Dynamical x-ray diffraction from quasicrystals

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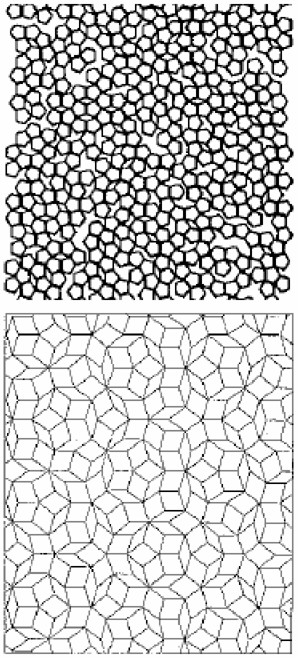
In 1984 D. Shechtman and coworkers published electron diffraction patterns from rapidly quenched, metastable samples of Al$_6$Mn that exhibited relatively sharp diffraction peaks arranged in a pattern with icosahedral point group symmetry (containing twofold, threefold, and fivefold symmetry axes) [1]. This marked the beginning of a new class of structures called "quasicrystals". Diffraction patterns from quasicrystals defied a century old belief that sharp diffraction peaks signify the presence of long-range periodic order while it is well known that periodic structures cannot exhibit crystallographically forbidden rotational symmetries (e.g., fivefold, eightfold, tenfold and twelve-fold rotation axes) [2]. It was soon realized that our notion of the equality of order and periodicity was a rather restrictive view of the full range of possibilities for ordered structures. While sharp diffraction spots are, indeed, the signature of long-range positional order, the positional order in the icosahedral phase alloys is called aperiodic rather than periodic.

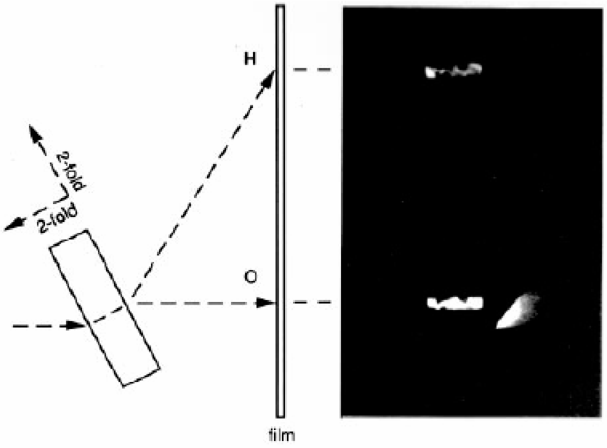
Theoretical models for the icosahedral phase alloys range from the icosahedral glass (or random packing) descriptions, which preserve bond-orientational order but lead to only relatively short positional coherence, to "perfect" Penrose tiling models (Fig. 1) which yield perfectly sharp Bragg peaks in an x-ray diffraction pattern. Soon after the discovery of the original Al-Mn quasicrystals, other alloys were discovered to exhibit stable or metastable icosahedral phases [3-5]. Prior to 1988, all known icosahedral alloys exhibited strong structural disorder evidenced by relatively broad peaks in x-ray diffraction patterns.

In 1988 a new class of quasicrystals was discovered and was labeled the Face Centered Icosahedral (FCI) alloys. A large number of ternary alloys such as Al-Cu-Fe, Al-Cu-Ru, Al-Pd-Mn, etc. fall into this category [6,7]. What was most surprising about this new set of alloys was that, when prepared properly, they presented no evidence of the disorder that plagues the original quasicrystals, now called Simple Icosahedral (SI) alloys [8,9]. Today, a large number of alloys have been discovered to present SI symmetry and FCI symmetry. The degree of disorder varies greatly from the SI alloy, Al-Li-Cu, with correlation lengths of ~300 Å to nearly perfect FCI alloys, Al-Cu-Ru and Al-Cu-Fe, with correlation lengths greater than 1 mm [8,9].

One of the most interesting and fundamental issues concerning quasicrystals has been the degree of perfection possible in aperiodic structures. The discovery of nearly perfect samples of FCI quasicrystals compelled us to ask "How



(Figure 1) (top) Shown is a random assortment of oriented pentagons viewed as a two dimensional analog of an icosahedral glass. (bottom) Penrose tiling is an example of a two dimensional quasiperiodic ordering of two types of tile, (in this case "thin" and "fat" rhombuses). Diffraction patterns from either structure would exhibit the crystographically forbidden 10-fold symmetry.



(Figure 2) Schematic (left) and results (right) of the Borrmann effect measurement. The sample is represented by the rectangle and the crystallographic orientation is illustrated directly above the sample. The dashed arrows passing through the sample depict the paths traced by the incident beam as well as the two exiting beams. The right side of the figure is an enlargement of a photograph taken down-stream of the sample in the Bragg condition. The H and O beams of the schematic have been drawn to correspond to the analogous images. When the sample is rotated about an axis perpendicular to the scattering plane, the H and the O beam disappear.

