

Acta Cryst. (1959). **12**, 412

Elimination of film shrinkage error in Weissenberg photographs. By SURENDRA NATH SRIVASTAVA,
Department of Physics, Allahabad University, Allahabad, India

(Received 29 November 1958 and in revised form 23 February 1959)

The unit-cell dimensions of a crystal are usually determined from Weissenberg photographs. For obtaining accurate values, it is essential to correct the values of Bragg angles of different reflexions for the errors arising due to 'film shrinkage' and uncertainty in the radius of the film due to its finite thickness.

These errors can be eliminated by the method of Bradley & Jay (1932), by casting on the film shadows of two knife edges at known angular separation. The second method, most commonly employed in this laboratory is to sprinkle pure aluminium dust on the crystal, so that powder photograph of aluminum is superimposed on the Weissenberg photograph of the crystal. Since the angles for the powder lines of aluminum are known, the film may be completely calibrated.

A method given in this note requires neither the sharp edges nor the standard substance for correcting the film of zero-layer Weissenberg photographs.

Consider the zero-layer Weissenberg photographs with b as the rotation axis. Let $h0l$ and $h0\bar{l}$ reflections be separated by a distance p along the translation of the film. Let us take the direction of motion of the film as the X axis and perpendicular to that as Y axis. It is easy to see that the distance p along the X axis corresponds to the distance of translation of the film, during which the crystal has rotated by 180° , since the two reflections are due to the $h0l$ and $\bar{h}0\bar{l}$ planes. In zero-layer photographs, Bragg planes are parallel to the rotation axis, which

therefore will give straight streaks of white radiation in Weissenberg photographs. Taking the angle of inclination of these streaks to the X axis as ψ , we can easily see that $p \tan \psi$ in Y -direction will also correspond to 180° of rotation of the crystal. Thus a knowledge of the Y coordinates only of the reflections will yield the Bragg angles θ in degrees of reflections by the following relation

$$\theta = 180Y/(p \tan \psi)$$

$\tan \psi$ may be determined from the coordinates of any two points on a very prominent white-radiation streak. Substituting this value of $\tan \psi$ to the above relation, all the quantities are known absolutely, and hence the film shrinkage errors are eliminated automatically without any extra standard line.

The Bragg angles which differed by even more than 3° on different films for Anthrone crystal, before this correction is applied, were found to agree within 0.5° (which corresponds to 0.5 mm. for the camera used by us).

The author is grateful to Prof. K. Banerjee for his very valuable suggestions and kind encouragement.

Reference

BRADLEY, A. J. & JAY, A. H. (1932). *Proc. Phys. Soc. Lond.* **44**, 563.

Acta Cryst. (1959). **12**, 412

On an analytic approximation to the atomic scattering factor. By J. B. FORSYTH and M. WELLS,
Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

(Received 22 December 1958)

In a recent paper by Vand, Eiland & Pepinsky (1957) it was shown that the atomic scattering factor, f , can be approximated as a function of $\sin \theta = x$, as far as $\theta = 90^\circ$ for Cu $K\alpha$ by an expression of the form

$$f(x) = A \exp(-ax^2) + B \exp(-bx^2)$$

and it was suggested that a better fit as far as $\theta = 90^\circ$ for Mo $K\alpha$ could be obtained by an expression

$$f(x) = A \exp(-ax^2) + B \exp(-bx^2) + C$$

We have calculated values of the parameters A, a, B, b and C using the following modifications to the method of Vand, Eiland & Pepinsky (1957):

(1) We have chosen as our reciprocal-space variable $s = \sin \theta / \lambda$ rather than $x = \sin \theta$; the values of a and b are then independent of the value of λ .

(2) We have relaxed the condition that

$$A + B + C = N$$

where N is the number of electrons in the atom or ion; the enforcement of this condition is equivalent to giving the point for $s = 0$ a weight equal to the sum of the weights of all the other points fitted, and we feel that its relaxation allows an improved fit over the more useful range of s values.

(3) Since most of the data used in crystallographic work occur around $s = 0.5$, we have applied a weighting factor of the form $\exp\{-(s-0.5)^2\}$ to the least-squares fitting procedure so that the 'middle' of the curve has the best agreement with the tabulated data.

