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Analytic Approximations to Form Factors

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Analytical constants are presented which describe the magnetic form factors for the firstgroup transition elements, their ions, and some rare-earth ions. Functions which peak at sin $\theta/\lambda=0$ are represented by a function $A\exp(-ax^2)+B\exp(-bx^2)+C$, where x is sin θ/λ. Contributions such as $\langle j_2\rangle$ and $\langle j_4\rangle$ *etc.*, which are zero at $x=0$, are represented by $[A\exp(-ax^2)+B\exp(-bx^2)+C]x^2$. An estimate for the goodness of fit between the function and its analytic approximation is given for each case.

Introduction

Analytic approximations to form factors are frequently used in the calculation of structure factors in preference to interpolation methods which involve an increase in computing time and, perhaps more importantly, more input data. Forsyth & Wells (1959) have used the expression

$$f(x)=A\exp(-ax^2)+B\exp(-bx^2)+C \quad (1)$$
(where $x=\sin\theta/\lambda$)

to fit X-ray atomic scattering factors, and further tables of the parameters A, a, B, b and C have been published subsequently by Hosoya & Sataka (1963, 1964).

Table 1. *Parameters for* $\langle j_0\rangle$ *scattering functions*

Atom or ion	A	a	B	b	C	ε
Ce^{3+}	0·2291	18·18	0·7897	5·807	−0·0191	0·1086
Pr^{3+}	0·2277	16·11	0·7923	5·277	−0·0204	0·0802
Nd^{3+}	0·2178	15·44	0·8031	4·904	−0·0211	0·0801
Sm^{3+}	0·2252	13·43	0·7964	4·245	−0·0220	0·0559
Eu^{2+}	0·2595	14·11	0·7603	4·092	−0·0205	0·0628
Gd^{3+}	0·2196	12·27	0·8031	3·752	−0·0229	0·0566
Dy^{3+}	0·2214	11·65	0·8014	3·371	−0·0229	0·0354
Er^{3+}	0·2332	10·59	0·7902	3·008	−0·0238	0·0489
Yb^{3+}	0·2316	9·898	0·7901	2·742	−0·0229	0·1223
Sc	0·5498	107·3	0·4493	18·27	−0·00253	0·3124
Sc^{+}	0·4633	54·18	0·5418	14·73	−0·00633	0·1508
Sc^{2+}	0·3910	36·16	0·6184	12·82	−0·00941	0·1585
Sc^{3+}	0·6550	20·84	0·3533	12·04	−0·00970	0·2269
Ti	0·4809	73·56	0·5200	13·67	−0·00450	0·3028
Ti^{+}	0·4243	42·69	0·5823	11·70	−0·00794	0·1381
Ti^{2+}	0·3667	30·66	0·6443	10·41	−0·0111	0·1245
Ti^{3+}	0·3318	22·84	0·6821	9·425	−0·0137	0·1338
V	0·4438	54·56	0·5589	10·86	−0·00607	0·2763
V^{+}	0·4080	34·87	0·5998	9·615	−0·00913	0·1274
V^{2+}	0·3595	26·30	0·6524	8·729	−0·0122	0·0846
V^{3+}	0·3452	19·90	0·6700	7·860	−0·0151	0·0945
Cr	0·4326	45·13	0·5710	8·997	−0·00681	0·2699
Cr^{+}	0·3957	29·01	0·6129	8·082	−0·0101	0·1257
Cr^{2+}	0·3774	21·97	0·6352	7·303	−0·0132	0·0650
Cr^{3+}	0·3574	17·47	0·6587	6·704	−0·0160	0·0607
Mn	0·4208	37·59	0·5834	7·615	−0·00738	0·2632
Mn^{+}	0·4041	25·15	0·6047	6·880	−0·0104	0·1368
Mn^{2+}	0·3714	19·26	0·6418	6·340	−0·0138	0·0510
Mn^{3+}	0·3839	15·11	0·6328	5·727	−0·0170	0·0417
Fe	0·4144	32·16	0·5902	6·578	−0·00758	0·2594
Fe^{+}	0·4062	21·99	0·6027	5·968	−0·0105	0·1421
Fe^{2+}	0·3715	17·49	0·6413	5·632	−0·0133	0·0517
Fe^{3+}	0·3854	13·45	0·6326	5·068	−0·0173	0·1692
Fe^{4+}	0·3924	11·23	0·6275	4·672	−0·0200	0·0252
Co	0·4064	27·45	0·5983	5·727	−0·00763	0·2518

