(*b*) for cs reflexions the relation $\theta^+ \simeq \theta_p^+$ and $\theta^+ \simeq -\theta_p^-$ are sufficiently accurate when $Q_i \geq 1$. Thus, information contained in cs phases proves to be not negligible compared with that provided by ncs phases.

6. Concluding remarks

The two main obstacles to overcome when one-wavelength methods are used exploiting the anomalous dispersion effect are: (*a*) finding the positions of the anomalous scatterers; (*b*) estimating phases of the complete crystal structure when the positions of the anomalous scatterers are known. In this paper a variety of new formulas has been derived, which may be used for both (*a*) and (*b*). The practical tests (on error-free diffraction data) show that the formulas are capable of making better estimates for certain magnitudes and phases, and also lead to the heavy-atom structure.

APPENDIX

In accordance with Stephens (1963) and Giacovazzo (1979) the following approximation holds:

$$1+2\sum_{m=1}^{\infty} D_m(x)D_m(y)D_m(z)\cos m(\varphi-q) \simeq 2\pi M(\varphi; q, \alpha), \qquad (A1)$$

where α is the solution of the equation

$$D_1(\alpha)=D_1(x)D_1(y)D_1(z),$$

and M is the Von Mises distribution.

In accordance with (A.1) we can write (10) as

$$A[I_0(2R^+R^-Y_{11})I_0(2R^+R_p^+Y_4)I_0(2R^-R_p^+Y_5)]^{-1} = 1+2\sum_{m=1}^{\infty} D_m(2R^+R^-Y_{11})D_m(2R^+R_p^+Y_4) \times D_m(2R_p^+R^-Y_5)\cos m(y_{11}-y_4-y_5) \simeq 2\pi M(y_4+y_5-y_{11}; 0, \alpha), \qquad (A2)$$

where α is given by (13).

Replacing (A.2) in (10) and in (9) gives (12).

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Powder Diffraction with Synchrotron Radiation. I. Absolute Measurements

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Abstract

Accurate measurements of the integrated intensities of several reflections from a standard powder sample of Ni have been made using monochromatic synchrotron X-ray radiation of wavelength 1·5413 Å from a perfect double-crystal Si(111) monochromator. A perfect Ge(111) analyzer crystal was mounted on the detector arm of the diffractometer to serve as a narrow 'angular' receiving slit. The intensities were placed on an absolute scale by application of the appropriate powder diffraction expressions, which require the incident photon counts, the axial and equatorial openings of the receiving 'slit', and the polarization factor to be known. The procedure for evaluating these instrumental parameters is described in some detail. The quantitative agreement between these and previous absolute measurements on a standard Ni sample with

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Cu $K\alpha$ radiation demonstrates that the synchrotron technique can be used for absolute measurements of high accuracy.

1. Introduction

Recently a novel powder diffraction method, which takes full advantage of the unique properties of synchrotron radiation, was reported by Hastings, Thomlinson & Cox (1984). This method uses the incident beam from a double-crystal monochromator, which has a vertical divergence of about 0·1 mrad and an energy band width of a few eV. These values are matched to an analyzer crystal, which is mounted on the detector arm of the diffractometer. The parallel-beam geometry eliminates displacement-type effects due to specimen flatness and transparency observed in conventional experiments, so that the principal remaining aberration is that due to the axial divergence. The instrumental resolution $\Delta(2\theta)$ with a Ge(111) or Si(111) analyzer is about 0·02° at $2\theta = 50°$ for a wavelength of 1·54 Å, and this makes possible very detailed studies of particle size and strain.

The earlier paper by Hastings *et al.* (1984) concentrated on peak-shape analysis and lattice-parameter determination. This work is now extended to the measurement of integrated intensities on an absolute scale. An intensity standard for powder diffraction was introduced by Suortti & Jennings (1977), and the absolute integrated reflections of Ni standard samples are known to better than 0·5% from measurements with Cu $K\alpha$ radiation. Thus similar measurements on one of these standard samples provide a very stringent test of the present method using synchrotron radiation.

2. Integrated reflections

The measurements were made at the A3 beamline of the Cornell High Energy Synchrotron Source (CHESS), with the geometrical arrangement of the experiment as shown in Fig. 1. The incident beam is monochromatized by an Si(111) double-crystal monochromator (Batterman & Berman, 1983). The first crystal is flat, and the second crystal is bent sagittally for horizontal focusing. The distances between the source, monochromator and sample correspond to $\frac{1}{3}$ magnification. The energy band width is determined by the vertical divergence, and $\Delta E = 4{\cdot}5$ eV at 1·5 Å when there is no slit in front of the monochromator. The incident-beam intensity is monitored by an ionization chamber.

