Acta Cryst. (1961). **14**, 231

Hartree–Fock Atomic Scattering Factors for the Neutral Atom Iron Transition Series

By A. J. Freeman

Materials Research Laboratory, Ordnance Materials Research Office, Watertown, Massachusetts, U.S.A.
and Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge,
Massachusetts, U.S.A.

and R. E. Watson*

Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge,
Massachusetts, U.S.A.

(*Received* 18 *April* 1960)

Atomic scattering factors for the lowest neutral atom $3d^{n-2}4s^2$ states have been calculated for the atoms Ti through Zn using recently computed Hartree–Fock analytic wave functions. Except for Cr and Cu, these calculations are for the ground state of the atom. Also given are tabulations of the individual transforms for the $3d$ and $4s$ electrons. The results are compared with previous calculations for these atoms and the effect of the $4s$ electrons on the form factors of the $3d$ and core electrons is discussed.

1. Introduction

In a previous paper (Watson & Freeman, 1961, referred to hereafter as W&F) we have reported on extensive calculations of atomic form factors for many atoms and ions of the iron transition series (Sc through Cu). These calculations were based on analytic Hartree–Fock wave functions as determined for these atoms and ions (Watson, 1959, 1960*a*) based on $3d^n$ configurations, where n denotes the total number of electrons outside the argon core. This restriction in configuration was imposed by the limited capacity of the computer (MIT's Whirlwind I) and led to the neglect of states involving $4s$ electrons ($3d^{n-2}4s^2$ and $3d^{n-1}4s$ for the neutral atoms and $3d^{n-1}4s$ for the singly ionized ions).

In this paper, we are reporting the results of calculations of the atomic form factors for the neutral atoms Ti to Zn using the $3d^{n-2}4s^2$ configuration analytic Hartree–Fock wave functions recently computed by Watson (1960*b*). (Except for Cr and Cu, for which $3d^{n-1}4s$ is the ground state configuration, these wave functions are for the ground state of the free atom.) Here too, certain computational difficulties led to this restriction. Also included are tabulations of the individual transforms for the $3d$ and $4s$ electrons. These results are compared with previous calculations for these atoms and the effect of the $4s$ electrons on the form factors of the $3d$ and core electrons is discussed.

2. Total free atom scattering factors

The atomic scattering factors for the atoms in the series Ti through Zn are listed in Table 1 as a function of $\sin\theta/\lambda$ in Å^{-1}. For the neutral atoms of the iron transition series there have been no previously published atomic scattering factors which have been calculated from accurate Hartree–Fock wave functions for the free atom ground state (Watson & Freeman, 1960*a*; Watson, 1961*a*).

As mentioned above, our earlier results for the neutral atoms were not for the appropriate ground state, so that except for Cr and Cu, the values given in Table 1 represent the first time that accurate Hartree-Fock results have been available for these atoms.

One of the more striking results of Watson's (1960*b*) neutral atom calculations was the finding that the $4s$ electrons have almost no effect on the inner electrons ($3d$ and core); i.e., the inner electrons of the neutral atom $3d^{n-2}4s^2$ states behave very much like the electrons of the doubly ionized $3d^{n-2}$ states. We therefore expect that a similar behavior is to be observed in the calculated form factors. If we compare the form factors for the neutral atoms reported here, from which the contribution due to the (two) $4s$ electrons has been subtracted, with the form factors for the doubly ionized atoms reported earlier (W&F) we find excellent agreement (i.e. the difference is nowhere greater than 0·05 electron units, or approximately 0·2%, with the maximum difference occurring at $\sin\theta/\lambda=0{\cdot}25$ Å^{-1}). This is an important result which has consequences for the form factors with which we are concerned.

The form factors for the $3d^{n-2}4s^2$ and $3d^{n-2}$ con-configurations give us bounds as to the effect on the form factors of the $4s$ electrons. Since this effect was found to be small, we are now able to predict, with a fair amount of certainty, a form factor for the *ground* state configuration of Cr and Cu, for which

---

* Now at AVCO, Research and Advanced Development Division, Wilmington, Massachusetts.

