Enhanced surface metallic density of states in icosahedral quasicrystals

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Valence and core-level photoemission spectra show that cleaved i-Al-Pd-Mn quasicrystals have a pronounced metallic signature. Spectra from states above E_F, populated by increasing the sample temperature, indicate the presence of a shallow pseudogap 0.09 eV above E_F. The Al $2p$ line asymmetry, on the other hand, which indicates metallic behavior, decreases with increasing photoelectron escape depth. This implies a decreasing density of states at E_F with increasing distance from the surface, consistent with indications that the density of states near E_F in the bulk is reduced. Our results thus help to resolve the apparent contradiction between the theoretical predictions for a bulk pseudogap, and the clear metallic Fermi edges in photoemission. [S0163-1829(98)05726-9]

The electronic structure of icosahedral quasicrystals is of great current interest, since in view of the unusual symmetry of these materials, conventional notions on electronic structure need to be adapted in order to provide a meaningful description of their properties. Among the striking features of quasicrystals are their high electrical resistivity and the low electronic contribution to the specific heat, compared to those of their metallic constituents. While several different effects may be responsible for these observations, a low density of states (DOS) at the Fermi level E_F has been suggested to play an important role, in particular for the electronic contribution to specific heat which is directly proportional to the DOS at E_F.[1] Theoretical considerations have been invoked to qualitatively account for this so-called pseudogap at E_F, based on the Hume-Rothery mechanism.[2] In high-resolution photoemission of four different icosahedral alloys, clear metallic Fermi edges have been observed, with the sampled DOS only weakly decreasing towards E_F.[3] Here we show that a high density of states at and above E_F is predominantly found in the surface region.

Our approach to electronic structure determination of the states near E_F by means of photoelectron spectroscopy is twofold. Electrons are sampled in the valence-band range, including the region thermally populated several 100 meV *above* E_F. The density of states near E_F is further investigated by analyzing the intrinsic core level line shape which, in metals, shows the well-known asymmetry towards higher binding energy due to intrinsic low-energy electron excitations from occupied to unoccupied states near E_F.[4] By tuning the kinetic energy of the core-level photoelectrons such that the electron escape depth, i.e., the probing depth, can be adjusted from a few Å to some tens of Å, we probe the density of states near E_F as a function of distance from the surface. From the decrease of the asymmetry parameter with increasing sampling depth we infer that the density of states at E_F is increased in the near-surface region. This suggests

that the presence of clearly developed Fermi edges in surface sensitive valence photoemission does not contradict the presence of a pseudogap near E_F in the bulk.

In order to avoid a possible influence of surface structure or composition perturbed by cleaning procedures, the icosahedral $Al_{70.5}Pd_{21}Mn_{8.5}$ single crystals were cleaved *in situ* perpendicular to the fivefold axis under UHV conditions yielding highly reflecting and in many cases smooth surfaces. The experiments were performed at the BESSY storage ring in Berlin using the monochromator TGM6. Electrons were detected by a VG ADES400 spectrometer system with a base pressure of 4×10^{-11} mbar. Valence and core-level spectra were taken with overall resolutions of 70 and 180 meV, respectively, the latter at a temperature of 120 K.

Valence-band spectra such as shown in Fig. 1 show a broad peak centered at about 4 eV below E_F, derived from Pd $4d$ electron states,[5] and a rounded shape of the valence-
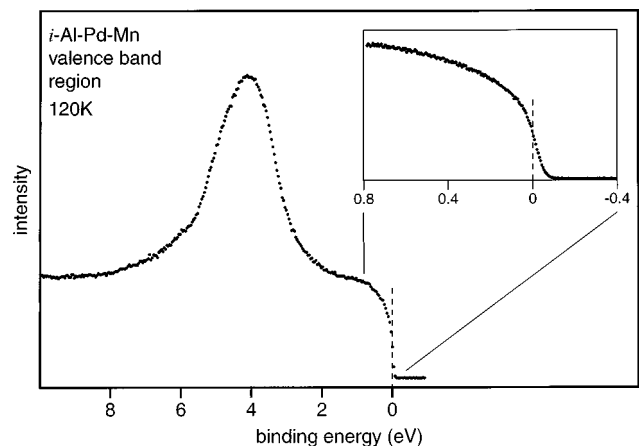

FIG. 1. Valence-band photoemission spectra of cleaved i-Al-Pd-Mn at 120 K and $\hbar\omega = 34.5$ eV. The inset shows a closeup displaying the rounded shape of the spectrum near the Fermi edge.

band region as the binding energy approaches E_F. This shape has been interpreted in terms of a pseudogap at E_F in previous photoemission studies at room and low temperature.[3,5,6] However, it is difficult to conclude on the presence of a pseudogap if only the experimentally broadened shape of valence-band spectra, cut off at E_F by the Fermi function, is considered; it is important to extend the measurements into the region above E_F. These states can be probed by photoemission if they are populated. Here we have used measurements at temperatures up to 570 K, such that a region of several 100 meV above E_F becomes accessible, according to Fermi-Dirac statistics. Even so it is difficult to obtain the exact spectral function, and thus the DOS, in the presence of experimental broadening. The conventional approach, successful in the interpretation of core-level data, is to assume a physical, parametrized model function, and to evaluate its parameters by minimizing the deviation from the experimental spectra in a least-squares fit. However, while the functional shapes of core lines are generally agreed on, no such agreement exists concerning the spectral shape of the valence-band region of quasicrystals near E_F.[3,6]

