Accurate Separation of X-ray $x_1-x_2$ Doublets by the 'Substitution Method'

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(Received 4 January 1982; accepted 1 June 1982)

Abstract

An improved 'substitution method' for the separation of X-ray diffraction $x_1-x_2$ doublets is based on the possibility of refining both the proportionality constant between the $x_1$ and $x_2$ contributions to the line intensity and the doublet separation expressed in terms of the diffraction angle or of a related variable in the reciprocal space. Optimization of these two parameters, with a proper evaluation of the error, clearly shows the statistical nature of the oscillations appearing on the high-angle side of the pure $x_1$ component after correction; their elimination by polynomial smoothing can therefore be performed and a procedure is suggested for achieving this result. A computer program, based on these principles, has been written and tested in many practical cases.

Introduction

Two methods are usually employed for the separation of the $x_1$ and $x_2$ components of the X-ray characteristic K radiation: the substitution method (Rachinger, 1948; DuMond & Kirkpatrick, 1931; Delhez & Mittemeijer, 1975), based on an algorithm originally proposed by Rachinger, and the Fourier method suggested by Gangulee (1970).

If $x$ is the diffraction angle or any suitable variable in the reciprocal space and $l(x)$ is the observed intensity of the $x_1-x_2$ composite profile, then for $I_1(x)$ and $I_2(x)$, the profiles of the two components, one can write

$$I_1(x) = \sum_{i=0}^{n} (-1)^i C^i l(x - iAx)$$

and

$$I_2(x) = \sum_{i=1}^{n} (-1)^{i+1} C^i l(x - iAx),$$

where $C$ is a proportionality constant derived from the commonly accepted assumptions of shape identity of the two profiles, $Ax$ is the doublet separation, and $n$ is an integer whose value is limited by the amplitude of the measurement interval. The dependence of $Ax$ on $x^*$ is given by

$$Ax = 2\sin^{-1}\left(\frac{\lambda_1}{\lambda_2}\sin x\right) - x,$$

where $\lambda_1$ and $\lambda_2$ are the wavelengths of the two components.

In this paper an improvement of the substitution method is proposed, in which optimization of the separation is achieved by minimizing the quantity $\sum \delta^2$, where $\delta$ is the difference between each value of the high-angle tail of the $x_1$ profile and the previous relative minimum of this function, and by an iterative procedure of refining $Ax$ and $C$. Thus the choice of these particular optimization criteria is based on the reasonable assumptions that the two profiles have the same shape and that the high-angle tail of the $x_1$ component is the part of the profile that is more sensitive to errors intrinsic in the separation method.

The improvement is based also on the fact that the optimization procedure does not require a previous determination of the background level and of the lattice constants and radiation wavelengths, thus eliminating the errors on $Ax$ and $C$ due to propagation of the measurement errors on these quantities.

Computing procedure and experimental

The following procedure was established as the basis of a computer program by which the $x_1-x_2$ separation can be performed:

(i) a grid of $5 \times 5$ equally spaced points (corresponding to five plausible values of both $C$ and $Ax$) is chosen;

(ii) the ratio $\lambda_1/\lambda_2$ is calculated for each of these five $Ax$ values;

(iii) at each grid point $\sum \delta^2$ values† are computed (for the definition of $\delta$, see the Introduction), following the $x_1-x_2$ separations based on the chosen 25 pairs of values of $C$ and $Ax$;

(iv) the 'best' $(C, Ax)$ pair is chosen on the basis of the criteria established in the Introduction;

(v) the found 'optimum' $(C, Ax)$ pair is taken as the mean value of a new set of 25 $(C, Ax)$ pairs (grid

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†The use of a $\chi^2$ parameter gives the same results in a longer computing time.

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points), characterized by smaller increments between any two nearest points;

(vi) the procedure (i) to (v) is iteratively repeated, defining grids with smaller and smaller increments until the required precision is achieved.

In order to test the above procedure and computer program (written in Fortran for a 370/138 IBM machine), \( x_1 - x_2 \) composite profiles have been synthesized by combining two Pearson VII (Hall, Veeraraghavan, Rubin & Winchell, 1977) distributions with suitable values of \( C \) and \( \Delta x \) (Figs. 1, 2) and 110 and 200 profiles have been measured from an iron powder sample characterized by an average grain of 2 \( \mu m \) and a lattice constant of 2.8663 \( \AA \) (Fig. 3 and 4). These experimental profiles constitute a critical test for the program due to narrowness of the \( x_1 \) and \( x_2 \) components, their high asymmetry, and the degree of their overlap. Considering the low diffraction angles at which these reflections have been measured, the corrections for both geometrical (Lorentz) and physical (polarization, thermal and scattering) factors were neglected.

**Results and discussion**

Consideration of the propagation of the experimental error on the \( x_1 \) and \( x_2 \) components of the line profile separated by the substitution method brings interesting conclusions.

Fig. 1. The substitution method applied to a synthesized line profile characterized by a distance between the two maxima of 0.120 and width of 0.178.

Fig. 2. The substitution method applied to a synthesized line profile characterized by a distance between the two maxima of 0.220 and width of 0.178.

Fig. 3. The substitution method applied to the 110 line profile of an Fe powder specimen collected by Mo white radiation.

Fig. 4. The substitution method applied to the 200 line profile of an Fe powder specimen collected by Mo white radiation.
With reference to (1) and (2) the expressions for the standard deviations $\sigma_1(x)$ and $\sigma_2(x)$ of $I_1(x)$ and $I_2(x)$ respectively are given by

$$\sigma_1(x) = \left[ \sum_{i=0}^{n} C^1 I(x - i \Delta x) \right]^{1/2} \quad (4)$$

and

$$\sigma_2(x) = \left[ \sum_{i=1}^{n} C^1 I(x - i \Delta x) \right]^{1/2}. \quad (5)$$

Application of (4) and (5) to both synthesized and experimental profiles (see previous section) shows that the error has an oscillating behaviour and that its maximum values are reached on the high-angle side of the $I_1(x)$ profile, exactly where the substitution method generates a tail characterized by damped oscillations.

The results of a $\chi^2$ test and the behaviour of the function representing the error on the two profiles clearly show that the observed deviations have a statistical nature even in the cases of the highest precision (corresponding to an error of 0.15%).

In Figs. 5 and 6 the results of the $\chi^2$ test and the ones of a polynomial smoothing (for the 110 and 200 reflections) are reported.

It is important to note that the described procedure (i) preserves all the information contained in the measured profile, (ii) offers two independent measurements of the same microstructural parameters, since both $I_1(x)$ and $I_2(x)$ are determined simultaneously, and (iii) constitutes a completely self-consistent method.

The suggested procedure is strongly recommended compared with the alternative route of the Fourier method, which leads to erroneous results owing to the unavoidable truncation error.

The authors are grateful to Professor Marcello Zocchi (Politecnico – Milano) for many stimulating and helpful discussions.

References