elemental structures from which standard CN 12
diameters are derived!

(2) It shows that an invariant parameter in a uniaxial
crystal structure may couple the variable parameters of
the structure, so as to produce apparent dependences of
the cell edges on the diameter of a component atom,
which could not possibly arise intrinsically through the
direct contacts of the atom with its neighbours.

(3) The observed variations of the cell dimensions of
phases with the A1Cr2C structure lead to some
interesting observations on the nature of the electronic
interactions in true interstitial phases. Hopefully, these
may stimulate band-structure calculations to confirm
or reject the reliability of such analyses.

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and $\xi$ in the $a^* b^*$ plane. Then,

$$d_{hkl}^2 = \xi^2 + \zeta^2. \quad (1)$$

$\zeta$ is measured on the oscillation photograph and is related to $c$ by

$$\zeta = le^{-1}. \quad (2)$$

$\xi$ is obtained from the $n$th-level film by measuring, in mm, $x$, the perpendicular distance from a reflection to the central line. One way of indicating the central line is to let the direct beam fall for a few seconds on both extremities of the film and join the centers of the spots with a fine pen. Alternatively, one can record the direct beam by manually moving the cassette throughout its range, but this tends to give a thicker trace. A relation between $\xi$ and $x$ can be derived from two expressions given by Buerger (1942, pp. 223, 254ff.) for the reflection angle $\Psi$,

$$2 \sin^{-1}(\xi/2 \cos \mu) = \Psi = C_1 x,$$

where $C_1$ is an instrumental constant equal to $2^\circ$/mm for a camera diameter of 57.3 mm and $\mu$ is the equi-inclination angle. For such a camera, $\xi$, expressed in $\AA^{-1}$, is given by

$$\xi = 2\lambda^{-1} \sin x \cos \mu. \quad (3)$$

The general expression for $d_{hkl}^*$ can be written in the form

$$l^2 c^*-2 + 2hla^* c^* \cos \beta^* + 2kib^* c^* \cos \alpha^* = d_{hkl}^2 - d_{hko}^2, \quad (4)$$

where

$$d_{hko}^2 = h^2 a^* + k^2 b^* + 2hka^* b^* \cos \gamma^*. \quad (5)$$

Equation (4) can be rewritten in terms of the observable quantities $\xi_{hko}^2 (=d_{hko}^2)$ and $\xi_{hkl}^2 (=d_{hkl}^2 - l^2/c^2)$:

$$l^2(c^*-c^{-2}) + 2hla^* c^* \cos \beta^* + 2kib^* c^* \cos \alpha^* = \xi_{hkl}^2 - \xi_{hko}^2. \quad (6)$$

Three reflections give rise to three equations of type (6) which may be solved by inverting the matrix of the indices

$$\begin{pmatrix}
2a^* c^* \cos \beta^* + 2h^2 a^* c^* \\
2b^* c^* \cos \alpha^*
\end{pmatrix}
= \begin{pmatrix}
l_1^2 & l_1 & l_1 & l_1^{-1} \\
l_2^2 & l_2 & l_2 & l_2^{-1} \\
l_3^2 & l_3 & l_3 & l_3^{-1}
\end{pmatrix}
\cdot
\begin{pmatrix}
\xi_{hkl}^2 - \xi_{hko}^2 \\
\xi_{hkl}^2 - \xi_{hko}^2 \\
\xi_{hkl}^2 - \xi_{hko}^2
\end{pmatrix},$$

whence

$$\begin{pmatrix}
\sigma + \tau = 360 - (\psi + \phi_{12} + \phi_{23})
\end{pmatrix}$$

$$\begin{pmatrix}
d_{123}^* \sin \sigma
\sin \phi_{12}
\sin \phi_{23}
\end{pmatrix}
= OP_2 \cdot \begin{pmatrix}
d_{123}^* \sin \tau
\sin \phi_{12}
\sin \phi_{23}
\end{pmatrix},$$

Frequently, the first level ($l=1$) will be the only upper level recorded in which case the inverse matrix simplifies to

$$\begin{pmatrix}
1 \\
1 \\
1
\end{pmatrix}
\begin{pmatrix}
h_3 & k_3 & h_2 & k_2 & h_1 & k_1 & h_3 & k_3 & h_2 & k_2 & h_1 & k_1 \\
k_3 & h_3 & k_2 & h_2 & k_1 & h_1 & k_3 & h_3 & k_2 & h_2 & k_1
\end{pmatrix}^{-1},$$

where the determinant $D = h_1(k_3 - k_2) + h_2(k_3 - k_1) + h_3(k_1 - k_2)$. Since $a^*$ and $b^*$ are known from the zero level, and $c^{-1}$ from the oscillation photograph, (7) yields the remaining r.l. parameters.

