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Abstract

We use hard x-ray photoemission to resolve a controversial issue regarding the mechanism for the formation of quasicrystalline solids, i.e., the existence of a pseudogap at the Fermi level. Our data from icosahedral fivefold Al-Pd-Mn and Al-Cu-Fe quasicrystals demonstrate the presence of a pseudogap, which is not observed in surface sensitive low energy photoemission because the spectrum is affected by a metallic phase near the surface. In contrast to Al-Pd-Mn, we find that in Al-Cu-Fe the pseudogap is fully formed; i.e., the density of states reaches zero at E_F indicating that it is close to the metal-insulator phase boundary.

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Bulk Electronic Structure of Quasicrystals

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We use hard x-ray photoemission to resolve a controversial issue regarding the mechanism for the formation of quasicrystalline solids, i.e., the existence of a pseudogap at the Fermi level. Our data from icosahedral fivefold Al-Pd-Mn and Al-Cu-Fe quasicrystals demonstrate the presence of a pseudogap, which is not observed in surface sensitive low energy photoemission because the spectrum is affected by a metallic phase near the surface. In contrast to Al-Pd-Mn, we find that in Al-Cu-Fe the pseudogap is fully formed; i.e., the density of states reaches zero at E_F indicating that it is close to the metal-insulator phase boundary.

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Although quasicrystals were discovered by Shechtman and co-workers [1] more than twenty-five years ago, and many aperiodically ordered alloys have been synthesized and even naturally occurring quasicrystals from a meteorite have been identified [2], the fundamental question of why nature prefers quasicrystalline order in some parts of the alloy phase diagram has remained controversial. The stability of quasicrystals has been ascribed to a mechanism that predicts the existence of a pseudogap in the electronic density of states (DOS) at the Fermi level (E_F) due to quasi-Brillouin zone and Fermi surface interaction [3,4]. Electronic structure calculations provide evidence for the pseudogap around E_F [4,5], but an experimental proof has been elusive, and the shape of the pseudogap specific to quasicrystals has not been identified to date.

Surface sensitive studies [6–9] using low photon energy photoelectron spectroscopy on a series of quasicrystals including icosahedral *i*-Al-Pd-Mn and *i*-Al-Cu-Fe show, instead of a pseudogap, a clearly developed metallic Fermi edge with a rounded shape of the spectral function decreasing in intensity towards E_F . Although a metallic Fermi edge was observed, this decrease in intensity was identified as the signature of the pseudogap [6–9]. On the other hand, bulk transport properties of quasicrystals such as high resistivity, negative temperature coefficient of resistivity, and low electronic specific heat indicate the presence of a pseudogap at E_F . This discrepancy was ascribed to an enhanced surface metallicity compared to the bulk [9], which thus masks the pseudogap in low energy (i.e., surface sensitive) photoemission.

One method to avoid such surface effects in photoemission is the use of high photon energies. The variation of the inelastic scattering cross section as a function of electron kinetic energy permits truly bulk sensitive data

to be recorded, with information depths of the order of 100 Å [10,11]. Hard x-ray photoelectron spectroscopy (HAXPES) has thus been increasingly applied to unravel the bulk electronic structure of materials. Here we demonstrate that this method convincingly reveals the pseudogap in icosahedral quasicrystals, and that it permits a semi-quantitative comparison with transport data from different quasicrystals: unlike in *i*-Al-Pd-Mn, the pseudogap reduces the density of states to zero at E_F in *i*-Al-Cu-Fe.

Single grain fivefold *i*-Al-Pd-Mn and *i*-Al-Cu-Fe quasicrystals (henceforth referred to as Al-Pd-Mn and Al-Cu-Fe) with bulk composition Al_{69.4}Pd_{20.8}Mn_{9.8} and Al₆₃Cu₂₅Fe₁₂, respectively were grown using the Bridgman technique and were subsequently polished and oriented to expose a fivefold axis. The native oxide layer on the quasicrystals was removed either by *in situ* cleaving or by 1.5 keV Ar⁺ ion sputtering for 30 mins. While cleaving retains the bulk composition at the surface, ion sputtering makes the surface Pd rich. Therefore, to restore the surface composition and quasicrystallinity, the sputtered specimens were annealed for 1.5 hours at 900–1000 K [12,13]. The measurements were performed at the P09 beam line [14] at Petra III, Deutsches Elektronen-Synchrotron, Hamburg and at ID32 beam line [15] at the European Synchrotron Radiation Facility, Grenoble using 7.93 and 5.95 keV x rays at 300 K and 40 K. Post-monochromators were used to improve the energy resolution and stability. At both the facilities, the spectra were recorded with a Phoibos 225 HVElectron energy analyzer from Specs Surface Nano Analysis GmbH, Germany. The inelastic mean free paths in Al-Pd-Mn and Al-Cu-Fe at 5.95 and 7.93 keV are 85 Å and 105 Å, respectively [16]. To maximize the bulk sensitivity and optimize the signal to the background ratio, the x rays were incident at almost grazing angle (5° with the surface) and the

