Multiple Bragg diffraction in quasicrystals: The issue of centrosymmetry in Al-Pd-Mn

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When a crystal is rotated around the scattering vector for a Bragg reflection **P**, another reflection **H** may be simultaneously excited for a particular value ψ of the azimuthal angle. The plot of the intensity $I_{\mathbf{P}}$ vs ψ (called the ''azimuthal plot'') shows peaks with asymmetric features from which phases of structure factors can be obtained. Multibeam diffraction data have been obtained with a high-quality Al-Pd-Mn quasicrystal using synchrotron x rays. Rocking widths of 36 arcsec have been obtained, which made it possible to obtain data that could be interpreted using dynamical theory without any need of smearing functions to take into account the mosaic spread or other instrumental resolution effects. The asymmetric features and the peak intensity of all azimuthal plots could be fitted with phases consistent with a noncentrosymmetric structure. This conclusion was reinforced by the results of a multibeam experiment with circularly polarized x rays. This is in contrast with several other diffraction experiments based on intensity measurements in the two-beam case. Possible reasons for this discrepancy are discussed. [S0163-1829(96)00422-5]

I. INTRODUCTION

Earlier multibeam experiments on the icosahedral phase of Al-Cu-Fe (Ref. 1) have demonstrated the feasibility of extracting phase information in quasicrystals using the Renninger effect.[2] Use is made of the notion of virtual Bragg scattering (VBS),[3] whereby a weak reflection, chosen to be the principal reflection (**P**), is monitored as a function of the azimuthal angle as the crystal is rotated around the scattering vector **P**. When one or more reflections are simultaneously excited, a peak with asymmetric features is normally observed. It has been shown[3] that the asymmetry effect results from interference between different Bragg reflections, so that phases can be recovered. More specifically, when only one simultaneous reflection **H** is excited (normally referred to as the three-beam case, because three beams are present, when the incident beam is taken into account) a quantity δ called the triplet invariant can be determined from the experiment,[4]

$$\delta = \phi_{\mathbf{H}} + \phi_{\mathbf{P}\text{-}\mathbf{H}} - \phi_{\mathbf{P}}, \tag{1}$$

where $\phi_{\mathbf{H}}$ is the phase of the **H** reflection, $\phi_{\mathbf{P}}$ is the phase of the **P** reflection, and $\phi_{\mathbf{P}\text{-}\mathbf{H}}$ is the phase of the coupling reflection **P**-**H**, whose Miller indices are the differences between those of the **P** and **H** reflections.[5] The quantity δ does not depend on the position of the origin in the unit cell.

The ingredients for a VBS situation are (i) a weak **P** reflection, which is always fully excited over the azimuthal scan; and (ii) a strong, but weakly excited, **H** reflection. In this situation the global interaction between photons and crystal is weak, and only single-scattering events are important. In such a situation dynamical and kinematic theories converge to the same results, which means that the interpretation of the experimental data does not depend on crystal perfection.

It has been shown[2,3,5,6] that in a VBS situation triplet invariants can be reliably determined even when some mosaic structure is present, and the shape of the crystal is not well defined. The method has been repeatedly tested with periodic crystals whose structures (i.e., phases) were well known, and it has invariably provided the right answers.

The question of whether or not the multibeam theory used to extract triplet invariants, originally developed for periodic crystals, can be applied to quasicrystals, has been discussed in Ref. 1, and the conclusion was that quasicrystals can be treated as periodic crystals from the point of view of diffraction theory. The peculiar kind of disorder present in a quasicrystal is no different from, say, disorder due to thermal vibrations, which do not prevent a crystal from diffracting dynamically. A recent treatment based on the Darwin approach has shown that a Fibonacci quasicrystal produces the same profile for the reflecting power as does a perfect periodic crystal.[7]

The main theme discussed in this paper is the issue of centrosymmetry, or lack of it. In periodic crystals, it is a well-defined notion, even though there are pathological situations in which a clear-cut decision is difficult to reach, in view of the inevitable experimental errors.[8] The question of defining what is meant by centrosymmetry in an aperiodic crystal, which is inherently noncentrosymmetric by definition, will be deferred to Sec. V. For the moment we will adopt the following definition: let $P_A(\mathbf{r})dV_{\mathbf{r}}$ be the probability of finding atom A at point **r**. A quasicrystalline specimen is considered to be centrosymmetric if a suitable origin can be chosen within the specimen such that $P_A(\mathbf{r}) = P_A(-\mathbf{r})$.

In a centrosymmetric crystal all phases are equal to 0° or 180°, if the origin is suitably chosen. Therefore, all triplet invariants are expected to be 0° or 180°.

Most quasicrystals are considered to be centrosymmetric, because all diffraction experiments do not show obvious deviations from centrosymmetry. For example, all precession photographs and electron-diffraction patterns of icosahedral and most decagonal quasicrystals look essentially centrosymmetric. When large sets of Bragg reflections are mea-

sured quantitatively for crystallographic analyses, the intensities of Friedel pairs (**H** and $-$**H** reflections) are approximately equal, within experimental error. It was with some surprise, therefore, that early *n*-beam experiments on the icosahedral phase of $Al_{63.6}Cu_{23.6}Fe_{12.7}$ gave a value for $\delta=67.5°$, for a particular combination of Bragg reflections.[1]

The work described in this paper has been done with a different icosahedral quasicrystal, Al-Pd-Mn, whose crystal perfection is far superior to that of Al-Cu-Fe.[9] In fact, small crystalline grains can be selected which exhibit very sharp rocking curves, about 30 arcsec wide, when exposed to highly collimated synchrotron x rays.[10] The diffraction pattern of Al-Pd-Mn is very similar to that of Al-Cu-Fe. They are both icosahedral, and face-centered-cubic in the six-dimensional space in which the Miller indices are expressed.

