

STRUCTURAL CHARACTERIZATION OF ADVANCED CERAMICS USING THE NEUTRON DIFFRACTOMETER DEVELOPED BY INSTITUTO DE PESQUISAS ENERGETICAS E NUCLEARES (IPEN)

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Abstract

Application of neutron diffractometer at the Instituto de Pesquisas Energéticas Nucleares, São Paulo, Brazil, in the structural investigations of advanced ceramics was presented. Methodology of the analysis of neutron diffraction patterns was tested with BaLiF₃ single crystals and also doped with Ni²⁺ or Pb²⁺ ions. The same methodology was used to investigate the HTSC phases in the system Bi-Sr-Ca-Cu-O. The system Bi_{1.7}Pb_{0.3}Sr₂Ca_{2.2}Cu_{3.5}O_{10.6} was also investigated. Addition of Pb²⁺ ions increased the fraction of high-T_c phase 2223. Symmetry in neutron multiple diffraction patterns, obtained for aluminium single crystal, was elaborated. Crystal lattice parameter for aluminium single crystal was determined at different temperatures using neutron multiple diffraction.

1. Development of the methodology for analysis of the crystalline quality of single crystals

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Recently, a study of the crystalline quality of Czochralski grown BaLiF₃ single crystals has been published [1]. In the study, intensity curves (rocking curves) obtained by neutron diffraction are related to several parameters involved in the growth method. Although the methodology employed in the study led to useful results, characterization of domains obtained by its employment lacks completeness. The present study is an attempt to develop a better methodology for the analysis of the crystalline quality of single crystals by using rocking curves measured by neutron diffraction. Neutrons are better than x-rays for this purpose since they can give information about the bulk of the crystal. X-ray, on the other hand, gives information about very small portion of crystal [1]. Tridimensional Intensity $\times \omega \times \chi$ plots, obtained from a single crystal as several Intensity $\times \omega$ rocking curves for χ stepping in a convenient interval, show, in general, more than a single mosaic domain. In principle, it is possible to determine number of domains, their relative intensities, mosaic spread of each one and angular dispersion between them. From a macroscopic point of view, determination of these characteristic corresponds to an evaluation of the crystalline quality of the single crystal under study. Figure 1 shows a tridimensional plot obtained from a BaLiF₃ single crystal and the corresponding contour map. A fit of Gaussians to a few of the individual Intensity $\times \omega$ rocking curves showed at least 5 mosaic domains. For the reason, one can say that the crystal has a bad crystalline quality. It should be noted that domains for the scans in the χ direction appear much more wider than in the ω direction. This is due to the worst resolution of the Soller collimator in the χ direction. Use of a special collimator for neutron multiple diffraction, which collimates in both vertical and horizontal directions, can partially eliminates this problem. Figure 2 is similar to Figure 1, except that it represents a BaLiF₃ single crystal with a much better crystalline quality. In fact, Gaussian fittings to a few individual Intensity $\times \omega$ rocking curves showed no more than 2 mosaic domains, one being dominant over the other.

Figure 3 shows 3 rocking curves obtained from a BTO single crystal. Such curves were measured with reflections 200, 002 and 020. Scattering vector of reflection 200 was parallel to the growth direction [100]. Scattering vectors of reflections 002 and 020 were perpendicular to growth direction. Gaussian fittings revealed the existence of several domains in the crystal.

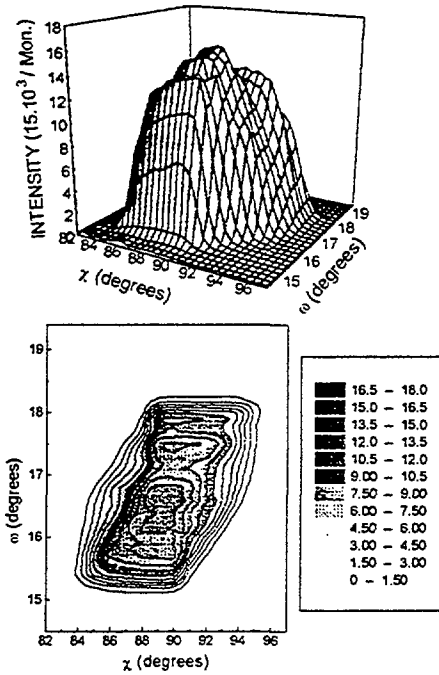


FIG. 1. Tridimensional plot (above) obtained with reflection 111 from a BaLiF₃ single crystal and corresponding contour map (below). Crystalline quality is very poor.

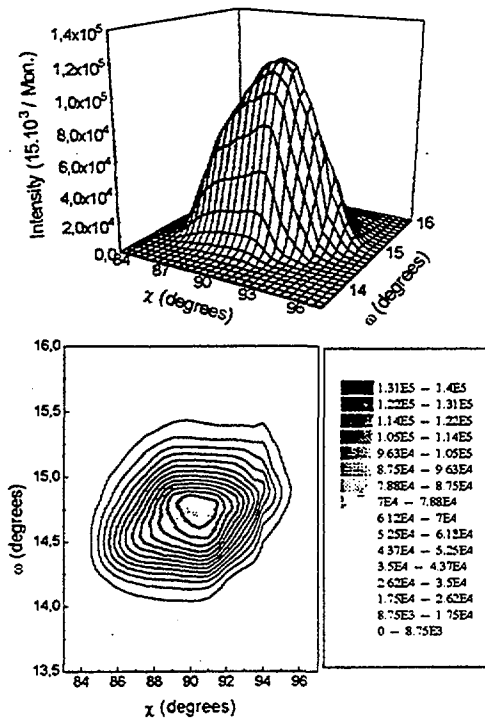


FIG. 2. Tridimensional plot (above) obtained with reflection 111 from a BaLiF₃ single crystal and corresponding contour map (below). Crystalline quality is good.

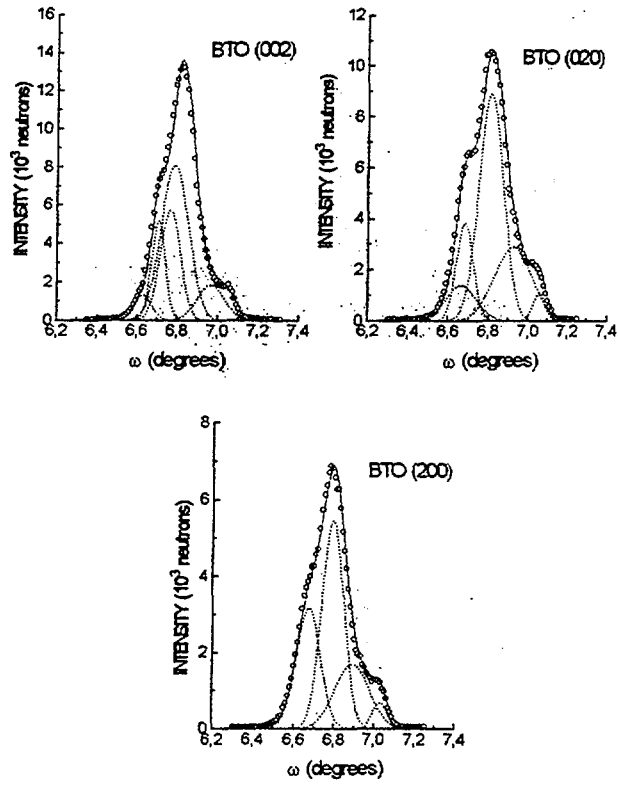


FIG. 3. Rocking curves for the growth direction, BTO (200), and for two directions perpendicular to growth direction, BTO (002) and (020) of a BTO single crystal. Gaussian fittings to curves reveal number, position and intensity of mosaic domains. Crystalline quality is poor.

