On the Determination of Accurate Intensities from Powder Diffraction Data. II. Estimation of Intensities of Overlapping Reflections

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Abstract

Even the best least-squares algorithm to extract intensities from a powder diagram will not be able to determine the separate intensities of completely overlapping peaks. In this paper a new method (DOREES) is presented to determine these intensities more accurately by applying relations between structure factors derived from direct methods and the Patterson function. The intensities obtained from the least-squares fit are used as a starting set for DOREES. Comparative tests on both artificially generated and real data show that DOREES improves the intensity set considerably.

1. Introduction

Crystal-structure determination from powder diffraction data by ab initio methods like direct methods such as MULTAN (Main, 1985) and SIMPEL88 (Peschar, 1990) requires accurate knowledge of the intensities for the majority of the reflections. However, peak overlap cannot be avoided in powder diffraction. Furthermore, the 20 range of detectable intensities will be smaller because the Lorentz factor decreases faster at higher diffraction angles θ than in single-crystal diffraction. In particular, the weaker intensities at higher θ are measured less accurately or will not be detected at all. These two problems, overlapping peaks and the small 20 range, complicate the structure-determination process. The latter problem can be tackled by more accurate measurements, for instance by using synchrotron radiation, the former by computation techniques as will be shown in this paper.

To determine a crystal structure from powder data the lattice parameters must first be determined from the observed diffraction angles. For this task very reliable programs were developed by, Visser (1969), Werner (1976), Louër & Louër (1972), Louër & Vargas, (1982) and van Vucht (Philips, 1989), among others.

The next step consists of the deconvolution of the intensities from the measured powder data. Since accurate integrated intensities are needed for the structure determination this separation should lead to as many reliable unique reflections as possible. From reviews (see, for example, Howard & Preston, 1989) it may be concluded that the best technique to achieve this aim is the whole-pattern-fitting procedure. Several programs have been developed to perform this refinement by, amongst others, Pawley (1981), Toraya (1986) and Jansen, Peschar & Schenk (1992). These fitting techniques proved to be successful for the determination of structures with small unit cells and a relatively small number of overlapping intensities.

However, even the best fitting procedure cannot retrieve accurate intensities for reflections whose diffraction angles differ by less than half of their half-width (Jansen et al., 1992). In that case only the total integrated intensity of each cluster of overlapping peaks will be measured accurately. The paper presented here will discuss ways in which the intensities of these reflections can still be predicted. The approach is based on the triplet and quartet relations from direct methods and the theory of the Patterson function. An alternative technique has been proposed by David (1987), who based his estimates on the entropy maximization of an |F|^2 Patterson function. This latter method has not been compared with the described procedure, although its potential implementation is obvious.

2. Five alternative techniques to estimate overlapping reflections

a. Introduction

In single-crystal crystallography, triplet and quartet relations are only successful in phasing reflections from intensity data (see, for example, Sayre, 1952; Cochran, 1955; Schenk, 1973, 1974; Hauptman, 1974; Peschar, 1987a). The basis for using triplets and quartets can be either probabilistic or algebraic. These relations correlate not only the phases of the reflections with the intensities, but also the intensities with each other. The latter feature will be used in the procedure presented here. The Patterson function will be used for the same purpose.

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b. Relations based on triplets

The triplet relations relate the value of the normalized structure factor $|E_H|$ to all pairs of structure factors $|E_K|$ and $|E_{-H-K}|$ with $K$ arbitrary. A heuristic argument for the ability to predict $|E_H|$ from $|E_K|$ and $|E_{-H-K}|$ is similar to Schenk’s argument that the triplet relation can be used in the phasing process (Schenk, 1979). If both $|E_K|$ and $|E_{-H-K}|$ are strong structure factors, the most probable situation is that most of the scatterers – the atoms in the crystal – will be situated near the intersecting lines of the $K$ and $-H-K$ planes. These intersecting lines are also contained in the $H$ planes, which suggests the structure factor $|E_H|$ to be strong as well. A similar argument suggests $|E_{-H-L}|$ to be weak if both $|E_K|$ and $|E_{H-L}|$ are weak.

1. Triplet product estimation. On the basis of the arguments given above it is reasonable to assume that the structure factor $|E_H|$ will be proportional to the product of $|E_K|$ and $|E_{-H-K}|$. Since $K$ is arbitrary, many such estimates are available. Averaging over all triplets defines the triplet product estimation of $|E_H|$.

$$|E_{H_{t,p}}| = (1/N_t) \sum_K |E_K||E_{-H-K}|,$$

(1)

where the subscript $t, p$ stands for triplet product and $N_t$ is the number of triplets used in the estimation procedure.

