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Natural crystals for use with the neutron diffraction technique

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Abstract

The purpose of this work is to develop a selection process for natural crystals that considers the major characteristics and performance as gratings for neutron monochromator and analyzers using the neutron diffraction technique. From the 350 naturally occurring types, 19 crystals have been selected and classified regarding their adequacy for use as neutron diffraction devices. Applying special criteria, method and with the help of the rocking curve determination technique, the measurements were established and the theoretically available values were confronted with experimental results, obtained directly from a Neutron Diffractometer, in operation at the IPEN-R1 (5 MW) nuclear research reactor. Natural occurring crystals allow the use of greater values of interplanar distance, providing measurements in the subthermal neutron energy range. The performance of the Merit Figure, introduced to evaluate the neutron reflectivity, was considered effective regarding the nuclear properties of the component crystalline materials. A total of 12 natural types and the respective main families of planes for neutron diffraction, which have affirmed their theoretical-experimental performance, were appointed for routine applications for complementary use together with the conventional-artificial crystals.

1. Introduction

Neutrons from a variety of sources have been used as microscopic probes to study the properties of materials in several applications. A review included some 70 works in different areas of neutron research, sources and applications (Date, 1993; DOE/

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ER-060P, 1994). In the last years, the steady state research reactors (neutron fluxes at 10^{15} n cm^{-2} s^{-1}) using crystals as neutron spectrometer and diffractometer, have been used in most of a great variety of investigations (Iyengar, 1987; Izumi, 1993).

The neutron diffraction technique (NDT) is appropriate to investigate both structure of solids and neutron inelastic scattering. Techniques to study the dynamics of solids and liquids have been traditionally carried out with steady state sources and spectrometers and diffractometers because of certain advantages on operating these instruments in such a specific manner. Historically, the main application for NDT was on condensed matter research, where the purpose was to obtain information about the crystal structure or spin configuration of magnetic materials. Later on, it was found that the inelastic scattering phenomena provides useful information about elementary excitations in solids, e.g. phonons and magnons (Lovesey, 1987; Hutchings and Windsor, 1987). Nowadays, there is an increasing interest in applying the NDT to the research on several materials, not only concerning to the basic sciences, chemistry, biology, earth and space sciences, but also to some industrial technologies (Zeyher, 1996; Schofield, 1983). Sometimes, the application of NDT is the sole available way for obtaining a particular parameter in some investigation on the condensed matter.

The analyzer crystal (or monochromator) is the most important part of the neutron diffraction instrument. Conventional artificial crystals of monoelements, those of simple crystalline structure and the metallic ones are the most usual choice in this priority rank: Pyrolytic graphite (PG), Be, Cu, Pb, Al, Zn, and the semiconductors of Ge and Si. The Heusler's ferromagnetic, ternary alloy (Cu_2MnAL or Cu_2MnSb) is used in neutron experiments concerning magnetism and polarization. To the main difficulties arising from the use of artificial crystals we could include these: doubtful quality control during the manufacture; limited choice on type and size; quasi-perfect crystalline formation structure; operational limit at an interplanar distance $d =$ 3.4 Å (Stasiulevicius and Rodrigues, 1995).

The quasi-perfect crystalline structure of the common mosaic blocks constituting the artificial crystals, generally, shows strong neutron reflectivity attenuation due to the predominance of the primary extinction phenomenon. On the contrary, the limited alignment periodicity of the crystalline mosaic blocks turns the ideally imperfect crystals more suitable, because they show larger widths on the neutron reflected distribution. With the ideally imperfect crystals occurs a less intense neutron attenuation phenomenon, called secondary extinction. Exception made to gems and high purity crystals, the great majority of natural occurring crystals are included in the class of ideally imperfect mosaic crystals. Both natural and conventional-artificial crystals pertaining to that class are preferred for applications with the NDT.

