5. Conclusion

The detailed argument above was not intended to suggest alternative methods of indexing the hexagonal system but rather to show why and when each particular choice of axes and indices is needed. The argument has incidentally shown that there is no alternative method having all the advantages of the Miller–Bravais system. Our general conclusions, of which (c) and (d) run counter to common assumptions, can be summarized as follows:

(a) a symmetric basis for the direct lattice is necessary for the equivalent indexing of symmetrically-related planes;

(b) the use of a redundant axis implies that a linear relation exists between the indices of a plane, this relation being equation (10) in the general case or, for the hexagonal lattice,

$$h+k+i=0; \qquad (1)$$

(c) the equation

$$\mathbf{h} \cdot \mathbf{u} = h_i u_i \qquad (12)$$

[and hence equation (4) for the hexagonal lattice] holds irrespective of the bases chosen and its validity implies nothing about 'best' choices nor about duality nor about equivalent indexing of planes and directions;

(d) it is always possible to find a basis $\mathbf{a}_i^\dagger$ $(i=1, \ldots, n+1)$ for the reciprocal lattice such that

$$\mathbf{h}=h_i\mathbf{a}_i^\dagger \qquad (14)$$

but the validity of this equation is not sufficient to define a unique basis;

(e) the equivalent indexing of symmetrically related directions implies that the indices of a direction must satisfy a linear relationship such as equation (30), e.g. for the hexagonal lattice

$$u+v+t=0; \qquad (3)$$

(f) duality between planes and directions in direct and reciprocal space can be made the final determinant of the choice of a reciprocal basis after symmetry conditions have been satisfied.

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The Variation with Wavelength of the Atomic Scattering Factor for Iron

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The atomic scattering factor for iron has been measured on five low-order reflexions from pure iron at eighteen wavelengths in the range 0·63 to 2·53 Å; measurements have also been made on nickel for Cu $K\alpha$ radiation to give additional checks with results of other workers. The variation of f for iron follows the Hönl theory for K-electrons quite closely, except for the 110 reflexion at wavelengths just short of the absorption edge. The dispersion corrections were independent of angle. The limiting values of f at high frequencies indicated by the results agree well with other theoretical and experimental values, except for the 110 reflexion.

1. Introduction

Measurements of the atomic scattering factor f as a function of wavelength determine the dispersion correction δf if a value of f_0, the limiting value for very high frequencies, can be assumed. The relation between f, f_0 and δf is

$$\delta f=|f|-f_0\simeq \Delta f' + \frac{(\Delta f'')^2}{2(f_0+\Delta f')}$$

$\Delta f'$ and $\Delta f''$ are the in-phase and out-of-phase parts of the dispersion term: in the present work, the wavelength variation of $|f|$ has been measured and no separate determination of $\Delta f'$ and $\Delta f''$ has been attempted.

The theory of anomalous dispersion effects shows how $\Delta f'$ and $\Delta f''$ can be calculated in terms of the oscillator strengths of the electron shells (see, for example, James, 1962). These in turn can be computed from atomic wave functions (Hönl, 1933a,b) or from

the wavelength dependence of the photoelectric absorption (Parratt & Hempstead, 1954; Dauben & Templeton, 1955; Cromer, 1965).

Systematic attempts to check the dispersion theory experimentally are reviewed in James (1962). None of this work is recent, and the discrepancies, between different experimenters and between experimental results and theory, are of the order of 50% to 100% of δf so that it can only be said that the results show the same general trend as the theoretical curves. Part of the difficulty in the early work lay in the uncertainty about the value of f_0. There have been some recent measurements of dispersion corrections at isolated wavelengths, for example on chlorine (Parthasarathy, 1962), on iodine (Hall & Maslen, 1966) and on uranium (Cromer, Larson & Roof, 1964).

The present work was undertaken for two main reasons. Firstly, the current interest in anomalous dispersion techniques for crystal structure analysis (see for example Black, 1965; Moncrief & Sims, 1969; Hope, Camp & Thiessen, 1969; Herriott, Sieker & Jensen, 1969) creates a need for experimental confirmation of the anomalous dispersion values that must be assumed in applying such techniques. Secondly, the measurements of the variation of f over a wide range of wavelengths can give a curve which can both confirm the theory and, when fitted to a theoretical curve, determine a value of f_0. Values of f_0 obtained in this way may be a useful contribution to attempts to measure f on an absolute scale, particularly because comparison of the wavelength variation of f for different diffraction spectra ought to give extra information about the effect of systematic errors in measurements of this type.

