

Diffraction from one- and two-dimensional quasicrystalline gratings

N. Ferralis, A. W. Szmodis, and R. D. Diehl^(a)

*Department of Physics and Materials Research Institute, Penn State University,
University Park, Pennsylvania 16802*

(Received 9 December 2003; accepted 2 April 2004)

The diffraction from one- and two-dimensional aperiodic structures is studied by using Fibonacci and other aperiodic gratings produced by several methods. By examining the laser diffraction patterns obtained from these gratings, the effects of aperiodic order on the diffraction pattern was observed and compared to the diffraction from real quasicrystalline surfaces. The correspondence between diffraction patterns from two-dimensional gratings and from real surfaces is demonstrated.

© 2004 American Association of Physics Teachers.

[DOI: 10.1119/1.1758221]

I. INTRODUCTION

In the past 5–10 years, there has been considerable interest in the structure of the surfaces of quasicrystal alloys, which provide realizations of quasicrystalline order in two dimensions.¹ The best-known examples of two-dimensional (2D) quasicrystal structures might be the tilings generated by Penrose² such as the one shown in Fig. 1, although many examples of aperiodic order exist in nature.³ The main differences between quasicrystal order and periodic crystal order are the absence of a periodically repeating structural unit and the possibility of “forbidden” rotational symmetries, such as 5-fold or 10-fold rotations in the quasicrystal structures. Quasicrystalline order in solids was discovered unexpectedly about 20 years ago in Al-based alloys, and subsequent metallurgical studies on such alloys have found that quasicrystal phases are generally restricted to small ranges of composition and temperature. A detailed understanding of the stability of these structures is beyond the scope of this paper, but the entropic factor in the free energy plays a significant role in many cases.

Recent scanning tunneling microscopy (STM) studies of the surfaces of the quasicrystalline phases of the alloys *i*-Al–Pd–Mn and *d*-Al–Ni–Co have identified tiling patterns similar to Penrose-type tilings.⁴ Figure 2 shows such tiling generated from the STM image of the 5-fold surface of icosahedral AlPdMn.⁵ This experimentally derived tiling has been shown to be identical in character to one of the mathematically derived Penrose tilings.⁶

Additional interest in quasicrystal surfaces has been generated by their unusual surface properties, such as low coefficients of friction, high hardness, good wear resistance, and good corrosion resistance.⁷ Quasicrystal coatings have been used as nonstick, wear-resistant surfaces in frying pans,⁷ and more recently polymeric composites of Al–Cu–Fe quasicrystal and polyethylene have been successfully tested as possible material candidates for acetabular cup prosthetics.⁸

It has been stated that the discovery of quasicrystals created a revolution in crystallography,^{9,10} which had previously treated order and periodicity as synonymous.¹¹ Diffraction is the primary technique for examining the structures of solid materials, and the consequences of aperiodicity on diffraction patterns provide a challenge and an opportunity to gain a deeper understanding of both diffraction and of quasicrystal structures.^{10,12,13} The most common procedures for analyzing diffraction measurements from crystalline solids were originally developed with the assumption of a periodic struc-

tural unit. The definition of a crystal included the requirement of periodicity until 1992.¹⁴ Aperiodicity and traditionally forbidden rotational symmetries introduce features in diffraction patterns that make interpretation by the traditional means more complex. Simulations can provide a means for building intuition of the effects of quasicrystalline order on diffraction patterns without resorting to a complicated analysis.

One of the most unexpected aspects of diffraction from quasicrystals is that they produce sharp, discrete diffraction peaks.¹⁵ A disruption of periodicity often leads to a loss of definition (broadening of peaks, increase in background intensity) in the diffraction pattern. However, aperiodicity by itself does not cause a broadening of diffraction peaks. This can be demonstrated in one dimension by looking at the Fourier transform of the well-ordered but aperiodic Fibonacci array.¹⁶

A Fibonacci array is a one-dimensional sequence of short (*S*) and long (*L*) elements generated by specific rules.¹⁷ In the limit of an infinite number of elements, the ratio of the number of *L* segments to *S* segments is given by the irrational number $\tau = (1 + \sqrt{5})/2$, known as the golden mean. A Fourier transform of this array does not show the broad peaks that are normally associated with a disordered structure. Unlike transforms from periodic arrays, the transform from a Fibonacci array forms a dense set of sharp peaks having different intensities. The positions of the peaks are related to each other by powers of the golden mean.