Table 1 (*cont.*)

Atom or ion	A	a	B	b	C	ε
Co^{+}	0·4060	19·60	0·6028	5·267	−0·0103	0·1428
Co^{2+}	0·3749	15·70	0·6375	4·996	−0·0131	0·0575
Co^{3+}	0·3754	12·65	0·6412	4·585	−0·0168	0·0208
Ni	0·4156	23·37	0·5894	4·995	−0·00771	0·2324
Ni^{+}	0·4002	17·62	0·6082	4·706	−0·00989	0·1398
Ni^{2+}	0·3798	14·12	0·6323	4·458	−0·0128	0·0607
Ni^{3+}	0·3684	11·73	0·6476	4·176	−0·0162	0·0245

More recently the determination of magnetic structures by neutron diffraction has led to the solution of relatively complex structures involving non-collinear spin arrays and a multiplicity of magnetically non-equivalent atoms. The consequent development of the appropriate least-squares refinement programs can be simplified by adopting an analytical approximation for the magnetic form factors. In contrast to the X-ray case the deviations from spherical symmetry of the magnetic moment density are frequently large and, in these cases, it is not sufficient to describe the form factor in terms of an angularly independent radial distribution. Watson & Freeman (1961) have calculated the spherical $\langle j_0 \rangle$ and aspherical $\langle j_2 \rangle$ and $\langle j_4 \rangle$ contributions to the form factors for the $3d$ electrons of the iron group transition element series Sc to Cu, and this work has been extended by Blume, Freeman & Watson (1962) to the rare earth ions where the full description requires $\langle j_6 \rangle$, $\langle g_2 \rangle$, $\langle g_4 \rangle$, $\langle g_6 \rangle$ and $\langle g_0 - \frac{1}{2} g_2 \rangle$ terms in addition to those required for the $3d$ elements.

The purpose of this paper is to report, in Tables 1 and 5, values for the analytical constants [equation (1)] required to describe the $\langle j_0 \rangle$ and $\langle g_0 - \frac{1}{2} g_2 \rangle$ contribu-

