are not to be considered as crystals or as nematic phases *etc.*

Considering the relatively thick water layers in the phases of higher order, probably permitting only the transmission of rather coarse asymmetries, it appears to be doubtful whether one could expect to find many space groups other than *Fm*3*m* (O_h^5), *Pmmm* (D_{2h}^1) or *P*6/*mmm* (D_{6h}^1).

In the case of tetragonal leaflets, for example, the transition energy smectic ⇌ tetragonal is probably too low to allow for the existence of the corresponding crystals of the space groups *P*4/*mmm* (D_{4h}^1). Special types of aggregation may then be produced by long range forces on account of geometric reasons only or of shape anisotropy with one or two (equal or different) dimensions comparable to the distance. The other kinds of asymmetry (Zocher & Török, 1953, 1954) may appear at short distances in one, two or all three directions, when the forces between surface charges and counter ions pass into the normal van der Waals forces. In spite of this restriction, the long range forces involved in the formation of superphases may be important in the formation of biological structures too.

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The Absolute Atomic Scattering Factor of Iron

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X-ray intensity measurements of the 110 reflexion from a carbonyl iron powder, using monochromatic Mo *Kα* radiation, were carried out on an absolute basis by direct intensity measurement of the incident beam. Effects of preferred orientation, porosity, and surface roughness were shown to be negligible. No contamination of specimens was found during storage for over one year under normal laboratory conditions. The absolute experimental scattering factor, *f*(110), of iron was found to be only 1·7% lower than the theoretical value for a free atom in the ground state. By combining this result with relative measurements made by one of the authors (T.P.), it was shown that the difference completely vanishes at $\sin\theta/\lambda = 0{\cdot}5$ Å^{-1}. This result contrasts with the measurements of Batterman, Chipman & DeMarco.

Introduction

In recent years, X-ray diffraction measurements have been undertaken to obtain information about the electron distribution in the transition metals of the iron group; these metals are especially interesting because of their incompletely filled 3*d* shell. Several authors (Batterman, Chipman & DeMarco, 1960; Cooper, 1962) have found that on a relative scale the experimental scattering factors agree with theoretical predictions for the free atom in the ground state, but that they are about 4–5% lower on an absolute scale. However, the reliability of the powder technique has been questioned concerning the time dependence of powder specimens (Hosoya, 1964) and the porosity effects (Harrison & Paskin, 1964).

The purpose of the experimental work reported in this paper is to study the suitability of carbonyl iron powder for highly accurate absolute measurements and to carry out an independent absolute measurement of the iron 110 reflexion, because it seems that the problem of deciding whether the discrepancy between theory and experiment is real or not should be carefully examined by improving the precision of the method of absolute intensity measurements, which is not always faultless at the present stage.

The samples

The carbonyl iron powder used in the present measurements was manufactured by General Aniline and Film Corporation. Controlled thermal decomposition of iron carbonyl gas produces spherical particles with a characteristic onion-skin structure due to minute carbon deposits in alternate layers (Jaumot & Muldawer, 1954). The mean size of the powder particles was 3–5 μ and the purity of the powder was 99·5%. Because the carbonyl process makes the coherently diffracting domains as small as some hundreds of Å in diameter, the extinction effects are negligible even for the strongest reflexions. Because of the spherical shape of particles, the domains are oriented at random, and we can expect that there is no preferred orientation as long as the moulding pressure does not crush the particles. According to our preliminary measurements, a safe moulding pressure limit is about 5000 kp.cm^{-2} for the powder used in the present study (carbon content 0·05%). Possible effects due to sample porosity were checked by observing the variation of the integrated intensity of the 110 reflexion with the sample density, which ranged from 0·40 to 0·70 relative to the bulk density. Our results did not show any effect of porosity. When the pressure was just sufficient to hold the powder together, the intensity decreased by about 2–5% by the absorption due to surface roughness. In this case also a sufficiently smooth surface could be made by using a binding agent. Our carbonyl iron specimens were stable under normal laboratory conditions, and no changes in the integrated intensity were found during a storage period for one year.

