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Photoemission studies of quasicrystals

Zbigniew M. Stadnik*

Department of Physics, University of Ottawa, Ottawa, Ont., Canada K1N 6N5

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Abstract

The results of the photoemission spectroscopy studies of the electronic structure of quasicrystals are reviewed. The presence and location of the features in the measured valence bands are in accordance with those in the calculated density of states. The existence of the theoretically predicted pseudogap at the Fermi level is confirmed. No evidence of the theoretically predicted spikiness of the density of states could be observed in the photoemission experiments of the highest energy resolution presently achievable.

Keywords: Quasicrystals; Electronic structure; Photoemission spectroscopy

1. Introduction

The physical properties of quasicrystals (QCs) are very unusual [1]. They are ultimately determined by the electronic structure of QCs. Knowledge and understanding of the electronic structure is thus essential if we are to understand the unexpected physical properties of QCs.

There are three major theoretical predictions of the electronic structure of icosahedral (i) and decagonal (d) alloys which are based on the calculations carried out for the corresponding crystalline approximants [2,26]. First, for the compositions at which the QCs form, the Fermi surface-effective Brillouin zone interaction results in the minimum of the electronic density of states (DOS) at the Fermi level (E_F) (Fig. 1). This means that a Hume–Rothery-type electronic mechanism is mainly responsible for the stabilization of QCs. This DOS minimum is enhanced by the hybridization of sp and d states [4]. Second, the DOS of QCs is very unusual in that it consists of many very fine spiked peaks with widths of about 10 meV (Fig. 1). This spikiness is believed to be responsible for the observation that the electrical conductivity of QCs is unusually sensitive to slight changes in their composition. The predicted minimum of DOS(E_F) (a pseudogap) is not a unique characteristic which distinguishes the electronic structure of QCs from that of crystalline and amorphous alloys since the structure induced pseudogap does occur in both crystalline and amorphous systems. However, the predicted DOS spikiness seems to be such a unique property which distinguishes QCs from other materials. Third, the i-Al-Pd-Re alloy is distinguished from all QCs in that it has the highest electrical resistivity and might be in fact an insulator [5]. A real gap in the DOS(E_F) is predicted for certain approximants to this i alloy [6].

We review here the results of the electronic structure studies of QCs obtained with the photoemission spectroscopy (PES). They are discussed in relation to theoretical models of the electronic structure of QCs which attempt to explain some of the unusual physical properties of these alloys.

2. Experimental procedure

Thermodynamically stable polyquasicrystalline i and d alloys were prepared as described elsewhere [7]. All polyquasicrystalline samples were characterized by X-ray diffraction and electron microscopy, both techniques showing the samples to be single phase. Bragg-peak widths were resolution limited.

The preparation of the single-grain i-$Al_{70.5}Pd_{21}Mn_{8.5}$ has been described in [8]. The preparation of the single-grain i-$Al_{70}Pd_{21.5}Mn_{8.5}$ used in the ultraviolet photoelectron spectroscopy (UPS) study [9] has been described in [10]. Its surface was oriented within 0.25° perpendicular to the fivefold axis. An inspection of the sample for the presence of second phases using scanning electron and scanning Auger miscroscopy indicated that, within a detection limit of 1%, the sample is single phase. The surface of the fivefold single-grain i-$Al_{70}Pd_{21.5}Mn_{8.5}$ was prepared for the UPS experiments by sputtering–annealing cycles. Annealing periods were typically 30 min during cleaning and several

* Corresponding author. Tel.: +1-613-562-5800/ext 6761; fax: +1-613-562-5190.
E-mail address: stadnik@physics.uottawa.ca (Z.M. Stadnik).

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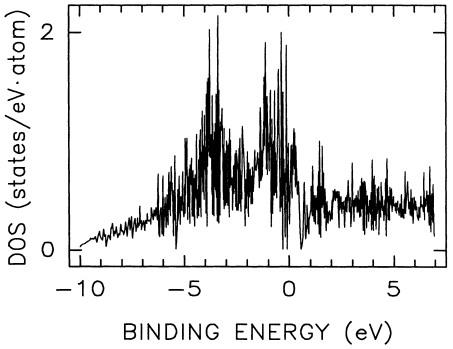

Fig. 1. Theoretical DOS for the 1/1 approximant of the i-Al-Pd-Mn alloy (model M2, [3]).

