On the Determination of Unit-Cell Dimensions from Inaccurate Powder Diffraction Data

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An upper limit for the volume of unit cells which can be verified by the de Wolff figure of merit [Wolff, P. M. de, J. Appl. Cryst. (1968). 1, 108–113] is given as a function of the errors in observed d spacings. In the use of the de Wolff figure of merit the requirement of information about the errors of measurement is emphasized. A number of examples are given where the unit cells that are found cannot be accepted as true, because of the lack of accuracy in the published data.

Introduction

With the availability of powerful computer methods it is now often possible to solve the indexing problem and derive symmetry and unit-cell dimensions solely from powder diffraction data. The indexing problem is divided into two consecutive steps. The first one is to find the unit-cell dimensions, and the second one is to prove the correctness of the cell derived. Although the most frequent reason for failure in obtaining a correct reciprocal lattice is the inaccuracy of the input data (Visser, 1969) it is not rare that the second step is the prohibitive one.

From experience gathered in using a trial-and-error indexing program written by the present author it has been found that very plausible unit-cell dimensions sometimes may be found also from inaccurate diffraction data. It may, however, be impossible to prove the correctness of the unit cell found, and thus the efforts to index the pattern will be wasted. The purpose of this paper is to derive an upper limit for the volume of unit cells which can be verified by the observed d values.

De Wolff's figure of merit

De Wolff(1968) presented a figure of merit for estimating the reliability of a unit cell derived exclusively from a given powder pattern. The figure of merit, $M_{20}$, is defined by the equation

$$M_{20} = Q_{20}/2\bar{\varepsilon}N_{20}$$

where $Q_{20} = 1/d^2$ for the 20th observed line, $N_{20}$ is the number of different calculated Q values up to $Q_{20}$ and $\bar{\varepsilon}$ is the average value of discrepancies $\varepsilon = |Q_{\text{obs}} - Q_{\text{calc}}|$. The following two statements were given by de Wolff:

I. $M_{20} < 6$ must give rise to considerable doubt about the result.

II. If the number of unindexed lines below $Q_{20}$ is not more than two, a value $M_{20} > 10$ guarantees that the indexing procedure is substantially correct.

As stated by de Wolff(1968) the number of unindexed lines is a very rough estimate of the contamination. To what extent it discredits the indexing depends also on the intensity of the unindexed lines. In order to avoid mistakes it may be better to strengthen statement II cited above:

III. If all lines below $Q_{20}$ are indexed, a value of $M_{20} > 10$ guarantees that the indexing is substantially correct.

The accuracy required

We may ask what accuracy is needed for the application of criterion III. A minimum value of $\bar{\varepsilon}$ may be estimated from the rounding errors.

$$\bar{\varepsilon} \approx \frac{1}{Q_{20}} \sum_{i=1}^{20} \left[ 1/(d_i^2 - 1/(d_i + \Delta_i)^2) \right]$$

where $\Delta_0 = 0.25 \times 10^{-n}$, and $n$ is the number of decimal places given in the observed $d$ value. As an approximate expression for $N_{20}$ in equation (1) we can use

$$N_{20} \approx \left( \frac{3}{8} \right) \pi \cdot (1/d_{20})^3 \cdot V/m$$

where $m$ is the multiplicity factor and $V$ is the cell volume. From (1) and (3) it follows that

$$M_{20,\text{max}} \approx \frac{3md_{20}}{8\pi\bar{\varepsilon}V}.$$

According to III a value of $M_{20} \approx 10$ is required. Therefore, we have a critical volume $V_{\text{crit}}$ for trial cells beyond which figures of merit give information about rounding errors but not about the correctness of the trial cell.

