Structure determination of Fe(II) spin-crossover complexes from powder diffraction data with direct-space methods
Dova, E.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
Chapter 3

Rietveld Refinement

3.1. Introduction

The determination of a structure is completed when the structure is successfully refined. The most widely used manner of refinement in powder diffraction is the Rietveld Refinement (RR) (Rietveld, 1969), first introduced for powder neutron diffraction data but later adapted for X-ray diffraction data (Malmros & Thomas, 1977; Young et al., 1977). In this method the powder diffraction pattern is used as is and no effort is made to separate overlapping reflections and to assign an observed intensity to each Bragg reflection. A reasonably good starting structural model is necessary, as RR is not a solution method. In RR a least-squares refinement is carried out until the best fit is obtained between the entire observed powder diffraction pattern and the entire calculated pattern based on parameters describing the crystal structure, diffraction optics effects, instrumental factors and other specimen characteristics. The quantity commonly minimized in the least-squares RR is the residual $S_y$.

$$S_y = \sum_i w_i (y_{oi} - y_{ci})^2$$  \hspace{1cm} (3.1)

where $y_{oi}$ is the observed intensity at the $i^{th}$ data point, $w_i = 1/y_{oi}$ is the weight assigned to each observed intensity, $y_{ci}$ is the calculated intensity at the $i^{th}$ data point and the summation is over all data points.

A powder diffraction pattern of a crystalline material can be considered as a superposition of individual reflection profiles, each of which has a peak height maximum, a peak position and a width. The contribution of a reflection to the powder diffraction pattern decays gradually with
distance from its peak height maximum while the total integrated peak area is proportional to the Bragg intensity $I_H$ plus background. The intensities, proportional to the square of the absolute value of the structure factor $(|F_H|^2)$, depend on the atomic positions but also on other specimen-related parameters such as absorption, extinction and preferred orientation. The peak shape is a convolution of several sample and instrumental effects such as geometry of the X-ray source, displacement of a flat specimen from the focusing circle, axial divergence of the X-ray beam, specimen transparency, effects of receiving slits and misalignment of the diffractometer (Klug & Alexander, 1974).

In general, at any point $i$ of an experimental powder pattern, several Bragg reflections contribute to the intensity $y_{oi}$. The calculated intensities $y_{ci}$ are determined by summing the calculated $|F_H|^2$ contributions from the neighbouring Bragg reflections plus the background.

$$y_{ci} = s \sum_H L_H m_H |F_H|^2 \phi(2\theta_i - 2\theta_H) P_H Y_H A_H + y_{bi}$$  (3.2)

where $s$ is the scale factor, $H$ denotes the Miller indices $hkl$ of a Bragg reflection, $L_H$ the Lorentz-polarization factor, $m_H$ the multiplicity of the $H$th reflection, $\phi$ is the reflection profile function, $2\theta_H$ is the calculated Bragg angle, $2\theta_i$ is the angle at the $i$th point in the pattern, $P_H$ is the preferred orientation function, $Y_H$ is the extinction correction function, $A_H$ is the absorption factor, $F_H$ is the structure factor for the $H$th Bragg reflection and $y_{bi}$ is the background intensity. The background is due to several factors such as fluorescence of the sample, amorphous phases in the sample, sample holder, the scattering of X-rays by air etc. It is quite common to model the background using polynomials (e.g. in $2\theta$) of which the coefficients are variables in the refinement.

The least-squares parameters can be divided into two groups. The first group of specimen-related parameters consists of background and profile parameters, the latter including the positions, the halfwidths and the possible asymmetry of the diffraction peaks, specimen displacement and transparency parameters, crystallite size and microstrain and preferred orientation. The second group of structural parameters consists of the unit cell parameters and the parameters describing the crystal structure model (atomic coordinates, atomic displacement parameters, occupation factors).

The least-squares minimization procedure leads to a set of normal equations involving derivatives of all the calculated intensities $y_{ci}$ with respect to each refinable parameter. Because this problem is not linear in the parameters, approximate values for all parameters are required in the first refinement cycle. These are refined in subsequent refinement cycles until a certain convergence criterion has been met.

### 3.2. Profile Shape Functions

The profile shape function describes the effects of both instrumental features (including reflection profile asymmetry) and specimen features (transparency, displacement, crystallite size, microstrain). The relatively large number of parameters, the correlation between them and the
small contribution of some of the sources to the profile shape, makes an analytical description very difficult. In addition, the contributions of the sources vary with instrumental configuration and with the specimen.

