Acta Cryst. (1962). **15**, 182

The Analytical Representation of Atomic Scattering Amplitudes for Electrons

By G. H. Smith and R. E. Burge

Medical Research Council, Biophysics Research Unit and Wheatstone Physics Laboratory,
University of London, King's College, Strand, W.C. 2, England

(*Received* 24 *March* 1961 *and in revised form* 18 *May* 1961)

A single analytical expression to represent the published values of the atomic scattering amplitudes for electrons $f_e(x)$ is given, and the parameters are determined for elements $Z=1$–18 and 20–104. Three terms are sufficient to fit the data accurately for all elements and all values of $f_e(x)$ are given equal weight. The standard deviation has an average value of 0·22% of $f_e(0)$.

Introduction

In connection with the preparation of the third volume of the *International Tables for Crystallography* Ibers (1958), Vainshtein & Ibers (1958) and Ibers & Vainshtein (1959) have published values of the atomic scattering amplitudes for electrons $f_e(x)$ for specific values of $x=\sin\theta/\lambda$ and for elements with atomic numbers Z in the ranges 1–18 and 20–104. In view of the importance of $f_e(x)$ both in electron diffraction, where Fourier methods are being used increasingly (e.g. Cowley & Rees, 1958), and in a study of the contrast arising by elastic electron scattering in electron microscopy (for references see Burge & Smith, 1961), it was considered desirable to express $f_e(x)$ for each element by a single analytical expression from which values could be calculated for any value of x and any electron energy.

The data given by Ibers & Vainshtein cover the range of x from 0 to 1·0 Å^{-1} for the elements $Z=1$–18 and the range from 0 to 1·5 Å^{-1} for $Z=20$–104. The atomic model used in the calculation of $f_e(x)$ is listed in Table 2 together with the corresponding analytic constants for the elements concerned.

A number of analytical expressions for $f(x)$ have been published (Vand, Eiland & Pepinsky, 1957; Freeman & Smith, 1958; Forsyth & Wells, 1959; Silverman & Simonsen, 1960). The forms of the curves for $f(x)$ and $f_e(x)$ are sufficiently similar to justify the assumption that any of these analytical forms would also fit the data for $f_e(x)$.

The analytical representation of $f_e(x)$

It was decided to use the expression

$$f_e(x) = \sum_j A_j \exp(-B_j x^2)\,, \tag{1}$$

since it was considered important that the terms should be of the same form with constant A_j and B_j for all values of x and that the terms should be easy to integrate over a range of x (for this application to the theory of elastic electron scattering at very small angles, see Burge & Smith, 1961). It was found that for all elements, only three terms in equation (1) were necessary to give a good fit.

Criterion of goodness of fit

The difference between the data value of the atomic scattering amplitude $f_e(x)$ and the analytical value $e(x)$ for each point was expressed as a percentage of $f_e(x)$ given by

$$G(x) = \left[\frac{e(x)-f_e(x)}{f_e(x)}\right]\times 100\,. \tag{2}$$

The sum of the squares of the percentage errors was then given by

$$W = \sum_{i=1}^{M}[G_i(x)]^2\,, \tag{3}$$

where M was the number of data points available, and W was minimized to give the best possible fit.

Equation (2) (Freeman & Smith, 1958) was regarded as a better criterion than expressing the difference between $e(x)$ and $f_e(x)$ as a percentage of $f_e(0)$ (Vand *et al.*, 1957), since it ensures the same degree of fit along the whole length of the curve. When the best fit had been obtained the standard deviation of the analytical curve from the data was expressed as a percentage of $f_e(0)$, by the equation

$$Y = (100/f_e(0)M^{\frac{1}{2}})\left\{\sum_{i=1}^{M}[e(x_i)-f_e(x_i)]^2\right\}^{\frac{1}{2}}\,. \tag{4}$$

Method of evaluating constants

(*a*) *First approximation* (*two terms*)

Initially two terms of equation (1) were considered. If the fit is perfect then

$$f_e(x)=A_1\exp(-B_1x^2)+A_2\exp(-B_2x^2)\,. \tag{5}$$

When $x=0$, then

$$A_2=f_e(0)-A_1\,. \tag{6}$$

In general one of the two exponential terms in equation (5) will decay faster than the other with increasing values of x; if $A_1\exp(-B_1x^2) \gg A_2\exp(-B_2x^2)$ for large x, and x_M is the largest value of x for which $f_e(x)$ is tabulated, we have, to a first approximation,

$$f_e(x_M) = A_1 \exp\left(-B_1 x_M^2\right),$$

i.e.

