

Electronic Band Dispersion and Pseudogap in Quasicrystals: Angular-Resolved Photoemission Studies on Icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$

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Angular-resolved photoelectron spectra from the fivefold surface of single-grain icosahedral $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ exhibit a quasiperiodic dispersion of 300 meV at 2.3 eV binding energy. Low energy electron diffraction studies confirm quasicrystalline order at the surface. A distinct pseudogap feature is observed with a density of states near the Fermi level decreasing as a square-root power law.

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After the discovery of quasicrystals [1], investigations focused mainly on their structural properties. An important feature of quasicrystals is the absence of periodic translational invariance, leading to the inapplicability of Bloch's theorem to quasicrystals and to the absence of Brillouin zones in the conventional sense. Yet long range positional order exists. The concept of a "quasi Brillouin zone" (QBZ) was introduced in models for the electronic structure of quasicrystals [2,3]. Energy bands have been used to describe many basic electronic properties of quasicrystals, e.g., electrical conductivity, optical properties, and magnetism [2]. Nevertheless, there has been no direct evidence for the existence in quasicrystals of energy bands, especially for energy vs momentum band dispersion, although dispersive phonon modes in quasicrystalline Al-Li-Cu, Al-Pd-Mn, and Al-Cu-Fe have been studied [4-6]. Another interesting feature of quasicrystals is their extremely low electrical conductivity. Composed of good metals, quasicrystals exhibit a conductivity thousands of times smaller than that of their constituents [2]. Proposed qualitative explanations fall into two major categories: (i) electron wave-function localization or criticality, and (ii) band structure effects and the Hume-Rothery rule. A pseudogap and aperiodic dispersion relations were predicted in some theoretical models favoring a Hume-Rothery explanation [7-10]. Specific heat measurements on quasicrystals indicate a significant reduction of the density of states at the Fermi level E_F compared with the free-electron value [2,11]. Angle-integrated photoemission measurements on Al-Cu-Fe icosahedral quasicrystals showed an anomalous valley at E_F [12,13]. That study was done on scraped surfaces with low energy resolution, and no surface structure information was available. To verify that the anomalous valley at E_F is an intrinsic feature of the sample one must first confirm that the surfaces are clean and ordered. Although electronic structure calculations are available for quasicrystals [7,8], band mapping using angle-resolved photoemission has not yet been reported.

In this Letter we demonstrate the quasiperiodic dispersion relations and pseudogaps in quasicrystals by angle-resolved photoemission on single-grain icosahedral

$\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$. We find a dispersionlike feature in the electronic structure which confirms that a QBZ indeed exists. We observe a pseudogap feature at E_F , consistent with the semimetal nature of this quasicrystal. The density of states decreases toward E_F in a power law relation that can be associated with the "Brillouin-zone"-Fermi-sphere interaction.

Large-grain samples of the $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ alloy were grown by the Bridgman method. Starting elements with purity 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. The furnace was then back-filled 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 \times 1 cm \times 1 cm were extracted from the ingot. A large grain was separated out of the alloy and cut with a crystallographic fivefold axis normal ($\pm 0.2^\circ$) to the surface, which was then mechanically polished to a mirror finish with 0.25 μm diamond compound. The sample was electropolished in a 1:1 solution of nitric and perchloric acids at approximately -70°C [14].

The photoemission studies were carried out on the Ames-Montana State beam line on Aladdin at the Synchrotron Radiation Center [15]. The overall (electron and photon) energy resolutions were 50 meV for the pseudogap measurements and 0.15 eV for the dispersion measurements. The base pressure was below 1×10^{-10} Torr during the measurements. The surface was prepared by 1 keV Ar-ion bombardment, followed by annealing at 600-700 °C. After several cycles of sputtering and annealing, low energy electron diffraction (LEED) patterns were taken, providing clear evidence of quasicrystalline ordering on the surface. In addition, separate LEED and Auger-electron spectroscopy (AES) studies were carried out. The surface cleanliness was verified by the sharpness and stability of the LEED patterns and by the Al 2p core level spectrum, which is very sensitive to contamination. The influence of oxygen and other contamination can also be monitored by a broad feature at about 7 eV below E_F .