The analytical reflection profile functions available for use vary from simple Gaussian, Lorentzian and pseudo-Voigt (combination of the first two) functions till complicated variations of the above (Pearson VII, Finger-Cox-Jephcoat modified pseudo-Voigt, split-type pseudo-Voigt, Tomandl etc). All profile shape functions are functions of the line position $2\theta_H$ and the Full-Width-at-Half-Maximum ($FWHM$ or $H_H$) (Table 3.1).

$H_H$ is commonly expressed a function of the diffraction angle as shown in the equation 3.3 (Cagliotti et al., 1958).

$$H_H^2 = U \tan^2 \theta_H + V \tan \theta_H + W$$

with $U$, $V$, $W$ being refinable parameters. For a specific sample their values depend on the instrumental configuration and the choice of profile shape function. This expression, however, does not incorporate peak broadening due to sample characteristics such as the crystallite size. It is possible to use a modified profile shape function to accommodate crystallite-size broadening. With respect to the structure determinations carried out in this thesis, modified expressions of $H_H$ have been used as incorporated in the programs GSAS (Larson & Von Dreele, 1994) and MRIA (Chernyshev & Schenk, 1998) (see Chapter 4).

**Table 3.1 Analytical profile shape functions.**

<table>
<thead>
<tr>
<th>$\phi(x)$</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2\sqrt{\ln 2}/H_H$</td>
<td>Gaussian (G)</td>
</tr>
<tr>
<td>$\frac{\sqrt{4}}{\pi H_H} \left[ 1 + 4(\sqrt{2} - 1)(x)^2 \right]^{1/2}$</td>
<td>Lorentzian (L)</td>
</tr>
<tr>
<td>$\eta L + (1 - \eta)G$</td>
<td>Pseudo-Voigt (P-V)</td>
</tr>
<tr>
<td>$\eta \left[ L(x) - \alpha \eta L^2(a_i x) \right] + (1 - \eta) \left[ G(x) - \alpha \eta (x + \alpha \eta)G(a_i; (x + \alpha \eta)) \right]$</td>
<td>Tomandl</td>
</tr>
</tbody>
</table>

$\phi(x)$ is the profile shape function at the $i^{th}$ point in pattern $x=(2\theta_r-2\theta_0)/H_H$

$2\theta_H$ Bragg angle

$\alpha$ is the asymmetry factor with $0<|\alpha|<0.5$

$a_L = 0.6$, $a_G = 0.85$, $\alpha_0 = 0.7$

$\eta = N_A + N_B \times 2\theta$. $N_A$ and $N_B$ refinable parameters

The fitting of an X-ray powder diffraction pattern is difficult due to the strong asymmetry of the peak profile and the angular dependence of their shapes. Both the pure Gaussian and the pure Lorentzian profile shape functions usually do not fit adequately the diffraction lines. The Pearson VII function approximates the convolution of a Lorentzian and a Gaussian function (i.e.
a Voigt function), the contribution of each being determined by the factor m. For m = 1, 1.5, 2, 10 a Pearson VII becomes a basic, intermediate, modified Lorentzian and Gaussian respectively (Bish and Post, 1989). Another option to model asymmetric peaks is to use a split profile function e.g. a split Pearson VII.

The profile shape function used in the Rietveld refinements carried out with GSAS was a variation on the pseudo-Voigt function (type number 3 in GSAS) that corrects for asymmetry due to axial divergence as described by Finger, Cox and Jephcoat (1994). In this function the mixing parameter η of the pseudo-Voigt function is a function of a modified expression of the FWHM incorporating a Gaussian broadening coefficient and a coefficient that describes an additional type of particle size broadening with Lorentzian character.

In Rietveld refinements carried out with MRIA, a split-type pseudo-Voigt function (Toraya, 1986) was used in several cases and a modified pseudo-Voigt function suggested by Tomandl (Young, 1993, p.117) in some others. Both profile functions accommodate to some extent peak profile asymmetry.

3.3. Preferred orientation correction

Preferred orientation (or texture) arises when the crystallites in a specimen show a strong tendency to be oriented in certain directions. As a result, the diffracted intensities related to the preferentially oriented directions become enhanced, thus leading to systematic deviations. The systematic increase or decrease of the reflection intensities can be modelled mathematically with preferred orientation functions. In this work, in order to correct for the texture, the spherical harmonics expansion method has been used as available in MRIA and GSAS and the March-Dollase method as implemented in Materials Studio. A description of the methods follows which intends to be informative rather than exhaustive.