The most common diffraction technique for studying surfaces is low-energy electron diffraction (LEED). In LEED, the electrons are backscattered from the surface in a geometry such as that shown in Fig. 3. Figure 4 shows LEED patterns from (a) the 5-fold surface of icosahedral AlPdMn¹⁸ and (b) the 10-fold surface of decagonal AlNiCo.¹⁹ In both cases, the distances between the diffraction spots are related by τ . In the first case, the LEED pattern is clearly 5-fold symmetric (that is, it has 5-fold rotational symmetry about the center of the pattern), and in the second, it is 10-fold symmetric. If these structures were periodic, it would be relatively simple to deduce the sizes and symmetries of the unit cells from the diffraction patterns by applying Bragg's law. However, extracting information about aperiodic structures is not so straightforward, particularly in the case of electron diffraction for which the pattern is not a simple Fourier transform of the structure, due to the complexities inherent in electron scattering. The complete analysis of LEED patterns generally involves the calculation of scattering from

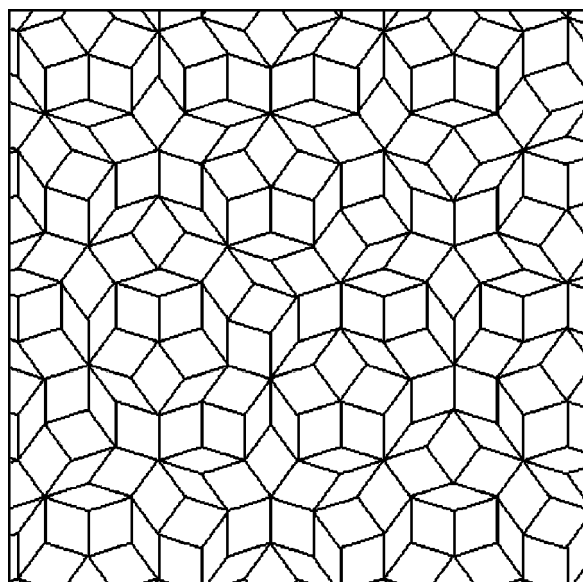


Fig. 1. Penrose tiling consisting of two sizes of rhombus.

model structures, but much can be learned by a kinematic (single-scattering) approach, which is sufficient to determine the locations of diffraction peaks in two dimensions.^{20,21}

In this paper, we present a method that gives insight into the diffraction from quasicrystal surfaces by studying the diffraction of light from one-dimensional and two-dimensional aperiodic gratings, and comparing these to diffraction from actual quasicrystal surfaces. Similar techniques were applied to aperiodic structures even before the discovery of quasicrystals.^{22,23}

II. METHOD

The first requirement for modeling quasicrystal surface diffraction is to establish a method for producing high-

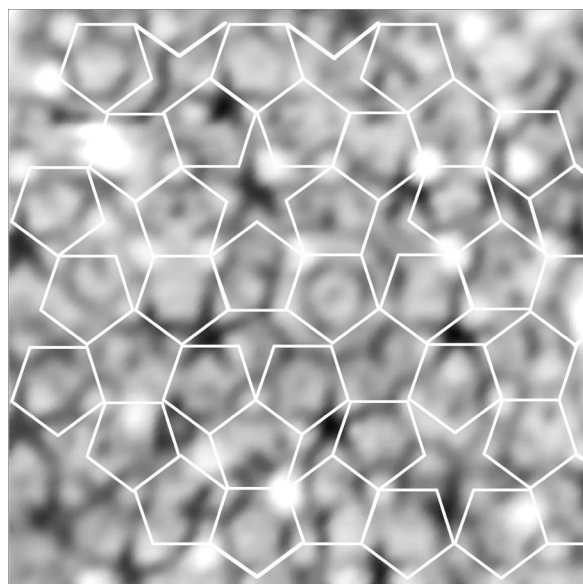


Fig. 2. High-resolution STM image ($75 \text{ \AA} \times 75 \text{ \AA}$) of the 5-fold surface of AlPdMn, with a tiling pattern superimposed. The tiling was generated by identifying similar features in the STM image and connecting them (see Ref. 6).