Table 2. *Parameters for* $\langle j_2 \rangle$ *scattering functions*

Atom or ion	A	a	B	b	C	ε
Sc	20·653	56·897	2·5834	9·3015	0·00833	3·809
Sc^{+}	9·6819	29·638	2·2081	7·0536	0·00937	2·228
Sc^{2+}	6·3663	19·781	1·8414	5·7114	0·00930	1·062
Sc^{3+}	5·6073	14·998	1·4465	5·2351	0·00752	0·5069
Ti	12·726	41·122	2·4102	7·4427	0·01244	3·535
Ti^{+}	7·0006	23·340	1·9611	5·8675	0·01246	1·828
Ti^{2+}	4·9870	16·955	1·7102	4·9451	0·01172	0·9526
Ti^{3+}	3·9338	12·898	1·4327	4·2234	0·01049	0·4913
V^{+}	5·4867	19·584	1·7722	5·0732	0·01529	1·5491
V^{2+}	4·0931	14·989	1·5937	4·3983	0·01403	0·8370
V^{3+}	3·2863	11·801	1·3847	3·8370	0·01274	0·3987
Cr	6·8257	25·561	1·8567	5·2937	0·01905	2·6118
Cr^{2+}	3·4152	13·510	1·5033	3·9839	0·01649	0·6899
Cr^{3+}	2·7839	10·947	1·3432	3·5414	0·01525	0·3294
Mn	5·5273	21·904	1·6815	4·6742	0·02209	2·1958
Mn^{+}	3·8539	15·571	1·5227	4·0849	0·02089	1·1456
Mn^{3+}	2·3850	10·213	1·2967	3·2916	0·01761	0·2504
Fe	5·7627	21·657	1·6054	4·3023	0·02571	2·273
Fe^{+}	3·2912	14·143	1·4210	3·7396	0·02336	0·9610
Fe^{2+}	2·5329	11·575	1·3614	3·4148	0·02163	0·4622
Fe^{4+}	1·7309	8·166	1·1632	2·8445	0·01949	0·1040
Co	3·9059	17·293	1·4373	3·8389	0·02769	1·5703
Co^{+}	2·8812	13·221	1·3549	3·4910	0·02607	0·8148
Co^{2+}	2·2130	10·882	1·3042	3·2067	0·02433	0·3863
Co^{3+}	1·8119	9·0380	1·2000	2·9066	0·02242	0·1712
Ni	3·3991	15·515	1·3249	3·5276	0·03004	1·259
Ni^{+}	2·5094	12·351	1·2931	3·2710	0·02881	0·6758
Ni^{2+}	1·9436	10·274	1·2499	3·0242	0·02686	0·3100
Ni^{3+}	1·6009	8·5706	1·1538	2·7540	0·02474	0·1338
Ce^{3+}	2·1284	8·9174	1·1229	2·8371	0·01108	0·6529
Pr^{3+}	1·8655	8·1948	1·0779	2·6641	0·01199	0·6399
Nd^{3+}	1·6588	8·1717	1·1067	2·6038	0·01364	0·4934
Sm^{3+}	1·3662	7·7069	1·0690	2·4118	0·01555	0·4531
Eu^{2+}	1·4865	7·7951	0·9980	2·3496	0·01543	1·2008
Gd^{3+}	1·1659	7·2776	1·0098	2·2256	0·01734	0·4814
Dy^{3+}	1·0661	7·1524	0·9551	2·0798	0·01816	0·3086
Er^{3+}	0·9824	6·7174	0·8747	1·9053	0·01805	0·2951
Yb^{3+}	0·8636	6·7786	0·8613	1·8515	0·02192	0·3454

