

Hartree-Fock Atomic Scattering Factors for the Iron Transition Series

BY R. E. WATSON

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

AND 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.*

(Received 7 December 1959)

Atomic scattering factors for thirty-five atoms and ions of the iron group transition series (Sc through Cu) have been determined from Watson's recently calculated Hartree-Fock wave functions and compared with the few other available calculations. Principal scattering factors were also computed, following the methods of Freeman, for the $3d$ electrons of those atoms containing non-spherical charge distributions. As shown by Weiss & Freeman these are all that are needed for determining (from the measured neutron form factor) the spatial symmetry of the outer electrons in magnetic materials. Argon core scattering factors were also calculated, and, on the basis of these new results, the question of the constancy of the argon core is discussed quantitatively. Analysis of the $3d$ transforms for different stages of ionization shows another difficulty for the Weiss-DeMarco experiments.

Introduction

For many years, the most widely used atomic scattering factors were those of Bragg & West (1928), Debye (1930) and Bewilogua (1931), calculated from Fermi-Thomas electron-distribution functions, and those of James & Brindley (1931), which were based for the most part on self-consistent field (SCF) wave functions without exchange. For those atoms for which no such wave functions were available, James & Brindley (J&B) used an interpolation procedure to determine form factors for these atoms from the ones they had already calculated. With the increase in precision of modern X-ray methods, showing the inadequacy of these J&B values (Bacon, 1952; Cochran, 1953 and others) there has arisen a determined effort to improve on these form factors in several ways (Viervoll & Øgrim, 1949; McWeeny, 1951; Parry, 1955), culminating in the use of Hartree-Fock wave functions to include the effects of exchange (Hoerni & Ibers, 1954, 1957). On a large and more inclusive scale Berghuis *et al.* (1955) and Freeman (1959*a*) calculated atomic scattering factors for many atoms and ions using latest Hartree-Fock wave functions. Recently, form factors for a large number of atoms and ions have been computed from Fermi-Thomas-Dirac functions by Thomas & Umeda (1957) as well, providing important data for many elements for which no SCF wave functions are available.

The X-ray experiments of Weiss & DeMarco (1958, 1959), on the number of $3d$ electrons in the transition metals, have stimulated a great deal of interest in determining accurate values of the atomic scattering factor (Batterman, 1959*a, b*, and Komura *et al.*, 1959).

Furthermore, the polarized neutron method of Shull has been shown to determine very accurate magnetic form factors for the $3d$ electrons (Nathans, Shull *et al.*, 1959; Nathans & Paoletti, 1959; Pickart & Nathans, 1959) while Weiss & Freeman (1959) were able to show theoretically that this data, when properly analyzed, gave charge densities which showed deviations from spherical symmetry. These developments emphasize the current need for accurate form factors, both for the total charge density and the individual $3d$ transforms, especially for the iron group transition elements.

Until recently, however, there have been few Hartree-Fock self-consistent field wave functions available for these elements, but of these none was an exact Hartree-Fock treatment. The calculations of Hartree (1954, 1956), were based in part on interpolation for the wave functions of the inner electrons in Mn^{+2} and in part on the use of the argon core ($1s^2 2s^2 2p^6 3s^2 3p^6$) wave functions from this calculation in the calculation of the outer electron ($3d, 4s$) wave functions for Ti^+ , V^{+2} , Mn^+ and Mn . Wood & Pratt (1957) carried out a modified Hartree-Fock calculation for atomic iron by using Slater's (1951) average exchange potential to simplify the variational problem.

In fact the V^{+2} calculation of Worsley (1958) was the first really accurate Hartree-Fock calculation for the case of an unfilled d shell in that no use was made of interpolations or other approximations and the numerical solution carried out to full self-consistency. More recently, Piper (1959) has calculated complete, accurate Hartree-Fock wave functions for Fe^{+3} , Mn^{+2} and Mn^{+4} and Mayers (1959) has done the same for some Fe series atoms. Simultaneously, one of us

(Watson, 1959) has calculated Hartree-Fock wave functions for the entire iron group series including atoms in many stages of ionization. These calculations used analytic wave functions, i.e., a linear combination of products of exponentials and powers of r , with coefficients determined by a Roothaan (1951) SCF procedure. The electronic configurations were limited to the $3d^n$ type only (e.g., neutral iron with a $3d^6 4s^2$ ground state is replaced by a $3d^8$ configuration). See Watson (1959) for more details about the wave functions and the accuracy of these calculations.

In this paper we are reporting on the calculation of a consistent set of atomic scattering factors for some thirty-five atoms and ions of the iron group transition series using Watson's (1959) wave functions. Included are argon core scattering functions and complete $3d$ atomic scattering functions, consisting of all the terms needed when the charge distribution is non-spherical (Freeman, 1959*a*; Weiss & Freeman, 1959). The numerical computations were carried out on Whirlwind I, the MIT high speed computer, using routines and techniques described earlier (Freeman, 1959*a*). As will be shown, the accuracy of the form factors agrees digitally with the few other such calculations available to date (Worsley, 1959; Piper, 1959).

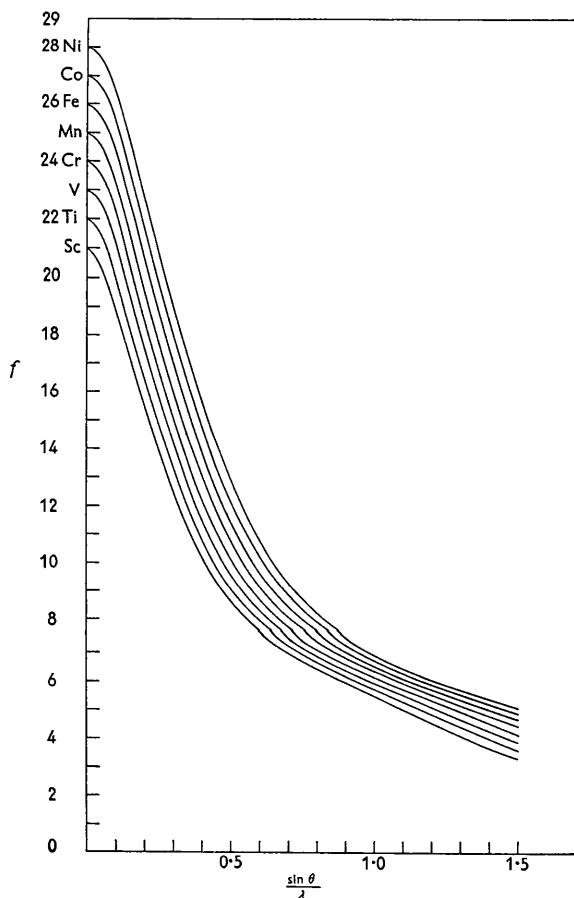


Fig. 1. Atomic scattering factors for the neutral atoms Sc through Ni as a function of $\sin \theta/\lambda$ in \AA^{-1} units.