$$V_{\text{crit}} \approx \frac{3md_{20}}{8\pi\bar{\varepsilon}10}.$$
Examples*

As an example, the powder pattern of (UO)₂P₂O₇ given by Burdese & Borlera (1963) may be used. The pattern contains 20 lines, and it may be indexed by a monoclinic cell: \( a = 10 \cdot 952, b = 12 \cdot 764, c = 6 \cdot 328 \text{ Å} \) and \( \beta = 120 \cdot 06^\circ \). All observed \( d \) values are given in Å to two decimal places, and all except the two first lines (cf. Table 1) have \( |d_{\text{obs}} - d_{\text{calc}}| < 0.005 \text{ Å} \) \( d_{\text{obs}} \) and \( d_{\text{calc}} \) treated as exact numbers). Unfortunately, \( V_{\text{crit}} \) calculated from equation (5) \( (m=4) \) is only \( 226.2 \text{ Å}^3 \). This clearly illustrates the importance of more accurate data when using the de Wolff figure of merit. As can be seen from the table the dominating contributions arise from the smallest \( d \) values.

In an article by Schaekers & Greybe (1973) a powder pattern from \( \text{U}_3\text{OsP}_2\text{O}_7 \) is given and compared with a pattern from a compound \( \text{(UO)}_3(\text{PO}_4)_2 \) published in the paper by Burdese & Borlera (1963) discussed above. Schaekers & Greybe claim that the two powder patterns arise from the same compound, \( \text{U}_3\text{OsP}_2\text{O}_7 \). In order to test if the pattern obtained by Schaekers & Greybe arises from one single phase one may try to find a unit cell by which the pattern can be indexed. A monoclinic cell with \( a = 16 \cdot 399, b = 9 \cdot 508, c = 10 \cdot 505 \text{ Å} \) and \( \beta = 102 \cdot 92^\circ \) was found. All lines are indexed, and the deviations \( |d_{\text{obs}} - d_{\text{calc}}| \) are less than the corresponding differences between the \( d_{\text{obs}} \) from \( \text{U}_3\text{OsP}_2\text{O}_7 \) and \( \text{(UO)}_3(\text{PO}_4)_2 \) respectively. Unfortunately, however, the 19 first \( d_{\text{obs}} \) in the \( \text{U}_3\text{OsP}_2\text{O}_7 \) pattern are given in Å to only two decimals. The critical volume is \( 1105 \text{ Å}^3 \), and since the volume of the trial cell is \( 1596 \text{ Å}^3 \) criterion III cannot be applied. If one line is omitted a figure of merit equals nine can be calculated from an average of the two patterns. This is, however, no evidence for the correctness of the trial cell.

In a paper concerning transition metal hexammines, by Muller, Bosch & Baran (1973), 12 unindexed powder patterns are given. At least five of them may be indexed by orthorhombic or monoclinic cells, but

