

Electronic Structure of Icosahedral Alloys Studied by Ultrahigh Energy Resolution Photoemission Spectroscopy

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The results of a systematic ultrahigh resolution ultraviolet photoemission study of the electronic structure of stable icosahedral alloys $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$, $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$, and $\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ are presented. It is shown that all icosahedral alloys have a clearly developed Fermi edge and are thus metallic down to the temperature of measurement (14–45 K). A marked decrease of the spectral intensity towards the Fermi level in these alloys is demonstrated to be consistent with the existence of the theoretically predicted pseudogap. With an experimental resolution of 6 meV, no evidence of the theoretically predicted spikiness of the density of states could be observed. [S0031-9007(96)01023-X]

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Quasicrystals are a new form of the solid state which differ 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 [1]. A central problem in condensed-matter physics is to determine whether quasiperiodicity leads to new physical properties which are significantly different from those of crystalline and amorphous materials. Such unusual properties have been found in icosahedral (*i*) alloys of high structural quality [1,2]. Some of their most striking features, which are not expected for alloys consisting of normal metallic elements, are the very high value of the electrical resistivity (up to $\sim 10 \Omega \text{ cm}$ at low temperatures in the *i*-Al-Pd-Re system [3–6]), a strong negative temperature coefficient of resistivity, an increase of resistivity with increased structural perfection of the samples along with an extreme sensitivity to sample composition, and a low electronic contribution to the specific heat and thus a low density of states (DOS) at the Fermi level E_F [1–6].

Several mechanisms have been proposed to allow a qualitative explanation of these unusual properties. Conventional mechanisms are based on band-structure effects and the Hume-Rothery rule and imply the existence of a pseudogap in the DOS around E_F , while rather more exotic mechanisms proposed invoke the concepts of tunneling, localization, and critical states [1–6]. The existence of a pseudogap is supported by electronic structure calculations performed for the crystalline approximants of *i* alloys [7,8]. These calculations also predict a very spiky structure of the DOS, with the width of spiky peaks of the

order of 10–20 meV. While the pseudogap can be related to the stability and high value of the electrical resistivity of *i* alloys, the spiked structure of the DOS is believed to be a signature of quasiperiodicity and to be responsible for several unusual temperature-dependent transport properties [7–9].

Photoemission spectroscopy (PES) measurements with ultrahigh energy resolution are essential [10] in order to unambiguously verify the hypothesis of the DOS spikiness in *i* alloys. So far, no direct evidence for the presence of this spikiness has been found as most of the previously published PES investigations were limited to resolutions larger than 230 meV [10,11]. Based on the claim of the absence of a sharp Fermi edge, two PES studies concluded that there is a pseudogap in the DOS(E_F) in *i*-Al-Cu-Fe [11] and in *i*-Al-Pd-Mn [12]. However, the conclusion common to these two previous studies must be questioned, given that they were both carried out at room temperature [11,12]. In order to establish the presence or absence of a Fermi edge reliably, measurements must be performed at low temperatures, where thermal broadening of the Fermi-Dirac function is small, and with an instrumental contribution of the same order of magnitude as $k_B T$ [13]. In this Letter we report the main results of an extensive study [14] of the electronic structure of most known, stable *i* alloys, where it is demonstrated that only through use of these stringent conditions can firm conclusions regarding the detailed form of the near- E_F DOS be drawn.

Four representative *i* alloys of nominal compositions $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$, $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$, $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$, and

$\text{Al}_{70.5}\text{Pd}_{21}\text{Re}_{8.5}$ were prepared as described elsewhere [3,14]. X-ray diffraction and electron microscopy studies showed that the samples are single phase and exhibit resolution-limited Bragg-peak widths. The samples were mounted on the cold finger of a liquid He cryostat and, while held at the lowest measurement temperature, were cleaned *in situ* ($\sim 10^{-10}$ Torr) by repeated scraping with a diamond file until no surface contamination could be detected [15]. Valence band spectra obtained from different regions of a given sample, as well as from several samples corresponding to a given composition, were reproducible. We therefore believe that the spectra represent the intrinsic features of the *i* alloys studied. The UPS spectrometer was equipped with a high-intensity He discharge lamp (Gammadata) and a high-resolution Scienta SES200 hemispherical analyzer. The instrumental resolution was determined by fitting the Fermi edge of Ag, evaporated *in situ* onto the previously measured samples, with the convolution of a Gaussian and the product of a linear DOS and the Fermi-Dirac function at the appropriate temperature [13]. The FWHM of the Gaussian is the only adjustable parameter in this procedure and gives directly the instrumental resolution. For high resolution spectra this was thus determined to be 6 meV. The uncertainty in the determination of E_F is less than 0.5 meV. The UPS valence bands presented here are corrected for the secondary-electron background [10].