electrons were detected in nearly normal emission geometry with the electric field vector and the dipole cone pointing into the direction of the analyzer. The overall resolution, including both the source and the analyzer contributions, was obtained by fitting the Au Fermi edge spectrum with a Gaussian function of FWHM given by 0.28 and 0.32 eV at 5.95 and 7.93 keV, respectively.

The valence band data of Al-Pd-Mn and Al-Cu-Fe are shown in Fig. 1 for low and high photon energies. In stark contrast to the low energy photoemission spectra [7,9] (dashed blue lines), the spectral weights of Al-Pd-Mn as well as Al-Cu-Fe recorded at 5.95 keV photon energy (red lines) are strongly reduced in the near- E_F region. This observation provides strong evidence for the existence of the pseudogap. The spectra in the near- E_F region are shown in an expanded scale in Figs. 1(c) and 1(d) together with the Fermi edge of a Au foil that was in electrical contact with the specimen. In order to quantitatively evaluate the depth and width of the pseudogap, we have recorded the valence band in the energy range near E_F with a smaller step size and better statistics (Fig. 2).

In order to emulate the pseudogap with only a few parameters, and to distinguish it from the Fermi edge, Stadnik *et al.* [7] used a Lorentzian function following the suggestion of Mori *et al.* [17]. We have performed

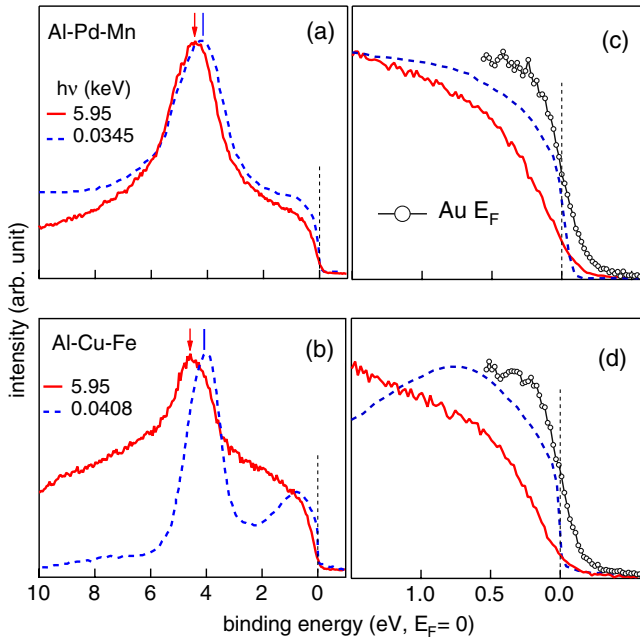


FIG. 1 (color online). HAXPES valence band spectra measured with $h\nu = 5.95$ keV at 300 K compared with surface sensitive low energy photoemission spectra from the literature [7,9] for (a) *i*-Al-Pd-Mn and (b) *i*-Al-Cu-Fe. The spectra have been normalized to the same intensity at the Pd $4d$ and Cu $3d$ main peak for Al-Pd-Mn and Al-Cu-Fe, respectively. The near- E_F region is shown along with the Au Fermi edge (black open circles) for (c) Al-Pd-Mn and (d) Al-Cu-Fe.

a line shape analysis in the near- E_F region using the expression

$$[I \times S(E) \times f(E, T)] \otimes G(E, \sigma), \quad (1)$$

where $S(E)$ is the spectral function that represents the shape of the pseudogap, $f(E, T)$ is the Fermi function at temperature T , $G(E, \sigma)$ is the Gaussian representing the instrumental resolution, and I is a multiplicative parameter. A Lorentzian function [7] centered at E_F is used,

$$S(E) = (aE + b) \left(1 - \frac{C_L \Gamma_L^2}{E^2 + \Gamma_L^2} \right), \quad (2)$$

