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Chapter 6

Application of the Broad-Energy X-ray Band Method

6.1 Introduction

In this chapter the broad-energy X-ray band method, utilising a bent-Laue monochromator\textsuperscript{11} (Chapter 5, Part A), is further developed. A test experiment to determine the structural changes in a LiNbO\textsubscript{3} crystal upon application of an external electric field was performed.

A discussion of the theory of refinement is presented together with the development of a refinement program based on relative changes in integrated intensities (§6.2). Followed by a discussion of the experimental conditions (§6.3), data reduction and results for LiNbO\textsubscript{3} (§6.4 and §6.5, respectively).

6.2 Refinement

Standard structure-refinement programs, like \textit{SHELXL93}\textsuperscript{12} and \textit{XTAL}\textsuperscript{13}, use integrated intensities \(I\) to refine a model structure. However, these programs are not suited for a refinement of structural parameters when relative changes in integrated intensities are experimentally observed, as is the case for the broad-energy X-ray band method, even though the strategy of refinement is not much different.

6.2.1 Theory of refinement

The refinement procedure\textsuperscript{14} is the iterative process of applying small changes to the atomic parameters of the used structure model in such a way that the calculated intensities approach the observed ones. In order to keep conformity with crystallographic practice, the refinement will be
discussed in terms of changes in structure factor instead of intensities (where both relate via Eq. 2-13).

The agreement between the observed ($\Delta F_{\text{obs}}$) and calculated difference structure factors ($\Delta F_{\text{calc}}$) is expressed in the $R$-factor and is defined as

$$
R = \frac{\sum |\Delta F_{\text{obs}}| - k|\Delta F_{\text{cal}}|}{\sum |\Delta F_{\text{cal}}|} \times 100\%.
$$

(6-1)

where $hkl$ is the whole set of measured reflections and $k$ is a scaling factor. The $R$-value will be low when the calculated difference structure factors approach the observations as closely as possible. Hence, the refinement should result in a low $R$-value.

A common refinement strategy is to minimise a function like $Q$,

$$
Q = \sum_{hkl} w(hkl) \left( |\Delta F_{\text{obs}}(hkl)| - |\Delta F_{\text{calc}}(hkl)| \right)^2
$$

(6-2)

as a function of the structural model by means of the method of least squares. The weight factor $w(hkl)$ of the observations ($\Delta F_{\text{obs}}$) is defined in terms of the standard deviation $\sigma(hkl)$ of $\Delta F_{\text{obs}}$,

$$
w(hkl) = \frac{1}{\sigma^2(hkl)}.
$$

Here, the scale factor $k$ is omitted for reasons that will become clear later.

The minimum of $Q$ can be obtained by varying the shift in atomic parameters $\Delta u_i$ that define the $|\Delta F_{\text{calc}}(hkl)|$, by setting the differentials of $Q$ with respect to all $\Delta u_j$ (with $j=1,\ldots,n$) to zero:

$$
\frac{\partial Q}{\partial (\Delta u_j)} = 0
$$

(6-3)

In this equation each $|\Delta F_{\text{calc}}(hkl)|$ depends on the shift in atomic parameters $\Delta u_i$, and $|\Delta F_{\text{obs}}(hkl)|$ is a constant. A solution can be found by expanding to a Taylor series, expressing $|\Delta F_{\text{calc}}(hkl)|$ into

$$
|\Delta F_{\text{calc}}(hkl;\Delta u)| = |\Delta F_{\text{calc}}(hkl;\Delta u)| + \sum_i \varepsilon_i \left[ \frac{\partial |\Delta F_{\text{calc}}(hkl)|}{\partial (\Delta u_i)} \right] + \frac{1}{2} \sum_i \sum_j \varepsilon_i \varepsilon_j \frac{\partial^2 |\Delta F_{\text{calc}}(hkl)|}{\partial (\Delta u_i) \partial (\Delta u_j)} + \ldots.
$$

(6-4)

where $|\Delta F_{\text{calc}}(hkl;\Delta u)|$ indicates that the $|\Delta F_{\text{calc}}|$ depends on the parameter $\Delta u$. The starting values of $\Delta u$ are $\Delta u$, and are changed by a small amount of $\varepsilon_i$ giving for the parameter $\Delta u_i = \varepsilon_i \Delta u_i$. The differential of $|\Delta F_{\text{calc}}(hkl;\Delta u)|$ with respect to $\Delta u_i$, calculated at the starting value $\Delta u_i$, is given by
If the $\epsilon$-values are small, the second and higher order terms can be neglected.