Table 1. *Atomic scattering factors for the lowest neutral atom* $3d^{n-2}4s^2$ *states*

sin θ/λ	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0·00	22·00	23·00	24·00	25·00	26·00	27·00	28·00	29·00	30·00
0·05	21·17	22·21	23·24	24·26	25·30	26·33	27·35	28·37	29·39
0·10	19·41	20·47	21·54	22·61	23·68	24·74	25·80	26·86	27·92
0·15	17·65	18·68	19·73	20·79	21·85	22·92	23·99	25·06	26·14
0·20	16·07	17·03	18·03	19·06	20·09	21·13	22·19	23·25	24·33
0·25	14·58	15·49	16·43	17·41	18·40	19·41	20·44	21·48	22·54
0·30	13·20	14·03	14·91	15·84	16·77	17·74	18·73	19·73	20·77
0·40	10·83	11·51	12·24	13·02	13·84	14·68	15·56	16·47	17·42
0·50	9·12	9·63	10·19	10·80	11·47	12·17	12·91	13·69	14·51
0·60	7·98	8·34	8·75	9·20	9·71	10·26	10·85	11·48	12·16
0·70	7·22	7·48	7·77	8·09	8·47	8·88	9·33	9·83	10·37
0·80	6·65	6·86	7·09	7·32	7·60	7·91	8·25	8·62	9·04
0·90	6·19	6·39	6·58	6·77	6·99	7·22	7·48	7·76	8·08
1·00	5·72	5·94	6·14	6·32	6·51	6·70	6·90	7·13	7·37
1·10	5·29	5·53	5·74	5·93	6·12	6·29	6·47	6·65	6·84
1·20	4·84	5·10	5·34	5·54	5·74	5·91	6·08	6·25	6·42
1·30	4·41	4·71	4·96	5·18	5·39	5·58	5·75	5·91	6·07
1·40	4·01	4·30	4·57	4·80	5·03	5·23	5·41	5·58	5·73
1·50	3·64	3·93	4·20	4·45	4·69	4·90	5·09	5·27	5·43

Table 2. 4*s scattering functions*

sin θ/λ	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0·00	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·05	0·7358	0·7540	0·7692	0·7819	0·7945	0·8050	0·8144	0·8228	0·8302
0·10	0·2838	0·3171	0·3466	0·3722	0·3985	0·4215	0·4426	0·4618	0·4792
0·15	0·0268	0·0482	0·0694	0·0892	0·1110	0·1312	0·1507	0·1693	0·1868
0·20	−0·0388	−0·0344	−0·0281	−0·0207	−0·0114	−0·0014	0·0089	0·0197	0·0306
0·25	−0·0281	−0·0327	−0·0355	−0·0367	−0·0367	−0·0353	−0·0330	−0·0298	−0·0259
0·30	−0·0055	−0·0118	−0·0174	−0·0220	−0·0261	−0·0291	−0·0313	−0·0327	−0·0333
0·40	0·0157	0·0136	0·0108	0·0076	0·0040	0·0004	−0·0032	−0·0067	−0·0099
0·50	0·0123	0·0136	0·0142	0·0141	0·0135	0·0124	0·0110	0·0092	0·0072
0·60	0·0045	0·0066	0·0084	0·0098	0·0110	0·0117	0·0121	0·0121	0·0118
0·70	0·0011	0·0024	0·0038	0·0051	0·0065	0·0077	0·0088	0·0096	0·0102
0·80	−0·0035	−0·0028	−0·0018	−0·0007	0·0005	0·0018	0·0031	0·0042	0·0053
0·90	0·0019	0·0014	0·0012	0·0013	0·0016	0·0022	0·0028	0·0035	0·0042
1·00	−0·0039	−0·0040	−0·0040	−0·0038	−0·0035	−0·0030	−0·0024	−0·0017	−0·0010
1·10	0·0034	0·0027	0·0020	0·0015	0·0011	0·0009	0·0008	0·0008	0·0010
1·20	−0·0018	−0·0021	−0·0024	−0·0026	−0·0028	−0·0030	−0·0030	−0·0030	−0·0029
1·30	0·0044	0·0040	0·0034	0·0028	0·0023	0·0017	0·0013	0·0009	0·0007
1·40	−0·0011	−0·0012	−0·0013	−0·0015	−0·0017	−0·0019	−0·0021	−0·0023	−0·0024
1·50	0·0038	0·0036	0·0034	0·0032	0·0028	0·0024	0·0021	0·0017	0·0014

accurate wave functions are not yet known. Since the ground state configurations for Cr and Cu are $3d^5 4s$ and $3d^{10} 4s$ respectively, it follows from the above that the most appropriate form factor for these atoms is formed by adding to the singly ionized results for Cr^+ and Cu^+ ($3d^5$ and $3d^{10}$ configurations respectively) given earlier (W&F) the corresponding 4*s* scattering factor for these atoms which is listed in Table 2. For completeness and for the convenience of readers, these form factors for Cr and Cu are given in Table 3. These are still not exact because of the use of the wrong 4*s* scattering factors (i.e. those obtained from a $4s^2$ instead of a $4s^1$ configuration).

