Acta Cryst. (1959). **12**, 274

A Study of the Compton Scattering of X-rays: Ne, Cu$^+$, Cu and Zn^{+2}

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(*Received 4 August* 1958 *and in revised form* 13 *October* 1958)

The complete Waller–Hartree theory has been employed to calculate the incoherent scattering intensities for Ne, Cu, Cu$^+$ and Zn^{+2}, using Hartree–Fock self-consistent field wave functions. It is found that inclusion of all the exchange integrals, usually neglected by James & Brindley and others, results in very large deviations from the values obtained by these authors. These exchange contributions are of increasing importance with increasing atomic number since the number of exchange integrals rises rapidly with the number of electrons. In agreement with certain experimental evidence, the results in all cases show a large decrease in the predicted Compton intensities, compared with the results of James & Brindley and others.

1. Introduction

In recent years the diffuse scattering of X-rays has become an increasingly important means for studying the properties of amorphous solids and imperfections in crystals (such as order–disorder, lattice vibrations, etc.). The scattering measured experimentally contains not only this diffuse scattering but also the incoherent Compton scattering. As the Compton scattering may frequently contribute a large part of the total radiation scattered, an accurate knowledge of the incoherent intensity is necessary if accurate measurements of the diffuse scattering are to be found. This contribution may be determined either theoretically or experimentally.

The usual procedure for correcting for the incoherent scattering intensity is to calculate its contribution theoretically. As no theory of crystalline scattering is available, the incoherent scattering intensity factor has been calculated by using free atom formulae. The most accurate of these is that due to Waller & Hartree (1929)

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

where

$$f_{ij} = \int \psi_i^*(\mathbf{r}) \exp{[iK\mathbf{S}.\mathbf{r}]}\psi_j(\mathbf{r})dv \qquad (2)$$

$K = 2\pi/\lambda$; λ is the wavelength of the incident radiation; $\mathbf{S} = \mathbf{s}-\mathbf{s}_0$, where $\mathbf{s}$, $\mathbf{s}_0$ are unit vectors along the reflected and incident directions: and the ψ's are appropriate one-electron wave functions. Equation (1), giving the intensity in electron units (e.u.) has been written (for convenience) without the Breit–Dirac correction factor $(\nu'/\nu)^3$, where ν and ν' are the frequencies of the X-rays before and after scattering.

The f_{ij} terms in the Waller–Hartree equation arise from application of the Pauli exclusion principle which forbids electronic transitions to an occupied state and so the summation is over one-electron wave functions of the same spin only. In general, almost all calculations of the Compton scattering have completely neglected these exchange contributions. To date, only the incoherent scattering function for carbon (Keating & Vineyard, 1956) has been calculated using Hartree–Fock SCF wave functions in the complete Waller–Hartree theory. Waller & Hartree (1929) calculated an $\mathscr{F}$ value for argon in which all f_{ij} terms between electrons in different shells were neglected. But as they used SCF wave functions without exchange, equation (1) may not properly be employed since the wave functions are not strictly orthogonal. The calculation by Harvey, Williams & Jauncey (1934) for neon was also approximate in that only the contribution of the $f_{2s,\,2p}$ term was calculated—all other exchange contributions were totally neglected. In all other calculations, these exchange effects have been completely neglected and the values of James & Brindley (1931) for $\Sigma_i|f_{ii}|^2$, based, in part, on interpolations for atoms for which no SCF wave functions are available, have been used extensively by X-ray workers.

It is the purpose of this work to calculate accurate incoherent scattering functions for atoms for which Hartree–Fock wave functions are available using the complete Waller–Hartree expression. In this paper the results of these calculations for Ne, Cu$^+$, Cu and Zn^{+2} are presented; the incoherent scattering functions for other atoms for which Hartree–Fock functions are available are being calculated and will be published at a later date.

2. Calculation of the f_{jk} integrals

If the total atomic charge distribution is spherically symmetrical, the scattering is independent of atomic orientation so that the matrix elements, f_{jk}, may be calculated by taking the vector $\mathbf{S}$ along the polar axis. Setting $k = K|\mathbf{S}| = 4\pi \sin\theta/\lambda$ (2θ is the angle of scattering, not to be confused with the polar angle in what follows), and using the expansion

$$\exp\,[ikr\cos\theta] = \sum_n i^n(2n+1)P_n\,(\cos\theta)\,j_n(kr)\,, \quad (3)$$

where the j_n are the spherical Bessel functions, we may write

$$f_{jk} = \sum_n i^n(2n+1)\int \psi_j^*(\mathbf{r})\psi_k(\mathbf{r})P_n\,(\cos\theta)j_n(kr)\,dv\,. \quad (4)$$