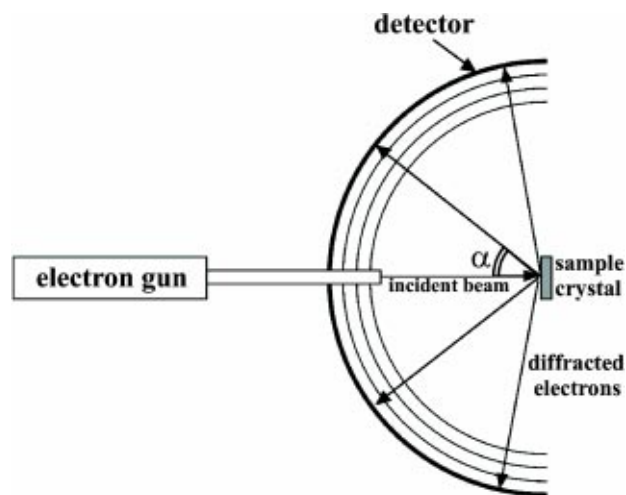


Fig. 3. The geometry of a typical LEED experiment. The incoming beam of electrons (from the left) is normally incident on a crystal surface. The diffracted beams are backscattered at various angles, α , which depend on the structure of the surface.

quality diffraction gratings. One-dimensional gratings can be constructed by first using a graphics program such as Adobe Illustrator[®] or CorelDraw[®] to draw the gridlines that make up the grating. Aperiodic gratings were generated by setting the spacing between the gridlines to those of the Fibonacci sequence. In this study, a typical short distance between the gridlines was 5 mm and the thickness of the gridlines was typically around 0.10 mm. An example of a one-dimensional grating is shown in Fig. 5. The drawing was then laser printed and photographed. Because the photographic negatives were to be used as diffraction gratings, the drawings were made in reverse polarity (black-white) to the desired grating. The photographs were taken using a Contax 137 MA quartz camera and Ilford PAN F black and white, 50 ASA film. This method is similar to one employed earlier by another group,²⁴ and we verified their finding that higher-resolution film produces a clearer diffraction pattern. An alternative and simpler way to produce high-resolution one-dimensional (1D)-gratings is to print the gratings onto overhead projector transparent sheets using a laser printer (nominal resolution of 600 dpi). This procedure produces gratings with a lower resolution than the photographic film, but is suitable for many diffraction investigations. To produce the diffraction pattern, a grating was placed on an x - y translation stage in front of a 0.95 mW He-Ne laser. The diffraction pattern was cast onto a white screen 100 cm in

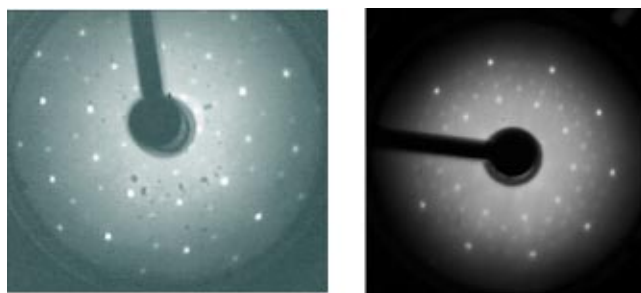


Fig. 4. LEED patterns from (left) the 5-fold *i*-AlPdMn (see Ref. 18) at 80 eV incident beam energy (see Ref. 35), and (right) the 10-fold *d*-AlNiCo (see Ref. 19) at 72 eV incident beam energy.

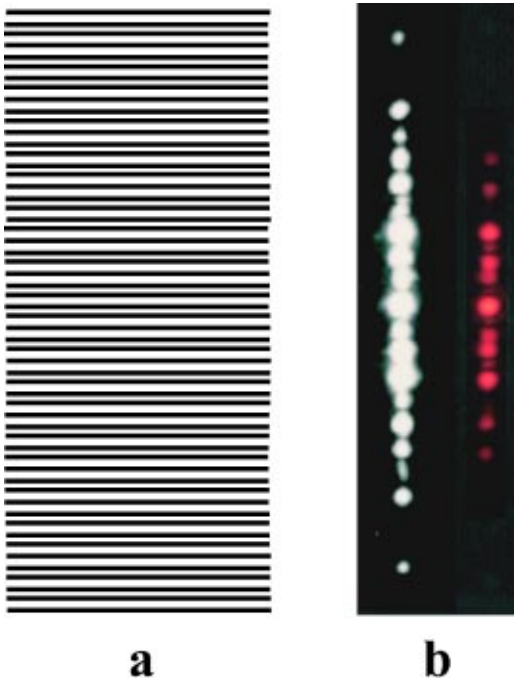


Fig. 5. (a) 1D diffraction grating comprising lines that are spaced according to the Fibonacci sequence. (b) Diffraction patterns obtained from such a grating using the photographic (left) and the laser printer (right) techniques.

front of the grating and photographed. Examples of the diffraction patterns from both methods are shown in Fig. 5.