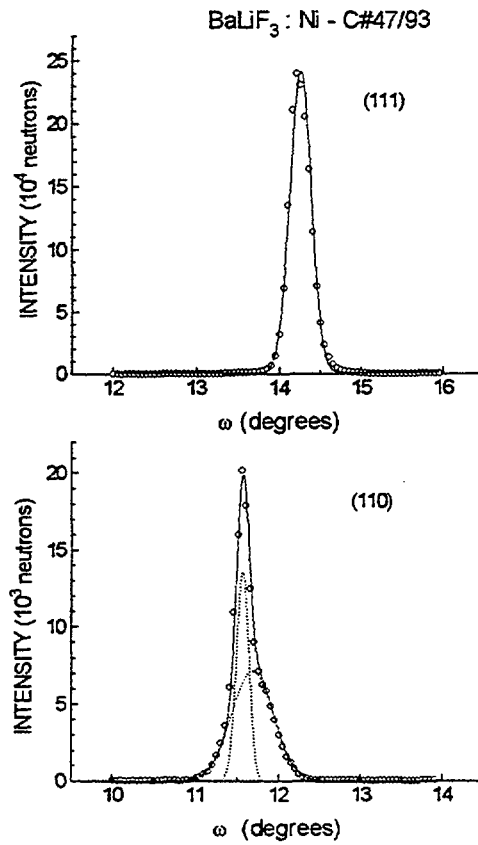


FIG. 4. Rocking curves for the growth direction (111) and a direction (110) perpendicular to growth direction of a Ni doped BaLiF₃ single crystal. Crystalline quality is good.

TABLE I- PARAMETERS FOR THE MOSAIC DOMAINS IN THE BTO SINGLE CRYSTAL, FOUND IN THE GAUSSIAN FITTINGS OF ROCKING CURVES.

domain	BTO (002)			BTO (020)			BTO (200)		
	center pos. (degrees)	f.w.h.m. (degrees)	height (counts)	center pos. (degrees)	f.w.h.m. (degrees)	height (counts)	center pos. (degrees)	f.w.h.m. (degrees)	height (counts)
1	6.6239	0.0876	1314.8	6.6600	0.1503	1387.3	6.6696	0.1182	3169.4
2	6.7007	0.0687	5217.9	6.6772	0.0831	3849.9	6.7899	0.1081	5463.2
3	6.8088	0.0997	5754.9	6.8067	0.1206	8903.5	6.8878	0.1690	1697.3
4	6.8310	0.1345	8112.0	6.9189	0.1855	2899.1	7.0270	0.0725	693.28
5	7.0101	0.1318	1870.8	7.527	0.0624	1081.2			

TABLE II. PARAMETERS FOR THE MOSAIC DOMAINS IN THE NI DOPED BaLiF₃ SINGLE CRYSTAL, FOUND IN THE GAUSSIAN FITTINGS OF ROCKING CURVES.

domain	BaLiF ₃ : Ni(111)			BaLiF ₃ : Ni(110)		
	center pos. (degrees)	f.w.h.m. (degrees)	height (counts)	center pos. (degrees)	f.w.h.m. (degrees)	height (counts)
1	14.24	0.1292	240600	11.55	0.0758	13530
2				11.67	0.2488	7173

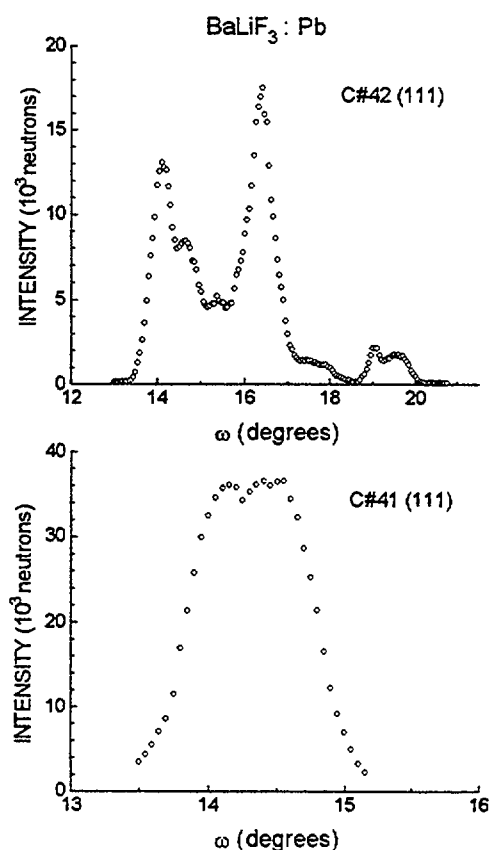


FIG. 5. Rocking curves for the growth direction of two Pb doped BaLiF₃ single crystals. Crystals C#41 and C#42 have concentrations 1% wt. and 2% wt. Pb, respectively. Although both have a bad crystalline quality, C#41 is much better than C#42.

Although obtained from a same crystal, rocking curves BTO (002) and BTO (020) revealed 5 mosaic domains whereas rocking curves BTO (200) revealed only 4 domains. It should be understood that it is impossible to determine unequivocally number and angular positions of domains from bidimensional rocking curves. Table I lists the parameters of the mosaic domains found for the rocking curves of Figure 3.

Figure 4 shows rocking curves obtained with reflections 111 and 110 from a Ni doped BaLiF₃ single crystal. Scattering vector of reflection 111 was parallel to the growth direction.

Scattering vector of reflection 110 was perpendicular to growth direction. For the growth direction only one domain is observed. The crystal has undoubtedly a quite good quality. As expected for the perpendicular direction, the quality is not so good as for the growth direction [1]. A Gaussian fitting in the case shows 2 domains with different spreads but very close one to other. Table II lists parameters found in the Gaussian fittings for both curves.

Figure 5 shows rocking curves for two Pb doped BaLiF₃ single crystals, both obtained in the growth direction. Crystals were doped with 5 % wt. and 2 % wt. of Pb and called C#41 and C#42, respectively. They were both grown by Czochralski method. Crystal C#42 has a very poor crystalline quality, probably due to extended defects produced by inclusion of Pb in the lattice. The same occurs with crystal C#41, although in a lesser degree owing to the smaller concentration of Pb in the lattice. It is expected that the crystalline quality be improved in next crystals in order to allow n.m.d. measurements. No Gaussian fittings were done for these samples.

2. Phases present in high - T_c ceramic superconductors of the Bi-Sr-Ca-Cu-O system.

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In a previous report, Parente and Mazzocchi [2] observed that the signal-to-background ratios, calculated for the peaks in neutron powder patterns of superconductors of the Bi-Sr-Ca-Cu-O system, have very low figures. Peaks are very broad with low intensity. This was ascribed to the small size of the crystallites in the samples. We have also observed that a heat treatment of samples, consisting of annealing at approximately 1000 K for several hours, produced no increase in the mean crystallite size. As a matter of fact, such annealing produced even a decrease in the mean size. Results also included a neutron powder pattern for a sample obtained by addition of lead during sintering of the superconductor. The signal-to-background ratios in this case have even lower figures, indicating that the mean crystallite size is smaller than in the case of annealed pure superconductors.