The low-temperature He II valence bands of four *i* alloys (Fig. 1) have a similar two-peak structure. The feature close to E_F is predominantly due to states of Fe 3*d*,

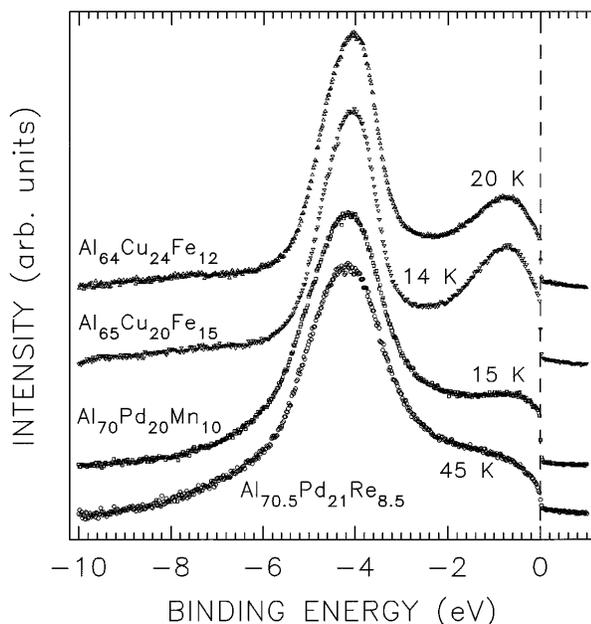


FIG. 1. Low-temperature He II valence bands of four *i* alloys. The energy resolution is ~ 30 meV. The spectra have been normalized to give a constant height between the maximum and minimum count.

Mn 3*d*, or Re 5*d* character, as appropriate, whereas the feature at a binding energy (BE) of about -4 eV is mainly due to the Cu 3*d*- or Pd 4*d*-derived states [14–16]. The intensity difference between the Fe 3*d* features of the *i* alloys $\text{Al}_{64}\text{Cu}_{24}\text{Fe}_{12}$ and $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ is consistent with the compositions of these alloys, confirming the validity of the surface preparation procedure. The two most salient features of the spectra in Fig. 1 are the presence of a Fermi edge in all the *i* alloys studied and, as compared to that in the Al-Cu-Fe and Al-Pd-Mn alloys, a significantly lower spectral intensity at E_F in the Al-Pd-Re system.

The valence band region of the *i* alloys close to E_F was examined with the highest energy resolution presently available to us. As an example, a high energy resolution spectrum for the *i*- $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ alloy is shown in Fig. 2(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 [Fig. 2(a)], is observed. Its temperature evolution follows exactly that of a Fermi-Dirac function [Fig. 2(b)]. Spectra as those in Fig. 2 were also observed for Al-Cu-Fe, Al-Cu-Ru, Al-Cu-Os, and Zn-Mg-Y *i* alloys [14]. This constitutes a direct and convincing proof that these *i* systems, in spite of their high electrical resistivity, are metallic and not semiconducting [17]. Furthermore, these results seem to show that the analysis of recent room temperature photoemission spectra from *i*- $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$, where the decrease in the DOS

