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Compton Incoherent Scattering Functions for Ions of the First Transition Series

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Compton incoherent scattering functions have been found for the transition elements Sc through Cu using the complete Waller–Hartree theory including the effects of the non-sphericity of the charge distributions. These calculations were based on analytic Hartree–Fock wave functions recently determined by Watson but restricted to $3d^n$ configurations. Results are given for three states of ionization ($+1$, $+2$, and $+3$) for each of the elements; the configurations $3d^n$ differ from the ground state only for the $+1$ ions other than Cr and Cu. These values are also compared with the few available earlier calculations for these ions and the role of the neglected $4s$ electrons is discussed.

Introduction

It is now generally accepted that in the absence of a theory for crystalline scattering the use of Hartree–Fock self-consistent field (SCF) wave functions in the Waller & Hartree (1929) free atom expression yields the best available incoherent scattering intensities. These have now been calculated for a large number of neutral atoms and ions (see Appendix I for a bibliography) and some of the general results may be summarized as follows:

(1) The exchange terms in the Waller–Hartree

equation must be included as these may be as large as the total intensity itself; the earlier James & Brindley (1931) values, which were based on SCF wave functions without exchange, are in error by at least the magnitude of the exchange terms. This error increases with Z, the atomic number.

(2) The properly calculated incoherent scattering intensities are in good agreement (except at very small scattering angles) with the few experimental determinations that have been made to date (Keating & Vineyard, 1956; Freeman, 1959a, b, c, and 1960a). While this means that free atom calculations may be used without loss of accuracy (despite all the differences between an atom in free space and one in a solid), it is also a disappointing result since it means

that information about the solid cannot be readily gotten from such experiments.

(3) For non-spherical charge distributions the dependence of the scattered intensity on the orientation of the scattering may be included in a straightforward way (Freeman, 1959d) and practical formulae, applicable to the case of scattering from randomly distributed free atoms, are available. These non-spherical effects are much smaller than the exchange contribution.

There have, until recently, been few Hartree–Fock self-consistent field wave functions available for the elements we are considering, but of these none (except for Cu^+ (Hartree & Hartree, 1936)) 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 iron series atoms. Simultaneously, one of us (Watson, 1959, 1960) has calculated Hartree–Fock wave functions for the entire iron group series including atoms in many stages of ionization. These

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* D. F. Mayers (unpublished) has just obtained some highly accurate numerical Hartree–Fock results for atoms up to Zn.

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 the results of calculations of the incoherent scattering functions for the first transition series (Sc to Cu). These calculations are based on analytic Hartree–Fock wave functions recently determined by Watson (1959 and 1960) but restricted to $3d^n$ configurations, i.e., no $4s$ electrons included. This restriction was imposed by the limited capacity of the computer (MIT's Whirlwind I). Results are given for three states of ionization ($+1$, $+2$, $+3$) for each of the elements Sc to Cu; the configurations $3d^n$ differ from the ground state only for the $+1$ ions other than Cr and Cu. These values are also compared with earlier data for some of these ions (Freeman, 1960b).

Formulas and method of calculation

The Waller–Hartree equation for the incoherent scattering intensity in electron units, e.u., without the Breit–Dirac (1926) correction factor $(\nu'/\nu)^3$ is

$$I_{e.u.} = Z - \Sigma_i |f_{ii}|^2 - \sum_{j\neq i}\sum |f_{ij}|^2 = Z - \mathscr{F}, \quad (1)$$

where

$$f_{ij} = \int \psi_i^*(\mathbf{r}) \exp[i\mathbf{k}\cdot\mathbf{r}]\psi_j(\mathbf{r})\,dv. \quad (2)$$

The ψ_j are the one-electron H–F atomic wave functions and $\mathbf{k}$ denotes the scattering vector. By using an appropriate expansion for the exponential, f_{ij} may be written as a sum of radial integrals involving the spherical Bessel functions with coefficients which are integrals of the product of three spherical harmonics. Details of the procedure may be found in an earlier

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Table 1. *Coefficients of the contribution to $\mathscr{F}$ from the $3d$ electrons for the ions listed along with their appropriate configuration and ground state*

