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Dynamical Three-Beam Diffraction in a Quasicrystal

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Abstract

Multiple Bragg scattering is a source of phase information. A quantity δ called the triplet invariant can be determined: $\delta = \phi_{\mathbf{H}} + \phi_{\mathbf{P}-\mathbf{H}} - \phi_{\mathbf{P}}$, where $\phi_{\mathbf{H}}$ is the phase of the simultaneous reflection **H**, **P** is the main reflection, and **P** − **H** is the coupling reflection. Previous experiments on Al–Pd–Mn have always yielded δ values far from 0 or 180°, the only values compatible with a centrosymmetric structure. In this work, a new approach is used. Instead of concentrating on the wings of the azimuthal plots, the central region is considered where the **H** reflection is fully excited. Circularly polarized X-rays are also used. The difference in the azimuthal plots between left and right polarization is a source of phase information. This approach is feasible with Al–Pd–Mn because the crystal perfection of this material is outstanding and dynamical theory can be applied to all regions of the azimuthal plot. A noticeable difference in the azimuthal plots is visible when the helicity is switched. *N*-beam dynamical theory without approximations is used to fit theoretical profiles to the experimental azimuthal plots. In all cases, a triplet invariant $\delta = 50 \pm 10°$ was found. It is confirmed that Al–Pd–Mn is not centrosymmetric.

1. Introduction

The feasibility of determining phases of X-ray reflections in quasicrystals by multiple Bragg scattering has been amply demonstrated (Lee *et al.*, 1993, 1996); in the following text, these two papers will be referred to as L1 and L2, respectively.

The principle of using multibeam diffraction for phase determination of X-ray Bragg reflections has been described in several review papers (Shen & Colella, 1986; Chang, 1987; Colella, 1995*a*,*b*; Weckert & Hümmer, 1997).

When two reflections are excited simultaneously (referred to as the 'three-beam case'), the quantity directly obtained from experiment is the so-called 'triplet invariant' (δ), a linear combination of phases for the three reflections involved in the experiment (Shen, 1986): the main reflection, whose scattering vector is **P**; the simultaneous reflection (scattering vector **H**), which is excited by a suitable rotation of the crystal around **P**; and the coupling reflection, whose scattering vector is **P** − **H**. A more complete description of the principles of multiple diffraction and phase determination in crystals and quasicrystals is given in recent review papers (Colella, 1995*a*,*b*).

The work described in L1 and L2 was on Al–Cu–Fe and $Al_{68.7}Pd_{21.7}Mn_{9.6}$, respectively. Both quasicrystals were in the icosahedral phase.

The problem debated in previous multibeam experiments is the issue of centrosymmetry. In a centrosymmetric crystal, all phases are 0 or 180° when the inversion point is chosen as origin. Since a triplet invariant does not depend on the origin chosen, it is expected that all triplet invariants determined in a multibeam experiment will turn out to be either 0 or 180°. In fact, all previous multibeam experiments have provided values quite far from 0 or 180°.

The conclusion seems inescapable: Al–Cu–Fe and Al–Pd–Mn quasicrystals are not centrosymmetric. This conclusion is in contradiction with several other experiments mentioned in L1 and L2.

The apparent controversy is discussed in great detail in L2, and the tentative conclusion given there is that a phase-sensitive experimental technique such as multibeam diffraction is enormously sensitive to even a small deviation from centrosymmetry. Since a quasicrystal, by its very nature, cannot be rigorously centrosymmetric, triple invariants can be quite different from 0 or 180° even though the overall structure is almost centrosymmetric.

To probe the issue further, we discussed in L2 (§III) the use of circularly polarized X-rays. We developed and applied to quasicrystals an idea originally suggested by Shen & Finkelstein (1990).

