0·68 Å, O^{2-} = 1·32 Å, the spacing below which puckering can be expected is 4·00 Å. In an examination of the structural transitions of $NaNbO_3$ and its solid solutions with $KNbO_3$, $Cd_{0.5}NbO_3$, and $Pb_{0.5}NbO_3$ (Francombe & Lewis, 1957) it was found that the temperature at which the multiple unit cell becomes single varies with composition from above 800° C. to below room temperature. The lattice spacing at this temperature, which may be called the puckering transition temperature, was in each case found to be close to 3·94 Å. In $AgNbO_3$ and $AgTaO_3$ the corresponding experimental values are 3·96 Å and 3·95 Å, respectively.

Ferroelectric or antiferroelectric effects appear to play only a minor role in the structural transitions of $AgNbO_3$. One criterion by which ferroelectric properties can be judged in the perovskite structures is the discontinuous nature of the Curie-point structure transition. Thus when unit-cell parameters are plotted against temperature, for substances like $BaTiO_3$ cr $KNbO_3$ which are strongly ferroelectric, or $PbZrO_3$ which is antiferroelectric, a very sharp discontinuity is apparent at the Curie temperature. $KNbO_3$ shows a sudden linear distortion of 1·6% at the Curie temperature (Shirane *et al.*, 1954) associated with a spontaneous polarization of 26 μC.cm.$^{-2}$ (Triebwasser & Halpern, 1955). For $AgNbO_3$ the discontinuous change of β from 90° to 90° 15′ at 325° C. corresponds to a linear distortion of 0·2%, and the spontaneous polarization observed is also small.

With $AgTaO_3$ the structure transition at 370° C. is comparatively smooth and this probably indicates the absence of ferroelectricity. In this connection it is notable that the effect of $AgTaO_3$ in solid solution with $AgNbO_3$ is to lower the measured values of permittivity. In $AgTaO_3$ the changes in structure observed at high temperatures probably arise almost entirely from ionic packing effects.

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Atomic Scattering Amplitudes for Electrons

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Some new values of atomic scattering amplitudes for electrons, intended primarily for use in the determination of crystal structures by electron-diffraction techniques, are presented. These new values are expected to be more reliable than previous ones since they are based on improved data, that is on Hartree–Fock or Hartree self-consistent fields rather than on interpolation techniques for the light atoms, and on the Thomas–Fermi–Dirac potential rather than on the Thomas–Fermi potential for the heavy atoms. Particular attention is given to the calculation of values of these scattering amplitudes at zero scattering angle. Some of the many factors which limit the usefulness of the atomic scattering amplitudes derived here are discussed.

Values of the atomic form factor for neutral magnesium were obtained in the course of the present calculations and are given in the Appendix.

Introduction

In the past several years a marked increase in the application of electron-diffraction single-crystal techniques to the determination of crystal structures has taken place (see for example, Cowley, 1953, 1956). Standard techniques of X-ray analyses, such as Patterson and Fourier syntheses, and the comparison of observed and calculated structure amplitudes, have been carried over to electron-diffraction studies and employed with success. In X-ray analyses a knowledge of atomic form factors $f_X(s)$ is essential. Similarly, in such electron-diffraction investigations a knowledge of atomic scattering amplitudes $f(s)$ is essential. It is the purpose of this paper to derive new, more reliable values of $f(s)$ for many of the elements. Particular attention will be given to the calculation of $f(0)$, the quantity analogous to $f_X(0) = Z$. It will become evident that our very limited knowledge of atomic fields in crystals is an even greater obstacle to the derivation of useful values of $f(s)$ than it is to the derivation of useful values of $f_X(s)$.

Notation

There exists, as yet, no uniform notation for those quantities in electron diffraction which have counterparts in X-ray diffraction. New notations are apt to cause more confusion than they prevent, and so in this paper the notation which is more or less standard in the theory of electron diffraction of gases will be used. By the quantity s we mean

$$s = (4\pi/\lambda) \sin \tfrac{1}{2}\varphi \ , \tag{1}$$

where λ is the wavelength of the electrons, and φ is the scattering angle, twice the Bragg angle. We use the symbol $f(s)$ for the atomic scattering amplitude for electrons, and the symbol $f_X(s)$ for the X-ray form factor.