For comparison to the diffraction from surfaces, a two-dimensional grating is required. Various two-dimensional gratings were made by superimposing two or more rotated 1D Fibonacci gratings. Figure 6(a) shows two grids rotated by 90° , and Fig. 6(b) shows the Fibonacci pentagrid achieved by superimposing five gratings rotated 72° from each other.

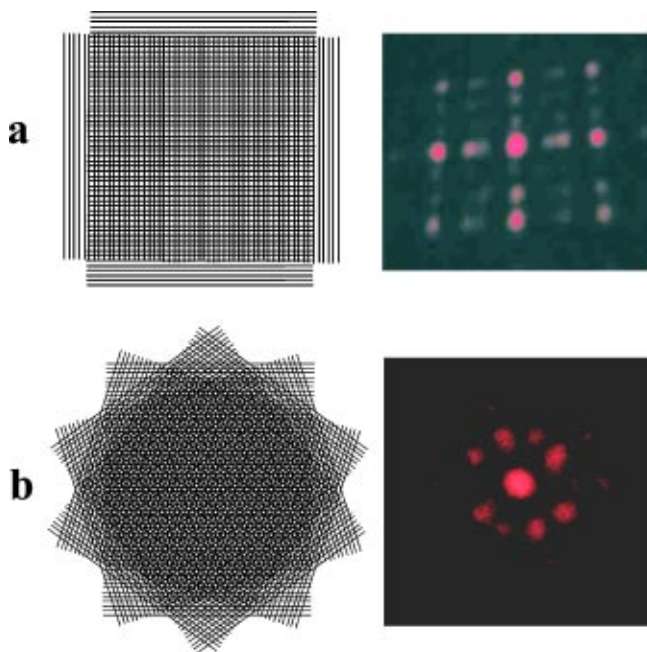


Fig. 6. The superposition of multiple 1D Fibonacci gratings produces 2D aperiodic diffraction grids. (a) The Fibonacci square and its laser diffraction pattern. (b) The Fibonacci pentagrid and its laser diffraction pattern.

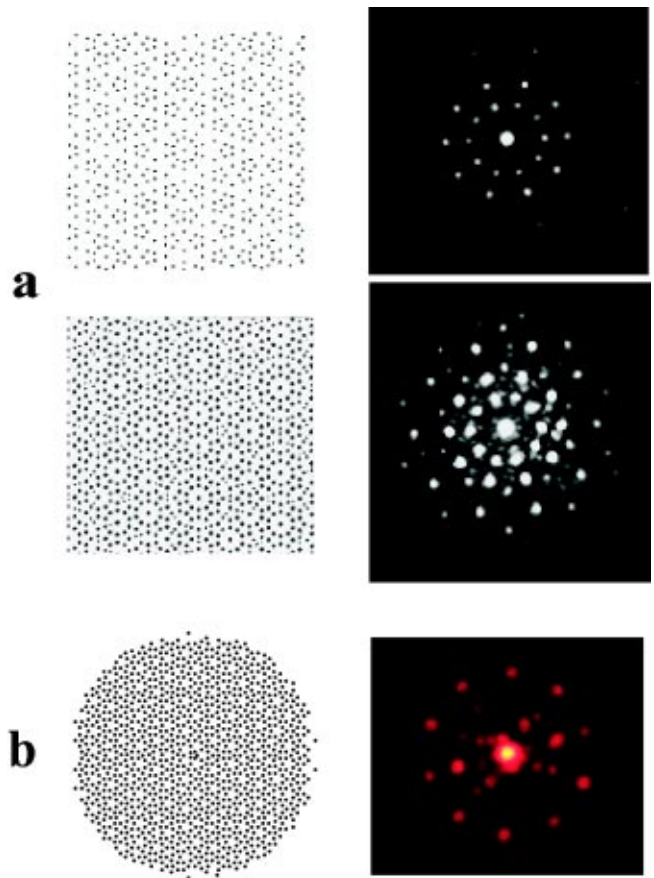


Fig. 7. Three 5-fold arrays of dots used to produce 2D aperiodic diffraction gratings. The arrays represent proposed atomic positions for (a) two different planes of a model structure for AlPdMn (see Ref. 25) and (b) plane of a model structure for AlNiCo (see Ref. 19).