The high quality of Al-Pd-Mn has opened up additional horizons for diffraction studies of this material. It has been found, in fact, that the mosaic structure of the material is essentially negligible, so that the azimuthal plots, that is to say, the plots of the intensity of the **P** reflection as a function of ψ, the angle of rotation around the scattering vector **P**—can be directly compared with theory without a need to convolute with *ad hoc* functions (i.e., Gaussians or similar), in order to take into account smearing effects due to mosaic structure. In this way, the widths of the azimuthal plots have no instrumental contributions, and the triplet invariants obtained in this way are very reliable.

In this paper another *n*-beam diffraction technique based on use of circularly polarized x rays will be discussed. The main idea goes back to an experiment made by Shen and Finkelstein,[11] in which they demonstrated that noncentrosymmetric phase information can be obtained with multibeam effect using circularly polarized x rays. The effect consists, for a noncentrosymmetric crystal such as GaAs, in a different response to circularly polarized x rays of different helicities, when three beams are excited simultaneously.

We propose to use the same principle to detect presence or absence of centrosymmetry in a quasicrystal. The theory developed in Ref. 11 predicts no change in the sidebands of an azimuthal plot when the helicity of the incident circularly polarized x rays is changed. Preliminary results on Al-Pd-Mn indicate small but perceptible changes for left and right circularly polarized x rays. These results will be presented and discussed in Secs. III and IV of this paper.

II. EXPERIMENT

A small grain ($0.20\times0.25\times0.33$ mm^3) of $Al_{68.7}Pd_{21.7}Mn_{9.6}$ was selected among several fragments cut with a razor blade from a large piece ($\simeq1$ mm^3) of material provided by de Boissieu. Precession photographs showed that single and sharp diffraction spots can be obtained if the selected grain is small enough. The crystal was oriented in the laboratory in such a way that the spindle axis was parallel to the (0 2 6 6 8 2),[12,13] whose scattering vector is perpendicular to the fivefold axis, and in between two adjacent spots of the several ten spots stars visible on 0-level precession photographs taken perpendicular to the fivefold axis.

The quasilattice constant a was found to be equal to 2.9040 Å, as deduced from many Bragg peaks determined in synchrotron experiments. The quasilattice constant a in this work is defined by the following equation for the reciprocal-lattice vector $\mathbf{G}_\parallel$ in Å^{-1}:

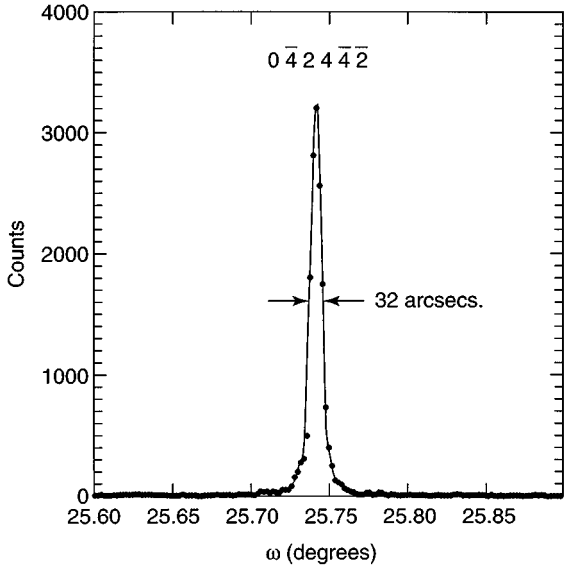

FIG. 1. Rocking curve of the $(0\,\overline{4}\,2\,4\,\overline{4}\,\overline{2})$. The counting time on each point was about 2 s. The increment $\Delta\theta$ was 0.002°. The width of the rocking curve corresponds to the instrumental resolution.

$$\mathbf{G}_\parallel = K\sum_{i=1}^{6} n_i \mathbf{e}^i, \quad G_\parallel = 2\sin\theta/\lambda,$$

where

$$K = 1/[2\pi a(1+\tau^2)^{1/2}], \quad \tau = \frac{(1+5^{1/2})}{2},$$

a is the quasilattice constant, and the xyz components of the $\mathbf{e}_\parallel^i$ basis vectors are

$$\mathbf{e}_\parallel^1 = \begin{pmatrix} 1 \\ \tau \\ 0 \end{pmatrix}, \quad \mathbf{e}_\parallel^2 = \begin{pmatrix} \tau \\ 0 \\ 1 \end{pmatrix}, \quad \mathbf{e}_\parallel^3 = \begin{pmatrix} 0 \\ 1 \\ \tau \end{pmatrix},$$

$$\mathbf{e}_\parallel^4 = \begin{pmatrix} -1 \\ \tau \\ 0 \end{pmatrix}, \quad \mathbf{e}_\parallel^5 = \begin{pmatrix} \tau \\ 0 \\ -1 \end{pmatrix}, \quad \mathbf{e}_\parallel^6 = \begin{pmatrix} 0 \\ -1 \\ \tau \end{pmatrix},$$

in agreement with the conventions of Ref. 13.

All multibeam experiments described in this paper have been done using synchrotron x rays, mostly at beamline X18-A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, at various x-ray energies between 7000 and 10 000 eV. The polarization experiment described in Sec. III was done at station $F3$ of the Cornell High Energy Synchrotron Source (CHESS). A typical rocking curve is shown in Fig. 1, whose sharpness is a clear indication of the high quality of the material.

Since the mosaic broadening is practically nonexistent in Al-Pd-Mn, sharp azimuthal plots can be obtained if the collimation in a plane perpendicular to the scattering plane is tight. For this reason all multibeam experiments were performed without a focusing mirror.