Theory

The present discussion will be restricted to coherent scattering from neutral, spherically symmetric atoms.

The atomic scattering function is a complex quantity, and calculations of the magnitudes and phases of the atomic scattering function for selected atoms have been carried out (Hoerni & Ibers, 1953; Ibers & Hoerni, 1954). These calculations are intended primarily for application to electron-diffraction studies of gases, and for reasons discussed in those papers they are based almost exclusively on the Thomas–Fermi (TF) potential function. They are therefore of limited application in the study of light atoms by electron diffraction from solids. Moreover, while the complex atomic scattering function is essential for the successful interpretation of electron-diffraction patterns obtained from gases containing both heavy and light atoms, there is good evidence (Cowley, 1956) that its use in the interpretation of electron-diffraction patterns obtained from solids represents a refinement which is not justified by the present experimental status of the latter technique. Accordingly, we make the approximation that the incident electron causes only a very slight perturbation of the atomic field (the Born approximation) and define a real atomic scattering amplitude as

$$f(s) = -\frac{8\pi^2 m}{h}\int_0^\infty V(r)\,\frac{\sin sr}{sr}\,r^2 dr \ . \tag{2}$$

In this equation $V(r)$ is the potential energy of the incident electron in the atomic field, and m is the actual mass, rather than the rest mass, of the electron.

The X-ray form factor $f_X(s)$ is given by the well known expression

$$f_X(s) = 4\pi\int_0^\infty \varrho(r)\,\frac{\sin sr}{sr}\,r^2 dr \ , \tag{3}$$

where $\varrho(r)$ is the probability that an electron in the atom lies within the spherical shell of radius R, where $r \le R \le r+dr$. By use of Poisson's equation it is not difficult to show that

$$f(s) = \frac{8\pi^2 me^2}{h^2}\left(\frac{Z-f_X(s)}{s^2}\right) . \tag{4}$$

Equation (4) is the usual basis for the calculation of $f(s)$ on the assumption of the Born approximation, since values of $f_X(s)$ are generally available in the literature. However, as s approaches zero, $f_X(s)$ approaches Z, and so equation (4) is not suitable for the calculation of $f(0)$. For this purpose we proceed as follows. We insert for $f_X(s)$ in equation (4) the formula of equation (3) and then expand the function $(\sin sr)/(sr)$ in a power series. Keeping in mind the definition of $\varrho(r)$, and letting s go to zero, we obtain

$$f(0) = \frac{4\pi^2 me^2}{3h^2}\,Z\langle r^2\rangle \ . \tag{5}$$

In equation (5) $\langle r^2\rangle$ is the mean-square radius of the atom. For light atoms $f(0)$ is calculated more readily by means of equation (5) than by equation (2) since usually the wave functions, but not the potentials, are tabulated in self-consistent field calculations.

Previous calculations

Values of $f(s)$ based on the Born approximation have been obtained by Vainshtein (1953). Vainshtein used equation (4) and the values of $f_X(s)$ of McWeeny (1951) for first row elements and those of James & Brindley (1931) for second row elements. He obtained values of $f(0)$ by extrapolation of $f(s)$ to zero s. For the heavier elements (argon and above) Vainshtein used equation (1) and the TF potential function.

In the last few years improved values of $f_X(s)$ have been calculated by several workers from Hartree–Fock (HF) or Hartree (H) wave functions. Values of $f_X(s)$ obtained from these wave functions should be more accurate than those obtained by McWeeny from Duncanson–Coulson variational wave functions and are certainly more accurate than those obtained from the interpolation techniques of James & Brindley. Thomas (1954) has evaluated the Thomas–Fermi–Dirac (TFD) potential function for atoms and Thomas & Umeda (1957) have evaluated $f_X(s)$ from this potential for a number of elements. The TFD potential represents a marked improvement over the TF potential since it takes into account the effects of electron exchange. The new values of $f_X(s)$ obtained from the TFD potential are thus more reliable than previous values. Finally, Vainshtein's values of the important quantity $f(0)$ are presumably unreliable, since he obtained them by an extrapolation technique; equation (5) offers a much more satisfactory way in which to evaluate $f(0)$. New values of $f(s)$ are calculated here, since, as is evident from the above discussion, there is reason to believe that more reliable values can now be obtained.