The sample is spun about the surface normal, and the axial (horizontal) divergence of the reflected beam is reduced by a Soller slit placed in front of the analyzer. The Ge(111) analyzer crystal is set to reflect the incident wavelength band, and any higher harmonics are essentially rejected by the pulse-height discriminator used with the NaI(Tl) scintillation counter.

The reflections were step-scanned at angular intervals smaller than $\frac{1}{6}$ of the full-width at half-maximum (FWHM), so that the probable error of the integrated intensity due to this sampling was 0·6% at most. A representative scan of the 111 reflection is shown in Fig. 2. The count rate of the peak is about 30 000 counts s^{-1}, and the peak-to-background ratio 550. About 50% of the background is thermal diffuse scattering (TDS) and amorphous scattering, which are passed by the analyzer. Background scattering that does not originate from the sample decreases at larger scattering angles to about 10 counts s^{-1}.

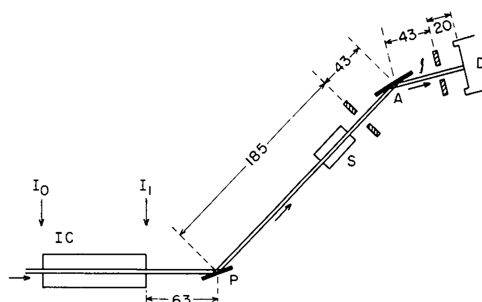

Fig. 1. Geometrical arrangement for the powder diffraction measurements. The monochromator (not shown) is a fixed-exit Si(111) perfect double-crystal non-dispersive monochromator, where the second crystal is bent sagittally for horizontal focusing. IC is the ionization counter, *P* the powder sample, *S* the Soller slit, *A* the Ge(111) analyzer crystal and *D* the scintillation detector. I_1 is the incident flux before absorption in air, and the numbers give the distances in mm.

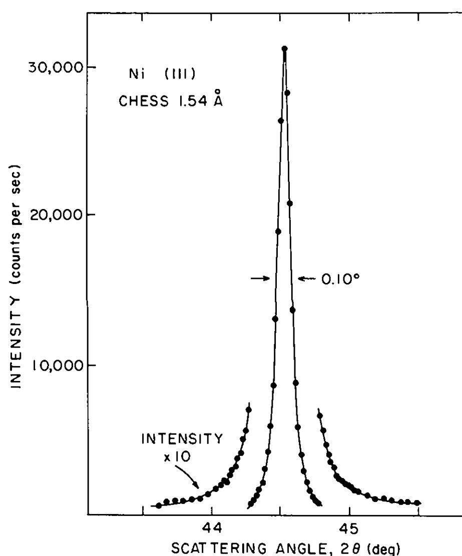

Fig. 2. Results of step scanning the Ni(111) reflection with the arrangement shown in Fig. 1. The solid line is a guide to the eye.

The scans were not wide enough to include all of the tails of the reflections. These were studied very carefully in the earlier measurements with Cu $K\alpha$ radiation, from which it was shown that the intensity in the tails can be described by the following function:

$$i(s)=i(s_1)(s/s_1)^{-p}+i_{\rm TDS}(s)+i_{\rm BG}, \qquad (1)$$

where $s=(\cos\theta/\lambda)\Delta(2\theta)$, the deviation from the peak of the reflection. The TDS contribution was calculated earlier (Suortti & Jennings, 1977), and the exponent p and the constant background $i_{\rm BG}$ were fitted to yield the observed $i(s)$ and the previously measured tail contributions outside the scan limits. The uncertainty resulting from this procedure is very small. The exponent p varied from 2·0 to 2·6, the latter value indicating effects of strain, which were also obvious in the measurements with Cu $K\alpha$ radiation. The net integrated count was then the total number of counts within the scan limits minus the constant and TDS background plus the integrated tails from the first term of (1).

The counting loss corrections for a regularly pulsed source have been discussed by Batterman (1980). During the present experiments the Cornell Electron Storage Ring (CESR) was operated in the 3 bunch mode, and the source frequency was $1/\tau=1/0{\cdot}853\ \mu s=1{\cdot}172$ MHz. As mentioned earlier, the energy window of the single-channel analyzer was set to accept only pulses due to the fundamental wavelength. As the bunch length is less than 1 ns, two pulses incident on the detector from the same bunch are counted as one of double energy. In addition, two pulses that come from successive bunches combine to form one that may fall outside the window of the analyzer if the dead-time of the electronics is comparable to the interval between the bunches. According to Batterman (1980), the observed count rate is

$$\begin{aligned}(n_{\rm obs})^1&=n[\exp(-n\tau)-n\tau\exp(-n\tau)]\\&\simeq n(1-2n\tau),\end{aligned} \qquad (2)$$

where n is the true count rate. The peak part of the profile can be approximated by a Gaussian function with a maximum count rate $n_{\rm max}$, and so the average count loss correction is that corresponding to a count rate $n_{\rm max}/\sqrt{2}$.