Substitution of Equation 6-4 into 6-3 gives the so-called normal equations:

$$
\sum_{hkl} w(hkl) \left\{ |\Delta F_{\text{calc}}(hkl)| - |\Delta F_{\text{calc}}(hkl; \Delta u)| \right\} \left[ \frac{\partial |\Delta F_{\text{calc}}(hkl; \Delta u)|}{\partial (\Delta u_j)} \right]_{\Delta u} = 0,
$$

(6-5)

giving $n$ equations ($j = 1, \ldots, n$).

Abbreviating Equation 6-5,

$$
a_j = \sum_{hkl} w(hkl) \left[ \frac{\partial |\Delta F_{\text{calc}}(hkl; \Delta u)|}{\partial (\Delta u_j)} \right]_{\Delta u},
$$

(6-6)

and

$$
b_j = \sum_{hkl} w(hkl) \left\{ |\Delta F_{\text{obs}}(hkl)| - |\Delta F_{\text{calc}}(hkl; \Delta u)| \right\} \left[ \frac{\partial |\Delta F_{\text{calc}}(hkl; \Delta u)|}{\partial (\Delta u_j)} \right]_{\Delta u},
$$

(6-7)

the normal equations can be expressed,

$$
\sum_j \varepsilon_j a_j = b_j
$$

(6-8)

or by a matrix, $[A][\varepsilon] = [B]$,

$$
\begin{bmatrix}
a_{11} & a_{21} & a_{31} & \cdots & a_{n1} \\
a_{12} & a_{22} & a_{32} & \cdots & a_{n2} \\
a_{13} & a_{23} & a_{33} & \cdots & a_{n3} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
a_{1j} & \cdots & \cdots & \cdots & a_{nj}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3 \\
\vdots \\
\varepsilon_j
\end{bmatrix}
= \begin{bmatrix}
b_1 \\
b_2 \\
b_3 \\
\vdots \\
b_j
\end{bmatrix}
$$

(6-9)

where $[A]$ is the normal matrix, which is a square and symmetric matrix, since $i$ and $j$ both run from 1 to $n$ parameters. By applying the basic rules of matrix multiplication for a square matrix one can obtain

$$
[\varepsilon] = [A]^{-1}[b].
$$

(6-10)
These equations can be solved and the resulting $\varepsilon$-values must be back-substituted into the variables $\Delta u$. Because of the truncation of higher order terms in the Taylor series the final values of $\Delta u$ are approached by iteration. In other words, in the next cycle of refinement the process is repeated until convergence is reached. For each cycle, new values of $|\Delta F_{\text{calc}}(hkl; \Delta u)|$ and its derivatives with respect to $\Delta u_i$ are calculated.

After the final convergence, the new obtained parameter value $\Delta u$ can be used to estimate the standard deviation of the parameter $\Delta u_i$ with the $a_{ij}$ of the inverse matrix $[A]^{-1}$ as follows

$$
\sigma^2(\Delta u_j) = a_{jj} \left( \frac{\sum_{h=1}^{p} w_h \{\Delta(\Delta F_h)\}^2}{p-n} \right) .
$$

(6-11)

where $p$ is the number of independent reflections, $n$ is the number of parameters, and $\Delta(\Delta F_h)=|\Delta F_{\text{obs}}(hkl)| - |\Delta F_{\text{calc}}(hkl)|$.

An illustration of the least-squares refinement procedure is shown in Figure 6-1. A derivative calculation is performed for the initial parameter $\Delta u_0$. The intersection between the derivative and $\Delta F_{\text{obs}}$ gives the new setting of $\Delta u_i$, that is $\Delta u_i'$, and $\Delta F_{\text{calc}}'$ can be calculated. At this point, the procedure repeats until $\Delta F_{\text{calc}}'$ approaches (or agrees to) the $\Delta F_{\text{obs}}$. The change in parameter $\Delta u$ is then the difference between the start $\Delta u_0$ and final values of $\Delta u_i'$. Of course there are more observations than variables so that the individual observations cannot be fitted exactly.

It should be noted that the refinement procedure, in fact, approximates a non-linear function by using a linear least-squares operation.

Figure 6-1: Visualisation of the linear least-squares refinement procedure of a non-linear function.
In principle, the refinement procedure of the data obtained by the broad-energy X-ray band method, can be achieved in two different ways. The first consists of a direct refinement of the changes in integrated intensities \( \Delta I \), whereas the second refines both the total integrated intensities \( I_0 + \Delta I \) and \( I_0 \). However, the first refinement procedure is used since the obtained structural changes are more accurate than the ones obtained by taking the difference of the refined absolute structures of the second procedure, see also §3.2.1. This is why standard structure-refinement programs like SHELXL93 and XTAL could not be used and a special program had to be developed.