Iron was chosen as the main subject of this investigation, because several other workers have attempted to measure f_0 for this element (see Table 3), because it can readily be obtained as a very fine powder, and because of current work in this laboratory on structures of compounds containing iron.

2. Experimental methods

The f factors were determined from measurements, on an absolute scale, of the integrated diffraction intensities from powder specimens. The specimens were mounted on the rotating specimen holder of a diffractometer. Monochromatic radiation was selected, from the output of a General Electric (XRD-6) generator, op eratedin the constant potential mode, by a

silicon crystal. Silicon was chosen because the very small $\lambda/2$ harmonic contribution meant that the potential on the X-ray tube could be set at almost three times the excitation limit of the required wavelength: X-ray intensities were measured with either a NaI(Tl) scintillation counter (for $\lambda < 1$ Å), or a Xe proportional counter for longer wavelengths ($\lambda > 1$ Å) where the reduced efficiency was of less importance than the improved resolution, particularly in the presence of intense fluorescence near the iron absorption edge. A single channel pulse height discrimination system was used. The plane monochromator and the diffractometer system were arranged to give Bragg–Brentano focusing from the line source of the X-ray tube. The horizontal and vertical divergences of the beam in the diffractometer were 0·3° and 1° respectively.

The intensity of a diffraction peak obtained by symmetrical reflexion from a powder is given (James, 1962) by the formula:

$$\frac{P}{I} = \frac{pN^2}{\mu} \left(\frac{e^2}{mc^2} \right)^2 \left(\frac{l}{R} \frac{\lambda^3}{16\pi} \right) \frac{(1+k\cos^2 2\theta)}{(1+k)\sin\theta\sin 2\theta} F^2$$

where F is the structure factor, P the total power diffracted into an arc of length l at a distance R from the specimen, I the incident beam intensity, p the multiplicity factor, N the number of unit cells per unit volume, μ the bulk linear absorption coefficient, (e^2/mc^2) the classical electron radius, λ the X-ray wavelength, k the polarization ratio of the monochromatic beam and θ the Bragg angle. This equation can be applied directly to measurements of diffracted intensity made with a stationary slit of width larger than the width of the diffraction peak: this method of measurement will be referred to below as the open slit method.

An alternative method is to use a narrow slit and scan the diffraction peak (with the usual coupled movement of the specimen). For this method F is related to the energy E diffracted into a receiving slit of area A scanning at angular velocity ω by the equation:

$$\frac{E\omega}{I} = \frac{pN^2}{\mu} \left(\frac{e^2}{mc^2} \right)^2 \left(\frac{A}{R^2} \frac{\lambda^3}{16\pi} \right) \frac{(1+k\cos^2 2\theta)}{(1+k)\sin\theta\sin 2\theta} F^2.$$

This method is referred to below as the scanned slit method.

For the pure iron and nickel used in this work, the atomic scattering factor f can be obtained from F by using the following relationship:

$$F = nf(1+\alpha) \exp\{-B(\sin\theta/\lambda)^2\}$$

Table 1. Atomic scattering factors of nickel for Cu Kα

Method	Specimen	111	200	220	311	222
{ Scanned narrow slit }	SO*	17·5±0·3	16·6±0·3	12·6±0·2	10·3±0·1	
	N(4)†	17·5±0·1	16·6±0·2	12·6±0·2	10·6±0·2	
{ Stationary open slit }	SO	16·5±0·15	15·9±0·2	12·1±0·2	10·0±0·2	9·4±0·2
	N(4)	16·6±0·15	15·8±0·2	12·1±0·2	10·0±0·2	9·4±0·2
{ Mean of I.U.Cr. results }	Many	16·5±0·4	16·1±0·3	12·1±0·3	10·0±0·3	9·4±0·4

* I.U.Cr. specimen.
† Specimen pressed from powder distributed for I.U.Cr. project.

where n is the number of atoms per unit cell, B the Debye–Waller factor and α a correction for the thermal diffuse scattering peak.

For measurements by either method, background was subtracted by linear interpolation from measurements taken on both sides of the peak well clear of appreciable thermal diffuse scattering effects.