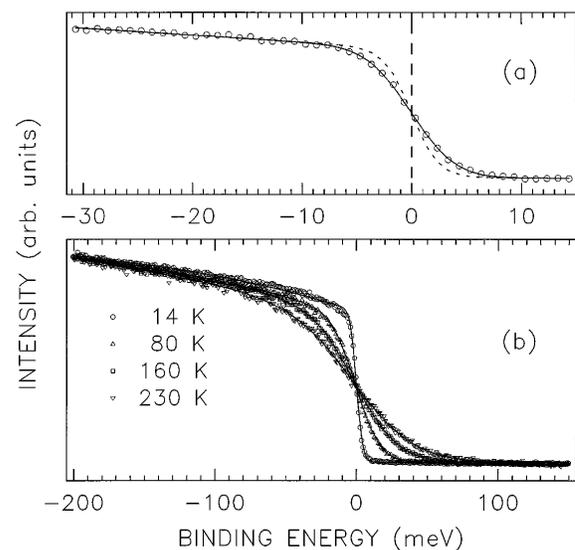


FIG. 2. (a) Near- E_F He I valence band of *i*- $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ at 14 K. The solid line is the fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 14 K (broken curve) and convoluted with a Gaussian whose FWHM = 6 meV. Note that the step between the data points is 1 meV. (b) Near- E_F He I valence bands of *i*- $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ measured at different temperatures. The solid lines are the fits as described in (a). Note the different binding energy scales in (a) and (b).

towards E_F is interpreted in terms of a power law, is invalid [12].

The behavior of the i -Al_{70.5}Pd₂₁Re_{8.5} alloy was found to be different from the other compounds studied in that we were unable to cool it down as far as all the other samples. The lowest temperature achieved was 45 K [18]. However, all the samples of this alloy displayed a clear Fermi edge. This can be seen by comparing a near- E_F spectrum of i -Al_{70.5}Pd₂₁Re_{8.5} with that of Ag evaporated onto the alloy (Fig. 3). The temperature dependence of the near- E_F spectra of this alloy was found to follow that of the Fermi-Dirac function. The i -Al-Pd-Re system is also distinct from the other i alloys in that it has a significantly lower spectral intensity at E_F (Fig. 1). This implies a DOS(E_F) that is smaller in the i -Al-Pd-Re system than in other i alloys, possibly one of the factors responsible for the anomalously low electrical conductivity [1–6]. We stress, however, that although the DOS(E_F) in the i -Al-Pd-Re system is very small, it is nevertheless finite and the alloy is thus metallic down to the temperatures measured.

Previous low energy resolution (233–500 meV), room-temperature PES data from the i alloys [10,11,15,16] could not convincingly demonstrate the existence of the theoretically predicted [7,8] pseudogap in the DOS around E_F , since the observed decrease of the spectral intensity towards E_F could not be distinguished from the Fermi edge cutoff. With the aim of obtaining simple parameters to characterize the pseudogap, one can simulate the observed structure close to E_F in the valence bands of the i alloys (Fig. 1) using the model proposed by Mori *et al.* [11]. As conventional alloys of the quasicrystal-forming elements do not generally display a DOS minimum close to E_F , we assume that a simple linear extrapolation of the spectra between BE's -1.2 and

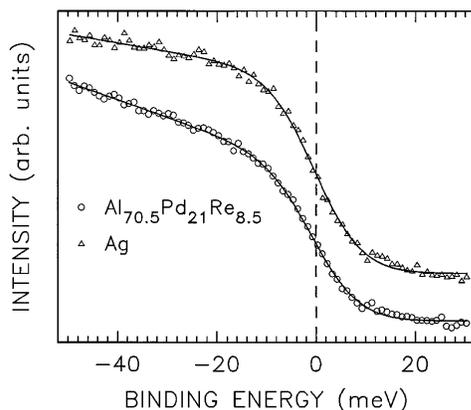


FIG. 3. Near- E_F He I valence bands of i -Al_{70.5}Pd₂₁Re_{8.5} and Ag evaporated onto it measured at 45 K with an experimental resolution of 6 meV. The solid curves are the fits to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 45 K (the convolution with the instrumental broadening function produces a negligible effect at this temperature).