For a given ion the contributions is a sum of all the terms in that row, i.e., a sum of products of coefficients (given here) and the appropriate radial integrals (not given)

Ion	Configuration	f_{3d}^2	$f_{3d,3d}^2(2)$	$f_{3d,3d}^2(4)$	$f_{1s,3d}^2$	$f_{2s,3d}^2$	$f_{3s,3d}^2$	$f_{2p,3d}^2(1)$	$f_{3p,3d}^2(1)$	$f_{2p,3d}^2(3)$	$f_{3p,3d}^2(3)$
Sc^{+2}, Ti^{+3}	$3d^1$, ^2D	1	$\frac{20}{49}$	$\frac{1}{49}$	2	2	2	$\frac{252}{105}$	$\frac{252}{105}$	$\frac{378}{105}$	$\frac{378}{105}$
Sc^+, Ti^{+2}, V^{+3}	$3d^2$, ^3F	2	$\frac{85}{49}$	$\frac{27}{49}$	4	4	4	$\frac{504}{105}$	$\frac{504}{105}$	$\frac{756}{105}$	$\frac{756}{105}$
Ti^+, V^{+2}, Cr^{+3}	$3d^3$, ^4F	3	$\frac{155}{49}$	$\frac{153}{49}$	6	6	6	$\frac{756}{105}$	$\frac{756}{105}$	$\frac{1134}{105}$	$\frac{1134}{105}$
V^+, Cr^{+2}, Mn^{+3}	$3d^4$, ^5D	4	$\frac{230}{49}$	$\frac{379}{49}$	8	8	8	$\frac{1008}{105}$	$\frac{1008}{105}$	$\frac{1512}{105}$	$\frac{1512}{105}$
Cr^+, Mn^{+2}, Fe^{+3}	$3d^5$, ^6S	5	$\frac{350}{49}$	$\frac{630}{49}$	10	10	10	12	12	18	18
Mn^+, Fe^{+2}, Co^{+3}	$3d^6$, ^5D	6	$\frac{370}{49}$	$\frac{631}{49}$	12	12	12	$\frac{1512}{105}$	$\frac{1512}{105}$	$\frac{2268}{105}$	$\frac{2268}{105}$
Fe^+, Co^{+2}, Ni^{+3}	$3d^7$, ^4F	7	$\frac{435}{49}$	$\frac{657}{49}$	14	14	14	$\frac{1764}{105}$	$\frac{1764}{105}$	$\frac{2646}{105}$	$\frac{2646}{105}$
Co^+, Ni^{+2}, Cu^{+3}	$3d^8$, ^3F	8	$\frac{505}{49}$	$\frac{783}{49}$	16	16	16	$\frac{2016}{105}$	$\frac{2016}{105}$	$\frac{3024}{105}$	$\frac{3024}{105}$
Ni^+, Cu^{+2}	$3d^9$, ^2D	9	$\frac{580}{49}$	$\frac{1009}{49}$	18	18	18	$\frac{2268}{105}$	$\frac{2268}{105}$	$\frac{3402}{105}$	$\frac{3402}{105}$
Cu^+	$3d^{10}$, ^1S	10	$\frac{700}{49}$	$\frac{1260}{49}$	20	20	20	24	24	36	36

paper (Freeman, 1959a) as may be a description of the numerical methods and an explanation of the notation (Freeman, 1959c).

For the ions discussed in this paper, the formulas for the contribution to $\mathscr{F}$, from the (in general) non-spherical shell of d electrons, are given in Table 1 for the appropriate configuration and ground state term value (Freeman, 1959a). To this contribution (i.e., the sum of all terms in a given row) must be added that of the core electrons ($1s^2 2s^2 2p^6 3s^2 3p^6$) which are common to all the atoms,

$$\mathscr{F}\,(\text{core}) = 2f_{1s}^2 + 2f_{2s}^2 + 6f_{2p}^2 + 2f_{3s}^2 + 6f_{3p}^2$$
$$+ 4(f_{1s,\,2s}^2 + f_{1s,\,3s}^2 + f_{2s,\,3s}^2)$$
$$+ 12(f_{1s,\,2p}^2 + f_{2s,\,2p}^2 + f_{3s,\,2p}^2 + f_{1s,\,3p}^2 + f_{2s,\,3p}^2 + f_{3s,\,3p}^2)$$
$$+ 12(f_{2p,\,2p}^2(2) + f_{3p,\,3p}^2(2) + f_{2p,\,3p}^2(0) + 2f_{2p,\,3p}^2(2)) \,. \quad (3)$$