All the multibeam experiments mentioned so far are based on the notion of virtual Bragg scattering (VBS) (Chapman *et al.*, 1981; Shen & Colella, 1987). In a VBS experiment, the **P** reflection is very weak but the **H** and **P** − **H** reflections are strong. In this situation, it has been shown that the plot of the intensity for the **P** reflection, $I_{\mathbf{P}}$, *vs* ψ, the angle of rotation around **P** (called an azimuthal plot), exhibits in general an asymmetric shape in the proximity of the peak owing to the excitation of the **H** reflection (*Umweganregung* or

Umweg peak for short). Such asymmetry, however, disappears when $\delta = 90°$. Shen & Finkelstein (1990) show that the asymmetry can be restored if circularly polarized X-rays are used instead of the usual plane-polarized beams. They also show that the asymmetry is reversed if the helicity of the X-rays is reversed. A key ingredient of their method is the use of a *noncentrosymmetric* crystal (GaAs). The effect disappears if a centrosymmetric crystal is used. The azimuthal plot is completely insensitive to the helicity of the X-rays in this case.

The great virtue of VBS is that crystal perfection is not an issue because the phase information is obtained from the wings of the azimuthal plots where the interaction between X-ray photons and the crystal is weak, so that multiple scattering (responsible for the so-called extinction effect in ordinary two-beam Bragg diffraction) is absent.

On the other hand, if the crystal is perfect, the central region of the *Umweganregung* peaks can also be utilized as a source of phase information. In this case, the *n*-beam dynamical theory developed by Colella (1974) can be applied rigorously even when multiple scattering is significant. It turns out that in this case the details of the *Umweg* peak are strongly dependent on the helicity of the X-rays, even when the crystal is centrosymmetric (Shen, 1993).

It appears, then, that use of circularly polarized X-rays adds a new twist to X-ray diffraction studies of crystal structures. The fact that the shape of an *Umweg* peak changes when the helicity of the incident X-rays is switched indicates that new structural information is available.

A previous VBS experiment (described in L2) on a small fragment of Al–Pd–Mn quasicrystal revealed a small but perceptible effect. The peak shape was slightly different for the left- and right-handed polarizations and such a difference could be qualitatively reproduced by theory.

In this paper, we describe a three-beam experiment in which a large Al–Pd–Mn quasicrystal was used. The specimen had a large surface exposed, of several mm^2, so that the boundary conditions were well defined over the whole cross section of the incident beam. The surface region exposed was carefully chosen to give sharp rocking curves in standard two-beam diffraction experiments. In this way, we were confident that dynamical *n*-beam diffraction theory could be applied to every point of the *Umweg* peak.

2. Experimental

A large slice of $Al_{71.0}Pd_{20.5}Mn_{8.5}$ quasicrystal was prepared with the surface perpendicular to a twofold axis, within 0.25°. The slice was approximately triangular in shape, with a long dimension of about 14 mm and a short dimension of 9 mm approximately. Berg–Barrett topography revealed the existence of large grains, several mm in size. The surface had been diamond polished, with one circular region electropolished. No difference in contrast was found between the electropolished and the diamond-polished regions, which was taken as proof that the whole surface was essentially strain free, except in the proximity of the grain boundaries. There the X-ray reflectivity was enhanced, an indication of strain. A suitable region, about 4 × 4 mm, was chosen and all the measurements were done within that region. Rocking curves taken with a double-crystal