$$B_1 = (-1/x_M^2) \ln\left(f_e(x_M)/A_1\right). \tag{7}$$

Substituting equations (6) and (7) in (5) gives

$$f_e(x) = A_1 \exp\left\{-(x/x_M)^2 \ln A_1/f_e(x_M)\right\} + (f_e(0) - A_1) \exp\left\{-B_2 x^2\right\}, \tag{8}$$

which contains only two unknown constants, A_1 and B_2.

Hence for any value of A_1,

$$B_2 = (-1/x^2) \times \ln\left\{\frac{f_e(x) - A_1 \exp\left[-(x/x_M)^2 \ln\left(A_1/f_e(x_M)\right)\right]}{f_e(0) - A_1}\right\}. \tag{9}$$

If the table contains M values of $f_e(x)$, equation (9) gives M values for the constant B_2, with an arithmetic mean $\bar{B}_2$, corresponding to the constant A_1.

Substituting $\bar{B}_2$ and A_1 in (8), gives the M values of $e(x)$. Hence $G(x)$ can be found for each point from equation (2) and W_1, the sum of the squares of the percentage difference, from (3).

Initially a very small value of A_1 was chosen (0·0001), and this was increased in steps of 0·1 until the condition

$$W_T - W_{(T-1)} > 0 \tag{10}$$

was satisfied, where T denotes the number of cycles, i.e. the number of values of A_1 tried.

When equation (10) is satisfied, the minimum value of W has been passed, and A_1 was changed in steps of $-0·01$ until equation (14) was again satisfied. The process was repeated, multiplying the increment by $-0·1$ each time until A_1 had reached a pre-set accuracy. This, together with the corresponding values of B_1, A_2, and B_2, gives the best fit with the approximations made.

(*b*) *Second approximation* (two terms)

The restrictions given by equations (6) and (7) were relaxed giving four independent variables. Using the method of Vand *et al.* (1957) we have, providing ΔA_j and ΔB_j are small,

$$\Delta e(x) = \sum_{j=1}^{2} \left(\frac{\partial e(x)}{\partial A_j} \Delta A_j + \frac{\partial e(x)}{\partial B_j} \Delta B_j\right) \tag{11}$$

and

$$\frac{\partial e(x)}{\partial A_j} = \exp\left(-B_j x^2\right)$$

$$\frac{\partial e(x)}{\partial B_j} = -A_j x^2 \exp\left(-B_j x^2\right). \tag{12}$$

This gives M equations for determining four unknowns (ΔA_1, ΔB_1, ΔA_2, ΔB_2). The equations were solved by the standard least-squares method. Table 1 (columns 3 to 5) gives the results obtained for gold at this stage.

(*c*) *Three-term approximation*

The three-term expression for $f_e(x)$ was then used, taking the final values of A_1, B_1, A_2, B_2 from part (*b*), and setting $A_3 = B_3 = 0$. Table 1 shows the results for gold; these are typical of those calculated for other elements.

The values of $e(x) - f_e(x)$ expressed as a percentage of $f_e(0)$ are included in Table 1; this criterion was not used in the calculations, but is inserted to illustrate the difference between it and the criterion adopted, which is shown in the preceding column.

Table 1. *A comparison of the two-term and three-term approximations to* $f_e(x)$ *for gold*