Present calculations

Values of $f(0)$ have been computed by means of equation (5), with values of $\langle r^2 \rangle$ obtained from HF or H wave functions, when available. (Reference to the wave functions used for individual atoms may be found in those papers which served as a source for values of $f_X(s)$. These are: Hoerni & Ibers, 1954; Berghuis *et al.*, 1955; and Ibers, 1957.) For heavy atoms, values of $f(0)$ were calculated by means of equation (2) from the TFD potential. The results of these calculations are shown in Fig. 1, and are tabulated in Table 1.

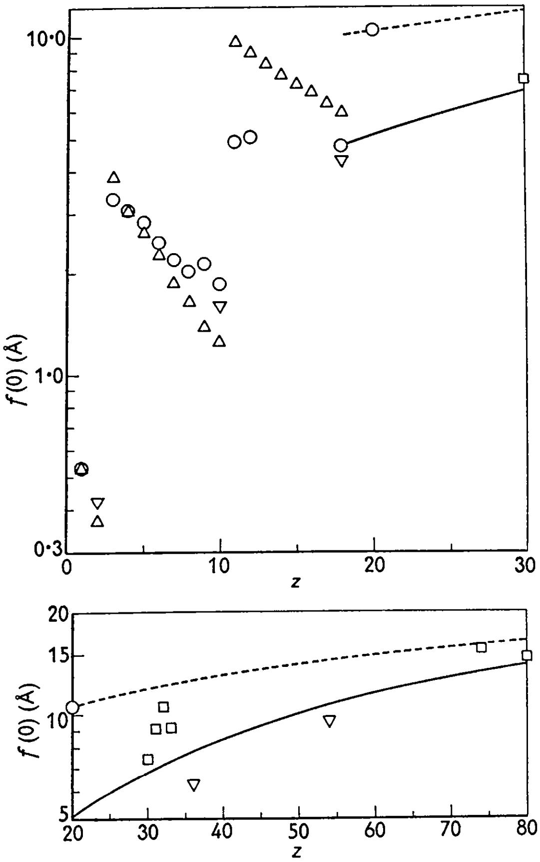

Fig. 1. Values of $f(0)$ versus Z. Present values from ○ HF, □ H, — TFD; Vainshtein's values △ for lighter elements, --- from TF; ▽ values from χ.

Values of $f(s)$ for s not equal to zero were computed by means of equation (4) from the corresponding values of $f_X(s)$. Since the TFD potential includes exchange effects it cannot be scaled, and so in Table 1 all results from this potential are given.

Calculations of $f(s)$ for atoms other than those listed in Table 1 do not seem worthwhile at this time. Since HF or H wave functions for most neutral atoms of the second row are as yet unavailable, the missing values of $f(s)$ can be obtained only by interpolation,* i.e. by direct interpolation on the values in Table 1, or from the values of $f_X(s)$ obtained by the interpolation technique of James & Brindley. In either case the results would be most uncertain. Values of $f(s)$ for $Z > 80$ could be obtained without undue difficulty from the TFD distribution of Thomas, or by extrapolation of the results of Table 1. This latter method is probably sufficiently reliable, since the values in Table 1 for high Z vary quite smoothly with Z. Such calculations were not carried out here because structures containing elements of atomic number greater than 80 are encountered so rarely in practice.