In continuation of the research, we have used a different heat treatment which will be described later on. We decided to use samples prepared by addition of lead although, as mentioned above, they produce poor figures for the signal-to-background ratio. Addition of lead is reported to increase the fraction of the higher T_c phase 2223 increasing the uniformity in the composition of this phase as well [3]. Both are desirable characteristics of the Bi-Sr-Ca-Cu-O system. For this reason, we have opted for this kind of superconductors. It should be mentioned that addition of Pb provokes a partial substitution of Pb for Bi in the lattice. A general formula, for the superconductor containing Pb can be written as Bi_{2-x}Pb_xSr₂Ca₂Cu₃O_y.

Samples of high-T_c ceramic superconductors are being currently prepared in the Materials Science Division at IPEN. A sample containing Pb to be used in this work was prepared by the solution technique [4]. The initial stoichiometry had an excess of 10 % at. of

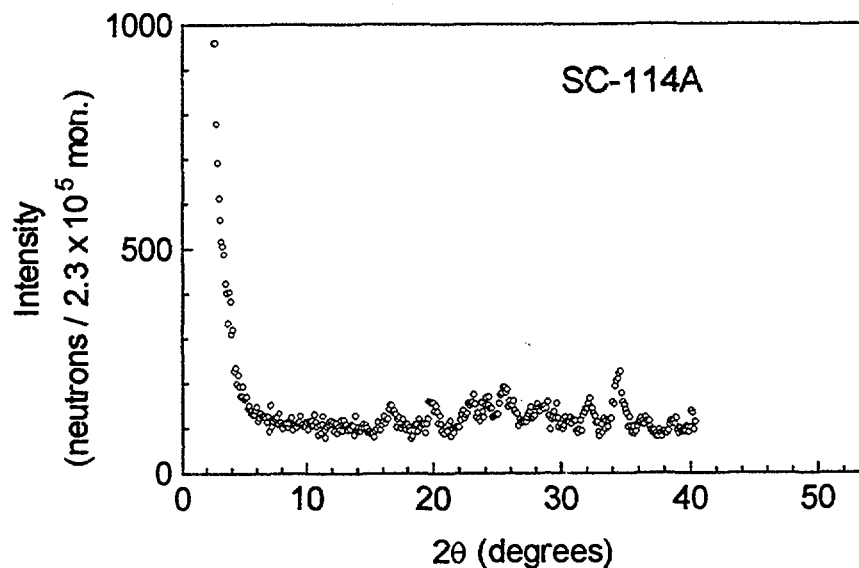


FIG. 6. Neutron powder pattern obtained with the high-Tc superconductor $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_{3.5}\text{O}_{10.6}$ after annealing at 1103 K for 30 h.

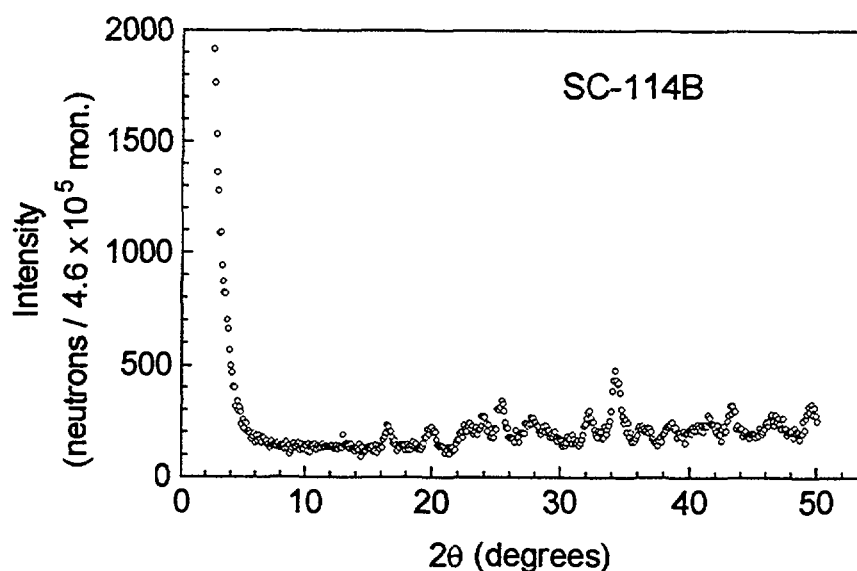


FIG. 7. Neutron powder pattern obtained with the same superconductor of Figure 6 above after a quick second annealing at ca. 1113 K for 30 minutes.

Ca and 16.7 % at. of Cu resulting in the high-Tc superconductor $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_2\text{Ca}_{2.2}\text{Cu}_{3.5}\text{O}_{10.6}$. The sample was annealed at circa 1103 K for 30 hours. With this sample, called SC-114A, we obtained the neutron powder pattern showed in Figure 6. After measurements, a new heat treatment was applied to the sample. It consisted of a quick annealing at 1113 K for 30 minutes. This temperature is about 5 K below the eutectic point of the compound. Fig. 7 shows the neutron powder pattern obtained with such sample, called SC-114B. It should be noted that the preset counting for the monitor in SC-114B pattern is twice that in SC-114A pattern. To allow an easy observation of differences between two patterns, intensity scale in SC-114A has an extension twice that in SC-114B. A simple

qualitative analysis of results shows that peaks for sample SC-114B are slightly greater than peaks for sample SC-114A. Another observation is that the background level in SC-114A is almost twice that in SC-114B. Both are evidences that crystallites in sample SC-114B have slightly greater sizes than in sample SC-114A.

3. Symmetry in multiple diffraction patterns

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In 1972, Parente studied the multiple diffraction of neutrons in an aluminium single crystal [5]. He measured a neutron multiple diffraction (m.d.) pattern with the 111 primary reflection from the crystal. The experimental neutron m.d. pattern had an extension sufficient to show two of the symmetry mirrors normally existing in a m.d. pattern. Figure 8 shows the pattern with indexing for the secondary reflections. It can be observed in Figure 8 that, for one of the mirrors (at $\phi = 60^\circ$ in the lower scale), in the unique pair of symmetrical peaks appearing in the pattern, peaks have different intensities. For the other mirror (at $\phi = 30^\circ$) 3 pairs exhibit a perfect symmetry, i. e. peaks are in symmetrical positions around the mirror and have same intensity. The author explained the differences in intensity by showing that a few of the secondary reflections, as well as the coupling reflections, involved in the formation of the peaks had different reflectivities. Different reflectivities imply different intensities. Recently, Sasaki [6] observed the same phenomenon in a X-ray m.d. pattern obtained with $\text{CuK}\alpha_1$ radiation and primary reflection 222 from a gallium arsenide (GaAs) single crystal. The crystal was epitaxially grown on top of an indium-gallium arsenide (InGaAs) substrate. The pattern obtained with the crystal is shown in Figure 9. Two symmetrical peaks having different intensities are indexed in this Figure.

