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It is shown that incomplete absorption of the X-ray beam in the phosphor of an area detector causes an incident-angle dependence of the recorded X-ray intensities. An energy scan of a SMART-6000 CCD (charge-coupled device) phosphor using synchrotron radiation shows the correction to be of importance above about 17 keV. Intensities of single reflections, each collected several times at different angles of incidence on the phosphor surface, show a pronounced angle-dependence at shorter wavelengths. Both conventional structural refinement and multipole charge density studies confirm that an oblique-incidence correction leads to improved quality of the results. Atomic displacement parameters will be systematically biased when the correction is not applied. For a \( \lambda = 0.394 \ \text{Å} \) data set, neglecting the correction gives rise to artifacts in the deformation density maps that are likely to lead to misinterpretation of the experimental results.

1. Introduction

CCD detectors are now widely used in both macromolecular and small-molecule crystallographic studies. While in macromolecular crystallography radiation with wavelengths above 1 Å is commonly used, in small-molecule structure analysis, and particularly in charge density studies, Mo K\( \alpha \) or shorter wavelength X-rays have distinct advantages and are widely employed. For such short wavelengths, the phosphor layer of the detector does not completely absorb the X-ray beam.

As was pointed out by Gruner (1993), but not always taken into account, when absorption is incomplete the phosphorescence will depend on the path length of the beam in the phosphor, and therefore on the angle of incidence \( \alpha \), defined as the angle between the diffracted beam and the normal to the CCD surface. This is the ‘thin phosphor regime’. On the other hand, in the ‘thick phosphor regime’, where absorption of the X-ray beam in the phosphor is very close to 100\%, as typically occurs for softer radiation, the efficiency of light transmission through the phosphor layer becomes the dominant effect. In the ‘thick phosphor regime’, less intensity may actually be recorded at larger angles of incidence, for which the absorption occurs closer to the entry surface of the phosphor (Gruner, 1993).

For incomplete absorption, the path length of the X-ray beam in the phosphor equals \( t/\cos(\alpha) \), where \( t \) is the thickness of the phosphor. Thus, while for perpendicular incidence the absorption is \( (1 - T_\perp) \), where \( T_\perp \) is the transmission at perpendicular incidence, it is \( [1 - \exp\{\ln(T_\perp)\/\cos(\alpha)] \) for a beam with incident angle \( \alpha \). In earlier work with imaging plates (Zaleski et al., 1998) and short-wavelength radiation, the observed intensity \( I_{\text{obs}} \) was reduced to an equivalent perpendicular-incidence intensity \( I_\perp \) with the expression

\[
I_\perp = I_{\text{obs}}(1 - T_\perp)/[1 - \exp\{\ln(T_\perp)\/\cos(\alpha)]
\]

This oblique-incidence correction proved to correct satisfactorily quite pronounced differences between the intensities of the same reflection recorded at different angles of incidence on BASF III imaging plates.

We show here that a similar correction is required for short-wavelength data collected with a SMART-6000 CCD detector using a Gd\(_2\)O\(_2\)S phosphor with a surface density of 50 mg cm\(^{-2}\), and that expression (1) leads to significant improvements in the experimental data sets. No other corrections were tested in this study.

2. Experimental

A 25 × 25 cm piece of a Gd\(_2\)O\(_2\)S phosphor with a surface density of 50 mg cm\(^{-2}\) and thickness of 0.2 mm, designed for the SMART-6000 CCD, was provided by Bruker AXS Inc. Its perpendicular transmission was measured at the SUNY X3 beamline at the National Synchrotron Light Source at Brookhaven National Laboratory, using both 19.3 keV (0.643 Å) and 31.45 keV (0.394 Å) radiation from sideways-mounted Si(111) and Si(220) crystals, respectively. To eliminate high-order contamination, the 312 reflection from a crystal of diaqua(bis(hydrogen phthalato)copper(II) (Bartl & Kuppers, 1980; Rodrigues et al., 2002), rather than the primary beam, was used. The perpendicular transmission was measured as 0.1237 and 0.5610 at the two wavelengths,
respectively. The perpendicular transmission of the phosphor in the full 17–32 keV energy range was recorded at the ChemMat CARS beamline at the Advanced Photon Source at Argonne National Laboratory. The results are shown in Fig. 1.

To examine the incidence dependence of the intensities, two sets of measurements were made at the X3 beamline on crystals of 2-dimethylsulfuranylidene-1,3-indanedione (0.643 Å) and diaquabis(hydrogen phthalato)copper(II) (0.394 Å), with the detector positioned at 2θ = 40, 30, 20, 10, 0 and −10°. At each position, 110 frames with an oscillation range of 0.3° were collected. All intensities were integrated with the SAINT (1999) program; no reflections were rejected. A vendor-supplied file for the floodfield correction, measured with Mo Kα radiation and a 17.5 cm source-to-detector distance, was used. The intensities were corrected for the decay of the synchrotron beam using as reference the counts in an ionization chamber located between the beam defining slits and the SMART shutter.

Finally, as summarized in Table 1, the oblique-incidence correction was tested on several complete data sets collected at the X3A1 beamline. Equivalent and multiple measured reflections were averaged using the program SORTAV (Blessing, 1997). The program SHELX (Sheldrick, 1990) was used for structure refinement.