The diffraction patterns obtained from these 2D grids also are shown. To draw a stronger correspondence between actual quasicrystal surfaces and these diffraction patterns, a grating can be made to consist of dots based on the locations of the intersections of superimposed 1D grids, or based on proposed atomistic models for quasicrystal planes. Figure 7 shows examples of such gratings that are based on models for the 5-fold surface of AlPdMn²⁵ and the 10-fold surface of AlNiCo.¹⁹ The resulting laser diffraction patterns also are shown. The gratings used in this study are available for download.²⁶ Additional resources for experiments using laser transforms and a broader range of gratings and images can be found in a comprehensive book on optical transforms²⁷ and at the related website.²⁸

III. RESULTS AND DISCUSSION

A. One-dimensional gratings

To gain insight into the diffraction patterns obtained with aperiodic gratings, the laser diffraction patterns can be compared with calculated diffraction patterns for both periodic and aperiodic arrays. Figure 8 shows a comparison of the laser diffraction and Fourier transforms of a Fibonacci array and a periodic array having a spacing equal to the long length in the Fibonacci array.

As pointed out in Sec. I, diffraction from a perfect periodic grating produces beams that have non-zero intensity only for values of k inversely proportional to the slit distance (the

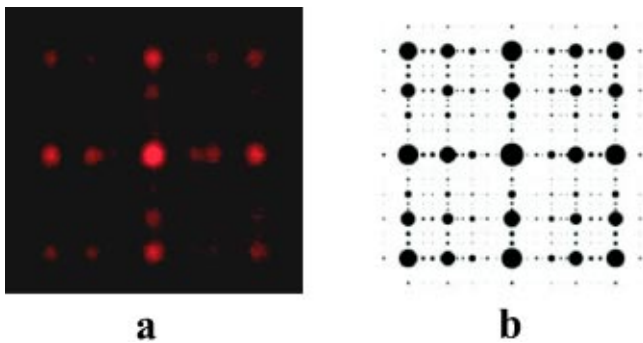


Fig. 12. The laser diffraction pattern of the square Fibonacci tiling (left) is compared with the Fourier transform of the same structure (see Ref. 32). The intensity at each point is proportional to the radius of the circle.

talline surfaces illustrates this point (see Fig. 4). In both cases the main beams are related to each other by powers of the golden mean, as shown in Fig. 14.

The background intensities also show similar behavior; what appears to be diffuse scattering in the LEED diffraction pattern is actually the sum of the intensities from a densely

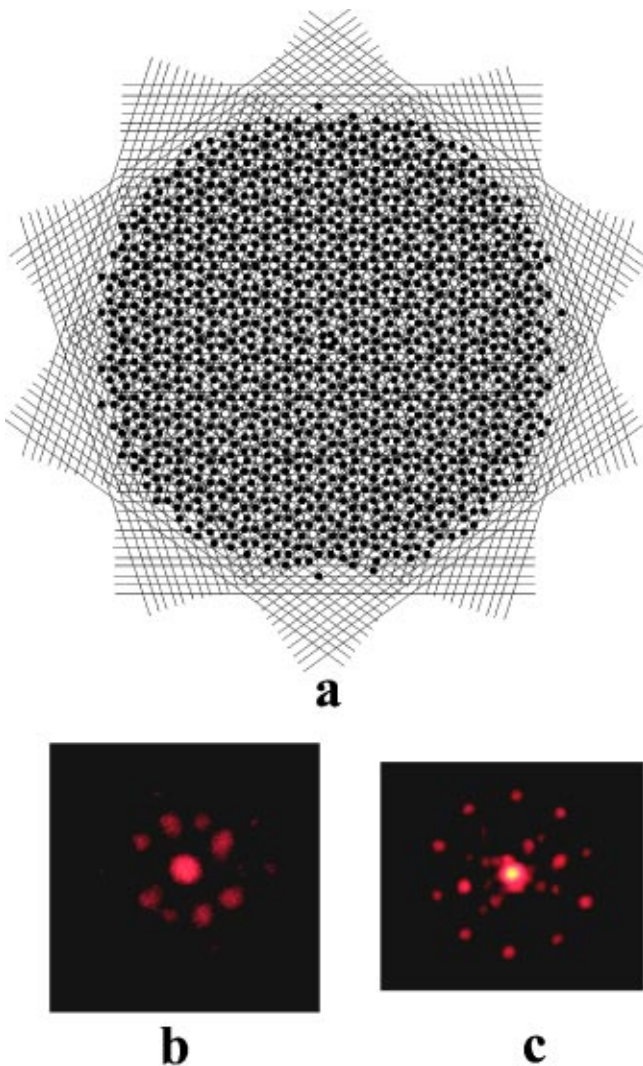


Fig. 13. (a) Superposition of the AlNiCo atomic coordinates with the Fibonacci pentagrid. (b) Diffraction pattern from the pentagrid. (c) Diffraction pattern from the grating obtained using the atomic coordinates.