Writing ψ_j in the separable form

$$\psi_j = P_j(r)/r\Theta(l_jm_j)\Phi(m_j)\,,$$

where $P_j(r)$ is the normalized radial function, $\Theta(l_jm_j)$ the normalized associated Legendre functions (as defined by Condon & Shortley (1953)), i.e., $P_l\,(\cos\theta) = \{2/(2l+1)\}^{\frac{1}{2}}\Theta(l, 0)$, and $\Phi(m_j)$ the ordinary normalized φ eigenfunctions, and denoting

$$C^n(l_1m_1;\ l_2m_2) = \left(\frac{2}{2n+1}\right)^{\frac{1}{2}}\int_0^\pi \Theta(n_1m_1-m_2)\Theta(l_1m_1)\Theta(l_2m_2)\sin\theta\,d\theta$$

we have upon substitution into equation (2) and its subsequent integration

$$f_{jk} = \sum_n i^n(2n+1)C^n(l_jm;\ l_km)\int_0^\infty P_j(r)P_k(r)j_n(kr)\,dr\,. \quad (5)$$

The coefficients $C_n(l_jm;\ l_km)$ are integrals of products of three associated Legendre functions and are tabulated in a convenient form by Condon & Shortley (1953).

Denoting the radial integrals in equation (5) by $\langle j_n\rangle$, we see that the f_{jk} terms of equation (1) are simply linear combinations of $\langle j_n\rangle$ with coefficients which depend only on the angular dependence of the one-electron wave functions. These coefficients are listed in Table 1 for the matrix elements, f_{jk}, of s-like, p-like and d-like one-electron wave functions; the 0, +, +2 subscripts denote the component of orbital angular momentum along the axis of quantization. When the individual one-electron charge density $\psi_j^*\psi_k$ is spherically symmetrical equation 5 reduces to the familiar form

Table 1. *Coefficients of $\langle j_n\rangle$ for the matrix elements of f_{jk}, for s, p and d electrons*

f_{jk}	Common coeff.	j_0	j_1	j_2	j_3	j_4
$f_{s,\,s}$	1	1	—	—	—	—
$f_{s,\,p_0}$	$\sqrt{3}i$	—	1	—	—	—
$f_{s,\,d_0}$	$\sqrt{5}$	—	—	-1	—	—
$f_{p_0,\,p_0}$	1	1	—	-2	—	—
$f_{p_+,\,p_+}$	1	1	—	1	—	—
$f_{p_0,\,d_0}$	$3i/\sqrt{15}$	—	2	—	-3	—
$f_{p_+,\,d_+}$	$3i/\sqrt{5}$	—	1	—	1	—
$f_{d_0,\,d_0}$	1	1	—	$-10/7$	—	18/7
$f_{d_+,\,d_+}$	1	1	—	$-\ 5/7$	—	$-12/7$
$f_{d_{+2},\,d_{+2}}$	1	1	—	$+10/7$	—	3/7

$$\int P_j(r)P_k(r)\sin kr/kr\,dr = \langle j_0\rangle\,. \quad (6)$$

In the work of James & Brindley (1931), Harvey *et al.* (1934) and others, the f_{ii}'s of equation (5) are replaced by the spherical approximation of equation (6), i.e., all $\langle j_n\rangle$ terms with $n \neq 0$ are neglected, so that aside from neglecting the exchange terms, the diagonal terms themselves are also approximated in all these calculations.

If the correct procedures, as outlined above, are followed, they result in the following formulae for the atoms considered in this paper:

(1) Ne$[(1s)^2(2s)^2(2p)^6,\ {}^1S]$:

$$\mathscr{F}_{\mathrm{Ne}} = 2f^2_{1s}+2f^2_{2s}+6f^2_{2p}+4f^2_{1s,\,2s}+12f^2_{1s,\,2p} +12f^2_{2s,\,2p}+12f^2_{2p,\,2p}\,. \quad (7)$$