The purpose of this work is the establishment of criteria and implementation of a methodology and experimental technique for the selection and classification of natural crystalline types, available from mineral resources in Brazil and other countries, for complementary use together with the conventional crystals. The performance verification of the selected crystals was accomplished with the IPEN-Neutron Diffractometer, close to the experimental channel of the IEA-R1 research nuclear

reactor, operating at 2 MW. The expected outcome of this work includes: the avoidance of some difficulties due to the exclusive use of the artificial crystals and, hence, the increase on the instrumental operational range; allowance for a greater flexibility on the choice of the suitable types and crystalline planes that best fits to the intended operational energy intervals; the improvement on the flexibility for use and a compromise term between higher intensity of diffracted neutrons and high resolution, which are, respectively, defined by the crystalline mosaic and the available collimation geometry of the experimental arrangement.

Moreover, the natural crystals show some qualities which are essential to NDT experiments: they provide optimal dimensions and formats with several cleavage planes and partitions; they allow for free choice of impurities according to their provenance; they provide greater interplanar distances and their costs are relatively low. The main obstacles to overcome in the selection of the natural crystalline types were the following: complexity on the chemical formulation; several crystalline systems; and lack of atomic-nuclear parameters necessary to the neutron reflectivity calculations. The last problem was overcome with the collection of the available data in the specialized literature and performing the calculations needed for the determination of that essential parameters. In order to evaluate the neutron reflectivity power for the different natural crystalline types, first was applied the formulations from literature usually used for the selection of artificial conventional crystals. It was also implemented a more comprehensive formula that provides a quantity, called crystalline Merit Factor (F_M), that best fits to the selection and classification processes for the natural crystals. This allowed the pre-classification of 19 types with the identification of main diffraction families of planes. Afterwards, it was made the experimental verification of 12 better natural crystals and their main planes. This was accomplished through the determination of the distributions around the monochromatic neutron beam emerging from the Neutron Diffractometer and obtaining their respective rocking curves.

2. Theoretical basis

The principle of the NDT is based on the Bragg relation: $n\lambda = 2d\sin\theta$, where: $n = 1,2,3,\ldots$,etc., λ is the associated neutron wavelength (de Broglie), $d = d_{hkl}$ refers to the distance between the crystalline planes, where h, k, l are the Miller indexes and θ is the incidence angle of the polychromatic neutron beam. The value of λ is given in Å by the approximation $\lambda \cong 0.286/(E)^{-1/2}$, where E is the energy of neutrons in eV.

As a general rule, the crystals used for NDT have mosaic blocks small enough ($\ll 5000$ Å), so that the primary extinction shall be considered negligible. The reduction of neutron beam intensity inside the crystal depends on the angular distribution $W(\Delta)$, relatively to the position of the blocks' normal lines, assumed an isotropic and normalized Gaussian function, given by:

$$W(\Delta) = [1/\eta(2\pi)^{-1/2}]\exp -(\Delta^2/2\eta), \tag{1}$$

where: Δ refers to the angular deviation of the distribution mean direction from the normal lines, η is the width of the crystal's mosaic approximated by $\eta \cong 0.427\beta$, i.e. characterized by the crystalline parameter β, directly derived from the measurement of angular full width at half maximum (FWHM) on the rocking curve (Stasiulevicius, 1998).

In the evaluation of the typical neutron diffraction crystal performance, a non-dimensional constant γ was introduced by Holm (1955). This constant accounts for this characteristic: the greater its value is, the better is the neutron reflectivity power of the crystal, according to the following expression:

$$\gamma = (8d^3 t_o N_c^2 F^2)/[(2\pi)^{1/2}\eta n^3] \tag{2}$$

where: t_0 is the crystal thickness, N_c is the number of cells per volume unit (V_c), and F is the characteristic structure factor of crystalline families of planes.

3. Selection process

Starting from an initial list of the natural crystals available on the mineralogical literature (Klein and Hurlbut, 1994; Lide, 1994), in a preliminary procedure to the selection process, in this basic criteria were considered: simplicity on the chemical composition and on the crystalline spatial group; compatibility of physical state; available dimension; preferential aggregations; difficulties on the acquisition of samples. Later on, the suitable selective process was implemented. It was divided into four stages targeting the main crystal operational characteristics: (1) Basic characteristics; (2) Macroscopic and atomic characteristics; (3) Microscopic and nuclear characteristics; (4) Experimental measurements with use of the IPEN-Neutron Diffractometer.

