Absence of fine structure in the photoemission spectrum of the icosahedral Al-Pd-Mn quasicrystal

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The results of the low-temperature ultrahigh-energy-resolution photoemission studies of a single-grain icosahedral alloy $Al_{70}Pd_{21.5}Mn_{8.5}$ have been presented. The existence of the theoretically predicted pseudogap in the density of states at the Fermi energy has been confirmed. No evidence of the theoretically predicted spikiness of the density of states could be observed. It has been suggested that the failure to detect the predicted spikiness of the density of states in icosahedral quasicrystals is consistent with the results of Zijlstra and Janssen [Europhys. Lett. **52**, 578 (2000)] who showed that the spikiness occurs only in lower-order periodic approximants to icosahedral quasicrystals, but does not survive in the quasiperiodic limit.

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I. INTRODUCTION

Quasicrystals (QC's) are a new form of the solid state which differs from the other two known forms, crystalline and amorphous, by possessing a new type of long-range translational order, *quasiperiodicity*, and a noncrystallographic orientational order associated with the classically forbidden fivefold (icosahedral), eightfold (octagonal), tenfold (decagonal), and twelvefold (dodecagonal) symmetry axes.¹ One of the central problems in condensed-matter physics is to determine whether quasiperiodicity leads to physical properties which are significantly different from those of crystalline and amorphous materials of the same/ similar compositions.

The physical properties of QC's, and especially their electronic transport properties, are very unusual.¹ They are ultimately determined by the electronic structure of these alloys. Knowledge and understanding of the electronic structure are thus essential if we are to understand the unexpected physical properties of QC's.

There are three major theoretical predictions of the electronic structure of icosahedral (*i*) alloys. The first one is the prediction of the existence of the pseudogap in the density of states (DOS) at the Fermi level E_F . The early calculations based on the nearly free-electron approximation concluded²⁻⁸ that such a pseudogap should exist in the *i* alloys. Modern electronic structure calculations performed for the approximants to various *i* alloys unanimously predict the presence of the pseudogap in the DOS(E_F).^{9–24} For the *i* Al-Pd-Re system, the possible existence of a real gap in the DOS around E_F was predicted.^{22,24} The predicted minimum of DOS(E_F) (a pseudogap) is not a unique characteristic which distinguishes the electronic structure of QC's from that of crystalline and amorphous alloys since the pseudogap does occur in both crystalline and amorphous systems.¹

The second theoretical prediction of the electronic structure calculations carried out for various approximants to QC's is the fine structure (spikiness) of the DOS.^{9–24} The (DOS) of QC's is believed to consist of many very fine spiked peaks with a width in the range 10–50 meV. The predicted DOS spikiness seems to be a unique property which distinguishes QC's from crystalline and amorphous alloys. This spikiness is invoked¹ to explain the experimental observation that the electrical resistivity ρ of QC's is unusually sensitive to slight changes in their composition: such changes shift the position of E_F , resulting in a strong change of the DOS(E_F), and consequently of ρ .

The electronic structure calculations are performed for the so-called quasicrystalline approximants,²⁵ which are periodic crystalline alloys with large unit cells whose local atomic structures are very similar to those in QC's. These approximants are characterized by the rational numbers τ_n $=F_n/F_{n+1}$, where F_n is a Fibonacci number. These $\frac{1}{1}, \frac{2}{1}$, $\frac{3}{2}$, $\frac{5}{3}$, $\frac{8}{5}$, ..., approximants approach the quasiperiodic limit as the numbers τ_n approach the golden mean $\tau = (1$ $(+\sqrt{5})/2$. By calculating the DOS for a series of approximants of increasing order, conclusions can be drawn regarding the DOS in the quasiperiodic limit. Because of the computational restrictions, the electronic structure calculations are carried out for the lowest-order approximants.⁹⁻²⁴ It has been pointed out by Haerle and Kramer²⁶ that the predicted DOS spikiness might be an artifact resulting from the restricted number of wave vector **k** points taken into account in the DOS calculations, leading to the lack of convergence with respect to the Brillouin-zone integration. Zijlstra and Janssen have shown²⁷ on the basis of quasiperiodic model Hamiltonians that, at a fixed level of computational resolution, the DOS spikiness disappears on approaching the quasiperiodic limit but persists in lower-order approximants. They argued that previously published electronic structure calculations suffered from the lack of convergence with respect to the number of the k points in a Brillouin zone and consequently the observed spikes in the DOS were not representative for the DOS of an ideal *i* QC.