**Horizontal measurements**

When vertical measurements cannot be made because the central line cannot be marked on the film, the $\zeta$'s can be calculated from horizontal measurements as shown below.

In Fig. 2, $P_1$ and $P_2$ are r.l. points in the $n$th layer and $O$ is the point of intersection of the oscillation axis with this layer. The angle, $\phi_{12}$, subtended by $P_1$ and $P_2$ at $O$ is measured on the film by the horizontal distance in mm (1 mm = $2^\circ$ in $\phi$) between lines of slope 2 passing through the corresponding reflections. Hulme (1966) has described two methods of using these measurements to determine the shift of the $n$th-level origin relative to $O$ and, thence, two angles of the direct cell: one method is a least-squares iteration necessitating the availability of a computer, and the other is graphical and, therefore, not very accurate. The following method is simple enough for hand calculation.

In Fig. 2, as the points $P_1$, $P_2$ and $P_3$ are r.l. points in the $n$th layer, the distances marked $d_{hkl}^*$ are deducible from the corresponding distances between r.l. points in the zero layer. Thus, $d_{hkl}^* = d_{hkl}^* - h_{kl}^*$ = $d_{hkl}^* - h_{kl}^* = h_{kl}^* - h_{kl}^*$ etc. These three distances define a triangle $P_1 P_2 P_3$ and the angle $\psi$. The values of $\xi_1$, $\xi_2$ and $\xi_3$ can be obtained via the angles $\sigma$ and $\tau$ as follows

$$\begin{pmatrix}
\sigma + \tau = 360 - (\psi + \phi_{12} + \phi_{23})
\end{pmatrix}$$

$$\begin{pmatrix}
d_{12}^* \sin \sigma
\sin \phi_{12}
\sin \phi_{23}
\end{pmatrix}
= OP_2 \cdot \begin{pmatrix}
d_{12}^* \sin \tau
\sin \phi_{12}
\sin \phi_{23}
\end{pmatrix},$$

whence

$$\begin{pmatrix}
\sin \sigma - \sin \tau
\sin \sigma + \sin \tau
\sin \sigma
\end{pmatrix}
= \begin{pmatrix}
d_{23}^* \sin \phi_{12} - d_{12}^* \sin \phi_{23}
0
0
\end{pmatrix}.$$
Table 1. Data for copper(II) sulphate pentahydrate

Cell parameters determined by Brooker & Nuffield (1966)

\[
a = 6.122, \quad b = 10.695, \quad c = 5.962 \text{ Å}, \quad \alpha = 97.58^\circ, \quad \beta = 107.17^\circ, \quad \gamma = 77.55^\circ
\]

\[
a^* = 0.1740, \quad b^* = 0.0960, \quad c^* = 0.1760, \quad \alpha^* = 85.80^\circ, \quad \beta^* = 74.00^\circ, \quad \gamma^* = 100.75^\circ
\]

(a) Cell parameters obtained from \( \phi \) measurements using three reflections