The LEED pattern in Fig. 1 was taken with 24 eV electron energy from the fivefold surface at normal electron

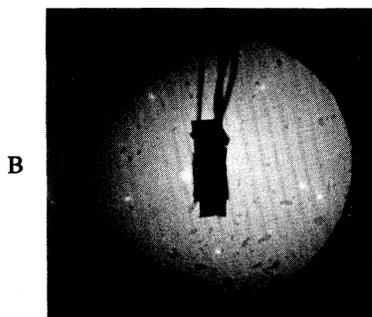


FIG. 1. LEED pattern from a fivefold symmetry surface of icosahedral quasicrystal $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ using 24 eV electrons.

incidence. At 18 eV the LEED pattern has tenfold symmetry, obtainable from an icosahedral or decagonal surface. At about 24 eV electron energy the LEED pattern shows fivefold symmetry, which can only be obtained from the fivefold icosahedral surface. At 33 eV the pattern shows fivefold symmetry with higher-order diffraction spots. The observed LEED patterns are characteristic of icosahedral quasicrystals, and can be observed from 5 to 240 eV electron energy. The quasicrystal surface ordering is stable over a large temperature range from room temperature up to about 700 °C. Details of surface LEED studies will be reported elsewhere [16].

Figure 2(a) shows the angular dependence of the photoelectron energy distribution curves (EDCs) using an incident photon energy of 13 eV. The photoelectron emission angles (θ , ϕ) were chosen to probe \mathbf{k} along the twofold axis of the quasisurface Brillouin zone (QSBZ). The QSBZ should be a decagon with tenfold symmetry, but the two \bar{F} points in the QSBZ are not equivalent with respect to the bulk QBZ, and the symmetry is reduced to fivefold [4]. In our convention the two nonequivalent \bar{F} points are designated \bar{F}_+ and \bar{F}_- as shown in the inset of Fig. 2(a). Three features were observed in the spectra, labeled A, B, and C, respectively. Feature A indicates the unusual shape of the Fermi edge, discussed in detail below. Feature B is at 2.34 eV binding energy at $\bar{\Gamma}$ and disperses upward by about 300 meV from $\bar{\Gamma}$ to \bar{F}_+ and \bar{F}_- . Feature C is the strongest peak in the valence band region. The peak position, 4.24 eV, is independent of the emission angle, and is due to the Pd 4d electrons by reference to the photoelectron spectra of Pd metal [17] and quasicrystalline Al-Li-Cu [18], Al-Cu-Fe [11], and AlPdMn [19].

An experimental E vs \mathbf{k}_{\parallel} relation is presented in Fig. 2(b), where the crystal momentum $\mathbf{k}_{\parallel} = 0.514 \times \sin\theta\sqrt{E_{\text{kin}}}$. The dispersion of the bandlike feature is very similar to that of a nearly-free-electron metal with a weak periodic potential, a free-energy-like parabola centered at $\bar{\Gamma}$ and distorted in the neighborhood of the Bragg "planes" \bar{F}_+ and \bar{F}_- where the curves have zero slope. The QBZ size is very small ($\sim 0.31 \text{ \AA}^{-1}$) so that one would expect relatively narrow free-electron bands. Although we use