Total atomic scattering factors

These are listed in Table 1 as a function of $\sin \theta/\lambda$ in \AA^{-1} units. Individual one-electron transforms were

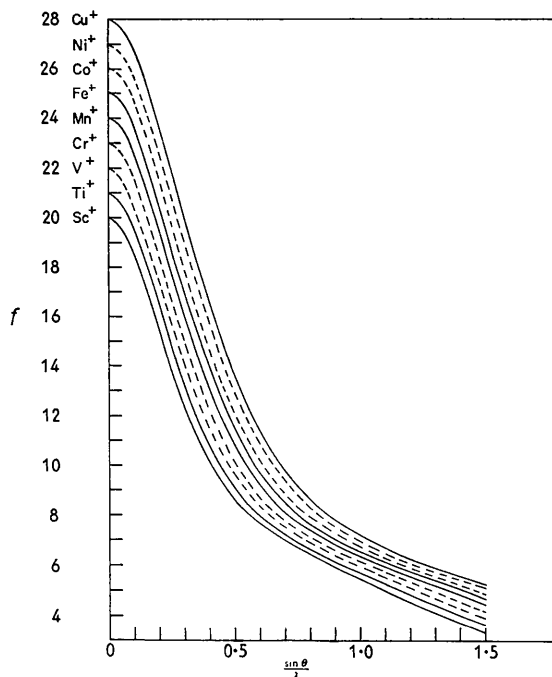


Fig. 2. Atomic scattering factors for the ions Sc^+ through Cu^+ as a function of $\sin \theta/\lambda$ in \AA^{-1} units.

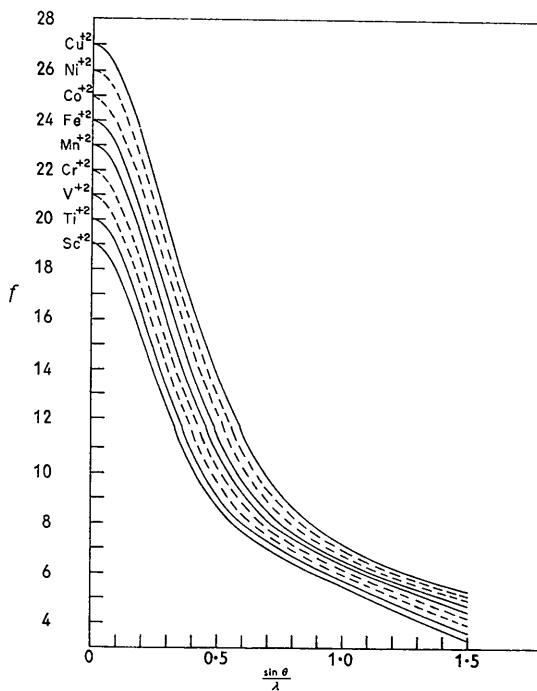


Fig. 3. Atomic scattering factors for the ions Sc^{+2} through Cu^{+2} as a function of $\sin \theta/\lambda$ in \AA^{-1} units.

also computed, but these are not listed here because of space limitations.*

Some of our results are more conveniently summarized in the accompanying figures (cf. Figs. 1-3). These show the total scattering factors for the neutral, singly and doubly ionized atoms to be smooth 'families' of functions of $\sin \theta/\lambda$ and Z , the atomic number.

For the transition elements there are few atomic scattering factors available to date which have been based on Hartree-Fock wave functions. Worsley (1959) has just published a scattering factor for V^{+2} and this agrees exactly with the values we have given in Table 1. Recently Piper (1959) has calculated accurate Hartree-Fock atomic form factors for Fe^{+3} , Mn^{+2} and Mn^{+4} . Our form factors for Fe^{+3} and Mn^{+2} (cf. Table 1) agree

with those of Piper's to the number of figures quoted, again giving an excellent check on the accuracy of our calculations.

Our values for Fe do not agree completely with those of Freeman & Wood (1959), who used the Hartree-Fock-Slater wave functions calculated by Wood & Pratt (1957) (see Fig. 4). For the intermediate and high angles, our form factors, although based on a d^8 configuration, should lead to no differences from the Wood & Pratt $3d^64s^2$ configuration. The observed differences in form factors indicate a real difference between the two sets of wave functions and in fact is probably due to the Slater approximation of treating exchange. Also shown in Fig. 4 are the form factors for four other ions of Fe. These show the usual agreement for large $\sin \theta/\lambda$ values, as has been observed earlier.

* They are available to interested persons on request.

Table 1. *Atomic scattering factors for the iron-transition elements*

	Sc	Sc ⁺	Sc ⁺²	Sc ⁺³	Ti	Ti ⁺	Ti ⁺²	Ti ⁺³
$\sin \theta/\lambda$	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.00	21.00	20.00	19.00	18.00	22.00	21.00	20.00	19.00
0.05	20.28	19.59	18.71	17.77	21.36	20.60	19.70	18.76
0.10	18.72	18.50	17.88	17.11	19.86	19.52	18.86	18.09
0.15	17.04	17.03	16.68	16.12	18.11	18.03	17.63	17.06
0.20	15.39	15.43	15.27	14.92	16.36	16.39	16.19	15.82
0.25	13.82	13.86	13.82	13.63	14.71	14.76	14.68	14.48
0.30	12.39	12.43	12.44	12.38	13.20	13.25	13.25	13.16
0.35	11.15	11.18	11.22	11.22	11.87	11.91	11.94	11.93
0.40	10.12	10.13	10.18	10.22	10.74	10.77	10.82	10.84
0.45	9.27	9.29	9.32	9.37	9.81	9.83	9.87	9.91
0.50	8.60	8.61	8.64	8.68	9.05	9.06	9.10	9.14
0.60	7.64	7.64	7.65	7.67	7.95	7.95	7.96	7.99
0.70	6.98	6.98	6.98	6.98	7.21	7.21	7.21	7.22
0.80	6.45	6.45	6.45	6.44	6.66	6.66	6.66	6.65
0.90	5.96	5.96	5.96	5.96	6.19	6.18	6.18	6.18
1.00	5.48	5.48	5.48	5.49	5.73	5.73	5.73	5.73
1.10	5.00	5.00	5.01	5.02	5.28	5.28	5.28	5.29
1.20	4.53	4.53	4.54	4.56	4.83	4.83	4.84	4.85
1.30	4.09	4.09	4.10	4.12	4.40	4.40	4.41	4.42
1.40	3.68	3.68	3.69	3.70	3.99	3.99	4.00	4.02
1.50	3.31	3.31	3.32	3.33	3.62	3.62	3.62	3.64

	V	V ⁺	V ⁺²	V ⁺³	Cr	Cr ⁺	Cr ⁺²	Cr ⁺³
$\sin \theta/\lambda$	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.00	23.00	22.00	21.00	20.00	24.00	23.00	22.00	21.00
0.05	22.42	21.61	20.70	19.76	23.45	22.62	21.70	20.76
0.10	20.99	20.54	19.86	19.07	22.05	21.58	20.87	20.07
0.15	19.22	19.05	18.62	18.03	20.26	20.10	19.62	19.02
0.20	17.40	17.37	17.14	16.76	18.41	18.40	18.13	17.72
0.25	15.66	15.69	15.60	15.37	16.62	16.68	16.55	16.30
0.30	14.07	14.11	14.10	13.99	14.96	15.03	15.00	14.87
0.35	12.65	12.69	12.72	12.69	13.46	13.53	13.55	13.50
0.40	11.42	11.46	11.51	11.52	12.16	12.21	12.26	12.26
0.45	10.40	10.42	10.47	10.51	11.04	11.08	11.13	11.16
0.50	9.55	9.57	9.61	9.65	10.11	10.13	10.18	10.22
0.60	8.30	8.31	8.32	8.36	8.70	8.71	8.74	8.77
0.70	7.47	7.47	7.47	7.48	7.75	7.75	7.76	7.78
0.80	6.87	6.87	6.86	6.87	7.09	7.09	7.09	7.09
0.90	6.39	6.39	6.38	6.38	6.59	6.58	6.58	6.58
1.00	5.95	5.95	5.95	5.95	6.15	6.14	6.14	6.14
1.10	5.53	5.52	5.52	5.53	5.74	5.74	5.72	5.74
1.20	5.10	5.10	5.11	5.11	5.34	5.34	5.34	5.34
1.30	4.69	4.69	4.69	4.70	4.94	4.94	4.95	4.96
1.40	4.28	4.29	4.29	4.30	4.55	4.55	4.56	4.57
1.50	3.91	3.91	3.91	3.93	4.18	4.18	4.19	4.20

Table 1 (cont.)

