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SINGLE-CRYSTAL X-RAY DIFFRACTOMETRY USING SYNCHROTRON RADIATION

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The properties of synchrotron radiation relevant to single-crystal X-ray diffractometry are: its high intensity over a wide spectral range, a small source size and a low divergence in the 0.1 mrad range, about 90% linear polarization in the horizontal plane, a pulsed time structure, and a time dependent intensity. The latter property requires monitoring of the primary beam intensity and its polarization state which slightly complicates data collection and needs particular attention in the data reduction stage. The other properties of synchrotron radiation, however, extend the range of X-ray diffractometry to experiments which are not feasable with sealed X-ray tubes. The high source intensity makes data collection possible on crystals down to and below 10 μm diameter. Measurement of weak and very weak ("forbidden") reflections profits from high intensity, low divergence, and a good peak-to-background ratio. Data collection at short wavelengths is useful to decrease both absorption and extinction effects and provides the resolution required for high precision structure analysis. Wavelength tunability is frequently used to exploit resonant X-ray scattering ("anomalous dispersion") for structure research. Examples are determination of absolute configuration, contrast variation, and phase determination from both single- and multiple-wavelength measurements ("MAD-phasing"). X-ray dichroism and double refraction are observed in the vicinity of absorption edges, causing an anisotropy and polarization dependence of anomalous scattering. This anisotropy may give rise to a violation of extinction rules for glide-planes and screw-axes, with orientation- and polarization-dependent intensities. More recently, these affects have been successfully used to derive (partial) phase information. Other applications are magnetic X-ray scattering and time-resolved X-ray diffraction, the latter exploiting the time structure of the synchrotron radiation source.

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1. Introduction

The properties of synchrotron radiation (SR in the following) relevant to single-crystal X-ray diffractometry are: its high intensity over a wide spectral range, a small source size and a low divergence in the 0.1 mrad range, about 90% linear polarization in the horizontal plane, and a pulsed time structure.

Another important property is the instability of the synchrotron radiation source: the stored electron beam has a limited lifetime, a decaying beam intensity, and both short and long term changes in the beam position. This is a potential source of problems and requires monitoring of the primary intensity and its polarization state. The result is a slightly more complex data collection strategy and data evaluation technique than that used with conventional X-ray sources.

Data collection and data processing techniques that apply to single-crystal X-ray diffraction at a synchrotron radiation source will be discussed in the following. Then a selection of typical applications of synchrotron radiation to structure research will be presented. A thorough review of the subject is, however, not intended.

2. Experimental problems

2.1. Beam monitorization

Since the beam intensity decays during a "fill", we need to monitor the beam intensity I_0 in order to normalize diffracted intensities. There are several methods; the most common are to use ionization chambers or the scattering from amorphous materials inserted in the beam. At HASYLAB we use a "polarimeter" [1] which simultaneously monitors intensity I_o and degree of linear polarization Q of the incident beam:

$$I_o = I_{\mathrm{h}} + I_{\mathrm{v}} \quad \text{and} \quad Q = (I_{\mathrm{h}} - I_{\mathrm{v}})/I_o, \tag{1}$$

I_{h} and I_{v} being the intensities of horizontally and vertically linear polarized beam components, respectively.

2.2. Beam polarization

Q depends on the position of the sample relative to the electron orbit and may change during a fill. Typically, $I_{\mathrm{v}} \approx 0.05 I_{\mathrm{h}}$, giving $Q \approx 90\%$. Errors in the assessment of the degree of polarization are much less dramatic than might be expected: for medium Bragg-angles between $30° \leq 2\theta \leq 50°$ and complete neglect of the polarization correction even a change of Q from 90% to 80% would affect the integral intensity by only about 2% [2].

The polarization factor derived from Q is

$$P = \frac{1}{2}[(1+Q) + (1-Q)\cos^2 2\theta] \tag{2}$$

assuming a vertical diffraction geometry where we have almost no intensity loss through polarization.

