Dynamical x-ray diffraction from quasicrystals

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In 1984 D. Shechtman and coworkers published electron diffraction patterns from nanoscale quasicrystals containing Au$_3$Pt$_7$ that exhibited relatively sharp diffraction peaks arranged in a pattern with icosahedral point group symmetry (containing six 5-fold, 10-fold, and 5-fold rotation 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, fourteenfold, and twentyfold rotation axes) [2]. It was soon realized that this notion of the equality of order and periodicity was rather restrictive view of the 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 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 x-ray diffraction pattern. Soon after the discovery of the original Al$_5$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-Co, 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 properly prepared, they presented no evidence of the disorder that plagued the original quasicrystals, now called Simple icosahedral (SI) alloys [8-9]. Today, a large number of alloys have been discovered to present 5I symmetry and FCI symmetry. The degree of disorder varies greatly from the SI alloy, Al$_5$Cu$_2$, with correlation lengths of ~30 Å to nearly perfect FCI alloys Al$_{25}$Cu$_{60}$ and Al$_{25}$Cu$_{50}$, with correlation lengths greater than 1 nm [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...
perfect can a quasicyrl 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 Pd-Al-Mn quasicrystals were prepared by means of a high-temperature growth technique. The growth parameters were optimized to produce individual grains as large as 2 cm x 3 cm x 1 cm. By means of neutron scattering, the mosaic width of the grains were found to be resolution limited (0.002°).

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 synchrotron technique [12] at the NSLS. The result was that the sample of Al-Pd-Mn quasicrystal scattered coherently over regions larger than 0.6 µm. The transverse width of diffraction peaks were resolution limited (0.0001°).

These results suggested that this alloy might be of sufficient quality to be considered a "perfect" isosceles trapezoidal quasicrystal. In general, as the defect density decreases and, therefore, the size of the coherent scattering region increases, the kinematic 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 E. P. Wigner in 1937 and reformulated by M. von Laue in 1931.

Briefly, the dynamical theory considers the interaction between the atom 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 [13]. The anomalous transmission of x-rays through an incommensurate or aperiodic crystal has been treated in some detail by Foner and Luban 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 (two forward scattering). The result of this multiple scattering is the existence of forward scattered waves as well as the propagation of a wavefield in the crystal. The periodicity of this wavefield is equal to the spacing of the reflecting planes. Some components of the wave field have minima of intensity at all the absorbing atomic positions, rather than 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.

We have shown direct evidence for dynamical diffraction of x-rays from single grains of the Al-Pd-Mn isosceles trapezoidal phase alloy through the observation of anomalous transmission (the Bremsstrahlung effect). For this experiment a single grain of the Al-Pd-Mn isosceles trapezoidal alloy was cut and polished in the form of a parallel-faced wafer. The diffraction pattern shown on the horizontal scale is equal to the angular range of the reflection.

2. A Pb sample was used and the x-ray beam was incident on the sample through the diffraction condition. For this experiment a single grain of the Al-Pd-Mn was used. In this configuration the 0.6 mm thick sample presented approximately ten absorption lengths for 1.5 keV x-rays (Fig. 2). The x-ray beam was incident on the sample at the correct Bragg angle for diffraction in the trapezoidal geometry. Two emerging beams were recorded on Kodak film placed behind the sample (right side of Fig. 2). The H beam is the diffracted Laue beam found at an angle of 2θ = 25° from the incident beam direction. The O beam is the anomalous transmitted (forward scattered) beam in the direction of the incident beam direction. When the sample was rotated by 0.01° 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 a substrate to isolate the O beam from the H beam.

![Graph](image-url)
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 

reflections (since the 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 diffractions 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 small range crystalline imperfections. The dynamical theory predicts an effective nonperiodic character for the perfect crystal causing interference fringes in the intensity exiting the crystal. The experiment is represent 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 205 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 12-ID-D CHESS. From the data shown in Fig. 5, we observe evidence of the characteristic Biermann 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-Fe-Mn, and presumably many of the other FCC 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 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 low-symmetry FCCs 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.

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