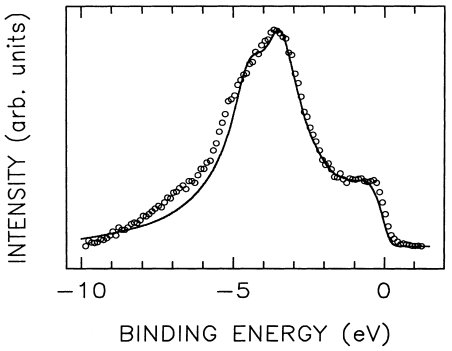

Fig. 2. Comparison of the room-temperature valence band of the i-$Al_{70}Pd_{20}Mn_{10}$ alloy measured at $h\nu$=100 eV with the energy resolution of 0.4 eV (open circles, [12]) with the broadened theoretical DOS for the 8/5 approximant of the i-Al-Pd-Mn alloy (solid line, [3]).

hours before the UPS experiments. Annealing was done at 773 K [11] which yielded a clear fivefold low-energy electron diffraction pattern [9].

PES experiments at various temperatures were carried out using an UPS spectrometer equipped with a high-intensity He discharge lamp producing a He I line at 21.2 eV and He II line at 40.8 eV [7,9], and also the synchrotron radiation facilities with different photon energies $h\nu$ [8,12].

3. Results and discussion

In order to make a meaningful comparison between the theoretical DOS, which is calculated for a bulk QC, and the valence band measured using the surface-sensitive PES technique, the former has to be appropriately broadened to account for the lifetime broadening effects inherent to the PES technique and for the finite energy resolution of a PES experiment [7]. Such a comparison for the i-$Al_{70}Pd_{20}Mn_{10}$ alloy shows a good agreement (Fig. 2). From the PES spectra measured for $h\nu$ values close to the Pd 4d Cooper minimum [12], the partial Mn 3d and Pd 4d DOSs can be determined. These experimental partial DOSs are compared with the appropriately broadened theoretical ones in Fig. 3. A relatively good agreement between the experimental partial DOSs and the corresponding theoretical ones is evident. It can be concluded that theoretical calculations of the DOS for approximant structure to i alloys account well for the experimentally observed DOSs in these alloys [13]. This is also true for d alloys [13].

The low-temperature He II valence bands of some representative i and d alloys (Fig. 4) have a two-peak structure. The feature at the binding energy of about −4.1 eV is mainly due to the Pd 4d- or Cu 3d-derived states, whereas the feature close to E_F is predominantly due to the states of Mn, Co, and Ni 3d or Re 5d character, in agreement with the theoretical DOS calculations for the approximants to i-Al-Pd-Mn [3], i-Al-Pd-Re [6], and d-Al-Co-Cu [14] alloys. There are three salient features of the valence bands of stable QCs (Fig. 4). First, there is a clear decrease of the spectral intensity as E_F is approached. Second, the presence of the Fermi edge is indicated in all studied QCs. Third, as compared to that of other QCs, a significantly lower spectral intensity at E_F is observed in the i-Al-Pd-Re alloy.

The decrease of the spectral intensity as E_F is approached, which is clearly distinguishable from the Fermi-edge cutoff (Fig. 4), can be shown to be compatible with the presence of a pseudogap, using a model proposed by Mori et al. [15]. As conventional alloys of QC-forming elements do not generally display a DOS minimum close to E_F, the model