(2) Cu$^+[(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^{10},\ {}^1S]$:

$$\begin{aligned}\mathscr{F}_{\mathrm{Cu+}} = \mathscr{F}_{\mathrm{Ne}}&+2f^2_{3s}+6f^2_{3p}+10f^2_{3d}+4f^2_{1s,\,3s}+4f^2_{2s,\,3s}\\ &+12(f^2_{3s,\,2p}+f^2_{1s,\,3p}+f^2_{2s,\,3p}+f^2_{3s,\,3p})+12f^{2(0)}_{2p,\,3p}\\ &+24f^{2(2)}_{2p,\,3p}+12f^2_{3p,\,3p}+20(f^2_{1s,\,3d}+f^2_{2s,\,3d}+f^2_{3s,\,3d})\\ &+24f^{2(1)}_{2p,\,3d}+36f^{2(3)}_{2p,\,3d}+24f^{2(1)}_{3p,\,3d}+36f^{2(3)}_{3p,\,3d}\\ &+700/49f^{2(2)}_{3d,\,3d}+1260/49f^{2(4)}_{3d,\,3d}\,.\end{aligned} \quad (8)$$

(3) Cu$[(1s)^2(2s)^2\ldots(3d)^{10}4s,\ {}^2S]$:

$$\begin{aligned}\mathscr{F}_{\mathrm{Cu}} = \mathscr{F}_{\mathrm{Cu+}}&+f^2_{4s}+2(f^2_{1s,\,4s}+f^2_{2s,\,4s}+f^2_{3s,\,4s})\\ &+6(f^2_{4s,\,2p}+f^2_{4s,\,3p})+10f^2_{4s,\,3d}\,.\end{aligned} \quad (9)$$

(4) Zn^{+2}: Same as Cu$^+$.

For each atom we have listed its configuration and its ground state term value. The notation* conforms to the following definitions:

$$\begin{aligned} f_{ns} &= \int P^2_{ns}(r)j_0(kr)\,dr\\ f_{np} &= \int P^2_{np}(r)j_0(kr)\,dr\\ f^{(m)}_{nd,\,nd} &= \int P^2_{nd}(r)j_m(kr)\,dr, \quad m = 0, 2, 4\\ f_{ns,\,n's} &= \int P_{ns}(r).P_{n's}(r)j_0(kr)\,dr\\ f_{ns,\,n'p} &= \int P_{ns}(r).P_{n'p}(r)j_1(kr)\,dr\\ f_{ns,\,n'd} &= \int P_{ns}(r).P_{n'd}(r)j_2(kr)\,dr\\ f_{np,\,np} &= \int P^2_{np}j_2(kr)\,dr\\ f^{(m)}_{np,\,n'p} &= \int P_{np}(r).P_{n'p}(r)j_m(kr)\,dr, \quad m = 0, 2\\ f^{(m)}_{np,\,n'd} &= \int P_{np}(r).P_{n'p}(r)j_m(kr)\,dr, \quad m = 1, 3\,. \end{aligned} \quad (10)$$

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* This notation is an extension of that introduced by Keating & Vineyard (1956) in order to avoid possible cases of ambiguity. For example $f^{(0)}_{2p,\,3p}$ and $f^{(2)}_{2p,\,3p}$ are now properly distinguished by the order of the spherical Bessel function given inside the parenthesis.

Table 2. *Calculation of the X-ray incoherent scattering functions for* Ne

$\sin\theta/\lambda$	f_{1s}	f_{2s}	f_{2p}	$f^{(2)}_{2p,2p}$	$f_{1s,2s}$	$f_{1s,2p}$	$f_{2s,2p}$	$\Sigma\|f_{ii}\|^2$	$\mathscr{F}$	$10-\mathscr{F}$
0·0	1·0000	1·0000	1·0000	0·000	0·0000	0·000	0·000	10·000	10·000	0·000
0·1	0·9976	0·9314	0·9153	0·032	−0·0021	0·019	0·186	8·764	9·184	0·816
0·2	0·9902	0·7570	0·7195	0·0992	−0·0081	0·0374	0·3044	6·331	7·461	2·539
0·3	0·9782	0·5435	0·5077	0·1554	−0·0174	0·0541	0·3377	4·341	5·745	4·255
0·4	0·9617	0·3479	0·3334	0·1827	−0·0292	0·0677	0·3100	3·160	4·372	5·628
0·5	0·9412	0·1975	0·2084	0·1840	−0·0423	0·0786	0·2539	2·517	3·373	6·627
0·6	0·9170	0·0958	0·1254	0·1695	−0·0560	0·0866	0·1923	2·139	2·685	7·315
0·7	0·8896	0·0343	0·0726	0·1485	−0·0693	0·0917	0·1371	1·882	2·228	7·772
0·9	0·8274	−0·0126	0·0201	0·1051	−0·0921	0·0944	0·0587	1·504	1·686	8·314
1·1	0·7587	−0·0132	0·0019	0·0706	−0·1077	0·0899	0·0172	1·212	1·359	8·641

From these formulae we see that the number of exchange terms rises rapidly with increasing atomic number; even for Ne the number of exchange terms is a large fraction of the total number of terms. For higher atomic number, the exchange contributions should therefore be important, and as will be shown later, they are definitely quite considerable.