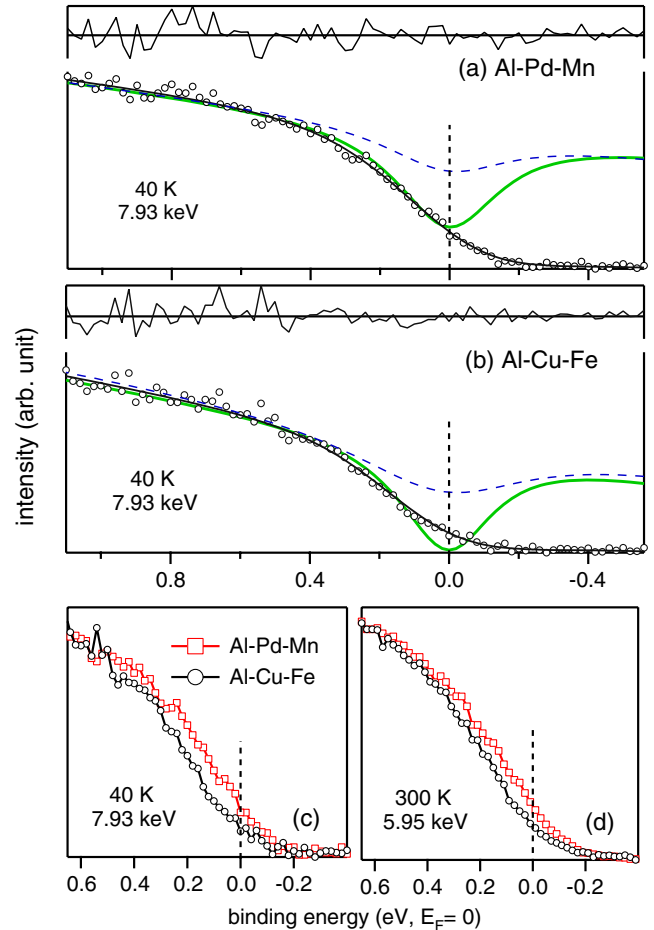


FIG. 2 (color online). HAXPES valence band spectra (black open circles) of (a) Al-Pd-Mn and (b) Al-Cu-Fe in the near- E_F region. The experimental valence band spectra, fitted with a Lorentzian function [$S(E)$, thick green line] broadened by the instrumental resolution and multiplied by the Fermi function, show the deep pseudogap at E_F . The resulting fitted curve is shown as a black line. The residuals are shown at the top of each panel. $S(E)$ for low energy photoemission (dashed blue line) is obtained from the parameters given in Ref. [7]. The near- E_F region of Al-Pd-Mn and Al-Cu-Fe HAXPES valence band spectra measured with 7.93 keV at 40 K and 5.95 keV at 300 K are directly compared in (c) and (d), respectively.

where $2\Gamma_L$ is the full width at half maximum of the Lorentzian function. If $C_L = 0$, the pseudogap is absent and the spectral function is a straight line ($aE + b$). The parameters a and b are obtained by fitting the spectrum in the range 0.7–1.2 eV with a straight line. If $C_L = 1$, then $S(E)$ is zero at $E = 0$, i.e., at E_F . The minimum of $S(E)$ occurs at E_F and corresponds to the DOS at E_F . So, the minimum value of $S(E)$ cannot be negative, and this implies $0 \leq C_L \leq 1$. The energy position of E_F , obtained by fitting the Au Fermi edge, is kept fixed. We find that the quality of the fit is excellent (Fig. 2), its results are presented below.

In Fig. 2(a), a well-developed pseudogap (thick green line) in the bulk is unambiguously observed in Al-Pd-Mn, and the resulting fitting parameters are $C_L = 0.72$ and $2\Gamma_L = 0.37$ eV. In contrast, for low energy photoemission, the parameters [7] ($C_L = 0.28$ and $2\Gamma_L = 0.44$ eV) defining the Lorentzian function (dashed blue line) clearly demonstrate the strong reduction of the pseudogap at the surface. For Al-Cu-Fe, the pseudogap [thick green line in Fig. 2(b)] is even more pronounced in the bulk, with the minimum of the spectral function reaching zero ($C_L = 1$, $2\Gamma_L = 0.33$ eV), in contrast to surface sensitive low energy photoemission where $C_L = 0.56$ and $2\Gamma_L = 0.64$ eV [7] (dashed blue line). Further it may be noted that the width ($2\Gamma_L$) in HAXPES is considerably smaller compared to the low energy photoemission value for both the quasicrystals, demonstrating that the pseudogap is not only deeper but also narrower in the bulk compared to the surface.