	Mn	Mn ⁺	Mn ⁺²	Mn ⁺³	Fe	Fe ⁺	Fe ⁺²	Fe ⁺³	Fe ⁺⁴
sin θ/λ	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.00	25.00	24.00	23.00	22.00	26.00	25.00	24.00	23.00	22.00
0.05	24.48	23.63	22.71	21.76	25.50	24.64	23.71	22.76	21.80
0.10	23.12	22.60	21.88	21.07	24.19	23.63	22.89	22.08	21.22
0.15	21.35	21.12	20.65	20.02	22.42	22.16	21.66	21.07	20.31
0.20	19.46	19.42	19.15	18.71	20.52	20.45	20.15	19.71	19.15
0.25	17.62	17.65	17.53	17.26	18.63	18.66	18.51	18.24	17.84
0.30	15.90	15.96	15.93	15.78	16.85	16.92	16.87	16.72	16.46
0.35	14.33	14.39	14.42	14.35	15.22	15.29	15.30	15.24	15.08
0.40	12.95	13.00	13.05	13.04	13.76	13.82	13.86	13.86	13.78
0.45	11.74	11.78	11.84	11.86	12.48	12.53	12.58	12.61	12.58
0.50	10.72	10.75	10.80	10.84	11.37	11.41	11.46	11.51	11.51
0.60	9.15	9.17	9.19	9.23	9.64	9.67	9.69	9.74	9.77
0.70	8.07	8.08	8.09	8.12	8.44	8.45	8.46	8.49	8.52
0.80	7.33	7.33	7.33	7.34	7.60	7.60	7.60	7.61	7.64
0.90	6.78	6.78	6.78	6.78	6.99	6.99	6.99	6.99	7.00
1.00	6.33	6.33	6.33	6.32	6.52	6.52	6.51	6.51	6.52
1.10	5.93	5.93	5.93	5.93	6.12	6.11	6.11	6.11	6.11
1.20	5.55	5.55	5.55	5.55	5.74	5.74	5.74	5.74	5.74
1.30	5.17	5.17	5.17	5.18	5.38	5.38	5.38	5.38	5.38
1.40	4.80	4.80	4.80	4.81	5.02	5.02	5.03	5.03	5.04
1.50	4.44	4.44	4.44	4.45	4.67	4.67	4.68	4.68	4.69

	Co	Co ⁺	Co ⁺²	Co ⁺³	Ni	Ni ⁺	Ni ⁺²	Ni ⁺³
sin θ/λ	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>	<i>f</i>
0.00	27.00	26.00	25.00	24.00	28.00	27.00	26.00	25.00
0.05	26.53	25.65	24.72	23.77	27.55	26.66	25.72	24.77
0.10	25.27	24.66	23.91	23.09	26.34	25.69	24.93	24.10
0.15	23.54	23.20	22.68	22.04	24.63	24.26	23.71	23.05
0.20	21.62	21.49	21.17	20.71	22.70	22.55	22.21	21.72
0.25	19.70	19.67	19.52	19.23	20.74	20.72	20.54	20.22
0.30	17.87	17.89	17.84	17.68	18.86	18.90	18.83	18.65
0.35	16.17	16.21	16.22	16.15	17.11	17.17	17.17	17.08
0.40	14.64	14.67	14.72	14.71	15.51	15.57	15.61	15.58
0.45	13.28	13.30	13.36	13.39	14.08	14.13	14.18	14.20
0.50	12.09	12.11	12.17	12.21	12.82	12.86	12.91	12.95
0.60	10.20	10.21	10.25	10.29	10.78	10.80	10.84	10.88
0.70	8.85	8.85	8.87	8.90	9.29	9.31	9.32	9.36
0.80	7.90	7.91	7.91	7.92	8.23	8.24	8.25	8.26
0.90	7.22	7.22	7.22	7.22	7.47	7.48	7.48	7.48
1.00	6.71	6.71	6.71	6.70	6.91	6.91	6.91	6.90
1.10	6.29	6.29	6.29	6.28	6.46	6.46	6.46	6.46
1.20	5.91	5.91	5.91	5.91	6.08	6.08	6.08	6.08
1.30	5.56	5.56	5.56	5.56	5.73	5.73	5.74	5.73
1.40	5.22	5.22	5.22	5.23	5.40	5.40	5.40	5.41
1.50	4.88	4.88	4.89	4.89	5.08	5.08	5.08	5.09

	Cu ⁺	Cu ⁺²	Cu ⁺³
sin θ/λ	<i>f</i>	<i>f</i>	<i>f</i>
0.00	28.00	27.00	26.00
0.05	27.67	26.73	25.77
0.10	26.73	25.95	25.11
0.15	25.32	24.75	24.07
0.20	23.61	23.24	22.75
0.25	21.78	21.57	21.24
0.30	19.93	19.84	19.65
0.35	18.15	18.14	18.05
0.40	16.49	16.52	16.50
0.45	14.99	15.04	15.06
0.50	13.64	13.70	13.74
0.60	11.43	11.47	11.53
0.70	9.79	9.82	9.86
0.80	8.61	8.62	8.64
0.90	7.76	7.76	7.77
1.00	7.13	7.13	7.13
1.10	6.65	6.65	6.64
1.20	6.25	6.25	6.24
1.30	5.90	5.90	5.89
1.40	5.57	5.57	5.57
1.50	5.25	5.26	5.26

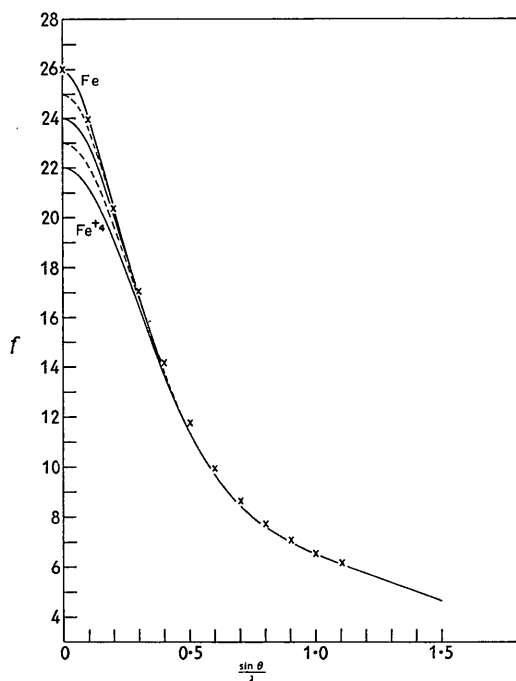


Fig. 4. Atomic scattering factors for Fe, Fe⁺, Fe⁺², Fe⁺³ and Fe⁺⁴; the x's denote the values for Fe as calculated by Freeman & Wood (1959).