2.3. Counter deadtime

Another thing to consider is the effect of higher harmonics and deadtime losses in the counting chains. Data reduction includes a deadtime correction for all the photon counters, including monitors. For NaI(Tl) scintillator counters deadtime is usually around $\tau = 3 \div 4$ μs. The usual correction (e.g. [3], [4])

$$N_{\text{corr}} = N_{\text{win}}/(1 - \tau N_{\text{int}}) \tag{3}$$

has to consider the total countrate N_{int}, including higher harmonics. N_{win} is the countrate in the Single Channel Analyzer (SCA) window set to reject higher harmonics. Since it is only a differential countrate, the often-used approximation

$$N_{\text{corr}} = N_{\text{win}}/(1 - \tau N_{\text{win}}) \tag{4}$$

is simply wrong. Assuming that $N_{\text{int}}/N_{\text{win}} = K$, i.e. a constant ratio of zero order to higher harmonics, we may write

$$N_{\text{corr}} = N_{\text{win}}/(1 - \tau K N_{\text{win}}) = N_{\text{win}}/(1 - \tau' N_{\text{win}}) \tag{5}$$

using an "effective" deadtime $\tau' = K\tau$. For practical purposes this approximation has been found to work satisfactorily, provided the relative higher-harmonics content does not change significantly during data collection. Repeated measurement of a couple of selected reflections during one or two fills has been found convenient to estimate τ' [2]. The preferred method, however, is to measure both zero order and higher harmonics simultaneously.

The separation of two bunches ($< 1\mu$s) is smaller than the deadtime of a NaI(Tl) counting chain. Thus, electronics cannot separate two or more photons per bunch; several photons per bunch will give — due to pile-up — a pulse of higher energy, which is rejected by the SCA. Thus, the maximum possible countrate appears to be limited by the time structure of a storage ring to

$$N_{\text{max}} = \frac{\text{electron frequency}}{\text{number of bunches}}, \tag{6}$$

NaI(Tl) is effectively "dead" for such high countrates. For countrates below 25000 cps, which we use (filters are inserted, if required), this is certainly no problem.

2.4. Reflection profiles and sample quality

Then, finally, the sample quality comes into play. The width of the rocking curve, i.e. the angular range over which a crystal diffracts as it is rotated through the Bragg position, has the following main contributions [5]:

$$\Delta\theta^2 = (\Delta\theta_{\text{S}}^2 + \Delta\theta_{\text{Q}}^2 + \Delta\theta_{\text{C}}^2) + \Delta\theta_{\text{M}}^2 + \Delta\theta_{\lambda}^2, \tag{7}$$

$\Delta\theta_{\text{S}}$: natural divergence of the SR beam ($\propto \lambda^{0.4}/E$)
$\Delta\theta_Q = \sigma_Q/R$: angle subtended by the source at the sample
$\Delta\theta_{\text{C}} = \sigma_{\text{C}}/R$: angle subtended by the sample at the source
$\Delta\theta_{\text{M}}$: mosaic spread of the crystal
$\Delta\theta_\lambda = (\Delta\lambda/\lambda)\tan\theta$: wavelength dispersion spread ($\propto \lambda^2$)

where σ_Q is the source size, σ_C is the crystal size, and R is the source-to-sample distance. This means, divergence is determined by the source, geometric factors, the sample quality, and the wavelength bandpass. Collecting θ-dependent and independent terms, the above equation reduces to the well-known formula

$$\Delta\theta^2 = A^2 + B^2 \tan^2\theta. \tag{8}$$

The natural divergence of the synchrotron radiation

$$\Delta\theta_S = \tfrac{1.33}{\gamma}\left(\tfrac{\lambda}{\lambda_c}\right)^{0.425} \quad [\mathrm{rad}] \tag{9}$$

$$\gamma = 1957E \quad [\mathrm{GeV}] \tag{10}$$

is of the order of the Darwin width of a Bragg reflection from perfect crystals (polarization neglected)

$$\Delta\theta_D = \frac{2r_e}{\pi V}\frac{\lambda^2}{\sin 2\theta}|F_H|. \tag{11}$$

The dispersion spread depends on

$$\Delta\lambda/\lambda = \cot\theta\ \Delta\theta_D \tag{12}$$

(neglecting the contribution from $\Delta\theta_Q$ and $\Delta\theta_S$).