As a further check on the result that the 4*s* electrons have little effect on the inner electrons, we have compared the form factor for Zn^{++} as calculated from Tables 1 and 2 with earlier Hartree–Fock calculations for Zn^{++} by Piper (1958). The agreement is again found to be excellent (the maximum difference is 0·04 e.u.'s).

In the last few years the atomic scattering factor for Fe has been the subject of a great deal of interest and controversy in experiments (Weiss & DeMarco, 1958, 1959; Batterman, 1959*a*, *b*; Komura *et al.*, 1959) and in their theoretical interpretation (Mott & Stevens, 1957; Lomer & Marshall, 1958; Hume-Rothery *et al.*, 1958; Freeman & Weiss, 1959, and many others). The analysis of the experimental results used the atomic form factor of Freeman & Wood (1959), which was

Table 3. *Atomic form factors for the ground state of* Cr *and* Cu

sin θ/λ	Cr	Cu	sin θ/λ	Cr	Cu
0	24·00	29·00	0·7	7·75	9·80
0·05	23·39	28·49	0·8	7·09	8·61
0·1	21·93	27·19	0·9	6·58	7·76
0·15	20·17	25·49	1·0	6·14	7·13
0·2	18·37	23·63	1·1	5·74	6·65
0·25	16·64	21·75	1·2	5·34	6·25
0·3	15·01	19·90	1·3	4·94	5·90
0·4	12·22	16·48	1·4	4·55	5·57
0·5	10·14	13·65	1·5	4·18	5·25
0·6	8·72	11·44			

Table 4. *3d atomic scattering functions (spherical part only)*

$\sin \theta/\lambda$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
0·00	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000
0·05	0·9542	0·9614	0·9668	0·9712	0·9741	0·9768	0·9790	0·9810	0·9827
0·10	0·8321	0·8568	0·8757	0·8913	0·9019	0·9115	0·9197	0·9268	0·9332
0·15	0·6703	0·7138	0·7480	0·7769	0·7970	0·8154	0·8315	0·8456	0·8584
0·20	0·5059	0·5620	0·6078	0·6479	0·6763	0·7030	0·7267	0·7477	0·7671
0·25	0·3628	0·4229	0·4742	0·5208	0·5548	0·5875	0·6170	0·6436	0·6686
0·30	0·2496	0·3068	0·3580	0·4060	0·4426	0·4783	0·5113	0·5416	0·5704
0·40	0·1049	0·1463	0·1872	0·2286	0·2629	0·2977	0·3311	0·3630	0·3943
0·50	0·0342	0·0588	0·0861	0·1159	0·1433	0·1719	0·2006	0·2289	0·2576
0·60	0·0030	0·0155	0·0314	0·0503	0·0698	0·0910	0·1132	0·1359	0·1596
0·70	−0·0086	−0·0037	0·0043	0·0149	0·0275	0·0419	0·0577	0·0747	0·0928
0·80	−0·0115	−0·0107	−0·0077	−0·0026	0·0048	0·0138	0·0243	0·0360	0·0491
0·90	−0·0108	−0·0120	−0·0117	−0·0101	−0·0064	−0·0014	0·0050	0·0127	0·0216
1·00	−0·0091	−0·0110	−0·0121	−0·0124	−0·0111	−0·0088	−0·0053	−0·0007	0·0049
1·10	−0·0072	−0·0092	−0·0110	−0·0122	−0·0123	−0·0117	−0·0103	−0·0079	−0·0046
1·20	−0·0055	−0·0074	−0·0093	−0·0109	−0·0119	−0·0123	−0·0121	−0·0113	−0·0097
1·30	−0·0041	−0·0058	−0·0075	−0·0093	−0·0106	−0·0117	−0·0123	−0·0124	−0·0119
1·40	−0·0030	−0·0044	−0·0060	−0·0076	−0·0091	−0·0104	−0·0115	−0·0122	−0·0125
1·50	−0·0022	−0·0034	−0·0047	−0·0062	−0·0076	−0·0090	−0·0103	−0·0113	−0·0121

