Neutron multiple diffraction used as a tool for structural studies

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Introduction

Multiple diffraction (MD) occurs when more than one reciprocal lattice point (in addition to the origin point) is located on the sphere of reflection. MD can occur accidentally or intentionally. Intentional X-ray multiple diffraction (XMD) has been measured and employed in innumerous crystallographic studies [1]. On the other hand, neutron multiple diffraction (NMD) has received scant attention in the literature. All studies presented in the following sections are related to the application of NMD in structural studies. They were carried out at the IPEN multipurpose neutron diffractometer, briefly described in Refrerence [2], installed at the IEAR1 research reactor of IPEN-CNEN/SP. An experimental arrangement, appropriate to perform NMD measurements, was installed in the diffractometer. Besides the usual components of a diffractometer, this arrangement included an extra neutron detector to measure the incident beam, a two-dimensional collimator for the incident beam and a five-circle goniometer to provide alignment of the crystal and its turning around the scattering vector [3].

In 1964, Moon and Shull developed a theory for NMD in mosaic single crystals. They proposed a Taylor-series expansion as a useful approximate solution for $P_1(x)$, the power of a primary reflected beam traversing a layer of thickness dx at depth x in a mosaic single crystal, calculated about the point $x = 0$ [4]. In order to check their theory, they measured several Fe(200) NMD patterns and compared the experimental peaks with simulated ones. They expanded the series till the second and third order. As they pointed out, expansions limited to few terms are valid only in the case of low secondary extinction and low absorption, which is commonly the case of thin crystals. The iron single crystals used in the measurements had the form of platelets 6.3 × 5.8 mm^2 with three different thicknesses. The thickest crystal was 1.4 mm thick.

In the 1970s, Parente and Caticha-Ellis, aiming to determine the mosaic spread of a single crystal in different directions, measured NMD patterns utilizing a large aluminum single crystal. The crystal was a 3 × 3 × 1 in^3 plate [5]. They first used the formulas already existing in the literature for their analysis. They soon realized that such formulas were not applicable to large crystals of the size of their aluminum sample. The solution they found was to work out a recurrence formula for the Moon and Shull's Taylor-series expansion [6]. They derived a formula that allows that as soon as the (n-1)th term of the series is calculated, the nth term can be calculated. Of course, this iterative way of calculating intensities is well suited for use of computers. It should be noted that, with the formula, the number of terms that can be calculated is unlimited. It only depends on the desired degree of approximation.

In 1994, Parente and coauthors [7] reformulated the recurrence formula in order to turn it into useful formulas applicable to any kind of beam (incident, primary or secondary) and in a many-beam case ($n \geq 4$). Two formulas were derived: one for reflected and another for transmitted beams. After deriving the formulas, they wrote a computer program for the simulation of NMD patterns.

Simulation of NMD patterns

MULTI [7], that is the name given to the program, calculates the intensity points of a NMD pattern as a function of the azimuthal angle φ for primary and transmitted (incident) beams. Patterns can be of any type, *Aufhellung*, *Umweganregung* or *mixed* [3], and there is no limitation in the number and types of the secondary beams involved in the phenomenon. MULTI also takes into account those secondary reflections that, even though not occurring at the same φ, are sufficiently close to interfere one another [7]. This is an important feature of the program that permits a good fitting of experimental NMD patterns, even in the case of high density of secondary reflections. One example is the application of MULTI in the fitting of an experimental NMD pattern. Figure 1 is a reproduction of Figure 2 of the paper by Mazzocchi and Parente which