Another correction to be applied to the measured count rate is due to attenuation by air after the incident-beam monitor and by the detector window. The total air path was 354 mm, and the calculated linear attenuation coefficient is $\mu_{\rm air}=0{\cdot}01148\ {\rm cm}^{-1}$ (Suortti, 1971). The absorption in the counter window, which was 0·125 mm Be plus a thin Al reflector, was not measured, but a typical earlier value of 0·96 was taken as the transmission factor. The total transmission factor is therefore $A=0{\cdot}642$.

3. Absolute scale

The integrated reflection P_{hkl} from a powder sample can be written as (Suortti & Jennings, 1977)

$$P_{hkl}=r_e^2M_0E_{hkl}=N_{hkl}/n_0A\,\Delta\varphi\,\Delta\psi K_{\rm pol}, \qquad (3)$$

where $r_e=e^2/m_0c^2$ is the classical electron radius, $M_0=1/V_c$ is the number of scattering units (atoms, unit cells) per unit volume, $N_{hkl}=\sum_i n(2\theta_i)\Delta(2\theta)$, the net cumulative count × step size, n_0 the number of incident photons per measured $n(2\theta_i)$, $\Delta\varphi$ the axial and $\Delta\psi$ the equatorial opening of the receiving 'slit', $K_{\rm pol}$ the polarization factor, and A the transmission factor between the monitor and the detector. For symmetrical reflection from a thick sample, the quantity E_{hkl} is related to the structure factor F_{hkl} through the expression

$$E_{hkl}=\frac{M_0\lambda^3 j_{hkl}}{8\pi\sin\theta_{hkl}\sin2\theta_{hkl}}\frac{F_{hkl}^2}{2\mu_0}, \qquad (4)$$

where λ is the X-ray wavelength, j_{hkl} the multiplicity, θ_{hkl} the Bragg angle, and μ_0 the linear attenuation coefficient of the diffracting material. The absolute values of E_{hkl} (in units of cm) have been measured for standard samples of Ni with Cu $K\alpha$ radiation, and the standard used in the present measurements deviates only slightly from the one described by Suortti & Jennings (1977).

As the aim of the present paper is to compare E_{hkl} with previous values, in order to evaluate the new method the parameters n_0, $\Delta\varphi$, $\Delta\psi$ and $K_{\rm pol}$ will be discussed in some detail.

(a) The incident flux was measured by an ionization chamber filled with N_2 at atmospheric pressure. The ion current is converted to voltage and this in turn to frequency. With the settings used, the flux through the chamber, I_1, was related to the monitor count rate, N_1, by

$$\begin{aligned}I_1=c_1N_1=1{\cdot}89\times10^5N_1(E/{\rm keV})^{-1}\\\times\exp(-\mu t)/[1-\exp(-\mu t)],\end{aligned} \qquad (5)$$

where E is the X-ray energy and $\exp(-\mu t)$ the absorption factor of the ionization chamber. From the measured reference points it was calculated that $\mu t(E)=39{\cdot}3\times[E({\rm keV})]^{-3}$, and so at 8·04 keV, $c_1=3{\cdot}0\times10^5$. The scattering from the sample, $n(2\theta_i)$, was measured for some fixed pre-set monitor count, $n_{\rm mon}$, and accordingly $n_0=c_1n_{\rm mon}$.

(b) A Soller slit was used before the analyzer crystal in order to reduce the effects of the axial divergence on the profiles of the low-angle reflections. The nominal divergence (foil spacing/foil length) of the Soller slit was ±1·62°; however, it must also be borne in mind that the rays that hit the Ta foils at angles smaller than the critical angle 0·53° pass the slit, while the open area is decreased because of the finite

thickness of the foils. The effective value of $\Delta\varphi$ was estimated to be $2{\cdot}0° = 0{\cdot}035$ rad.