In a classic X-ray diffraction experiment \( I \) is observed which scales to \( |F_{\text{calc}}| \) by a factor \( k \) (Eq. 2-13), which is refined together with the structural parameters. In the perturbation experiments the observed quantity is \( \Delta I/I_0 \) and the scaling is automatic and not needed:

\[
\left( \begin{array}{c} \Delta I \\ I_0 \end{array} \right)_{\text{obs}} = \frac{k \left\{ |F_{\text{calc}}(+)|^2 - |F_{\text{calc}}(-)|^2 \right\}}{|F_{\text{calc}}(0)|^2} \tag{6-12}
\]

Since \( |F_{\text{calc}}(0)|^2 \) is a known quantity the observables can be defined more conveniently as

\[
\Delta_{\text{obs}} = \left( \begin{array}{c} \Delta I \\ I_0 \end{array} \right)_{\text{obs}} |F_{\text{calc}}(0)|^2 , \tag{6-13}
\]

so Equation 6-12 becomes

\[
\Delta_{\text{obs}} = \left\{ |F_{\text{calc}}(+)|^2 - |F_{\text{calc}}(-)|^2 \right\} . \tag{6-14}
\]

On the basis of Equation 6-14 the least-squares object function \( Q \) can be defined as

\[
Q = \sum_{\text{obs}} w_{\text{obs}} \left\{ |\Delta_{\text{obs}} - |F_{\text{calc}}(+)|^2 - |F_{\text{calc}}(-)|^2 | \right\} . \tag{6-15}
\]

Assuming that

\[
|F_{\text{calc}}(+)|^2 = |F_{\text{calc}}(0)|^2 + \frac{1}{2} \Delta |F_{\text{calc}}|^2 \tag{6-16a}
\]

and

\[
|F_{\text{calc}}(-)|^2 = |F_{\text{calc}}(0)|^2 - \frac{1}{2} \Delta |F_{\text{calc}}|^2 \tag{6-16b}
\]

Equation 6-15 reduces to

\[
Q = \sum_{\text{obs}} w_{\text{obs}} \left\{ |\Delta_{\text{obs}} - |\Delta F_{\text{calc}}| | \right\} . \tag{6-17}
\]
This implies that in the normal equations (Eq. 6-5 – 6-11) as calculated in practice, the $\Delta F_{\text{obs}}$ is replaced by $\Delta F_{\text{obs}}$ and the $\Delta F_{\text{calc}}$ by $\Delta F_{\text{calc}}$.

The refinement program (REFINE) was developed in the IDL\cite{IDL} environment using SHELXL93 for the calculation of the structure factors, whereas the calculation of derivatives is performed numerically by REFINE.

Solving the normal equation is performed by the built-in IDL procedure called Single Value Decomposition (SVDC), which is based on the routine SVDCMP as described in Numerical Recipes\cite{NumericalRecipes}.

The refinement software was tested extensively by using a simulated data set of LiNbO$_3$ and proved to be working correctly for a shift in atomic positions up to $\sim 1 \times 10^{-2}$ Å, which is acceptable since the expected shifts are in the order of $\sim 1 \times 10^{-4} - 1 \times 10^{-5}$ Å.

### 6.3 Experimental

The experimental work was performed at the Materials Science beam-line (§3.4.2) using a bent-Laue optics set-up generating a broad-energy X-ray band-pass (Chapter 5, Part A). The monochromator set-up consisted of a rectangular Si(311) crystal with an asymmetry angle of $25.24^\circ$ (§5.4). Furthermore, a tilt-stage was built into the set-up to allow for corrections in $\psi$. To obtain a low background, the monochromator set-up was shielded by a castle made of 5 cm thick lead. The Ge-detector (Chapter 4) and a pin-diode were positioned together with a pair of slits on a 4-circle diffractometer (Huber 511.1). The application of the electric field and gating was identical to that described in §5.6.

The sample was a 1 mm thick plate like shaped (7x5 mm$^2$) LiNbO$_3$ crystal with Al electrodes evaporated on both the large surfaces (§3.3). The experiment was performed with a broad-energy X-ray band beam of 44 keV (mean energy) and $\Delta E/E$ of 1.8%. The applied electric field was $1.5 \times 10^6$ Vm$^{-1}$ with a frequency of 33 Hz. Rocking curve scans were performed in order to be able to correct for the phase contrast (§5.7.1) in the broad-energy X-ray band beam. The scan range was $0.00156 + 0.00895 \times \tan \theta$ about the peak position $\theta$, and the rocking curve contained 100 data points each measured 0.1 s.