For Mn⁺² and Mn⁺ our form factors agree with those of Freeman (1959*a*) but not so well with his data for V⁺², Ti⁺ and Mn. This is to be expected since his calculations were based on the use of Hartree's (1956) interpolated set of wave functions for the argon core of Mn⁺². Forsyth & Wells (1959) calculated a form factor for Ti⁺, using a Ti⁺² (interpolated) core, which is in agreement with our present values, but which again shows deviations from Freeman's (1959*a*) values. (In the next section we discuss the question of the constancy of the argon core, so frequently assumed but never proven). The interpolated form factors obtained by Forsyth & Wells (1959) from the Ti⁺, Mn⁺² and Cu⁺ data show fairly good agreement with our values for V⁺² and Cr⁺² but not for Co⁺² and Ni⁺² (in agreement with their predictions).

Berghuis *et al.* (1955) and Veenendaal, MacGillavry *et al.* (1959) calculated form factors for Cr⁺² and Co⁺² respectively from SCF wave functions without exchange. Our values are everywhere greater than these values, which is the well known effect of the inclusion of exchange. These differences have a maximum of about 0.5 electron units (e.u.'s) in the region about $\sin \theta/\lambda = 0.3$.

Argon core scattering functions

For X-ray measurements of the outer electron charge distributions, as carried out by Weiss & DeMarco (1958, 1959), Batterman (1959*a, b*), and Komura *et al.* (1959), it is important to know accurate values of the

argon core scattering function. (This is defined as the contribution to the total scattering factor arising from the inner electrons—1*s* through 3*p*, inclusive.) Furthermore, many people have assumed that the argon core scattering function is fairly constant with *Z*, the atomic number, and independent of degree of ionization. Since we have computed the individual one-electron transforms we are able to investigate these questions quantitatively.

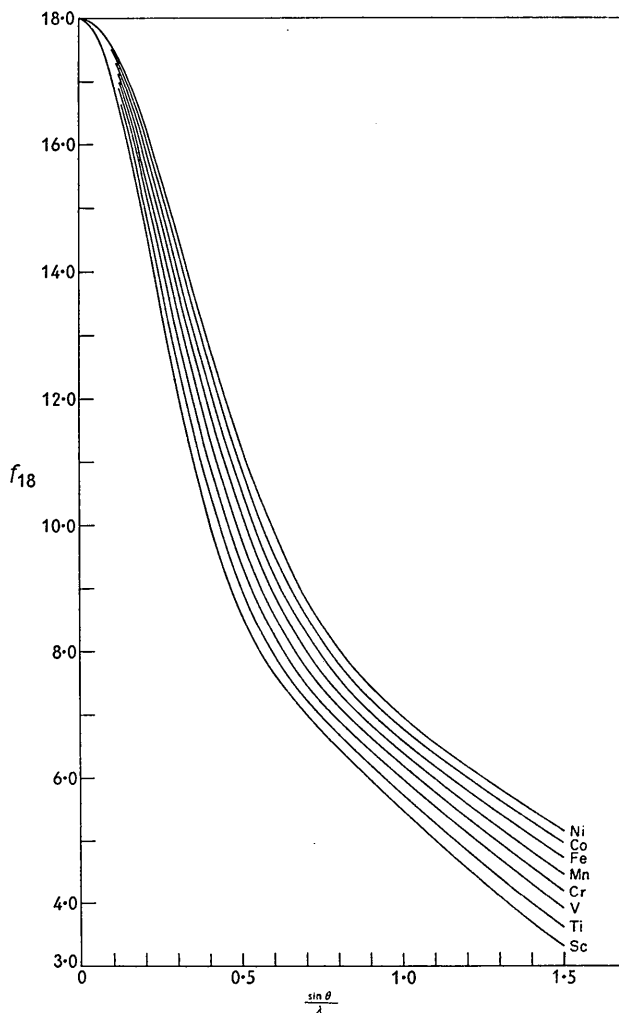


Fig. 5. Atomic scattering functions for the argon core of the neutral atoms Sc through Ni.

In Fig. 5 we plot f_{18} , the argon core scattering function, for the neutral atoms Sc through Ni (the f_{18} 's for the ionized atoms show the same behavior). As is readily seen from Fig. 5 there is a large variation in the argon core scattering functions and therefore the assumption of constancy is in fact false. The values of f_{18} are given in Table 2, for the neutral atoms.

The variation in f_{18} with degree of ionization, however, is found to be small for all the atoms considered.

Table 2. Argon core scattering functions

$\sin \theta/\lambda$	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
0.00	18.00	18.00	18.00	18.00	18.00	18.00	18.00	18.00
0.05	17.75	17.78	17.81	17.83	17.85	17.86	17.87	17.88
0.10	17.04	17.16	17.25	17.33	17.40	17.46	17.51	17.55
0.15	15.99	16.21	16.40	16.57	16.70	16.82	16.93	17.02
0.20	14.73	15.06	15.35	15.61	15.82	16.01	16.18	16.32
0.25	13.41	13.83	14.20	14.54	14.83	15.09	15.32	15.52
0.30	12.14	12.62	13.05	13.44	13.79	14.10	14.39	14.64
0.35	11.01	11.50	11.95	12.38	12.77	13.12	13.45	13.74
0.40	10.04	10.51	10.96	11.40	11.80	12.18	12.53	12.85
0.45	9.24	9.68	10.10	10.52	10.93	11.31	11.67	12.00
0.5	8.59	8.98	9.37	9.77	10.15	10.52	10.88	11.22
0.6	7.65	7.95	8.26	8.58	8.91	9.23	9.56	9.87
0.7	7.00	7.24	7.48	7.74	8.07	8.28	8.55	8.83
0.8	6.47	6.69	6.91	7.13	7.35	7.57	7.81	8.04
0.9	5.97	6.21	6.43	6.64	6.84	7.04	7.24	7.44
1.0	5.49	5.75	5.99	6.20	6.40	6.59	6.78	6.96
1.1	5.00	5.29	5.55	5.79	6.00	6.19	6.38	6.55
1.2	4.54	4.84	5.13	5.38	5.61	5.81	6.01	6.19
1.3	4.09	4.41	4.70	4.97	5.22	5.44	5.65	5.84
1.4	3.68	4.00	4.30	4.58	4.84	5.08	5.30	5.50
1.5	3.31	3.62	3.92	4.20	4.47	4.72	4.95	5.16

Even though the change in the number of outer electrons is appreciable (4 for Fe, 3 for the others) the change is never more than 0.2 e.u.'s (0.3 e.u.'s for Fe). Argon core transforms have been calculated for all the atoms and ions considered here, but are not tabulated in order to conserve space.

Form factors for the 3d-electrons

The iron transition series elements have many important physical properties which are attributable to their unfilled 3d shell. For this reason a great deal of theoretical and experimental work has centered on determining the electronic charge distribution of these 3d electrons. Since the form factor is a direct measure of the charge density, accurate form factors are required if accurate electronic charge distributions are to be determined.

As has been stated earlier, the polarized neutron technique of Shull has already been used to determine highly accurate form factors for the spin densities of the unpaired 3d electrons in Fe, Co, Ni, and Fe₃Al. Weiss & Freeman (1959) have shown that the polarized neutron data, when properly analyzed, gave charge densities which showed deviations from spherical symmetry. They further showed that a theoretical analysis of the effect of various crystalline environments on non-spherical charge distributions led to a determination of the spatial symmetry of the outer electrons.