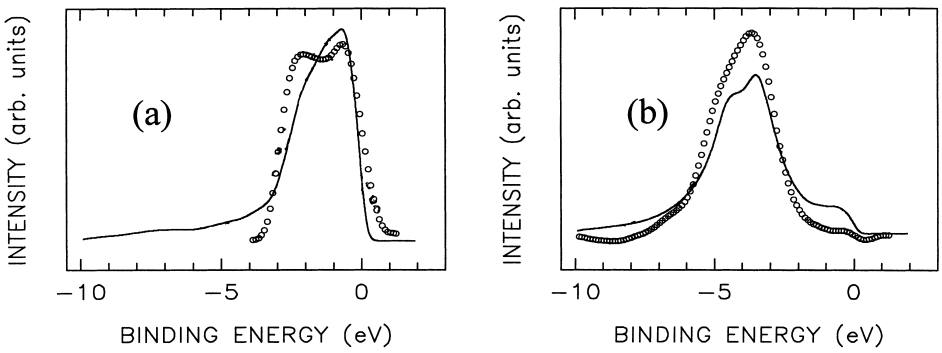

Fig. 3. Comparison of the partial DOS in the i-Al-Pd-Mn alloy of the (a) Mn 3d; (b) Pd 4d character obtained from the PES spectra (open circles, [12]) with the corresponding broadened theoretical partial DOS (solid line, [3]).

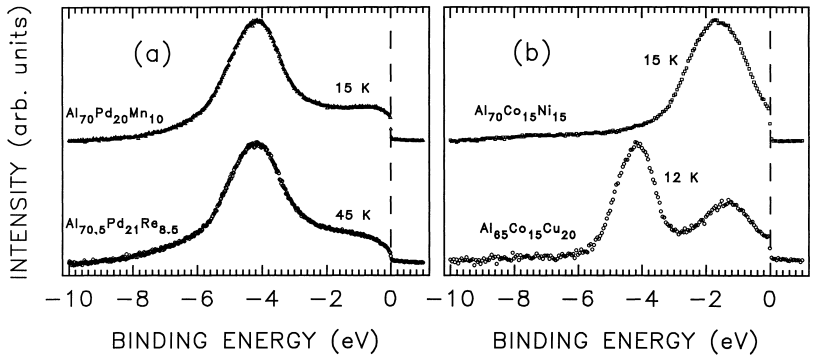

Fig. 4. Low-temperature He II valence bands of (a) i alloys; (b) d alloys. The energy resolution is about 30 meV. The spectra have been normalized to give a constant height between the maximum and minimum count.

assumes that a simple linear extrapolation of the spectra for the binding energy range directly before the peak of the valence band feature close to E_F represents the DOS of an alloy without a pseudogap (the normal DOS). The presence of the pseudogap would result in an intensity dip which is assumed to be of Lorentzian shape. Thus the observed intensity close to E_F is the convolution of the normal DOS multiplied by the pseudogap Lorentzian function and by the Fermi–Dirac distribution function, and the experimental resolution Gaussian function [7]. This model (Fig. 5) fits well the near-E_F region of the valence bands of i-$Al_{70}Pd_{20}Mn_{10}$ and of other i and d alloys [7]. The high-resolution UPS data are in support for the theoretically predicted presence of the pseudogap in QCs.

An unambiguous experimental evidence for the presence of the pseudogap was provided by an elegant PES experiment at 570 K with an energy resolution of 70 meV [8] on a single-grain i-$Al_{70.5}Pd_{21}Mn_{8.5}$, whose surface was perpendicular to the fivefold axis. In this experiment, the states both below and above E_F were probed. The PES technique can also probe the states above E_F is they are populated. According to Fermi–Dirac statistics, in metallic systems these states become populated at nonzero temperatures. At a temperature of 570 K, a region of several hundred meV above E_F becomes accessible. A spectral function, which is proportional to the DOS, can be reconstructed from the 570 K valence band [8]. It clearly shows a minimum of DOS located at 90 meV above (Fig. 6). For binding energies higher than about 0.3 eV, a considerable scatter of the reconstructed spectral function, which is due to the small probability that the states are populated, prevents a meaningful evaluation of the DOS.