Due to the small vertical divergence of the synchrotron radiation (≈ 0.1 mrad), source size ≤ 1 mm, and the large source distance (30–40 m) the full width at half maximum (FWHM) of the rocking curve is mainly determined by the sample. The divergence is dominated by the sample (or collimator) size $\Delta\theta_C$, its mosaic spread $\Delta\theta_M$, and by the wavelength bandpass $\Delta\lambda/\lambda$. As a result, reflection profiles from good quality mosaic crystals have a FWHM of typically 0.02–0.03°, which is about a tenth of what one observes with a sealed X-ray tube.

This results in a much improved peak-to-backgrund ratio, a very welcome feature. However, the highly collimated beam makes the sample quality readily apparent. Poor quality samples have rocking curves that consist of several, more or less well separated peaks, often combined with a highly anisotropic peak width (dependent on sample orientation). Measurement of an integrated reflectivity

$$R = \int I(\omega)\mathrm{d}\omega \tag{13}$$

requires integration over all domains and mosaic blocks. For “bad” quality crystals this means:

1. Integration in the vertical direction may be more efficient by using continuous scans instead of (traditional) step scans.
2. We have to start worrying about proper integration in the horizontal plane perpendicular to the scan direction.
3. The scattering volume at each point of the scan is only part of the total sample volume. This may lead to appreciable intensity losses.

In the worst case it may turn out impossible to measure true integrated intensities for all reflections of a sample with highly anisotropic mosaic spread (no such problem might be encountered for the same sample using sealed X-ray tubes).

2.5. Peak-to-background ratio

In order to measure weak and very weak ("forbidden") reflections the background has to be kept as low as possible. A source of parasitic scatter often overlooked is the sample itself and its mounting: some brands of glue and glass fiber may create additional — and often structured — background. A check prior to the SR experiment is always worth the trouble. Usually, however, the main source is absorption and parasitic scatter by the air in the beam path. An effective and simple solution is to use He-flushed collimator tubes. Another possibility is to cover the whole instrument with a He-flushed plastic tent.

Since synchrotron radiation is already highly collimated, all kinds of "collimators" mainly serve to reduce the beam size and the parasitic background from air scattering rather than affecting the beam divergence which is determined by the geometric factors discussed above.

Air absorbs and scatters X-rays, preferrably at wavelengths above 1 Å. The absorption for Cu K_α radiation is close to 1% per cm, i.e. 70 cm air absorb 50% of the beam. In addition, changes in barometric pressure may produce significant intensity changes caused by changed air absorption. With He in the beam path, background may be as low as $\approx$ 1 cps, depending on the θ-angle. The intensity gain observed with He is about a factor of 2 at 1.5 Å, and 4 at 2.0 Å with a corresponding improvement of the peak-to-background ratio.

2.6. Working conditions

Last but not least, we have to consider the typical working conditions at a synchrotron radiation facility: 24 hours running and always limited time allocated to experiments in an unfamiliar environment.

3. Data collection

There is no unique answer to the question how to collect single crystal diffraction data with synchrotron radiation. Some of the problems related to data collection with synchrotron radiation have been discussed by Wendschuh-Josties and Wulf [6] and by Kirfel and Eichhorn [2]. The latter deal with high precision structure factor measurement, the former address aspects of data collection on small and/or poor-quality crystals (though the authors do not state this explicitly).

In general, one wants to collect a "complete" data set of sufficient quality in the shortest possible time. The finer details of data collection depend on the general aims of the experiment, the synchrotron radiation spectrum, sample quality, sample absorption and scattering power, peak width and shape, and both absorption and parasitic scatter in air. Most of these factors are wavelength-dependent and partly counteractive (e.g. a decreasing integral reflectivity with decreasing wavelength, but smaller absorption, smaller Darwin width and generally a better peak-to-background ratio at shorter wavelengths). The optimum wavelength for some given conditions is not always obvious and sometimes difficult to determine. So far, there exists no clearcut answer to this question, and further investigations are still required on this subject.

3.1. Data collection strategies

For each reflection we want to optimize a scan width and a step size, counting time per step, and we need to determine the proper filter combination. Therefore, the data collection algorithm implemented on HASYLAB's 4-circle diffractometer [7] has the following main features:

- location of the reflection position, if required by making a pre-scan,
- determination of the proper filter combination, if required,
- evaluation of the optimum scan parameters, and
- a subsequent step scan with real-time monitoring of the beam intensity and polarization for data reduction.