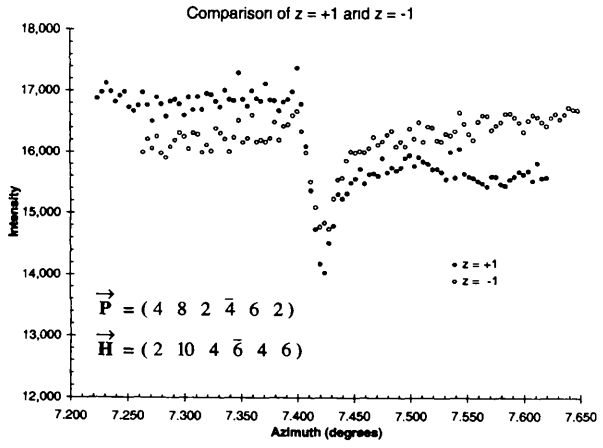

Fig. 1. Azimuthal plot of the **P** reflection in the neighborhood of the simultaneous excitation of the **H** reflection. The difference between the two plots is solely due to different helicity. The azimuthal angle ψ is defined in such a way that, when the reference axis **M** (024024) is on the scattering plane, mostly antiparallel to the incident beam, $\psi = \psi_0 = 137.244°$. The z values ($\pm$ 1 mm) refer to the position of the horizontal slit with respect to the orbital plane of the storage ring ($z = 0$). The upper position ($z = +1$) selects right-handed circular polarization, meaning clockwise rotation for an observer looking along the direction of travel for the X-ray beam.

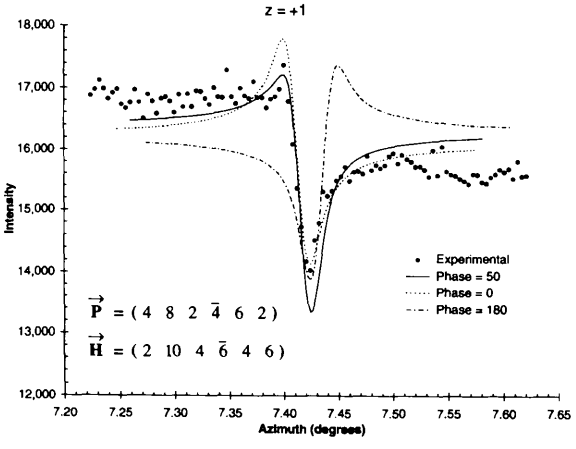

Fig. 2. The experimental points are the same as in Fig. 1 for $z = +1$ (right-handed circular polarization). The continuous lines are theoretical fits for different values of the triplet invariant δ.

spectrometer, equipped with a Ge(111) monochromator and Cu $K\alpha$ radiation in the dispersive arrangement, gave sharp and well separated α_1 and α_2 peaks.

The multibeam experiment was done at the Cornell High Energy Synchrotron Source (CHESS), at station F3. Circularly polarized X-rays were obtained by picking up X-rays out of the orbital plane by moving a slit 1 mm up and down from the orbital plane. The percentage and sense of circular polarization were obtained from a previous experiment that provided all the Stokes–Poincaré parameters of the beam (Shen & Finkelstein, 1993).

The main reflection **P** was the (482$\bar{4}$62), located on an axis which was 15.5° off a twofold axis. The indexing is done using a six-Miller-indices notation due to Cahn *et al.* (1986). See also L2 for more details. Fig. 1 shows the three-beam perturbation due to excitation of the simultaneous reflection **H** (= 2,10,4,$\bar{6}$,4,6). The **P**, **H** and **P** − **H** reflections are medium–strong and of comparable intensities. Two profiles are shown in Fig. 1 for the two different helicities.

Figs. 2 and 3 show fits done using n-beam dynamical theory (without approximations) with different values of the triplet invariant δ for the two different helicities. The theory used was the one developed by Colella (1974) for plane-polarized X-rays, with some modifications in the expressions for the boundary conditions to make it applicable to circularly polarized X-rays. More details are given in L2 (last paragraph of §IV).

The structure factors used in the fits were calculated using a large set (about 65 000 atoms) of atomic sites in a cubic box with 100 Å side, calculated using a program kindly provided by M. de Boissieu (LTPCM, Grenoble, France). The general principles of the theory used in writing the program are explained in a paper by Boudard *et al.* (1992). Thermal factors were ignored in these calculations.

A Gaussian smearing function with FWHM = 0.02° was convoluted with the theoretical profiles in order to take into account mosaic spread and beam divergence.