Table 3. *Parameters for* $\langle j_4 \rangle$ *scattering functions*

Atom or ion	A	a	B	b	C	ε
Sc	2·3127	19·022	0·5647	4·2687	0·01014	2·430
Sc^{+}	1·1870	7·9530	0·2906	2·4070	0·00350	2·581
Sc^{2+}	1·0152	4·1972	−1·2280	55·241	0·02184	2·333
Sc^{3+}	1·0735	4·0281	−1·2238	29·432	0·01884	1·228
Ti	1·2896	12·885	0·4944	3·3216	0·01135	2·156
Ti^{+}	0·9768	4·3318	−1·3890	112·48	0·02441	3·1002
Ti^{2+}	0·8246	3·4906	−0·9708	42·851	0·02315	1·4970
Ti^{3+}	0·7477	3·0355	−0·8367	24·408	0·02258	0·7036
V^{+}	0·8095	3·6667	−0·9575	68·325	0·02620	2·0910
V^{2+}	0·6982	3·0186	−0·8060	34·797	0·02380	0·9249
V^{3+}	0·6392	2·6655	−0·7021	21·009	0·02322	0·4140
Cr	0·6737	7·4807	0·3388	2·1652	0·00901	1·8320
Cr^{2+}	0·6029	2·6589	−0·6674	28·196	0·02406	0·5579
Cr^{3+}	0·5570	2·3792	−0·5993	18·221	0·02350	0·2559
Mn	0·6098	5·5244	0·2239	1·3058	−0·00699	1·7753
Mn^{+}	0·5990	2·8534	−0·6890	42·223	0·02818	0·9279
Mn^{3+}	0·4910	2·1427	−0·5206	16·011	0·02338	0·1193
Fe	0·6054	3·2286	−0·9535	121·57	0·03446	2·5536
Fe^{+}	0·5273	2·5758	−0·5953	35·271	0·02845	0·6322
Fe^{2+}	0·4725	2·1691	−0·5025	20·608	0·02408	0·1698
Fe^{4+}	0·4115	1·7728	−0·4302	10·977	0·02141	0·0145
Co	0·5275	2·8973	−0·6739	76·357	0·03526	1·8362
Co^{+}	0·4718	2·3685	−0·5151	29·789	0·02895	0·4338
Co^{2+}	0·4240	1·9835	−0·4429	18·148	0·02371	0·0918
Co^{3+}	0·3941	1·7868	−0·4135	13·010	0·02257	0·0492
Ni	0·4763	2·6905	−0·5966	54·957	0·03600	1·3260
Ni^{+}	0·4209	2·1608	−0·4512	25·383	0·02862	0·2550
Ni^{2+}	0·3825	1·8218	−0·3981	16·169	0·02327	0·0517
Ni^{3+}	0·3574	1·6461	−0·3764	11·972	0·02190	0·0286
Ce^{3+}	0·4221	1·7572	−0·4087	14·604	0·01465	0·3034
Pr^{3+}	0·3827	1·5924	−0·3589	12·6798	0·01384	0·3226
Nd^{3+}	0·3565	1·4851	−0·3306	11·2048	0·01359	0·3010
Sm^{3+}	0·3075	1·2546	−0·2842	10·219	0·00961	0·4629
Eu^{2+}	0·2956	1·2777	−0·2746	12·994	0·01142	0·2114
Gd^{3+}	0·2659	1·0646	−0·2358	9·4324	0·00614	0·3345
Dy^{3+}	0·2351	0·9727	−0·2269	9·9402	0·00723	0·2633
Er^{3+}	0·2099	0·8708	−0·1850	9·3512	0·00619	0·2548
Yb^{3+}	0·1939	0·7638	−0·1803	9·2104	0·00160	0·2932

Table 4. *Parameters for* $\langle j_6 \rangle$ *scattering functions*

Ion	A	a	B	b	C	ε
Ce^{3+}	0·13076	0·8650	−0·15173	5·6704	0·00281	0·4212
Pr^{3+}	0·12917	0·9376	−0·13886	4·1666	0·00793	0·4655
Nd^{3+}	0·11089	0·7271	−0·12147	4·4742	0·00245	0·4583
Sm^{3+}	0·10872	0·8963	−0·1282	3·3559	0·01145	0·4941
Eu^{2+}	0·11729	0·30145	−0·10436	6·1637	−0·03682	0·5386
Gd^{3+}	0·09564	0·30904	−0·08487	4·0469	−0·02168	0·3903
Dy^{3+}	0·23632	0·07179	−0·07037	4·4593	−0·17553	0·4542
Er^{3+}	0·01501	0·16841	0·0	0·0	0·0	3·928
Yb^{3+}	0·04002	0·13149	0·0	0·0	0·0	3·693

Table 5. *Parameters for* $\langle g_0 - \frac{1}{2}g_2 \rangle$ *scattering functions*

Ion	A	a	B	b	C	ε
Ce^{3+}	0·3816	9·165	0·6053	2·595	0·0118	0·1441
Pr^{3+}	0·3623	8·435	0·6230	2·432	0·0132	0·1417
Nd^{3+}	0·3429	8·064	0·6408	2·313	0·0149	0·1151
Sm^{3+}	0·3140	7·480	0·6657	2·110	0·0188	0·1051
Eu^{2+}	0·3065	8·304	0·6709	2·127	0·0214	0·1195
Gd^{3+}	0·2822	7·068	0·6939	1·951	0·0227	0·0930
Dy^{3+}	0·2784	6·669	0·6962	1·776	0·0244	0·0906
Er^{3+}	0·2665	6·343	0·7050	1·641	0·0274	0·0947
Yb^{3+}	0·2410	6·271	0·7254	1·560	0·0329	0·0618