2. Triplet algebraic estimation. From the definition of the normalized structure factors an algebraic relation can be derived (Giacovazzo, 1980) which leads to the triplet algebraic estimation of $|E_H|$.

$$|E_{H_{t,a}}| = \left( \frac{N}{N_t} \sum_K [(|E_K|^2 - 1)(|E_{-H-K}|^2 - 1)] + 1 \right)^{1/2},$$

(2)

where the subscript $t, a$ stands for triplet algebraic and $N$ is the number of atoms in the crystallographic unit cell.

c. Relations based on quartets

In direct methods the quartet invariants are used to determine phases. If the four main terms $|E_{-H-L}|$, $|E_K|$, $|E_{-H-K}|$, and $|E_{H-L}|$ are strong, the quartet phase sum can be estimated to be zero if the cross terms $|E_{K-L}|$, $|E_{K+L}|$, and $|E_{H-K-L}|$ are strong, and to be $\pi$ if the cross terms are weak reflections (Schenk, 1973, 1974; Hauptman, 1974; Peschar, 1987a). This suggests that quartet relations can be used to distinguish between strong and weak cross terms. For these quartet-based relations, a similar heuristic argument as for the triplet-based relations holds. The quartets considered contain the reflection $H$ – whose intensity is to be predicted – as one of the four main terms. The value of $|E_H|$ is then to be predicted from the known values of the intensities of the four main terms and of the two other cross terms.

3. Quartet number estimation. The reflection $H$ forms triplets with two pairs of the main terms of one quartet. It can therefore be stated that the probability that a weak cross term appears in a quartet for which the main terms are strong is low. It is thus more likely that this cross term will be strong. This argument leads to the quartet number estimation for $|E_H|$.

$$|E_{H_{q,#}}| = \text{number of quartets with } E_H \text{ as cross term and for which}$$

$$\left( |E_{-H-K}| |E_K| |E_L| |E_{H-L}| \right) / N \geq \delta,$$

(3)

where the subscript $q, # \text{ stands for quartet number and } \delta \text{ is a positive real number which has to be optimized experimentally. Detailed research (Jansen, 1991) has shown that the quartet number estimation becomes more reliable with increasing } \delta \text{ but is useless if there are not enough quartets for which the inequality of expression (3) holds. It turned out that for most structures } \delta \text{ should be approximately 0.4.}$$

4. Quartet algebraic estimation. An algebraic relation to estimate the intensity of a cross term of a quartet was derived by van der Putten, Schenk & Tsoucaris (1982). They intended to predict reflections outside the Ewald sphere, assuming all reflections inside the sphere to be known. In the powder diffraction case under investigation, unknown reflections inside a reflection sphere are to be estimated from the known intensities inside the same sphere. The procedure of van der Putten, Schenk & Tsoucaris, which employs a scale factor based on the knowledge of all magnitudes inside a sphere, is not directly applicable and has to be replaced by an average over all quartets which are used in the estimation process. This leads to the definition of the quartet algebraic estimation for $|E_H|$.

$$|E_{H_{q,a}}| = \left( 1/N_q \right) \sum_{\text{quartets}} |E_{H-K}| |E_K||E_L||E_{-H-L}| \cos \Phi_4,$$

(4)

where the subscript $q, a \text{ stands for quartet algebraic, } N_q \text{ is the number of quartets used and } \Phi_4 \text{ is the quartet phase sum,}$$

$$\Phi_4 = \varphi_{H-K} + \varphi_K + \varphi_L + \varphi_{-H-L}.$$

(5)

The value of $\cos \Phi_4 \text{ can be estimated from the six known intensities in the quartet as (Peschar, 1987b)}$

$$\cos \Phi_4 = Bq(E^2_4).$$

(6)
Bq is a quotient of two modified Bessel functions or a hyperbolic tangent:

$$Bq(E^*_*) = \begin{cases} \left[ \frac{I_1(2E^*_*)}{I_0(2E^*_*)} \right] & \Phi_4 \text{ general phased;} \\ \tanh (E^*_*) & \Phi_4 \text{ phase restricted.} \end{cases}$$ (7)