Since further neutron studies are already underway (with more anticipated) and since there is continuing interest in the Weiss-DeMarco experiments (as described above), we have calculated the 3d transforms including the terms needed when the charge distribution is aspherical. As shown by Freeman (1959a, b) the basic transform of a one-electron wave function, ψ_i , given by

$$f_i = \int \psi_i^* \psi_i \exp [i \mathbf{k} \cdot \mathbf{r}] dv \quad (1)$$

can be written as

$$f_i = \sum_n i^n (2n+1) C_n(l_i m_i; l_i m_i) \langle j_n \rangle. \quad (2)$$

Where the coefficients $C_n(l_i m_i; l_i m_i)$ are integrals of products of Legendre functions and $\langle j_n \rangle$ symbolizes the integral

$$\langle j_n \rangle = \int U_i(r) j_n(kr) dr. \quad (3)$$

$U_i(r)$ is the radial charge density arising from $\psi_i^* \psi_i$ and $j_n(kr)$ are the spherical Bessel functions. The usual spherical approximation is to replace (eq. 2) by the first term

$$\langle j_0 \rangle = \int U_i(r) \sin kr / kr dr.$$

As shown earlier (Freeman, 1959a) there are three 'principal' one-electron transforms for d electrons in a free atom, as calculated from eq. (2). These principal scattering factors (which are different linear combinations of the $\langle j_n \rangle$) are needed to describe the dependence of the scattering on the orientation of the scattering vector, \mathbf{k} .

The scattering from d electrons in various crystalline environments for the actual Bragg reflections, as discussed by Weiss & Freeman (1959), may also be described in terms of the principal scattering factors. (Complete expressions may be found in the reference cited.) We have calculated the $\langle j_n \rangle$ for the 3d electrons of the transition series according to the methods already described (Freeman, 1959a). They are listed in Table 3. No $\langle j_2 \rangle$ or $\langle j_4 \rangle$ terms are listed for d^5 configurations since a half-closed shell is spherically symmetric, and its form factor is just 5 $\langle j_0 \rangle$.

Unlike the case for the total scattering function, the 3d scattering function is strongly dependent on the degree of ionization. This is illustrated in Fig. 6 where the $\langle j_0 \rangle$ part of the transform, labeled f_{3d} , is plotted for Fe and some of its ions. This has particular

Table 3. *3d Atomic scattering functions*

$\sin \theta/\lambda$	Sc			Sc ⁺			Sc ⁺²		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.8421	0.0591	0.0028	0.9196	0.0313	0.0006	0.9466	0.0210	0.0002
0.10	0.5598	0.1380	0.0235	0.7290	0.0976	0.0074	0.8069	0.0727	0.0032
0.15	0.3501	—	—	0.5205	—	—	0.6275	—	—
0.20	0.2193	0.1546	0.0651	0.3489	0.1796	0.0453	0.4530	0.1732	0.0289
0.25	0.1364	—	—	0.2245	—	—	0.3086	—	—
0.30	0.0828	0.1212	0.0710	0.1393	0.1703	0.0759	0.2003	0.1950	0.0662
0.35	0.0482	—	—	0.0826	—	—	0.1239	—	—
0.40	0.0260	0.0875	0.0657	0.0460	0.1318	0.0848	0.0719	0.1654	0.0884
0.45	0.0123	—	—	0.0228	—	—	0.0376	—	—
0.5	0.0039	0.0603	0.0570	0.0085	0.0937	0.0803	0.0157	0.1241	0.0924
0.6	-0.0035	0.0403	0.0475	-0.0049	0.0641	0.0698	-0.0055	0.0875	0.0857
0.7	-0.0051	0.0265	0.0384	-0.0083	0.0430	0.0579	-0.0114	0.0596	0.0743
0.8	-0.0052	—	—	-0.0083	—	—	-0.0113	—	—
0.9	-0.0038	0.0114	0.0240	-0.0066	0.0187	0.0375	-0.0093	0.0262	0.0501
1.0	-0.0034	—	—	-0.0054	—	—	-0.0072	—	—
1.1	-0.0014	0.0041	0.0156	-0.0035	0.0078	0.0235	-0.0052	0.0113	0.0316

$\sin \theta/\lambda$	Sc ⁺³			Ti			Ti ⁺		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9554	0.0176	0.0001	0.8946	0.0403	0.0013	0.9384	0.0241	0.0004
0.10	0.8341	0.0636	0.0020	0.6761	0.1095	0.0130	0.7850	0.0792	0.0047
0.15	0.6676	—	—	0.4745	—	—	0.6020	—	—
0.20	0.4921	0.1705	0.0218	0.3247	0.1637	0.0511	0.4355	0.1688	0.0337
0.25	0.3356	—	—	0.2183	—	—	0.3024	—	—
0.30	0.2122	0.2113	0.0608	0.1436	0.1501	0.0698	0.2029	0.1822	0.0658
0.35	0.1239	—	—	0.0918	—	—	0.1315	—	—
0.40	0.0656	0.1836	0.0929	0.0563	0.1199	0.0739	0.0817	0.1556	0.0827
0.45	0.0295	—	—	0.0324	—	—	0.0477	—	—
0.5	0.0085	0.1337	0.1030	0.0165	0.0894	0.0702	0.0252	0.1195	0.0856
0.6	-0.0087	0.0899	0.0958	0.0000	0.0640	0.0627	0.0013	0.0870	0.0799
0.7	-0.0118	0.0589	0.0811	-0.0056	0.0447	0.0537	-0.0075	0.0615	0.0701
0.8	-0.0106	—	—	-0.0071	—	—	-0.0097	—	—
0.9	-0.0084	0.0252	0.0516	-0.0061	0.0210	0.0367	-0.0089	0.0295	0.0492
1.0	-0.0065	—	—	-0.0055	—	—	-0.0076	—	—
1.1	-0.0049	0.0112	0.0314	-0.0036	0.0094	0.0244	-0.0057	0.0137	0.0327

$\sin \theta/\lambda$	Ti ⁺²			Ti ⁺³			V	V ⁺		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
0.05	0.9562	0.0173	0.0002	0.9658	0.0135	0.0001	0.9230	0.9501	0.0196	0.0002
0.10	0.8391	0.0612	0.0023	0.8713	0.0497	0.0013	0.7479	0.8216	0.0668	0.0033
0.15	0.6826	—	—	0.7369	—	—	0.5638	0.6594	—	—
0.20	0.5216	0.1575	0.0219	0.5874	0.1433	0.0147	0.4104	0.5018	0.1567	0.0261
0.25	0.3790	—	—	0.4442	—	—	0.2921	0.3674	—	—
0.30	0.2642	0.1951	0.0552	0.3204	0.1986	0.0444	0.2036	0.2607	0.1851	0.0568
0.35	0.1771	—	—	0.2212	—	—	0.1388	0.1796	—	—
0.40	0.1135	0.1808	0.0808	0.1460	0.1984	0.0752	0.0919	0.1198	0.1703	0.0778
0.45	0.0685	—	—	0.0914	—	—	0.0585	0.0769	—	—
0.5	0.0375	0.1464	0.0916	0.0529	0.1677	0.0934	0.0350	0.0466	0.1392	0.0861
0.6	0.0034	0.1101	0.0909	0.0090	0.1299	0.0977	0.0080	0.0117	0.1067	0.0849
0.7	-0.0094	0.0793	0.0834	-0.0090	0.0958	0.0927	-0.0034	-0.0036	0.0791	0.0780
0.8	-0.0125	—	—	-0.0146	—	—	-0.0076	-0.0093	—	—
0.9	-0.0117	0.0382	0.0614	-0.0145	0.0480	0.0715	-0.0079	-0.0103	0.0411	0.0590
1.0	-0.0097	—	—	-0.0124	—	—	-0.0075	-0.0095	—	—
1.1	-0.0076	0.0178	0.0413	-0.0098	0.0226	0.0498	-0.0058	-0.0079	0.0206	0.0414

