Absorption correction for crystals in capillary tubes. By D. J. WATKIN, Chemical Crystallography Laboratory, Oxford University, 9 Parks Road, Oxford OX1 3PD, England

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An inexpensive calculation is outlined for determining those reflexions suffering large absorption errors, and for correcting those with smaller errors.

For a Bragg angle $\theta$ of less than $57^\circ$, the Hilger and Watts Y290 four-circle diffractometer usually records data in bisecting geometry, that is, with the plane of the $\chi$ circle parallel to the scattering vector. For greater $\theta$ values, $\chi$ is fixed at $\pm 90^\circ$ and $\omega$ and $\phi$ are adjusted.

During a recent redetermination of the crystal structure of naphthalene, bisecting geometry was used with copper $K\alpha$ radiation up to $\theta=57^\circ$. In order to obtain scaling data in addition to those of the standard reflexions, the fixed $\chi$ geometry was then used from $\theta=50^\circ$ to $\theta=80^\circ$. During the scaling of the data sets it was evident that some reflexion intensities measured in both geometries differed by factors of up to 10. These reflexions were ones that had been observed with the incident or emergent beam inclined at a small angle to the tube axis.

The crystal used for the data collection was a small rectangular block (0.3 x 0.6 x 0.9 mm) grown by sublimation in a 2 mm diameter Pantak tube. An empirical absorption correction (North, Phillips & Mathews, 1968) was applied using the 120 and 240 reflexions to obtain transmission factors as a function of $\phi$. The maximum correction applied on this basis was 1.41.

The discrepancies were reduced by applying the following additional absorption-correction factor, based on the oblique incidence of the incident and emergent beam on the specimen and tube.

Fig. 1 represents a lateral section through a point crystal supported on the axis of a capillary tube. The ray $S(1)$ is diffracted by a plane whose normal is perpendicular to the tube axis, so that the correction for transmission of the rays through the tube is

$$A^* = \exp \left( \frac{\mu t}{\sin \gamma_0} \right) \cdot \exp \left( \frac{\mu t}{\sin \gamma} \right).$$

if the tube wall is of uniform thickness. For a more general ray, the incident beam is inclined to the axis of the tube at an angle $\gamma_0$ in, say, the plane of the paper, and the emergent beam at an angle $\gamma$ to the tube axis. The emergent beam is not necessarily also in the plane of the paper. The correction factor in this situation becomes

$$A^* = \exp \left( \frac{\mu t}{\sin \gamma_0} \right) \cdot \exp \left( \frac{\mu t}{\sin \gamma} \right).$$

Since programs to apply the North–Phillips–Mathews or other orientation-linked corrections need to compute the angular relationships between the crystal and the incident and diffracted beams, it is possible to compute this additional correction at little extra cost.

If $\omega'$, $\chi'$ and $\phi'$ are the settings required to make the tube axis horizontal and normal to the X-ray beam, then the effective 'indices' of the tube are

$$h' = [\phi']^{-1} \cdot [\chi']^{-1} \cdot [\omega']^{-1} \left[ \begin{array}{c} 1 \\ \sin 2\theta \\ -\cos 2\theta \\ 0 \end{array} \right].$$

where $[\phi']$ is the appropriate form of the $\phi$ rotation matrix.

In the reflecting position the components of the tube axis are

$$v_i = [\omega] \cdot [\chi] \cdot [\phi] \cdot h',$$

or

$$v_i = [R] \cdot h',$$

the components of the incident beam are

$$v_i = [R] \cdot \left[ \begin{array}{c} 0 \\ 1 \\ 0 \end{array} \right],$$

and the components of the diffracted beam are

$$v_d = [R] \cdot \left[ \begin{array}{c} \sin 2\theta \\ -\cos 2\theta \\ 0 \end{array} \right].$$

for a coordinate system in which $+y$ points from the crystal.
to the X-ray source and +x is in the equatorial plane and on the same side of the X-ray beam as +θ. The angles between v₁ and v₂(γ₀) and v₄ and v₅(γ) can be computed, and hence A*. The rise in the correction as a function of γ is very sharp at small γ values (Table 1), so that there is the possibility of large errors being introduced through small errors in either μ or in ω', χ' or φ'. In the program therefore, if either part of A*, or the final A* was greater than a preset limit, that part was set to the limit, and the reflexion marked as being in error.

Table 1. Variation of the absorption correction (A*) as a function of angle of incidence

<table>
<thead>
<tr>
<th>γ(°)</th>
<th>A* = exp (0.2/sin γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>92038-08</td>
</tr>
<tr>
<td>2</td>
<td>307-97</td>
</tr>
<tr>
<td>4</td>
<td>17-46</td>
</tr>
<tr>
<td>8</td>
<td>4-22</td>
</tr>
<tr>
<td>16</td>
<td>2-08</td>
</tr>
<tr>
<td>32</td>
<td>1-46</td>
</tr>
<tr>
<td>64</td>
<td>1-25</td>
</tr>
</tbody>
</table>

For non-spherical crystals, crystals not on the axis of the tube and rays not passing through the centre of the crystal this treatment is only approximate (Krieger, Chambers, Christoph, Strout & Trus, 1974). In the naphthalene experiment a value of μt=0.2 was found appropriate for the particular crystal-tube combination by looking at several reflexions suffering from strong attenuation and adjusting μt for an adequate fit (μ for naphthalene ≈ 6.05 cm⁻¹ for Pyrex glass about 50 cm⁻¹). Some examples of the results are shown in Table 2.

Table 2. Examples of the correction applied to naphthalene

<table>
<thead>
<tr>
<th>h k l</th>
<th>Fixed χ setting (uncorrected)</th>
<th>Fixed χ setting (corrected)</th>
<th>Bisecting setting (corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 4</td>
<td>314</td>
<td>703</td>
<td>754</td>
</tr>
<tr>
<td>5 0 5</td>
<td>4748</td>
<td>5221</td>
<td>5291</td>
</tr>
<tr>
<td>4 7 4</td>
<td>354</td>
<td>2284*</td>
<td>2319</td>
</tr>
<tr>
<td>3 2 6</td>
<td>1029</td>
<td>1147</td>
<td>1065</td>
</tr>
</tbody>
</table>

* The incident or emergent-beam correction exceeded the maximum permitted (5.0) and was thus set to 5. The reflexion was flagged as in error.

When the capillary tube is approximately parallel to the axis of rotation, the variation in this correction factor is not large for measurements made in bisecting geometry. However, if it is unavoidable that the tube be inclined to the rotation axis, then the calculation allows a correction to be made, or allows the operator to determine and reject those measurements that may contain a large systematic error.

References


Lattice parameters of some binary and ternary copper alloys. By S. C. CHATTERJEE and M. P. GUPTA, Department of Physics, Ranchi University, Ranchi-834008, India

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Lattice parameters of some binary and ternary alloys of copper, aluminum, cadmium, indium and tin are given, based on X-ray powder diffraction measurements.

In course of the determination of stacking-fault parameters for a number of α-phase binary and ternary copper alloys, we have evaluated the lattice parameters (LP) of these alloys using powder X-ray diffraction and the extrapolation method of Nelson & Riley (1945). The photographic technique was used throughout. The results are summarized in Tables 1 and 2.

As may be seen from Table 1, the relation between lattice