Spherical-harmonics expansion method: The preferred orientation of crystallites in a polycrystalline sample can be described by its orientation–distribution function (ODF), which is a mapping of the probability occurrence of each of the possible crystallite orientations with respect to the sample coordinates (Roe and Krigbaum, 1964). The preferred orientation effects can be modelled by expanding the ODF of the crystallites in spherical harmonics. The harmonics are chosen according to the Laue class and the coefficients are the parameters being refined.

In a special case of the spherical-harmonic model (symmetrized harmonics expansion), developed by Ahtee et al (1989) and Jarvinen (1993), it is assumed that the ODF of the sample is axially symmetric, as may be realized for example by spinning of the sample. In the program MRIA the texture correction is implemented according to this principle. Von Dreele (1997) has implemented in the program GSAS the generalized spherical harmonics description of texture.

When a sample is spinning during the measurement, the rotation axis becomes the polar axis and every crystallite has a specific direction in relation to it defined by the spherical coordinates θ and φ. If dV is the total volume of the crystallites whose polar axes fall in a solid-angle element dΩ in a direction (θ, φ), the polar-axis density W(θ,φ) is given by the equation

\[ W(\theta,\phi) = \frac{dV}{V_o} \frac{d\Omega}{4\pi} \]

(3.4)
where $V_o$ is the total volume of the illuminated crystallites. The polar-axis density is a characteristic quantity of the orientation distribution of the grains in the sample. It can be represented as a density map on the surface of the unit sphere. In an ideal sample the orientation distribution is uniform, thus $W_{ide} = 1$.

If $\alpha$ is the angle between the polar axis and the scattering vector, the integrated intensity $I_{obs}$ measured for a reflection $hkl$ will be proportional to the average value of the polar-axis density along the circle O on the unit sphere, which is intercepted by a cone with apex angle $2\alpha$,

$$I_{obs}^{hl} = \overline{W}(hkl, \alpha) I_{ide}^{hl}$$ (3.5)

where $I_{ide}^{hl}$ is the intensity in absence of texture. The average polar-axis density $\overline{W}(hkl, \alpha)$ can be expressed in Legendre polynomials $P_l(cos \alpha)$ and a set of symmetrized harmonics $Y_{lm}$,

$$\overline{W}(hkl, \alpha) = \sum_{lm} C_{lm} Y_{lm}(\theta_{hkl}, \varphi_{hkl}) P_l(cos \alpha)$$ (3.6)

with $C_{00}=1$, $C_{lm}$ the refinable parameters and $(\theta_{hkl}, \varphi_{hkl})$ the spherical coordinates of the normal to the plane $(hkl)$.

The texture correction as applied in GSAS is described below. The factor that describes the changes in intensity due to texture is given by Von Dreele (1997).

$$A(h, y) = 1 + \sum_{l \geq 2} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \sum_{\mu=-l}^{l} C_i^{m0} k_l^m(h) k_l^m(y)$$ (3.7)

where the two harmonic terms $k_l^m(h)$ and $k_l^m(y)$ take values according to the crystal and sample symmetry respectively. In the case of cylindrical sample symmetry (all cases in this work) only $k_l^0(y)$ terms are nonzero and only the set of $C_i^{m0}$ parameters is used. $L$ is the maximum order of the spherical harmonics used and its value depends on the complexity of the texture and the quality of the data. In general one should try to have an order as low as possible. The crystal reflection coordinates $(\varphi, \beta)$ in $k_l^m(h)$ are determined by the choice of reflection index $(hkl)$ while the sample coordinates $(\psi, \gamma)$ in $k_l^m(y)$ are determined by the sample orientation on the diffractometer. Then, equation 3.7 becomes

$$A(\varphi, \beta, \psi, \gamma) = 1 + \sum_{l \geq 2} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \sum_{\mu=-l}^{l} C_i^{m0} k_l^m(\varphi, \beta) k_l^m(\psi, \gamma)$$ (3.8)
The harmonic terms $k_l^m(\phi, \beta)$ and $k_l^n(\psi, \gamma)$ can be expanded in Legendre polynomials as pointed out by Bunge (Bunge, 1982; Von Dreele, 1997). The harmonic coefficients $C_l^m$ are the refinable parameters in the least-squares refinement.