Table 3 (cont.)

sin θ/λ	V ⁺²			V ⁺³			Cr			Cr ⁺
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000
0.05	0.9628	0.0147	0.0001	0.9703	0.0118	0.0001	0.9366	0.0247	0.0005	0.9587
0.10	0.8618	0.0529	0.0017	0.8873	0.0437	0.0010	0.7858	0.0773	0.0057	0.8495
0.15	0.7227	—	—	0.7671	—	—	0.6164	—	—	0.7057
0.20	0.5738	0.1442	0.0173	0.6301	0.1306	0.0118	0.4671	0.1532	0.0332	0.5585
0.25	0.4357	—	—	0.4944	—	—	0.3465	—	—	0.4262
0.30	0.3189	0.1912	0.0469	0.3725	0.1905	0.0375	0.2526	0.1683	0.0582	0.3158
0.35	0.2257	—	—	0.2706	—	—	0.1807	—	—	0.2280
0.40	0.1543	0.1890	0.0734	0.1896	0.2014	0.0668	0.1266	0.1537	0.0720	0.1603
0.45	0.1011	—	—	0.1277	—	—	0.0863	—	—	0.1094
0.5	0.0625	0.1621	0.0883	0.0819	0.1800	0.0875	0.0566	0.1286	0.0769	0.0720
0.6	0.0165	0.1284	0.0923	0.0253	0.1468	0.0962	0.0198	0.1022	0.0757	0.0257
0.7	-0.0040	0.0968	0.0885	-0.0017	0.1134	0.0954	0.0019	0.0783	0.0707	0.0030
0.8	-0.0114	—	—	-0.0125	—	—	-0.0060	—	—	-0.0070
0.9	-0.0127	0.0507	0.0702	-0.0153	0.0617	0.0793	-0.0084	0.0432	0.0559	-0.0104
1.0	-0.0116	—	—	-0.0144	—	—	-0.0088	—	—	-0.0109
1.1	-0.0097	0.0253	0.0500	-0.0122	0.0312	0.0586	-0.0075	0.0228	0.0409	-0.0097

sin θ/λ	Cr ⁺²			Cr ⁺³			Mn		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9679	0.0127	0.0001	0.9738	0.0104	0.0001	0.9475	0.0205	0.0003
0.10	0.8797	0.0463	0.0013	0.9000	0.0389	0.0008	0.8178	0.0669	0.0041
0.15	0.7552	—	—	0.7917	—	—	0.6635	—	—
0.20	0.6177	0.1321	0.0139	0.6655	0.1197	0.0097	0.5198	0.1449	0.0273
0.25	0.4854	—	—	0.5372	—	—	0.3986	—	—
0.30	0.3689	0.1852	0.0399	0.4184	0.1819	0.0319	0.3008	0.1693	0.0523
0.35	0.2723	—	—	0.3156	—	—	0.2233	—	—
0.40	0.1952	0.1931	0.0663	0.2309	0.2014	0.0595	0.1630	0.1624	0.0684
0.45	0.1355	—	—	0.1638	—	—	0.1165	—	—
0.5	0.0904	0.1739	0.0839	0.1120	0.1884	0.0815	0.0811	0.1418	0.0762
0.6	0.0330	0.1439	0.0915	0.0442	0.1603	0.0933	0.0347	0.1171	0.0777
0.7	0.0043	0.1130	0.0912	0.0086	0.1288	0.0960	0.0098	0.0933	0.0749
0.8	-0.0082	—	—	-0.0080	—	—	-0.0025	—	—
0.9	-0.0124	0.0637	0.0772	-0.0143	0.0752	0.0851	-0.0077	0.0551	0.0628
1.0	-0.0127	—	—	-0.0154	—	—	-0.0094	—	—
1.1	-0.0114	0.0339	0.0580	-0.0140	0.0406	0.0662	-0.0089	0.0308	0.0483

sin θ/λ	Mn ⁺			Mn ⁺²	Mn ⁺³			Fe		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9638	0.0143	0.0001	0.9720	0.9766	0.0093	0.0000	0.9553	0.0176	0.0002
0.10	0.8666	0.0508	0.0018	0.8943	0.9105	0.0349	0.0007	0.8415	0.0590	0.0031
0.15	0.7354	—	—	0.7826	0.8123	—	—	0.7001	—	—
0.20	0.5970	0.1346	0.0171	0.6558	0.6958	0.1101	0.0080	0.5628	0.1567	0.0228
0.25	0.4688	—	—	0.5299	0.5748	—	—	0.4429	—	—
0.30	0.3587	0.1791	0.0431	0.4153	0.4597	0.1733	0.0274	0.3433	0.1679	0.0471
0.35	0.2683	—	—	0.3169	0.3573	—	—	0.2623	—	—
0.40	0.1964	0.1829	0.0662	0.2358	0.2704	0.1995	0.0530	0.1976	0.1673	0.0646
0.45	0.1406	—	—	0.1709	0.1994	—	—	0.1464	—	—
0.5	0.0980	0.1642	0.0806	0.1202	0.1429	0.1939	0.0755	0.1063	0.1512	0.0743
0.6	0.0424	0.1370	0.0863	0.0522	0.0652	0.1711	0.0896	0.0514	0.1291	0.0780
0.7	0.0126	0.1096	0.0853	0.0153	0.0214	0.1422	0.0953	0.0199	0.1061	0.0772
0.8	-0.0022	—	—	-0.0029	-0.0013	—	—	0.0028	—	—
0.9	-0.0088	0.0654	0.0727	-0.0106	-0.0117	0.0883	0.0892	-0.0055	0.0665	0.0680
1.0	-0.0110	—	—	-0.0130	-0.0151	—	—	-0.0091	—	—
1.1	-0.0109	0.0371	0.0564	-0.0127	-0.0151	0.0504	0.0727	-0.0097	0.0392	0.0546

Table 3 (cont.)