Reflection profiles from good quality mosaic crystals have a full width at half maximum (FWHM) of typically 0.02–0.03°, which is much smaller than those obtained with a sealed X-ray tube. Such narrow profiles require small steps for measuring, typically 0.002–0.003°, in order to allow for a proper integration. The accuracy of calculated angular positions is, for good quality crystals, after refinement of the orienting matrix, in the order of 0.005–0.010°. For poor-quality samples, however, position errors may easily exceed 0.010°. Since the peak position is therefore not always accurately known, a pre-scan may be required.

The following are the data collection strategies we commonly use [7]:

- Make a quick and narrow pre-scan, locate the peak center, select filters, set the time per step, and proceed with an optimized main scan.
- Make a wider pre-scan and remeasure only significant reflections in the main scan; use the pre-scan result for the weaker reflections.
- Work without any pre-scan, provided that we can tolerate the offset of the calculated from the true peak position.

In the first method, the only purpose of the pre-scan is to locate the peak maximum. Therefore, it can be rather fast, with a stepsize typically about twice that of the main scan. Use of a spread in the ensuing main scan may help to further optimize counting time.

The second method, however, requires a fairly wide pre-scan, since all the "weaker" reflections will not be re-measured in the main scan. Significance level is set by a threshold, $I > x\sigma(I)$, where x may well be 5–10 or even larger. It may be chosen such that only reflections that require a filter are actually remeasured in the main scan.

The third method is applicable to good-quality crystals when the orienting matrix is well known and calculated positions are accurate to within a couple of steps. For strong reflections, the proper filter combination may then be safely determined starting with the countrate at the calculated position. If this countrate exceeds the "filter-threshold" a filter search is initiated which works as follows: a couple of steps are measured across the initial position; the maximum count step is located and used in a cyclic procedure until the proper filter combination has been found, and the counting time per step is adjusted accordingly.

When filters are not required, or if there are only a few strong reflections, it is usually much more economic to by-pass the filter search step and to remeasure the affected reflections, if any, at the end of data collection.

Since normal data sets span reflections from very weak to very strong, it may be a good idea to pre-sort reflections into classes according to expected intensity, and to collect batches with individually optimized measurement parameters. This would help to make the most efficient use of allocated beam time. An optimized data collection strategy allows one to collect a large number of data in the shortest possible time, in particular if one can tolerate a certain percentage of "unobserved" reflections.

3.2. Scan modes

Many crystals have reflection profiles with sharp peak and long tails. A traditional step scan requires therefore, due to the small stepsize, a large number of steps to safely reach the background, yet to sample the peak region with sufficient accuracy to determine a reliable integrated intensity. Actually, an appreciable amount of measuring time is then "wasted" on measuring the tails and the background. A better distribution between peak and tails may be achieved by using spread step scans with finer steps in the peak center, and wider steps in the tails. Such unequal step-width scans require, however, that the peak position is precisely known.

To further reduce the number of profile sampling points, and the amount of output, we may apply a continuous scan mode with counter read-out "on the fly" at fixed time intervals. This provides a true integration over the peak, and a small number of "steps" is sufficient to sample the peak profile. Since each step is actually an integral, we may run into problems with the deadtime correction for higher countrates. This is certainly a drawback of the continuous scan method, but it works fine for weaker and medium intensity reflections, tolerating peak offsets of 0.01° and even larger, without pre-scan. Continuous scan mode is often the best scan-type to choose for poor-quality samples with split reflection peaks and anisotropic peak shapes.

4. Data reaction and data analysis

4.1. Normalization

The time-dependence of the SR source intensity requires a decay correction and normalization of the measured reflection intensities. Let us assume that for each profile count $C_i, i = 1, \cdots, n$, there are additional counts from beam monitors C_{hi} and C_{vi}, and that all counts have been properly corrected for deadtime loss. Defining a local beam intensity $I_i = (C_{hi} + C_{vi})$ and a polarization ratio $Q_i = (C_{hi} - C_{vi})/I_i$, the simplest approach would be to scale each step count C_i for its local I_i and Q_i individually. This, however, has a serious disadvantage: for all but the weaker reflections the accuracy of the data would then be determined by the monitor counts rather than by the reflection shape and intensity. A better approach is to use averages $\langle C_\mathrm{h}\rangle$ and $\langle C_\mathrm{v}\rangle$, provided that we can correct any drift or fluctuation in the beam. Averaging should improve statistics by a factor $\sqrt{n}$, where n is the number of profile points. Since n is typically about 100, the error can thus be reduced by an order of magnitude relative to the "simple" point-to-point scaling approach.