Comparison with previous calculations and discussion

We have pointed out above that the values in Table 1 should be intrinsically more reliable, within the framework of the assumptions made, than the previous calculations of Vainshtein. It seems worthwhile to check our calculations in some independent manner, and, although this cannot be done in general, it can be done for a few values of $f(0)$, the quantity most sensitive to many of our assumptions. The molar diamagnetic susceptibility χ, according to the Langevin theory, is proportional to $\langle r^2 \rangle$ and may be expressed for neutral atoms as

$$-\chi = \frac{Nh^2}{8\pi^2 m^2 c^2} f(0) = 4{\cdot}492 f(0)\,, \qquad (6)$$

where $f(0)$ is in Ångström units, and χ in the units of 10^{-6} cm.^{3}/mole. In Fig. 1 we plot the values of $f(0)$ derived by equation (6) from the experimental values of χ for the rare gases (Landolt–Börnstein, 1950). It is seen that these values are generally in much better agreement with the present calculations than with those of Vainshtein. Reliable measurements of χ for neutral atoms are available only for the rare gases, and so we must be satisfied with this limited comparison.

In Fig. 2 we plot for selected atoms both our values of $f(s)$ and those of Vainshtein. The rather large deviations, particularly at low s, arise from those factors mentioned to some extent above and discussed in more detail below.

Particular attention should be given to the calculation of the quantity $f(0)$, which plays the same role in electron-diffraction studies as does Z in X-ray diffraction studies. Values of $f(0)$ are useful for the approximate calculation of shapes of peaks on Fourier maps, for the calculation of unitary structure am-

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* Values of $f(s)$ for neutral atoms can be obtained reliably for $(\sin(\frac{1}{2}\varphi)/\lambda)$ greater than perhaps 0·3 Å^{-1}, using equation (4) and the corresponding values of $f_X(s)$ for the ion, if available. Compare the values of $f_X(s)$ for Mg and Mg^{++} in the Appendix.

Table 1. *Atomic scattering amplitudes for electrons*[a]