The Fig. 1 shows a consolidated listing of the 19 selected natural crystals compared with eight usual types of the conventional-artificial ones, plotted as a function of their respective d_{hkl} or d_{HKIL}(using Miller–Bravais index) values for use with NDT. In Table 1 are presented the data of 19 available natural occurring crystals for use with NDT, selected after stage (3).

Usually, the natural crystals are more complex compounds having many primary constituent elements or several impurities that exhibit high neutron cross sections. So, the conditions are very different from those existing with the conventional-artificial crystals, which, normally, are constituted by a single element that may have a low absorption cross-section. In order to establish a more complete and suitable method to the selection and pre-qualification process of natural occurring crystals, the expression called crystalline Merit Factor, F_M, derived from the Holm's formula Eq. (2), is here introduced. The constant γ was considered because the implication of most crystallographic and atomic parameters, being more representative for a given crystal and its families of planes for NDT applications. In the Holm's original expression it was, initially, added three parameters, namely: λ according to the Bragg

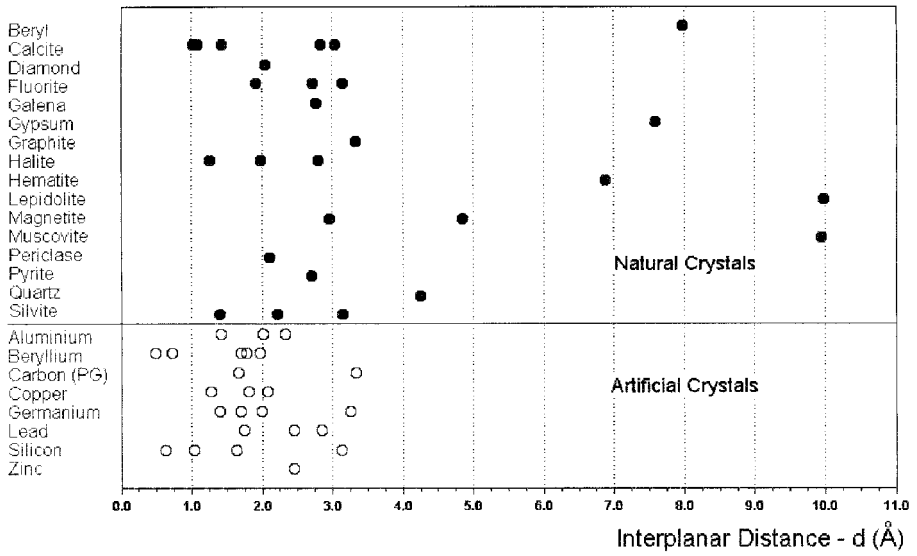

Fig. 1. A consolidated listing of 16 selected main natural crystal and eight types of usual conventional-artificial ones, as a function of their respective interplanar distances, according to their main families of planes for NDT applications. The interplanar distances of the artificial crystals are limited to only 3.4 Å. Natural occurring crystals, on account of their greater interplanar distances (ranging up to almost 10 Å), allow for measurements with NDT be also made in the subthermal and cold neutron energy ranges.

relation; β obtained directly from the rocking curve; and the isotropic temperature factor influence, represented by exp $(-M)$, where $M = B(\sin^2\theta/\lambda)$, with $B = 8\pi^2\mu_m^2$, and μ_m accounting for the quadratic mean displacement of the atoms referring to their mean positions, perpendicular to the families of planes (Mazzocchi, 1994). The Holm's formula takes the new form:

$$\Gamma = [3.758d^2\lambda t_0 N_c^2(\exp^{-M} F)^2]/\beta n^2 \sin\theta \tag{3}$$

The modified Holm's expression Eq. (3) is more complete, but it still remains dependent of parameters related to the geometrical, crystallographic and atomic properties of the crystalline material. The principal contribution of this report is also to consider the nuclear properties of the crystalline material. In this sense, it is suggested the introduction of a correcting factor defined by the ratio between the macroscopic elastic coherent scattering cross section ($\Sigma_{\text{coher.}}$), and the sum of the absorption macroscopic cross section (Σ_A) and other competitive parasite macroscopic scattering cross sections ($\Sigma_{\text{paras.}}$), where:

$$\Sigma_{\text{paras.}} = \Sigma_{\text{inc.}} + \Sigma_{\text{inel.}} + \Sigma_{\text{residual}}$$