Therefore, our data normalization strategy looks like the following [2]: normalization to $(\langle C_\mathrm{h}\rangle + \langle C_\mathrm{v}\rangle)$ provided both $C_{\mathrm{h}i}$ and $C_{\mathrm{v}i}$ do not show a significant drift or scatter; otherwise we try to correct with a least-square fit to $(C_{\mathrm{h}i} + C_{\mathrm{v}i})$ before averaging. If such a correction turns out insufficient, a point-to-point normalization is applied. Since the contribution from the monitors to $\sigma(I)$ is taken into account, "bad" reflections are automatically given a larger standard deviation than "good" reflections and a smaller weight in subsequent data processing and structure refinement.

4.2. Data reduction

Post-processing of the raw intensities after beam decay correction includes — among others — a Lorentz-polarization correction, and an absorption correction using data from azimuthal scans or an analytical procedure if the sample has well-developed and indexable faces. It may also include an internal scaling relative to the standard reflections correcting, e.g. for a sample decay.

Structure factors are obtained from the integrated intensities by

$$F^2 = SI/LP \tag{14}$$

$$\sigma(F^2) = S\sigma(I)/LP \tag{15}$$

and Ref. [8]

$$F = \begin{cases} \sqrt{F^2}, & F^2 > 0 \\ 0, & F^2 \le 0 \end{cases} \tag{16}$$

$$\sigma(F) = \begin{cases} \sigma(F^2)/2F, & F^2 > \sigma(F^2) \\ \frac{1}{2}\sqrt{\sigma(F^2)}, & F^2 \le \sigma(F^2) \end{cases} \tag{17}$$

where LP is the usual Lorentz-polarization factor which is obtained from the polarization ratio Q as

$$LP = \frac{(1+Q) + (1-Q)\cos^2 2\theta}{2\sin 2\theta} \tag{18}$$

The scaling factor

$$S = \frac{C_\mathrm{mon}}{\langle C_\mathrm{h}\rangle + \langle C_\mathrm{v}\rangle} \tag{19}$$

takes the beam monitorization into account. It serves to scale the data to a common preset monitor countrate C_mon which is essentially arbitrary; a reasonable value is about the average countrate during a fill.

4.3. Checks and data analysis

Statistical analysis of the test reflections may give a first hint on data quality. It is a common practice to check the intensity of the standards vs. time, and to correct for fluctuations, if required. In principle one might check for dependence on various experimental parameters; such checks are, however, rarely done.

The time-dependence of the synchrotron radiation source may easily introduce time-dependent errors not known from measurements with sealed X-ray tubes, which may pass unnoticed without an extra analysis. Improper treatment may easily offset the advantages to be gained from high intensity and low divergence of the synchrotron radiation source. Data evaluation should therefore include additional checks to make sure there are no such errors left uncorrected. It has been found that the deadtime correction is frequently a source of such type of error. The simplest and quickest method is to plot the intensity of the test reflections vs. the monitor countrate; ideally such a plot exhibits only random scatter.

The usual procedure to obtain a higher accuracy is to extend the counting time per profile step. If we do so at the synchrotron source we will, however, encounter a significant decay of primary beam intensity over the reflection profile; the decay rate depends on the lifetime of the electron beam in the storage ring. Such a decay requires a correction; in the worst case we are back to a point-per-point scaling, loosing the factor $\sqrt{n}$ in accuracy. This leads to the paradox situation that increasing the measurement time may actually decrease the data quality.

To obtain data of higher accuracy it is generally preferred to measure symmetrically equivalent reflections and to improve data by averaging rather than to expand the counting time to more than 1–2 s/step. Typically, we use 0.1–1 s/step for data collection.

5. Applications

Diffraction experiments with synchrotron radiation make use of the high intensity, the good collimation, the polarization, and the wavelength-tunability over a fairly wide spectral range.