Fig. 4 shows the azimuthal plot for the same main reflection **P** in the neighborhood of another multiple reflection **K** (= 6,10,6,$\bar{2}$,4,4). Figs. 5 and 6 show theoretical fits for the two different helicities. The two simultaneous reflections **H** and **K** are equivalent, even with respect to the noncentrosymmetric icosahedral point group (235). They are, in fact, located symmetrically in the azimuthal plot around **P** with respect to a plane defined by **P** and **M** with **M** = (024$\bar{0}$24), which is a mirror plane. The outcome of an experiment with circularly polarized X-rays is sensitive to helicity as long as the incident and the two diffracted beams ($\mathbf{k_P}$ and $\mathbf{k_H}$ or $\mathbf{k_K}$) are not coplanar (Shen & Finkelstein, 1992).

A parameter K_c can be defined, which is a measure of the noncoplanarity of the three beams. Such a parameter

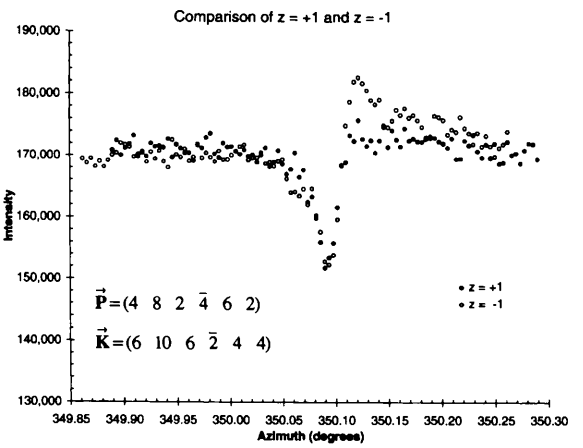

Fig. 4. The same as Fig. 1, except for **K** (the simultaneous reflection) = (6,10,6,$\bar{2}$,4,4).

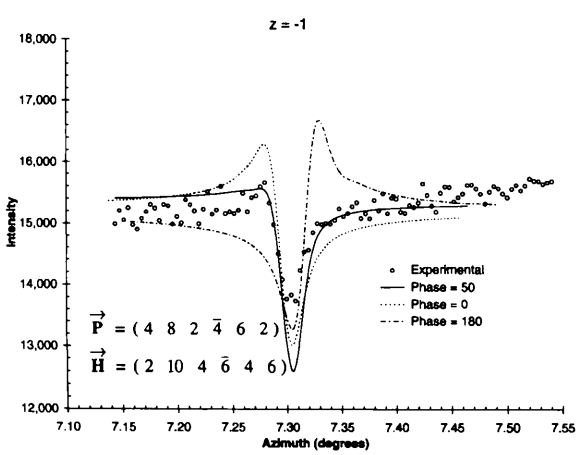

Fig. 3. The same as for Fig. 2, except for $z = -1$ (left-handed circular polarization).

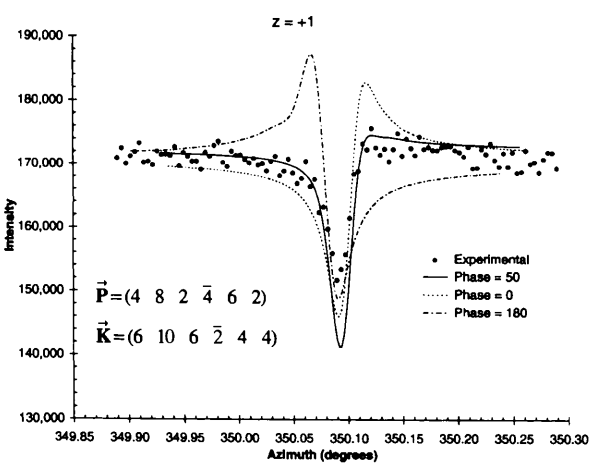

Fig. 5. The experimental points are the same as in Fig. 4, for $z = +1$ (right-handed circular polarization).

is defined (for the **H** reflection) by

$$k_c = \lambda(\sin\beta)r_\perp,$$

where λ is X-ray wavelength, $\mathbf{r}_\perp$ is the vector component, normal to **P**, of the **H** vector, and β is the angle between $\mathbf{r}_\perp$ and the $(\mathbf{k_o}, \mathbf{k_P})$ plane. The parameter k_c is equal to 0.21 for both reflections **H** and **K**. Since **H** and **K** are equivalent reflections, they have the same phases and the triplet invariants in the two cases are expected to be equal. Such is indeed the case, as the fits of Figs. 2, 3, 5 and 6 clearly show. A common value of 50° gives the best fit in all cases. When the centrosymmetric values of 0 and 180° are used, poor fits are obtained.