The terms f_{ij}, with $i \neq j$ are the exchange terms which arise from application of the Pauli exclusion principle; the summation in equation (1) is over wave functions i, j having the same spin.

Results and discussion

The results of the calculations are summarized in Table 2 which gives $I_{\text{e.u.}}$ as a function of $\sin\theta/\lambda$ in

$Å^{-1}$ units. In previous work values of f_{ij} were also given in order to facilitate interpolation for atoms for which no such computations were available. Since we have obtained values for the entire series no such interpolations are necessary and in order to conserve space the f_{ij} integrals have not been tabulated. (They are available to interested persons from the authors.) The exchange terms amount to 50% of $I_{\text{e.u.}}$ at low $\sin\theta/\lambda$ in agreement with earlier results, and so cannot be neglected.

In Fig. 1 we show the calculated results for Fe^+ ($3d^7$), Fe^{+2} ($3d^6$), Fe^{+3} ($3d^5$) and also Fe $3d^6 4s^2$ taken from the earlier work of Freeman (1960b). We see that the results form a 'family' of non-intersecting curves and, at each $\sin\theta/\lambda$, show a roughly equal spacing between them. Let us see what some consequences of this result might be. First, it implies that one can readily interpolate (or extrapolate) available data to obtain incoherent scattering functions for ions for which such data is not known. Secondly, it offers the possibility of determining, from Compton scattering experiments, the number of $3d$ electrons in the (say) transition metals, whereas (and for a similar reason) such a determination based on measurements of the atomic scattering factor as suggested by Weiss & DeMarco

Table 2. *X-ray incoherent scattering functions for the transition elements* Sc *through* Cu

$\sin\theta/\lambda$	Sc$^+$	Sc^{+2}	Sc^{+3}	Ti$^+$	Ti^{+2}	Ti^{+3}	V$^+$	V^{+2}	V^{+3}	Cr$^+$
0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
0·05	0·52	0·35	0·22	0·50	0·35	0·27	0·49	0·34	0·26	0·46
0·10	1·74	1·26	1·01	1·72	1·32	1·01	1·67	1·25	1·00	1·62
0·20	4·53	3·78	3·21	4·56	3·81	3·25	4·56	3·81	3·24	4·50
0·30	7·00	6·16	5·43	7·08	6·24	5·56	7·13	6·31	5·60	7·11
0·40	8·99	8·08	7·25	9·17	8·28	7·49	9·30	8·42	7·64	9·35
0·50	10·52	9·57	8·67	10·83	9·89	9·03	11·07	10·14	9·29	11·23
0·60	11·66	10·68	9·75	12·10	11·14	10·21	12·46	11·51	10·61	12·74
0·70	12·53	11·54	10·59	13·07	12·09	11·14	13·54	12·58	11·63	13·93
0·90	13·89	12·89	11·90	14·50	13·51	12·53	15·11	14·11	13·14	15·66
1·10	15·00	14·00	12·99	15·64	14·63	13·64	16·27	15·28	14·29	16·90