In general, the eigenvalue spectrum of a Hamiltonian can be categorized as absolutely continuous, point-like, or singular continuous, corresponding respectively to extended, localized, and critical eigenstates.^{28,29} Extended and localized eigenstates are characteristic for periodic and strongly disordered systems, respectively. Critical eigenstates, which are neither extended nor localized, are characterized by a powerlaw decay of their amplitudes. They seem to be inherent to one-dimensional (1D), 2D, and possibly 3D QC's.^{28,29}

The anomalously large ρ and a low electronic specific heat coefficient γ were taken as an experimental evidence for the existence of a pseudogap in the DOS at E_F .^{30–33} A universal experimental relation $\rho \sim \gamma^{-1/2}$, discovered independently by Mizutani³² and Rapp³³ for many *i* alloys, is indicative of the minimum of the DOS(E_F) in these alloys. The results of NMR,^{34–37} optical conductivity,^{38–43} and photoconductivity⁴⁴ experiments were interpreted in terms of the pseudogap in the DOS(E_F) in the *i* alloys.

The theoretically predicted spikiness of the DOS in *i* QC's has been claimed to be consistent with the variations of various physical parameters which probe the DOS indirectly. The temperature/composition dependencies of γ ,⁴⁵ the Hall coefficient and the thermoelectric power,^{30,46} and the NMR Knight shif *K* and the spin-lattice relaxation rate $1/T_1$ (Refs. 37, 47, and 48) were interpreted as evidence for the presence of the fine structure of the DOS. However, other experiments were interpreted as being against the presence of the DOS spikiness. The results of the temperature/composition/ pressure dependencies of $1/T_1$ and K,^{36,37,49} the magnetic susceptibility,⁵⁰ and the specific heat^{32,51} were taken as evidence for a smooth DOS.

The possible existence of the critical eigenstates in the *i*-Al-Pd-Re alloy was invoked in the interpretation of the unusual power-law-like increase of ²⁷Al-NMR $(T_1T)^{-1}$ with decreasing temperature below 20 K.⁵²

A common characteristic of the measurements mentioned above is the fact that they probe the DOS *indirectly* via, sometimes complex, dependencies of the measured parameters upon DOS. Studies using spectroscopic techniques which probe DOS *directly* in the vicinity of E_F are therefore desirable to determine the predicted presence of the pseudogap in the DOS(E_F) and of the DOS fine structure in QC's. The experiments carried out with high energyresolution photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) established conclusively the presence of the pseudogap in the *i* alloys Al-Li-Cu, Al-Cu-Fe, Al-Cu-Os, Al-Pd-Mn, and Al-Pd-Re alloys.^{53–60}

PES/IPES experiments with high energy resolution are fully capable^{57,61} of detecting DOS spikiness at low and/or room temperatures. The predicted DOS spikiness has not been observed in any of the PES/IPES experiments carried out so far on various QC's. Experiments carried out with the tunneling spectroscopy (TS) technique, which has an energy resolution of $\sim k_B T$ (better than 1 meV at 4.2 K), detected at liquid helium temperatures one sharp feature, located at E_F , of width \sim 50–60 meV in the *i* Al-Cu-Fe, Al-Pd-Mn, and Al-Pd-Re alloys.^{62–65} However, in another TS study,⁶⁶ this feature was found to be much narrower (\sim 20 meV) in the *i* Al-Cu-Fe and Al-Pd-Mn alloys, but very wide (\sim 100 meV) in the Al-Pd-Re alloys. No other spikes could be observed in the tunneling spectra of i alloys.^{62–66}

Different reasons have been invoked⁶⁷ to explain the failure to detect the DOS spikiness even in the low-temperature PES valence bands of QC's measured with the highest energy resolution presently achievable. The main concern was associated with the fact that the majority of the studied QC's were in a polyquasicrystalline form; the studied surfaces consist of small polyquasicrystalline grains with arbitrary orientation which, in principle, may lead to a smoothing of the existing fine structure of the DOS. In addition, the surfaces are prepared by in situ mechanical scraping and/or cleaving which, in principle, may lead to the destruction of the surface quasicrystallinity. Here we report low-temperature, high energy-resolution PES measurements on a single-grain i Al-Pd-Mn alloy with a well characterized surface. We demonstrate that the predicted DOS spikiness cannot be detected in the valence band of this alloy when measured with the highest energy resolution currently achievable.