		Two terms			Three terms		
x	$f_e(x)$	$e(x)$	$\frac{100[e(x)-f_e(x)]}{f_e(x)}$	$\frac{100[e(x)-f_e(x)]}{f_e(0)}$	$e(x)$	$\frac{100[e(x)-f_e(x)]}{f_e(x)}$	$\frac{100[e(x)-f_e(x)]}{f_e(0)}$
0 Å^{-1}	12·90	12·70	−1·51	−1·51	12·90	−0·01	−0·01
0·05	12·45	12·32	−1·04	−1·01	12·42	−0·22	−0·22
0·10	11·13	11·26	1·17	1·01	11·16	0·31	0·26
0·15	9·51	9·77	2·70	1·99	9·53	0·17	0·13
0·20	7·92	8·14	2·78	1·71	7·92	−0·04	−0·02
0·25	6·60	6·64	0·57	0·29	6·58	−0·34	−0·18
0·30	5·58	5·41	−3·03	−1·31	5·55	−0·47	−0·20
0·35	4·78	4·50	−5·84	−2·16	4·78	0·02	0·01
0·40	4·14	3·87	−6·58	−2·11	4·17	0·74	0·24
0·50	3·19	3·13	−1·89	−0·47	3·22	1·02	0·25
0·60	2·53	2·69	6·21	1·22	2·52	−0·44	−0·09
0·70	2·05	2·31	12·76	2·03	2·02	−1·61	−0·26
0·80	1·70	1·95	14·91	1·96	1·67	−1·72	−0·23
0·90	1·43	1·62	12·95	1·44	1·43	−0·27	−0·03
1·00	1·22	1·31	7·06	0·67	1·24	1·60	0·15
1·10	1·05	1·03	−1·64	−0·13	1·08	3·19	0·26
1·20	0·92	0·80	−13·19	−0·94	0·94	2·66	0·19
1·30	0·80	0·60	−24·51	−1·52	0·82	2·13	0·13
1·40	0·71	0·45	−37·10	−2·04	0·70	−1·45	−0·08
1·50	0·64	0·32	−49·54	−2·46	0·59	−7·38	−0·37
		S.D. = 1·53% of $f_e(0)$			S.D. = 0·19% of $f_e(0)$		

Table 2

(*a*) Analytic constants for the electron scattering amplitudes ($Z=1$–18)

Z	A_1	B_1	A_2	B_2	A_3	B_3	$Y\%$	Ref.
1	0·2022	30·8679	0·2437	8·5444	0·0825	1·2726	0·10	E
2	0·052	17·333	0·196	5·686	0·120	0·980	0·09	H
3	1·772	105·507	1·217	24·456	0·304	1·863	0·40	HF
4	1·333	63·623	1·426	16·206	0·323	1·486	0·21	HF
5	1·046	47·281	1·399	11·983	0·356	1·361	0·34	HF
6	0·462	52·702	1·488	11·734	0·463	1·452	0·72	HF
7	0·331	52·839	1·359	9·817	0·498	1·319	0·32	HF
8	0·303	38·003	1·177	8·193	0·524	1·230	0·23	HF
9	0·206	46·008	1·092	8·334	0·618	1·273	0·22	I
10	0·174	47·002	1·011	7·824	0·659	1·233	0·25	HF
11	2·613	102·813	1·368	16·207	0·896	1·520	0·38	HF
12	2·578	62·166	1·599	13·634	0·837	1·313	0·21	HF
13	3·289	41·567	1·431	9·456	0·726	1·070	0·41	I
14	2·447	43·317	2·359	13·290	0·848	1·204	0·37	H
15	1·784	39·795	2·729	12·216	0·855	1·170	0·28	H
16	1·472	36·984	2·756	10·493	0·823	1·050	0·41	H
17	0·728	55·553	3·103	11·703	1·006	1·235	0·60	I
18	0·268	538·892	3·150	13·345	1·291	1·542	0·55	HF

E: Exact; I: Interpolation; H: Hartree (Hydrogen-like atom method); HF: Hartree Fock.

(*b*) Analytic constants for the electron scattering amplitudes ($Z=20$–104). Based on T.F.D. model