5.1. Micro-crystals

In the kinematic fraction theory, the integral reflection intensity is given by

$$I = \left(\frac{r_e\lambda^2}{V}\right) V_c \frac{\lambda}{\sin 2\theta} P|F_H|^2 \tag{20}$$

(V_c is the sample volume), or, combining constants into a scale factor K,

$$I = KV_c\lambda^3F^2. \tag{21}$$

Thus, there are two applications of SR that are immediately obvious: smaller samples and/or weak reflections.

Comparison of the intensity of the SR beam with that of conventional source is not straightforward, and numbers given for the photon flux at the sample position are often misleading. The intensity gain depends on the sample itself and is greatest for crystals with low mosaic spread.

The high source intensity makes experiments possible that require a small sample volume, e.g. the use of high-pressure cells [9]. Data collection is feasable on crystals down to and below 10 μm diameter. In principle it is feasable to use a powder grain for a single-crystal structure analysis. A demonstration was given by Schulz and co-workers [10] who succeeded to collect a complete data set on a 6 μm CaF_2 crystal at HASYLAB. 130 significant reflections were averaged to 17 unique observations that refined to $R = 3\%$. The smallest crystal used to date had a volume of only 2.2 μm^3 [11]. Mounting and orienting such small samples is not a trivial task, and determination of an orienting matrix is the crucial step of data collection on micro-crystals. It is an advantage when the cell constants are already known, e.g. from powder diffraction.

Often crystals cannot be grown to sizes which allow single-crystal diffraction with conventional sources. SR makes particle sizes accessible between 5 and 50 μm and bridges a gap that could not be treated satisfactorily with either single-crystal or powder diffraction. Zeolites are a typical class of compounds, as an example [12]. At HASYLAB samples between 30 and 50 μm are handled routinely by some of our "customers", but I do not know of an unknown crystal structure that has been solved from $a < 10$ μm crystal so far.

5.2. *Accurate structure analysis*

Instead of using smaller samples we may use normal-size crystals to measure weak (or even "forbidden") reflections. Weak reflections carry often information about fine details of a crystal strcuture like thermal vibrations, electron density distribution, disorder, defects, pseudosymmetry, and more.

Measurement of weak and very weak ("forbidden") reflections profits from high intensity low divergence, almost θ-independent polarization and a good peak-to-background ratio.

A first indication of the accuracy that can be obtained at a SR source was obtained by Coppens and co-workers [13] who performed an electron density study on the inorganic complex $Cr(NH_3)_6Cr(CN)_6$. Data were collected at the Cornell A2 beamline, using $\lambda = 0.302$ Å wavelength. 7224 reflections were measured (2329 unique) to $\sin\theta/\lambda = 1.15$ Å^{-1} with an internal agreement factor of $R_i = 0.021$, and refined to $R_f = 0.0252$ (HO-refinement). A comparison with conventional tube data was not, however, made.

In order to assess the accuracy that can be obtained with SR, Kirfel and Eichhorn [2] and Eichhorn, Kirfel, Grochowski and Serda [14] collected single crystal X-ray diffraction data on the 5-circle diffractometer at HASYLAB [15] using three well-known crystal structures: cuprite (Cu_2O), corundum (α-Al_2O_3), and borazon (cubic BN). These three compounds were chosen because of their structural simplicity and since they can be cross-checked against deposited structure factors from careful X-ray tube measurements which have been analyzed in terms of the electron-density distributions (Cu_2O, [16]; Al_2O_3, [17]; BN, [18–19]).

Cuprite, Cu_2O crystallizes in cubic space group $Pn\bar{3}m$. Its outstanding feature is a linear and symmetric O–Cu–O bond (Cu–O 1.848 Å) as a result of two interpenetrating lattice complexes of Cu and O which are F and I, respectively.

Corundum, α-Al_2O_3, crystallizes in hexagonal space group $R\bar{3}c$. It is composed of AlO_6 octahedra with oxygen tetrahedrally coordinated by Al atoms.

Borazon, cubic BN, has similarities with the isoelectronic diamond structure (space group $Fd\bar{3}m$). It is, however, non-centrosymmetric (space group $F\bar{4}3m$).