$\sin\theta/\lambda$	Cr^{+2}	Cr^{+3}	Mn$^+$	Mn^{+2}	Mn^{+3}	Fe$^+$	Fe^{+2}	Fe^{+3}	Co$^+$	Co^{+2}
0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
0·05	0·33	0·26	0·45	0·32	0·25	0·44	0·32	0·25	0·43	0·31
0·10	1·23	0·99	1·60	1·20	0·97	1·57	1·19	0·94	1·54	1·17
0·20	3·79	3·23	4·54	3·74	3·21	4·53	3·74	3·15	4·51	3·72
0·30	6·33	5·64	7·21	6·31	5·65	7·25	6·38	5·62	7·28	6·40
0·40	8·52	7·75	9·50	8·55	7·82	9·60	8·69	7·85	9·68	8·77
0·50	10·33	9·51	11·45	10·46	9·66	11·63	10·67	9·76	11·77	10·82
0·60	11·80	10·93	13·07	12·04	11·19	13·33	12·34	11·38	13·56	12·58
0·70	12·98	12·06	14·36	13·32	12·42	14·72	13·71	12·72	15·05	14·04
0·90	14·67	13·71	16·22	15·19	14·24	16·75	15·73	14·71	17·24	16·22
1·10	15·90	14·92	17·53	16·51	15·52	18·14	17·13	16·11	18·74	17·72

| $\sin\theta/\lambda$	Co^{+3}	Ni$^+$	Ni^{+2}	Ni^{+3}	Cu$^+$	Cu^{+2}	Cu^{+3}
0·00	0·00	0·00	0·00	0·00	0·00	0·00	0·00
0·05	0·25	0·41	0·31	0·24	0·40	0·30	0·24
0·10	0·94	1·50	1·14	0·92	1·45	1·12	0·90
0·20	3·15	4·47	3·69	3·13	4·42	3·66	3·09
0·30	5·65	7·28	6·40	5·66	7·26	6·39	5·64
0·40	7·95	9·72	8·82	8·01	9·73	8·85	8·03
0·50	9·95	11·86	10·93	10·07	11·92	11·02	10·16
0·60	11·65	13·73	12·76	11·85	13·85	12·92	12·01
0·70	13·07	15·30	14·31	13·37	15·51	14·55	13·65
0·90	15·22	17·67	16·67	15·68	18·06	17·06	16·09
1·10	16·71	19·29	18·29	17·29	19·82	18·81	17·82
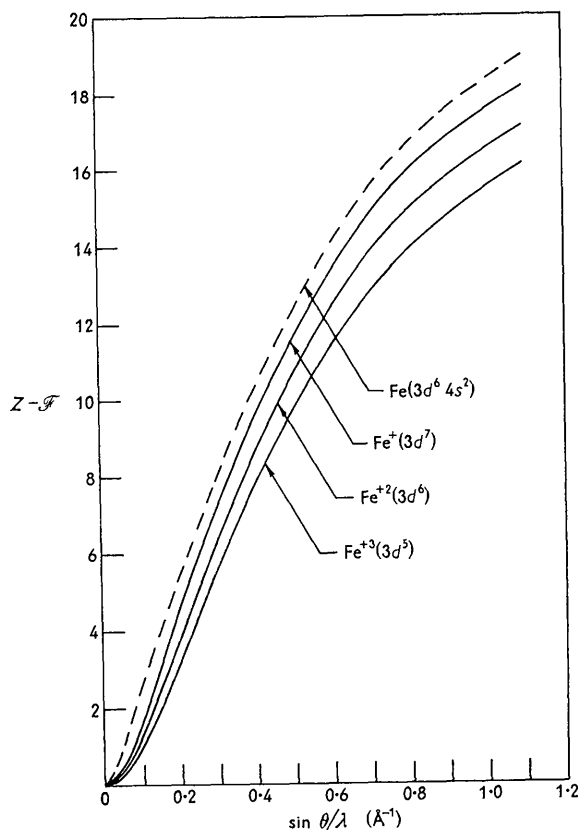
Fig. 1. Incoherent scattering intensity, $Z-\mathscr{F}$, for $Fe^+(3d^7)$, $Fe^{+2}(3d^6)$, $Fe^{+3}(3d^5)$ of this work and the $Fe(3d^6, 4s^2)$ result of Freeman (1960b).

Fig. 2. Incoherent scattering intensity for Mn^{+2} (this work), solid curve, compared with the earlier result of Freeman (1960b), dashed curve.