II. EXPERIMENTAL PROCEDURE

A single-grain i Al70Pd21.5Mn8.5 alloy was grown by the Bridgman technique. Appropriate quantities of Al (99.999% pure), electron-beam-melted purified Pd (99.99%), and distilled Mn (99.999%) were cleaned and arc melted several times under an argon atmosphere. The buttons were then remelted and the alloy drop cast into a copper chill cast mold to ensure compositional homogeneity throughout the ingot. The as cast ingot was placed in an alumina crucible and heated under a pressure of 1.3×10^{-4} Pa up to 673 K to degas the crucible and melt. The furnace was backfilled with argon gas to a pressure of 2.06×10^5 Pa. This overpressurization is necessary in order to maintain stoichiometry and minimize porosity formation. Following pressurization, heating was continued until the ingot reached a temperature of 1373 K and held for 1 h before being withdrawn from the furnace at a rate of 1 mm/h. A flat wafer approximately 10 $mm \times 8 mm \times 2 mm$ was cut from a single grain of a boule and oriented by an x-ray Laue technique within 0.25° perpendicular to the fivefold axis. The surface was then polished using standard metallographic techniques. An inspection of the sample for the presence of second phases using scanning electron and scanning Auger spectroscopy indicated that, within a detection limit of 1%, the sample is single phase.

The surface of the fivefold single-grain $i \text{ Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ was prepared for the PES experiments by sputteringannealing cycles. Annealing periods were typically 30 min during cleaning and about 2 h before the PES experiments. Choosing an appropriate annealing temperature is crucial in producing a quasicrystalline surface.^{68,69} Annealing was done at 773 K which yielded a clear fivefold low-energy electron diffraction pattern.^{68,69} The surface cleanliness was verified using Auger electron spectroscopy.

Ultrahigh-energy-resolution PES experiments were carried out in an angle-integrated mode using a spectrometer equipped with a high-intensity He discharge lamp (Gammadata) producing a He I line at 21.2 eV and He II line at 40.8 eV, and a high-resolution Scienta SES200 hemispherical analyzer.⁵⁷ The instrumental resolution was determined by



FIG. 1. (a) He II angle-integrated valence band of the singlegrain *i* $Al_{70}Pd_{21.5}Mn_{8.5}$ at 12 K measured with an energy resolution of 8.6(1) meV. The amplitude of the error bars is equal to one standard deviation. (b) The model of the DOS at 0 K which is used to fit the near- E_F region of the angle-integrated valence band of single-grain *i* $Al_{70}Pd_{21.5}Mn_{8.5}$ at 12 K from (a). The solid line represents the normal DOS at 0 K, whereas the broken line represents the dip which must be subtracted from the normal DOS in order to fit the near- E_F region of the valence band. (c) The near- E_F region of the angle-integrated valence band of single-grain *i* $Al_{70}Pd_{21.5}Mn_{8.5}$ at 12 K from (a) (open circles) fitted (solid line) to the model DOS shown in (b) which is multiplied by the Fermi-Dirac function at 12 K and convoluted with the experimental Gaussian function of FWHM=8.6 meV.

fitting the Fermi edge of an atomically clean Ta foil in direct thermal and electrical contact with the sample with the convolution of a Gaussian and the product of a linear DOS and the Fermi-Dirac function at the appropriate temperature. The full width at half-maximum (FWHM) of the Gaussian is the only adjustable parameter in this procedure and gives directly the instrumental resolution. PES measurements were performed at a base pressure of better than 5×10^{-11} Torr. The PES valence bands presented here are corrected for the secondary-electron background.⁶¹

III. RESULTS AND DISCUSSION

The low-temperature He II valence band of the singlegrain sample $i \text{ Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ [Fig. 1(a)] differs from the corresponding valence band of a polyquasicrystalline $i \text{ Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ sample⁵⁶ in that the main feature at the binding energy E_B of -4.1 eV of the former has a clear shoulder at $E_B \approx -5$ eV. The main feature of the valence band is mainly due to the Pd 4*d*-derived states, whereas the feature close to E_F is predominantly due to states of Mn 3*d* character. This assignment is based on previous room-temperature synchrotron-radiation PES studies^{70,71} carried out on the polyquasicrystalline $i \text{ Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ sample with an energy resolution of 400 meV. They established a good agreement between the theoretical¹⁷ and experimental^{70,71} partial DOS of the Mn 3*d* and Pd 4*d* character and the total experimental^{70,71} and theoretical¹⁷ DOS.

