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Dynamical x-ray diffraction from an icosahedral quasicrystal

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We present direct evidence of dynamical diffraction of x rays from a quasicrystal. High-resolution x-ray-diffraction measurements of the Al-Pd-Mn face-centered icosahedral quasicrystal were performed, revealing a mosaic full width at half maximum of less than 0.001°. In a second experiment, the anomalous transmission of x rays (the Borrmann effect) was observed. These measurements show that nearly perfect quasicrystals may be grown to centimeter-size dimensions allowing x-ray techniques based upon dynamical diffraction to be brought to bear on the analysis of icosahedral structures.

One of the most interesting and fundamental issues concerning the quasicrystalline alloys has been the degree of perfection, relative to periodic crystals, that can be realized in these novel systems.[1] 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 lengths, to "perfect" Penrose tiling models which yield perfectly sharp Bragg peaks in an x-ray-diffraction pattern. Prior to 1988, all known icosahedral alloys exhibited strong structural disorder evidenced by relatively broad peaks in x-ray-diffraction patterns. In 1988, the discovery of the face-centered icosahedral (FCI) alloys such as Al-Cu-Fe and Al-Cu-Ru changed this picture.[2] Powder-diffraction measurements on Al-Cu-Ru and single-grain diffraction experiments on Al-Cu-Fe demonstrated that the range of positional order, as inferred from the diffraction peak widths, exceeded 1 μm.[3]

One clear indication of the degree of structural perfection for a particular material is whether the diffraction from a sample is best described by the kinematical or dynamical scattering theory. The kinematical theory, applicable in most cases, treats diffraction as a single scattering process where the scattered photon exits the sample without further interactions. This theory is appropriate to "imperfect" materials containing a high density of defects which reduce the coherent scattering volume of the sample. As the defect density decreases and, therefore, the size of the coherent scattering region increases, the dynamical scattering theory becomes the more appropriate description of diffraction. The theory of dynamical scattering in crystalline materials has been thoroughly reviewed in several excellent articles.[4] 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 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.[5]

In this paper we show evidence of dynamical diffraction from single grains of the Al-Pd-Mn icosahedral phase alloy. High-resolution x-ray-diffraction microprobe measurements have been made to assess the quality of the sample over length scales on the order of tens of μm. The longitudinal and transverse diffraction peak widths were found to be resolution limited. The "mosaic" of the sample is less than 0.001° full width at half maximum (FWHM), less than one-third of the intrinsic Darwin width of Si(111). In a second experiment, we show direct evidence for dynamical diffraction from the Al-Pd-Mn alloy through the observation of anomalous transmission (the Borrmann effect).

There are important implications for the study of quasicrystals that result from these measurements. First, we have demonstrated that icosahedral quasicrystals of high perfection can be grown to centimeter-size dimensions. One consequence, of importance to the determination of quasicrystalline structures, is that primary extinction corrections to the integrated intensities of diffraction peaks for structural refinements of some icosahedral quasicrystals, such as Al-Pd-Mn, are important. Second, we have demonstrated that dynamical diffraction theory, originally proposed for periodic crystalline systems, may be used to describe the diffraction process in aperiodic crystals. Scattering techniques, based upon dynamical diffraction, may be brought to bear on the study of quasiperiodic alloys.

Single crystals were grown from the $Al_{70}Pd_{21.5}Mn_{8.5}$ alloy by the Bridgman method.[6] Starting elements with purity of 99.99% were arc melted and chill cast into a copper mold. The as-cast ingot was placed in an alumina crucible in a Bridgman apparatus, and heated to 1050 °C under a vacuum of 1.3×10^{-4} Pa in a Pt-Rh resistance furnace. The furnace was then backfilled with Ar gas to 2.06×10^{5} Pa. The crystal-growth rate was approximately 1 mm/h.