Values in Ångström units

Element	Z	Ref[b]	$[\sin(\phi/2)]/\lambda$ (A^{-1})											
			0.00	0.05[c]	0.10	0.15	0.20	0.25	0.30	0.35	0.40	0.50	0.60	0.70
H	1	E	0.529	0.508	0.453	0.382	0.311	0.249	0.199	0.160	0.130	0.089	0.064	0.04
Li	3	HF	3.31	2.78	1.88	1.17	0.75	0.53	0.40	0.31	0.26	0.19	0.14	0.11
Be	4	HF	3.09	2.81	2.23	1.63	1.16	0.83	0.61	0.47	0.37	0.25	0.19	0.14
B	5	HF	2.82	2.62	2.23	1.78	1.37	1.04	0.80	0.62	0.49	0.33	0.24	0.18
C	6	HF	2.45	2.26	2.06	1.74	1.43	1.15	0.92	0.74	0.60	0.41	0.30	0.22
N	7	HF	2.20	2.09	1.91	1.68	1.44	1.20	1.00	0.83	0.69	0.48	0.35	0.27
O	8	HF	2.01	1.95	1.80	1.61	1.42	1.22	1.04	0.88	0.75	0.54	0.40	0.31
F	9	HF	2.12	2.01	1.90	1.71	1.50	1.29	1.11	0.95	0.81	0.60	0.45	0.35
Ne	10	HF	1.85	1.80	1.69	1.55	1.40	1.24	1.09	0.95	0.83	0.63	0.49	0.38
Na	11	HF	4.89	4.21	2.97	2.11	1.59	1.29	1.09	0.95	0.83	0.64	0.51	0.40
Mg	12	HF	5.01	4.60	3.59	2.63	1.94	1.50	1.21	1.01	0.87	0.67	0.53	0.43
A	18	HF	4.71	4.40	4.07	3.56	3.03	2.52	2.07	1.71	1.42	1.00	0.74	0.57
Ca	20	HF	10.46	8.71	6.40	4.54	3.40	2.69	2.20	1.84	1.55	1.12	0.84	0.65
Mn	25	TFD	6.2	5.93	5.34	4.49	3.66	2.97	2.43	2.04	1.73	1.29	0.99	0.79
Fe	26	TFD	6.4	6.13	5.48	4.62	3.76	3.05	2.51	2.10	1.79	1.33	1.03	0.82
Co	27	TFD	6.5	6.32	5.62	4.73	3.87	3.14	2.58	2.16	1.84	1.37	1.06	0.84
Ni	28	TFD	6.7	6.41	5.74	4.85	3.97	3.22	2.65	2.23	1.89	1.41	1.09	0.87
Cu	29	TFD	6.8	6.61	5.89	4.97	4.06	3.30	2.72	2.29	1.95	1.45	1.13	0.90
Z	30	H	7.4	6.70	5.67	4.61	3.75	3.11	2.63	2.26	1.97	1.53	1.21	0.97
		TFD	7.0	6.70	6.03	5.08	4.16	3.38	2.79	2.35	2.00	1.49	1.16	0.92
Ga	31	H	9.1	8.42	6.49	4.95	3.90	3.19	2.68	2.29	1.99	1.54	1.23	0.99
		TFD	7.2	6.89	6.15	5.20	4.25	3.46	2.86	2.41	2.05	1.53	1.19	0.95
Ge	32	H	10.4	9.76	7.40	5.37	4.13	3.33	2.75	2.33	2.01	1.56	1.24	1.01
		TFD	7.3	7.08	6.29	5.32	4.35	3.54	2.93	2.46	2.10	1.57	1.22	0.97
As	33	H	9.2	8.52	7.04	5.52	4.33	3.46	2.85	2.39	2.05	1.58	1.26	1.02
		TFD	7.5	7.18	6.41	5.43	4.44	3.62	2.99	2.52	2.15	1.61	1.25	1.00
Se	34	TFD	7.6	7.37	6.56	5.53	4.54	3.70	3.06	2.58	2.20	1.65	1.28	1.02
Br	35	TFD	7.8	7.47	6.68	5.63	4.63	3.78	3.13	2.64	2.25	1.69	1.32	1.05
Kr	36	TFD	7.9	7.56	6.80	5.74	4.71	3.85	3.19	2.69	2.31	1.73	1.35	1.08
Rb	37	TFD	8.0	7.75	6.92	5.85	4.80	3.93	3.26	2.75	2.35	1.77	1.38	1.10
Sr	38	TFD	8.2	7.85	7.04	5.96	4.89	4.00	3.32	2.80	2.40	1.80	1.41	1.13
Y	39	TFD	8.3	8.04	7.16	6.06	4.98	4.07	3.38	2.86	2.45	1.84	1.44	1.15
Zr	40	TFD	8.5	8.14	7.28	6.16	5.06	4.15	3.45	2.91	2.50	1.88	1.47	1.17
Nb	41	TFD	8.6	8.23	7.40	6.27	5.15	4.22	3.51	2.97	2.54	1.92	1.50	1.20
Mo	42	TFD	8.7	8.42	7.52	6.36	5.24	4.29	3.57	3.02	2.59	1.95	1.53	1.22
Tc	43	TFD	8.9	8.52	7.63	6.47	5.31	4.36	3.63	3.08	2.64	1.99	1.56	1.25