The least-squares fitting was performed on EDSAC II using as an initial approximation the values given by Vand, Eiland & Pepinsky (1957) after suitable conversion of the values of a and b ; the results obtained are given in Table 1 together with the value of

$$\varepsilon = \frac{100}{f_0} \left(\frac{\sum \omega_i \delta_i^2}{\sum \omega_i} \right)^{\frac{1}{2}}$$

Table 1. *Analytic constants for some previously published scattering factors*

		<i>A</i>	<i>a</i>	<i>B</i>	<i>b</i>	<i>C</i>	ϵ
H	MeW	0.3882	7.151	0.6011	30.18	0.0076	0.3465
He	MeW	0.9144	3.078	1.045	11.51	0.0370	0.1597
Li	MeW	1.731	2.652	1.072	110.3	0.1767	0.5553
Be	B	1.621	1.531	2.096	53.27	0.2631	0.2926
B	VO	1.574	1.210	2.936	54.04	0.4026	0.9660
C	B	1.455	1.462	3.775	22.49	0.7241	0.5178
N	B	1.459	2.001	4.471	17.02	1.023	0.4807
O	B	2.113	2.867	4.637	14.75	1.211	0.4048
F	B	3.258	3.484	4.360	15.44	1.344	0.3758
F ⁻	B	4.408	4.565	4.101	24.91	1.406	0.6035
Ne	B	4.032	3.189	4.538	12.52	1.397	0.2658
Na	B	7.525	4.016	1.755	52.84	1.616	0.7921
Mg	VO	7.507	3.354	2.781	60.34	1.661	0.7257
Mg ²⁺	B	4.497	2.022	4.093	6.126	1.402	0.0657
Al	VO	7.675	2.834	3.411	67.03	1.772	0.8457
Si	VO	7.741	2.395	4.275	69.49	1.862	0.6517
Si ₄ ⁺	B	5.138	1.459	3.442	3.982	1.420	0.0193
P	VO	7.680	1.946	5.334	50.51	1.874	0.4182
S	VO	7.603	1.637	6.354	39.98	1.924	0.3877
Cl	VO	7.511	1.328	7.487	31.76	1.881	0.3743
Cl ⁻	B	7.579	1.328	8.336	27.01	1.955	0.4024
A	B	7.430	1.087	8.616	19.31	1.884	0.2460
K ⁺	B	7.330	0.8785	8.860	14.48	1.759	0.1779
Ca	B	7.325	1.807	8.301	19.59	3.787	1.318
Cr	VO	8.442	2.052	10.17	20.21	4.648	1.322
Cr ²⁺	B	6.839	1.575	10.44	10.77	4.581	0.4178
Fe	VO	11.04	2.788	8.630	24.38	5.441	1.413
Co	VO	12.13	2.890	8.308	23.44	5.671	1.341
Ni	VO	12.76	2.637	8.638	19.88	5.650	1.263
Cu	VO	12.87	2.288	9.932	13.92	5.583	0.7682
Cu ⁺	B	12.85	2.401	9.215	10.13	5.853	0.2435
Zn	B	17.07	3.091	6.338	25.40	6.372	0.5615
Ga	B	18.27	3.031	5.919	31.45	6.533	0.5983
Ge	B	19.11	2.887	5.968	38.88	6.637	0.5903
As	B	19.31	2.616	6.864	35.61	6.642	0.4421
Rb ⁺	B	19.51	1.759	9.886	21.53	6.527	0.1642
Se	JB	15.36	1.980	11.44	21.84	6.804	0.5638
Br	JB	15.73	1.950	11.81	21.41	7.082	0.5660
Kr	JB	16.18	1.933	12.09	21.43	7.336	0.5741
Sr	JB	17.18	1.906	12.60	21.38	7.814	0.5688
Y	JB	17.63	1.878	12.89	20.92	8.066	0.5550
Zr	JB	18.18	1.861	13.13	20.85	8.270	0.5356
Nb	JB	18.52	1.879	13.39	20.38	8.676	0.5234
Mo	JB	18.97	1.854	13.65	19.89	8.903	0.5558
Ma	JB	19.33	1.842	14.00	19.72	9.172	0.5681
Ru	JB	19.66	1.797	14.43	19.00	9.359	0.6067
Rh	JB	20.15	1.824	14.54	19.24	9.771	0.5883
Pd	JB	20.72	1.818	14.66	19.11	10.05	0.6150
Ag	JB	21.23	1.857	14.67	19.20	10.50	0.6206
Cd	JB	21.67	1.793	15.13	19.01	10.57	0.6220
In	JB	22.03	1.750	15.59	18.46	10.75	0.6094
Sn	JB	22.32	1.722	16.06	17.93	10.98	0.6011
Sb	JB	23.00	1.745	16.04	18.16	11.34	0.5715
Te	JB	23.38	1.710	16.43	17.69	11.56	0.5747
I	JB	23.98	1.699	16.61	17.93	11.77	0.5745
Xe	JB	24.27	1.647	17.22	17.44	11.87	0.5353
Cs	JB	24.98	1.786	16.74	18.56	12.76	0.4619
Ba	JB	25.47	1.742	17.15	18.16	12.86	0.4589
La	JB	25.58	1.649	17.91	16.98	12.87	0.5372
Ce	JB	25.97	1.585	18.52	16.38	12.86	0.5462
Pr	JB	26.46	1.610	18.53	16.53	13.33	0.5387
Nd	JB	26.97	1.625	18.62	16.73	13.74	0.5173
Il	JB	27.50	1.625	18.82	16.80	14.02	0.5170
Sm	JB	27.74	1.601	19.26	16.36	14.28	0.5413
Eu	JB	28.30	1.587	19.50	16.25	14.49	0.5385
Gd	JB	28.74	1.577	19.77	16.27	14.78	0.5400
Tb	JB	29.16	1.589	19.88	16.04	15.19	0.5814
Dy	JB	29.71	1.610	19.87	16.02	15.62	0.5725
Ho	JB	30.21	1.612	20.09	15.95	15.92	0.5535
Er	JB	30.66	1.597	20.39	15.90	16.13	0.5679
Tu	JB	31.13	1.555	20.83	15.70	16.23	0.5478