The incident beam intensity I was measured with the use of absorber foils. Wherever possible, absorber foils with K absorption edges between λ and $\lambda/2$ were chosen so that the foils attenuated any $\lambda/2$ harmonic (and some of the harder radiation) by more than they attenuated the main wavelength. This precaution, together with the reduction of $\lambda/2$ by the monochromator and the restriction of the X-ray tube potential to avoid $\lambda/3$, served to eliminate harmonic effects: attenuation of some absorbers was measured at various values of the X-ray tube potential, from just above excitation (V_k) to almost $3V_k$, and found to be independent of potential. The difference in absorption between the $K\alpha_1$ and $K\alpha_2$ components means that the wavelength composition of the beam changes as it passes through a set of foils (Chipman, 1969). Calculations on this effect showed that it would affect the f values by about 0·1%. To check on the accuracy of the foil attenuations several of the diffraction measurements were made with different numbers of absorbers. For one wavelength (Mo $K\alpha$) measurements of incident and diffracted beams were made first with the incident beam so weak that only one foil, with an attenuation factor of about 10, was needed, and subsequently, using higher tube potentials, with beams needing attenuation by factors from 10 to 10^4. All of these checks gave consistent results for the f values.

For the scanned slit method the slit width, S, was measured with an X-ray beam by comparing a wide slit measurement of I with the intensity C collected by scanning the main beam at angular velocity ω; it is easily shown that

$$S = \omega R \left(\frac{C}{I} \right)$$

The polarization factor k for the monochromater was measured by an adaptation of a method suggested by Jennings (1968) (see Miller & Black, 1969). For some of the measurements, the monochromator selected wavelengths from the white spectrum of the X-ray tube: the polarization of the white radiation was also checked and found to be negligible at the wavelengths and operating potentials used. The absorption coefficient values were taken from *International Tables for X-ray Crystallography* (1962). The values assumed for B were $0·359 \times 10^{-16}$ cm^2 for iron and $0·295 \times 10^{-16}$ cm^2 for nickel. The values of the correction factor for thermal diffuse scattering were taken from Chipman & Paskin (1959). All measurements were taken at room temperature.

The specimens of iron were made by pressing carbonyl iron powder (of about 3 micron size) at pressures between 11×10^7 and 14×10^7 Nm^{-2}, a range chosen to minimize preferred orientation and surface roughness effects (Weiss, 1966). These specimens had a relative density of 0·56.

One specimen of nickel was supplied by the I.U.Cr. project on the measurement of f factors from nickel powder with Cu $K\alpha$ radiation (Jennings, 1969). Other specimens were made from powder supplied by the project which was pressed at 25×10^7 Nm^{-2} to give a relative density of 0·60.

The nickel specimens were measured with Cu $K\alpha$ radiation only. The iron specimens were measured at eighteen wavelengths, using characteristic lines from six different targets together with four different wavelengths selected from the white radiation of a tungsten tube (see Table 2). One of the white wavelengths was chosen to be exactly on the iron K absorption edge: for this wavelength, a 12 micron iron foil placed in the beam removed all wavelengths shorter than the edge, so that the wavelength profile for this measurement was asymmetric.

The five lowest order reflexions were measured for iron: all of these are within the range of measurement for all wavelengths shorter than the K edge.

Suorrti & Paakari (1966) have analysed and measured several aberration effects which can cause errors in integrated intensities measured from powders, and their experimental checks were repeated for the specimens and equipment used in this work. Only two effects were found to be significant. For the first of these, the θ–2θ ratio error, good agreement was obtained between theoretical prediction and experimental results, when missetting errors were deliberately introduced, for the Fe (110) spectrum with Mo $K\alpha$ and the Ni (111) with Cu $K\alpha$ radiation. However, measurements on the second, the parallel displacement error, with a scanned
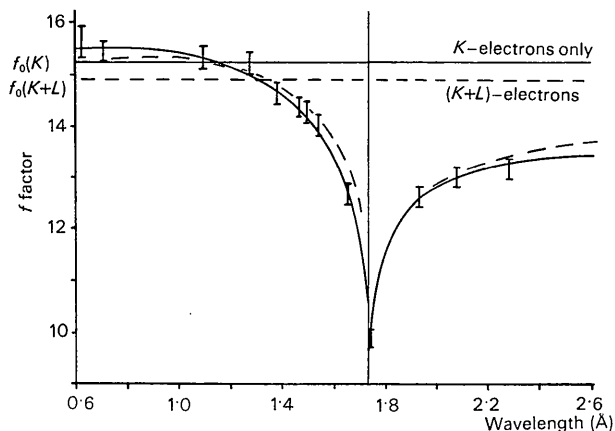

Fig. 1. Variation with wavelength of experimental values of f for iron calculated from measurements on the 200 reflexion, showing fitted curves and values of f_0 for Hönl theory for K-electrons, and for K- and L-shell theory using the parameters for oscillator strengths and absorption power laws quoted in § 4.