Ru	44	TFD	9.0	8.62	7.75	6.56	5.40	4.43	3.69	3.13	2.68	2.03	1.58	1.27
Rh	45	TFD	9.1	8.81	7.85	6.66	5.48	4.50	3.75	3.18	2.73	2.06	1.61	1.30
Pd	46	TFD	9.3	8.90	7.97	6.75	5.56	4.57	3.81	3.23	2.77	2.10	1.64	1.32
Ag	47	TFD	9.4	9.00	8.07	6.85	5.64	4.64	3.87	3.28	2.82	2.13	1.67	1.34
Cd	48	TFD	9.5	9.19	8.19	6.95	5.72	4.71	3.93	3.34	2.86	2.17	1.71	1.37
In	49	TFD	9.6	9.29	8.31	7.03	5.80	4.78	3.99	3.39	2.91	2.20	1.73	1.39
Sn	50	TFD	9.8	9.38	8.40	7.13	5.88	4.84	4.05	3.44	2.95	2.24	1.76	1.41
Sb	51	TFD	9.9	9.48	8.50	7.22	5.95	4.91	4.10	3.49	3.00	2.27	1.79	1.44
Te	52	TFD	10.0	9.57	8.62	7.31	6.03	4.97	4.16	3.54	3.04	2.31	1.81	1.46
I	53	TFD	10.1	9.77	8.71	7.39	6.11	5.04	4.22	3.59	3.08	2.34	1.84	1.48
Xe	54	TFD	10.2	9.86	8.81	7.49	6.19	5.10	4.27	3.64	3.13	2.38	1.87	1.51
Cs	55	TFD	10.4	9.96	8.93	7.57	6.26	5.17	4.33	3.68	3.17	2.41	1.90	1.53
Ba	56	TFD	10.5	10.05	9.02	7.66	6.34	5.23	4.39	3.73	3.21	2.45	1.93	1.55
La	57	TFD	10.6	10.15	9.12	7.75	6.40	5.30	4.44	3.78	3.26	2.48	1.95	1.57
Ce	58	TFD	10.7	10.24	9.21	7.84	6.49	5.36	4.50	3.83	3.30	2.51	1.98	1.60
Pr	59	TFD	10.8	10.44	9.31	7.92	6.56	5.42	4.55	3.88	3.34	2.55	2.01	1.62
Nd	60	TFD	10.9	10.53	9.41	8.01	6.63	5.48	4.60	3.93	3.38	2.58	2.03	1.64
Pm	61	TFD	11.0	10.63	9.53	8.10	6.70	5.55	4.66	3.97	3.43	2.61	2.06	1.66
Sm	62	TFD	11.1	10.72	9.62	8.17	6.77	5.61	4.71	4.02	3.47	2.65	2.09	1.69
Eu	63	TFD	11.2	10.82	9.72	8.25	6.85	5.67	4.77	4.07	3.51	2.68	2.11	1.71
Gd	64	TFD	11.4	10.91	9.79	8.34	6.91	5.73	4.82	4.11	3.55	2.71	2.14	1.73
Tb	65	TFD	11.5	11.01	9.88	8.42	6.98	5.79	4.87	4.16	3.59	2.74	2.17	1.75
Dy	66	TFD	11.6	11.11	9.98	8.50	7.05	5.85	4.92	4.20	3.63	2.78	2.19	1.77
Ho	67	TFD	11.7	11.20	10.08	8.58	7.12	5.91	4.98	4.25	3.67	2.81	2.22	1.80
Er	68	TFD	11.8	11.30	10.17	8.66	7.19	5.97	5.03	4.30	3.71	2.84	2.25	1.82
T	69	TFD	11.9	11.49	10.27	8.74	7.26	6.03	5.08	4.34	3.75	2.87	2.27	1.84
Yb	70	TFD	12.0	11.58	10.36	8.82	7.33	6.09	5.13	4.39	3.79	2.91	2.30	1.86
Lu	71	TFD	12.1	11.68	10.44	8.90	7.40	6.15	5.18	4.43	3.83	2.94	2.32	1.88
Hf	72	TFD	12.2	11.78	10.53	8.98	7.46	6.20	5.23	4.48	3.87	2.97	2.35	1.90
Ta	73	TFD	12.3	11.87	10.63	9.05	7.53	6.26	5.28	4.52	3.91	3.00	2.38	1.93
W	74	TFD	12.4	11.97	10.72	9.13	7.59	6.32	5.33	4.56	3.95	3.03	2.40	1.95
Re	75	TFD	12.5	12.06	10.79	9.21	7.66	6.38	5.38	4.61	3.99	3.06	2.43	1.97
Os	76	TFD	12.6	12.16	10.89	9.29	7.72	6.43	5.43	4.65	4.03	3.19	2.45	1.99
Ir	77	TFD	12.7	12.25	10.96	9.36	7.79	6.49	5.48	4.70	4.06	3.12	2.48	2.01
Pt	78	TFD	12.8	12.35	11.06	9.44	7.86	6.54	5.53	4.74	4.19	3.16	2.50	2.03
Au	79	TFD	12.9	12.45	11.13	9.51	7.92	6.60	5.58	4.78	4.14	3.19	2.53	2.05
Hg	80	TFD	13.0	12.54	11.23	9.58	7.98	6.66	5.63	4.83	4.18	3.22	2.55	2.07