$\sin \theta/\lambda$	Fe ⁺			Fe ⁺²			Fe ⁺³	Fe ⁺⁴		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	1.0000	0.0000	0.0000
0.05	0.9681	0.0126	0.0001	0.9748	0.0100	0.0001	0.9791	0.9818	0.0072	0.0000
0.10	0.8817	0.0453	0.0014	0.9043	0.0372	0.0008	0.9196	0.9294	0.0277	0.0004
0.15	0.7622	—	—	0.8015	—	—	0.8382	0.8494	—	—
0.20	0.6325	0.1251	0.0142	0.6828	0.1128	0.0095	0.7226	0.7507	0.0925	0.0051
0.25	0.5089	—	—	0.5625	—	—	0.6086	0.6429	—	—
0.30	0.3998	0.1738	0.0379	0.4507	0.1712	0.0300	0.4978	0.5349	0.1573	0.0191
0.35	0.3077	—	—	0.3524	—	—	0.3968	0.4333	—	—
0.40	0.2325	0.1844	0.0608	0.2696	0.1930	0.0543	0.3088	0.3423	0.1959	0.0411
0.45	0.1724	—	—	0.2018	—	—	0.2349	0.2641	—	—
0.5	0.1252	0.1715	0.0767	0.1475	0.1867	0.0742	0.1745	0.1988	0.2041	0.0645
0.6	0.0609	0.1480	0.0847	0.0719	0.1654	0.0865	0.0881	0.1036	0.1906	0.0830
0.7	0.0242	0.1221	0.0862	0.0282	0.1386	0.0914	0.0363	0.0452	0.1661	0.0941
0.8	0.0043	—	—	0.0047	—	—	0.0074	0.0116	—	—
0.9	-0.0057	0.0771	0.0772	-0.0068	0.0881	0.0858	-0.0074	-0.0061	0.1119	0.0966
1.0	-0.0102	—	—	-0.0116	—	—	-0.0137	-0.0143	—	—
1.1	-0.0114	0.0460	0.0623	-0.0128	0.0523	0.0705	-0.0154	-0.0170	0.0687	0.0842

$\sin \theta/\lambda$	Co			Co ⁺			Co ⁺²		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9619	0.0150	0.0002	0.9716	0.0112	0.0001	0.9773	0.0090	0.0000
0.10	0.8627	0.0516	0.0023	0.8938	0.0409	0.0012	0.9134	0.0337	0.0007
0.15	0.7345	—	—	0.7842	—	—	0.8193	—	—
0.20	0.6046	0.1277	0.0187	0.6626	0.1168	0.0120	0.7086	0.1048	0.0081
0.25	0.4872	—	—	0.5438	—	—	0.5942	—	—
0.30	0.3866	0.1651	0.0418	0.4364	0.1680	0.0336	0.4856	0.1639	0.0262
0.35	0.3028	—	—	0.3438	—	—	0.3881	—	—
0.40	0.2341	0.1710	0.0602	0.2664	0.1842	0.0560	0.3041	0.1906	0.0493
0.45	0.1785	—	—	0.2031	—	—	0.2338	—	—
0.5	0.1340	0.1596	0.0718	0.1523	0.1765	0.0728	0.1763	0.1898	0.0694
0.6	0.0708	0.1404	0.0776	0.0805	0.1567	0.0825	0.0934	0.1729	0.0831
0.7	0.0325	0.1187	0.0788	0.0373	0.1328	0.0859	0.0429	0.1487	0.0900
0.8	0.0102	—	—	0.0123	—	—	0.0139	—	—
0.9	-0.0018	0.0785	0.0725	-0.0013	0.0880	0.0803	-0.0016	0.0994	0.0882
1.0	-0.0077	—	—	-0.0082	—	—	-0.0092	—	—
1.1	-0.0099	0.0486	0.0606	-0.0110	0.0549	0.0673	-0.0122	0.0618	0.0752

$\sin \theta/\lambda$	Co ⁺³			Ni			Ni ⁺		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9809	0.0076	0.0000	0.9670	0.0130	0.0001	0.9747	0.0100	0.0001
0.10	0.9263	0.0288	0.0004	0.8791	0.0459	0.0017	0.9047	0.0368	0.0009
0.15	0.8437	—	—	0.7615	—	—	0.8044	—	—
0.20	0.7431	0.0945	0.0058	0.6379	0.1203	0.0155	0.6907	0.1086	0.0101
0.25	0.6349	—	—	0.5228	—	—	0.5771	—	—
0.30	0.5280	0.1571	0.0207	0.4220	0.1622	0.0375	0.4721	0.1617	0.0295
0.35	0.4288	—	—	0.3367	—	—	0.3795	—	—
0.40	0.3408	0.1921	0.0427	0.2657	0.1725	0.0567	0.3005	0.1829	0.0511
0.45	0.2654	—	—	0.2074	—	—	0.2346	—	—
0.5	0.2025	0.1984	0.0647	0.1599	0.1646	0.0696	0.1805	0.1803	0.0686
0.6	0.1100	0.1853	0.0814	0.0906	0.1480	0.0766	0.1017	0.1643	0.0798
0.7	0.0520	0.1625	0.0911	0.0465	0.1282	0.0790	0.0522	0.1427	0.0851
0.8	0.0177	—	—	0.0193	—	—	0.0221	—	—
0.9	-0.0012	0.1117	0.0934	0.0035	0.0890	0.0751	0.0046	0.0989	0.0828
1.0	-0.0106	—	—	-0.0052	—	—	-0.0050	—	—
1.1	-0.0143	0.0702	0.0822	-0.0092	0.0577	0.0650	-0.0098	0.0643	0.0718

Table 3 (cont.)

$\sin \theta/\lambda$	Ni^{+2}			Ni^{+3}		
	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$	$\langle j_0 \rangle$	$\langle j_2 \rangle$	$\langle j_4 \rangle$
0.00	1.0000	0.0000	0.0000	1.0000	0.0000	0.0000
0.05	0.9795	0.0082	0.0000	0.9825	0.0069	0.0000
0.10	0.9214	0.0307	0.0006	0.9325	0.0265	0.0004
0.15	0.8348	—	—	0.8561	—	—
0.20	0.7315	0.0975	0.0068	0.7621	0.0881	0.0049
0.25	0.6229	—	—	0.6596	—	—
0.30	0.5178	0.1567	0.0230	0.5569	0.1496	0.0182
0.35	0.4216	—	—	0.4599	—	—
0.40	0.3372	0.1873	0.0446	0.3723	0.1875	0.0386
0.45	0.2651	—	—	0.2959	—	—
0.5	0.2050	0.1915	0.0647	0.2311	0.1984	0.0599
0.6	0.1158	0.1788	0.0795	0.1329	0.1896	0.0772
0.7	0.0590	0.1575	0.0880	0.0689	0.1701	0.0884
0.8	0.0246	—	—	0.0293	—	—
0.9	0.0049	0.1101	0.0897	0.0061	0.1219	0.0940
1.0	-0.0056	—	—	-0.0064	—	—
1.1	-0.0107	0.0713	0.0792	-0.0124	0.0798	0.0855

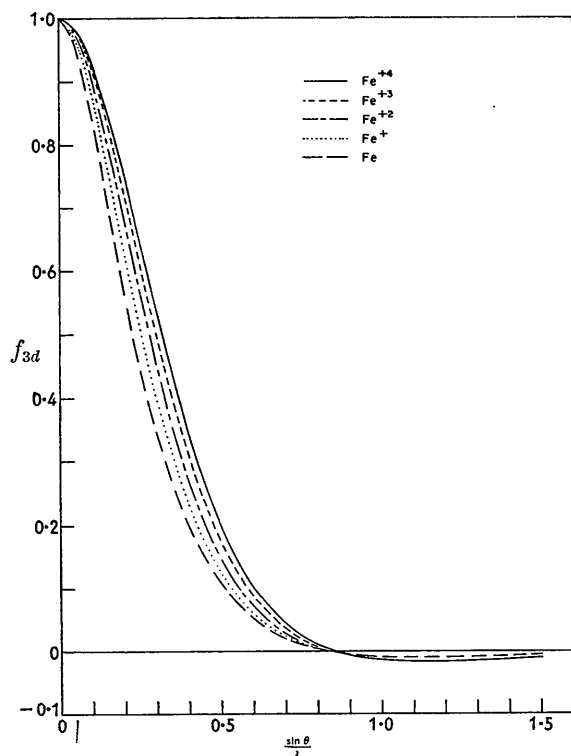


Fig. 6. Spherical part of the $3d$ transforms for Fe , Fe^+ , Fe^{+2} , Fe^{+3} and Fe^{+4} .

importance for the experiments mentioned above, especially for the X-ray determinations of the number of outer electrons in metals, since the use of an incorrect f_{3d} (i.e., one based on the wrong number of electrons) would alter the 'count'. This implies that one must know the number of $3d$ electrons to begin with in order to use the correct form factor to determine the number of $3d$ electrons (the ' $3d$ count'). The difficulty in such a situation is obvious, but is one

which may be resolved by some self-consistent procedure. In any event, the results illustrated in Fig. 6 point out another one of the difficulties involved in this type of experiment. In all cases, accurate $3d$ transforms are essential.