In order to find multiple-diffraction peaks, the following strategy was adopted. After deciding on a given weak reflection to be used as main reflection, called **P**, all the azimuthal angles corresponding to strong Bragg nodes lying on the Ewald sphere at the same time as the **P** reflection were calculated using a computer program, called UMWEGQXTAL, based on an algorithm described several years ago by Cole, Chambers, and Dunn[14] (CCD). The program tries with several candidate Bragg reflections and decides whether or not an angle ψ can be found such that a given candidate lies on the Ewald sphere. While for ordinary crystals Bragg reflections can be generated by considering triplets of integer numbers hkl, within a parallelepiped in reciprocal space defined by the maximum and minimum values of hkl, such a procedure cannot be used for quasicrystals, in view of the more complicated relationship between the six Miller indices and the distance of a given node from the origin. Instead, a number of reflections were considered as candidates, using a set of 360 Bragg reflection intensities obtained in the course of a crystallographic analysis.[15] All intensity values were corrected for Lorentz-polarization and absorption factors. The first 33 reflections were selected, with intensities ranging from 290 to 8.8, under the assumption that weaker reflections would not play an appreciable role in multiple diffraction. When all equivalent reflections were considered, a total of 1384 reflections were taken to be candidates in the UMWEGQXTAL program.

The orientation of the crystal with respect to the diffractometer was defined by its orientation matrix. A provision was added to CCD's algorithm to calculate the angle ψ formed by an arbitrary reference axis **M**, not parallel to **P**, with the scattering plane. In CCD's algorithm ψ is zero when **M** lies on the scattering plane, on the side of the incident beam. In order to find a given multiple-diffraction peak, the diffractometer angles are set in order to excite the **P** reflection in bisecting geometry, then a ψ scan is performed in order to bring the reference axis **M** to the desired azimuthal position. If the initial azimuth of **M** in bisecting position is ψ_0, and the angle given by CCD's algorithm, using **M** as a reference axis, is β, then the ψ scan consists in a rotation around the scattering vector by $(\beta-\psi_0)$ degrees.

In this way multiple-diffraction peaks are found usually where they are expected, except that some scanning in θ and ψ is usually required (a few hundredths and a few tenths of a degree, respectively) due to the high collimation of synchrotron beams, and unavoidable experimental errors in the orientation matrix.

A number of experimental results are shown in Figs. 2–5. In all figures the smooth profiles are theoretical fits from Shen's perturbation theory,[4,16] and the points are experimental peak intensities in θ scans. While there is no guarantee that the peak intensities are proportional to the integrated intensities (vs θ), in whose terms the theory is formulated, our practice has invariably shown that the peak shape of the θ scans over the ψ range corresponding to a multiple-diffraction peak does not change appreciably, a sure indication that our approximation is correct. A possible reason for this fact is that the intrinsic width of our θ scans is probably very small in view of the fact that the **P** reflection is usually chosen among the weakest observable reflections, and that the observed rocking width (usually around 30 arcsec) is dominated by the instrumental resolution.

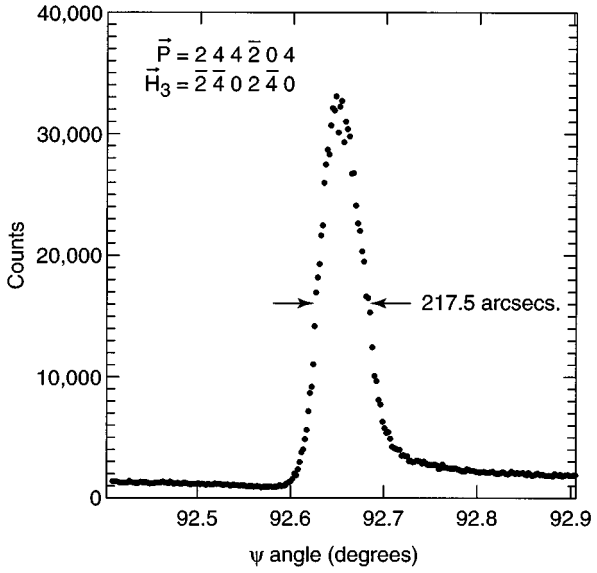

FIG. 2. Azimuthal plot of the $(2\,4\,4\,\bar{2}\,0\,4)$ reflection, a three-beam case. The simultaneous reflection **H** is the $(2\,4\,0\,2\,4\,0)$. The x-ray energy is 7000 eV. The azimuthal angle is zero when the $(0\,0\,0\,0\,1\,0)$ axis is in the scattering plane, mostly antiparallel to the incident beam, and the diffractometer angle $\psi_0=249.771°$. The counting time on each point was about 1 s. The increment on ψ was 0.002°.

Another bonus of the good quality of crystal perfection is that all profiles shown in Figs. 2–5 have been obtained without any need of convoluting the theoretical profile, calculated under the assumption of a perfectly parallel incident beam, with a smearing function, to take into account broadening to mosaic spread and instrumental resolution. The profiles of

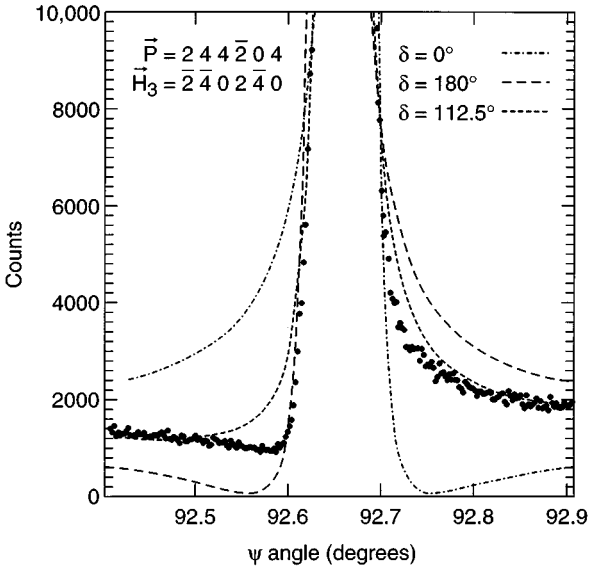

FIG. 3. The same as Fig. 2, except that the multiple diffraction peak (heavy dots) was truncated at the counting number of 10 000. The short-dashed line is a fit with a triplet invariant $\delta=0°$, and the long-dashed line is the one with $\delta=180°$. The small dashed line is the best fit, with $\delta=112.5°$.