Strikingly, the pseudogap is clearly deeper for Al-Cu-Fe compared to Al-Pd-Mn [Figs. 2(a) and 2(b)], although the widths are similar. This is also portrayed by the raw data shown in Figs. 2(c) and 2(d): the Al-Cu-Fe spectra have lower intensity at E_F in comparison to Al-Pd-Mn for both 7.93 and 5.95 keV photon energy data recorded at 40 and 300 K, respectively. In fact, for Al-Cu-Fe, $S(E)$ shows that the DOS is zero at E_F , which indicates that it is close to the metal-insulator phase boundary, in agreement with the specific heat and transport measurements [18].

Fitting the spectra with a third order polynomial function (see Ref. [19] for details) yields results as good as the Lorentzian function, as judged from the residual. The pseudogap is clearly observed in both Al-Pd-Mn and Al-Cu-Fe [19]. For Al-Cu-Fe, it also yields zero DOS at E_F , showing that the pseudogap is independent of the model function.

The Al-Cu-Fe near- E_F spectra measured at 40 K and 300 K do not exhibit significant differences [Fig. 3(a)]. Thus, it can be concluded that there is no qualitative change in the shape of the pseudogap at low temperatures. The influence of temperature on the Fermi function could not be identified because the thermal broadening between 40 K and 300 K is much smaller than the resolution broadening.

Evidence that the surface electronic structure of Al-Pd-Mn is modified, explaining the surface sensitive low energy

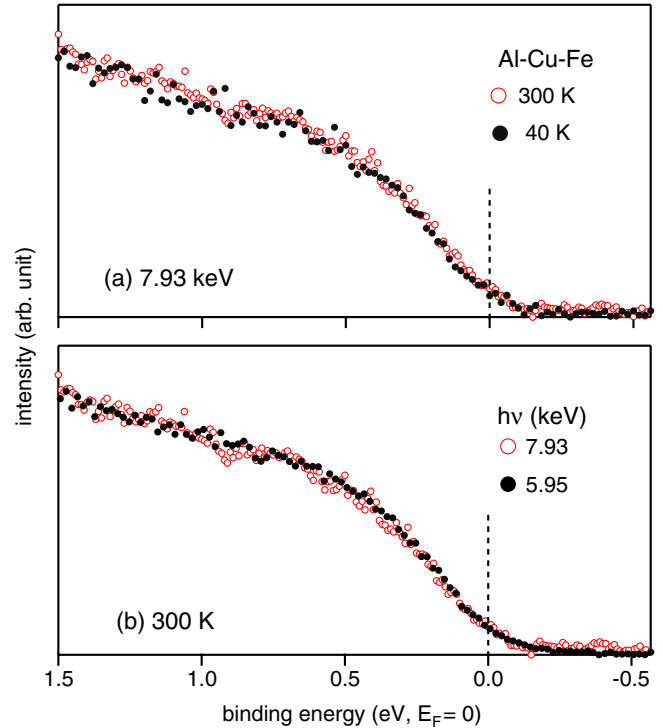


FIG. 3 (color online). The near- E_F region of the HAXPES valence band spectra of Al-Cu-Fe measured with (a) 7.93 keV photon energy at 40 K and 300 K and (b) 7.93 and 5.95 keV photon energies at 300 K.

photoemission data [6–9], was provided by a density functional theory based calculation performed by Krajčí and Hafner [20]. They decomposed a 2/1 approximant into a sequence of slabs of three different thicknesses denoted as S , M , and L slabs, respectively. The calculation considered two models on the basis of existing experimental results on the surface structure [21,22]: an M slab with five atomic layers and an MS slab (i.e., M and S slab) of 6.6 Å thickness consisting of eight layers of atoms [20]. In both models, the partial DOS (PDOS) shows a shift of the Mn 3d states towards E_F and an enhancement of Al s , p states in comparison to the bulk PDOS (see Fig. 10 of Ref. [20]). Thus, the pseudogap that is clearly observed in the bulk is completely filled up and ceases to exist at the surface. This explains the absence of the pseudogap in surface sensitive low energy photoemission [6–9]. The width of the pseudogap obtained from the bulk electronic structure calculation of Al-Pd-Mn [20] is in good agreement with HAXPES ($2\Gamma_L = 0.37$ eV). Significantly, this width is much larger than what has been observed in scanning tunneling spectroscopy (STS) for Al-Pd-Mn (0.02–0.05 eV) [23] and Al-Cu-Fe (0.1 eV) [24]. This might be related to the higher surface sensitivity of STS compared to low energy photoemission for quasicrystals, because the surface DOS around E_F is higher than the bulk DOS [20]. Dynamical low energy electron diffraction study showed that the topmost layer of Al-Pd-Mn consists of 90% Al and 10% Mn [21]. Thus, the

pseudogap observed in STS is possibly a characteristic of this topmost Al-Mn surface layer, whereas HAXPES probes the bulk pseudogap of Al-Pd-Mn.