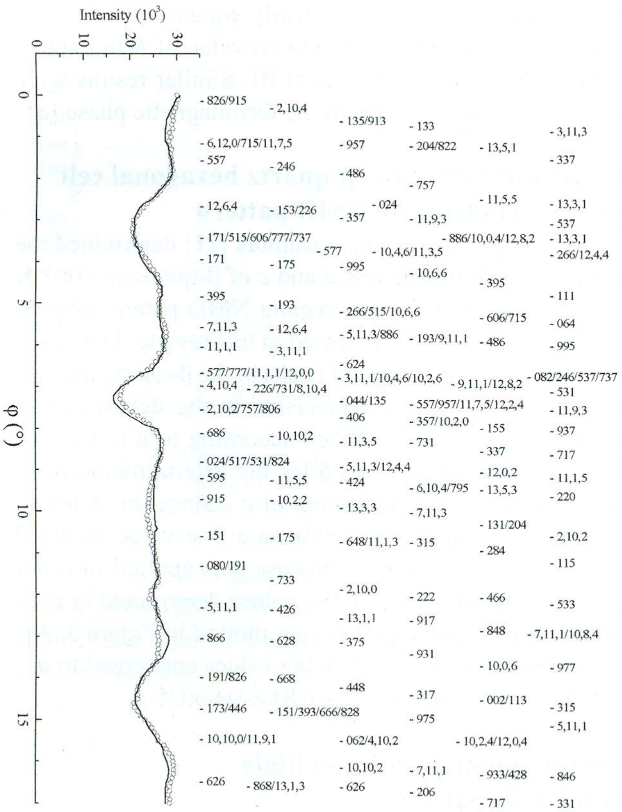

Figure 1. Indexing of a partial NMD pattern measured with Fe_3O_4 (magnetite) in the ferrimagnetic phase. Experimental (small circles) and simulated (continuous line) patterns are compared. Simulated patterns were calculated by MULTI with refined parameters [8]. © IUCr. Reproduced by permission of IUCr. Permission to reuse must be obtained from the rightsholder.

deals with the refinement of the ferri- and paramagnetic phases of magnetite using MULTI [8]. It shows the indexing of the secondary reflections contributing to the NMD pattern of the ferrimagnetic phase of magnetite. Despite the high density of secondary reflections in the pattern, a good fitting was obtained in the last cycle of refinement.

Use of MULTI in the study of β-quartz

The first application of MULTI to structural studies was a comparison between two models of structure for the β phase of quartz (SiO_2). At approximately 846 K, the room temperature phase of quartz, α-quartz, undergoes a reversible transition to β-quartz. In a study dealing with the mechanism of the α-β transition in quartz, Young proposed three different models for the structure of the β-phase. In two models the structure was disordered. In the third model, it was ordered. After a detailed intensity analysis, Young opted for the ordered model [9]. Using high-resolution neutron diffraction, Wright and Lehmann studied the α- and β-quartz structures. They determined that the β-quartz structure was disordered [10]. In 1994, Mazzocchi and Parente used NMD to study β-quartz making a comparison between the Young's model and the Wright and Lehmann's model. They measured a β-quartz (00.1) *Umweganregung* NMD pattern from a large natural quartz crystal, shaped into an orthocylinder 5 cm diameter × 5 cm height. The crystal was heated to 1003 K inside a special electrical furnace designed to be used in NMD measurements. Using MULTI, they simulated NMD patterns retaining terms up to the 30th order for both ordered and disordered models. They used structural parameters found in the literature for each model. Agreement between the observed and calculated intensities was verified by calculating the reliability factor R for the comparisons between the models and the experimental pattern. Values found were $R = 0.143$ for the Young's ordered model and $R = 0.110$ for the Wright and Lehmann's disordered model. The comparisons favored the Wright and Lehmann's disordered model though the difference between the Rs is only 3.3% [3].

Refinement of the ferri- and paramagnetic phases of magnetite

At room temperature, magnetite (Fe_3O_4) is a Néel A-B ferrimagnet. Above the Curie temperature, *ca.* 853 K, magnetite becomes a paramagnet. In 1998 Mazzocchi and Parente, using a natural single crystal with a volume of about 5 cm^3, measured NMD patterns of magnetite at room temperature and 976 K. The same furnace used in the work described in the above section, with minor modifications, was used to heat the crystal. Using MULTI, these authors refined structural and thermal parameters for both phases. The lattice parameter a and the position parameter x were refined along with thermal parameters in three different refinements: an overall isotropic thermal parameter was assumed for all ions in the structure (I); different isotropic parameters were assumed for the special positions in the space group (II); anisotropic parameters were assumed (III). Figure 2 shows the final results obtained in the refinements I, II and III of the paramagnetic phase of magnetite. Table 1 gives the values for the lattice, positional and thermal parameters, scale factor c and calculated R found in respective refinements. The mosaic spread η was only refined in refinement III. A qualitative evaluation of the refinements I, II and III