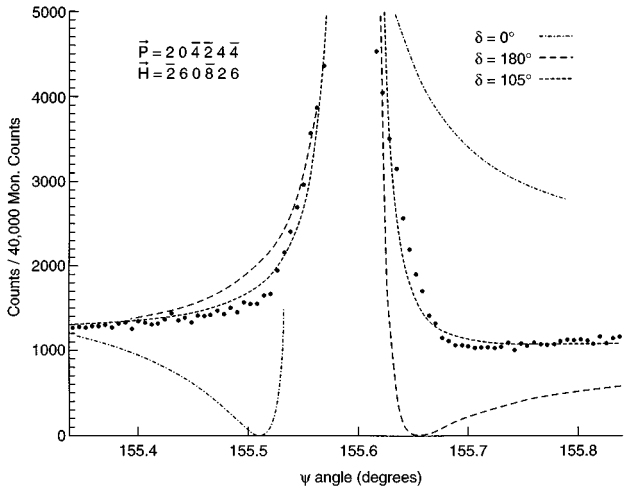

FIG. 4. Similar to Fig. 3. The main reflection **P** (2 0 $\overline{4}$ $\overline{2}$ 4 $\overline{4}$) is equivalent to the **P** reflection of Fig. 3, but the simultaneous reflection **H** is different. [**H**=(2 6 0 8 2 6)]. The azimuthal angle is zero when the (0 1 0 0 0 0) is in the scattering plane, mostly antiparallel to the incident beam, and is equal to β=145.605° for the three-beam case shown in this figure. The angle ψ, different from β, shown on the horizontal axis of this figure, is the diffractometer angle, that is, the departure from the value corresponding to the bisecting geometry in the four-circle diffractometer.

Figs. 1 and 2 have been obtained at NSLS, where the beam divergence normal to the scattering plane was about 15 arcsec. A comparison between Fig. 1, which shows a θ scan 30 arcsec wide, and Fig. 2, which shows a three-beam azimuthal peak whose width is 218 arcsec, indicates that smearing effects are indeed negligible.

The fits of Figs. 3, 4, and 5 have been done using the structure factors calculated by Boudard *et al.*[15] (see Table I). Initially, it was not possible to obtain any kind of a reasonable fit, because the experimental profiles were thinner than those calculated from theory. Usually, the opposite situation is found, which requires the use of convoluting smearing functions (Gaussians, or similar) to bring about agreement between theory and experiment. The only explanation for this awkward situation is the use of incorrect values of structure factors. We assumed that the strong structure factors are reasonably well calculated by theory, but that the weak ones are probably not too reliable. This assumption has been corroborated by recent experiments in our laboratory.[17]

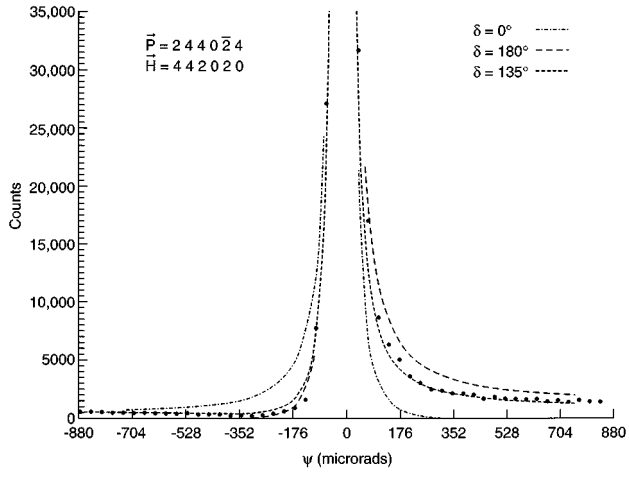

FIG. 5. Similar to Fig. 3. The main reflection **P** (2 4 4 0 $\overline{2}$ 4) is equivalent to the **P** reflection of Fig. 3. In this case the **H** and the **P**-**H** reflections are equivalent. The azimuthal angle β is 9.105°. The ψ angle shown on the horizontal axis of this figure is the departure of the diffractometer angle from the exact value for three-beam diffraction (see the caption to Fig. 4 for explanation of symbols: β and ψ). Again, a good fit is obtained with δ=135°, while the centrosymmetric values (0° and 180°) give poor fits.

It will be recalled here that the width of an azimuthal profile, according to Shen's theory,[4] is very sensitive to the magnitude $F_{\mathbf{P}}$ of the structure factor for the **P** reflection. If the structure factor of the **P** reflection is treated as an adjustable parameter, then good fits are obtained. It is essential to stress that changing $F_{\mathbf{P}}$ only changes the width, without affecting the asymmetry effect. Thus it appears that three-beam diffraction is also a good method for measuring the magnitudes of weak structure factors, provided the strong ones are well known. The F values used in the fits of Figs. 3, 4, and 5 are listed in Table I.