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slit method, gave error effects about twice the size of those predicted theoretically. These tests were with Cu $K\alpha$ radiation on Ni (111); a similar discrepancy was found by Suorrti & Paakari (1966) with Mo $K\alpha$ on Fe (110). Porosity and surface roughness effects were checked by measuring the fluorescence intensity with Mo $K\alpha$ radiation. The intensities were within 3% of intensities obtained with solid specimens for iron and within 1% for nickel, and the fluorescence intensity was independent of angle over a wide range. Tests for preferred orientation showed no significant effects.

Other checks showed that reduction of the horizontal or vertical divergences, and selection of different parts of the incident beam by an extra lead slit, did not effect the f values obtained. Full details of all of these tests are available elsewhere (Miller, 1969).

3. Results

Results obtained with the nickel specimens were compared with the values obtained by other participants in the I.U.Cr. project. The first measurements made in this work, which were reported as part of that project, were made with a scanned slit method only and gave values of f which were about 5% higher than the mean of the I.U.Cr. results (Table 1). Subsequent measurements by an open slit method gave results smaller than those of the scanned slit method and in close agreement with results of other workers. It has been found that if the narrow receiving slit were rotated slightly by about (0·5)° on replacement, the discrepancy could be explained: the apparatus would appear to permit such rotation, although a detailed check on the possible range has not been made. Because of this possible error, all of the measurements on iron powders have been made by the open slit method.

The results for iron are given in Table 2. The open slit method made it possible to obtain measurements with weak radiations which could not have been used so easily with the scanned slit method. The errors quoted in Table 2 are in the range 1% to 1·5% for most of the measurements; the error estimate includes allowance for counting statistics, the effect of errors in the measurements of background and of polarization ratio, an estimate of the error in the absolute scaling from the agreement of repeated measurements of the diffracted to incident beam ratio and an estimate of the effect of diffractometer alignment errors. No allowance has been made in Table 2 for the effect of possible errors in the absorption coefficients. The values in
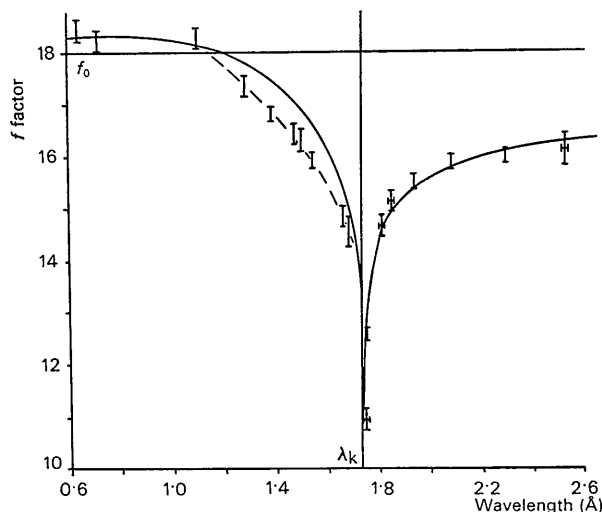

Fig. 2. Variation with wavelength of experimental values of f for iron calculated from measurements on the 110 reflexion, showing theoretical curve for Hönl K-shell theory fitted at the shortest wavelengths and wavelengths greater than the absorption edge. A range of error is shown in the wavelength measurement for those data obtained with monochromatised white radiation.