Data collection with 0.56 Å wavelength yielded (after averaging) 258 unique reflections ($\sin\theta/\lambda \leq 1.1$ Å^{-1}) for Al_2O_3, and 162 ($\sin\theta/\lambda \leq 1.45$ Å^{-1}) for Cu_2O, including 19 "forbidden" (hho)-reflections (only reflection (221) could be measured with a sealed tube, and (223) and (421) were shown to have $I > \sigma(I)$). For Al_2O_3 all reflections were significantly observed. Comparison with the published data gave an overall agreement of 1.5% for both compounds. Refinements using multipole models yielded agreement factors of $R = 0.0096$ and $R = 0.0078$ for Cu_2O and Al_2O_3, respectively. Most results, including deformation density maps, are in satisfactory agreement with the published results.

For borazon X-ray diffraction data were collected at $\lambda = 0.50$ Å up to $\sin\theta/\lambda = 1.45$ Å^{-1}. Comparison with accurate tube data resulted in an agreement factor $R = 0.0135$ (0.006 omitting the four lowest-order reflections). Refinements with a multipole expansion yielded R-values as low as 0.0046. Ensuing deformation maps agree well with expectation.

These analyses indicate that high-quality data can be obtained at a SR source in much shorter time than with conventional sources, provided proper attention is given to data collection strategies and data reduction procedures. Though little is gained for strong reflections, the improvement is very pronounced for weak reflections, which can be measured in much shorter time than with conventional sources. SR allows an unprecedented accuracy for weak diffraction intensities. In this context it is important to note that high-order reflections are also generally "weak". In particular the latter increase effective resolution, resulting in reduced parameter correlation and increased accuracy of refined structure parameters. Due to this increased resolution deformation density maps from SR data were observed to show remarkably little noise in the regions away from the atoms.

The analysis on borazon is of particular importance: data collection was carried out using — without lengthy analyses — our established "standard" data collection procedure developed on Cu_2O and Al_2O_3. Thus, accurate structure analysis with SR does not mean excessive work, but it is possible in relatively short time. (We like to repeat this kind of measurement once in a while, using our standard crystals, in order to check diffractometer, software and methods.)

Summarizing, SR provides significant advantages for precise structure analyses. The results above give confidence to single-crystal diffraction using SR sources quite in general.

5.3. Anomalous dispersion for structure research

Wavelength tunabilty offers an opportunity to reduce both absorption and extinction effects and to avoid corrections for anomalous dispersion, f' and f''. Short wavelengths are particularly favorable, and they provide the high resoluton required by accurate structure analyses. On the other hand, energies be chosen deliberately which maximize dispersion effects in order to exploit them for structure research.

The wavelength can be tuned over a fairly wide range ($0.3 \leq \lambda \leq 2.5$ Å), giving access to the $4K$- or L-edges of all elements beyond Ti. The real and imaginary parts, f' and f'', of the atomic scattering factors may show large variations near the absorption edges; in particular at the L-edges (e.g. [20]). Theoretical developments and a limited number of experiments give rise to expectation that anomalous dispersion effects may have considerable impact on crystal structure determination. In particular protein crystallography can be expected to profit from anomalous dispersion effects. There is also much untapped potential for small-molecule crystallography, however.

Traditional applications of anomalous dispersion may profit from maximizing dispersion effects. Examples are determination of absolute configuration, location of heavy atoms, and an aid to phase determination.

Most promising for structure research is "differential anomalous dispersion" which makes use of measurements at several wavelengths around an absorption edge. Examples are contrast variation to distinguish elements of similar atomic number [21], and phase determination from both single- and multiple-wavelength measurements (MAD-phasing), using Patterson-syntheses [22] or an algebraic approach suggested by Karle [23] and developed by Hendrickson (e.g. [24]).

Most of the above applications will remain restricted to SR sources though in certain cases suitable wavelengths may also be available from sealed tubes.

5.4. *Anisotropy of* f' *and* f''

The corrections f' and f'' may, close to absorption edges, exhibit a pronounced anisotropy: their magnitude may depend on the sample orientation with respect to the electric vector of the incident radiation. The result is X-ray dichroism and double refraction. Such anisotropies have been studied for several compounds like vanadyl bisacetyl acetonate, rubidium uranyl acetate and sodium bromate [25–27]; $LiNbO_3$ [28]; Cu_2O, TiO_2, MnF_2 [29], and more.