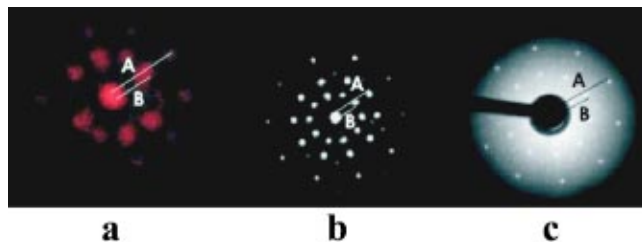


Fig. 14. The laser diffraction patterns obtained from grating from (a) the Fibonacci pentagrid and (b) from atomic coordinates show similar features to (c), the LEED diffraction pattern of the 10-fold AlNiCo surface (see Ref. 19). In particular the ratio A/B is equal to the golden mean.

spaced array of weak spots. As for the 1D case, the diffraction pattern presents a dense set of discrete points in k -space, with self-similar features. To illustrate the density and self-similarity of the pattern, laser diffraction patterns were acquired using two exposure times are shown in Fig. 15. Although the main order beams appear overexposed in the longer exposure picture, it is possible to see additional diffraction spots. If diffuse scattering predominated, we would see an overall homogeneous increase of the background intensity.

A significant difference that emerges by comparing the laser diffraction pattern to the LEED patterns from the real structures is the presence in one case of 5-fold symmetry [the AlPdMn quasicrystalline surface, see Fig. 4(a)]. All of the laser diffraction patterns and the Fourier transforms show 10-fold symmetry. This inversion symmetry is a general property of the Fourier transform, and also of 2D diffraction, and, in particular, a 5-fold 2D structure will produce a 10-fold diffraction pattern.¹⁶

So why does the AlPdMn surface display a 5-fold symmetry in the LEED pattern? Electron diffraction from real surfaces differs from laser diffraction in several respects. First, different chemical entities can be present in a real surface (quasicrystals are usually alloys), each having different scattering properties. More importantly, electrons penetrate the surface, scattering from more than one plane of atoms. In addition, most of the scattered electrons undergo more than one scattering event. The net result is that there is a decrease in intensity of the scattering from each successive layer of the material. Even if the scattering from just the top layer is 10-fold in nature, the scattering from the next layer, which has a different path length, breaks this 10-fold symmetry. In general, surfaces having 5-fold or 10-fold symmetry therefore give 5-fold LEED patterns, but under special circum-

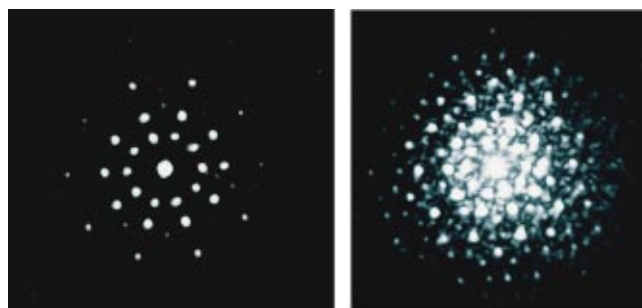


Fig. 15. Photographs of two laser diffraction patterns taken at different exposures. The diffraction pattern of a quasicrystalline structure has an infinite number of diffraction spots, in every point in k -space.

stances 10-fold patterns are observed.¹⁶ Nevertheless, the correspondence between the positions of the peaks in the laser diffraction patterns with those in the LEED patterns does provide insight into the nature of the order in the real quasicrystal.

IV. CONCLUSIONS

Interpreting diffraction patterns generated by quasicrystal surfaces has been challenging because the traditional analysis methods were based on periodic structures. We have presented an approach that involves the production of high quality 1D and 2D diffraction gratings using both traditional chemical photography and laser printing. These gratings can be modified to reproduce different types of aperiodic structures and observe the effects on the diffraction patterns. By investigating the intermediate steps between the simple case of the Fibonacci sequence and the more sophisticated Fibonacci pentagrid, we can trace the origins of the diffraction features (self-similarity and inversion symmetry) from the simple 1D case to the 2D cases. Employing different methodologies in the identification of the grating matrix (for example, the use of the pentagrid compared to atomic coordinates) provides a correspondence of these models to the real structures.