Table 1
Results from the selection process of 19 available natural crystals for the application of the NDT

Crystal and plane (h,k,l) or (H,K,I,L)	Crystalline system and spatial group	Crystalline parameters a_0, b_0, c_0 (Å) or β_0 (°)	Vc (10^{-24} cm^3)	d_{hkl} or d_{HKIL} (Å)
Beryl ($10\bar{1}0$)	Hexagonal (beryl) — P6/mmc	8.215; 9.192	675.98	7.9804
Calcite ($10\bar{1}1$)	Trigonal-R (calcite) — R3c	4.9899; 17.064	121.90	3.0348
Corundum (0002)	Trigonal-R (corundum) — R3c	4.7591; 12.9894	129.75	6.4947
Diamond (111)	Isometric (diamond) — Fd3m	3.5670	45.39	2.0594
Fluorite (111)	Isometric (fluorite) — Fm3m	5.4638	163.41	3.1545
Galena (200)	Isometric (halite) — Fm3m	5.9360	209.16	2.7680
Gypsum (020)	Monoclinic — C2/c	5.68; 15.18; 6.29; 113.83°	496.10	7.5910
Graphite (0002)	Hexagonal (graphite) — P6mcc	2.4612; 6.7079	35.19	3.3511
Halite (200)	Isometric (halite) — Fm3m	5.6402	179.43	2.8138
Hematite (0002)	Trigonal-R (corundum) — R3c	5.0329; 13.7492	301.61	6.8746
Lepidolite (0002)	Monoclinic (mica) — C2/c	9.2; 5.3; 20.0; 98.0°	965.70	9.9903
Magnetite (111)	Isometric (spinel) — P3121	8.3940	591.43	4.8463
Muscovite (0002)	Monoclinic (mica) — C2/c	5.203; 8.995; 20.030; 94.47°	934.57	9.9614
Periclase (200)	Isometric (halite) — Fm3m	4.2117	74.71	2.1059
Pyrite ($20\bar{0}$)	Isometric (pyrite) — Pa3	5.4175	159.00	2.7088
Quartz ($10\bar{1}0$)	Trigonal-R — P3121	4.91304; 5.40463	113.01	4.2550
Scheelite (101)	Tetragonal (scheelite) — I41/a	5.242; 11.372	312.49	4.7610
Silvite (200)	Isometric (halite) — Fm3m	6.2931	249.23	3.7419
Topaz (303)	Orthorhombic — Pmna	8.394; 8.792; 4.649	343.10	1.3560

i.e. respectively, macroscopic scattering cross sections incoherent, inelastic and residual. The value of the $\Sigma_{\text{coher.}}$ should prevail over the sum of Σ_{A} and $\Sigma_{\text{paras.}}$. Applying this correcting factor, the formula F_{M} can be written as:

$$F_{\text{M}} = \Gamma[\Sigma_{\text{coher.}}/(\Sigma_A + \Sigma_{\text{paras.}})] \tag{4}$$

The application of the F_{M} expression is done at the final stage before the experimental evidence in the selection and pre-classification processes of natural occurring crystals, and it is also useful to evaluate the performance of a given variety of crystalline type depending on the neutron diffracted intensity.

4. Experimental results

The experiments for the final verification and selection of the natural crystals and their families of planes for neutron diffraction, were carried out using the neutron diffractometer installed close to the horizontal neutron extraction channel #6, allotted to experiments, on the research nuclear reactor IEA-R1 (5 MW) at the "Instituto de Pesquisas Energéticas e Nucleares- IPEN/CNEN-SP". With the Neutron Diffractometer was used the conventional monochromator Cu (220). A total of 62 samples of selected 12 representative natural crystals were examined through their respective rocking curve plots.