### 6.4 Data Analysis and Reduction

The data has to be analysed in order to determine $I_0$ and $M$, as follows.

#### 6.4.1 Determination of $I_0$

The rocking curve scans, which were needed to account for the phase contrast in the X-ray beam, of $I_0$ (see for example Fig. 6-2c) were corrected for the background by the IDL based program ANALYSER. This correction consisted of linear fit through the points $B$ with
\[ B < B_{\text{min}} + 0.05(P_{\text{max}} - B_{\text{min}}), \]  

where \( B_{\text{min}} \) is the lowest point in the left and right tail of the rocking curve, respectively and \( P_{\text{max}} \) is the maximum of the rocking curve. The flat region of rocking curve was selected by

\[ P > 0.95P_{\text{max}}, \]

where \( P \) is a point on the plateau and \( P_{\text{max}} \) is the maximum of the rocking curve after background correction.

### 6.4.2 Determination of \( \Delta I \)

The same points \( P \) on the \( I_0 \) plateau were selected on all the curves measured by the DLIA (\( x\)-val, \( y\)-val and \( r\)-val, §4.3.2). The average of the points \( P \) on the \( r\)-val curve determined \( \Delta I \), whereas the sign of \( \Delta I \) was determined by the average of points \( P \) on the \( x\)-val curve. It should be noted that no background correction was necessary for the determination of \( \Delta I \).

The IDL-functions, *Poly_fit*, *Total* and *Moment*, where used to fit a line for the background correction procedure, for calculating the average of \( \Delta I \) and \( I_0 \), and the standard deviation, respectively.

The reflections were selected manually using the following criteria:

1. The peak intensity of \( I_0 \) must be high (>1\times10^3 \text{ ph s}^{-1}).
2. The \( x\)-val must show the theoretical expected profile of Figure 6-2c,
3. The \( y\)-val must be significantly smaller than \( x\)-val and
4. The flat part of all curves should consist of at least 5 points.

Finally, the selected reflections where merged by *SORTAV*\(^{[7]}\) and the resulting data with \(|\Delta / I| > 3\sigma\) were used for the refinement procedure.

### 6.5 Results and Discussion

Figure 6-2 shows typical profiles of the experiment. Here the profiles of the (1-29) reflection are shown for the \( x\)-val, \( r\)-val and diode signal (Fig. 6-2a, b and c, respectively).

In total 55 measured reflections fulfilled the given criteria of acceptance and were merged by *SORTAV*, which gave 16 unique reflections with internal \( R_I \) and \( R_\delta \) values of 39% and 69%, respectively.

These 16 reflections were used to refine the structural parameters of LiNbO\(_3\). The crystallographic parameters, based on the parameters of the congruent phase obtained by Abrahams and Marsh\(^{[8]}\), are listed in Table 6-3. The congruent LiNbO\(_3\) satisfies the formula \([\text{Li}_{1.5x}\text{Nb}_{5.5}\text{]}\text{Nd}_{1.4x}\text{O}_3\) with \( x=0.0118 \), which corresponds to an overall charge neutrality. All relevant atomic/ionic factors such
as scattering factors are taken from the \textit{SHELXL93} package. Since the applied electric field along the \( c \)-direction of the crystal does not break the symmetry, the refinement was performed in the same space group settings, i.e. R
definition as

\begin{align*}
\text{Figure 6-2: Typical profiles: } x\text{-val (a), } r\text{-val (b) and diode signals (c) of (1-29) reflection.}
\end{align*}

The Nb(2) atom was selected to be the fixed origin\textsuperscript{[9]} because of its special position at \((0,0,0)\). A correction for the induced change in the unit cell parameter \( c \) (\( \Delta c = 0.000156 \) Å) was applied by using the \( d_{33} \), as was determined in §3.6.1. Since the \( x \)- and \( y \)-parameters of the Li(1) and Nb(1) atom are fixed (special position (6a) in R3c), only the \( z \)-parameter was allowed to change unconstrained. Furthermore, the positional parameters of O(1) atom were allowed to change since the atom lies on a general position (18b). The anisotropic atomic displacement factors and the occupancy were not refined. If the latter would be allowed to change, it implies that the electric field induces site-hopping of atoms, which is unlikely. So, a total of five parameters were used in the refinement procedure. The final \( R \)-factor was 83\% \((R\_e=92\%)\) using a weighting scheme based on the experimentally obtained standard deviation, where \( R\_e \)-factor is defined as
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\[ R_u = \frac{\sum_{hkl} w(hkl) |\Delta I_{obs} - k| |\Delta I_{calc} |}{\sum_{hkl} |\Delta I_{obs}|} \times 100\% . \] (6-20)

Tables 6-4 and 6-5 list the final refinement results of the changes in $\Delta l/l$ and positional parameters, respectively.