The decrease of the spectral intensity towards E_F [Fig. 1(a)], which is clearly distinguished from the decrease due to the Fermi cutoff, results from the presence of a pseudogap in the $DOS(E_F)$. With the aim of obtaining simple parameters to characterize the pseudogap, one can simulate the observed structure close to E_F in the valence band using the model proposed by Mori *et al.*⁵⁴ As conventional alloys of the quasicrystal-forming elements do not display a DOS minimum close to E_F , it is assumed that a simple linear extrapolation of the spectrum for E_B energy range directly before the peak in the valence band feature close to E_F accounts for the DOS without the gap (the normal DOS). The presence of a pseudogap would result in an intensity dip which is assumed to be of Lorentzian shape centered at E_F , characterized by the half-width Γ_L , and the dip depth relative to the normal DOS C. The observed intensity $I(E_B)$ is the convolution of the normal DOS multiplied by the pseudogap Lorentzian function and by the Fermi-Dirac function $f(E_R,T)$, and the experimental resolution Gaussian function

$$I(E_B) = \int N(ax+b) \left(1 - \frac{C\Gamma_L^2}{x^2 + \Gamma_L^2} \right) f(x,T)$$
$$\times \exp\left[-\frac{(x-E_B)^2}{2s^2} \right] dx, \qquad (1)$$

where N is a normalization factor, the experimental Gaussian FWHM is related to s through FWHM= $2\sqrt{2 \ln 2s}$, and the constants a and b are determined from a linear fit of the spectrum for E_B energy range between -1.2 to -0.7 eV. The C values of 0 and 100% correspond, respectively, to the normal DOS (no pseudogap) and no $DOS(E_F)$. There is some arbitrariness in the model expressed by Eq. (1) regarding the choice of the E_B range for which the data are fitted to a line aE_B+b representing a normal DOS, which results in nonunique values C and Γ_L characterizing the pseudogap. Nevertheless, one obtains a reasonable estimate of the width and depth of the pseudogap with this procedure. A good fit of the near- E_F region of the valence band of the single-grain $i \operatorname{Al}_{70}\operatorname{Pd}_{21.5}\operatorname{Mn}_{8.5}$ alloy [Fig. 1(c)] with this model [Fig. 1(b)] is achieved for parameter values C = 33.9(1.9)% and Γ_L =0.13(1) eV. The values of these parameters obtained from the similar fit of the near- E_F region of the valence band of the polyquasicrystalline $i \operatorname{Al}_{70} \operatorname{Pd}_{20} \operatorname{Mn}_{10}$ alloy⁵⁶ are, respectively, 28.1(1.0)% and 0.22(2) eV. Thus it can be concluded that the high-resolution PES data obtained from both polyquasicrystalline and single-grain samples are in support of the theoretically predicted¹⁷ presence of the pseudogap in the *i* Al-Pd-Mn system.

The predicted DOS spikes have amplitudes of up to $\sim 100\%$ of the average DOS and the widths in the range 10–50 meV [Fig. 2(a)]. In order to assess whether such spikes can be detected in a PES valence band, the following analysis is applied. In principle, a PES spectrum is proportional to the total DOS.^{72,73} However, a number of corrections have to applied to the measured valence band in order



FIG. 2. (a) Total DOS of the $\frac{1}{1}$ approximant Al₈₈Pd₂₀Mn₂₀ from Ref. 17. (b) Occupied part of the DOS from (a) multiplied by the Fermi-Dirac function at 12 K and convoluted with a Lorentzian (curve 1), to account for the lifetime broadening effects, and with a Gaussian, to account for the experimental resolution, with the resolution of 200 meV (curve 2), 100 meV (curve 3), 50 meV (curve 4), and 8.6 meV (curve 5). The separation between the two neighboring ticks on the ordinate axis corresponds to 0.5 states/(eV atom).

to compare it to a theoretical DOS. In practice, the recovery of the DOS from the measured spectrum is difficult and therefore one usually generates a synthetic spectrum from the theoretical DOS to which the known corrections are applied, and then compares this synthetic spectrum with the experimental one.^{72,73} The theoretical DOS in Fig. 2(a) has to be modified to account for the lifetime broadening effects inherent to the PES technique, the finite energy resolution of an experiment, and the temperature of the sample. The lifetime broadening effects are represented by the Lorentzian whose FWHM= $\Gamma_l^0 E_B^2$, where Γ_L^0 is a parameter which fixes the scale of the broadening.^{73,74} The Γ_L^0 parameter was set at the value of 0.04 eV⁻¹ which is a typical value used for other metallic alloys.^{71,73,74} The instrumental broadening is represented by a Gaussian with FWHM Γ_G equal to the energy resolution of the PES experiment. The synthetic PES spectra [Fig. 2(b)] have been obtained from the theoretical DOS from Fig. 2(a) by multiplying it by the Fermi-Dirac function at 12 K, and then convoluting it with a Lorentzian and a Gaussian with the values Γ_G equal to 0.0 (infinitely high energy resolution), 200, 100, 50, and 8.6 meV. It is evident [curve 1 in Fig. 2(b)] that the lifetime broadening effects smear out the DOS spikiness for E_B 's smaller than -1.2 eV, i.e., in a hypothetical PES experiment with an infinitely high energy resolution one could expect to detect them only in the