### Table 1
Comparison of Rmerge and final agreement factors with and without correction of the data for oblique incidence.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>λ (Å)</th>
<th>(sin2θλ)_{max} (Å⁻¹)</th>
<th>Tmax</th>
<th>α°</th>
<th>Rmerge (no correction)</th>
<th>Rmerge (with correction)</th>
<th>Rrefinement (no correction)</th>
<th>Rrefinement (with correction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuC₆H₄BN₂F₄S₂§</td>
<td>20</td>
<td>0.643</td>
<td>0.89</td>
<td>0.1237</td>
<td>0.33–62.18</td>
<td>6.01%</td>
<td>5.48%</td>
<td>3.59%</td>
</tr>
<tr>
<td>ZrC₆H₄Pt</td>
<td>25</td>
<td>0.643</td>
<td>0.97</td>
<td>0.1237</td>
<td>0.45–68.16</td>
<td>7.05%</td>
<td>6.70%</td>
<td>4.35%</td>
</tr>
<tr>
<td>Cu(C₆H₄O₄)_2·2H₂O</td>
<td>30</td>
<td>0.394</td>
<td>1.55</td>
<td>0.561</td>
<td>0.13–61.02</td>
<td>5.85%</td>
<td>4.30%</td>
<td>5.03%</td>
</tr>
<tr>
<td>Cu(C₆H₄O₄)_2·2H₂O§</td>
<td>30</td>
<td>0.394</td>
<td>1.02</td>
<td>0.561</td>
<td>1.49–51.16</td>
<td>4.17%</td>
<td>4.06%</td>
<td>3.98%</td>
</tr>
<tr>
<td>SrTiO₃§</td>
<td>35</td>
<td>0.394</td>
<td>1.62</td>
<td>0.561</td>
<td>1.13–60.70</td>
<td>6.80%</td>
<td>6.06%</td>
<td>2.92%</td>
</tr>
<tr>
<td>SrHfO₃§</td>
<td>32</td>
<td>0.394</td>
<td>1.58</td>
<td>0.561</td>
<td>0.15–61.57</td>
<td>9.67%</td>
<td>8.51%</td>
<td>5.14%</td>
</tr>
</tbody>
</table>

† The angle between the diffracted beam and the vector normal to the CCD phosphor surface. § Measured at T = 17 K. §§ Measured at T = 293 K.

3. Analysis of the angle dependence

As shown in Fig. 1, for the phosphor tested the absorption at perpendicular incidence is not complete even at 17 keV, at which the transmission is about 5%. This means that even with Mo Kα radiation (E = 17.45 keV) the correction is desirable if an accuracy of better than 5% in the intensities is required, and a large detector positioned close to the crystal is employed. Temperature factors will be biased if the correction is ignored under such conditions. In the data collection procedure used with SMART detectors, a floodfield correction is applied to account for variation of the sensitivity across the

**Figure 1**
The transmission versus energy of the phosphor of the SMART 6000 CCD.

**Figure 2**
Observed (dot) and calculated (solid line) intensity versus angle of incidence for selected reflections of a C₆H₄O₄S crystal collected at 0.643 Å. The calculated values are from expression (1) with Tmax = 0.1237.
detector surface using a pixel by pixel correction file, supplied with the detector or determined in a separate experiment. Such a correction would account for the differential absorption in the phosphor only if the same wavelength is employed and the source-to-detector distance is identical to the crystal-to-detector distance used in the diffraction experiment. These conditions are generally not fulfilled. At synchrotron sources the wavelength can be matched approximately by using an appropriate fluorescent foil as source, but this requires a much larger source-to-detector distance to avoid diffuse powder lines from the foil affecting the correction.

At the higher energies often used at synchrotron beamlines, the oblique-incidence correction becomes imperative. In accordance with the absorption curve of Fig. 1, the measurements at both 0.643 Å and 0.394 Å show a clear incident-angle dependence of the recorded intensities (Figs. 2 and 3). The full line represents the correction according to expression (1). As expected, the correction is most pronounced for the shorter wavelength.

4. Effect of the correction

In Table 1, \( R_{\text{merge}} \) values and \( R \) factors from conventional structure refinements of a number of data sets collected at different wavelengths and different resolutions are tabulated before and after the oblique-incidence correction. In all cases both \( R_{\text{merge}} \) and the \( R \) factor from the least-squares refinement improve on application of the correction. The effect of the correction on \( R_{\text{merge}} \) may be especially large for data collected for charge density studies, in which several detector angles are often used. Thus, identical or equivalent reflections are very likely collected at different angles of incidence, leading to a significant deterioration in \( R_{\text{merge}} \) prior to correction.

The correction tends to decrease the intensity of the high-order reflections, which, given that the selection of the detector angle is optimized for efficient data collection, tend to occur at larger incident angles. Thus, the temperature factors are artificially lowered before the correction is applied. This is confirmed by the results shown in Table 2.

The effect on the model deformation density in the plane of the hydrogen phthalate anion in diaquabis(hydrogen phthalate)copper(II) (17 K data), obtained after refinement with the program XD (Koritsanszky et al., 1997), is illustrated in Fig. 4. Remarkably, the double peaks appearing in the cova-
lent bonds before correction disappear when the corrected data are used. The 'double bond peak' feature has been observed in other studies, some of which may require re-examination.

5. Concluding remarks

The study reported here concerns one particular type of phosphor. It is clear that a wider examination of the different phosphors being used in crystallographic experiments is needed to ensure the elimination of the systematic errors identified in this study.

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References