Although diffraction from real structures presents some technical differences from the laser diffraction from aperiodic gratings, common features can be easily observed and understood. A deviation from the expected behavior can be used to determine the presence of defects or imperfections in the quasicrystal. Finally, laser diffraction allows an inductive approach for understanding complex aperiodic structures, and can provide educators with an innovative tool for introducing and extending the traditional concept of diffraction.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Julian Ledieu for providing some of the figures. This research was supported by NSF, DMR-0208520, DGE-9979579 and DMR-0097769.

^{a)}Electronic mail: rdiehl@psu.edu

¹R. McGrath, J. Ledieu, E. J. Cox, and R. D. Diehl, "Quasicrystal surfaces: Structure and potential as templates," *J. Phys.: Condens. Matter* **14**, R119–R144 (2002).

²R. Penrose, "Pentaplexity," *Math. Intell.* **2**, 32–37 (1979).

³T. H. Garland, *Fascinating Fibonacci: Mystery and Magic in Numbers* (Dale Seymour, Palo Alto, CA, 1987).

⁴R. McGrath, J. Ledieu, E. J. Cox, and R. D. Diehl, "Tilings and coverings of quasicrystal surfaces," in *Coverings of Discrete Quasiperiodic Sets: Theory and Applications to Quasicrystals*, edited by P. Kramer and Z. Papadopolos (Springer, Berlin, 2003), pp. 257–268.

⁵J. Ledieu, R. McGrath, R. D. Diehl, T. A. Lograsso, D. W. Delaney, Z. Papadopolos, and G. Kasner, "Tiling of the fivefold surface of Al₇₀Pd₂₁Mn₉," *Surf. Sci.* **492** (3), L729–L734 (2001).

⁶Z. Papadopolos, G. Kasner, J. Ledieu, E. J. Cox, N. V. Richardson, Q. Chen, R. D. Diehl, T. A. Lograsso, A. R. Ross, and R. McGrath, "Bulk termination of the quasicrystalline fivefold surface of Al₇₀Pd₂₁Mn₉," *Phys. Rev. B* **66** (18), 184207–184213 (2002).

⁷J. M. Dubois, "The applied physics of quasicrystals," *Phys. Scr.*, T **49**, 17–23 (1993).

⁸B. C. Anderson, P. D. Bloom, K. G. Baikerikar, V. V. Shear, and S. M. Mallapragada, "Al–Cu–Fe quasicrystal/ultra-high molecular weight polyethylene composites as biomaterials for acetabular cup prosthetics," *Biomaterials* **23**, 1761–1768 (2002).

⁹J. W. Cahn, "Epilogue," in *Proceedings of the 5th International Conference on Quasicrystals*, edited by C. Janot and R. Mosseri (World Scientific, Singapore, 1996), p. 807.

¹⁰M. Senechal, *Quasicrystals and Geometry* (Cambridge U.P., Cambridge, 1995).

¹¹R. Lifshitz, "The rebirth of crystallography," *Z. Kristallogr.* **217**, 342–343 (2002).

¹²R. Lifshitz, "Quasicrystals: A matter of definition," *Found. Phys.* **33** (12), 1703–1711 (2003).

¹³R. Lifshitz, "The symmetry of quasiperiodic crystals," *Physica A* **232**, 633–647 (1996).

¹⁴"Report of the Executive Committee for 1991, International Union of Crystallography," *Acta Crystallographica* **48**, 922–946 (1992).

¹⁵L. Pauling, "Apparent icosahedral symmetry is due to directed multiple twinning of cubic crystals," *Nature (London)* **317**, 512–514 (1985).

¹⁶R. D. Diehl, J. Ledieu, N. Ferralis, A. W. Szmodis, and R. McGrath, "Low-energy electron diffraction from quasicrystal surfaces," *J. Phys.: Condens. Matter* **15** (3), R63–R81 (2003).

¹⁷C. Janot, *Quasicrystals: A Primer* (Clarendon, Oxford, 1992).

¹⁸M. Gierer, M. A. Van Hove, A. I. Goldman, Z. Shen, S.-L. Chang, P. J. Pinhero, C. J. Jenks, J. W. Anderegg, C.-M. Zhang, and P. A. Thiel, "Fivefold surface of quasicrystalline AlPdMn: Structure determination using low-energy electron diffraction," *Phys. Rev. B* **57**, 7628–7641 (1998).