Individual grains as large as 2 cm×1 cm×1 cm were located by means of neutron scattering. A large grain was then separated out of the alloy and cut with a crystallographic twofold direction normal (±0.2°) to the surface which was polished to a mirror finish with 0.05 μm alumina compound. A series of monochromatic x-ray precession photographs were taken of a second sample from the same piece, ground to a spherical shape. All of the diffraction spots were consistent with those for a face-centered icosahedral quasicrystalline structure. There were no apparent shifts or broadening of the diffraction peaks.

X-ray-diffraction line-shape measurements were done on the X25 wiggler beamline at the National Synchrotron Light Source (NSLS) using a double-crystal Si(111) monochromator set to diffract 7 keV ($\lambda=1.77$ Å) x rays. An 18 μm collimator pinhole was used before the sample and a 33 μm pinhole, 1.03 m from the sample, before the detector. Longitudinal scans (Q scans) were made for the 4/4, 8/12, 20/32, and 52/84 peaks along the icosahedral twofold axis, indexed by the shorthand notation introduced by Cahn, Shechtman, and Gratias.[7] The observed diffraction peak positions were all within $\Delta q=\pm0.001$ Å^{-1} of the values calculated for an FCI quasicrystal with a three-dimensional quasilattice constant of $a_0=6.453$ Å. The longitudinal peak widths were all resolution limited. Similarly, transverse scans (θ scans) across several peaks, such as the 8/12 shown in Fig. 1, yielded resolution-limited transverse widths. We point out that the resolution limit of the peak width in the transverse direction is determined by the acceptance of the detector pinhole (approximately 0.001°).

The small mosaic observed for the Al-Pd-Mn icosahedral sample suggested that this alloy might be of sufficient perfection for the observation of anomalous transmission. For this experiment a 0.4 mm thick, single grain of the Al-Pd-Mn icosahedral alloy was cut with twofold axes parallel and perpendicular to the smallest dimension (see Fig. 2). The experiment was performed on beamline X23A3 at the NSLS using 12 keV x rays from a silicon double-crystal asymmetric-cut monochromator set at the (111) reflection. The sample was set at the correct Bragg angle for the 20/32 reflection along the twofold axis in the Laue (transmission) geometry. This reflection is one of the most intense found for icosahedral Al-Pd-Mn. In this configuration the sample is at the thick crystal limit, presenting approximately ten absorption lengths for 12 keV x rays.

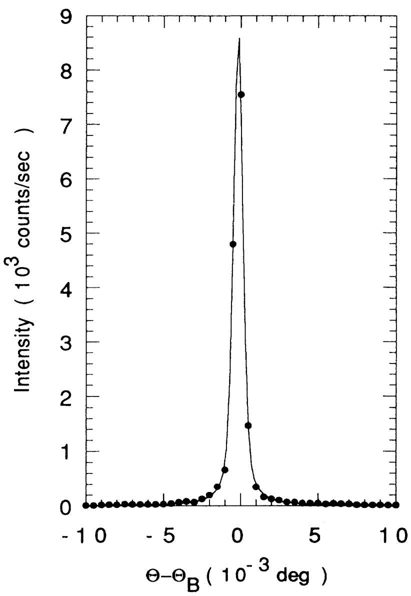

FIG. 1. Transverse scan (θ scan) of the Al-Pd-Mn 8/12 peak. The solid line through the data is intended as a guide to the eye.

The experiment is shown schematically on the left side of 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 3.5 cm 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 anomalously transmitted (forward diffracted) beam

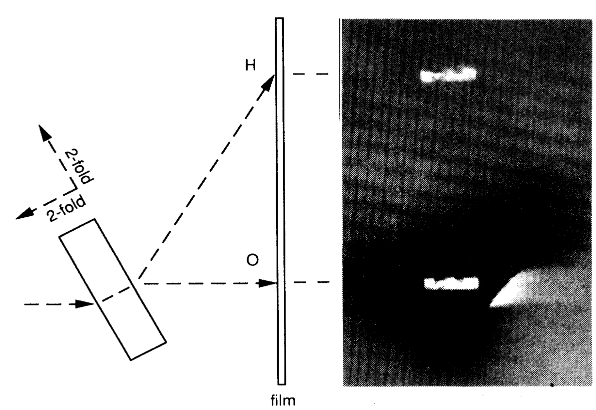

FIG. 2. A schematic of the configuration used to observe the Borrmann effect from Al-Pd-Mn. The photograph at right was taken 3.5 cm behind the sample and shows the O- and H-diffracted beams as well as the dark outline of the sample. The bright spot at the lower right resulted from spillover of the incident beam at the edge of the sample.