It will be noted that all **P** reflections listed in Table I are equivalent. Their calculated and fitted values, however, are quite different for 8124 and 7000 eV. This reflects the fact that the **P** reflection, which is exceedingly weak, is one in which the atoms are almost exactly out of phase. In this situation, small changes in individual scattering factors give rise to large changes in F values. This is reflected in the table of calculated values,[15] which shows a large variation for the weak reflection, but small, if any, effects, on the strong reflections, when the x-ray energy is changed. The ratio between fitted and calculated values for the **P** reflection at 8124 eV is quite large (3.8), which corresponds to a ratio of 14.5 in the intensities. However, if we consider the ratio, squared, between a strong reflection such as **H** (=4 4 2 0 2 0) and the **P** reflection (=2 4 4 0 2 4), using the value from Ref. 15 for the **H** reflection and our fitted value (=0.011 08) for the **P** reflection, we find a value of 1988, which is only a factor of 2 off the experimental value (−923) from Ref. 15. A factor of 2 can easily be accounted for by extinction on the strong **H** reflection. It is clear from Figs. 3–5 that the triplet invariants for which the best fits are obtained are far from 0° and 180°, the only values consistent with centrosymmetry. When we try to fit with δ=0° or 180°, we obtain profiles inconsistent with the experimental results, as shown in Figs. 3 and 5.

III. POLARIZATION EXPERIMENT

Use of circularly polarized x rays in n-beam experiments can enhance the sensitivity to phase effects, especially when the major issue of concern is the presence or absence of centrosymmetry. When a noncentrosymmetric crystal is used for a three-beam experiment, and the triplet invariant δ is equal to zero, there is no asymmetry effect, as shown by Eqs. (23-a) and (23-b) of Ref. 4.

The latter equations, however, have been obtained for linearly polarized x rays. It has been pointed out[11] that the asymmetry effect with δ=90° becomes visible if circularly polarized x rays are used, and that the asymmetry is reversed when the helicity of the incident photons is changed. For a centrosymmetric crystal, all δ's are equal to 0° or 180°, and

TABLE I. Structure factor values used in three-beam experiments (Figs. 3–5). The values listed in the central column are the magnitudes of those calculated by de Boissieu *et al.* (Ref. 15). The values on the right column (F_f) are those actually used in the fits. All **P** reflections listed are equivalent. The calculated values are not necessarily all equal because anomalous dispersion is taken into account (see text, Sec. II). The parameters M and N depend only on the Miller indices, and are defined in Ref. 13.

	Miller indices	M	N	F values (electrons/Å^3)	X-ray energy (eV)	F_f values (electrons/Å^3)
P	$2\,4\,4\,\bar{2}\,\bar{0}\,4$	176	112	0.006 27	7000	0.006 27
H	$2\,4\,0\,\bar{2}\,\bar{4}\,0$	128	80	0.490	7000	0.490
P-H	$4\,8\,\bar{4}\,\bar{4}\,\bar{4}\,\bar{4}$	464	288	0.252	7000	0.252
P	$2\,0\,4\,\bar{2}\,\bar{4}\,4$	176	112	0.006 27	7000	0.006 27
H	$2\,\bar{6}\,0\,\bar{8}\,2\,6$	464	288	0.252	7000	0.252
P-H	$4\,\bar{6}\,4\,\bar{6}\,2\,\bar{10}$	672	416	0.355	7000	0.355
P	$2\,4\,4\,0\,\bar{2}\,4$	176	112	0.002 91	8124	0.011 08
H	$\bar{4}\,4\,2\,0\,\bar{2}\,0$	128	80	0.494	8124	0.494
P-H	$\bar{2}\,0\,2\,0\,4\,4$	128	80	0.494	8124	0.494

there is no asymmetry effect for circularly polarized x rays.[18]

With a perfect noncentrosymmetric crystal such as GaAs, whose phases are all well known, these results can be exploited to characterize the polarization parameters, called Stokes-Poincaré parameters.[19] The same technique can be used to decide between centrosymmetry or the lack of it.

An experiment has been performed with circularly polarized x rays on beamline $F3$ at the Cornell High-Energy Synchrotron Source (CHESS), in which a quasicrystal was used as a specimen. In order to obtain a good percentage of circularly polarized x rays, the receiving slit before the monochromator was moved up and down by 1 mm, so that x rays emitted outside of the orbital plane were used for the experiment. The Stokes-Poincaré parameters of the beam, under those conditions, had been determined earlier in a previous independent experiment.[19] The percentage of circular polarization P_c was calculated to be 0.648.

The sensitivity of a n-beam experiment to polarization parameters depends on the extent to which the scattering vector of the simultaneous reflection **H** is out of the scattering plane for the **P** reflection. In the coplanar case there is no sensitivity to polarization parameters. Such sensitivity can be measured by a parameter[18,20] $k_c=[\mathbf{H}-(\mathbf{H}\cdot\mathbf{P})\mathbf{P}/\mathbf{P}]\lambda\sin\beta$, where β is the angle between the normal component of **H**, perpendicular to **P**, and the scattering plane for the **P** reflection. In choosing the Miller indices for an n-beam experiment, there are some constraints which limit the number of options available. The x-ray energy sets a limit on the q values of the accessible reflections ($q=2\sin\theta/\lambda$) but the most important constraint is the fact that the **P** reflection must be weak, and the **H** and **P-H** reflections must both be strong. It turns out that one of the best combinations we could find, yielding a relatively high value for k_c ($=0.19$) is a four-beam case. The Miller indices are the following: $\mathbf{P}=(2\,0\,4\,2\,4\,4)$, $\mathbf{H}_1=(6\,0\,0\,4\,4\,6)$, and $\mathbf{H}_2=(2\,0\,\bar{10}\,8\,8\,4)$. The x-ray energy was 10 000 eV.

The experimental azimuthal profiles are shown in Fig. 6. It is clear that near the sidebands of the peak there is a perceptible difference between the two polarizations, which tends to vanish at the extreme ends of the ψ range. Such a difference can only be explained as a result of lack of centrosymmetry in the structure of the quasicrystal.

We do not see in this case a reversal of the asymmetry effect, as observed in Ref. 11 for GaAs. Conversely, we see that for one polarization the intensity on the sidebands is slightly greater on both sides than for the other polarization.