$E^*_*$ can be expressed in terms of the weight $w_i$, which depends on the space group, and the observed intensities,

$$E^*_* = -2w_1|E_{H-K}E_{L}E_{-H-L}|/N$$
$$+ (w_2|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$\times Bq(2w_2|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$+ (w_3|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$\times Bq(2w_2|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$+ (w_4|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$\times Bq(2w_2|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$+ (w_5|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2})$$
$$\times Bq(2w_2|E_{H-K}E_{L}E_{H-K+L}|/N^{1/2}).$$ (8)

d. Relation based on the Patterson function

The final estimation method is based on the Patterson function. The Patterson method has proved to be successful in solving structures with a small number of heavy atoms (Patterson, 1934). The Patterson function is the Fourier transform of the squared absolute (normalized) structure factors. The peaks of the Patterson function represent the interatomic vectors.

5. The Patterson estimation. The $E^2$ Patterson function is calculated using only those reflections which can be determined accurately. It is assumed that this set contains sufficient structural information for the peaks to be at almost the correct positions $u_j$. A second assumption models these peaks with delta functions of height $H_j$. The Fourier transform of this new Patterson function yields the Patterson estimation for $|E_H|$:

$$|E_H|_p = \left[ \sum_j H_j \exp (2\pi i \mathbf{H} \cdot \mathbf{u}_j) \right]^{1/2}. \quad (9)$$

e. The reliability of the relations

In our experience (Jansen, 1991), each of the five estimation techniques can be used only qualitatively. Apparently, the correlation between the magnitudes is not sufficient to ensure reliable quantitative estimates. This result is not unexpected since a minimum of independent data is required to describe a minimum of independent atomic variables. A high correlation between (all) intensities would exclude such a description.

In spite of the lack of quality of the individual quantitative estimates, they are still useful in a qualitative way. If the predicted value of $|E|$ of one of the methods is large, it is very likely that the structure factor will be a strong one and, when the predicted value is low, the structure factor is probably weak. In the next section a procedure will be described that incorporates these indications into a quantitative estimation of the intensities of the overlapping reflections.

3. An algorithm to estimate intensities of overlapping reflections (DOREES)

a. Introduction

Fig. 1. shows the newly developed algorithm to extract from a powder diffractogram the correct intensities of overlapping reflections, DOREES (double reflection estimation), in relation to the other steps to be performed. These other routines will be discussed briefly, since a complete description can be found elsewhere.

LSQPROF is the direct-intensity-fitting procedure, which was discussed in the previous paper (Jansen et al., 1992). All reflections are divided into clusters. A cluster contains (a set of) reflections which are distant, on the $2\theta$ scale, by less than a certain value, $d_{min}2\theta$, from at least one of the other peaks of the cluster and are a distance larger than $d_{min}$ to peaks from all the other clusters. $d_{min}$ is usually expressed as a fraction of the half-width of a peak.

It has been shown that LSQPROF can determine the intensity of a reflection when its distance to the next neighbouring peak is more than about 0.5 times the half-width of the peak. This distance is taken as $d_{min}$. In this way the intensity of a reflection belonging to a cluster of only one element, a single peak, is known accurately.

$\text{I \_TO \_ F}$ is a newly developed procedure to transform intensities to $F$ values. It corrects for

![Flow diagram showing the process of accurate intensity determination from powder data.](image)
Lorentz–polarization and multiplicity factors of the reflections. The cluster structure is left unchanged. If there are no overlapping peaks the resulting \( F \) values are almost the same as those for single-crystal data.

**NORMAL** is the normalization procedure of Main (1985) modified to incorporate the cluster structure.

**FOUR** is the fast Fourier program from the MoLEN package of Enraf–Nonius (Enraf–Nonius, 1990) modified to calculate an \( E^2 \) Patterson from the single reflections.

**TRIQUA**.88 is a modified version of the triplet- and quartet-generation part taken from SIMPEL88 (Peschar, 1990). It calculates all quartets with the four main terms and two of the cross terms selected from the single peaks and one cross term from the overlapping peaks. Triplets are calculated with the first term being an overlapping reflection and the second and third term being single reflections.

**b. Double reflection estimation, DOREES**

**DOREES** is a newly developed computer procedure to rearrange intensities within the clusters of overlapping peaks in such a way that the resulting arrangement is more likely to be the correct distribution of intensities than the initial set of intensities. The latter may have been determined by the least-squares refinement LSQPROF or calculated in a previous cycle of **DOREES**. The program applies the five estimation procedures described in the previous paragraph.