Z	A_1	B_1	A_2	B_2	A_3	B_3	$Y\%$
20	2·670	28·184	1·956	5·739	0·722	0·665	0·36
21	2·811	28·254	2·014	5·450	0·719	0·638	0·35
22	2·872	28·795	2·112	5·576	0·758	0·642	0·19
23	3·035	27·450	2·084	5·254	0·766	0·625	0·19
24	3·033	28·656	2·229	5·536	0·821	0·642	0·16
25	3·213	26·504	2·167	5·109	0·806	0·604	0·15
26	3·292	27·225	2·264	5·116	0·831	0·602	0·22
27	3·367	26·715	2·296	5·130	0·866	0·603	0·18
28	3·382	27·163	2·399	5·216	0·899	0·607	0·21
29	3·535	26·480	2·396	4·963	0·900	0·590	0·16
30	3·558	26·885	2·496	5·063	0·931	0·590	0·18
31	3·563	28·112	2·630	5·294	0·987	0·607	0·21
32	3·693	27·373	2·629	5·176	1·005	0·603	0·18
33	3·708	27·925	2·716	5·307	1·055	0·615	0·19
34	3·785	27·657	2·754	5·297	1·086	0·619	0·18
35	3·822	28·247	2·854	5·290	1·105	0·614	0·16
36	3·930	27·397	2·841	5·105	1·110	0·596	0·18
37	4·018	27·126	2·885	5·032	1·119	0·587	0·18
38	4·047	27·610	2·963	5·156	1·167	0·597	0·18
39	4·129	27·548	3·012	5·088	1·179	0·591	0·17
40	4·105	28·492	3·144	5·277	1·229	0·601	0·17
41	4·237	27·415	3·105	5·074	1·234	0·593	0·18
42	4·294	27·501	3·162	5·103	1·263	0·593	0·18
43	4·318	28·246	3·270	5·148	1·287	0·590	0·15
44	4·358	27·881	3·298	5·179	1·323	0·594	0·18
45	4·431	27·911	3·343	5·153	1·345	0·592	0·17
46	4·436	28·670	3·454	5·269	1·383	0·595	0·17
47	4·499	28·259	3·483	5·196	1·392	0·587	0·19
48	4·623	27·995	3·482	5·083	1·410	0·586	0·18
49	4·633	27·983	3·547	5·136	1·441	0·589	0·18
50	4·628	28·786	3·659	5·258	1·483	0·594	0·18
51	4·684	28·559	3·679	5·226	1·509	0·593	0·19
52	4·785	27·999	3·688	5·083	1·500	0·581	0·19
53	4·761	28·670	3·786	5·273	1·568	0·598	0·17
54	4·881	28·016	3·767	5·105	1·565	0·584	0·19
55	4·890	28·839	3·884	5·207	1·597	0·586	0·19
56	4·933	28·610	3·907	5·192	1·627	0·589	0·18
57	4·940	28·716	3·968	5·245	1·663	0·594	0·19
58	5·007	28·283	3·980	5·183	1·678	0·589	0·18
59	5·083	28·588	4·043	5·143	1·684	0·581	0·17
60	5·151	28·304	4·075	5·073	1·683	0·571	0·16
61	5·201	28·079	4·094	5·081	1·719	0·576	0·17
62	5·255	28·016	4·113	5·037	1·743	0·577	0·18

Table 2 (*cont.*)