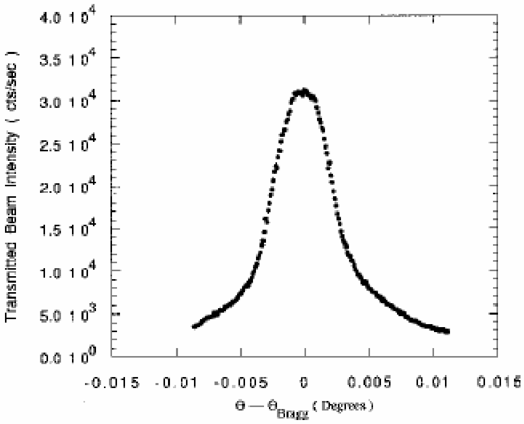
perfect can a quasicrystal be?" The resolution of this question was our initial goal. We have focused on revealing the degree of order achievable by quasicrystalline alloys by performing x-ray diffraction studies on carefully prepared samples of Al-Pd-Mn quasicrystal. This work has led to the study of dynamical diffraction in quasicrystals.

Samples of FCI Al-Pd-Mn quasicrystals were prepared by means of a Bridgman slow growth technique. The growth parameters were optimized to produce individual grains as large as 2 cm × 1 cm × 1 cm. By means of neutron scattering, the mosaic width of the grains were found to be resolution limited ($\Delta\theta < 0.02°$).

In order to resolve disorder over length scales longer than 1 mm, rather than applying typical high resolution diffraction techniques, we decided to take advantage of the coherent x-ray speckle technique [13] at the X25 wiggler source at NSLS. The results of the experiment was that the sample of Al-Pd-Mn quasicrystal scattered coherently over regions larger than 6 µm. The transverse width of diffraction peaks were resolution limited ($\Delta\theta < 0.001°$).

These results suggested that this alloy might be of sufficient quality to be considered a "perfect" icosahedral quasicrystal. In general, as the defect density decreases and, therefore, the size of the coherent scattering region increases, the kinematical scattering theory fails to be an appropriate description of the diffraction from crystalline solids. For an accurate description of the diffraction of x-rays from a perfect crystal it is necessary to apply the dynamical theory of x-ray scattering, first introduced by P. P. Ewald in 1917 and reformulated by M. von Laue in 1931.

Briefly, the dynamical theory considers the interaction between the atoms and the wave field in the crystal which is a solution of Maxwell's equations in a medium with a periodic, or perhaps aperiodic, complex dielectric constant. One consequence of the dynamical theory, discussed in more detail below, is the anomalous transmission of x-rays through a thick crystal set at the correct angle for diffraction. The theory of dynamical scattering in crystalline materials has been thoroughly reviewed in several articles [14]. The anomalous transmission of x-rays through an incommensurate or aperiodic crystal has been treated in some detail by Berenson and Birman for the special case of a one-dimensional Fibonacci lattice [15]. The effect is present when scattering from a strongly reflecting set of planes in a perfect crystal. The x-rays that scatter once also satisfy the Bragg condition for the same set of planes and can be reflected again (into the forward direction). The result of this multiple scattering is the existence of forward scattered x-rays as well as the promotion of a wavefield in the crystal, the periodicity of this wavefield is equal to the d-spacing of the reflecting planes. Some components of the wave field have minima of intensity at the absorbing atomic positions, suffer relatively small absorption and are capable of passing through even a thick sample. If the crystal is rocked out of the Bragg condition, the wavefield is eliminated and the x-rays are attenuated by the usual amount.



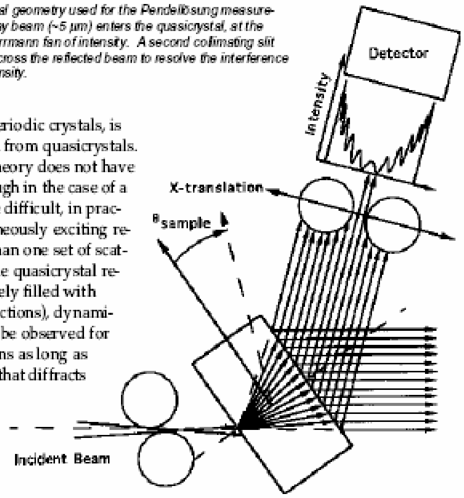
(Figure 3) Intensity of the forward diffracted beam (O beam) as the sample is rotated through the diffraction condition. The nominal zero of the horizontal scale was chosen at the center of the angular range of the reflection.