a) These values are based on the rest-mass of the electron. For diffraction studies using electrons of velocity v these values should be multiplied by $(1-(v/c)^2)^{-\frac{1}{2}}$.

b) E: Exact wave function. HF: Hartree–Fock wave function. H: Hartree (non-exchange) wave function. TFD: Thomas–Fermi–Dirac potential function.

c) The second decimal places are not significant in this column.

Corrections to above table: The symbols for the elements $Z=18$ and $Z=30$ should read Ar and Zn respectively.

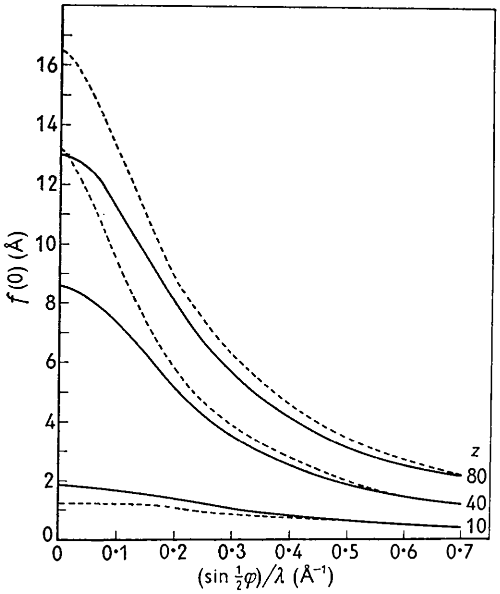

Fig. 2. Values of $f(s)$ versus $(\sin \frac{1}{2}\varphi)/\lambda$ for selected Z.

plitudes, and for the evaluation of the relative scattering power for electrons of the various atoms. It is to be emphasized, however, that since $f(0)$ is directly proportional to the mean-square radius of the atom, it is sensitive to a variety of factors, many of which are difficult to take into account adequately. Factors which affect $f(0)$ and also $f(s)$ for $(\sin(\frac{1}{2}\varphi)/\lambda)$ less than perhaps 0·4 Å^{-1} include: (1) the shell structure of the atoms; (2) exchange effects; (3) errors either of omission or of calculation in the contributions to the atomic fields of the outer electrons; (4) the deviations of the electron distribution, and hence of the potential distribution, in the crystal from that imposed by our assumption of spherical, neutral atoms. These factors will now be considered in more detail.

The effects of the shell structure of the atoms on values of $f(s)$ can be seen quite clearly in Fig. 1. It is obvious then that the assumption of the TFD potential, a potential which averages-out shell effects, is a poor one for the calculation of $f(s)$ at low s. Because of the general unavailability of more accurate atomic functions (H or HF), there is little choice but to use the TFD potential if one wishes to calculate any save a very few values of $f(s)$. We expect the effects of shell structure to be less pronounced as the atomic number increases, and to make the TFD values unreliable primarily when the atoms are of unusual size, as is the case in Groups I and VII of the periodic table. The TFD potential should give reasonably reliable estimates of $f(s)$ for most of the heavier atoms. The limited comparison available here for Z between 30 and 33 indicates that this is the case. These comparisons are not as meaningful as would be desired, since only H (non-exchange) values for Z of 30–33 can be compared with the TFD values, and we do not know whether neglect of exchange or of shell structure is the more serious error.

The effects of electron exchange are such as to cause a decrease in the effective size of the atomic shell. This is clearly illustrated in Fig. 1 by the results for argon from H and from HF wave functions, and by the fact that Vainshtein's values, based on the TF potential, are significantly higher than those based on the TFD potential. In fact, the results shown in Fig. 2 indicate that even for heavy atoms at $(\sin \frac{1}{2}\varphi)/\lambda) =$ 0·5 Å^{-1} Vainshtein's values of $f(s)$ are some 10% higher than the values obtained here.