The valence band region of QCs close to E_F was examined with the highest energy resolution presently available [7,16]. As an example, a high energy resolution spectrum for the i-$Al_{70}Pd_{20}Mn_{10}$ alloy [16] is shown in Fig. 7(a). A clearly developed Fermi edge, which can be perfectly fitted using a Fermi–Dirac function convoluted with a Gaussian function representing the instrumental broadening, is observed. Its temperature evolution follows exactly that of a Fermi–Dirac function (Fig. 7(b)). Spectra as those in Fig. 7 were also observed [7] for other polyquasicrystalline samples of QCs. This constitutes a direct and convincing proof that these systems, in spite of their high electrical resistivity, are metallic.

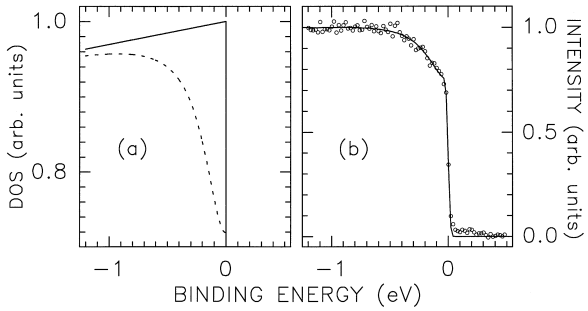

Fig. 5. (a) The model of the DOS at 0 K which is used to fit the near-E_F region of the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ at 15 K from Fig. 4(a). The solid line represents the normal DOS at 0 K, whereas the broken line represents the dip which must be subtracted from the normal DOS in order to fit the near-E_F region of the valence band. (b) The near-E_F region of the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ at 15 K from Fig. 4(a) (open circles) fitted (solid line) to the model DOS shown in (a) which is multiplied by the Fermi–Dirac function at 15 K and convoluted with the experimental resolution Gaussian function of FWHM=32(3) meV.

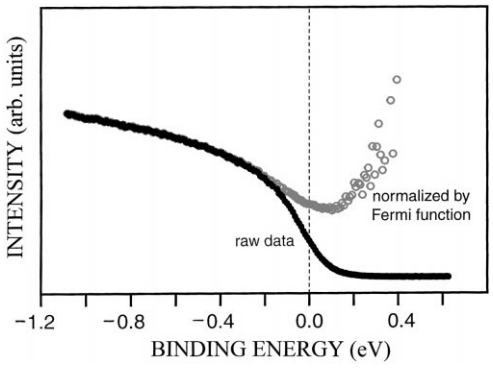

Fig. 6. Valence band of the single-grain i-$Al_{70.5}Pd_{21}Mn_{8.5}$ at 570 K measured at $h\nu$=32.3 eV (full circles) and the reconstructed spectral function (open circles) near-E_F [8].

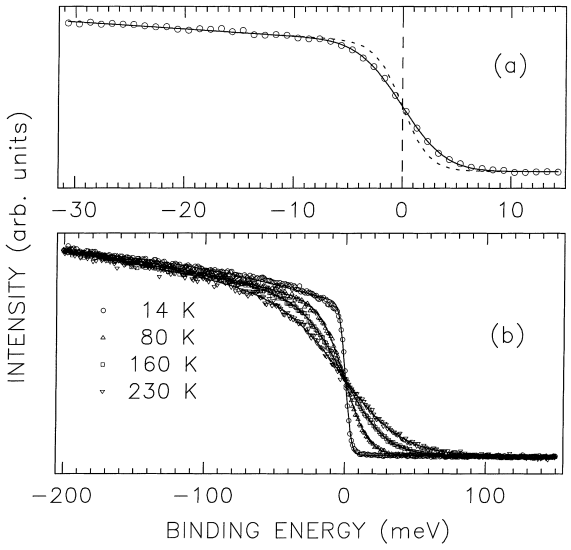

Fig. 7. (a) Near-E_F He I valence band of i-$Al_{70}Pd_{20}Mn_{10}$ at 14 K. The solid line is the fit to a linearly decreasing intensity multiplied by the Fermi–Dirac function at 14 K (broken curve) and convoluted with a Gaussian whose FWHM=5.8(2) meV. Note that the step between the data points is 1 meV. (b) Near-E_F He I valence bands of i-$Al_{70.5}Pd_{21}Mn_{8.5}$ measured at different temperatures. The solid lines are the fits as described in (a). Note that the different binding energy scales in (a) and (b).