Table 1 (cont.)

		A	a	B	b	C	ϵ
Yb	JB	31.55	1.581	20.86	15.76	16.73	0.5866
Lu	JB	32.12	1.582	21.01	16.03	17.04	0.5681
Hf	JB	32.44	1.604	21.15	16.12	17.55	0.5792
T	JB	32.90	1.621	21.25	16.15	18.01	0.5677
W	JB	33.26	1.590	21.69	15.86	18.21	0.5756
Re	JB	33.66	1.558	22.16	15.57	18.33	0.5715
Os	JB	33.98	1.545	22.55	15.39	18.63	0.5625
Ir	JB	34.45	1.523	22.85	15.12	18.79	0.5798
Pt	JB	34.85	1.542	22.61	14.94	19.30	0.7066
Au	JB	35.32	1.502	23.37	14.74	19.35	0.5729
Hg	JB	35.65	1.509	23.56	14.62	19.83	0.5817
Tl	JB	36.83	2.150	19.37	18.86	24.11	1.296
Pb	JB	36.43	1.552	23.70	14.86	20.89	0.5973
Bi	JB	37.03	1.538	23.91	14.72	21.07	0.6055
Po	JB	37.37	1.510	24.31	14.30	21.26	0.6178
85	JB	37.56	1.498	24.76	14.10	21.61	0.6121
Em	JB	38.25	1.487	24.88	13.90	21.76	0.6241
87	JB	38.55	1.485	25.21	13.77	22.11	0.6159
Ra	JB	38.82	1.442	25.86	13.44	22.18	0.6072
Ac	JB	39.36	1.426	26.14	13.24	22.31	0.6173
Th	JB	39.88	1.462	25.98	13.41	22.98	0.5986
Pa	JB	40.21	1.451	26.38	13.31	23.27	0.5872
U	JB	40.59	1.477	26.34	13.35	23.88	0.5977

Source of the atomic scattering factor used:

B: Berghuis *et al.* (1955).

McW: McWeeny (1951).

JB: James & Brindley (1931).

VO: Viervoll & Øgrim (1949).

i.e. the error as a percentage of the scattering factor at $s = 0$.

In preparing Table 1 the most recent published values of the atomic scattering factor have been used. Some new values for scattering factors are listed in Table 2, where the same values of $\sin \theta/\lambda$ as those used by Berghuis *et al.* (1955) have been adopted:

0.00, (0.05), 0.40, (0.1), 1.30 \AA^{-1} .