Z	A_1	B_1	A_2	B_2	A_3	B_3	$Y\%$
63	5·286	27·951	4·174	5·026	1·752	0·571	0·19
64	5·225	29·158	4·314	5·259	1·827	0·586	0·20
65	5·272	29·046	4·347	5·226	1·844	0·585	0·19
66	5·332	28·888	4·370	5·198	1·863	0·581	0·19
67	5·376	28·773	4·403	5·174	1·884	0·582	0·20
68	5·436	28·655	4·437	5·117	1·891	0·577	0·20
69	5·441	29·149	4·510	5·264	1·956	0·590	0·18
70	5·529	28·927	4·533	5·144	1·945	0·578	0·19
71	5·553	28·907	4·580	5·160	1·969	0·577	0·19
72	5·588	29·001	4·619	5·164	1·997	0·579	0·18
73	5·659	28·807	4·630	5·114	2·014	0·578	0·18
74	5·709	28·782	4·677	5·084	2·019	0·572	0·19
75	5·695	28·968	4·740	5·156	2·064	0·575	0·19
76	5·750	28·933	4·773	5·139	2·079	0·573	0·17
77	5·754	29·159	4·851	5·152	2·096	0·570	0·19
78	5·803	29·016	4·870	5·150	2·127	0·572	0·17
79	5·849	29·096	4·906	5·130	2·143	0·571	0·19
80	5·841	29·335	4·973	5·198	2·186	0·577	0·18
81	5·932	29·086	4·972	5·126	2·195	0·572	0·19
82	5·953	28·999	5·016	5·121	2·209	0·568	0·18
83	6·091	27·802	4·924	4·927	2·193	0·560	0·16
84	6·070	28·075	4·997	4·999	2·232	0·563	0·17
85	6·133	28·047	5·031	4·957	2·239	0·558	0·17
86	6·137	28·283	5·105	4·981	2·257	0·556	0·17
87	6·201	28·200	5·121	4·954	2·275	0·556	0·17
88	6·215	28·382	5·170	5·002	2·316	0·562	0·17
89	6·278	28·323	5·195	4·949	2·321	0·557	0·18
90	6·264	28·651	5·263	5·030	2·367	0·563	0·18
91	6·306	28·688	5·303	5·026	2·386	0·561	0·18
92	6·345	28·752	5·347	5·008	2·401	0·559	0·19
93	6·323	29·142	5·414	5·096	2·453	0·568	0·19
94	6·415	28·836	5·419	5·022	2·449	0·561	0·19
95	6·378	29·156	5·495	5·102	2·495	0·565	0·20
96	6·460	28·396	5·469	4·970	2·471	0·554	0·19
97	6·502	28·375	5·478	4·975	2·510	0·561	0·18
98	6·548	28·461	5·526	4·965	2·520	0·557	0·19
99	6·526	28·806	5·605	5·038	2·560	0·559	0·18
100	6·559	28·924	5·644	5·044	2·586	0·561	0·19
101	6·570	29·214	5·708	5·070	2·612	0·562	0·19
102	6·619	29·184	5·730	5·055	2·632	0·561	0·21
103	6·598	29·686	5·817	5·142	2·674	0·566	0·20
104	6·627	29·815	5·860	5·161	2·701	0·567	0·21

With three terms, it can be seen that each point is fitted with an error of less than 2% of $f_e(x)$ up to $\sin\theta/\lambda = 1{\cdot}0$ Å^{-1}. This is typical for all elements with $Z > 20$, but for $Z = 1$–18 this accuracy of fit only extends out to 0·6 Å^{-1} in general. For points where the error is larger than 2% the differences are still regarded as being sufficiently small to be ignored for most practical purposes.

Results

The values of the parameters calculated for all elements (excluding $Z = 19$) are listed in Table 2, where the last column gives the standard deviation of the analytical curve expressed as a percentage of $f_e(0)$; the average value of the standard deviation is 0·22%. These values are for electrons of mass m_0.

The relativistic correction is obtained by multiplying the three A parameters by

$$\left[1 - \frac{v^2}{c^2}\right]^{-\frac{1}{2}},$$

where v is the electron velocity and c is the velocity of light.

It is interesting to compare the values of the parameters obtained for different elements. For light atoms ($Z < 20$) the shell structure affects the value of $f_e(x)$ greatly, and hence there are larger fluctuations in the parameters. However, for elements with $Z > 20$, where the T.F.D. model of the atom was used to obtain $f(x)$ and hence $f_e(x)$ the A values were found to increase fairly smoothly with increasing Z, and the values of A_3, for example, lie within 4% of the line

$$\log_{10}(A_3) = 0{\cdot}82\,[\log_{10}(Z) - 1{\cdot}5]\,.$$

Similar equations were obtained for A_1 and A_2. The B parameters did not exhibit any such smooth variation with Z.

We wish to thank Prof. J. T. Randall, F.R.S. for facilities and the University of London Computer Unit for permission to use the digital computer

'Mercury'. One of us (G. H. S.) is indebted to the Medical Research Council for a Research Scholarship.

References

Burge, R. E. & Smith, G. H. (1961). *Proc. Phys. Soc.* (In press).
Cowley, J. M. & Rees, A. L. G. (1958). *Rep. Phys. Soc. Progr.* **XXI**, 165.
Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.
Freeman, H. C. & Smith, J. E. W. L. (1958). *Acta Cryst.* **11**, 819.
Ibers, J. A. (1958). *Acta Cryst.* **11**, 178.
Ibers, J. A. & Vainshtein, B. K. (1959). *Kristallografiya*, **4**, 641.
Silverman, J. N. & Simonsen, S. H. (1960). *Acta Cryst.* **13**, 50.
Vainshtein, B. K. & Ibers, J. A. (1958). *Kristallografiya*, **3**, 416.
Vand, V., Eiland, P. F. & Pepinsky, R. (1957). *Acta Cryst.* **10**, 303.