The magnitude of the texture can be evaluated from the texture index by

$$ J = 1 + \sum_{l=2}^{N} \frac{1}{2L+1} \sum_{m=-l}^{l} \sum_{n=-l}^{l} |C_l^m|^2 $$

(3.9)

In absence of texture $J = 1$, otherwise $J > 1$: for a single crystal $J = \infty$. Until now, there are no generally accepted rules established about the value of J. In the GSAS tutorial pages at http://www.ccp14.ac.uk/, there is reference to a comment of Scott Belmonte stating that a texture index of 3 indicates strong texture while higher values could be an indication of overfitting. It has been suggested (Von Dreele, 1997) that the number of spherical harmonic parameters used for texture correction should be kept as low as possible, as the use of too many parameters may result in fitting other phenomena as well (e.g. atomic displacements). In practice, though, it is very difficult to judge whether other effects have been incorporated into the texture correction.

**March-Dollase method:** Dollase (1986) proposed a single pole-density profile based on functions used by March (1932). Preferred orientation results usually from processes such as compaction, settling or deformation acting on non-isotropic crystallite shapes. Dollase (1986) defined as the preferred orientation plane (HKL) the prominent planar surface for platy crystallites and the plane normal to the prominent elongation axis for rod-shaped crystallites. If a diffraction plane hkl(= H) makes an angle $\alpha$ with (HKL) the March-Dollase pole-density profile is given by

$$ P_H = (r^2 \cos^2 \alpha + (1/r) \sin^2 \alpha)^{-3/2} $$

(3.10)

with $r$ characterizing the strength of the preferred orientation and giving the effective sample compression or extension along the cylinder axis due to preferred orientation. For platy crystallites $r = d/d_o$ while for rod-shaped crystallites $r = d_o/d$, with $d_o$ the thickness of a hypothetical sample that does not exhibit preferred orientation and d the sample thickness after axial extension or compression. If there is no preferred orientation $r = 1$. In Materials Studio, the values of the normal to the preferred orientation plane are expressed in fractions of the reciprocal lattice vectors $a^*$, $b^*$, and $c^*$.

### 3.4. Criteria of fit

The purpose of the Rietveld refinement process is to obtain the set of parameters that minimizes the least-squares difference between the calculated and measured profiles. A number of criteria-of-fit (listed in Table 3.2) have been developed to help one judge how well the refinement proceeds and to assess the quality of the final fit.
TABLE 3.2. Criteria of fit in Rietveld refinement

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_p = \frac{\sum</td>
<td>y_{oi} - y_{ic}</td>
</tr>
<tr>
<td>$R_{wp} = \left[ \frac{\sum w_i (y_{oi} - y_{ic})^2}{\sum w_i y_{oi}^2} \right]^{1/2}$</td>
<td>R-weighted pattern</td>
</tr>
<tr>
<td>$\chi^2 = \left[ \frac{\sum w_i (y_{oi} - y_{ic})^2}{N - P + C} \right]^{1/2}$</td>
<td>Goodness-of-fit (GOF)</td>
</tr>
</tbody>
</table>

The subscript i denotes all points in the pattern range undergoing refinement.

$w_i = 1/y_{oi}$

$N =$ the number of observations

$P =$ the number of refined parameters

$C =$ number of constraints applied

From a mathematical point of view, $R_{wp}$ is the most meaningful indicator of a calculated-to-observed pattern fit because the numerator is the residual minimized during the refinement (Young, 1993). The effect of weighting is to reduce the contributions of the errors due to the misfit at the tops of the peaks. In contrast, the contribution of the misfit in the regions near the tails will be significant. As a result, discrepancies will be observed mainly at the peak profile maxima while the agreement will be better at the tails.

The effectiveness of the derivative-based algorithm in the RR is affected by factors such as the quality of the initial estimates of the parameters, the degree of correlation between the parameters and the number of parameters undergoing refinement. For example, both an increase of the number of parameters and a parameter correlation increase the number of cycles required for convergence and reduce the ability of the algorithm to determine the optimum parameter values (Young, 1993).

Although numerical criteria are useful, they should be considered as indicators of the progress of the refinement and not be interpreted in absolute sense. The difference plot and the refined structural model should be judged critically in order to assure the correctness of the refinement procedure (Mc Cusker et al., 1999). Visual inspection of the difference pattern can be very informative and may reveal various kinds of misfits, such as inadequately calculated profile tails, an inappropriate background or incorrect lattice parameters. A check of the structural model is essential, especially in case of organic fragments (with a specific geometry), as a highly distorted model might be hidden behind a very satisfactory R-value. Moreover, R-values can be misleadingly small in case of a high background.