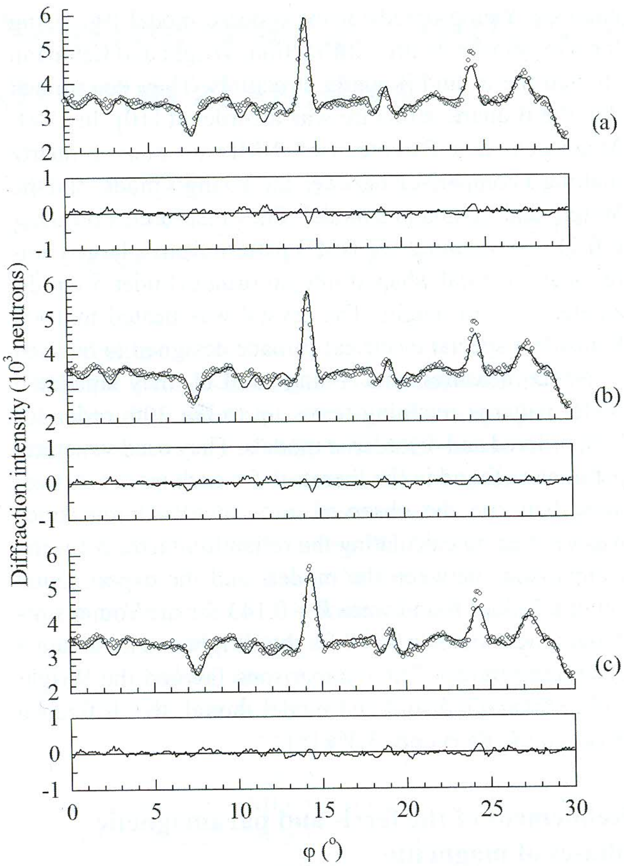

Figure 2. Experimental NMD pattern (small circles), measured with Fe_3O_4 (magnetite) in the paramagnetic phase, compared with simulated patterns (continuous lines) calculated by MULTI for refinements I, II and III [8]. © IUCr. Reproduced by permission of IUCr. Permission to reuse must be obtained from the rightsholder.

of Figure 2 does not show clearly which is the best refinement. Nevertheless, the lowest value of *R* in Table 1 is that listed for the refinement III. Similar results were found for the refinements of the ferrimagnetic phase [8].

Determination of the β-quartz hexagonal cell parameters from an NMD pattern

Recently, Campos and coauthors [11] determined the hexagonal cell parameters *a* and *c* of β-quartz at 1003 K using the (00.1) *Umweganregung* NMD pattern already used in the first study presented in this review. They used the azimuthal φ positions of peaks in the β-quartz pattern. In order to improve the precision in the determination of φ, the peaks were selected according to a test which defined if a peak was 'good for the determination of *a*' or 'good for the determination of *c*'. Since the determination of a parameter depends on a first value assumed for the other, an iterative process was applied in order to determine final values. The values determined in each cycle of the iterative process are plotted in Figure 3. After twelve cycles of iteration the values converged to $a = 4.9957 \pm 0.0014$ and $c = 5.46184 \pm 0.00035$ Å.

Mirror symmetries in multiple diffraction patterns

More recently, Parente and coauthors made a study of the symmetry mirrors appearing in NMD and XMD patterns. Several different 360° NMD and XMD patterns were simulated by MULTI and MULTX for different face-centered cubic (f.c.c.) crystals. MULTX is a version of MULTI for XMD. The patterns, plotted in cir-

Table 1. Lattice, positional and thermal parameters found in the three refinements of the paramagnetic phase of magnetite [8].