The theory indeed shows that this is what we expect in a case like this. Figure 7 shows two calculated plots, for the two different polarizations, obtained with parameters appropriate to the experimental situation of Fig. 6. Details on how these plots have been obtained from theory will be given in Sec. IV. The points correspond to one of the two experimental profiles shown in Fig. 6. On the scale of Fig. 7, the two experimental profiles would look practically identical.

Even though the calculated profiles show a difference much greater than the one observed experimentally, the difference is qualitatively reproduced by the theory and it is in the right direction. A possible explanation for the discrep-

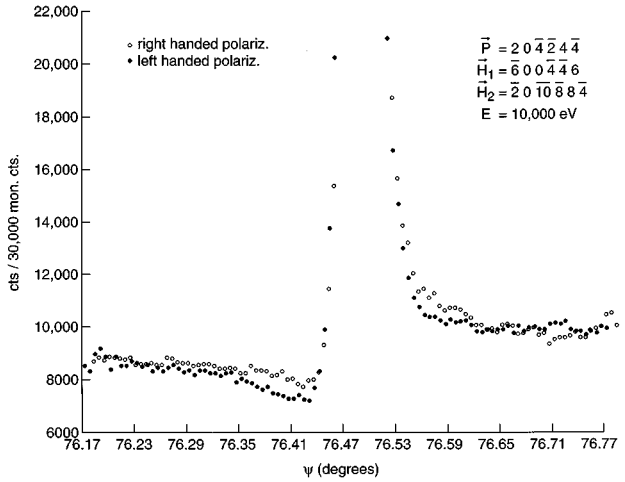

FIG. 6. Effect of changing the helicity of circularly polarized x rays. Main reflection $\mathbf{P}=(2\,0\,4\,2\,4\,4)$; simultaneous reflections: $\mathbf{H}_1=(6\,0\,0\,4\,4\,6)$, $\mathbf{H}_2=(2\,0\,\bar{10}\,8\,8\,4)$. A difference is clearly visible on the sidebands near the central peak, and tends to disappear as the two-beam condition is restored, at the extreme ends of the plot. A centrosymmetric crystal would not show any difference between the two polarizations. The percentage of circular polarization was $P_c=0.648$.

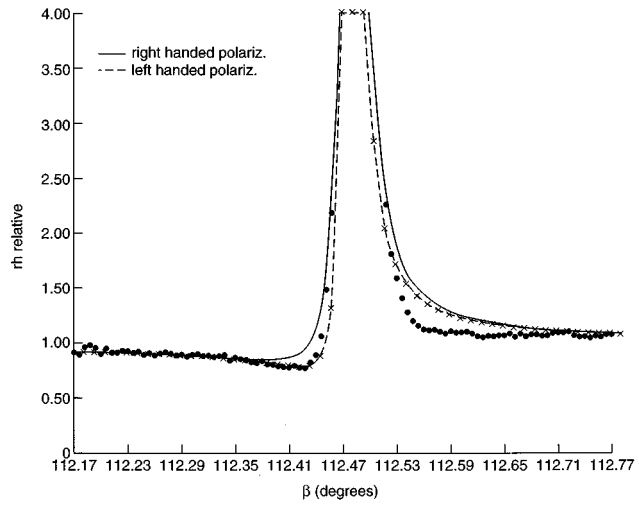

FIG. 7. Calculated profiles for the multibeam experiment of Fig. 6. The experimental points correspond to one of the experimental profiles of Fig. 6 (filled circles). The angle β in this plot is the azimuthal angle, defined to be zero when the (0 1 0 0 0 0) is on the scattering plane, mostly antiparallel to the incident beam. The multibeam intensity plotted here vs β is relative to the two-beam intensity. The right-handed polarization corresponds to a profile systematically higher than the left-handed one, in agreement with experiment.

ancy between experiment and theory is the effect of the unpolarized component that exists in the beam, which was not taken into account in the computations.

IV. COMPUTATIONAL DETAILS

We will explain in this section how the computed profiles of Fig. 7 have been obtained. For this part we used the program NBEAM,[21] which is based on exact solutions to the diffraction problem, as opposed to the perturbational approach[4] used in the fittings described in Sec. II. There is no special reason to use an exact theory for this analysis. Since we are looking at the sidebands of the multiple-diffraction peak, the perturbational approach would have been legitimate. However, a version of Shen's program set up for four beams was not available, so the only way out was to use NBEAM. Since the difference between the two plots, corresponding to the two polarizations, is very small, we initially disregarded this difference, and used a version of NBEAM set up for linear polarization.

Since this is a four-beam case, there are two triplet invariants to consider:

$$\delta_1 = \delta_{\mathbf{H}_1} + \phi_{\mathbf{P}\text{-}\mathbf{H}_1} - \phi_{\mathbf{P}}\,,$$
$$\delta_2 = \phi_{\mathbf{H}_2} + \phi_{\mathbf{P}\text{-}\mathbf{H}_2} - \phi_{\mathbf{P}}\,. \tag{2}$$

Several combinations of δ_1 and δ_2 were used in the attempt to find the best fit. In the end we were able to decide that the best fit was obtained with $\delta_1 = 180°$ and $\delta_2 = 67.5°$. The magnitudes of the structure factors were obtained from de Boissieu,[15] except for the weak **P** reflection, whose structure factor was too small, causing a much too broad multiple-diffraction peak. A reasonable fit was obtained by multiplying de Boissieu's value by 2.65. The set of structure factors and phases used in the fit with NBEAM is shown in Table II.

At this point the program NBEAM was modified for circular polarization. This was done by changing a few numbers in the boundary conditions. The only changes were in Eqs. (15) of Ref. 21, in which δ_σ and δ_π were suitably modified in magnitude and phase so as to correspond to an elliptically polarized incident beam, with a percentage of polarization $P_c = 0.685$. With these changes in place, the program NBEAM produced the two plots of Fig. 7.