The integrals

$$\int_0^{r_{\max.}} P^2(r) \frac{\sin \mu r}{\mu r} \cdot dr,$$

where $\mu r = \sin 4\pi r y$ and $P^2(r)$ is the spherically averaged charge density for each group of electron orbitals, were calculated using the Gaussian 12-point formula, each interval being divided into a number of sub-intervals. All interpolations were carried out by the Lagrangian

Table 2. Atomic scattering factors

NS: Electron densities calculated for the normal state

VS: Electron densities calculated for the valence state

X: The electron distribution has been calculated with exchange

	Ca ²⁺	Al ³⁺	Al ⁰	Ti ⁺	Mn ²⁺	Mn ⁰	Fe ⁰	Mo ⁺
$\sin \theta/\lambda$	NSX (1)	NSX (2)	NSX (2)	VSX (3), (4)	VSX (3), (5)	NSX (5)	NSX (6)	VS (7)
0.00	18.00	10.00	13.00	21.00	23.00	25.00	26.00	41.0
0.05	17.72	9.93	12.58	20.60	22.72	24.25	25.41	40.1
0.10	16.93	9.74	11.54	19.52	21.91	22.57	23.95	38.0
0.15	15.77	9.42	10.35	18.04	20.68	20.75	22.15	35.2
0.20	14.41	9.01	9.32	16.39	19.19	19.01	20.36	32.5
0.25	13.01	8.52	8.52	14.77	17.58	17.39	18.65	30.0
0.30	11.71	7.97	7.87	13.27	15.97	15.80	17.05	27.8
0.35	10.57	7.40	7.30	11.94	14.45	14.32	15.54	25.9
0.40	9.62	6.81	6.76	10.80	13.07	12.99	14.15	24.2
0.50	8.26	5.68	5.71	9.08	10.81	10.79	11.76	21.5
0.60	7.39	4.68	4.73	7.95	9.20	9.20	9.95	19.3
0.70	6.75	3.85	3.90	7.21	8.10	8.09	8.64	17.4
0.80	6.22	3.19	3.23	6.65	7.33	7.34	7.72	15.7
0.90	5.70	2.69	2.72	6.16	6.77	6.77	7.07	14.0
1.00	5.10	2.31	2.33	5.76	6.33	6.33	6.57	12.6
1.10	4.68	2.04	2.04	5.28	5.92	5.93	6.19	11.2
1.20	4.18	1.83	1.83	4.78	5.47	5.48	5.77	10.1
1.30	3.77	1.68	1.68	4.38	5.13	5.13	5.40	9.1

(1) Hartree & Hartree (1938).

(2) Froese (1957).

(3) Hartree (1956).

(4) Hartree, private communication.

(5) Hartree (1954).

(6) Wood & Pratt (1957).

(7) Ridley (1955).

4-point method, which produces a cubic fitting curve (Hartree, 1952).

The scattering factors for Al^{3+} , Ca^{2+} , Mn^{2+} and Mn^0 agree with those given by Freeman (1958) to within a few units in the last figure quoted. Freeman's data are given at intervals

$$0.00, (0.1), 1.1 \text{ \AA}^{-1}.$$

The scattering factor curve for Ti^+ does not agree so well, and it is possible that Freeman (1958) has used the $(3d)^3$ wave functions for Ti^+ (Hartree, 1956) with the argon-core scattering factor for Mn; we have used the values for the Ti^{2+} core to compute our curves. Our calculations have been checked with those of Berghuis *et al.* (1955) for Na, Cu^+ , Rb^+ and Ca^0 and the agreement is again good.

As wave functions with exchange are now available for Ti^+ , Mn^{2+} and Cu^+ , interpolations have been made to find the scattering factors for V^{2+} , Cr^{2+} , Co^{2+} and Ni^{2+} . These results are listed in Table 3. The f -values for Fe^0