Special positions	Parameters	Refinement I	Refinement II	Refinement III
8(a)	a (Å)	8.486(0)	8.490(5)	8.491(3)
	B (Å^2)	1.42(5)	—	—
	B_a (Å^2)	—	1.8(5)	—
	B_{11} (Å^2)	—	—	0.26(0)
16(d)	B_d (Å^2)	—	1.1(5)	—
	B_{11} (Å^2)	—	—	0.41(0)
	B_{12} (Å^2)	—	—	–0.00(9)
32(e)	x	0.381(5)	0.381(5)	0.381(7)
	B_e (Å^2)	—	1.8(0)	—
	B_{11} (Å^2)	—	—	0.19(8)
	B_{12} (Å^2)	—	—	0.18(3)
	η (rd)	—	—	0.0051(2)
	c (×10^5)	2.040	1.995	2.380
	R (%)	3.56	3.46	3.32

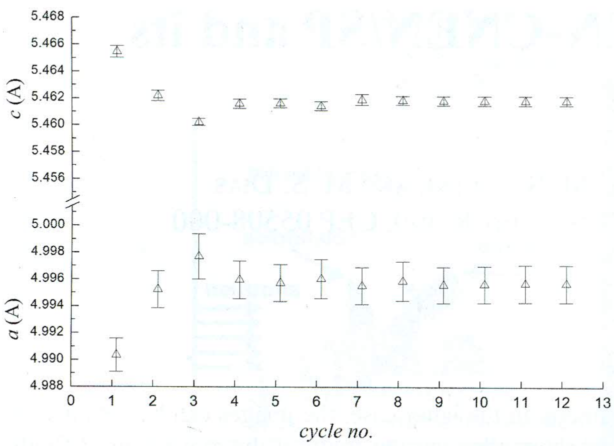

Figure 3. Plot showing the convergences of parameters a and c determined in the 12 cycles of iteration [11]. © IUCr. Reproduced by permission of IUCr. Permission to reuse must be obtained from the rightsholder.

cular plots, showed that two types of symmetry mirrors coexist: isomorphic (IM) and anamorphic (AM) mirrors. Number and types of mirrors depend on the *n*-fold symmetry of the scattering vector of the primary reflection. For *n* even, only *n* IMs appear in the patterns. For *n* odd, *n* IMs are formed intercalated between *n* AMs [12]. The results above are important for a correct and quick indexing of both NMD and XMD patterns obtained with f.c.c. crystals. Figures 4 and 5 are examples of NMD patterns simulated for this study.

Acknowledgments

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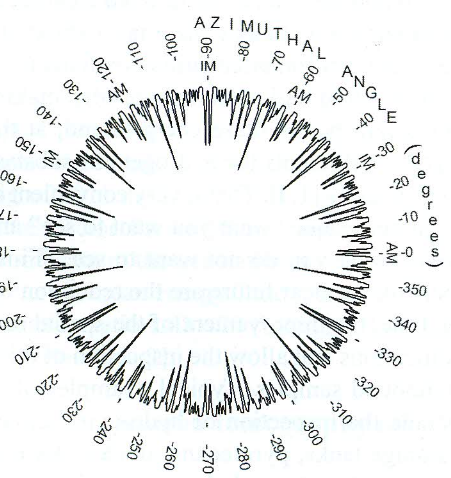

Figure 4. Simulated NMD pattern for Al(111) showing equal numbers of IMs and AMs [12]. © IUCr. Reproduced by permission of IUCr. Permission to reuse must be obtained from the rightsholder.

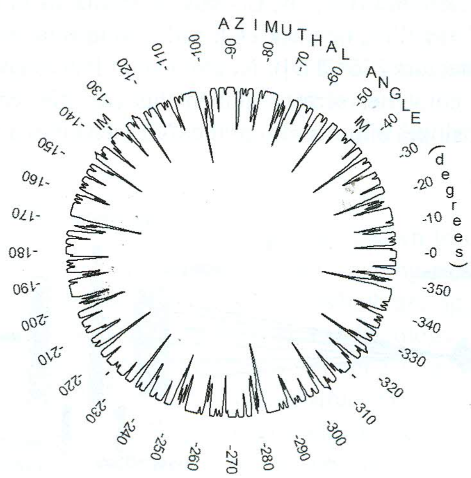

Figure 5. Simulated NMD pattern for Al(220) showing only IMs [12]. © IUCr. Reproduced by permission of IUCr. Permission to reuse must be obtained from the rightsholder.