V. DISCUSSION

All the evidence from n-beam diffraction experiments points in the direction of a noncentrosymmetric structure. However, as indicated in Sec. I, all conventional diffraction experiments (such as electron diffraction, precession photography, and crystallographic analysis) do not show obvious deviations from centrosymmetry.

The question has been directly addressed in an experiment specifically designed to probe the issue of centrosymmetry, or lack of it.[22] A large number of Friedel-related pairs (reflections with opposite diffraction vectors: **H** and $-\mathbf{H}$) have

TABLE II. Structure factor values used in the fitting of the four-beam experiment (Fig. 7). The structure of this table is similar to that of Table I. Since in this case an exact multibeam calculation was performed, as opposed to a perturbational treatment used for the fittings of Figs. 3–5 and Table I, the cross-term structure factor $\mathbf{H}_2$-$\mathbf{H}_1$ appears in the table. Since anomalous dispersion is weak at 10 KeV, it is assumed in Table II that $F_{\mathbf{H}} = F_{\mathbf{H}}^{*}$. Note how different F_f is for the **P** reflection from F, and how different are both values from the corresponding values at different x-ray energies (see Table I). See comments in the text (Sec. II) about the question of sensitivity of weak reflections to x-ray energy. The phases given in the right column were chosen as those giving the best fits. The parameters M and N depend only on the Miller indices, and are defined in Ref. 13.

	Miller indices	M	N	F values Magnitude (electrons/Å^3)	X-ray energy (eV)	F_f values Magnitude (electrons/Å^3)	F_f values phase (degrees)
P	$2\,0\,4\,\bar{2}\,4\,\bar{4}$	176	112	0.000 906	10 000	0.125	0.0
$\mathbf{H}_1$	$\bar{6}\,0\,0\,4\,4\,6$	336	208	0.593	10 000	0.593	67.5
$\mathbf{H}_2$	$\bar{2}\,0\,\bar{10}\,8\,8\,\bar{4}$	800	496	0.140	10 000	0.140	180.0
$\mathbf{P}$-$\mathbf{H}_1$	$8\,0\,\bar{4}\,2\,8\,\bar{10}$	800	496	0.140	10 000	0.140	0.0
$\mathbf{P}$-$\mathbf{H}_2$	$4\,0\,6\,\bar{6}\,\bar{4}\,0$	336	208	0.593	10 000	0.593	0.0
$\mathbf{H}_2$-$\mathbf{H}_1$	$8\,0\,\bar{10}\,\bar{4}\,12\,\bar{10}$	1328	848	0.332	10 000	0.332	0.0

been measured in the neighborhood of the Pd K edge, in order to increase the imaginary component of the Pd scattering factor, thereby enhancing the difference in intensity between $\mathbf{H}$ and $-\mathbf{H}$ reflections. It is well known, in fact, that in absence of an imaginary component in the scattering factors, Friedel-related pairs have exactly the same intensity, even for noncentrosymmetric structures (Friedel's law).

Most pairs have intensities that are practically identical within experimental error. However, there are isolated cases of large deviations. In a list of 38 pairs analyzed in Ref. 22, there are five pairs for which the observed difference between $\mathbf{H}$ and $-\mathbf{H}$ exceeds 10%, which is outside of the experimental error, reaching values of 25% and 44% in two extreme cases.

The data point toward a centrosymmetric structure, but the evidence is not conclusive. In the words of the authors, ''. . . these results strongly suggest that the icosahedral Al-Pd-Mn phase is centrosymmetrical or at least presents a weak noncentrosymmetric character . . . ''

In the same paper the authors analyze in detail the very meaning of centrosymmetry for a quasicrystal. It is obviously impossible to define centrosymmetry in a rigorous sense for a nonperiodic structure.

To make things quantitative, the authors consider a two-dimensional (2D) square lattice, which generates, by the cut and projection method, a one-dimensional quasicrystal. The 2D lattice is then ''decorated'' by means of atomic surfaces, which in this case are segments perpendicular to the straight line used for projection. These segments are projected as points on the straight line, indicating atomic sites. Two atoms are associated to each lattice point. If the atomic surfaces, that is to say if the segments, are identical and symmetrically located with respect to each atomic site, the structure is centrosymmetric in 2D space. However, when we look at the 1D projection, the set of atomic sites is not centrosymmetric. Actually, it looks centrosymmetric over limited regions, but the overall distribution of atomic sites lacks an inversion symmetry point. Centrosymmetry can only be observed on a local basis. It is most likely this kind of noncentrosymmetry which is responsible for the noncentrosymmetric values of the triplet invariants found in multiple-beam experiments.

It may be mentioned here that noncentrosymmetric phases, close to 90°, or 270°, have been found for some intense structure factors calculated for $P2_13$ cubic approximants of Al-Cu-Fe in the icosahedral phase.[23] An alternative definition of centrosymmetry for quasicrystals has been put forward by Chung and Durbin.[7] It is based on information obtainable from standing-wave experiments. The authors of Ref. 7 consider a Fibonacci sequence of two different atomic layers (Ga and As), and calculate the expected fluorescence dependence on rocking angle. Despite the fact that the atomic layers of Ga and As are not periodically arranged, distinctive signatures of standing-wave patterns can be observed in the computed profiles, in agreement with the fact that some kind of periodicity exists even in a Fibonacci sequence, as proved by the fact that well-developed Bragg reflections have been observed.[24] The authors of Ref. 7 have constructed histograms of all phases ϕ_i encountered by the standing waves in this model structure, for several Bragg reflections. They show that if the Ga and As layers were identical while retaining the Fibonacci sequence of planar separations, the phase distributions could be centrosymmetric even though the real quasicrystal cannot.