(1958) is *not* possible (Watson & Freeman, 1961). This is so because the atomic scattering factors at low $\sin \theta/\lambda$ (the measurements are most accurate at the first Bragg reflection and so are done there) is surprisingly insensitive to the number of $3d$ electrons in the atom (Watson & Freeman, 1961). 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 un- ambiguously determine the $3d$ configuration of iron in the range $3d^8$ 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 $3d^4$ con- figuration from this range.

Incoherent scattering functions have been calculated previously only for a few ions of the transition series (Freeman, 1959c, 1960b). For Cu^+ we find almost exact agreement between the results given in Table 2 and those reported earlier (Freeman, 1959c). This is an encouraging result for it means that even though there are small differences between the methods that were used to determine the wave functions (analytic
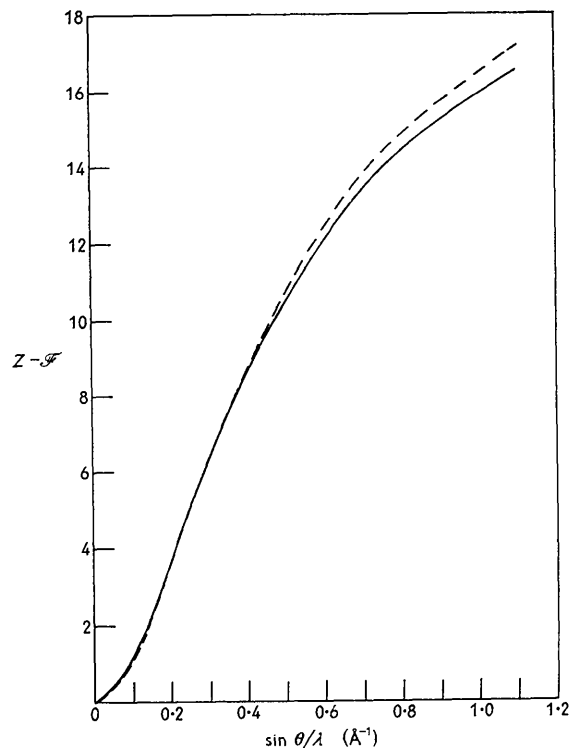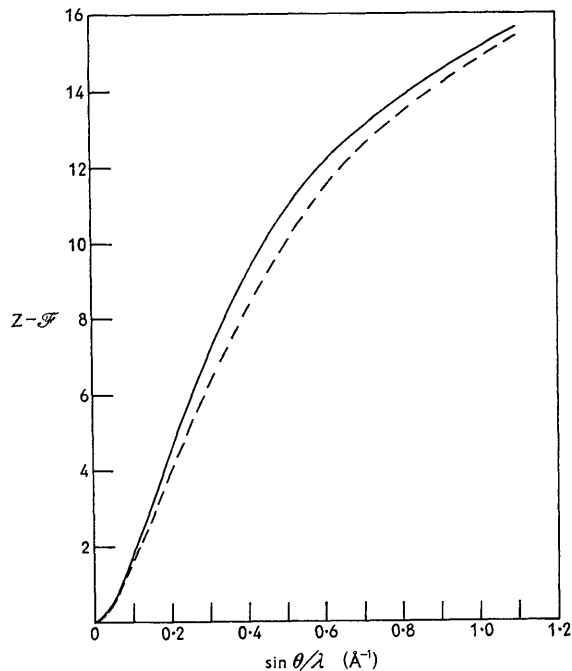

Fig. 3. Incoherent scattering intensity for Ti^+ (this work), solid curve, compared with the earlier result of Freeman (1960b), dashed curve.
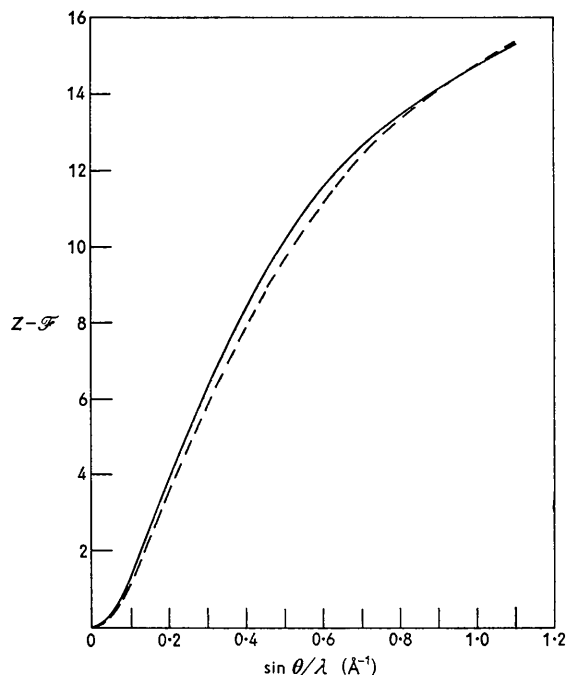
Fig. 4. Incoherent scattering intensity for V^{+2} (this work), solid curve, compared with earlier result of Freeman (1960b), dashed curve.