As indicated already, each individual estimation method suggests a reflection to be strong or weak or of unknown magnitude. From our experiments it appears that more reliable estimates of the intensities are obtained by combining the individual qualitative indications. For this purpose the estimates from each method are ranked according to a decreasing estimation value. In this way every reflection is given an estimation value. In this way every reflection is given

\[
M_H = \left( \frac{N_{H,t,p} w_{t,p} + N_{H,i,a} w_{i,a} + N_{H,q,a} w_{q,a} + N_{H,q,#} w_{q,#} + N_{H,#} w_{#}}{w_{t,p} + w_{t,a} + w_{q,a} + w_{q,#} + w_{#}} \right)
\]

(10)

In a default run of **DOREES** all five estimation criteria are employed with an equal unit weight. The \( |E_H| \) is expected to be large for small \( M_H \) and small for large \( M_H \). Occasionally, zero weights are used to exclude one or more criteria which are known beforehand to be unreliable. For example, the Patterson estimation is not reliable when the total number of overlapping reflections is larger than the number of known single reflections (Jansen, 1991). Subsequently, the reflections are divided into three groups, strong, weak and intermediate. Two threshold values, \( M_{\text{strong}} \) and \( M_{\text{weak}} \), are selected which define the number of strong and weak reflections respectively. If the ratio of single and overlapping reflections is much smaller than one, these numbers are initially kept low to avoid errors. \( M_H \) is used to determine to which group the reflection \( H \) belongs. The \( M_{\text{strong}} \) reflections with the lowest values of \( M_H \) are put into the strong group and the \( M_{\text{weak}} \) reflections with the highest \( M_H \) into the weak group. The rest of the reflections form the intermediate group.

In a next step the division into the three groups is used to arrive at better normalized structure factors \( |E_H| \) within the clusters of overlapping reflections. To achieve this, it is recalled that the scale factor of the normalization procedure relating the intensities to \( |E| \) values depends only on the Bragg angle \( \theta \). Since reflections in a cluster have almost the same reflection angle, a large normalized structure factor implies a relatively large intensity in a cluster and a small normalized structure factor implies a relatively small intensity. This can be used to rearrange the intensities within one cluster. It is assumed that a part of the intensity of the reflections in the weak group should be transferred to the strong group and to a lesser extent to the intermediate group. On the other hand, the strong group is expected to gain intensity both from the weak and to a lesser extent from the intermediate group. Finally, only small changes are expected for the intermediate group, since it both loses and gains some intensity.

These considerations lead us to the following rearrangement scheme for a cluster consisting of \( N \) reflections of which \( N_S \) are strong and \( N_w \) weak.

For strong reflections,

\[
I'_i(\theta) = (1/2N_S) \sum_{\theta_i} \left\{ I_i(\theta) \left[ \frac{(d_{\text{min}} - d_i)/d_{\text{min}}} {H(d_{\text{min}} - d_i) + \frac{1}{N - N_w}} \right] \right\} \sum_{\theta_i} \left\{ I_w(\theta) \right\} \times \frac{d_{\text{min}} - d_i}{d_{\text{min}}} H(d_{\text{min}} - d_i) + I_S(\theta).
\]

(11)

For weak reflections,

\[
I'_w(\theta) = - \left[ \frac{1}{2(N - N_w)} \right] I_w(\theta) \times \sum_{\theta_i} \left\{ \left[ \frac{(d_{\text{min}} - d_i)/d_{\text{min}}} {H(d_{\text{min}} - d_i)} \right] \right\} \times \frac{1}{N - N_w} I_w(\theta)
\]

(12)
For intermediate reflections,

\[ I'_\text{int}(\theta) = \left[ \frac{1}{2} (N - N_\text{w}) \right] \sum_{\theta_\text{weak}} \{ I_{\theta_\text{weak}}(\theta) \} \]

\[ \times \left[ \left( \frac{d_{\text{min}} - d_j}{d_{\text{min}}} \right) \frac{H(d_{\text{min}} - d_j)}{H(d_{\text{min}} - d_j)} \right] \]

\[ - \left( \frac{1}{2N_\text{w}} \right) I_\text{w}(\theta) \sum_{\theta_\text{strong}} \left\{ \left[ \left( \frac{d_{\text{min}} - d_j}{d_{\text{min}}} \right) \right] \right\} \]

\[ \times H(d_{\text{min}} - d_j) + I_\text{w}(\theta). \]  \hspace{1cm} (13)

In (11), (12) and (13), \( d_j \) is the distance

\[ d_j = |2\theta - 2\theta_j|, \]  \hspace{1cm} (14)

which can be expressed conveniently in units of the half-width of a peak. \( H(x) \) is the Heaviside function. The intensities on the right-hand side of (11), (12) and (13) are those determined by the least-squares pattern fit (for instance \( \text{LSQPROF} \)) or by a previous cycle of \( \text{DOREES} \).