FIG. 3. Near- E_F He I angle-integrated valence band (open circles) of the single-grain *i* Al₇₀Pd_{21.5}Mn_{8.5} at 12 K. The error bars are much smaller than the size of the circles. The solid line is the fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 12 K (broken curve) and convoluted with a Gaussian whose FWHM=8.6(1) meV.

vicinity of E_F , up to 1.2 eV below E_F . An inspection of curves 2–4 in Fig. 2(b) indicates that one should be able to observe the fine structure in the PES valence band of the *i*-Al-Pd-Mn alloy measured with an energy resolution better than about 50 meV up to 1.0 eV below E_F . For such an energy resolution the amplitudes of the spikes reach up to about 50% of the average spectral intensity [curves 4 and 5 in Fig. 2(b)].

It is apparent from the valence band shown in Fig. 1 that the measured intensity is a smooth function of E_B . The statistical error of the spectral intensity is an order of magnitude smaller than the expected maximum amplitude of the spikes. The He I valence band of the single-grain $i \text{ Al}_{70}\text{Pd}_{21.5}\text{Mn}_{8.5}$ alloy measured in the vicinity of E_F , where the lifetime broadening effects are negligible, on a dramatically expanded E_B scale (Fig. 3) shows no evidence for the spiky variation of the spectral intensity. A clearly developed Fermi edge confirms that this alloy, in spite of its high ρ ,³³ is metallic. It must be then concluded that the high energyresolution PES results cannot confirm the reality of the predicted¹⁷ spikiness of the DOS in the *i* Al-Pd-Mn system.

Other room and low-temperature PES experiments^{55,58–60} on fivefold and twofold surfaces of the *i* Al-Pd-Mn system carried out with an energy resolution in the range 25–70 meV also failed to detect the presence of any spiky variation of the spectral intensity of the valence bands close to E_F . Recent room-temperature PES measurements⁷⁵ on a tenfold surface of the decagonal Al-Co-Ni QC carried out with an energy resolution of 55 meV were also unable to detect the presence of the predicted⁷⁶ spikiness in the DOS. Thus it can be concluded that, in agreement with the theoretical prediction of Zijlstra and Janssen,²⁷ the fine structure of DOS does not exist in *i* QC's.

For the He I and He II photon energies used here, the PES is a surface-sensitive technique probing only a few atomic layers.⁷² The PES spectra thus reflect, simultaneously and in different proportions, both bulk and surface properties. The electronic structure of a quasicrystalline surface can, in principle, be different form that of the bulk. There are indications, based on the PES studies of the Al 2p, Mn 2p, and Pd 3d core-level lines in the single-grain *i*-Al-Pd-Mn

alloys, 58,77 that the pseudogap in the DOS(E_F) is shallower at the surface than in the bulk; this could be interpreted as evidence that the bulk and surface states are different. It is predicted that the DOS spikiness can be smoothed out by a surface.⁷⁸ It is thus conceivable, given the larger contribution to the He I and He II PES spectra from the surface than from the bulk, that the observed absence of the fine structure in the PES spectra indicates the nonexistence of the DOS spikes in the surface DOS rather than in the bulk. However, the absence of the spikiness observed in the PES spectra measured with different photon energies, 55,58-60 and thus for different probing depths, would seem to indicate that the spectra presented here are representative of the bulk electronic structure. For all known QC's, even the most "perfect" ones, diffuse scattering is observed in their diffraction spectra.^{79,80} The diffuse scattering results from the presence of some disorder in the diffracting structure. It is possible⁸¹ that this disorder might smooth out the DOS spikiness.

IV. SUMMARY

The low-temperature valence band of the single-grain i alloy $i \operatorname{Al}_{70}\operatorname{Pd}_{21.5}\operatorname{Mn}_{8.5}$ has been measured with the ultrahigh-

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energy-resolution PES technique. The alloy has a clearly developed Fermi edge, and is therefore metallic. The decrease of the spectral intensity toward E_F has been shown to be compatible with the presence of the theoretically predicted pseudogap in the DOS around E_F . The presence of the theoretically predicted fine structure of the DOS has not been observed with an energy resolution of 8.6 meV. It has been suggested that the failure to detect the predicted DOS spikiness in QC's is compatible with the theoretical results of Zijlstra and Janssen [Europhys. Lett. **52**, 578 (2000)] who showed that the DOS spikiness occurs only in lower-order periodic approximants to *i* QC's, but does not survive in the quasiperiodic limit.

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