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 sample, as might be expected, is not perfect across the entire 3×1 mm extent of the beam. There is structure in both the O and H beams related to the existence of defects in the quasicrystal. Laue topographs of the sample were taken to analyze the defect structure for the sample, and will be presented elsewhere.[8] Nevertheless, 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. Figure 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. The measured angular width of the forward diffracted beam, of 0.006° FWHM, results from the convolution of the incident beam profile and the rocking curve (the angular range over which there is total reflection) of the quasicrystal. The divergence of the incident monochromatic beam was limited to 0.004° by a 1 mm vertical slit before the sample. From this measurement a reasonable upper limit on the intrinsic rocking curve of the 20/32 reflection is 0.004°.

Having demonstrated the phenomenon of anomalous transmission in icosahedral Al-Pd-Mn we now consider how the dynamical theory, originally formulated for perfect periodic crystals, is relevant to diffraction from quasicrystals. The two-beam dynamical theory of diffraction predicts that at the Bragg angle there are two sets of electromagnetic waves present inside the crystal for each of the two linear polarization states of the incident beam. Since the present experiment was performed using synchrotron radiation, which is to a large extent linearly polarized in the orbital plane of the circulating electrons, we will limit our discussion to a single incident polarization state (σ polarization), perpendicular to the vertical scattering plane of the experiment. For a simple crystalline system, the phenomenon of anomalous transmission may be pictured as follows. At the Bragg condition one of the sets of electromagnetic waves (the α-branch solution in the nomenclature of the dynamical theory) produces a standing-wave pattern with planes of constant intensity parallel to the diffracting planes and nodes at the atomic planes while the other set (β-branch solution) produces a standing-wave pattern with antinodes at the atomic planes. The flow of energy inside the crystal is parallel to the diffracting planes. The total field inside the crystal for the α- or β-branch solutions may be written as

$$\mathbf{E}(\mathbf{r})=\mathbf{E}_O\exp(-i\mathbf{K}_O\cdot\mathbf{r})\pm\mathbf{E}_H\exp(-i\mathbf{K}_H\cdot\mathbf{r}) \ , \quad (1)$$

where the positive sign corresponds to the β-branch solution and the negative sign to the α-branch solution. $\mathbf{E}_O$, $\mathbf{K}_O$ and $\mathbf{E}_H$, $\mathbf{K}_H$ are the electric field vectors and wave vectors of the incident and diffracted beams, respectively. $\mathbf{K}_H$ satisfies the Bragg condition $\mathbf{K}_H=\mathbf{K}_O+\mathbf{H}$. The reciprocal lattice vector $\mathbf{H}$ for a Bragg reflection from a periodic crystal is defined by $\mathbf{H}=\Sigma n_i\mathbf{a}_i^*$, where the $\mathbf{a}_i^*$ are the three basis vectors of the reciprocal lattice and the n_i are integers. A similar definition for the reciprocal lattice vector for an icosahedral quasicrystal can be written as $\mathbf{H}=\Sigma n_i\mathbf{a}_i^*$, where the $\mathbf{a}_i^*$ are now the six basis vectors of the icosahedral reciprocal lattice and the n_i are integers.[7] At the central angle of the reflection $\mathbf{E}_H=\mathbf{E}_O$ and the field intensity is given by

$$\mathbf{E}(\mathbf{r})^2=2\mathbf{E}_O^2[1\pm\cos(\mathbf{H}\cdot\mathbf{r})] \ . \quad (2)$$