Each summation in (11) appears with a minus sign in (12) or (13). Furthermore, the term with a plus sign in (13) appears with a minus sign in (12). Overall, this rearrangement keeps the total intensity within a cluster constant. Moreover, the dependence of the least-squares fit on the separation of the peaks has been incorporated in the rearrangement of intensities. When the peak separation increases, less intensity is shifted from one peak to the other while, if the peak separation is larger than \( d_{\text{min}} \), no intensity is shifted at all.

In its current implementation the redistribution of the intensities of the weak reflections follows the ratio 2:1:1 for strong, intermediate and weak reflections respectively. This ratio, which proved to be successful, is empirically based and somewhat arbitrary. It will be subject to optimization in future versions of \( \text{DOREES} \).

After a run of \( \text{DOREES} \) the \( M_{\text{strong}} \) and the \( M_{\text{weak}} \) intensities are assumed to be sufficiently determined and they are handled henceforth as single reflections. This applies also to the intermediate reflections which remain as a single element of a cluster after removal of the strong and weak reflections.

All the steps of Fig. 1 except \( \text{LSQPROF} \) are iterated either until enough single reflections have been obtained to start the structure determination or until no further significant changes occur in the intensity distribution.

4. Experimental results

a. Powder diagram simulated from single-crystal data

The procedure described in the previous paragraph has been tested for the structure CPCN (cyclopropanecarbonitrile, \( \text{C}_4\text{H}_5\text{N} \)) (Kiers, de Boer, Heijdenrijk, Stam & Schenk, 1985). Single-crystal data of this structure were available. From these data a powder diffractogram was generated using Gaussian peaks with peak-form parameters \( u = 0.2, v = -0.2 \) and \( w = 0.1 \). The intensities were extracted from the powder diagram by the program \( \text{LSQPROF} \). The intensities of both the original single-crystal data and those of the powder diagram were normalized. In Fig. 2 the absolute differences between the \(|E|\)'s estimated with the direct-intensity-fitting technique, \( \text{LSQPROF} \), and the \(|E|\)'s calculated from the single-crystal data are plotted for all 361 structure factors as a function of the normalized structure factors obtained with the direct-intensity-fitting technique (Jansen et al. 1992).

This figure shows that many reflections that are estimated by the least-squares procedure as weak reflections, having an \(|E|\) value less than 0.7, are actually much stronger. The opposite holds for reflections estimated to be strong – those reflections with an \(|E|\) value larger than 1.5. Since these two groups of reflections are the most important in direct methods, it is not very likely that direct methods will lead to the correct solution. Indeed, with the intensities from \( \text{LSQPROF} \) the direct-methods program \( \text{SIMPEL88} \) (Peschar, 1990) failed to solve the structure, whether using all reflections or only the single reflections.

In a second trial to solve the structure, the rearrangement of the intensities was performed by executing four iterations with the program \( \text{DOREES} \) with different threshold values \( M_{\text{strong}} \) and \( M_{\text{weak}} \) for the numbers of strong and weak reflections. The threshold values together with the main results of \( \text{DOREES} \) are summarized in Table 1. It can be seen that the number of deconvoluted single reflections increases rapidly and after four cycles all intensities are deconvoluted. After this deconvolution the 361

![Fig. 2. Differences of absolute normalized structure factors obtained by \( \text{LSQPROF} \) and from single-crystal data as a function of the structure factors obtained by \( \text{LSQPROF} \) for the structure CPCN.](image-url)
Table 1. Review of the reflections used in DOREES for the generated data of CPCN

<table>
<thead>
<tr>
<th>Step</th>
<th>( M_{\text{strong}} )</th>
<th>( M_{\text{weak}} )</th>
<th>Number of single reflections</th>
<th>Number of overlapping reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>114</td>
<td>247</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>10</td>
<td>179</td>
<td>182</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>40</td>
<td>247</td>
<td>114</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>40</td>
<td>333</td>
<td>28</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>15</td>
<td>361</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2. \( \chi \) values for various ranges of \( E_{\text{estimated}} \) of the structure CPCN obtained with data after LSQPROF and DOREES respectively

\[
\begin{array}{ccc}
| E_{\text{estimated}} | \chi_{\text{LSQPROF}} | \chi_{\text{DOREES}} |
\hline
0.0--0.7 & 0.265 & 0.253 \\
0.7--1.5 & 0.272 & 0.277 \\
1.0--\infty & 0.318 & 0.303 \\
\end{array}
\]