This work is a systematic search for the phenomenon observed by authors above in X-ray and neutron m.d. patterns. Present authors intend to make a further investigation of the phenomenon by measuring a simulating m.d. patterns for different primary reflections from several different crystals. Simulated patterns are calculated by the computer programs MULTI [7] and MULTX [8], for neutrons and x-rays, respectively. Till now, several simulated m.d. patterns have been calculated, for a full extension of the azimuthal angle ϕ ranging from 0 to 360° . Data were plotted in circular plots, where the intensity axis is radial and the ϕ axis is circular. A circular plot allows a better visualization of the pattern symmetry. Using such a type of plot simulated patterns, we have identified two types of symmetry mirrors. One of them is a normal mirror we called "isomorphic mirror". It produces only pairs of fully symmetrical peaks like those in Figure 8, around $\phi = 30^\circ$ in the lower scale. Other is an abnormal mirror we called "anamorphic mirror". It produces pairs of symmetrical peaks having different intensities like those in Figure 8, around $\phi = 60^\circ$. It should be mentioned that such a type of mirror also produces pairs of fully symmetrical peaks. Another point to be noted is that, depending on some sample characteristics, partially symmetrical peaks can appear with so minute differences that they can be misinterpreted as being fully symmetrical peaks. Figure 10 shows a pair of peaks, simulated by MULTI, corresponding to the experimental pair at $\phi = 60^\circ$ in the lower scale of Figure 8. For the simulations, a cylindrical Al single crystal was considered. By varying radius (r), height (h) of the cylinder and mosaic spread (η) of the crystal, peaks change their shapes and intensities in an astonishing way. It can be easily verified that η plays a much more important role in the shape modification than r or h does. Figure 11 is the equivalent for Figure 10, except that the

simulated pair corresponds to the experimental pair at $\phi = 30^\circ$ in Figure 8. In this case, although a great variation in shape and intensity occurs, peaks are rigorously equal for a same pair.

Concerning the existence of isomorphic and anamorphic mirrors, we have simulated several different m.d. patterns. Examples of simulated patterns are shown in Figures 12, 13 and 14 corresponding to the primary reflections 111, 220 and 042 from a cylindrical Al single crystal. In cubic symmetry, direction [111] has a 3-fold symmetry, [220] a 2-fold symmetry and [042]. As can be readily seen in Figures 12, 13 and 14, each plot form a figure having the symmetry of the corresponding direction. Furthermore, circular plots for n odd have both anamorphic and isomorphic mirrors. Mirrors of one type intercalate into mirrors of other type, in a regular sequence. Circular plots for n even have only isomorphic mirrors. The number of isomorphic mirrors equals the order of the symmetry axis parallel to the scattering vector of primary reflection, i. e. $m_i = n$. For anamorphic mirrors $m_a = m_i = n$, if n is odd, and $m_i = 0$, if $n = \text{even}$. Of course, number total of mirrors m_t is given by $m_t = m_i + m_a$. In equalities above m_i is the number of isomorphic mirrors, m_a is the number of anamorphic mirrors and n is the order of symmetry axis. It should be noted that, the number of mirrors is twice that in a circular plot, a same mirror passing through a certain azimuthal position also passes through a position 180° from the first one. In a normal plot, these two positions are considered as being individual mirrors.

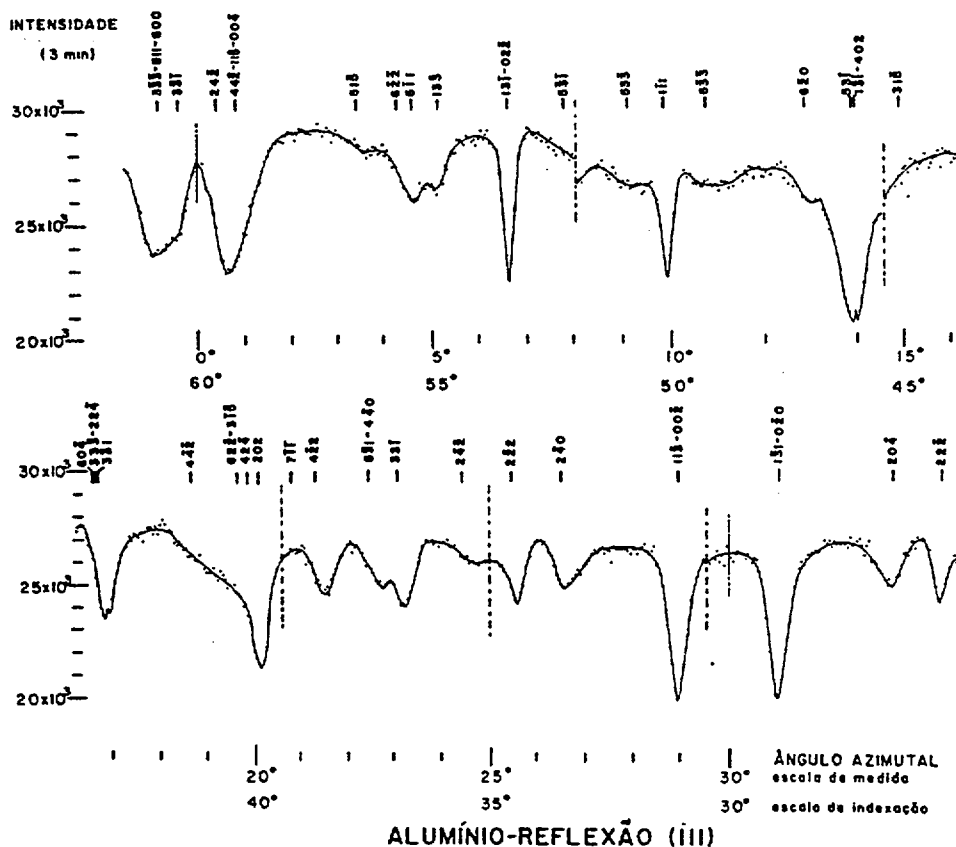


FIG. 8. Neutron m.d. pattern obtained with reflection 111 from an aluminium single crystal [5]. An anamorphic symmetry mirror is positioned at $\phi = 60^\circ$ in lower scale; an isomorphic at 30° .