After some preliminary measurements, we concluded that carbonyl iron powder is a very suitable material for highly accurate absolute studies. For the final absolute measurements we selected the following three samples:

A. Moulding pressure 4000 kp.cm^{-2}

B. Moulding pressure 2000 kp.cm^{-2}

C. The powder was impregnated with a binding material (Tensol Cement no. 6).

The surface of each sample was treated with fine emery papers.

Absolute measurement

The intensity measurements were carried out with Mo $K\alpha$ radiation (30 kV) using a Siemens X-ray generator (Kristalloflex 4). The recording apparatus consisted of a NaI(Tl)-scintillation counter followed by a linear amplifier, a pulse height analyser and a scaler. The over-all dead time measured by the multiple foil technique was 2·5 ± 0·5 μ sec. We used the counting method in all measurements; the line profiles were recorded only for inspection.

The total energy diffracted by an ideal powder specimen received at a slit of height l and breadth d is, according to James (1962),

$$E=r_e^2\,\frac{\lambda^3 A_0 I_0 l d}{64\omega\pi\mu_\varrho R^2 MV}\cdot\frac{pF^2(1+\cos^2 2\theta_M\cos^2 2\theta)}{\sin^2\theta\cos\theta}\,, \quad (1)$$

where $r_e = e^2/mc^2$ is the classical electron radius, A_0 the cross-section of the primary beam with the intensity I_0, ω the angular velocity of the detector, λ the X-ray wavelength, R the distance from the specimen to the receiving slit, μ_ϱ the mass absorption coefficient, p the multiplicity, θ the Bragg angle, θ_M that at the monochromator, and F the structure factor of a cell of mass M and volume V.

The total energy of the primary beam was measured by driving the detector across the beam. The beam intensity was reduced to a countable rate by use of a zirconium absorber. The attenuation ratio, 62·50 ± 0·30, of the absorber was determined using both the direct beam and a strong reflexion from a single crystal. The agreement between the results showed that the attenuation did not depend on the wavelength distribution in each case. The path of the direct beam relative to slits and the specimen was inspected by photographic means. When a monochromator is placed behind the receiving slit we have

$$E_0=\frac{d}{\omega R}A_0 I_0\cdot\tfrac{1}{2}(1+\cos^2 2\theta_M)\,. \quad (2)$$

The absolute scattering factor of a reflexion hkl is given as

$$F(hkl)=\frac{4}{r_e}\left[\frac{\pi M V\mu_\varrho R}{p\lambda^3 l}\cdot\frac{\sin\theta\sin 2\theta(1+\cos^2 2\theta_M)}{(1+\cos^2 2\theta_M\cos^2 2\theta)}\cdot\frac{E(hkl)}{E_0}\right]^{\frac{1}{2}}. \quad (3)$$

The absorption coefficient, μ_ϱ, of iron for Mo $K\alpha$ radiation was measured using square foils. The value obtained, $\mu_\varrho = 37{\cdot}90 \pm 0{\cdot}30$ cm^2.g^{-1}, is in good agreement with Cooper's (1965) value of 37·61 ± 0·33 cm^2.g^{-1}. Inserting the measured ratio $R/l = 41{\cdot}36 \pm 0{\cdot}15$ and other parameters into (3), we have

$$F(110)=(8039\pm 40)\sqrt{\frac{E(110)}{E_0}}\,. \quad (4)$$

We did not use Soller slits because of a very small vertical divergence. This was conditioned by a small height of the direct beam of only 1 mm at the specimen site and by a small length of the receiving slit of only about 4 mm. The horizontal divergence was symmetrical and was about 0·8°. This would increase the integrated intensity of 110 reflexion by 0·4%, if the intensity in the primary beam were equally distributed in the horizontal direction. This small increase was practically cancelled by an asymmetrical intensity distribution in the primary beam (Suortti & Paakkari, 1966). The accuracy of the zero alignment for the X-ray focus, the centre of the goniometer, the specimen surface, and the receiving slit was of the order of 0·003° in 2θ; this gives rise to a probable error of only about $\pm 0{\cdot}1\%$ in the integrated intensity of the 110 reflexion (Suortti & Paakkari, 1966). The area of the detector required in measurement of the reflexion was the same as that in measurement of the primary beam.