Recent low-temperature, high-energy-resolution UPS experiments on a fivefold single-grain i-$Al_{70}Pd_{21.5}Mn_{8.5}$ alloy [9] confirm the main conclusions reached from the similar experiments carried out on polyquasicrystalline i-Al-Pd-Mn alloys [16]. The valence band of this single-grain sample (Fig. 8(a)) differs from that of a polyquasicrystalline

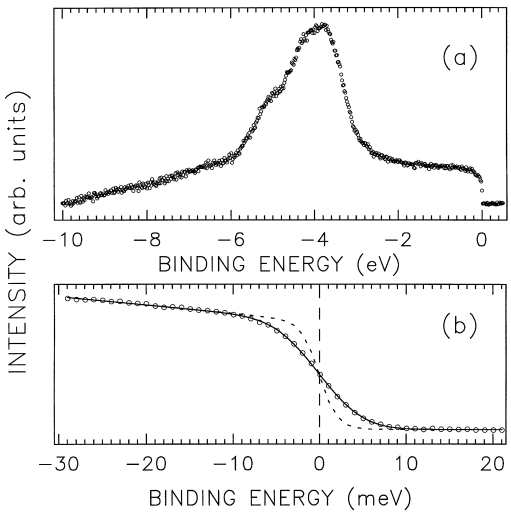

Fig. 8. (a) He II valence band of the single-grain i-$Al_{70}Pd_{21.5}Mn_{8.5}$ at 12 K measured with the resolution of 38(3) meV. (b) Near-E_F He I valence band of the single-grain i-$Al_{70}Pd_{21.5}Mn_{18.5}$ at 12 K. The solid line is the fit to a linearly decreasing intensity multiplied by the Fermi–Dirac function at 12 K (broken curve) and convoluted with a Gaussian whose FWHM=8.6(1) meV. Note that the different binding energy scales in (a) and (b).

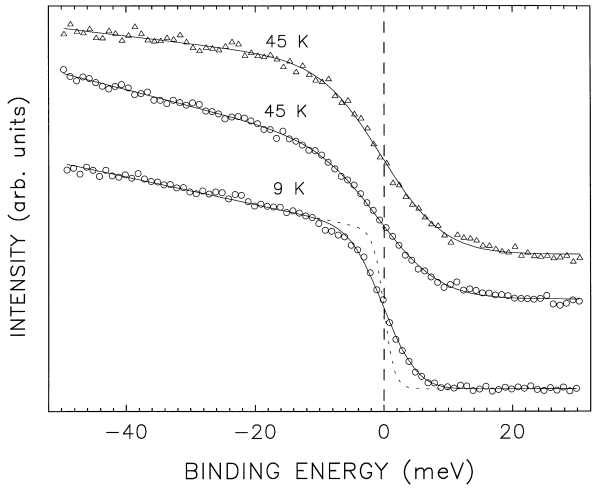

Fig. 9. Near-E_F He I valence band of i-$Al_{70.5}Pd_{21}Re_{8.5}$ (circles) and Ag (triangles) evaporated on it. The solid lines are the fits to a linearly decreasing intensity multiplied by the Fermi–Dirac function at 45 and 9 K (broken curve) and convoluted with a Gaussian whose FWHM is respectively, 6.0(5) and 9.2(3) meV for the spectra measured at 45 and 9 K.

i-$Al_{70}Pd_{20}Mn_{10}$ sample (Fig. 4(a)) in that the main feature at the binding energy of −4.1 eV of the former has a clear shoulder at about −5 eV [9]. The decrease of the spectral intensity toward E_F (Fig. 8(a)) can be successfully fitted [9] to the model of Mori et al. [15], yielding similar pseudogap parameters as those obtained from a similar fit of a polyquasicrystalline i-$Al_{70}Pd_{20}Mn_{10}$ (Fig. 5). As in the case of polyquasicrystalline i-$Al_{70}Pd_{20}Mn_{10}$ (Fig. 7(a)), a clearly developed Fermi edge is observed for the single-grain i-$Al_{70}Pd_{21.5}Mn_{8.5}$ alloy (Fig. 8(b)).