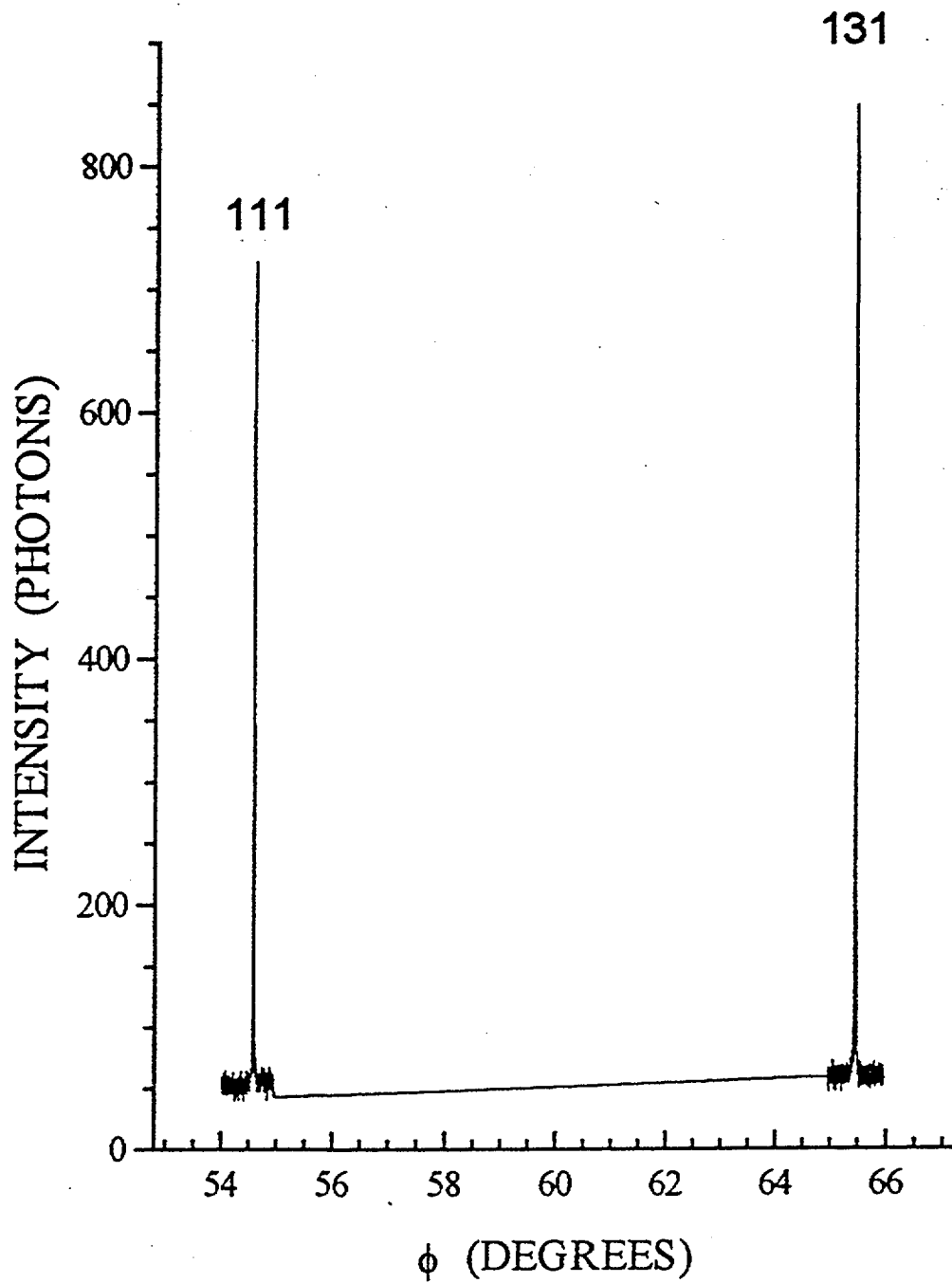


FIG. 9. X-ray m.d. pattern obtained with $\text{CuK}\alpha_1$ radiation and reflection 222 from a GaAs/InGaAs single crystal [6]. Symmetrical secondary reflections have different intensities.

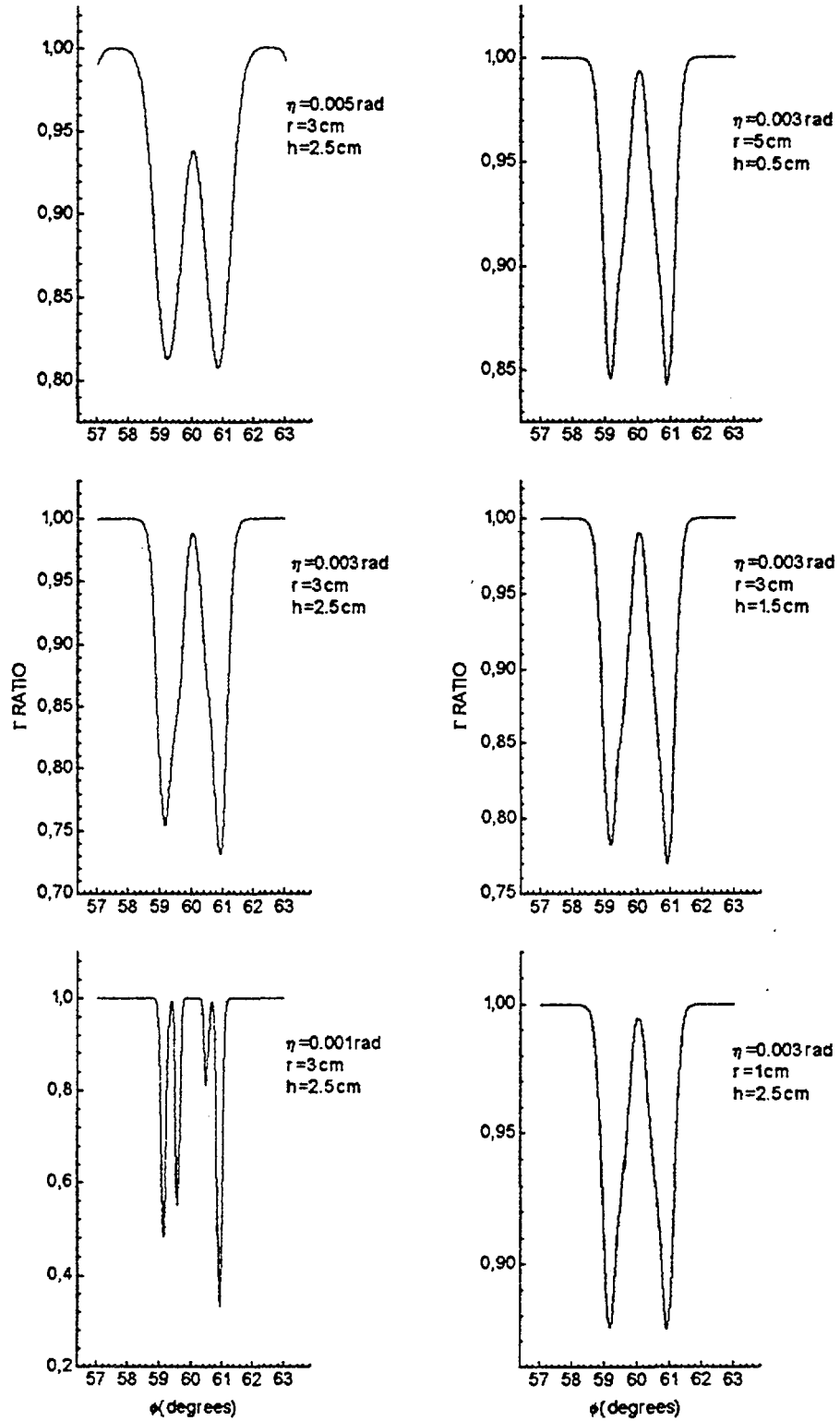


FIG. 10. Al (111) simulated peaks around an anamorphic mirror located at $\phi = 60^\circ$. Different values for the radius (r) and height (h) of a cylindrical single crystal as well as for the mosaic spread (η) were assumed in the calculations.