Table 2. *Experimental f factors, f_0 and δf values*

Radiation	λ (Å)	λ/λ_k	hkl 110 f_0 18·0±0·1	200 15·2±0·1	211 13·15±0·1	220 11·6±0·1	310 10·45±0·1
					$f \pm$ error $\pm \delta f$		
Mo $K\beta$	0·632	0·36	18·4±0·2+0·4	15·6±0·3+0·4	13·6±0·3+0·5	12·0±0·3+0·4	10·9±0·3+0·4
Mo $K\alpha$	0·711	0·41	18·2±0·2+0·2	15·4±0·2+0·2	13·4±0·2+0·3	12·0±0·2+0·4	10·9±0·2+0·4
W $L\gamma$	1·099	0·63	18·2±0·2+0·2	15·4±0·2+0·2	13·4±0·2+0·3	11·9±0·3+0·3	10·9±0·3+0·4
W $L\beta$	1·282	0·74	17·3±0·2−0·7	15·2±0·2+0·0	13·1±0·2+0·0	11·2±0·3−0·4	10·1±0·3−0·4
Cu $K\beta$	1·392	0·80	16·8±0·15−1·2	14·6±0·2−0·6	12·7±0·2−0·5	11·0±0·2−0·6	9·9±0·2−0·6
W $L\alpha$	1·476	0·85	16·4±0·2−1·6	14·3±0·2−0·9	12·3±0·2−0·8	10·9±0·2−0·7	9·9±0·2−0·6
Ni $K\beta$	1·500	0·86	16·2±0·2−1·8	14·3±0·2−0·9	12·3±0·2−0·9	10·7±0·2−0·9	9·7±0·2−0·8
Cu $K\alpha$	1·542	0·89	15·9±0·15−2·1	14·1±0·2−1·1	12·0±0·2−1·1	10·5±0·2−1·1	9·1±0·3−1·3
Ni $K\alpha$	1·659	0·95	14·7±0·2−3·3	12·9±0·2−2·3	10·7±0·2−2·5	9·3±0·3−2·3	
W Ll	1·678	0·96	14·5±0·3−3·5		10·2±0·4−2·9		
White	1·75±0·1	1·003	10·9±0·2−7·1				
Fe $K\beta$	1·756	1·007	12·6±0·15−5·4	9·9±0·2−5·3	7·9±0·2−5·3	6·2±0·2−5·4	
White	1·81±0·1	1·04	14·6±0·2−3·4				
White	1·85±0·1	1·06	15·1±0·2−2·9				
Fe $K\alpha$	1·937	1·11	15·4±0·15−2·6	12·6±0·2−2·6	10·5±0·2−2·6		
Cr $K\beta$	2·085	1·20	15·8±0·15−2·2	13·0±0·2−2·2	10·8±0·2−2·3		
Cr $K\alpha$	2·291	1·31	16·0±0·15−2·0	13·2±0·2−2·0			
White	2·53±0·1	1·45	16·1±0·3−1·9				

International Tables for X-ray Crystallography (1962) were used because they appeared to provide the best set of values covering the wide range of wavelength required. More recent tabulations (Heinrich, 1966; Kelly, 1966; Theisen, 1965) are derived by semi-empirical methods from experimental measurements, and differ appreciably amongst themselves, whilst good direct measurements (*e.g.* those of Cooper, 1965) are available for only a few wavelengths. Table 3 lists the correction factors which would have to be applied to the values of Table 2 if these various results for absorption coefficients were used: the most reliable values, those of Cooper, would indicate the need for corrections, of the order of the estimated error, which would vary with wavelength and so effect the detailed form of the wavelength variation of f.

Table 3. *Correction factors to be applied to values of Table 2 if different absorption coefficients are used*

Factor quoted is K where

$$f(\text{new } \mu) = Kf(\text{old } \mu), \text{ so } K \propto (\mu_1/\mu_2)^{1/2}$$

λ (Å)	Cooper* 1965	Theisen 1965	Kelly 1966	Heinrich 1966
0·63	—	0·98	1·03	—
0·71	0·99	1·03	1·03	0·99
1·10	—	1·03	1·03	0·99
1·28	—	1·02	1·03	0·99
1·39	—	1·02	1·04	1·00
1·48	—	1·00	1·05	1·00
1·50	—	0·99	1·05	1·00
1·54	1·01	1·01	1·05	1·01
1·66	—	1·04	1·06	1·01
1·68	—	—	1·07	1·02
K edge				
1·75	—	1·09	1·06	1·05
1·76	—	1·09	1·06	1·05
1·81	—	1·08	1·06	1·04
1·85	—	1·08	1·05	1·04
1·94	1·02	1·06	1·04	1·04
2·09	—	1·05	1·02	1·03
2·29	1·02	1·05	1·00	1·02
2·53	—	1·05	0·99	1·02

* Experimental values.

4. Discussion of results

For each diffraction spectrum, a graph of f against wavelength was plotted and attempts were made to fit various theoretical curves to the data. In the fitting, the value of f_0 was not specified; thus there was one degree of freedom available and the best fit of any theoretical curve would serve to determine f_0.

