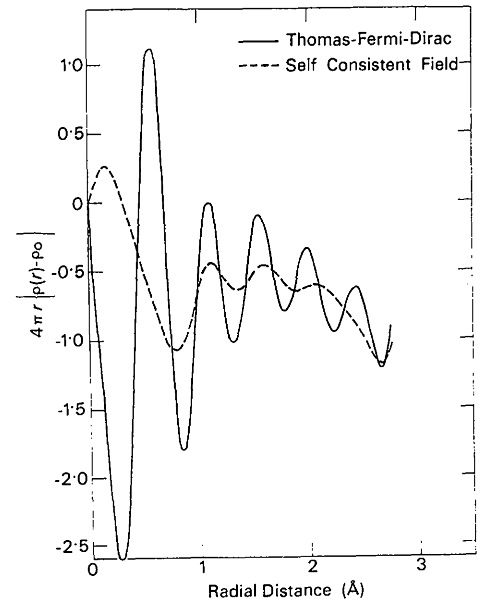

Fig. 2. Oscillations in radial distribution function due to slowly varying error in reduced intensity functions for tin.

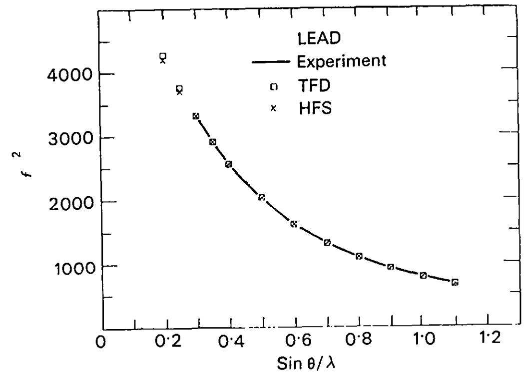

Fig. 3. Lead scattering factors.

lead, except at high angles where they drop off a little too rapidly. None of the calculations are in good agreement with the experimental values for mercury, but the TFD is best at high angles (relative to sin $\theta/\lambda = 0{\cdot}6$) and the TFD, and HFS are better than the others at low angles.

Discussion

It should be noted that improper normalization of the data to the initial scattering factor values and termination effects due to the finite range of data also produce oscillations in $G(r)$ at small values of r. The latter, however, are easily removed because of their characteristic forms (KSA), and they have been removed in the curves shown in Fig. 2. Errors in correcting for Compton modified scattering, for which the theoretical values may not be known precisely, might also introduce oscillations in $G(r)$ which could be mistaken for an erroneous shape in the f^2 function, particularly at large angles. In these experiments, however, the Compton corrections were negligible, because of the large atomic numbers of the elements, and because the monochromator in the diffracted beam eliminated the modified scattering at high angles. If the Compton corrections were at fault, the error would be expected to be considerably worse for tin than the two heavier elements. In fact, the tin results are seen to be in excellent agreement with the most recent calculations.

It is interesting to note that the TFD calculations are in best agreement with the high angle shapes for both lead and mercury; in the latter instance the TFD shows no negative deviation. This result is surprising since the energy terms calculated from other wave functions are in better agreement with experimental values (Cohen, 1960). For both these elements, however, the complex part of the dispersion correction amounts to about 15% of f^2 at sin $\theta/\lambda = 1{\cdot}1$ compared with 6% at sin $\theta/\lambda = 0{\cdot}6$. The distinction between the various calculations therefore lies within the alteration in shape caused by the theoretical dispersion terms, which have not been separately validated. There does not appear to be an explanation for the low angle mercury deviations, but the low angle fits for tin and

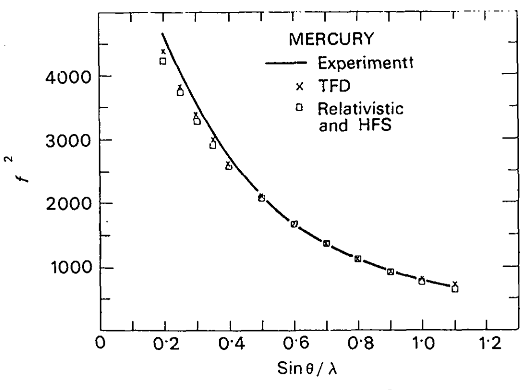

Fig. 4. Mercury scattering factors.