Other features in the HAXPES spectra and their comparison to low energy photoemission also reveal differences in the bulk and surface electronic structure. The position of the Pd 4*d* related main peak in Al-Pd-Mn valence band spectra appears at 4.45 eV in the HAXPES spectra recorded with both 5.95 keV and 7.93 keV; this is a clear shift by 0.3 eV towards higher binding energy compared to low energy photoemission [Fig. 1(a)]. A similar effect is also observed for Al-Cu-Fe: the Cu 3*d* main peak at 4.6 eV is shifted by 0.6 eV towards higher binding energy [Fig. 1(b)]. Note that both the *M* and the *MS* slabs considered in the density functional theory calculation [20] are Pd rich (26% Pd) compared to the bulk content of 21% Pd. The PDOS shows that the Pd 4*d* peak is shifted by about 0.5 eV towards lower binding energy in the surface compared to the bulk [20]. This shift is thus a surface effect and might be further influenced by excess Pd content in the surface slab. The latter possibility is based on the observation from our low energy photoemission studies on Al-Pd-Mn that the Pd 4*d* peak shifts towards higher binding energy as the surface Pd content decreases [19]. For example, for the sputtered Al-Pd-Mn surface (36% Pd content), the Pd 4*d* peak is at 3.5 eV. For the cubic crystalline Al-Pd-Mn phase (32% Pd content) obtained by annealing at 630 K [25], the binding energy of Pd 4*d* increases to 3.7 eV. For HAXPES that probes bulk Al-Pd-Mn, the Pd concentration (21%) is lower than the surface region (about 3–5 Å) that is probed by low energy photoemission (26%) [21]. Thus, the higher binding energy of the Pd 4*d* peak observed in HAXPES compared to the low energy photoemission can be ascribed to a bulk versus surface effect, possibly enhanced by excess Pd at the surface.

The recoil of the emitted photoelectron, an intriguing effect observed in HAXPES data, may cause a shift of the photoemission peaks to seemingly higher binding energies [10,26]. However, such a recoil effect can be excluded to have a significant influence on the presented data. If the near- E_F states are dominated by Al 3*s*, the E_F of the quasicrystal also might exhibit a recoil shift as in Al metal [26], which is about 40 meV between 6 and 8 keV [27]. However, between the near- E_F spectra of Al-Cu-Fe measured with 7.93 and 5.95 keV, no such shift is observed and the spectra are indistinguishable [Fig. 3(b)]. Moreover, according to the single particle approximation of the recoil effect, the expected shift for a shallow core level such as Al 2*s* at 6 (8) keV is about 120 (160) meV. But in comparison with the XPS data, the HAXPES data do not reveal any shift of the Al 2*s* binding energy [19]. Apart from Al 3*s* states, in Al-Cu-Fe and Al-Pd-Mn the states close to E_F are dominated by 3*d* states of the heavier Fe and Mn, respectively [20,28,29], which would reduce any recoil effect. On the basis of these arguments, we rule out any significant recoil effect in the states near E_F to be responsible for a

reduction in the observed spectral function at E_F . For the Pd 4*d* peak in Al-Pd-Mn [Fig. 1(a)], an estimate of the recoil shift is 0.03 eV [10], while the observed shift (0.3 eV) is an order of magnitude larger. Pd is heavier than Mn and so is not expected to exhibit the recoil effect. This is further confirmed by the absence of any shift in the Pd 3*p* core-level between HAXPES and XPS [19].

In summary, we demonstrate that a well-developed pseudogap is observed in the icosahedral quasicrystals when bulk specific data are recorded by employing hard x-ray photoelectron spectroscopy. Contrasting spectral features observed earlier by low energy photoelectron spectroscopy, i.e., a high contribution to spectral function at E_F , can be assigned to surface effects. By modeling the spectral line shape near E_F , we are able to quantitatively account for the differences between Al-Pd-Mn and Al-Cu-Fe, showing that the pseudogap is fully formed in the latter.

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