3. Numerical methods

Since the results of the computations depend directly on the choice of one-electron basis functions, it was decided to use Hartree–Fock self-consistent field solutions as these represent the best free atom wave functions available to date. The numerical integrations were carried out on Whirlwind I, the M.I.T. digital computer using a j_n generation routine written by Wood (1957). The numerical wave functions were used as direct input data, after being interpolated to a mesh suitable for machine calculation by a routine written by Corbató (1956). The effect of the interpolation procedure on the numerical accuracy was checked by the normalization condition.

4. Results

In the accompanying Tables are listed, for each atom, the calculated values of f_{ij}, $\mathscr{F}$ and $Z-\mathscr{F}$ as a function of $\sin\theta/\lambda$ in Å^{-1} units. Also included, for purposes of comparison with other calculations, are values of the diagonal terms $\Sigma i|f_{ii}|^2$, since the difference between $\mathscr{F}$ and this quantity gives us the magnitude of the exchange contribution.

(A) *Neon*

Recently calculated Hartree–Fock wave functions* (Allen, 1957) were used in the present work. The numerical results are given in Table 2. For comparison the earlier results of James & Brindley (1931) and Harvey *et al.* (1934) are plotted along with our results in Fig. 1. The J&B values differ from ours by 75% at $\sin\theta/\lambda = 0{\cdot}2$, decreasing to 20% at $\sin\theta/\lambda = 0{\cdot}5$. The Harvey *et al.* values are considerably better than the J&B values over most of the range of $\sin\theta/\lambda$; the inclusion of the exchange terms neglected by Harvey *et al.* lowers the Compton intensity by 25% at $\sin\theta/\lambda = 0{\cdot}2$ and by 10% even at $\sin\theta/\lambda = 0{\cdot}5$. These percentage deviations are summarized in Table 3 as they clearly indicate the importance of the exchange contribution to the incoherent scattering intensities.

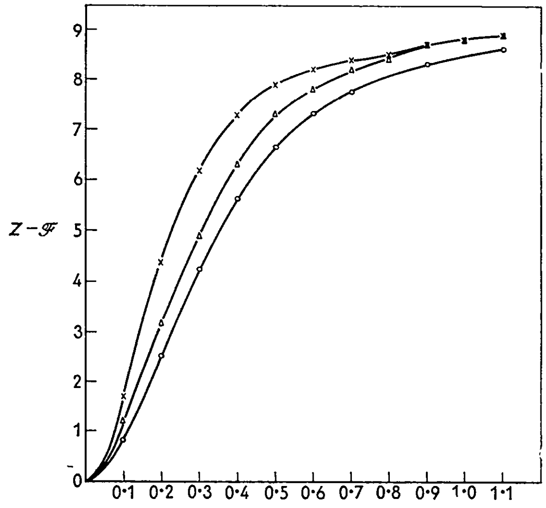

Fig. 1. Incoherent scattering function for Ne: (*a*) the x's denote the values of J&B, (*b*) the triangles those of Harvey *et al.* (1934) and (*c*) the circles our values using the complete Waller–Hartree equation.

Table 3. *Comparison of results for* Ne *with other calculations: Percentage deviations from our values*

$\sin\theta/\lambda$	J&B	Harvey *et al.*
0·1	107	48
0·2	74	27
0·3	46	15
0·4	30	12
0·5	19	10
0·6	12	6·6
0·7	8·4	5·8
0·9	4·8	4·8
1·1	3·1	3·1

(B) *Copper*

The numerical results for Cu$^+$ and Cu are presented

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* I am grateful to Dr L. C. Allen for allowing me the use of his unpublished results.

Table 4. *Calculation of the X-ray incoherent scattering functions for* Cu⁺ *and* Cu