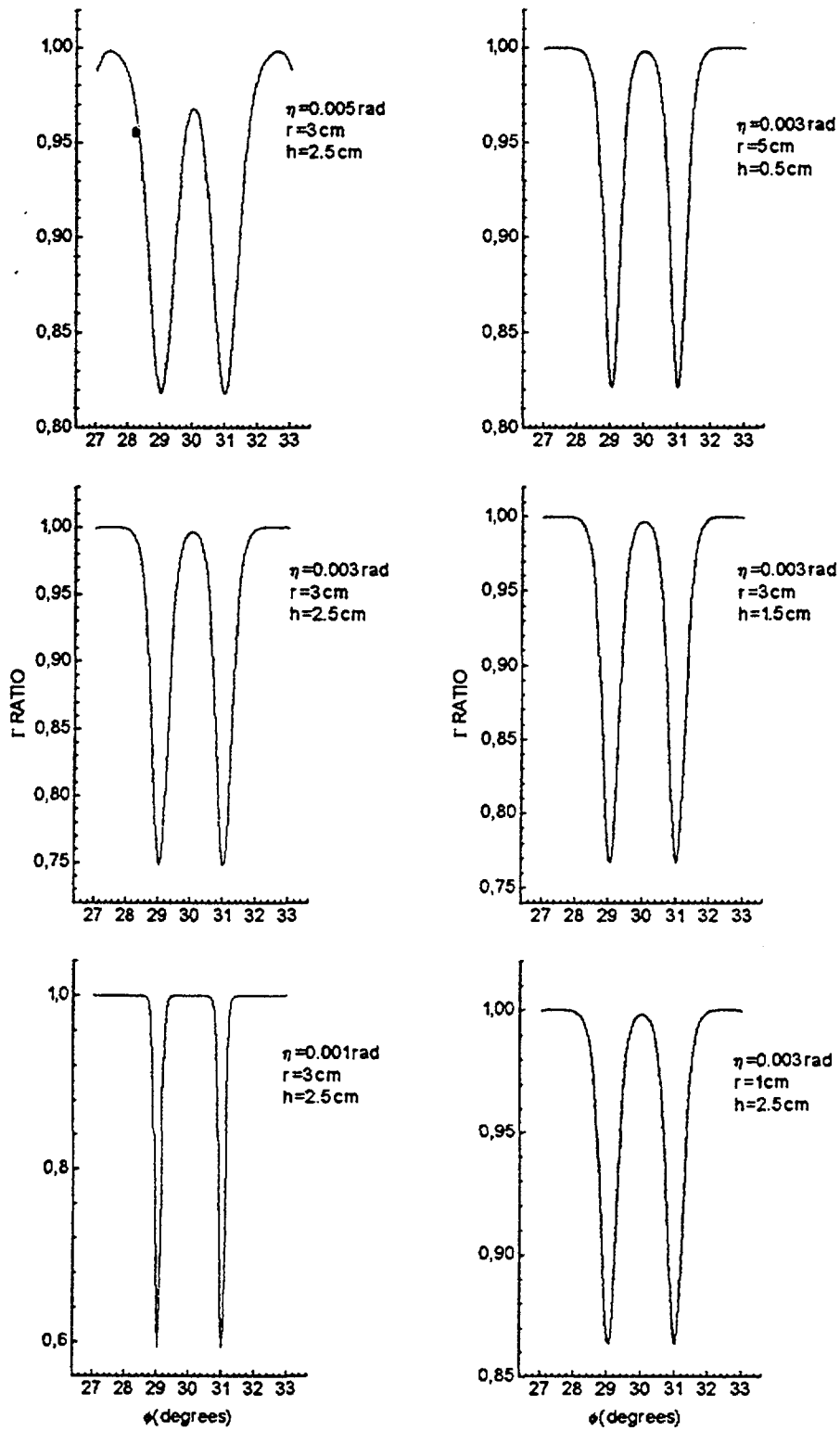


FIG. 11. Al (111) simulated peaks around an isomorphous mirror located at $\phi = 30^\circ$. Different values for the radius (r) and height (h) of a cylindrical single crystal as well as for the mosaic spread (η) were assumed in the calculations.

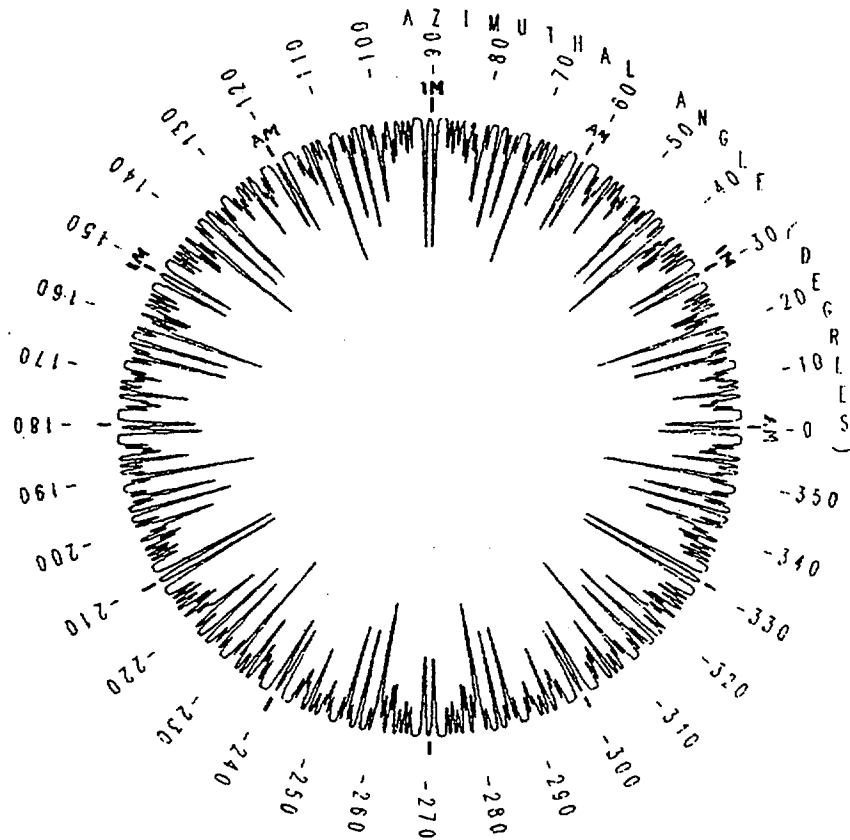


FIG. 12. Simulated Al (111) neutron m.d. pattern in a circular plot. The 3-fold symmetry of direction 111 is clearly visible in the plot. Three isomorphous mirrors (IM) intercalated into three anamorphous mirrors (AM) are shown in the plot.

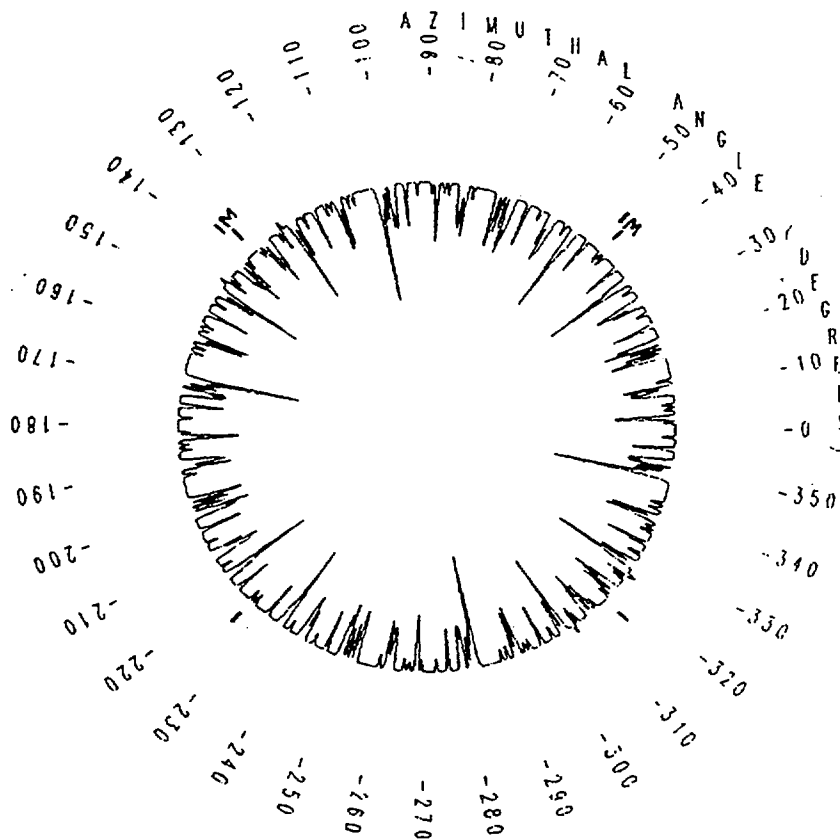


FIG. 13. Simulated Al (220) neutron m.d. pattern in a circular plot. Only two isomorphous mirrors (IM) are defined for the 2-fold symmetry of direction 110.