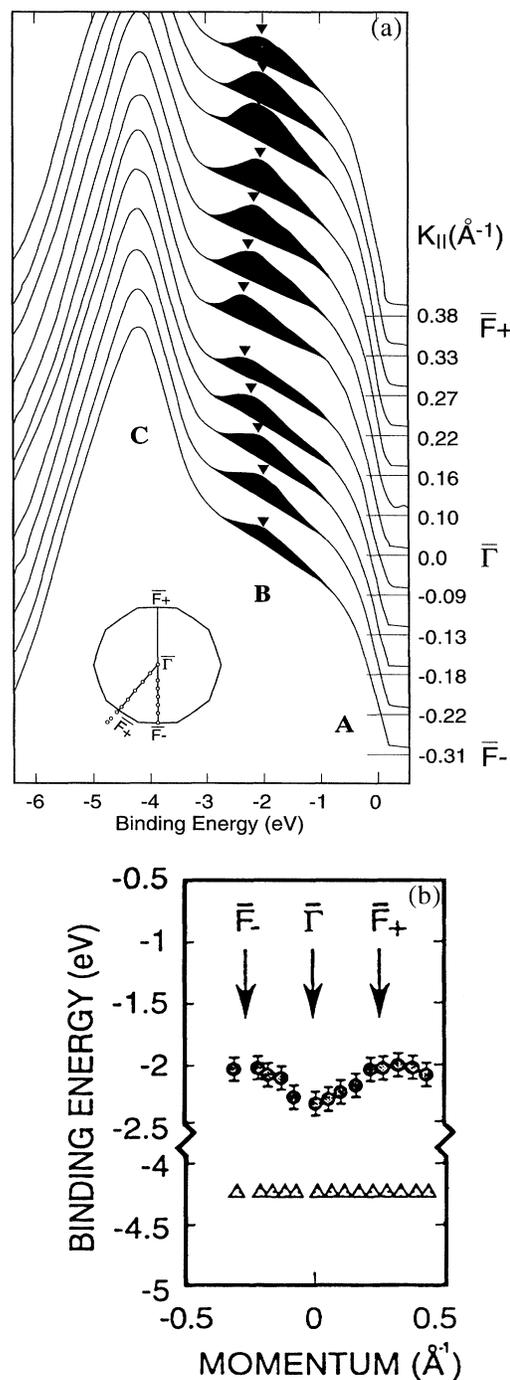


FIG. 2. Angle-resolved valence band photoemission spectra of icosahedral quasicrystal $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$. The inset shows the surface quasi Brillouin zone for the fivefold symmetry axis. $\bar{\Gamma}$ to \bar{F}_+ and \bar{F}_- are the directions along a twofold symmetry axis. The circles indicate the corresponding \mathbf{k} value of feature B. (b) The experimental E vs \mathbf{k} relation as measured on the fivefold surface along the twofold symmetry axis directions ($\bar{\Gamma}$ to \bar{F}_+ and \bar{F}_-). The points correspond to the points in the inset of (a).

a QSBZ to present our data, it must be remembered that the real dispersion relation is three dimensional. We also scanned the photon energy in normal emission from 12 to 34 eV and found that the dispersion relation along the fivefold symmetry axis is difficult to obtain; the 2.3 eV feature quickly disappears as the photon energy is increased or decreased from 13 eV, indicating that 13 eV photon energy corresponds to one of the high symmetry points in k space along the fivefold symmetry axis. Interestingly, an incident photon energy of 28 eV also produces a weak feature approximately 2.3 eV below E_F . Krajcǐ *et al.* [20] reported calculations of the electronic structure for higher-order rational approximants of an icosahedral Al-Pd-Mn alloy with up to 41 068 atoms in the unit cell, based on a tight-binding linear muffin tin orbital (LMTO) Hamiltonian and the recursion technique. They predict a pseudogap at E_F . They calculated the spectral density $A(\mathbf{k}, E)$ for \mathbf{k} along the twofold symmetry axis. Our nondispersing band at 4.24 eV appears to correspond to their strong (large A) band at 4.5 eV, which, however, disperses. A strong dispersing band runs between 1 and 2 eV in the calculation, but it has no intensity at Γ , unlike our dispersing band, 2.34 eV, at Γ .

To examine the detailed structure of feature A, in Fig. 3(a) we present high resolution photoemission spectra near E_F . Pt and Ta foils were used as references for E_F . The Pt spectra were taken at low temperature (~ 20 K) to reduce the temperature broadening of the Fermi edge while the quasicrystal spectra were recorded at room temperature in order to get fresh clean surfaces after Ar ion bombardment and annealing. The quasicrystal spectra do not show a sharp Fermi edge. The "edge" is much broader than the instrumental resolution and the 3×26 meV intrinsic width of the Fermi edge at room temperature. The density of states (DOS) associated with this limited region of the QBZ drops smoothly toward the Fermi level and can be represented by an expression of the form $g(E - E_F) \propto (1 - E/E_F)^\alpha$, where α is a constant. To fit the experimental curve, the assumed partial DOS is multiplied by a linear background term and a Fermi distribution function, then convoluted with a Gaussian energy resolution function. A least-squares fit [Fig. 3(b)] gives $\alpha = 0.50 \pm 0.05$; i.e., we observe local scaling behavior of the density of states near E_F [21]. While a sharp Fermi edge is the fingerprint of a metallic phase in periodic crystalline materials, the absence of a sharp Fermi edge in the quasicrystal suggests a pseudogap has opened at E_F . It is interesting to note that in three-dimensional periodic crystals, if the electron energy varies as $E = E_0 - a\mathbf{k}^2$ for $E < E_0$, the density of states will be of the form [22] $g(E - E_0) \propto (1 - E/E_0)^{1/2}$ for $E < E_0$.