Cu⁺

$\sin\theta/\lambda$	f_{1s}	f_{2s}	f_{2p}	f_{3s}	f_{3p}	f_{3d}	$f_{1s,2s}$	$f_{1s,2p}$	$f_{2s,2p}$	$f_{2p,2p}$	$f_{1s,3s}$
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	0·0000	0·0000	0·0000	0·0000	0·000
0·1	0·9998	0·9951	0·9961	0·9565	0·9513	0·9123	0·0008	0·0087	−0·0475	0·0016	0·000
0·2	0·9989	0·9806	0·9846	0·8368	0·8195	0·7131	0·0016	0·0178	−0·0941	0·0062	0·000
0·3	0·9976	0·9567	0·9657	0·6687	0·6404	0·5036	0·0029	0·0270	−0·1387	0·0136	0·0004
0·4	0·9956	0·9244	0·9399	0·4856	0·4535	0·3330	0·0047	0·0357	−0·1801	0·0239	0·0009
0·5	0·9932	0·8845	0·9081	0·3165	0·2887	0·2090	0·0069	0·0443	−0·2178	0·0359	0·0016
0·6	0·9902	0·8382	0·8708	0·1790	0·1610	0·1241	0·0096	0·0527	−0·2509	0·0498	0·0025
0·7	0·9866	0·7866	0·8292	0·0798	0·0727	0·0681	0·0128	0·0606	−0·2792	0·0651	0·0034
0·9	0·9780	0·6729	0·7363	−0·0166	−0·0088	0·0109	0·0202	0·0761	−0·3199	0·0972	0·0057
1·1	0·9675	0·5534	0·6369	−0·0268	−0·0167	−0·0083	0·0290	0·0901	−0·3397	0·1288	0·0085

$\sin\theta/\lambda$	$f_{2s,3s}$	$f_{3s,2p}$	$f_{1s,3p}$	$f_{2s,3p}$	$f_{3s\ 3p}$	$f_{3p,3p}$	$f^{(0)}_{2p,3p}$	$f^{(2)}_{2p,3p}$	$f_{1s,3d}$	$f_{2s,3a}$
0·0	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
0·1	0·0040	0·0105	0·0026	0·0174	−0·1568	0·0193	0·0033	−0·0012	0·0000	−0·0017
0·2	0·0133	0·0198	0·0053	0·0330	−0·2807	0·0690	0·0119	−0·0046	0·0000	−0·0064
0·3	0·0279	0·0263	0·0080	0·0458	−0·3514	0·1298	0·0253	−0·0097	0·0000	−0·0138
0·4	0·0463	0·0295	0·0105	0·0545	−0·3664	0·1820	0·0422	−0·0158	0·0004	−0·0231
0·5	0·0666	0·0290	0·0131	0·0587	−0·3367	0·2135	0·0610	−0·0221	0·0005	−0·0333
0·6	0·0873	0·0246	0·0156	0·0581	−0·2799	0·2214	0·0804	−0·0279	0·0006	−0·0439
0·7	0·1067	0·0169	0·0181	0·0533	−0·2127	0·2094	0·0990	−0·0324	0·0008	−0·0536
0·9	0·1366	−0·0059	0·0229	0·0337	−0·0922	0·1521	0·1290	−0·0362	0·0014	−0·0695
1·1	0·1504	−0·0324	0·0273	0·0072	−0·0190	0·0876	0·1460	−0·0322	0·0019	−0·0781

$\sin\theta/\lambda$	$f_{3s,3d}$	$f^{(2)}_{3d,3d}$	$f^{(1)}_{2p,3d}$	$f^{(3)}_{2p,3d}$	$f^{(1)}_{3p,3d}$	$f^{(3)}_{3p,3d}$	$f^{(4)}_{3d,3d}$	$\Sigma\|f_{ii}\|^2$	$\mathscr{F}$	$28-\mathscr{F}$
0·0	0·0000	0·000	0·0000	0·0000	0·0000	0·0000	0·0000	28·00	28·00	0·00
0·1	0·0194	0·033	0·0254	0·0000	−0·1624	−0·0025	0·0008	25·54	26·52	1·48
0·2	0·0679	0·101	0·0492	0·0005	−0·2775	−0·0172	0·0089	20·46	23·54	4·46
0·3	0·1240	0·155	0·0704	0·0017	−0·3263	−0·0449	0·0264	15·87	20·70	7·30
0·4	0·1683	0·1796	0·0880	0·0038	−0·3181	−0·0774	0·0467	12·73	18·23	9·77
0·5	0·1915	0·1817	0·1015	0·0069	−0·2751	−0·1055	0·0640	10·76	16·06	11·94
0·6	0·1936	0·1699	0·1107	0·0108	−0·2176	−0·1241	0·0761	9·47	14·15	13·85
0·7	0·1795	0·1513	0·1157	0·0153	−0·1594	−0·1320	0·0827	8·48	12·50	15·50
0·9	0·1273	0·1096	0·1151	0·0251	−0·0661	−0·1228	0·0842	6·82	9·95	18·05
1·1	0·0723	0·0737	0·1045	0·0341	−0·0111	−0·0963	0·0759	5·44	8·19	19·81