scattering contribution of the other electrons. If from the earlier Fe $(3d^6 4s^2)$ results (Freeman, 1960b) we compute the contribution to $\mathscr{F}$ from all terms $(|f_{ii}|^2$ and $|f_{ij}|^2)$ involving the $4s$ electrons we find that like the $4s$ form factor this contribution is negligible except at very low $\sin \theta/\lambda$ and that the contribution $(2 - \mathscr{F})$ to the intensity equals $2 \cdot 00 \ (\pm 0 \cdot 08)$ except at $\sin \theta/\lambda = 0 \cdot 1$. (It is, of course, zero at $\sin \theta/\lambda = 0$). This means that, over most of the range in angle, one could estimate I for say a $3d^{n-2}4s^2$ atom by using the I given in Table 2 for the $3d^{n-2}$ state and adding 2 as the $4s$ contribution or, much better still, adding the square of the $4s$ form factor. (See Freeman & Watson (1961) for a tabulation of these for the neutral iron series atoms.) If one follows this procedure and adds the $4s$ contribution to the intensity listed in Table 2 for Fe^{+2} one does not reproduce the earlier results (Freeman, 1960b). This is not surprising in view of the Slater (1951) approximation of exchange which Wood & Pratt (1957) used to calculate the earlier wave functions. The effect of this approximation is discussed more fully by Watson & Freeman (1960). The possibility of following a procedure such as the one just discussed for treating the $4s$ contribution means that the results given in Table 2 may be applied without large errors to atomic configurations

versus numerical) the results are insensitive to these. Further it provides us with evidence that both calculations were carried out fairly accurately.

In Figs. 2, 3, and 4, we show a comparison of the present results for Ti^+, V^{+2}, and Mn^{+2} with those reported earlier (Freeman, 1960b). We see that over most of the range of $\sin \theta/\lambda$ the results for Mn^{+2} agree very well; only at very large angles do the results diverge. Several factors may be responsible for this but most probably the main reason lies in the fact that the earlier results were based on Hartree's (1954) wave functions which were obtained from an incomplete self-consistent field treatment and it is the outer region in $\sin \theta/\lambda$ which would reflect the differences in wave function density near the nucleus. The results for Ti^+ and V^{+2} show greater differences but this is not surprising since the wave functions used in the earlier calculation (Freeman, 1960b) were based on Hartree's (1954) core wave functions for Mn^{+2} and $3d$ functions calculated with these as the core potential (Hartree, 1956), and so are even more approximate than those for Mn^{+2}.

The calculations have one obvious shortcoming— they do not include the contribution of the $4s$ electrons. Let us now see how serious this is and how to go about overcoming this deficiency. First we must observe that it was previously found (Watson & Freeman, 1961) that the presence of $4s$ electrons had no effect on either the distribution of the other electrons or their scattering factors. Hence we expect that we can separate out the effect of the $4s$ electrons from the incoherent

Table 3. *Incoherent scattering intensities based on Hartree–Fock wave functions*