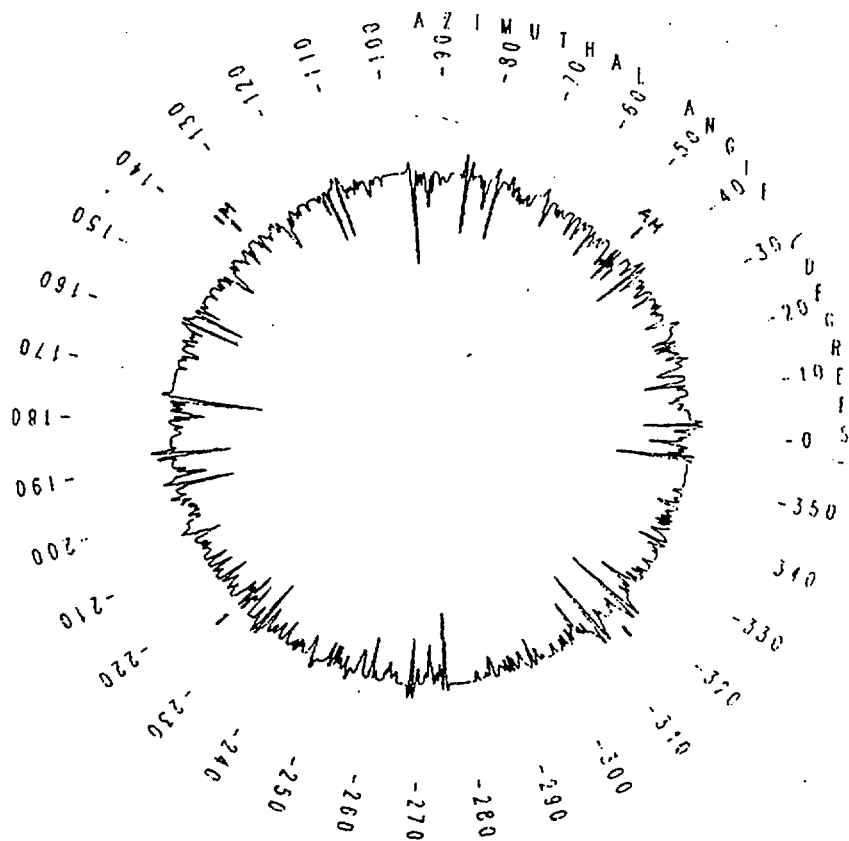


FIG. 14. Simulated Al (042) neutron m.d. pattern in a circular plot. According the 1-fold symmetry of direction 021 only one isomorphous mirror (IM) and one anamorphic mirror (AM) appear in the plot.

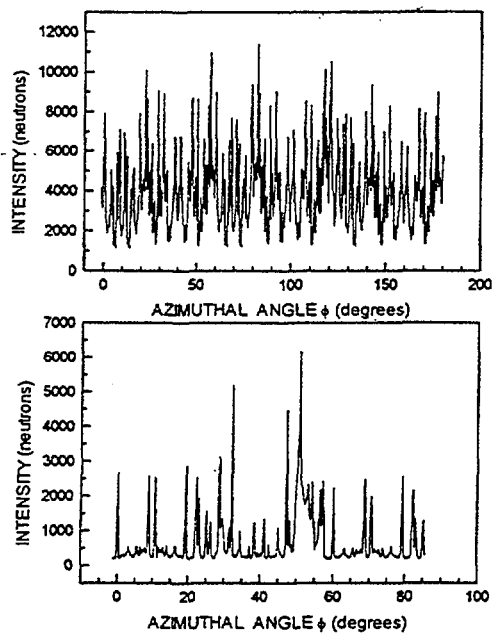


FIG: 15. Neutron m.d. patterns obtained with reflection 00.1 from a quartz (SiO_2) single crystal in phase a (above) and b (below) [9].

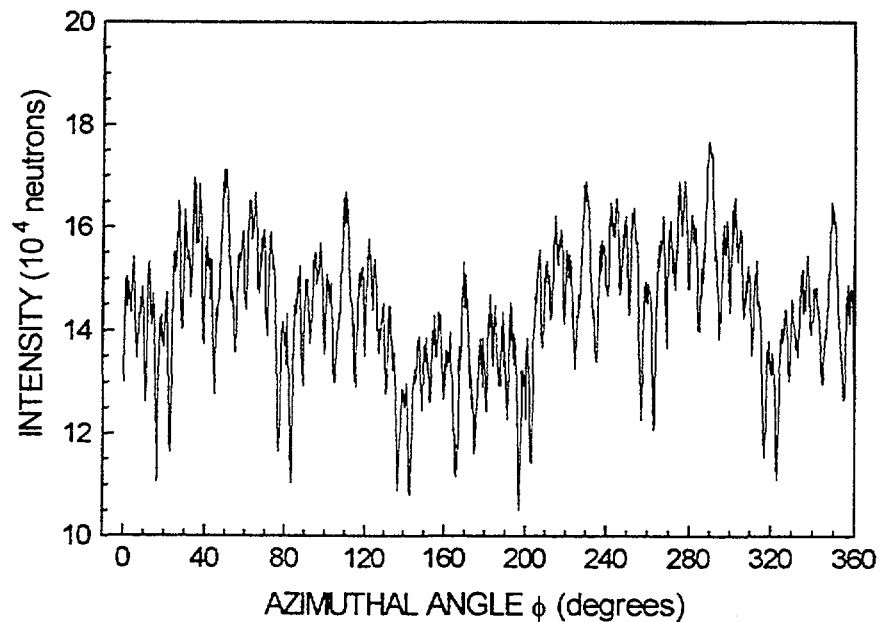


FIG. 16. Full neutron m.d. pattern measured with reflection 111 from a BaLiF₃ single crystal.