Cu

$\sin\theta/\lambda$	f_{4s}	$f_{1s,4s}$	$f_{2s,4s}$	$f_{3s,4s}$	$f_{4s,2p}$	$f_{4s,3p}$	$f_{4s,3d}$	$\Sigma\|f_{ii}\|^2$	$\mathscr{F}$	$29-\mathscr{F}$
0·0	1·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	29·00	29·00	0·00
0·1	0·6550	−0·0043	−0·0192	−0·0729	0·0032	0·0671	−0·0487	25·96	27·01	1·99
0·2	0·1668	−0·0043	−0·0171	−0·0057	0·0062	0·0868	−0·1105	20·48	23·74	5·26
0·3	−0·0240	−0·0041	−0·0137	0·0589	0·0087	0·0565	−0·1104	15·87	20·85	8·15
0·4	−0·0330	−0·0040	−0·0091	0·0937	0·0107	0·0074	−0·0711	12·73	18·30	10·70
0·5	−0·0041	−0·0038	−0·0036	0·0961	0·0120	−0·0331	−0·0273	10·76	16·10	12·90
0·6	0·0142	−0·0036	0·0025	0·0777	0·0124	−0·0548	0·0054	9·47	14·18	14·82
0·7	0·0185	−0·0033	0·0088	0·0517	0·0118	−0·0593	0·0248	8·48	12·54	16·46
0·9	0·0099	−0·0027	0·0208	0·0097	0·0079	−0·0409	0·0352	6·82	9·98	19·02
1·1	0·0015	−0·0020	0·0298	−0·0064	0·0015	−0·0171	0·0276	5·44	8·20	20·80

in Table 4. To the Hartree–Fock wave functions for Cu⁺ (Hartree & Hartree, 1936) was added a 4*s* electron taken from an SCF calculation with exchange of Piper (1957) for germanium* to form neutral copper. While this 4*s* charge density is a poor approximation to the actual atomic 4*s* electron for Cu, neither one is a good representation of the 4*s* conduction band electrons in the metal. Furthermore, since the 4*s* contribution will vary little between the two choices, the approximation we are making is really of second order, possibly important only for very small $\sin\theta/\lambda$.

These results are plotted in Fig. 2 along with the earlier results of James & Brindley (1931). The differences between our values and those of J&B are very large over the entire range of $\sin\theta/\lambda$; even at very high angles this difference amounts to 20% of our results, or an absolute deviation of 4 electron units (e.u.). At $\sin\theta/\lambda = 0{\cdot}3$ this difference is 7 e.u. or 85% of our calculated values. As this type of comparison clearly illustrates the essential features of these results, we list in Table 5 both the absolute and percentage differences between the J&B data and our own. An indication of the crudeness of the J&B interpolation procedure, is shown in Fig. 2 by the fact that a smooth curve cannot be put through the J&B values.

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* I am grateful to Dr W. Piper for making available his unpublished results for Ge and Zn^{+2}.

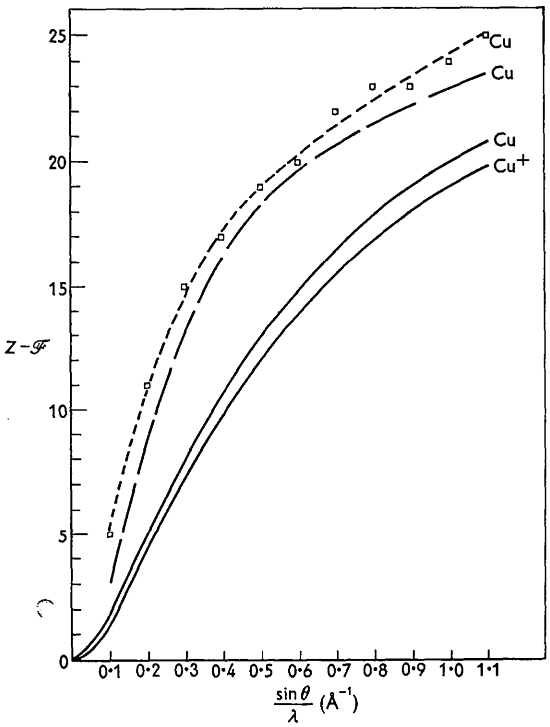

Fig. 2. Incoherent scattering function for Cu^+ and Cu: (*a*) the solid curves are our values using the complete Waller–Hartree equation, (*b*) the long dashed curve gives our values for Cu without the inclusion of exchange and (*c*) the —□— are the J&B values.