Table 6-3: Structural parameters for the congruent LiNbO$_4$ with space group R$3c$ and unit cell parameters of $a=b=5.150523(45)\,\text{Å}$ and $c=13.864961(21)\,\text{Å}$.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>occ</th>
</tr>
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<td>0</td>
<td>27909(53)</td>
<td>0.313729</td>
</tr>
<tr>
<td>Nb(1)</td>
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<td>0</td>
<td>27909(53)</td>
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</tr>
<tr>
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<td>0</td>
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</tr>
<tr>
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<td>4790(12)</td>
<td>34299(12)</td>
<td>6385(9)</td>
<td>1.0</td>
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</table>

<table>
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<tr>
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<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
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<td>2558</td>
<td>3092(223)</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nb(1)</td>
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<td>448</td>
<td>359(5)</td>
<td>224</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Nb(2)</td>
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<td>448</td>
<td>359(5)</td>
<td>224</td>
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<td>0</td>
</tr>
<tr>
<td>O(1)</td>
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<td>593(13)</td>
<td>761(10)</td>
<td>339(15)</td>
<td>-134(15)</td>
<td>-228(10)</td>
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Table 6-4: The refinement results for $\Delta l/l$.

<table>
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<tr>
<th>$h$</th>
<th>$k$</th>
<th>$l$</th>
<th>$\Delta l/l_{calc}$ [%]</th>
<th>$\Delta l/l_{obs}$ [%]</th>
<th>$\sigma_{obs}$ [%]</th>
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<td>1</td>
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</tr>
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<td>1</td>
<td>15</td>
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</tr>
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</tr>
<tr>
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</tr>
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<td>3</td>
<td>20</td>
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<td>1.8923</td>
<td>0.5808</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>20</td>
<td>0.0486</td>
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<td>0.4366</td>
</tr>
<tr>
<td>3</td>
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<td>16</td>
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</tr>
<tr>
<td>4</td>
<td>2</td>
<td>20</td>
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<td>2.8295</td>
<td>0.5271</td>
</tr>
</tbody>
</table>
The obtained refinement results are shown to be significant, although the changes are larger than the ones observed by Fujimoto\textsuperscript{11}. Unfortunately, Fujimoto gives no information on the sample composition. Furthermore, the refinement may indicate that the Li(1) atom moves more than the Nb(1) or O(1) atoms.

However, it should be noted that these results must be approached with caution since the listed values in Table 6-5 are close to the limit of the refinement procedure (~1\texttimes{}10^{-2} \text{ Å}) and the R-factor is high.

### Table 6-5: Refinement results of LiNbO$_3$ upon application of an external electric field of 2.6\texttimes{}10$^5$ Vm$^{-1}$ along the c-direction.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta x$ [\texttimes{}10^{-3} \text{ Å}]</th>
<th>$\Delta y$ [\texttimes{}10^{-3} \text{ Å}]</th>
<th>$\Delta z$ [\texttimes{}10^{-3} \text{ Å}]</th>
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<tbody>
<tr>
<td>Li(1)</td>
<td>-75(8)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nb(1)</td>
<td>12(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(1)</td>
<td>-27(7)</td>
<td>-30(11)</td>
<td>2.6(9)</td>
</tr>
</tbody>
</table>

### 6.6 Conclusion

The developed refinement program proved to refine a test model correctly, with the limit for refinement of changes in the atomic positions of ~1\texttimes{}10^{-2} \text{ Å}. Furthermore, it was shown that in the future, a small data set can be measured easily using the broad-energy X-ray band method.

A refinement of a LiNbO$_3$ data set showed large changes in the atomic parameters. However, these results should be taken with caution since the R-factor (83\%) is, of course, much too high and even higher than expected based on the merging statistics ($R_{merge}=39\%$). The fact that the R-factor is high indicates that either the data contain (systematic) errors, or that the used model is insufficient or incorrectly describes the data. One known problem is the phase contrast, which introduces rather large uncertainties in the data. Possible absorption and extinction effects might occur because of the large and relatively perfect LiNbO$_3$ crystal sample which was used. Furthermore, the refinement was carried out with a very limited set of reflections, whereas the total number of refinement parameters was relatively large.

However, it should be stressed that the primary purpose of the experiment was to test the experimental procedures needed to perform an automatic collection of an extended data set, as well as to develop and test the data reduction and data refinement algorithms. Therefore less emphasis was placed on the accuracy of the data, which would be an issue in future experiments.

### References

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