Mathematically, anisotropic f' and f'' can be described by 2nd rank tensors

$$\hat{f} = f_o\hat{I} + \hat{f}' + \mathrm{i}\hat{f}'' \qquad (22)$$

$\hat{I}$ being a 3×3 identity matrix. The structure factor will then also become a tensor

$$\hat{F} = \sum_j \hat{f}_j \exp[2\pi\mathrm{i}\boldsymbol{r}_j\boldsymbol{H}] \qquad (23)$$

and the observed integral intensity

$$I(\boldsymbol{H}) = |\varepsilon^T\hat{F}(\boldsymbol{H})\varepsilon_o|^2 \qquad (24)$$

is both orientation- and polarization-dependent.

The effect of anomalous anisotropic dispersion (AAD) on single-crystal Bragg-diffraction was first discussed by Templeton and Templeton [25]. As a particularly interesting consequence anisotropy of f' and f'' may give rise to violation of systematic absences due to screw axes and glide planes, with a polarization dependent intensity of those "extinct" reflections. The reason for this is that crystallographically equivalent atoms do not have the same scattering power any more exactly (both magnitude and phase may differ). Experimental evidence for the occurence of space-group extinct reflections due to AAD has been reported by Templeton and Templeton [27, 30–31] for cubic $NaBrO_3$, by Petcov, Kirfel and Fischer [28] for $LiNbO_3$, and by Kirfel, Petcov and Eichhorn [29] for Cu_2O, TiO_2 and MnF_2.

It has been demonstrated that this effect may be used for selectively determining the positions of the anisotropically scattering atoms. The possibility of partial structure analysis by AAD has been discussed by Kirfel and Petcov [32] for the special case of space group $P2_12_12_1$ having one anomalous scatterer in the asymmetric unit. They proposed a method to extract structural information from the ψ-dependence of "forbidden" axial reflextions ($(h00)$, $h = 2n + 1$; $(0k0)$, $k = 2n + 1$; $(00l)$, $l = 2n + 1$).

At the Br K-absorption edge of $NaBrO_3$ Templeton and Templeton [31] observed screw-axis extinct reflections $(00l)$, $l = 1, 3, 5, 7, 9, 11$. In their analysis they showed that the intensity variation of these "extinct" reflections with azimuthal angle ψ could be used to determine the phases of the corresponding (allowed) $(002l)$ reflections.

In this context I would like to point out that AAD is not at all bound to the use of synchrotron radiation or to single crystals. It is also observed with unpolarized radiation, and it has been shown to be observable also for powder diffraction [33].

5.5. Other applications

The high intensity permits measurement of weak effects such as (thermal) diffuse scattering, elastic, magnetic and nuclear scattering, and satellite reflections. The low divergence yields a high intrinsic collimation, high resolution and a good signal-to-noise ratio. Thus features close to the main peaks and from twinned crystals can be resolved.

The time structure of the SR source can be used for time-resolved experiments on a nanosecond time scale. Spectroscopists exploit this time structure for time-resolved measurements; time-resolved small-angle X-ray scattering is also frequently used on biological systems. Applications to small-molecule X-ray scattering, however, are still rare. An example is the time resolved analysis of laser annealing of Si-wafers by Larson, Tischler and Mills [34], performed at the Cornell SR source (CHESS).

Magnetic X-ray scattering profits from the polarization properties of the SR source: magnetically and electronically scattered photons may be discriminated by their different polarization dependence [35].

6. Conclusions

Crystallographers are using synchrotron radiation facilities for experiments that take advantage of the characteristics of synchrotron radiation, namely, a wide distribution of wavelengths, high intensity, low divergence, linear polarization, and a pulsed time structure.

Single-crystal X-ray diffraction with synchrotron radiation helps us to solve traditional problems. Synchrotron radiation helps also to extend the range of X-ray diffractometry to experiments which are not feasable with sealed X-ray or rotating anode tubes. Thus, in addition to the more familiar diffraction experiments new types of crystallographic studies are progressing rapidly with more general access to synchrotron radiation sources.

Crystallographic experiments place stringent demands on the long-term stability of source, optics, and detector linearity. However, existing and new sources and diffractometers have undoubtedly properties attractive to crystallographers. X-ray diffraction with synchrotron radiation can be expected to be in the forefront of crystallographic research in the next several years.

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