### Table 1. Calculated X-ray diffraction powder pattern for a monoclinic unit cell

<table>
<thead>
<tr>
<th>( hkl )</th>
<th>( d_{\text{calc}} ) (Å)</th>
<th>( 10^\circ e_3 )</th>
<th>( d_{\text{calc}} ) (Å)</th>
<th>( 10^\circ e_2 )</th>
<th>( d_{\text{calc}} ) (Å)</th>
<th>( d_{\text{obs}} ) (Å)</th>
<th>( 10^\circ e )</th>
<th>( I/I_0 )</th>
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<tr>
<td>010</td>
<td>6.303</td>
<td>2</td>
<td>6.30</td>
<td>20</td>
<td>6.30</td>
<td>0.348</td>
<td>6.30</td>
<td>131</td>
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<td>001</td>
<td>5.047</td>
<td>4</td>
<td>5.05</td>
<td>39</td>
<td>5.04</td>
<td>7.07</td>
<td>5.06</td>
<td>200</td>
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<tr>
<td>012</td>
<td>4.485</td>
<td>6</td>
<td>4.48</td>
<td>56</td>
<td>4.48</td>
<td>4.77</td>
<td>4.48</td>
<td>106</td>
</tr>
<tr>
<td>021</td>
<td>4.156</td>
<td>7</td>
<td>4.16</td>
<td>69</td>
<td>4.15</td>
<td>6.30</td>
<td>4.16</td>
<td>103</td>
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<tr>
<td>110</td>
<td>3.782</td>
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<td>3.78</td>
<td>92</td>
<td>3.78</td>
<td>2.29</td>
<td>3.78</td>
<td>85</td>
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<tr>
<td>101</td>
<td>3.637</td>
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<td>3.64</td>
<td>104</td>
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<td>6.81</td>
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<td>132</td>
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<td>114</td>
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<td>6.56</td>
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<td>157</td>
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<tr>
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<td>132</td>
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<td>212</td>
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<td>174</td>
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<td>11</td>
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<td>2.77</td>
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<td>308</td>
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<tr>
<td>502</td>
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<td>563</td>
<td>2.07</td>
<td>0.29</td>
<td>2.07</td>
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<td>202</td>
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<td>64</td>
<td>1.98</td>
<td>643</td>
<td>1.98</td>
<td>0.07</td>
<td>1.98</td>
<td>18</td>
</tr>
<tr>
<td>532</td>
<td>1.911</td>
<td>72</td>
<td>1.91</td>
<td>716</td>
<td>1.91</td>
<td>0.96</td>
<td>1.91</td>
<td>275</td>
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<tr>
<td>513</td>
<td>1.841</td>
<td>80</td>
<td>1.84</td>
<td>801</td>
<td>1.84</td>
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<td>1.84</td>
<td>443</td>
</tr>
<tr>
<td>071</td>
<td>1.730</td>
<td>96</td>
<td>1.73</td>
<td>964</td>
<td>1.73</td>
<td>0.09</td>
<td>1.73</td>
<td>35</td>
</tr>
<tr>
<td>062</td>
<td>1.680</td>
<td>105</td>
<td>1.68</td>
<td>1052</td>
<td>1.68</td>
<td>0.00</td>
<td>1.68</td>
<td>0</td>
</tr>
</tbody>
</table>
since the $d$ values are all given in Å with only two decimals the critical volumes are too small, and none of the unit cells found can be tested by criterion III. Furthermore, the numbers of observed lines are less than 20 which makes the figure-of-merit calculations somewhat statistically uncertain. The unit-cell dimensions, critical volumes, $e_{\text{max}}$ and figures of merit are shown in Table 2. Only unit cells where all $d_{\text{obs}}$ can be indexed are given. As can be seen from the table, figures of merit above 6 have been calculated for all five compounds. From the critical volumes given in Table 2 figures of merit above 6 have been calculated for all five indexed are given. As can be seen from the table, figures of merit above 6 have been calculated for all five compounds.

It may be concluded that at least the figures of merit of the unit cells found can be tested by criterion III, which can be easily seen from a differentiation of the type discussed above for the (UO)$_2$P$_2$O$_7$ pattern. It may also be mentioned that it is possible to index all lines of the $\text{[Ni(NH}_3)_6]\text{WO}_2\text{S}_2$ pattern using an orthorhombic cell with $a=13.301$ Å, $b=10.262$ Å and $c=9.247$ Å. All $d_{\text{obs}}$ are indexed and used in the figure-of-merit calculations.

The observed and the two alternative calculated patterns are given in Table 3.

### Table 2. ‘Possible’ (not necessarily true) unit-cell dimensions for five transition-metal hexammines derived from X-ray diffraction powder patterns observed by Müller, Bösch & Baran (1973)

$e = |1/d_{\text{obs}} - 1/d_{\text{calc}}|$. In the calculation of $e_{\text{max}}$, $d_{\text{calc}}$ are treated as exact numbers (no rounding off). All $d_{\text{obs}}$ are given in Å with two decimal places. All $d_{\text{obs}}$ are indexed and used in the figure-of-merit calculations.