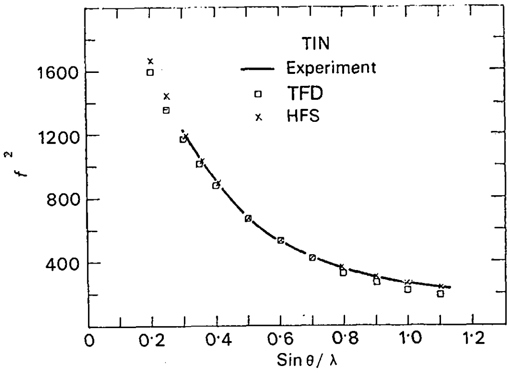

Fig. 5. Tin scattering factors.

lead indicate that these are not due to systematic experimental errors.

With respect to experimental errors, it is apparent that the derived values of f^2 will be in error to the same extent that the measured intensities are in error. However, if sufficient care is taken in the alignment of the diffractometer and in the recording of the data, the relative intensities should be quite exact. In particular, with liquid specimens one need not worry about extinction, preferred orientation, Debye–Waller factors or the separation of peak and diffuse intensity, all of which are possible sources of error when using solid specimens to check the shape of f^2.*

We are grateful for the use of the facilities of the M.I.T. Computation Center. We wish to thank A. J. Freeman and R. E. Watson for the use of their unpublished results. We appreciate, also, the sponsorship by the Office of Naval Research, whose continuing support has made this work possible.

References

COHEN, S. (1960). *Phys. Rev.* **118**, 489.
CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
CROMER, D. T., LARSON, A. C. & WABER, J. T. (1964). *Acta Cryst.* **17**, 1044.
CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104.
DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **8**, 841.
FREEMAN, A. J. & WATSON, R. E. (1965). Private communication of unpublished results.
HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
IBERS, J. A. (1958). *Acta Cryst.* **11**, 447.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JAMES, R. W. (1954). *The Optical Principles of the Diffraction of X-rays.* London: Bell.
KAPLOW, R., STRONG, S. L. & AVERBACH, B. L. (1965). *Phys. Rev.* **138**, A1336.

---

* A multiple scattering correction is required, however, when elements of low absorption are investigated.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1965). **19**, 1046

Crystal data for monobenzoylosmocene.

By A. C. MACDONALD and J. TROTTER, *Department of Chemistry, University of British Columbia, Vancouver* 8, *B.C., Canada*

(*Received* 28 *June* 1965)

Crystals of monobenzoylosmocene, C_5H_5.Os.C_5H_4.CO.C_6H_5, are yellow needles (Rausch, Fischer & Grubert, 1960) elongated along **a**. The unit-cell dimensions and space group were determined from rotation, Weissenberg and precession films, and on the General Electric Spectrogoniometer.

Crystal data (λ, Cu $K\alpha$ = 1·5418 Å; λ, Mo $K\alpha$ = 0·7107 Å).
Monobenzoylosmocene, $C_{17}H_{14}OOs$; M.W. 424·5; m.p. 134·5 °C.
Monoclinic, a = 6·07, b = 15·49, c = 14·53 Å, β = 106°40′.
U = 1308·8 Å^3.
D_m (flotation in aqueous silver nitrate) = 2·18, Z = 4, D_x = 2·15$_4$ g.cm^{-3}.
Absorption coefficients for X-rays: μ(Cu $K\alpha$) = 185 cm^{-1}, μ(Mo $K\alpha$) = 103 cm^{-1},
F(000) = 800.
Absent reflexions: $h0l$ when l is odd, $0k0$ when k is odd.
Space group $P2_1/c$ (C_{2h}^5).

No further work is planned.

The authors thank Dr M. D. Rausch for the crystal sample, the National Research Council of Canada for financial support, and the Department of Scientific and Industrial Research, United Kingdom, for a research studentship (to A.C.M.).

References

RAUSCH, M. D., FISCHER, E. O. & GRUBERT, H. (1960). *J. Amer. Chem. Soc.* **82**, 76.