based on wave functions obtained from a *modified* Hartree–Fock procedure (Wood & Pratt, 1957) using Slater's (1951) method of averaging out the effects of exchange. A comparison of this scattering factor with the one for iron reported in Table 1 shows differences between them—about 0·3 e.u.'s for small and intermediate scattering angles and 0·1 e.u.'s at large angles. This indicates a considerable difference between the Wood & Pratt (1957) wave functions and those of Watson (1960*b*), both for small and large distances, *r*, from the nucleus. This is attributable to the Slater method of averaging exchange which is not correct when the electronic charge density is small (i.e., at either small or large *r*). It is also to be noted that the one-electron energies as calculated by Wood & Pratt are in error by some 60 Rydbergs (8100 e.V.) for the 1*s* electrons (out of 520 Rydbergs), 3 Rydbergs (40 e.V.) for the 2*s* electrons (out of 64 Rydbergs), etc. Despite these large errors in one-electron energies, the Wood & Pratt functions are not as bad as this might suggest. Further details are given by Watson & Freeman (1960).

3. Scattering factors for the 4s electrons

No accurate Hartree–Fock form factors have previously been available for the iron series transition elements which included the 4*s* electrons. It is, of course, well known that the contribution to the scattering factor is important only for low $\sin \theta/\lambda$, and therefore, accurate values are of importance only for small angle scattering measurements. In order to quantitatively assess their importance, we give in Table 2 our results for the 4*s* transforms from which the variation in scattering with Z (the atomic number) and $\sin \theta/\lambda$ is readily observed and so needs no further discussion.

From the data given in Tables 1 and 2, and the 3*d* atomic scattering factors, which are listed in Table 4, the argon core scattering functions, which are of importance for the Weiss–DeMarco type of experiment, can readily be computed.

4. 3*d* scattering factors

These are listed in Table 4 since they are important for experiments involving the magnetic scattering of neutrons. Only the spherical part of the form factor is given in the table. Since, as was stated above, these differ but little from the ones for the doubly ionized $3d^{n-2}$ states given previously (W&F), we expect that the aspherical terms will correspondingly also agree. For this reason these terms were not calculated. For work involving non-spherical effects one may combine the 3*d* (spherical) transforms of Table 4 with the earlier results for the aspherical parts of the form factor (W&F). As was shown by Freeman (1959) and Weiss & Freeman (1959), these terms are all that are needed for determining from neutron diffraction data the symmetry of the outer electron distributions in magnetic materials.

We are pleased to thank Mrs Athena Harvey and Mrs Anna Hansen for their help with some of the computations.

References

Batterman, B. W. (1959*a*). *Phys. Rev. Letters*, **2**, 47.

Batterman, B. W. (1959*b*). *Phys. Rev.* **115**, 81.

Freeman, A. J. (1959). *Acta Cryst.* **12**, 261.

Freeman, A. J. & Weiss, R. J. (1959). *Phil. Mag.* **4**, 1086.

Freeman, A. J. & Wood, J. H. (1959). *Acta Cryst.* **12**, 271.

Hume-Rothery, W., Brown, P. J., Forsyth, J. B. & Taylor, W. H. (1958). *Phil. Mag.* **36**, 1466.

Komura, Y., Tomiie, Y. & Nathans, R. (1959). *Phys. Rev. Letters*, **3**, 268.

Lomer, W. M. & Marshall, W. (1958). *Phil. Mag.* **3**, 185.

MOTT, N. F. & STEVENS, K. W. H. (1957). *Phil. Mag.* **2**, 1364.

PIPER, W. (1958). Unpublished results.

SLATER, J. C. (1951). *Phys. Rev.* **81**, 385.

WATSON, R. E. (1959). *Technical Report* No. 12, Solid State and Molecular Theory Group, M.I.T. (Unpublished.)

WATSON, R. E. (1960*a*). *Phys. Rev.* **118**, 1036.

WATSON, R. E. (1960*b*). *Phys. Rev.* **119**, 1934.

WATSON, R. E. & FREEMAN, A. J. (1961*a*). *Acta Cryst.* **14**, 27.