This relation describes the well-known square-root Van Hove singularity and is coincident with our experimental result if one allows $E_0 = E_F$. This suggests that the DOS at E_F is not only a minimum but also its energy derivative at E_F is divergent. Since angle-integrated photoemission

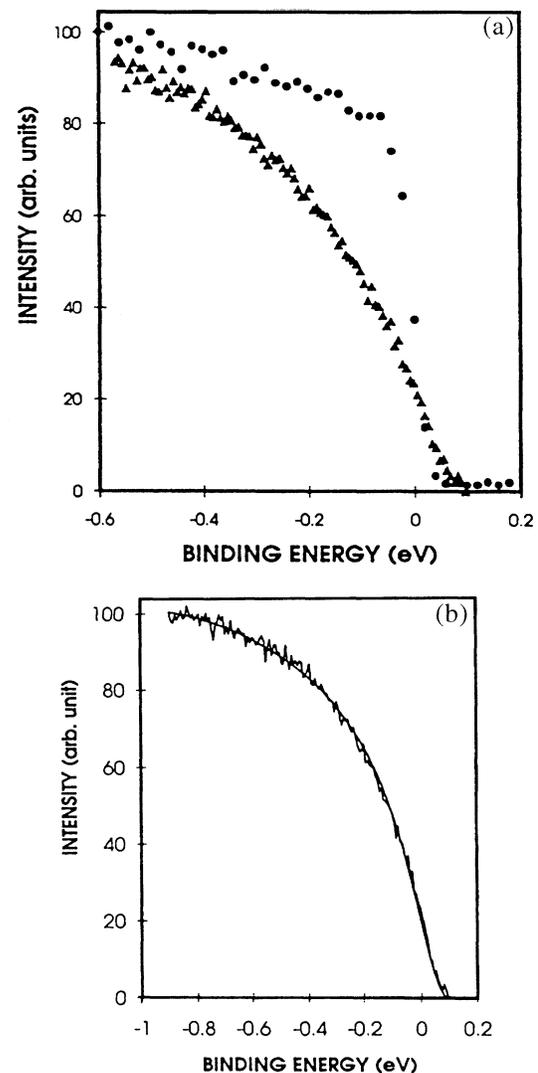


FIG. 3. High resolution (50 meV) photoemission spectra near the Fermi level region. The spectra were taken at about 20 K for Pt (dots) and at room temperature for quasicrystal $\text{Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ (triangles). (b) Least-squares fit of the spectra of (a).

[12] found a dip, our partial DOS evidently is similar to the full DOS. The observed dip is analogous to a similar feature in solid bismuth, which is a semimetal [23].

Possible sources of such a dip include: (1) a Van Hove singularity, (2) surface contamination, (3) a surface amorphous phase. The second is unlikely, since close monitoring of the Al $2p$ core level spectra before and after each valence band scan reveals no contamination by oxygen during the course of our measurement. An oxygen-related feature could be observed at about 2 eV below the Al $2p$ peak if the surface has chemisorbed oxygen or is oxidized [11]. We detected no such feature after sputter-anneal cycles. The third possibility also is unlikely. While a surface

amorphous phase is induced by Ar ion sputtering, proper annealing restores surface order, as shown by LEED before and after taking data. We believe the observed dip is an intrinsic feature of this quasicrystal. These measurements, then, provide direct evidence of a pseudogap in the density of states of icosahedral Al-Pd-Mn near E_F .

Matsubara *et al.* [18] have reported a gaplike feature in the inverse photoemission spectra of the icosahedral phase of Al-Li-Cu, but a distinct gaplike feature was not found in the photoemission spectra, although the band calculation of the crystalline R phase predicts that the pseudogap is situated below E_F .

Our data are consistent with the early observation of Mori *et al.* [12] of an anomalous valley at E_F in AlCuFe samples. In their case the clean surface was obtained by scraping with a diamond file in ultrahigh vacuum. Surface structure information was not available. The decrease in the density of states near E_F was also reported for icosahedral AlCuFe [11] and AlPdMn [19], but with low energy resolution (0.4–0.5 eV) one cannot easily distinguish whether it is an intrinsic effect or is due to the Fermi edge cutoff.