We have shown direct evidence for dynamical diffraction of x-rays from single grains of the Al-Pd-Mn icosahedral phase alloy through the observation of anomalous transmission (the Borrmann effect). For this experiment a single grain of the Al-Pd-Mn icosahedral alloy was cut and polished in the form of a parallel faced wafer. The experiment was performed on beamline X23A3 at the NSLS using 12 keV x-rays. The sample was set at the correct Bragg angle for a reflection in the Laue (transmission) geometry. The chosen reflection was one of the most intense found for icosahedral Al-Pd-Mn. In this configuration the 0.4 mm thick sample presented approximately ten absorption lengths for 12 keV x-rays (Fig. 2). The x-ray beam is incident from the left and strikes the sample at the correct Bragg angle for diffraction in the Laue (or transmission) geometry. Two emerging beams were recorded on Polaroid film placed behind the sample (right side of Fig. 2). The H beam is the diffracted Laue beam found at an angle of $2\theta_{Bragg}$ from the incident beam direction. The O beam is the anomalous transmitted (forward diffracted) beam parallel to the incident beam direction. When the sample was rotated by 0.04° away from the correct Bragg angle, no intensity at these positions was recorded. The observation of the O beam is clear evidence of dynamical diffraction from the sample.

The intensity profile of the O beam was recorded by replacing the film with a NaI scintillation detector and aperture to isolate the O beam from the H beam and other background radiation. Fig. 3 shows the intensity in the forward scattering direction as the crystal angle is scanned through the diffraction condition, again clearly showing the phenomenon of anomalous transmission. From this measurement a reasonable upper limit on the intrinsic rocking curve of the reflection is 0.004°. This can be compared to the rocking curve width of the (111) reflection of silicon which is approximately 0.002°.

Having demonstrated the phenomenon of anomalous transmission in icosahedral Al-Pd-Mn we next considered how the dynamical theory, originally for-

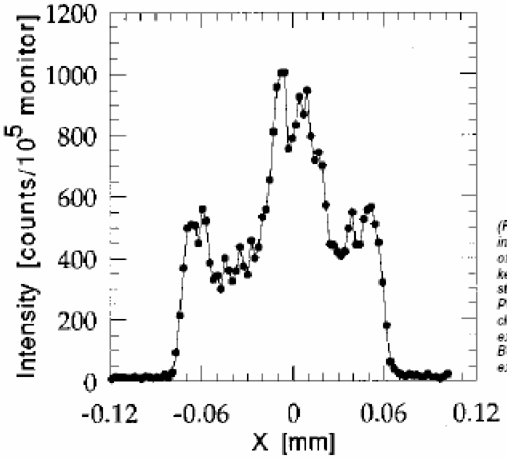
(Figure 4) The experimental geometry used for the Pendellösung measurements. The collimated x-ray beam (~5 µm) enters the quasicrystal, at the Bragg angle, creating a Bormann fan of intensity. A second collimating slit (~5 µm) can be scanned across the reflected beam to resolve the interference fringes in the reflected intensity.



mulated for perfect periodic crystals, is relevant to diffraction from quasicrystals. It turns out that the theory does not have to be modified, although in the case of a quasicrystal it may be difficult, in practice, to avoid simultaneously exciting reflections from more than one set of scattering planes (since the quasicrystal reciprocal space is densely filled with strong and weak reflections), dynamical diffraction should be observed for the strongest reflections as long as the size of the region that diffracts is sufficiently large for dynamical, rather than kinematical, scattering.

We tested this conclusion through an attempt to observe the phenomenon of Pendellösung fringes, a dynamical diffraction effect that is sensitive to subtle long-range crystalline imperfections. The dynamical theory predicts an effective birefringent character for the perfect crystal causing interference fringes in the intensity exiting the crystal. The experiment is represented schematically in Fig. 4. In our experiment, the thickness of the sample, 0.4 mm, places it in the thin crystal limit (~2 absorption lengths for the 20.5 keV x-rays) allowing all the components of the wave field to suffer a relatively small degree of attenuation. The experiment was carried out at beamline B2 at CHESS. From the results shown in Fig. 5, we observe evidence of the characteristic Borrmann Fan as predicted by the dynamical theory and although the expected fringe pattern was not observed, definite fringes are present. In addition to the Pendellösung pattern there is a large contribution to the scattering intensity due to what appears to be kinematical scattering of x-rays in the sample.

The observation of dynamical diffraction from quasicrystals holds some important implications for structural investigations of these phases. First, we point out that primary extinction effects associated with diffraction from single grains of Al-Pd-Mn, and presumably many of the other FCI alloys, may be very significant and should be carefully corrected for prior to the use of diffraction data as input to structural determinations. Second, we note that several probes based upon dynamical diffraction effects, such as x-ray standing wave fluorescence techniques multiple beam interference effects and x-ray transmission topographs, may now be employed to study the bulk and surface structure of some quasicrystals. More generally, the observation of dynamical diffraction from icosahedral Al-Pd-Mn is a striking confirmation of the fact that quasicrystals can present a degree of structural perfection comparable to that found in the best periodic intermetallic crystals.



(Figure 5) The intensity distribution of the reflected 20.5 keV x-rays from a strong reflection of Al-Pd-Mn. The pattern clearly shows the existence of the Bormann Fan of the expected width.

Acknowledgments. The authors gratefully acknowledge useful discussions with B. W. Batterman and R. Colella. Ames Laboratory is operated by Iowa State University for the USDOE under Contract No. W-7405-Eng-82.

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