Two theoretical curves were fitted to the data. For the first the Hönl theory for K electrons was used. For the second, oscillator strengths of 1·33, 1·37 and 6·11 were used for the 1s, 2s, and 2p electrons respectively [the 2s and 2p values are from Cromer (1965)] and the absorption law powers (n in $\mu \alpha \lambda^n$ for $\lambda < \lambda_{edge}$) were assumed to be 2·75 for 1s, 2·33 for 2s and 2·5 for 2p. Two such curves [for the (200) data] are shown in

Fig. 1, from which it is evident that the Hönl theory, for K-electrons only, gives the better fit. A third curve, not shown in Fig. 1, was calculated using the parameters for K-electron absorption employed for the second curve but omitting the effects of the L-electrons: this curve shows a small deviation at short wavelengths but fits well over the rest of the range. The inclusion of L-electron effects appears to give poorer agreement with the data on all of the reflexions except the 110: attempts to fit curves with L-electrons included would give lower values of f_0 than those given by K-electron curves. No explanation of this unexpected result has been found although attempts to account for it by systematic error effects have been considered. It is possible that errors in the absorption coefficients could provide an explanation: use of the factors in the last three columns of Table 3 would give f values which would not fit as well with either curve, whilst the values of Cooper cannot be used without assuming an interpolation law. The contribution of M-electrons should be negligible for the wavelengths of Table 2.

The 110 reflection does not follow any theoretical curve. A fit has been obtained by relying on values measured at the shortest wavelengths, where our results are supported by the results of several other workers to within $\pm 0·4$, and on values at wavelengths beyond the absorption edge where the general trend follows the theoretical curve quite closely. If this fitted curve is accepted (Fig. 2) it indicates that the measured f is between 0·6 and 1·0 lower than the theoretical f in the range $0·75 < \lambda/\lambda_k < 0·96$. It seems likely that this divergence is a systematic error effect which shows up only on the lowest angle spectrum when the absorption effect is at a maximum. These conditions rule out extinction effects but are consistent with porosity and/or surface roughness effects, although these would be expected to diverge more rapidly near the edge. It is not possible to make theoretical predictions of these effects without further extensive investigations of our specimens (see for example Harrison & Paskin, 1964).

From the δf values given in Table 2 it can be seen that the observed δf is independent of angle (in the range $0·25 < \sin \theta/\lambda < 0·55$) except for the 110 reflexion on the short wavelength side near the edge. f does depend on f_0 when $\Delta f''$ is not zero, but this effect on δf for wavelengths less than the absorption edge should be smaller than the experimental error.

Table 4 shows the f_0 values obtained from fitting the results of Table 2 to theoretical curves, together with theoretical and experimental results obtained for iron by other workers, which have recently been reviewed by Sirota (1969). Apart from the results of Batterman (1959) and Batterman, Chipman & de Marco (1961) there is good agreement for all reflexions except that the present result for 110 is smaller than expected. Results for chromium (Cooper, 1962), aluminum (Batterman *et al.*, 1961) and copper (Hosoya & Yamgishi, 1966) all show f values lower than theoretical values for the lowest angle only.

Table 4. *Iron f_0 values by different authors*

Author	110	200	Spectrum 211	220	310	Method used
Freeman & Watson (1961)	18·51	15·27	13·13	11·61	10·49	Theoretical
Wakoh (1968)	18·34	15·12	12·98	11·48	10·36	Theoretical
Batterman (1959)	19·0	15·7	13·9	12·4	—	Experimental Fe $K\alpha$
Batterman *et al.* (1961)	17·63	14·70	12·62	11·13	10·10	Experimental Mo $K\alpha$
Radchenko & Tsvetkow (1965)	18·38	15·23	13·09	11·43	10·45	Experimental Mo $K\alpha$
Paakari & Suorrti (1967)	18·19	15·19	13·01	11·60	10·47	Experimental Mo $K\alpha$
Paakari & Suorrti (1968)	18·50	15·41	13·17	11·74	10·58	Experimental Mo $K\alpha$
Hosoya (1968)	18·38	15·13	13·18	11·60	10·39	Experimental Mo $K\alpha$
Watanabe, Uyeda & Fukahara (1968)	18·34	—	—	—	—	Electron diffraction
Present work	18·0	15·2	13·15	11·6	10·45	Experimental several wavelengths

Fourier syntheses of [f(theory)–f(experimental)] have been computed for the present results and the theoretical f's of Freeman & Watson (1961) and of Wakoh (1968). For the former, the difference map shows a peak of 1% excess on the atom centre, but for the theoretical values of Wakoh there is no clear systematic effect and the differences do not amount to more than 0·3% of the electron density at any point. The Freeman and Watson values were calculated for a free atom, whereas those of Wakoh are for an atom in a crystal.

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