Table 5. *Comparison of results for* Cu *with those of J&B: Percentage and absolute deviations from our values*

$\sin\theta/\lambda$	% Deviation	Absolute deviation (e.u.)
0·1	150	3·0
0·2	109	5·7
0·3	84	6·9
0·4	59	6·3
0·5	47	6·1
0·6	35	5·2
0·7	34	5·5
0·9	21	4·0
1·1	20	4·1

Also included in Fig. 2 is a plot of our results with the exchange terms neglected. This comparison shows that the major deviation between our complete results and those of J&B is due to the exchange contribution. These large contributions to the scattering show that the exchange terms may not be neglected.

In order to determine the effects of changes in ionicity on the scattering, the incoherent scattering function for Cu^+ was calculated as well. (See Table 4 and Fig. 2 for these results.) To a fair degree of approximation, one may say that $\mathscr{F}$, but not $Z-\mathscr{F}$ is independent of the state of ionization of the atom at high $\sin\theta/\lambda$ values. This is in keeping with the same well-known results for the coherent scattering factors as both depend on the fact that the contribution of the outer electrons is largest for small $\sin\theta/\lambda$ values.

(C) *Zinc*

An incoherent scattering function for Zn^{+2} has been calculated using new Hartree–Fock wave functions as calculated by Piper (1957). The results are given in Table 6.

As no J&B values are available for Zn^{+2}, no such comparisons can be made.

5. Comparison with experiment

At present, there is only very little experimental information on X-ray Compton scattering. No direct measurements have been made for the atoms considered in this paper.

Chipman & Paskin (1958), however, have used our data to determine experimentally the thermal diffuse scattering (TDS) from copper to test the reliability of current TDS theory. They find that our values for the Compton scattering affects their measured TDS values in an important way. Using our results Chipman & Paskin find ten percent more measured TDS than they would using the J&B data, in agreement with theory.

These encouraging results are in keeping with recent results obtained for aluminum. In another paper, the author (Freeman, 1959) has calculated the incoherent scattering function for aluminum using Hartree–Fock wave functions in the complete Waller–Hartree theory as extended to include the effects of the inherent non-sphericity of atomic charge distributions. Comparison with the experimental results of Walker (1956) showed very good agreement, within the estimated experimental error quoted by Walker (1956), over the whole range of $\sin\theta/\lambda$. Only for low $\sin\theta/\lambda$, was the agreement with Laval's (1942) data not as good as this. Simultaneously, the J&B values were shown to be consistently too high, the discrepancy being as much as 25%, again proving the importance of including the exchange terms in the Waller–Hartree theory.

6. Conclusion

It has been shown that the exchange terms in the Waller–Hartree theory contain important contributions to the incoherent scattering intensities. These terms, usually neglected in the James & Brindley calculations, and in other work as well, account for the large differences between our results and those of these authors. These differences may be as much as 90% and are largest where the exchange terms are largest—for small and intermediate values of $\sin\theta/\lambda$. While individually the exchange terms may be small their sum is not and hence they may not be neglected (as was done by Waller & Hartree (1929) and Harvey *et al.* (1934)). This effect is more pronounced for higher

Table 6. *Calculation of the X-ray incoherent scattering functions for* Zn^{+2}

$\sin\theta/\lambda$	f_{1s}	f_{2s}	f_{3s}	f_{2p}	f_{3p}	$f^{(0)}_{3d,\,3d}$	$f^{(2)}_{2p,\,2p}$	$f^{(2)}_{3p,\,3p}$	$f^{(2)}_{3d,\,3d}$	$f^{(4)}_{3d,\,3d}$	$f_{1s,\,2p}$
0·0	1·0000	1·0000	1·0000	1·0000	1·0000	1·0000	0·0000	0·0000	0·0000	0·0000	0·0000
0·1	0·9997	0·9955	0·9601	0·9964	0·9561	0·9332	0·0014	0·0174	0·0250	0·0004	0·0085
0·2	0·9990	0·9820	0·8494	0·9858	0·8361	0·7680	0·0057	0·0630	0·0855	0·0053	0·0174
0·3	0·9977	0·9599	0·6915	0·9683	0·6693	0·5732	0·0126	0·1207	0·1423	0·0183	0·0263
0·4	0·9959	0·9299	0·5157	0·9445	0·4900	0·3984	0·0219	0·1733	0·1776	0·0369	0·0347
0·5	0·9936	0·8928	0·3487	0·9149	0·3262	0·2619	0·0333	0·2086	0·1902	0·0559	0·0431
0·6	0·9908	0·8494	0·2083	0·8802	0·1939	0·1634	0·0464	0·2222	0·1855	0·0714	0·0513
0·7	0·9875	0·8009	0·1029	0·8412	0·0978	0·0956	0·0607	0·2162	0·1705	0·0820	0·0593
0·9	0·9795	0·6932	−0·0083	0·7537	+0·0001	0·0221	0·0914	0·1667	0·1297	0·0896	0·0744
1·1	0·9695	0·5787	−0·0282	0·6590	−0·0182	−0·0055	0·1221	0·1032	0·0910	0·0846	0·0882