The planes of constant intensity in the standing-wave pattern are spaced a distance $d=2\pi/H$ apart, which is the same period as the component of the charge distribution which produces the diffraction peak. Antinodes of the electric field for the α-branch (β-branch) solution are located at minima (maxima) in the charge distribution, resulting in lower (higher) than normal absorption. For a sufficiently thick perfect crystal (on the order of ten absorption lengths or greater at the energy of the incident beam) only the α branch survives to produce the O and H beams. For more complicated crystals, with several atoms per unit cell, the charge density may be nonzero at the antinodes of the electric field for the α-branch solution resulting in significant photoelectric absorption that limits the intensity of the O beam. Such is the case for the (111) reflection of silicon. This may also be anticipated for an incommensurate structure such as a quasicrystal which is characterized by an aperiodic rather than periodic charge distribution. Even though the charge distribution in a quasicrystal is aperiodic, Bragg diffraction is observed. Therefore, anomalous transmission should be observed for the strongest reflections [where $\cos(\mathbf{H}\cdot\mathbf{r})$ in Eq. (2) is close to 1] as long as the size of the region that diffracts coherently is sufficiently large for dynamical, rather than kinematical, scattering.

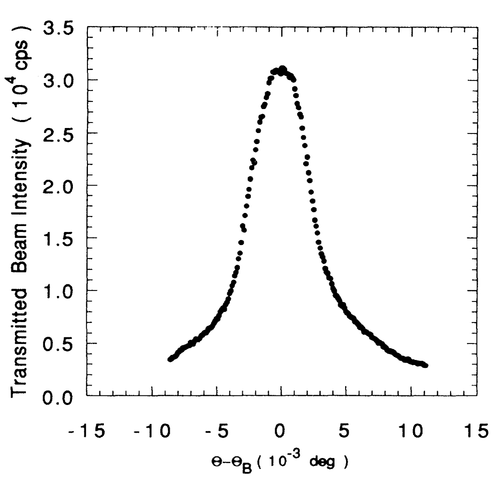

FIG. 3. Intensity of the forward diffracted beam (O beam) as the sample is rotated through the diffraction condition. The nominal zero of the horizontal scale was chosen at the center of the angular range of the reflection.

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 metallic crystals. Furthermore, these measurements demonstrate that the two-beam dynamical diffraction theory applies generally to ordered systems, not simply those with translational periodicity. We point out, however, that a more sophisticated n-beam approach to dynamical diffraction may be required since the reciprocal space of a quasicrystal is, in principle, densely filled with Bragg peaks. When the diffraction condition for a particular strong peak is met, multiple scattering from the dense set of other reciprocal lattice points sufficiently close to the Ewald sphere will contribute to the scattering. These other points, though, generally contribute vanishingly small intensities.[5,9]

The observation of dynamical diffraction from quasicrystals also 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, can be significant and primary extinction corrections should be made prior to the use of diffraction data as input to structural determinations. Second, 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. Indeed, efforts are already underway to use multiple diffraction interference effects to determine whether quasicrystalline systems are centrosymmetric.[9]

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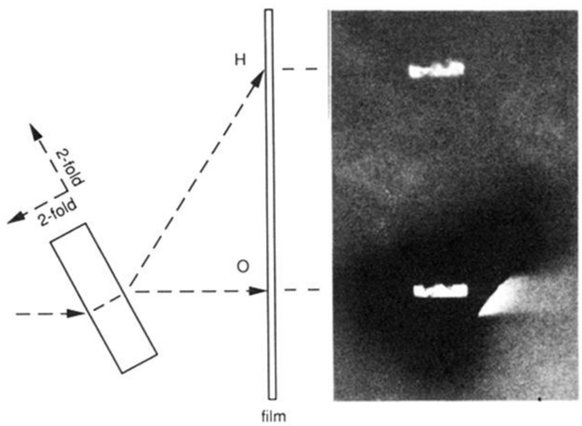

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