Even for the i-Al-Pd-Re alloys, which have the highest values of the electrical resistivity among all QCs, the near-E_F spectra also exhibit a Fermi edge. This can be seen by comparing the near-E_F spectrum at 45 K of i-$Al_{70.5}Pd_{21}Re_{8.5}$ with that of Ag evaporated onto the alloy (Fig. 9). This is also evidenced by the fits of the spectra of this alloy measured at 45 and 9 K (Fig. 9). It is concluded that in spite of its high electrical resistivity, the i-Al-Pd-Re alloy is a metal.

In order to assess the possible existence of the predicted DOS spikiness, a meaningful comparison between the measured DOS spectra and the calculated DOS has to be made. This involves modifying the theoretical DOS to account for the finite energy resolution of an experiment, the lifetime broadening effects inherent to a given spectroscopic technique used to measure the DOS, and the sample temperature [7]. It is clear [7,13] that the possible DOS spikiness can be observed in a QC sample at room and/or low temperatures with the PES technique with an energy resolution better than about 100 meV, and only in the vicinity of E_F. However, such spikes are not observed in the UPS valence bands measured with high and ultra high energy resolution (Figs. 4, 6–9).

There are several possible reasons which might explain the failure to detect the predicted DOS spikiness in high energy resolution PES experiments. The preparation of surfaces for PES experiments by using a standard procedure of scraping or fracturing (carried out at low temperatures to prevent any structural reorganization of the sample) the polyquasicrystalline samples could, in principle, lead to a destruction of their quasicrystalline order, and thus the disappearance of the fine structure of the DOS. However, the valence bands of well-characterized single grains of i-Al-Pd-Mn alloys [8,9,17] are virtually the same as those of polyquasicrystalline alloys [7,16], which indicates that the employed surface preparation procedures [7,16] maintained the sample surface quasicrystallinity. It may not be possible to detect the predicted DOS spikiness even with the PES experiments of the highest energy resolution because of the existence of chemical and topological disorder in QCs of high structural quality. Such disorder, which is not taken into account in the electronic structure calculations, may wash out the DOS spikiness induced by quasiperiodicity. Furthermore, the concept of quasiperiodicity implies that no two crystallographic positions of a given atom are exactly the same, which can be viewed as a sort of topological disorder. There is growing experimental evidence that the chemical and topological disorder are present in these structurally 'perfect' QCs. Diffuse scattering is often observed in X-ray-, electron-, and neutron-diffraction patterns of high-quality QCs [18–20]. Its presence indicates that some disorder must exist in the diffracting structure. Local probes, such as Mössbauer spectroscopy [21], nuclear magnetic resonance [22,23], and nuclear quadrupole resonance [22,24], clearly detect the distribution of the electric quadrupole splittings in high-quality stable QCs. Such a distribution can be detected only if there is a chemical and/or topological order in the investigated samples [21]. The apparent success of quantum interference theories (the electron–electron interaction and the weak-localization effects), which were originally developed for highly disordered conductors, in accounting for the temperature and field dependencies of electrical resistivities of high-quality QCs [5] also indicates the importance of chemical disorder. The experiments mentioned above demonstrate that chemical and/or topological disorder is present in the stable QCs and therefore, may smear out the DOS spikiness predicted for disorder-free QCs. And finally, it is conceivable that the predicted DOS spikiness is an artifact of the calculations. It has been recently demonstrated [25] that unphysical spikes do appear in the calculated DOS of a toy model with an assumed a priori smooth DOS as a result of insufficient computational precision necessary for analyzing structures with large unit cells. It was concluded that the predicted fine structure at the level of about 100 meV may be an artifact. This is rather an alarming possibility and it is important to investigate it in more detail.

Acknowledgements

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