The integrated intensity of the 110 reflexion was about 2500 counts when ω was $\frac{1}{8}°$ per minute and the width of the receiving slit was 0·1 mm. It was, therefore, necessary to minimize the background scattering. The incoherent part was eliminated by placing a quartz crystal monochromator behind the receiving slit. In this case the background was mainly (90%) due to the dark current of the counter. The accuracy of the correction for background was estimated to be better than $\pm 0{\cdot}5\%$ of the integrated intensity. The monochromator crystal was proved to be ideally mosaic. The measured primary beam contained about 2200 c.p.s. The dead time correction was then $0{\cdot}6 \pm 0{\cdot}2\%$. Variations in the direct beam power were inspected by alternately measuring the intensities of direct beam and reflexion.

Absolute scattering factor

The results of the absolute measurements on the three samples are given in Table 1. There is no noticeable difference between the samples. The standard error over all thirty measurements was $\pm 0{\cdot}5\%$. Inserting the mean value of the results given in Table 1 into (4), we obtain the absolute structure factor $F(110)$ of iron for Mo $K\alpha$ radiation

$$F(110) = 36{\cdot}30 \pm 0{\cdot}40\ .$$

Table 1. *The ratio of the total counts of the* 110 *reflexion of the three samples to that of the primary beam*

Sample	*A*	*B*	*C*
$E(110)/E_0 \times 10^5$	2·038	2·039	2·041

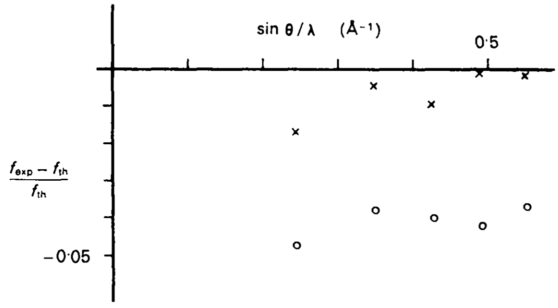

Fig. 1. Relative differences between experimental and theoretical atomic scattering factors. Crosses: present values; open circles: Batterman *et al.* (1960).

The thermal diffuse scattering (TDS) under the Bragg reflexion makes the total measured integrated intensity somewhat larger than the real intensity of the Bragg reflexion. According to the formula by Chipman & Paskin (1959) the correction in $F(110)$ was estimated to be $-0{\cdot}04$. To simplify comparison with the work of other authors we convert $F(110)$ to the atomic scattering factor $f(110)$ which corresponds to the atom at rest and is independent of the X-ray wavelength. With correction for TDS and using the same values as Batterman *et al.* (1960) for the dispersion correction $\Delta f' = 0{\cdot}35$, and for the temperature factor $B = 0{\cdot}36$ Å², we obtain

$$f(110) = 18{\cdot}19 \pm 0{\cdot}20\ .$$

Discussion of results

In order to give an idea of the general behaviour of the experimental scattering factors as a function of $\sin\theta/\lambda$, we have cited in Table 2 some unpublished values obtained by one of us (T.P.), who measured the relative integrated intensities of all reflexions up to the value $\sin\theta/\lambda = 1{\cdot}3$ Å⁻¹. We have normalized these data on the basis of the absolute value for $f(110)$. Comparison with the theoretical values shows that disagreement completely vanishes at $\sin\theta/\lambda = 0{\cdot}5$ Å⁻¹, and that there is no appreciable discrepancy between the experimental scattering factors of iron and the theoretical Hartree–Fock values for the free atom in the ground state on the absolute scale.