The question then that remains to be answered is the following: if the structure of icosahedral quasicrystals is almost centrosymmetric, how can the values found for the triplet invariant be so far from the centrosymmetric values (0° and 180°)? The best way to answer this question is to consider a ''gedanken experiment.'' Consider a three-beam experiment with GaAs, for example the combination of $\mathbf{P}=222$ and $\mathbf{H}=511$. The 222 reflection in GaAs is weak, because it is due to the difference in atomic numbers of Ga ($Z=31$) and As ($Z=33$). The electron transfer Δ is equal to 2. Suppose that by virtue of a ''magic knob'' we can change Δ arbitrarily between 0 and 2. Suppose, also, that the electron density is spherically distributed around each atomic site.

We start with $\Delta=2$, and perform a three-beam experiment. The triplet invariant we deduce from the experiment is 90°. We then reduce Δ to very small values. The 222 becomes weaker and weaker, but the triplet invariant is always the same: 90°, because δ only depends on structure, it does not depend on Δ.

This situation persists even when Δ is infinitesimal. At this point, we perform the same kind of experiment described in Ref. 22. We measure the intensities of a large number of Friedel-related pairs near an absorption edge. Since the electron densities of Ga and As are almost identical, the difference between members of each pair will be vanishingly small. We would deduce that the crystal is centrosymmetric. Actually, it is *almost* centrosymmetric. The triplet invariant we measure is always 90°, irrespective of Δ. When Δ is set equal to zero, the 222 disappears, and the experiment is no longer feasible.

VI. CONCLUSIONS

Several multiple-beam diffraction experiments have been performed with a small specimen of Al-Pd-Mn quasicrystal of high quality. The peaks observed in azimuthal scans were found to be unaffected by mosaic broadening, or other sources of instrumental resolution effects, so that no smearing functions were used to be convoluted with the calculated profiles, for a meaningful comparison between theory and experiment. The triplet invariants obtained from all experiments are consistent with a noncentrosymmetric structure. Azimuthal plots obtained with circularly polarized x rays having different helicities exhibited a small but perceptible difference, which can only happen with noncentrosymmetric structures. These results are in contradiction with other experimental data based on conventional diffraction experiments, such as electron diffraction, precession x-ray photography, x-ray crystallographic analysis, and quantitative measurements of Friedel pairs near an absorption edge.

It is concluded that a weak deviation from centrosymmetry must exist in icosahedral Al-Pd-Mn, observable over a wide range of atomic sites. Multiple-beam diffraction, being sensitive to phases rather than intensities, can detect small deviations from centrosymmetry that cannot be observed with other diffraction techniques. It is shown how the values of the triplet invariants can be very far from the centrosym-

metric values (0° and 180°) even when the deviation from centrosymmetry is very small.

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[1] H. Lee, R. Colella, and L. D. Chapman, Acta Crystallogr. A **49**, 600 (1993).
[2] Q. Shen and R. Colella, Nature **329**, 232 (1987).
[3] L. D. Chapman, D. R. Yoder, and R. Colella, Phys. Rev. Lett. **46**, 1578 (1981).
[4] Q. Shen, Acta Crystallogr. A **42**, 525 (1986).
[5] A fairly detailed review article on multiple diffraction has been published recently. See R. Colella, Comments Condens. Matter Phys. **3**, 175 (1995); **4**, 199 (1995).
[6] M. C. Schmidt and R. Colella, Phys. Rev. Lett. **55**, 715 (1985).
[7] J. S. Chung and S. Durbin, Phys. Rev. B **51**, 14 976 (1995).
[8] R. E. Marsh, Acta Crystallogr. A **50**, 450 (1994).
[9] A. P. Tsai, A. Inoue, Y. Yokohama, and T. Masumoto, Philos. Mag. Lett. **61**, 9 (1990).
[10] H. Lee, Ph.D. thesis, Purdue University, 1993 (unpublished).
[11] Q. Shen and K. D. Finkelstein, Phys. Rev. Lett. **65**, 3337 (1990).
[12] The indexing system used in this paper is based on a six Miller indices notation described in Ref. 13.
[13] J. W. Cahn, D. Schechtman, and D. Gratias, J. Mater. Res. **1**, 13 (1986).
[14] H. Cole, F. W. Chambers, and H. M. Dunn, Acta Crystallogr. **15**, 148 (1962).
[15] M. Boudard, M. de Boissieu, C. Janot, G. Heger, C. Beeli, H. U. Nissen, H. Vincent, R. Ibberson, M. Audier, and J. M. Dubois, J. Phys. Condens. Matter **4**, 10 149 (1992). Tables of observed intensities and calculated structure factors were kindly provided in the form of a private communication by M. de Boissieu and M. Boudard.
[16] Q. Shen and R. Colella, Acta Crystallogr. A **44**, 17 (1988).
[17] Y. Zhang and R. Colella (unpublished).
[18] Q. Shen and K. D. Finkelstein, Phys. Rev. B **45**, 5075 (1992).
[19] Q. Shen and K. D. Finkelstein, Rev. Sci. Instrum. **64**, 3451 (1993).
[20] Q. Shen, Acta Crystallogr. A **49**, 605 (1993).
[21] R. Colella, Acta Crystallogr. A **30**, 413 (1974).
[22] M. de Boissieu, P. Stephens, M. Boudard, and C. Janot, J. Phys. Condens. Matter **6**, 363 (1994).
[23] E. Cockaine, R. Phyllips, X. B. Kan, S. C. Moss, J. L. Robertson, T. Ishimasa, and M. Mori, J. Non-Cryst. Solids **153**–**154**, 140 (1993).
[24] R. Merlin, K. Bajema, R. Clarke, F. Y. Juang, and P. K. Bhattacharya, Phys. Rev. Lett. **55**, 1768 (1985); J. Todd, R. Merlin, R. Clarke, K. M. Mohanty, and J. D. Axe, *ibid*. **57**, 1157 (1986).