In summary, photoemission on the icosahedral Al₇₀Pd_{21.5}Mn_{8.5} quasicrystal demonstrates 300 meV dispersion in an electronic band 2.3 eV below E_F , which suggests the concept of a quasi Brillouin zone is applicable to describe the electronic energy bands of quasicrystals. A diplike pseudogap was detected. The pseudogap is well represented by a power law scaling relation with scaling index 0.5. We suggest this local scaling behavior might originate from Van Hove singularities at or near E_F .

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- [1] D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, *Phys. Rev. Lett.* **53**, 1951 (1984).
- [2] S. J. Poon, *Adv. Phys.* **41**, 303 (1992).
- [3] A. E. Carlsson and R. Phillips, in *Quasicrystals: The State of the Art*, edited by D. P. DiVincenzo and P. Steinhart (World Scientific, Singapore, 1991).
- [4] M. de Boissieu, M. Boudard, R. Bellissent, M. Quilichini, B. Hennion, R. Currat, A. I. Goldman, and C. Janot, *J. Phys. Condens. Matter* **5**, 4945 (1993).
- [5] A. I. Goldman, C. Stassis, M. de Boissieu, R. Currat, C. Janot, R. Bellissent, H. Moudden, and F. W. Gayle, *Phys. Rev. B* **45**, 10280 (1992).
- [6] M. Quilichini, G. Heger, B. Hennion, S. Lefebure, and A. Quiry, *J. Phys.* **51**, 1785 (1990).
- [7] J. Hafner and M. Krajci, *Phys. Rev. Lett.* **68**, 2321 (1992).
- [8] T. Fujiwara and T. Yokokawa, *Phys. Rev. Lett.* **66**, 333 (1991).
- [9] A. P. Smith and N. W. Ashcroft, *Phys. Rev. Lett.* **59**, 1365 (1987).
- [10] A. E. Carlsson, *J. Non-Cryst. Solids* **153 & 154**, 386 (1993).
- [11] Z. M. Stadnik and G. Stroink, *Phys. Rev. B* **47**, 100 (1993).
- [12] M. Mori, S. Matsuo, T. Ishimasa, T. Matsuura, K. Kamiya, H. Inokuchi, and T. Matsukawa, *J. Phys. Condens. Matter* **3**, 767 (1991).
- [13] E. Belin, Z. Dankhazi, A. Sadoc, and J. M. Dubois, *J. Phys. Condens. Matter* **6**, 8771 (1994).
- [14] S. W. Kycia, Ph.D. thesis, Iowa State University, 1995.
- [15] C. G. Olson, *Nucl. Instrum. Methods Phys. Res., Sect. A* **266**, 205 (1988).
- [16] X. Wu, C. G. Olson, and D. W. Lynch (to be published).
- [17] F. J. Himpsel and D. E. Eastman, *Phys. Rev. B* **18**, 5236 (1978).
- [18] H. Matsubara, S. Ogawa, T. Kinoshita, K. Kishi, S. Takeuchi, K. Kimura, and S. Suga, *Jpn. J. Appl. Phys.* **30**, L389 (1991).
- [19] G. W. Zhang, Z. M. Stadnik, A.-P. Tsai, and A. Inoue, *Phys. Lett. A* **186**, 345 (1994); *Phys. Rev. B* **50**, 6696 (1994).
- [20] M. Krajci, M. Windisch, J. Hafner, G. Kresse, and M. Mihalkovic, *Phys. Rev. B* **51**, 17355 (1995).
- [21] M. Kohmoto, B. Sutherland, and C. Tang, *Phys. Rev. B* **35**, 1020 (1987).
- [22] L. van Hove, *Phys. Rev.* **89**, 1189 (1953).
- [23] Y. Baer and H. P. Myers, *Solid State Commun.* **21**, 835 (1977).

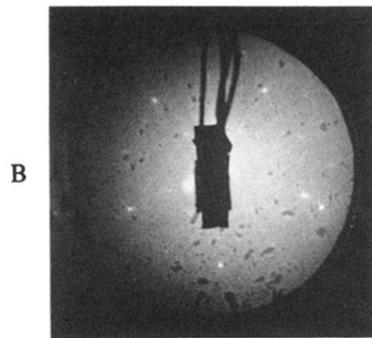


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