$$
\begin{align*}
\text{Cr(NH}_3)_6\text{(ReO}_4\text{)}_3 & : a = 16.768\, \text{Å} & V = 1291.3\, \text{Å}^3 \\
b & = 5.186\, \text{Å} & V_{\text{calc}} = 970\, \text{Å}^3 \\
c & = 16.048\, \text{Å} & M_{16} = 9 \\
\beta & = 112.27^\circ & e_{\text{max}} = 0.00032 \text{ for } hkl = 304 \\
\text{Ni(NH}_3)_6\text{MoO}_2\text{S}_2 & : a = 13.149\, \text{Å} & V = 1264.5\, \text{Å}^3 \\
b & = 10.107\, \text{Å} & V_{\text{calc}} = 672\, \text{Å}^3 \\
c & = 9.514\, \text{Å} & M_{18} = 9 \\
\beta & = 112.27^\circ & e_{\text{max}} = 0.00021 \text{ for } hkl = 220 \\
\text{Ni(NH}_3)_6\text{WO}_2\text{S}_2 & : a = 13.309\, \text{Å} & V = 767.9\, \text{Å}^3 \\
b & = 4.776\, \text{Å} & V_{\text{calc}} = 299\, \text{Å}^3 \\
c & = 12.088\, \text{Å} & M_{15} = 7 \\
\beta & = 92.21^\circ & e_{\text{max}} = 0.00027 \text{ for } hkl = 400 \\
\text{Ni(NH}_3)_6\text{WS}_2 & : a = 8.025\, \text{Å} & V = 550.9\, \text{Å}^3 \\
b & = 10.511\, \text{Å} & V_{\text{calc}} = 374\, \text{Å}^3 \\
c & = 6.736\, \text{Å} & M_{18} = 7 \\
\beta & = 104.34^\circ & e_{\text{max}} = 0.00041 \text{ for } hkl = 002 \\
\text{Ni(NH}_3)_6\text{MnO}_4 & : a = 15.136\, \text{Å} & V = 1503.6\, \text{Å}^3 \\
b & = 11.887\, \text{Å} & V_{\text{calc}} = 1034\, \text{Å}^3 \\
c & = 8.357\, \text{Å} & M_{18} = 7 \\
\beta & = 104.34^\circ & e_{\text{max}} = 0.00033 \text{ for } hkl = 501 \\
\end{align*}
$$

It is not the purpose of the present paper, however, to prove that all or any one of these hexammine patterns are correctly indexed by the unit cells given in Table 2. Judging from the de Wolff criterion I they may all be termed ‘possible’, but from the quality of data, as expressed by the critical volumes, it seems impossible to prove anything about the correctness of the unit cells found solely from the de Wolff figures of merit. On the other hand, even a third decimal approximated as 0 or 5 in the observed $d$ values (Å) should double the critical volumes. The unreliable unit cells given above are intended to focus the attention on this commonly occurring fact.

### General remarks

From the values of $e_3$ and $e_2$ given in Table 1, one may get the impression that the errors in $d_{\text{obs}}$ increase with increasing diffraction angles. This is of course not true, which can be easily seen from a differentiation of Bragg's law. The pronounced increase in $e$ with decreasing $d$ values is here only an effect of rounding errors. An explicit statement of the estimated experimental errors in $\theta$ and a sufficient number of decimals for each line is of course recommended. Although two decimals in $d_{\text{obs}}$ (Å) may be relevant for low-angle lines, it may not be sufficient for the high-angle lines. Since the limit for two- and three-decimal $d$ values in Å is dependent on the errors of measurement it is not possible to state a general limit here. A ‘guard digit’, however, i.e. an additional digit retained to reduce the effects of rounding errors is not a bad scientific practice. Furthermore, the superiority of $\theta$ or $1/d^2$ values
over $d$ values is well known but unfortunately they are still not very often published.

It is obvious from the examples given above that it is in general a very unprofitable task to determine unknown cell dimensions from inaccurate powder diffraction data. Unless better data can be collected or other sources of information are available, however, it seems reasonable to save computing time by the introduction of the critical volume as an upper limit in the indexing program.

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References