Acta Cryst. (1962). **15**, 186

The Crystal Structure of K_3SiF_7

By D. L. Deadmore and W. F. Bradley
Illinois State Geological Survey, Urbana, Ill., U.S.A.

(*Received* 24 *March* 1961 *and in revised form* 22 *May* 1961)

A fine-grained homogeneous powder of composition K_3SiF_7 results from dry ignition of K_2SiF_6 to about 700 °C. Analysis of the powder data establishes that K_3SiF_7 is tetragonal with $a = 7{\cdot}740$, $c = 5{\cdot}564$ Å. A calculated powder diffraction diagram for a structure in $P4/mbm\text{–}D_{4h}^5$ agrees with the observed diagram with average departures less than 30%. The structure is a tetragonal honeycomb of composition K_2SiF_6 which adducts strings of alternating K and F ions.

A previous investigation by one of us (Deadmore, 1960) of the thermal stability of K_2SiF_6 in dry air revealed that at temperatures of 700 to 750 °C. it loses SiF_4 until the composition K_3SiF_7 is reached.

The K_3SiF_7 used here was prepared by heating K_2SiF_6 in dry air for 2 hr. at 750 °C. A chemical analysis gave 41·4% K, 10·2% Si, and 47·4% F, which agrees well with the calculated composition of 42·0% K, 10·2% Si, and 47·8% F. The measured density was 2·86 g.cm.$^{-3}$, and the calculated density, using the cell constants given below and $Z=2$, is 2·78 g.cm.$^{-3}$.

The product is fine-grained, and affords only a powder diffraction diagram, but inspection of the data suggests isomorphism with the $(NH_4)_3SiF_7$ crystal analyzed by Hoard & Williams (1942). Powder lines were all found to be indexable on the basis of a tetragonal cell with $a=7{\cdot}740$ and $c=5{\cdot}564$ Å (both ± about 1/20 of 1%), with $a/c=1{\cdot}391$, and a trial structure in $P4/mbm\text{–}D_{4h}^5$ afforded reasonable interatomic distances. The crystallization has a large temperature amplitude, and complete $\alpha_1\text{–}\alpha_2$ resolution is not realized within the range of unambiguous indexing. The accuracy estimate for lattice parameters is based on the absence of significant drift in calculated values between 50° and 70° 2θ with Cu radiation.

The disadvantage of being confined to powder data was in part offset by the advantage that the scattering power of potassium substantially exceeds that of the other constituents, with the result that some large index lines were probably properly indexed to d values as small as 0·889 Å.

Table 1. *Atom parameters for* K_3SiF_7 *in* $P4/mbm$*

$2K_I$	in	$2(a)$	$0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, 0$
$4K_{II}$	in	$4(h)$	$x, x+\frac{1}{2}, \frac{1}{2}$, etc. with $x=0{\cdot}205$
$2Si$	in	$2(d)$	$0, \frac{1}{2}, 0;\ \frac{1}{2}, 0, 0$
$2F_I$	in	$2(b)$	$0, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
$4F_{II}$	in	$4(g)$	$x, x+\frac{1}{2}, 0$, etc. with $x=0{\cdot}155$
$8F_{III}$	in	$8(k)$	$x, x+\frac{1}{2}, z$, etc. with $x=0{\cdot}390$ and $z=0{\cdot}216$

* Correspondence with the Hoard & Williams analysis is effected by the substitution $x=-x$.

Variable parameters are most sensitive to intensities of the reflections for which $h+k$ is odd. Fourteen of these were observed, resolved from neighboring features, among reflections up to $\sin\theta/\lambda=0{\cdot}5$, and five more fell at positions where lines could have been observed if present. The parameters selected in Table 1 are those affording apparent best agreement under an assumption that the six SiF_6 octahedral distances were equal. After application of an arbitrary temperature factor, they give average departures of $|I_o-I_c|/I_o$ of 0·28 (comparable with a reliability factor of about 0·15) for the 14 observations, and calculated intensities for the 5 possibilities not found or doubtful, were all trivial. Eight other $h+k$ odd reflections fell in mutual doublets, for which intensity sums show adequate agreement.