### 3.5. Restraints and constraints in Rietveld Refinement

The loss of information because of the collapse of the three-dimensional single-crystal data to an one-dimensional powder diffraction pattern is the main reason of the poor ratio observation/variables, which in turn hinders the efficiency of a refinement. A way to
compensate for this loss is to introduce additional stereochemical information e.g. by inclusion of interatomic distances and angles (Waser, 1963; Baerlocher, 1982). The additional observations can be included as hard constraints or restraints (soft constraints). Constraints are imposed rigorously so that the relationship specified must be fulfilled exactly. Restraints are relationships that are imposed approximately, with the degree of approximation being given by a finite weight, so allowing for deviations from the prescribed values. The use of restraints increases the number of the observations (so improves the observation/variables ratio) thereby allowing more parameters to be refined and keeping the geometry of the structural model sensible.

The function of restraints or pseudo-observations to be minimized can be written as

$$ S_R = \sum_i w_i (R_{oi} - R_{c}(x))^2 $$

(3.11)

with $R_o$ an expected value (e.g. distance, angle or any other stereochemical quantity), $R_c(x)$ the value calculated from the atomic positions or other structural variables and $w$ the inverse of the variance of the pseudo-observation. The whole minimization function can be written as

$$ S = S_y + c_w S_R $$

(3.12)

with $c_w$ a common weight factor which can be used to vary the contribution of the restraints in the refinement progress. The larger the $c_w$ the more dominant the restraints in the result will be. $c_w$ should be decreased as the refinement progresses and ideally be removed at the end.

In MRIA, only distance restraints can be applied. Angle and planar restraints are expressed as distance requirements when restraining more distances additional to the bond distances (Waser, 1963). The $c_w$ factor in (3.12) is given by

$$ c_w = 10S_y / \langle w_i \rangle $$

(3.13)

with $S_y$ a user defined constant and $\langle w_i \rangle$ the average experimental weight ($w_i=1/y_i$).

In GSAS it is possible to use constraints and restraints. A set of the expected values of stereochemical restraints with a standard deviation each can be supplied and used as a set of observations. In this work, bond distance, bond angle and planar restraints have been applied in the refinements. In this case the minimization function can be expressed by

$$ S_R = f_d \sum_{i=1}^{N} w_i (d_{oi} - d_{ci})^2 + f_a \sum_{i=1}^{N} w_i (a_{oi} - a_{ci})^2 + P_c \sum_{i=1}^{N} w_i (-p_{ci})^2 $$

(3.14)
with $w_i = 1/\sigma_i^2$ the individual weight of the restraint and $\sigma_i$ a standard deviation set by the user. The weight factors $f_a$, $f_b$, $f_p$, are used to increase or decrease the effect of each restraint component on the minimization function. The planar group restraint is computed by determining the distance of each atom to the best plane through a group of atoms.

### 3.6. Estimates of precision in Rietveld Refinement

The refinement can be stopped when several convergence criteria are met. The most commonly used criterion (Young, 1993) is based on the estimated standard deviations (e.s.d.) calculated as $\sigma_j$ in the $j^{th}$ parameter, which can be derived from the errors associated with the measured intensity values.

$$
\sigma_j^2 = \left[ \frac{M_{jj}^{-1} \sum_i w_i (y_{ij} - y_{cj})^2}{N - P + C} \right]^{1/2}
$$

(3.15)

where $M_{jj}^{-1}$ is the corresponding diagonal element in the inverted normal equation matrix, $N$ is the number of observations, $P$ the number of parameters adjusted and $C$ the number of constraints applied. Convergence is achieved when all the parameter shifts $\Delta x_i$ calculated in a given cycle satisfy the condition $|\Delta x_i| < a \sigma_i$, where $a$ is a user-defined value (~0.3 according to Young, 1993).

The e.s.d.'s are not the experimental errors but, as formulated by Young (1993, p. 26), *minimum probable possible errors arising from random errors (counting statistics) alone*. However, as noted by Langford and Louër (1996), systematic errors arising e.g. from inadequate modelling of preferred orientation, description of line profiles etc can introduce a bias in the calculation of e.s.d.'s and the precision and accuracy of the parameter estimates cannot be assessed validly by statistical methods.

The estimates of precision obtained from profile-fitting algorithms should be regarded only as estimates of how well the values of the parameters could be determined for a particular set of data and not as an indication of how close the parameter values are to the true values, that is to say, e.s.d.'s are measures of precision and not of accuracy. The true errors and the accuracy of the Rietveld refinement results are best assessed by comparison to single-crystal results for the same material.

### References