Table 3. Review of the reflections used in DOREES for \( \text{Ba}_2\text{YCu}_3\text{O}_{8-x} \)

<table>
<thead>
<tr>
<th>Step</th>
<th>( M_{\text{strong}} )</th>
<th>( M_{\text{weak}} )</th>
<th>Number of single reflections</th>
<th>Number of overlapping reflections</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
<td>71</td>
<td>174</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
<td>10</td>
<td>82</td>
<td>145</td>
</tr>
<tr>
<td>2</td>
<td>5</td>
<td>10</td>
<td>100</td>
<td>128</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>10</td>
<td>117</td>
<td>128</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>10</td>
<td>137</td>
<td>108</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
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<td>178</td>
<td>67</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
<td>20</td>
<td>216</td>
<td>29</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>18</td>
<td>245</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 4. E-map peak heights obtained from solutions of SIMPEL88 for \( \text{Ba}_2\text{YCu}_3\text{O}_{8-x} \) applying the intensities of LSQPROF and of DOREES respectively

<table>
<thead>
<tr>
<th>Peak</th>
<th>Height ( \text{LSQPROF} )</th>
<th>Height ( \text{DOREES} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>4909</td>
<td>4129</td>
</tr>
<tr>
<td>Y</td>
<td>1635</td>
<td>4085</td>
</tr>
<tr>
<td>Cu1</td>
<td>3186</td>
<td>3088</td>
</tr>
<tr>
<td>Cu2</td>
<td>1626</td>
<td>2348</td>
</tr>
<tr>
<td>5</td>
<td>1015</td>
<td>819</td>
</tr>
<tr>
<td>6</td>
<td>921</td>
<td>811</td>
</tr>
<tr>
<td>7</td>
<td>737</td>
<td>745</td>
</tr>
</tbody>
</table>

single intensities resulting from DOREES were normalized. The absolute differences of these estimated \( |E| \) values and those of the original single-crystal data are plotted in Fig. 3. The means of the absolute differences of the estimated and the single-crystal normalized structure factors (\( \chi \)) are presented in Table 2 for various ranges of the estimated structure factors. Clearly, the differences are much smaller than after using LSQPROF only. The number of wrongly estimated structure-factor magnitudes – those differing by more than 1 (the average value of the \( E^2 \) values) – is reduced by a factor of 3. In particular, the regions which are important for direct-methods procedures – the very strong and very weak structure factors – are improved considerably. As a result, it was a simple task to determine the atomic positions by the direct-methods program SIMPEL88 (Peschar, 1990) with the intensities obtained from DOREES.

b. A real X-ray powder diagram

A second test of the procedure concerned the powder pattern of the superconductor \( \text{Ba}_2\text{YCu}_3\text{O}_{8-x} \). The atomic positions of this structure were determined from single-crystal data by Le Page and co-workers (Le Page, McKinnon et al., 1987; Le Page, Siegrist et al., 1987). In the preceding paper (Jansen et al., 1992), it was shown that this structure can be solved from powder data if the direct-intensity-fitting technique is used to extract the intensities from the diagram. The program DOREES was applied to these intensities according to the scheme displayed in Table 3. In a subsequent run of SIMPEL88 the structure was solved from these data. The results are even more convincing than with application of LSQPROF only. As shown in Table 4, the peak heights of the DOREES-generated E map correspond better to the atomic weights and the gap between the atomic peaks and the noise peaks becomes much larger.

5. Concluding remarks and suggestions

The procedure presented here to rearrange intensities improves the set of intensities by a whole-pattern-
fitting technique for all structures considered. Previously only structures with five to ten atoms in the asymmetric unit could be solved from standard laboratory diffraction data by direct methods. Applying the method presented here, we expect that structures with up to 20 atoms in the asymmetric unit can be solved from standard laboratory powder diffraction data.

The rearrangement formulae (11), (12), (13) have been composed rather empirically. Although they seem to work satisfactorily, an advanced study is planned to improve them. Further improvements may be obtained from employing other, possibly more reliable, relations to estimate the absolute values of the structure factors.

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References