$\sin\theta/\lambda$	$f_{2s,\,2p}$	$f_{3s,\,2p}$	$f_{1s,\,3p}$	$f_{2s,\,3p}$	$f_{3s,\,3p}$	$f^{(0)}_{2p,\,3p}$	$f^{(3)}_{2p,\,3d}$	$f^{(3)}_{3p,\,3d}$	$f_{1s,\,2s}$	$f_{1s,\,3s}$	$f_{2s,\,3s}$
0·0	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000	0·0000
0·1	−0·0458	0·0102	0·0025	0·0171	−0·1502	0·0028	0·0001	−0·0020	0·0003	0·0001	0·0030
0·2	−0·0906	0·0191	0·0051	0·0327	−0·2717	0·0109	0·0005	−0·0142	0·0010	0·0003	0·0119
0·3	−0·1334	0·0257	0·0078	0·0455	−0·3459	0·0236	0·0016	−0·0388	0·0022	0·0007	0·0256
0·4	−0·1737	0·0292	0·0102	0·0547	−0·3684	0·0399	0·0037	−0·0699	0·0039	0·0011	0·0430
0·5	−0·2106	0·0292	0·0127	0·0595	−0·3474	0·0579	0·0066	−0·0994	0·0060	0·0018	0·0626
0·6	−0·2434	0·0257	0·0152	0·0600	−0·2974	0·0767	0·0103	−0·1215	0·0086	0·0025	0·0827
0·7	−0·2718	+0·0190	0·0177	0·0564	−0·2340	0·0950	0·0147	−0·1337	0·0116	0·0034	0·1019
0·9	−0·3141	−0·0017	0·0223	0·0391	−0·1119	0·1259	0·0246	−0·1316	0·0187	0·0055	0·1328
1·1	−0·3370	−0·0270	0·0267	0·0138	−0·0310	0·1451	0·0341	−0·1086	0·0272	0·0081	0·1493

$\sin\theta/\lambda$	$f^{(2)}_{2p,\,3p}$	$f^{(1)}_{2p,\,3d}$	$f^{(1)}_{3p,\,3d}$	$f_{1s,\,3d}$	$f_{2s,\,3d}$	$f_{3s,\,3d}$	$\Sigma\lvert f_{ii}\rvert^2$	$\mathscr{F}$	$28-\mathscr{F}$
0·0	0·0000	0·0000	0·0000	0·000	0·0000	0·0000	28·00	28·00	0·00
0·1	−0·0011	0·0257	−0·1547	0·000	−0·0016	0·0175	25·99	26·89	1·11
0·2	−0·0043	0·0502	−0·2705	0·000	−0·0064	0·0624	21·45	24·36	3·64
0·3	−0·0091	0·0722	−0·3284	0·0002	−0·0137	0·1172	16·86	21·61	6·39
0·4	−0·0149	0·0906	−0·3318	0·0003	−0·0230	0·1642	13·48	19·13	8·87
0·5	−0·0211	0·1052	−0·2977	0·0004	−0·0334	0·1929	11·29	16·93	11·07
0·6	−0·0269	0·1155	−0·2445	0·0006	−0·0441	0·2012	9·88	14·99	13·01
0·7	−0·0316	0·1217	−0·1865	0·0009	−0·0544	0·1923	8·84	13·29	14·71
0·9	−0·0364	0·1234	−0·0867	0·0015	−0·0714	0·1447	7·17	10·61	17·39
1·1	−0·0341	0·1145	−0·0228	0·0022	−0·0818	0·0880	5·77	8·71	19·29

atomic number since the number of exchange terms rises rapidly with increasing number of electrons.

The results in all cases show a large decrease in the predicted Compton scattering, compared with the J&B values, in agreement with the experimental results available to date. In the absence of a theory for crystalline scattering, the best theoretical calculation of the incoherent scattering is found from the complete Waller–Hartree equation using SCF wave functions with exchange.

I am pleased to acknowledge the help given by Dr John Wood with some of the Whirlwind routines. Thanks are due Mrs Joan Stekler of the Joint Computing Group at M.I.T. and Mrs Anna Hansen of the Materials Research Laboratory for their help with the hand computations.

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