Table 2
Twelve of the main natural crystal types and their best families of neutron diffraction planes, tested in the Neutron Diffractometer, IPEN. The F_{M} calculated values, for each crystalline type is confronted with the respective values of the relative maximum intensity, obtained from the rocking curves. The very wide range of the F_{M} values, presenting a direct proportionality to the neutron intensity, reflects a better condition for measurements and lower statistical errors. A high F_{M} value for a certain crystal indicates a good condition on the neutron reflectivity power for an experiment with NDT

Order	Crystal and plane	Mosaic β parameter $\times 10^{-3}$ (rd)	F_{M}	Relative intensity
1st	Calcite $(10\bar{1}1)$ — RJ[a]	4.487	6 083.8	9.96 ± 0.09
2nd	Hematite (0002) — MG	5.881	1 929.4	8.78 ± 0.09
3rd	Beryl $(10\bar{1}0)$ — MG	7.850	1 746.5	7.57 ± 0.08
4th	Quartz $(10\bar{1}0)$ — MG	8.80	978.7	4.25 ± 0.07
5th	Magnetite (111) — MG	10.41	316.0	3.98 ± 0.07
6th	Pyrite (200) — MG	5.75	58.3	2.73 ± 0.07
7th	Fluorite (111) — A	5.64	31.9	1.52 ± 0.06
8th	Galena (200) — MG	15.70	28.8	1.10 ± 0.06
9th	Halite (200) — RFA	6.77	7.0	2.25 ± 0.07
10th	Gypsum (020) — MEX	16.25	5.1	1.73 ± 0.06
11th	Muscovite (0002) — MG	11.74	4.1	0.17 ± 0.01
12th	Lepidolite (0002) — MG	25.91	0.4	0.02 ± 0.01

[a] RJ, Rio de Janeiro, Brazil; MG, Minas Gerais, Brazil; A, Argentina (North); RFA, Federal Republic of Germany ("Asse Mine Salt"); MEX, Mexico (North).

The rocking curve was obtained rotating the examined crystalline sample around its vertical axis, once fixed the geometry in 2θ relative to the neutron counter (BF_3) position. For each selected crystalline type, the rocking curve more suitable to represent the families of planes was obtained, i.e. curve having a form close to the Gaussian shape, a reasonable mosaic width and having the best diffracted maximum intensity. For each rocking curve, to the experimental set of points was adjusted a curve by the minimum squares method with aid of a computer program. As the case, the resulting curve was unfolded in other Gaussian components, characterized by theirs parameters.

In Table 2, for each crystal type and main plane, are shown the calculated values F_M, the respective βs and experimental relative intensity values, obtained from 12 samples of the selected main natural crystals. The confrontation between theoretical values of the Merit Figure as directly proportional to the experimental results of the relative maximum intensity, for each crystal and families of planes, were considered satisfactory within the experimental error.

5. Conclusions

The natural crystals exhibit greater values for the interplanar distances (d ranging up to almost 10 Å) whereas with the artificial conventional crystals it is limited to only 3.4 Å. This feature of the natural crystals allows for measurements with the NDT be also made in the subthermal and cold neutron energy range.

The usefulness of the F_M expression was considered effective to take in account the nuclear properties of the crystalline constituent materials. Another advantage on the use of the F_M expression for a same crystal type is that it allows for the choice of the more suitable variety for an available experimental arrangement, optimizing the diffracted intensity and providing the expected instrument resolution. In Table 2, it can be observed that, with the application of the F_M expression as directly proportional to the relative intensity, there is only a small discrepancy in the ranking for intermediary classified crystals, imputed to the presence of great quantity of impurities having high neutron cross sections in the investigated crystalline samples.

In this study was included the diamond and graphite crystals both considered as the best natural neutron monochromators, but they were only considered here as references on the calculations. Calcite crystal is indicated for most experiments including use in low neutron flux reactors. The quartz is recommended for experiments that require better resolutions and higher energies. The magnetite or ferrita crystals are useful in measurements with magnetism and neutron polarization, as substitutes for the conventional Heusler's alloy. The crystal pyrite, galena, halite are helpful for general experiments. The fluorite (111) replaces the conventional semiconductor Ge (111) and Si (111), in the suppression of second order contamination. The crystals beryl, hematite, gypsum, muscovite and lepidolite are indicated for use with lower energy neutrons (subthermal). The crystal periclase, topaz, schelite and corundum are also indicated for use with the NDT, with great prominence of the first, and corundum (or saphire) is a good subthermal neutron filter.

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