WATSON, R. E. & FREEMAN, A. J. (1960). *Phys. Rev.* **120**, 1125.

WEISS, R. J. & DEMARCO, J. J. (1958). *Revs. Mod. Phys.* **30**, 59.

WEISS, R. J. & DEMARCO, J. J. (1959). *Phys. Rev. Letters*, **2**, 148.

WEISS, R. J. & FREEMAN, A. J. (1959). *J. Phys. Chem. Solids*, **10**, 147.

WOOD, J. H. & PRATT, G. W., JR. (1957). *Phys. Rev.* **107**, 995.

Acta Cryst. (1961). **14**, 234

The Crystal Structure of Gadolinium Trichloride Hexahydrate*

BY MASSIMO MAREZIO,† H. A. PLETTINGER AND W. H. ZACHARIASEN

Department of Physics, University of Chicago, Chicago, Illinois, U.S.A.
and Division of Physics, Argonne National Laboratory, Argonne, Illinois, U.S.A.

(*Received* 24 *June* 1960)

$GdCl_3.6\,H_2O$ is monoclinic with space group $P2/n$ and two molecules in the cell

$$a=9{\cdot}651,\ b=6{\cdot}525,\ c=7{\cdot}923\ \text{Å};\ \beta=93{\cdot}65^\circ.$$

All atomic positions (except for hydrogen) were determined with high precision.

The structure contains complexes $[Cl_2Gd(OH_2)_6]$ which are held together by $O\text{–}H\cdots Cl$ bonds. Thus one third of the chlorine atoms are not bonded to gadolinium atoms. The only symmetry element of a complex is a twofold axis. The bond lengths are:

$$Gd\text{–}Cl=2{\cdot}768,\ Gd\text{–}O=2{\cdot}39\text{–}2{\cdot}42,\ O\text{–}H\cdots Cl=3{\cdot}14\text{–}3{\cdot}24\ \text{Å}.$$

Introduction

The investigation to be reported on in the following is part of the general crystal chemical studies of 4*f* and 5*f* elements in which this laboratory has been engaged over a number of years.

The specific compound to be discussed, $GdCl_3.6\,H_2O$, is representative of an isostructure series with numerous members. It is definitely known that the corresponding compounds of neodymium, samarium, erbium (Pabst, 1931; Iveranova, Tarasova & Umanskii, 1951) and of plutonium have the same structure as $GdCl_3.6\,H_2O$, and it is probably true that most of the analogous chlorides and bromides of 4*f* and 5*f* elements, of yttrium and possibly of scandium belong to the same structure type.

Because of the ease with which large (although hygroscopic) single crystals can be prepared extensive magnetic and spectroscopic measurements have been made on many of these compounds. It is hoped that the structure results will be useful in the interpretation of these data.

Goniometric measurements have been reported (Pabst, 1931) for $GdCl_3.6\,H_2O$ and $SmCl_3.6\,H_2O$, and unit-cell dimensions have been published (Iveranova *et al.*, 1951) for the samarium and neodymium chlorides.

The single crystals used in the present investigation were furnished by Prof. G. H. Dieke of Johns Hopkins University.

$GdCl_3\ 6\,H_2O$ is monoclinic with two molecules in a unit cell of dimensions

$$a=9{\cdot}651\pm0{\cdot}001,\ b=6{\cdot}525\pm0{\cdot}001,$$
$$c=7{\cdot}923\pm0{\cdot}001\ \text{Å};\ \beta=93{\cdot}65\pm0{\cdot}02^\circ.$$

The calculated density is 2·478 g.cm.$^{-3}$. The only regular absences among the reflections are $H0L$ when $H+L$ is odd, corresponding to space group symmetry $P2/n$ or Pn.

Determination of the structure

All intensity measurements were made on a General Electric XRD-3 spectrometer rebuilt for single crystal work, using a proportional counter and filtered Cu $K\alpha$ radiation. All data were taken on one crystal which had been ground into a sphere of radius

$$2{\cdot}83\pm0{\cdot}02\times10^{-2}\ \text{cm}.$$

Since the crystals are hygroscopic, the sphere was coated with a solution of Canada balsam in benzene.

---

* Work done under the auspices of the Atomic Energy Commission.

† On leave from Istituto di Chimica Generale e Inorganica dell'Universita di Roma.