(c) The equatorial opening is determined by the analyzer crystal, and is the integrated reflectivity of the analyzer,

$$\begin{aligned}\Delta\psi &= \int R(\theta_A)\,\mathrm{d}\theta_A \\ &= (r_e\lambda^2|F'e^{-M}|/\pi V \sin 2\theta_A) \\ &\quad \times (n_{hkl,\sigma}R^y_\sigma + n_{hkl,\pi}|\cos 2\theta_A|R^y_\pi)/n_{hkl}. \qquad (6)\end{aligned}$$

Here $|F'e^{-M}|$ is the real part of the structure factor of the unit cell of volume V, $n_{hkl,\sigma}$ is the scattered flux of the σ-polarized component, $n_{hkl,\pi}$ that of the π component, n_{hkl} the sum of the two, and R^y_σ and R^y_π the integrated reflectivities on the y scale (Zachariasen, 1945). The measured polarization of the incident beam indicates that $n_{hkl,\pi}$ varies from 5% of n_{hkl} (at $2\theta = 45$ and 135°) to 0 (at $2\theta = 90°$). Therefore, although the integrated reflectivity of the analyzer is in principle a function of 2θ, in the present case this can be ignored since $R^y_\sigma = 2{\cdot}4025$ and $|\cos 2\theta_A|R^y_\pi = 2{\cdot}1084$ do not differ too much. These values as well as those of the other parameters were taken from the work by Jennings (1969). The resulting value of $\Delta\psi$ at the Cu $K\alpha$ wavelength is $9{\cdot}013 \times 10^{-5}$.

(d) The polarization of the incident beam was measured using the instrument described by Materlik & Suortti (1984). It is basically a powder diffractometer that can be rotated about the incident beam. When a reflection at $2\theta = 90°$ is measured, only that component of the incident beam that has its electric vector perpendicular to the plane of diffraction contributes to scattering. In the present case the Mo(220) reflection at 87·68° was used, and the polarization ratio $K = n_{0,\perp}/n_{0,\parallel}$ was found to be 0·11. Here $n_{0,\perp}$ refers to the component perpendicular to the plane of the electron orbit and $n_{0,\parallel}$ to the parallel component. In the present measurements the plane of diffraction was vertical, and so the polarization factor becomes

$$K_{\text{pol}} = (1 + K\cos^2 2\theta)/(1+K). \qquad (7)$$

4. Results

The net integrated counts N_{hkl} of several reflections from the standard Ni sample are given in Table 1. These are corrected for the average counting loss and converted to the integrated reflections P_{hkl} through (3). The resulting values are given together with the results from the earlier absolute measurement with Cu $K\alpha$ radiation.

The very close agreement is perhaps somewhat fortuitous, because the actual accuracy of the conversion factor between N_{hkl} and P_{hkl} may not be better than 5–10%. However, this agreement clearly demonstrates that the details of the method are well understood, and that it can be used for powder diffraction measurements that require high accuracy. The nickel standard sample can be used to determine the absolute intensity scale at 1·542 Å to better than 1%, and this can be extended to nearby wavelengths, because the relative values of the parameters in (3) and (4) can be measured or calculated quite accurately. Many of the subtle difficulties involved in absolute measurements, such as the effects of harmonic wavelengths, can be circumvented by the use of a standard scatterer. Scattering from any other sample can easily be placed on an absolute scale, which opens up a whole new dimension to diffraction measurements and makes many new types of experiment possible.

Table 1. *Absolute integrated reflections of the standard Ni sample*

The wavelength was 1·5413 Å. N_{hkl} is the integrated number of counts before the counting loss corrections given in the next column. The conversion factors are $n_0 = 2{\cdot}99 \times 10^5 \times n_{\text{mon}}$, $\Delta\varphi = 0{\cdot}035$, $\Delta\psi = 9{\cdot}013 \times 10^{-5}$ and $A = 0{\cdot}642$. E_{hkl} refers to a primitive unit cell of Ni, and $r_e^2 M_0 = 7{\cdot}2577 \times 10^{-3}$ cm^{-1}. The column indicated by Cu $K\alpha$ gives $r_e^2 M_0 E_{hkl}$ of the earlier absolute measurement with Cu $K\alpha$ radiation.

hkl	N_{hkl}	$\sqrt{2}n_{\max}\tau$	n_{mon}	K_{pol}	$r_e^2M_0E_{hkl}$ ($\times 10^3$)	Cu $K\alpha$ ($\times 10^3$)
111	102·48	0·036	2×10^5	0·951	0·923	0·928
200	57·62	0·014	2×10^5	0·938	0·515	0·514
220	34·43	0·006	2×10^5	0·905	0·316	0·314
311	38·26	0·005	2×10^5	0·900	0·353	0·347
222	22·14	0·000	4×10^5	0·902	0·101	0·099
400	23·49	0·000	8×10^5	0·928	0·052	0·052
331	47·00	0·000	4×10^5	0·967	0·201	0·210

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