Table 6. *Parameters for* $\langle g_2 \rangle$ *scattering functions*

Ion	A	a	B	b	C	ε
Ce^{3+}	0·9191	6·7749	0·7037	1·8889	0·03302	0·5145
Pr^{3+}	0·8083	6·2423	0·6566	1·7520	0·03201	0·3770
Nd^{3+}	0·7188	6·1288	0·6479	1·7225	0·03419	0·3141
Sm^{3+}	0·5969	5·2668	0·5711	1·5302	0·03156	0·1419
Eu^{2+}	0·6575	6·3330	0·6140	1·6486	0·03628	0·3166
Gd^{3+}	0·4955	5·7275	0·5850	1·5452	0·03707	0·2531
Dy^{3+}	0·4583	5·4798	0·5370	1·4323	0·03571	0·2083
Er^{3+}	0·3999	5·4202	0·5134	1·4001	0·03888	0·2036
Yb^{3+}	0·3739	5·0025	0·4661	1·2673	0·03468	0·2358

Table 7. *Parameters for* $\langle g_4 \rangle$ *scattering functions*

Ion	A	a	B	b	C	ε
Ce^{3+}	0·1885	1·1911	−0·1664	8·0750	0·01974	0·3156
Pr^{3+}	0·1649	0·9648	−0·1674	9·0049	0·01319	0·3057
Nd^{3+}	0·1515	0·7873	−0·1554	9·3635	0·00611	0·2377
Sm^{3+}	0·1308	0·7836	−0·1192	6·8486	0·01189	0·4517
Eu^{2+}	0·1296	0·8038	−0·1167	8·5749	0·01217	0·3403
Gd^{3+}	0·1158	0·6692	−0·1152	6·6378	0·00874	0·2259
Dy^{3+}	0·1008	0·6786	−0·1100	6·8429	0·01353	0·4924
Er^{3+}	0·1223	0·2911	−0·0905	8·1898	−0·03044	0·2321
Yb^{3+}	0·1017	0·3201	−0·0675	6·1564	−0·01608	0·2451

tions for the form factors given by Watson & Freeman (1961) and Blume *et al.* (1962), and, in addition, to propose a new form of approximation to the asymmetric contributions which are zero at $\sin\theta/\lambda = 0$. This expression is given by

$$\langle j_n \rangle = [A \exp(-ax^2) + B \exp(-bx^2) + C]x^2, \quad (2)$$
$$n = 2, 4, 6 \text{ etc.}$$

[Equation (2) is suitable for describing data which increase monotonically with increasing $\sin\theta/\lambda$ from zero at the origin to a maximum value, and thereafter decrease monotonically.] Tables 2, 3, 4, 6, 7 and 8 contain the constants for these aspherical contributions.

Table 8. *Parameters for* $\langle g_6 \rangle$ *scattering functions*

Ion	A	a	B	b	C	ε
Ce^{3+}	0·04187	0·2535	0	0	0	4·122
Pr^{3+}	0·03632	0·18472	0	0	0	3·911
Nd^{3+}	0·03164	0·11471	0	0	0	3·937
Sm^{3+}	0·02667	0·05837	0	0	0	3·836
Eu^{3+}	0·02835	0·11317	0	0	0	3·462
Gd^{3+}	0·02165	−0·0209	0	0	0	4·150
Dy^{3+}	0·01958	−0·03825	0	0	0	3·552

Weighting and errors

Forsyth & Wells (1959) weighted their least-squares fit with a factor designed to obtain the best fit in the region about $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1}. Our results have been obtained without this weighting scheme since, in general, the aspherical data peaks in the regions between $\sin\theta/\lambda = 0{\cdot}4 - 0{\cdot}8$ Å^{-1} and the fit will necessarily be best in these regions.

The spherical contributions to the magnetic scattering are less extended in reciprocal space than the total X-ray scattering factors and again it seems more appropriate to adopt a unit weighting scheme.