Note added in Proof. Dr B. W. Batterman has called to our attention following, for which we are grateful. Of the measurable X-ray scattering factors for iron, the one corresponding to the lowest order Bragg reflection, the (110) at $\sin \theta/\lambda = 0.247$ should be most sensitive to the distribution of $3d$ electrons whereas the calculated form factor at $\sin \theta/\lambda = 0.25$ is surprisingly insensitive to the number of $3d$ electrons in the atom. In fact, the form factor is actually smaller for an atom with eight ($3d$) electrons than for one with seven ($3d$) electrons. If these results are applicable to atoms in the solid, it means that an X-ray measurement cannot unambiguously determine the $3d$ configuration of iron in the range $3d^3$ to $3d^5$, and would be fairly insensitive down to $3d^4$. With reasonable experimental error one could not determine by X-ray measurements whether iron had from five to eight electrons in $3d$ like orbits and could just, outside of error, resolve a $3d^4$ configuration from this range. The peculiar behavior of the form factor in these calculations is not a result of an appreciable change in the argon core electron distribution but is due to the change in the charge distribution of each $3d$ electron with degree of ionization. A similar behavior of the form factor as a function of ionization has been reported by Thomas and Umeda (1957) who used the statistical TFD method. However, one cannot readily ascertain from their results whether it is only the wave functions of the $3d$ electrons which vary with ionization, or if the change is distributed throughout all the electrons of the atom.

We are pleased to thank Mrs Anna Hansen and Mrs Athena Harvey of the Materials Research Laboratory

for their help with the computations and Dr James Ibers for helpful correspondence and suggestions.

References

- BACON, G. E. (1952). *Acta Cryst.* **5**, 492.
 BATTERMAN, B. W. (1959a). *Phys. Rev. Letters*, **2**, 47.
 BATTERMAN, B. W. (1959b). *Phys. Rev.* **115**, 81.
 BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.
 BEWILOGUA, L. (1931). *Phys. Z.* **32**, 740.
 BRAGG, W. L. & WEST, J. (1928). *Z. Kristallogr. A*, **69**, 118.
 COCHRAN, W. (1953). *Acta Cryst.* **6**, 812.
 DEBYE, P. (1930). *Phys. Z.* **31**, 419.
 FORSYTH, J. B. & WELLS, M. (1959). *Acta Cryst.* **12**, 412.
 FREEMAN, A. J. (1959a). *Acta Cryst.* **12**, 261.
 FREEMAN, A. J. (1959b). *Phys. Rev.* **113**, 169.
 FREEMAN, A. J. & WOOD, J. H. (1959). *Acta Cryst.* **12**, 271.
 HARTREE, D. R. (1954). *Proc. Camb. Phil. Soc.* **51**, 206.
 HARTREE, D. R. (1956). *J. Opt. Soc. Amer.* **46**, 350.
 HOERNI, J. A. & IBERS, J. A. (1954). *Acta Cryst.* **7**, 744.
 HOERNI, J. A. & IBERS, J. A. (1957). *Acta Cryst.* **10**, 86.
 JAMES, R. W. & BRINDLEY, G. W. (1931). *Phil. Mag.* (7), **12**, 81.
 KOMURA, V., TOMIIE, Y. & NATHANS, R. (1959). *Phys. Rev. Letters*, **3**, 268.
 MAYERS, D. F. (1959). *Proc. Roy. Acad. A*. (To be published.)
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 NATHANS, R. & PAOLETTI, A. (1959). *Phys. Rev. Letters*, **2**, 254.
 NATHANS, R., SHULL, C. G., SHIRANE, G. & ANDRESON, A. (1959). *J. Phys. Chem. Solids*, **10**, 133.
 PARRY, G. S. (1955). *Acta Cryst.* **8**, 593.
 PICKART, S. J. & NATHANS, R. (1959). *J. Appl. Phys.* (To be published.)
 PIPER, W. (1959). Private communication.
 ROTHAAAN, C. C. J. (1951). *Revs. Mod. Phys.* **23**, 69.
 SLATER, J. C. (1951). *Phys. Rev.* **81**, 385.
 THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.
 VEENENDAAL, A. L., MACGILLAVRY, C. H., STAM, B., POTTERS, M. L. & RÖMGENS, M. J. H. (1959). *Acta Cryst.* **12**, 242.
 VIERVOLL, H. & ØGRIM, O. (1949). *Acta Cryst.* **2**, 277.
 WATSON, R. E. (1959). Technical Report No. 12, S.S.M. T.G., MIT. (Unpublished.)
 WATSON, R. E. (1960). *Phys. Rev.* **118**, 1036.
 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.
 WORSLEY, B. H. (1958). *Proc. Roy. Soc. A*, **247**, 390.
 WORSLEY, B. H. (1959). *Canad. J. Phys.* **37**, 967.

Acta Cryst. (1961). **14**, 37

The Thermal Vibrations in Diketopiperazine

BY KATHLEEN LONSDALE

University College, London, England

(Received 10 February 1960)

An analysis of the anisotropic atomic thermal parameters obtained by Degeilh & Marsh for diketopiperazine has shown that the principal rigid-body translations of the molecules are along the directions towards neighbouring parallel chains of molecules and are of the order of amplitude 0.13–0.14 Å. The translational amplitude within the chain is a little less. The rigid-body libration about the normal to the molecule is very small (semi-amplitude 1.8°), and results in tangential movements of C₁, C₂ and N of the order of 0.04 Å, and of O of 0.08 Å. There are very large out-of-plane librational movements about in-plane axes (semi-amplitudes 7.0° and 4.7°) the larger being about an axis making an angle of about 45° with [101] and about 10° with the C=O bond. The O and C₁ atoms appear to have vibrational movements approximately along [101] which are independent of the rigid-body vibrations. The coefficient of expansion should be minimum along [101] and maximum normal to (10 $\bar{1}$).

In a recent paper by Degeilh & Marsh (1959), to which we shall refer as DM, the crystal structure of diketopiperazine has been refined. This study shows that Corey's original (1938) X-ray determination was remarkably accurate. Vainshtein (1955) later gave hydrogen positions, based on an electron-diffraction study. The latest refinement (DM) gives individual

anisotropic temperature factors, but does not attempt more than a qualitative interpretation of these data in terms of rigid-body translations and librations.

Since their *R*-factor (for 1144 observed reflexions with non-zero weight) is 0.072, it does seem possible to analyze the DM thermal-vibration data with some confidence (Lonsdale & Milledge, 1959).