-0.7 eV (Fig. 1) accounts for the DOS without the pseudogap (the normal DOS). The presence of the 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 [Fig. 4(a)]. As an example, we show the application of this model to the near- E_F region of the valence band of i -Al₇₀Pd₂₀Mn₁₀. One obtains a good fit of the near- E_F region of the valence band of i -Al₇₀Pd₂₀Mn₁₀ with this model [Fig. 4(b)] for parameter values $C = 28.1\%$ and $\Gamma_L = 0.22$ eV. The same procedure applied to the near- E_F valence band spectrum of Al₆₄Cu₂₄Fe₁₂ gives a similarly good fit for $C = 55.5\%$ and $\Gamma_L = 0.32$ eV, and likewise for Al₆₅Cu₂₀Fe₁₅ ($C = 56.8\%$, $\Gamma_L = 0.34$ eV) and Al_{70.5}Pd₂₁Re_{8.5} ($C = 48.2\%$, $\Gamma_L = 0.21$ eV). Although this model is purely phenomenological, the values arrived at for the width of the pseudogap are in good accord with the order of magnitude expected from calculations [7]. Thus we conclude that the observed intensity depression close to E_F in the valence bands of i alloys is accounted for by the existence of the Hume-Rothery pseudogap in the DOS.

As was shown earlier [10], the predicted DOS spikiness should be detectable in ultrahigh energy resolution PES experiments in the vicinity of E_F , where the influence of lifetime broadening effects is negligible. No trace of such spikiness could be observed in this study (Figs. 1–3), even with an energy resolution as high as 6 meV (Fig. 2). Such spikiness was also not observed in a recent PES study [12] of i -Al-Pd-Mn with an energy resolution of 50 meV. Furthermore, no DOS spikiness could be detected in a nuclear magnetic resonance pressure study of i -Al-Cu-Ru [19]. Assuming that the predicted spikiness is not an

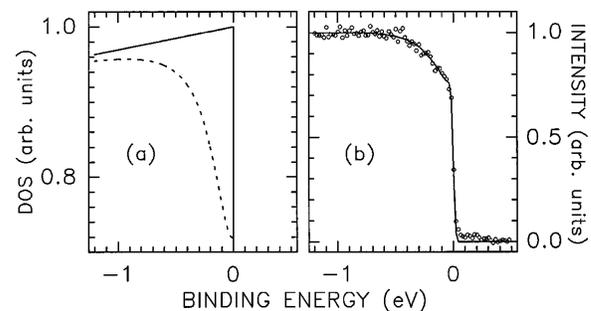


FIG. 4. (a) The model of DOS at 0 K which is used to fit the near- E_F region of the valence band of i -Al₇₀Pd₂₀Mn₁₀ at 15 K from Fig. 1. The solid line, which is obtained from a linear fit of the band between BE's -1.2 and -0.7 eV, represents a normal DOS (without a pseudogap). The broken line represents 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 -Al₇₀Pd₂₀Mn₁₀ at 15 K from Fig. 1 (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 meV.

artifact of the electronic structure calculations [7,8], the failure to detect it experimentally may be explained by the presence of disorder even in the structurally “perfect” (phason free) i alloys. Local probes, such as Mössbauer spectroscopy [20], nuclear magnetic resonance [21], and nuclear quadrupole resonance [21,22], clearly show the presence of distributions of the hyperfine parameters in the structurally perfect i alloys. Such distributions can only occur if there is chemical or topological disorder in the samples. Diffuse scattering is often observed in x-ray and electron diffraction patterns of high-quality quasicrystals [23], also indicating that some disorder must be present in the diffracting structure. A recent study on the propagation of acoustic shear waves in a single-grain i -Al-Pd-Mn shows [24] similarities between the acoustic properties of this alloy and those of amorphous metals. Additionally, the success of quantum interference theories [1,2], which were originally developed for disordered conductors, in accounting for the temperature and field dependencies of the electrical conductivity and magnetoresistance of several stable i alloys, indicates that these alloys are electronically disordered. Thus the presence of this disorder, which may be an intrinsic feature of the quasiperiodic systems, washes out the predicted spikiness in the DOS.

In summary, we have demonstrated that the stable i alloys of high structural quality have a clearly developed Fermi edge and are thus metallic. The decrease of the spectral intensity towards E_F in these alloys has been shown to result from the presence of the theoretically predicted pseudogap in the DOS around E_F . The presence of the theoretically predicted spikiness in the DOS could not be observed even with a resolution of 6 meV.

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