Errors of omission or of calculation in the contributions to the H or HF fields can have a large effect on $f(s)$, particularly at low s. In Fig. 1 there appear to be two inconsistencies. On the basis of the departure of $f(0)$ for fluorine from the smooth curve one suspects that the self-consistent field calculations for fluorine are in error. Actually these calculations were made on the assumption that exchange effects only modify the $2p$ wave functions (Brown, 1933), and this assumption may account for the apparent inconsistency in the derived value of $f(0)$. The other apparent inconsistency concerns the effects of shell structure on $f(0)$ for atoms in Rows 2 and 3 of the periodic table. The very slight decrease of $f(0)$ from Na to Ar is certainly most surprising in view of the large decrease found in going from K (and Ca) to Kr. In an attempt to resolve this inconsistency, previously unavailable values of $f_X(s)$ and $f(s)$ were computed for neutral Mg (see Appendix) from the HF wave functions. Although $f(0)$ for Mg does turn out to be somewhat higher than that for Na, there is no indication of a large error in the $f(0)$ value for Na. This apparent inconsistency in the effects of shell structure on $f(0)$ for atoms in Rows 2 and 3 of the periodic table must remain unresolved until further data are available. Small inconsistencies in the values for the $4p$ wave functions may also account for the unexpected behavior of those values of $f(0)$ for Z between 31 and 33. Similar remarks apply to the results for W and Hg.

The deviation of the actual potential distribution in the crystal from that imposed by our assumption of spherical, neutral atoms beyond doubt limits the usefulness of the values of $f(s)$ calculated here. At this time, however, there appears to be no convenient theoretical model which will lead to more meaningful values of $f(s)$, particularly since one knows so little about the actual distribution of electrons or of potential in crystals.

One other remark should be made about the reliability of the values of $f(s)$ given above. All these values are based on non-relativistic solutions to the many-electron problem. As far as is known, only for Cu^+ has the relativistic Hartree–Fock solution been computed (Williams, 1940). The differences between the relativistic and non-relativistic solution for this relatively light ion appear to be too small to have much effect on $f(s)$ or $f_X(s)$. However, one expects such differences to be much larger for heavier atoms.

The above factors present a greater obstacle to the calculation of meaningful values of $f(s)$ than they do for the calculation of reliable values of $f_X(s)$. This is because many of the factors mentioned above have a larger effect on $f(s)$ than on $f_X(s)$, particularly at small values of s. Moreover, the quantity and range of data are more limited in electron-diffraction studies than they often are in X-ray techniques. Whereas in X-ray diffraction studies it is sometimes possible to use the data at high s values to evaluate anisotropic temperature factors, and hence to compensate for possible asymmetries in the electron distribution, errors in the form factors, and other sundry effects, such a procedure is not possible with the limited data available in electron-diffraction studies. Nevertheless, in our present state of knowledge the values of $f(s)$ derived above should be useful for the calculations necessary in the investigations of crystal structures by electron diffraction, and it is hoped that they may serve as a basis for improved theoretical work.

Table 2. *Atomic form factor for magnesium*

Values in electrons

$\sin(\frac{1}{2}\varphi)/\lambda$	$f_X(\mathrm{Mg})$	$f_X(\mathrm{Mg})-f_X(\mathrm{Mg}^{++})$
0·00	12·00	2·00
0·05	11·52	1·61
0·10	10·50	0·84
0·15	9·53	0·27
0·20	8·75	0·00
0·25	8·09	−0·06
0·30	7·46	−0·05
0·35	6·83	−0·02
0·40	6·20	0·00
0·50	5·01	0·02
0·60	4·06	0·03
0·70	3·30	0·02
0·80	2·72	0·01
0·90	2·30	0·00
1·00	2·01	0·00
1·10	1·81	0·00
1·20	1·65	0·00
1·30	1·54	0·00

APPENDIX

Incidental to the calculation described above, values of the atomic form factor $f_X(s)$ for neutral magnesium have been computed. The contribution to $f_X(s)$ of the $3s$ electrons have been obtained from the $3s$ ground-state Hartree–Fock wave functions for neutral magnesium given by Biermann & Trefftz (1949). The necessary Fourier transform was computed in the manner previously described (Ibers, 1957). $f_X(s)$ for neutral Mg was then obtained by addition of this contribution to the values of $f_X(s)$ for Mg^{++} given by Berghuis *et al.* (1955). The results, together with differences between the form factor for neutral and dipositive magnesium, are given in Table 2.

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