Table 2. *Absolute experimental and theoretical atomic scattering factors for iron corresponding to an atom at rest*

The values $f_{\rm BCD}$, from Batterman *et al.* (1960), and the present values $f_{\rm PS}$ are corrected for TDS and for anomalous dispersion. The theoretical values $f_{\rm th}$, taken from Freeman & Watson (1961), are interpolated with the use of a Gaussian representation. The probable errors quoted for $f_{\rm PS}$ are those relative to the 110 reflexion; all values will have an additional uncertainty of 1·1 %, corresponding to the error in the absolute scale.

hkl	$\sin\theta/\lambda$	$f_{\rm BCD}$	$f_{\rm PS}$	$f_{\rm th}$
110	0·247	17·63 ± 0·20	18·19	18·51
200	0·349	14·70 ± 0·23	15·19 ± 0·08	15·27
211	0·427	12·62 ± 0·21	13·01 ± 0·08	13·13
220	0·493	11·13 ± 0·20	11·60 ± 0·05	11·61
310	0·551	10·10 ± 0·19	10·47 ± 0·05	10·49

As shown in Fig. 1 the results of Batterman *et al.* (1960) are quite similar to ours in relative values, but there is a systematic difference of 3·5% in absolute scale. Only $f(110)$ in our results is noticeably lower than the theoretical value. This *reduction* does not seem to be due to specimen effects because qualitatively a similar reduction has been found for copper (Hosoya & Yamagishi, 1966) and for nickel (Inkinen & Suortti, 1964), although in these two examples the reduction already almost vanishes at the second reflexion, which is very close to the first one in angular position. The reduction found in the present study, however, is too small to conclude therefrom the existence of solid state effects. It is also to be mentioned that the present X-ray diffraction data do not give any information about the region below $\sin\theta/\lambda = 0{\cdot}25$ Å^{-1}.

It is apparent that the contradictory results found by various authors are related to the techniques used for determining the intensity data on the absolute basis. In measurements of this kind, it is necessary to pay much attention to detailed experimental conditions. For example, we have found that an inaccuracy of $\pm 0{\cdot}2°$ (in 2θ) in the zero alignment (Batterman *et al.*, 1960) may result in an error of $\pm 5\%$ in the integrated intensity when $\theta = 10°$, if the receiving slit is very narrow.

As was pointed out at the Seventh International Congress of Crystallography in Moscow 1966 (Informal Session on the Powder Intensity Project), it is very desirable to have a standard powder specimen for X-ray intensity measurements, because with such a specimen a relative measurement can readily be converted to an absolute one. In the light of our measurements, carbonyl iron seems to be suitable for the purpose. This powder is stable, and identical specimens will be available in different laboratories because of a well standardized procedure for the preparation of this substance.

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A Linear Analysis of the Non-Crystallographic Symmetry Problem

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Linear equations are derived which express constraints on the structure factors of a crystal having more than one identical molecule or subunit in the asymmetric unit. Solution of these equations leads to a series of functions having the required non-crystallographic symmetry. Any structure having the postulated symmetry can be expressed as a linear combination of these functions. This approach has the advantage that far fewer variables are needed to describe the system to a given resolution than in the conventional method using amplitudes and phases. The reduction in the number of variables is used as a measure of the information content of the equations.

Introduction

It has been shown (Rossmann & Blow, 1963; Main & Rossmann, 1966) that, when a crystal contains more than one identical molecule or subunit per asymmetric unit, equations can be set up which imply constraints on the phases of the structure factors. These equations contain certain parameters relating to the relative rotational and translational positioning of the subunits within the asymmetric unit. However, there exist methods for determining these parameters (Rossmann & Blow, 1962; Rossmann, Blow, Harding & Coller, 1964) and it is assumed in all that follows that their values are known.

Iterative methods for solution of the equations have been proposed which, for a number of simple trial structures, appear to converge to a unique answer, agreeing well with the known phases (Rossmann & Blow, 1964; Main & Rossmann, 1966). Both these papers attempt to derive values for the unknown phases and in doing so formally separate the amplitudes and phases of the structure factors as they appear in the equations. This means that the equations to be solved are non-linear from the beginning of the calculation.

The methods described in this paper formally keep the amplitude and phase together as an unknown complex structure factor. The equations are now linear in