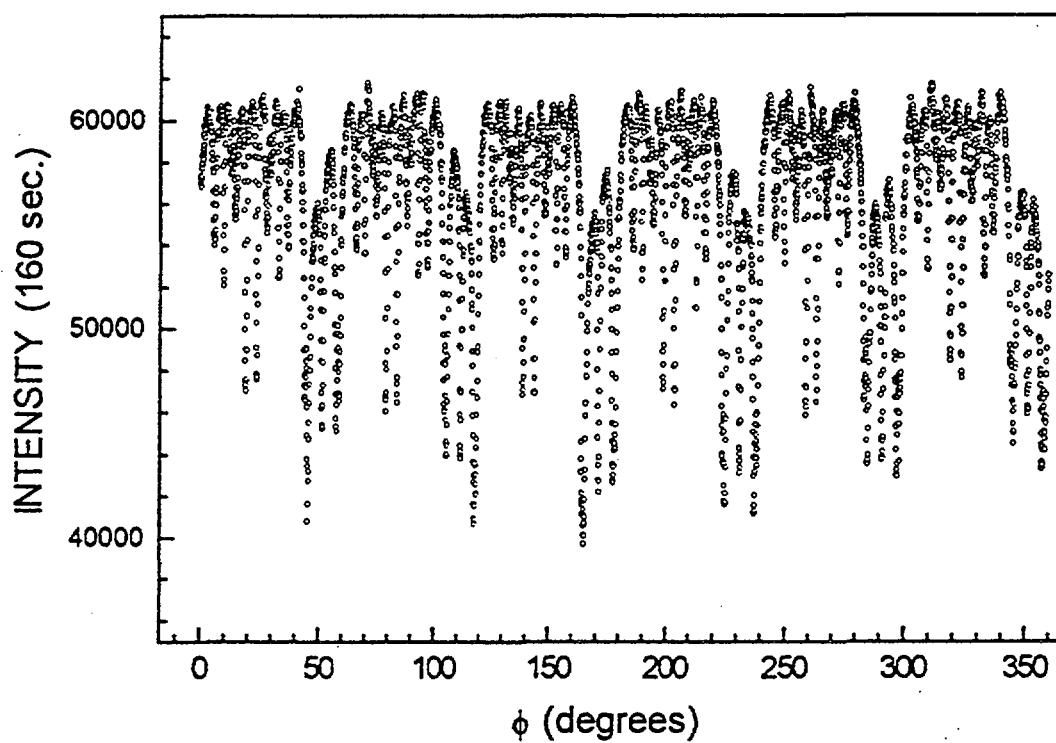


FIG. 17. Full neutron m.d. pattern measured with reflection 111 from a Cu single crystal.

We have also studied several experimental X-ray and neutron m.d. patterns in search for isomorphic and anamorphic mirrors. For instance, we have analysed the experimental 00.1 α - and β -quartz patterns measured by Mazzocchi [9]. We observed that they present no anamorphic mirrors. In this case, in a circular plot, m_a is equal to zero but m_i is still equal to n . It should be mentioned that α -quartz has a hexagonal structure. Consequently, the [00.1] direction has 6-fold symmetry and $m_i = 6$. On the other hand, β -quartz has a trigonal structure and [00.1] direction has a 3-fold symmetry with $m_i = 3$. The patterns are shown in Figure 15.

Although conclusions like those just above have been drawn from experimental patterns, existing patterns have limited extensions and are, in general, of poor quality. For this reason, we have decided to obtain full experimental patterns with good quality. It should be noted that obtainment of a full (360°) pattern is a very time-consuming procedure, particularly in a low flux reactor like ours. Nevertheless, we have already measured two full patterns. One of them is shown in Fig. 16. It was obtained with the 111 primary reflection from a BaLiF_3 single crystal. Other recently measured full pattern was obtained by measuring reflection 111 from a cylindrical copper single crystal. The scattering vector of this reflection was parallel to the cylinder axis. In this case, a quite good pattern was obtained. Fig. 17 shows such a pattern like in the pattern of Fig. 12, intercalated isomorphic and anamorphic mirrors can be observed. It should be noted that copper and aluminium are isostructural. The number of mirrors, 12 in the normal plot, is in accordance with reflection 111 from the copper cubic structure.

4. Determination of the lattice parameter of aluminium at different temperatures by neutron multiple diffraction

C. B. R. Parente, V. L. Mazzocchi

In a m.d. pattern the azimuthal position of a peak depends on the wavelength of the incident radiation as well as on the cell parameters of the crystal under investigation [10]. If the wavelength assumes a fixed value, azimuthal position becomes dependent only on the cell parameters. In this work, the cell parameter a of an Al single crystal is determined for different temperatures. The azimuthal angular positions of several peaks in a neutron Al m.d. pattern, obtained at a certain temperature, are used to determine the \underline{a} -value for that temperature. In a first method, the absolute position of a peak, i. e. its position referred to an arbitrary origin, is used. In this method, each peak produces an \underline{a} -value. In a second method, the relative positions of two neighbour peaks are used. In this method each pair of peaks produces an \underline{a} -value. Values of \underline{a} are found by comparing the absolute azimuthal position of a peak with azimuthal positions of the corresponding peak in simulated patterns, calculated by assuming different \underline{a} -values. When the azimuthal position of corresponding peaks match for a particular simulated pattern, the \underline{a} -value assumed in the simulation is assigned to the peak. In the second method, relative positions, i. e. azimuthal angular distances between two peaks, are used instead. For this method, angular distances are compared to find the \underline{a} -value for a particular temperature. For both methods, the final \underline{a} -value can be attained by linear regression of the several individual \underline{a} -values plotted.

Figure 18 shows partial neutron m.d. patterns obtained with an Al single crystal at 3 different temperatures. The azimuthal positions of the peaks are listed in the bottom of Figure 18. They resulted from Gaussian fittings of the patterns (full lines). Figure 18 illustrates how the peaks change their positions with temperature. Peak 402, for example, goes to left as

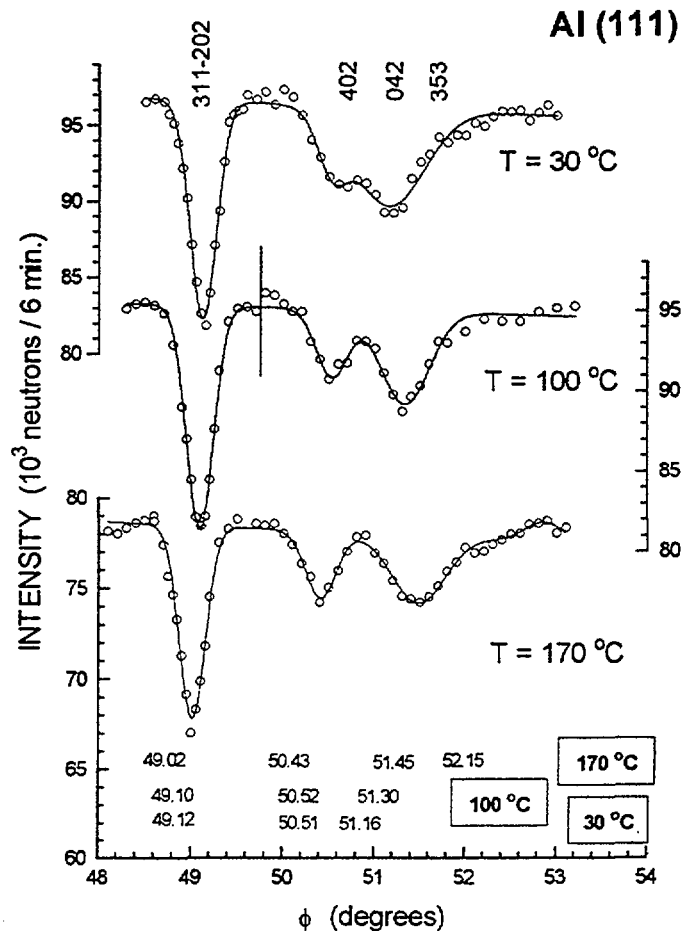


FIG. 18. Partial Al (111) neutron m.d. patterns measured at 30, 100 and 170 °C. They illustrate how peaks change positions with the temperature variation.

the temperature increases. Peak 042, on the other hand, goes to right. They form a pair with opposite behaviours and could be used in the second method. Nevertheless, each one separately could also be used in the first method.

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