3. Discussion

The problem of centrosymmetry (or lack of it) in quasicrystals has been addressed by Weckert & Hümmer (1997) using the same technique of three-beam diffraction but different methodology. These authors make use of triplets for which the **P**, **H** and **P** − **H** are all strong and of comparable intensities, which is also the situation of the experiments described in this paper. The difference, however, between Hümmer & Weckert's experiments and ours is that they have used linearly polarized X-rays, whereas we have made use of circularly polarized X-rays. In such a situation, the details within the rocking curve are very sensitive to the helicity of the X-rays, as shown by Shen (1993), and it is this extra sensitivity that is exploited in our work as a source of phase information. Using plane-polarized X-rays, there is no hope to detect slight deviations from centrosymmetry using strong reflections for **P**, **H** and **P** − **H**. In a separate paper (Eisenhower *et al.*, 1998), we show in detail an example of a three-beam computer experiment on InSb, a slightly noncentrosymmetric crystal. We consider first the case of three strong reflections, for **P**, **H** and **P** − **H**, and show that the azimuthal scan is hardly distinguishable from that of grey tin, which is centrosymmetric, between In and Sb in the Periodic Table. On the other hand, when the computer experiment is performed according to the prescriptions of VBS (**P** reflection very weak, **H** and **P** − **H** quite strong), the azimuthal plots of InSb and grey tin are quite different and the signatures of centrosymmetry (or lack of it) are evident at first sight. The key point is that the **P** reflection is weak not because of a large value of $\sin\theta/\lambda$ but because of destructive interference between the atoms. We believe that this simple example of InSb and grey tin explains the discrepancy between Weckert & Hümmer's experiments and ours.

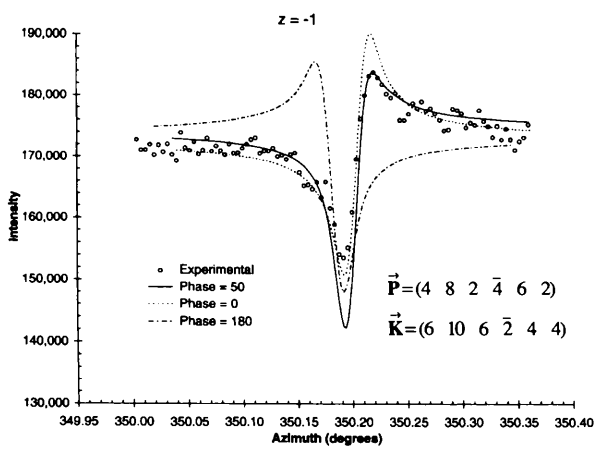

Fig. 6. The same as for Fig. 5, except for $z = -1$ (left-handed circular polarization).

4. Conclusions

The results of this work, therefore, reinforce the conclusions reached in L2, namely that the crystal structure of Al–Pd–Mn in the icosahedral phase is not centrosymmetric. As discussed in L2 (§V), the deviation from centrosymmetry is probably very small but phases can depart from their centrosymmetric values (0 and 180°) by large amounts even in the case of infinitesimal deviations from centrosymmetry.

It is gratifying to see that this three-beam experiment, done under conditions quite different from those present in the work described in L2, leads to the same qualitative conclusions.

It appears that the helicity of circularly polarized X-rays can be used as a supplementary probe in crystal structure analysis based on *n*-beam diffraction.

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