Table 3. Interpolated atomic scattering factors with allowance for exchange

$\sin \theta/\lambda$	V^{2+}	Cr^{2+}	Co^{2+}	Ni^{2+}
0.00	21.00	22.00	25.00	26.00
0.05	20.70	21.71	24.70	25.69
0.10	19.85	20.86	23.84	24.82
0.15	18.60	19.60	22.46	23.50
0.20	17.10	18.10	21.00	21.92
0.25	15.54	16.51	19.30	20.21
0.30	14.03	14.95	17.60	18.49
0.35	12.66	13.48	16.00	16.85
0.40	11.46	12.21	14.52	15.32
0.50	9.59	10.16	12.04	12.72
0.60	8.33	8.74	10.19	10.74
0.70	7.48	7.77	8.86	9.29
0.80	6.87	7.10	7.92	8.25
0.90	6.38	6.57	7.24	7.49
1.00	5.95	6.17	6.74	6.92
1.10	5.49	5.70	6.27	6.50
1.20	5.05	5.26	5.86	6.05
1.30	4.67	4.92	5.48	5.63

given in Table 2 were not used in the interpolation as the $(3d)$ wave functions vary considerably with a change in the state of ionization. The wave functions for iron (Wood & Pratt, 1957) were calculated using the unrestricted Hartree-Fock method, and include the effect of exchange polarization arising from the net spin of the atom. This produces a more compact atom and the

f -curve is displaced from its interpolated value towards the curve for cobalt. It seems probable that the interpolated values for Co^{2+} and Ni^{2+} may be a little low for the same reason, though the exchange polarization effect would be smaller than for iron. The interpolated values for V^{2+} do not agree well with those of Freeman (1958), and it is thought that this may be for the same reason as in the case of Ti^+ .

The constants of the analytic expression for these new scattering factors are given in Table 4.

One of us (M. W.) wishes to thank the Department of Scientific and Industrial Research for the award of a Research Studentship. This research forms part of a project supported by the Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office, under Contract No. AF. 61(052)-50.

Dr R. J. Weiss supplied the figures for the argon-core charge density of Ti^{2+} which were contained in a private letter from the late Prof. D. R. Hartree.

We are indebted to Prof. N. F. Mott, Dr W. H. Taylor and Dr H. D. Megaw for the provision of facilities and for their interest and encouragement, and we wish to thank Dr M. V. Wilkes, of the Mathematical Laboratory, for permission to use the EDSAC.

References

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 FREEMAN, A. J. (1958). Quarterly Progress Report No. 28. Solid State and Molecular Theory Group. Massachusetts Institute of Technology.
 FROESE, C. (1957). *Proc. Camb. Phil. Soc.* **53**, 206.
 HARTREE, D. R. & HARTREE, W. (1938). *Proc. Roy. Soc. A*, **164**, 167.
 HARTREE, D. R. (1952). *Numerical Analysis*, p. 84. Oxford: University Press.
 HARTREE, D. R. (1954). *Proc. Camb. Phil. Soc.* **51**, 126.
 HARTREE, D. R. (1956). *J. Opt. Soc. Amer.* **46**, 350.
 JAMES, R. W. & BRINDLEY, G. W. (1931). *Phil. Mag.* (7), **12**, 81.
 McWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 RIDLEY, E. C. (1955). *Proc. Camb. Phil. Soc.* **51**, 702.
 WOOD, J. H. & PRATT, G. W. (1957). *Phys. Rev.* **107**, 995.
 VAND, V., EILAND, P. F. & PEPINSKY, R. (1957). *Acta Cryst.* **10**, 303.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.

Table 4. Analytic constants for the new scattering factors proposed in this paper

	A	a	B	b	C	ϵ
Ca^{2+}	7.062	0.8174	8.893	11.63	2.017	0.1318
Al^{3+}	5.151	1.806	3.402	5.078	1.442	0.0402
Al^0	7.622	2.492	3.697	39.84	1.655	0.2445
Ti^+	6.523	1.288	10.50	11.88	3.808	0.4898
Mn^{2+}	6.742	1.447	11.53	8.418	4.659	0.2397
Mn^0	12.40	3.343	6.625	24.07	5.653	0.9000
Fe^0	13.68	3.227	6.297	22.52	5.829	0.6564
Mo^+	19.93	1.442	13.09	18.78	7.668	0.4600
V^{2+}	6.335	1.166	10.71	9.761	3.885	0.2649
Cr^{2+}	6.502	1.331	11.08	9.203	4.340	0.2679
Co^{2+}	8.822	2.077	10.56	9.206	5.565	1.555
Ni^{2+}	10.35	2.173	9.919	9.328	5.679	0.8194