We have estimated the goodness of fit by computing a factor

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

where N is the number of points fitted and f_0 is the maximum point of the curve. Values of ε are included in each Table.

It can be seen that the fitting is in general good, but that it is systematically worse for approximations which involve large values for the coefficients a and b. This correlation indicates that the expressions are less able to approximate to the form factors which vary more sharply with $\sin\theta/\lambda$.

Some of the form factors for the $\langle j_6 \rangle$ and all of those for the $\langle g_6 \rangle$ form do not reach their maximum within the tabulated range ($\sin\theta/\lambda = 1{\cdot}3$ Å^{-1}). This limitation prevents the proper fitting to equation (2) and we have arbitrarily obtained a rather poorer fit to these small terms by setting B, b and C to zero.

Table 9. *Input data and corresponding calculated values for the* $\langle j_0 \rangle$ Fe^{2+} *scattering function*

$\sin\theta/\lambda$ (Å^{-1})	Input values	Calculated values
0·0	1·0000	0·9995
0·05	0·9748	0·9746
0·10	0·9043	0·9047
0·15	0·8015	0·8023
0·20	0·6828	0·6831

Table 9 (*cont.*)

$\sin\theta/\lambda$ (Å^{-1})	Input values	Calculated values
0·25	0·5625	0·5622
0·30	0·4507	0·4499
0·35	0·3524	0·3519
0·40	0·2696	0·2697
0·45	0·2018	0·2024
0·50	0·1475	0·1482
0·60	0·0719	0·0718
0·70	0·0282	0·0273
0·80	0·0047	0·0041
0·90	−0·0068	−0·0066
1·00	−0·0116	−0·0110
1·10	−0·0128	−0·0126

Table 10. *Input data and corresponding calculated values for the* $\langle j_4 \rangle$ Fe^+ *scattering function*

$\sin\theta/\lambda$ (Å^{-1})	Input values	Calculated values
0·05	0·0001	0·0000
0·1	0·0014	0·0012
0·2	0·0142	0·0144
0·3	0·0379	0·0380
0·4	0·0608	0·0601
0·5	0·0767	0·0763
0·6	0·0847	0·0853
0·7	0·0862	0·0871
0·9	0·0772	0·0761
1·1	0·0623	0·0627

Tables 9 and 10 give the input data and the equivalent values for the two examples; the $\langle j_0 \rangle$ form for Fe^{2+} and the $\langle j_4 \rangle$ form for Fe^+.

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Lattice Parameters and Thermal Expansion Coefficients of Al, Ag and Mo at Low Temperatures. Comparison with Dilatometric Data*

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Lattice parameters and thermal expansion coefficients of Al, Ag and Mo were determined at temperatures between 30 and 180°K in a special X-ray camera without the use of liquid gases. The powder samples were cooled by a mechanical refrigerator, and symmetrical back-reflections patterns of the three metals were prepared. The purpose was to check the reliability of this method by comparing the lattice parameters and expansion coefficients calculated from X-ray patterns with those obtained by other well established, interferometric-dilatometric methods. The expansion coefficients were reproduced with reasonable precision, but the lack of reliable measurements of low-temperature parameters in the literature prevented a conclusion from being reached concerning the accuracy of the lattice parameters calculated. Values of the expansion coefficients and the lattice parameters are given.

The aim of the present investigation was to determine, with high precision, the lattice parameters of crystalline substances at low temperatures without the use of liquid gases for sample cooling. The powder sample (grain size about 20μ) was placed on a silver sample holder, tightly screwed to the cold head of a cooling machine. A symmetrical back-reflection vacuum camera provided the vacuum shroud for the cold head. The high-angle interference were registered on a film (on which six exposures can be made) fastened in a movable cylindrical film holder within the camera. Lattice-parameter determinations between 30 and 180°K were possible. Since more advanced refrigerators are now available, temperatures as low as 3·6°K (according manufacturers, claims), can be reached. The camera for

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