For the ground state configuration only the unfilled outer shell is given

Atom or ion	Ground state	Reference		Atom or ion	Ground state	Reference
Li^+	$1s^2, {}^1S$	F(e)		Al	$3p, {}^2P$	F(b)
Li	$2s, {}^2S$	F(e)		Si^{+4}	$2p^6, {}^1S$	F(d)
Be	$2s^2, {}^1S$	F(e)		Si^{+3}	$3s, {}^2S$	F(d)
B	$2p, {}^2P_{\frac{1}{2}}$	M–B		Si	$3p^2, {}^3P$	F(d)
C	$2p^3, {}^4S$	K–V		Cl^-	$3p^6, {}^1S$	F(e)
N	$2p^3, {}^4S$	F(d)		K^+	$3p^6, {}^1S$	F(e)
N^-	$2p^4, {}^3P$	F(d)		Ca^{++}	$3p^6, {}^1S$	F(e)
O^{+3}	$2p, {}^2P$	F(d)		Ca^+	$3p^6, 4s, {}^2S$	F(e)
O^{+2}	$2p^2, {}^3P$	F(d)		Ca	$3p^6, 4s^2, {}^1S$	F(e)
O^+	$2p^3, {}^4S$	F(d)		Ti^+	$3d^3, {}^4F$	F(f)
O	$2p^4, {}^3P$	F(d)		V^{+2}	$3d^3, {}^4F$	F(f)
O^-	$2p^5, {}^2P$	F(d)		Mn^{+2}	$3d^5, {}^6S$	F(f)
F	$2p^5, {}^2P$	F(d)		Mn^+	$3d^6, {}^5D$	F(f)
F^-	$2p^6, {}^1S$	F(d)		Mn	$3d^5, 4s^2, {}^6S$	F(f)
Ne	$2p^6, {}^1S$	F(c)		Cu^+	$3d^{10}, {}^1S$	F(c)
Na^+	$2p^6, {}^1S$	F(e)		Cu	$3d^{10}, 4s, {}^2S$	F(c)
Na	$3s, {}^2S$	F(e)		Zn^{+2}	$3d^{10}, {}^1S$	F(c)
Al^{+3}	$2p^6, {}^1S$	F(e)		Ge	$4s^2, 4p^2, {}^3P$	F(d)
Al^+	$3s^2, {}^1S$	F(e)				

F(b) = Freeman (1959b)
F(c) = Freeman (1959c)
F(d) = Freeman (1959d)
F(e) = Freeman (1960a)
F(f) = Freeman (1960b)
K–V = Keating & Vineyard (1956)
M–B = Milberg & Brailsford (1958)

other than $3d^n$ for which the calculations were carried out.

Comparison with experiment

There have been very few experimental determinations of the incoherent scattering intensities (for C, Al, KCl, CaF_2 and NaCl) but these have not included any of the atoms considered in this paper. While the agreement between theory and experiment has been very good for these cases, it would be valuable to have accurate measurements for the transition elements, both for their own inherent interest and to compare with theory in order to test its validity. While the experiments are not easy to perform we hope that they will soon be undertaken.

APPENDIX A

We give in Table 3 a listing of the atoms and ions for which accurate incoherent scattering functions are now known in order to provide a convenient summary of the data available to date. The results of the present work are not included.

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Some Calculations using the Ewald Transformation

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The calculation of the energy, dispersion relations of the normal modes, and elastic constants of a crystal requires a knowledge of the long-range Coulomb interactions between the atoms. The summations involved can be expressed in dimensionless form and converted to a rapidly convergent form by using the Ewald transformation. Machine programs have been written to calculate the Madelung coefficients, Coulomb coefficients, and the expansions of the Coulomb coefficients, (which are required to calculate the elastic constants), for crystals which have at least orthorhombic symmetry. Both the Madelung coefficients, and the Coulomb coefficients for wave-vectors parallel to the ferro-electric axis, have been calculated for barium titanate, using the atomic positions both of the paraelectric phase and of the ferroelectric phase at 20 °C.

The total energy of a non-metallic crystal is usually divided into two parts—one from the Coulomb interaction of point charges, dipoles and higher multipole moments representing the long-range interactions between the atoms in the crystal, and the other from the short-range or repulsive forces. Although the potential for the interaction of point charges and multipoles is readily obtained from classical electrostatics, the short-range interaction is essentially of a quantum-mechanical nature, and cannot usually be