Data from Hulme's (1966) Table 2

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>( \varphi_m )</th>
<th>( hkl )</th>
<th>( \varphi_m )</th>
<th>( hkl )</th>
<th>( c^* )</th>
<th>( \alpha^* )</th>
<th>( \beta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 1</td>
<td>81.0</td>
<td>0 2 1</td>
<td>83.8</td>
<td>1 0 1</td>
<td>0.1760</td>
<td>86.1</td>
<td>73.9</td>
</tr>
<tr>
<td>1 0 1</td>
<td>85.5</td>
<td>0 3 1</td>
<td>79.5</td>
<td>1 0 1</td>
<td>0.1760</td>
<td>86.2</td>
<td>73.9</td>
</tr>
<tr>
<td>2 1 1</td>
<td>103.0</td>
<td>0 3 1</td>
<td>108.0</td>
<td>1 1 1</td>
<td>0.1756</td>
<td>85.7</td>
<td>74.5</td>
</tr>
<tr>
<td>1 1 1</td>
<td>71.0</td>
<td>2 2 1</td>
<td>84.2</td>
<td>1 2 1</td>
<td>0.1758</td>
<td>84.7</td>
<td>74.7</td>
</tr>
<tr>
<td>1 1 1</td>
<td>103.0</td>
<td>0 2 1</td>
<td>83.8</td>
<td>1 0 1</td>
<td>0.1762</td>
<td>86.0</td>
<td>73.7</td>
</tr>
<tr>
<td>0 3 1</td>
<td>79.5</td>
<td>1 0 1</td>
<td>85.0</td>
<td>1 3 1</td>
<td>0.1765</td>
<td>86.2</td>
<td>73.3</td>
</tr>
</tbody>
</table>

(b) Cell parameters calculated from \( \xi \) derived from Brooker & Nuffield's data

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>( \xi^2 )</th>
<th>( \xi^2_{kk} - \xi^2_{k0} )</th>
<th>( c^* )</th>
<th>( \alpha^* )</th>
<th>( \beta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 8 0</td>
<td>0.7128</td>
<td>0.0732</td>
<td>0.1759</td>
<td>85.81</td>
<td>73.99</td>
</tr>
<tr>
<td>3 8 1</td>
<td>0.7860 (0.073)</td>
<td>0.1758 (85.79) (74.06)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 7 0</td>
<td>0.6599</td>
<td>0.0193</td>
<td>0.1758</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 7 1</td>
<td>0.6792 (0.019)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 2 0</td>
<td>1.0520 (0.103)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 2 1</td>
<td>0.9486 (0.103)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Let

\[
\tan \rho = \frac{d^*_{23} \sin \varphi_{23}}{d^*_{12} \sin \varphi_{12}},
\]

then,

\[
\tan \frac{\sigma - \tau}{2} = \tan (45 - \rho) \tan \frac{\sigma + \tau}{2}.
\]

The angles \( \sigma \) and \( \tau \) can be calculated from their sum (8) and difference (9). Now, with three elements known in both triangles \( P_2P_1O \) and \( P_2P_3O \), the \( \xi \)'s can be calculated and \( c^*, \beta^* \) and \( \alpha^* \) derived from (7).

Examples

The parameters \( c^*, \alpha^* \) and \( \beta^* \) of copper(II) sulphate pentahydrate have been calculated for both methods described above. The data for this compound given by Brooker & Nuffield (1966) are quoted below. In Table 1(a), the values of \( \varphi_m \) have been taken from Hulme's (1966) Table 2 and these lead to estimates that are generally within ±0.3% for \( c^* \) and ±0.5° for \( \alpha^* \) and \( \beta^* \). In Table 1(b), the values of \( \xi \) have been calculated from Brooker & Nuffield data. The values of \( (\xi^2_{kk} - \xi^2_{k0}) \) in parentheses have been rounded and give the parameters in parentheses: evidently, this method of estimation is not unduly sensitive to experimental errors.

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References


Diffractometric angles for rotation around the diffraction vector. By PATRICE DE MEESTER, Chemical Crystallography Laboratory, Imperial College, London SW7 2AY, England

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Abstract

It is shown that the azimuthal angle \( \psi \) of rotation around the diffraction vector and the four angles \( \chi_1, \chi, \varphi_1 \) and \( 90 - \omega_1 \) all belong to one right spherical triangle from which the new relations \( \sin \psi = \sin \chi \sin \varphi_1 \) and \( \cos \varphi_1 = \cos \omega \cos \psi \) are derived. These angles are in fact related by ten trigonometric equations which can also be derived by matrix methods. The setting angles for a full \( \psi \) rotation of 360° are easily determined when results of both methods are used together.

Several methods have been proposed to calculate the setting angles \( \omega, \chi \) and \( \varphi \) for a given \( \psi \) rotation around the

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