¹⁹N. Ferralis, K. Pussi, E. J. Cox, M. Gierer, J. Ledieu, I. R. Fisher, C. J. Jenks, M. Lindroos, R. McGrath, and R. D. Diehl, "Structure of the 10-fold d-Al-Ni-Co quasicrystal surface," *Phys. Rev. B* **69**, 075410 (2004).

²⁰D. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science* (Cambridge U.P., Cambridge, 1986).

²¹M. A. Van Hove, W. H. Weinberg, and C.-M. Chan, *Low-Energy Electron Diffraction: Experiment, Theory and Surface Structure Determination* (Springer-Verlag, Berlin, 1986).

²²R. Mosseri and J. F. Sadoc, "Two and three dimensional non-periodic networks obtained from self-similar tiling," in *The Structure of Non-Crystalline Materials 1982*, edited by P. H. Gaskell, J. M. Parker, and E. A. Davis (Taylor and Francis, London, 1982), pp. 137–150.

²³A. L. Mackay, "Crystallography and the Penrose pattern," *Physica A* **114**, 517–522 (1982).

²⁴S. Y. Litvin, A. B. Romberger, and D. B. Litvin, "Generation and experimental measurement of a one-dimensional quasi-crystal diffraction pattern," *Am. J. Phys.* **56** (1), 72–75 (1988).

²⁵M. Boudard, M. de Boussieu, C. Janot, G. Heger, C. Beeli, H.-U. Nissen, H. Vincent, R. Ibberson, M. Audier, and J. M. Dubois, "Bulk structure of AlPdMn," *J. Phys.: Condens. Matter* **4**, 10149–10168 (1992).

²⁶(<http://alpdmn.phys.psu.edu/gratings.html>). Links to downloadable images of periodic and quasiperiodic diffraction gratings.

²⁷G. Harburn, C. A. Taylor, and T. R. Welberry, *Atlas of Optical Transforms* (G. Bell & Sons, London, 1975).

²⁸([http://rsc.anu.edu.au/~welberry/Optical transform/](http://rsc.anu.edu.au/~welberry/Optical%20transform/)). This site includes information on producing optical transforms as well as slides of various diffraction gratings.

²⁹A. R. Smith, K.-J. Chao, Q. Niu, and C.-K. Shih, "Formation of atomically flat silver films on GaAs with a 'silver mean' quasi periodicity," *Science* **273**, 226–228 (1996).

³⁰P. Ebert, K.-J. Chao, Q. Niu, and C.-K. Shih, "Dislocations, phase defects, and domain walls in a one-dimensional quasiperiodic superstructure of a metallic thin film," *Phys. Rev. Lett.* **83** (16), 3222–3225 (1999).

³¹J. Ledieu, J.-T. Hoefl, D. E. Reid, J. Smerdon, R. D. Diehl, T. A. Lograsso, A. R. Ross, and R. McGrath, "Pseudomorphic growth of a single element quasiperiodic ultrathin film on a quasicrystal substrate," *Phys. Rev. Lett.* **92**, 135507 (2004).

³²R. Lifshitz, "The square Fibonacci tiling," *J. Alloys Compd.* **342**, 186–190 (2002).

³³M. Gierer, A. Mikkelsen, M. Gräber, P. Gille, and W. Moritz, "Quasicrystalline surface order on decagonal Al_{72.1}Ni_{11.5}Co_{16.4}: An investigation with spot profile analysis LEED," *Surf. Sci. Lett.* **463**, L654–L660 (2000).

³⁴W. Steurer, T. Haibach, B. Zhang, S. Kek, and R. Lück, "The Structure of decagonal Al₇₀Ni₁₅Co₁₅," *Acta Crystallogr., Sect. B: Struct. Sci.* **B49**, 661–675 (1993).

³⁵M. Gierer, M. A. Van Hove, A. I. Goldman, Z. Shen, S.-L. Chang, C. J. Jenks, C.-M. Zhang, and P. A. Thiel, "Structural analysis of the fivefold symmetric surface of the Al₇₀Pd₂₁Mn₉ quasicrystal by low energy electron diffraction," *Phys. Rev. Lett.* **78**, 467–470 (1997).

³⁶T. Cai, J. Ledieu, R. McGrath, V. Fournée, T. Lograsso, A. Ross, and P. Thiel, "Pseudomorphic starfish: Nucleation of extrinsic metal atoms on a quasicrystalline substrate," *Surf. Sci.* **526** (1–2), 115–120 (2003).