In order to obtain the spectral function for the valence-band states around E_F we use the following reasoning: the measured spectrum $I(E)$ arises from the spectral function $S(E)$ by a multiplication with the Fermi function $f(E)$, to account for the reduced occupation probability for states near and above E_F, and a convolution with the instrumental function $A(E)$. Thus, $I(E)=\int dE' S(E) \cdot f(E) \cdot A(E-E')$. To reconstruct the spectral function $S(E)$ we utilize an experimentally determined Fermi edge taken from a thick polycrystalline silver film, freshly evaporated onto the sample kept at the same temperature. In order to eliminate counting statistics, the Ag spectra were modeled by a Fermi function proportional to a spectral function $S_{Ag}(E)=1$, convoluted by a Gaussian which approximates the instrumental function $A(E)$. This spectrum can be written as $I_{Ag}(E)=\int dE' f(E) \cdot A(E-E')$, since both the instrumental and the Fermi function are identical. If the width of $A(E)$ is small compared to the width of $f(E)$, the spectral function $S(E)$ can be approximated by $S(E) \approx I(E)/I_{Ag}(E)$. The accuracy of this reconstruction procedure was tested numerically by calculating model spectra from a chosen spectral function. These spectra were subjected to the reconstruction procedure and the results were found to resemble the original spectral functions with less than 10% deviation. Accessing electronic states slightly above E_F via this scheme is superior to inverse photoemission because of the much higher resolution.

The result of this analysis for the valence band of cleaved i-Al-Pd-Mn is shown in Fig. 2 for a spectrum taken at 570 K. The open circles indicate the spectral function reconstructed from the raw spectrum (filled circles) by the procedure described above. Neglecting variations in the transition matrix element, the spectral function is equivalent to a partial DOS. It is evident that no extremal point is observed in this DOS at E_F. Instead we find a weakly decreasing DOS at E_F, interestingly with a minimum at 90 meV above E_F; previous attempts to determine the shape of the density of states near E_F were based on the assumption of a Lorentzian shape and the location at an energy $E=E_F$.[3] Our numerical tests show that this position cannot be accounted for by the error inherent to the reconstruction procedure if a dip is assumed in the
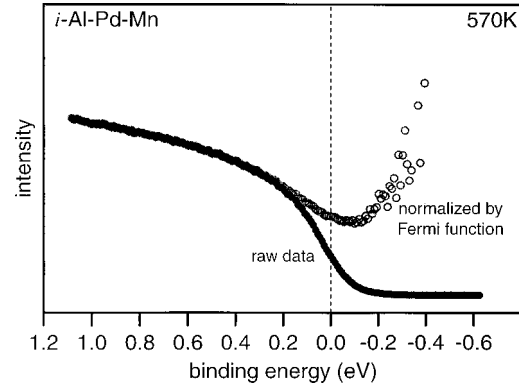

FIG. 2. Photoemission spectrum (filled circles, $\hbar\omega=32.3$ eV) and reconstructed spectral function (empty circles, see text) of the valence band near E_F of i-Al-Pd-Mn. To populate states above E_F the sample was measured at 570 K.

true spectral function right at E_F. At energies higher than 0.3 eV, counting statistics lead to a considerable scatter in the reconstructed DOS which inhibits a meaningful evaluation. In the electronic structure calculations of the so-called approximants, the location of the center of the pseudogap was found to be about 0.8 eV above E_F, shifting towards E_F for the higher-order approximants.[2]

The reconstructed valence-band data show that, while a dip in the DOS seems to be present at an energy slightly above E_F, there is considerable DOS at E_F which, it may be argued, is in contradiction to the observation of a low electronic contribution to the specific heat. The DOS at E_F, however, is also reflected in the core-level photoelectron spectrum, although in a less obvious manner. In metallic systems, core-level lines shape assume an asymmetric shape, because of intrinsic losses through the excitation of electrons from below E_F into unoccupied states above E_F. The probability for such processes depends on the density of states $\rho(E_F)$.[4] In core-level line-shape analysis, this asymmetry is often modeled by the Doniach-Sunjic formula which provides an adequate description for systems where ρ does not vary strongly near E_F. The asymmetry in the line shape of the Al $2p$ peak from i-Al-Pd-Mn can be clearly seen in the spectra of Fig. 3. Fits to the data are also displayed, which consist of one spin-orbit doublet of Gauss-broadened asymmetric Doniach-Šunjić lines[7] and a rising background, due to secondary electrons, modeled by a third-order polynomial. The residual—also displayed—shows that the fits excellently model the data within the Poisson statistics (upper and lower straight line corresponding to $\pm\sqrt{N}$, where N is the number of collected electrons per channel). Other commonly used background models[8] were tested but found to give either bad fits or vanishing extra background parameters. The so-called Shirley step background in particular was found to be inappropriate; this background model has previously been shown to be unphysical on general grounds.[8] All spectra can be fitted by one common model function with a fixed spin-orbit splitting of 411 meV (Ref. 9) and a Lorentzian width 2γ of 20 meV; this ensures the high reliability of the values for the asymmetry parameter derived from the fits. The line position, intensity, branching ratio, Gaussian width σ, and singularity parameters α as well as the third-order polynomial background were free parameters of the fits. However, out of
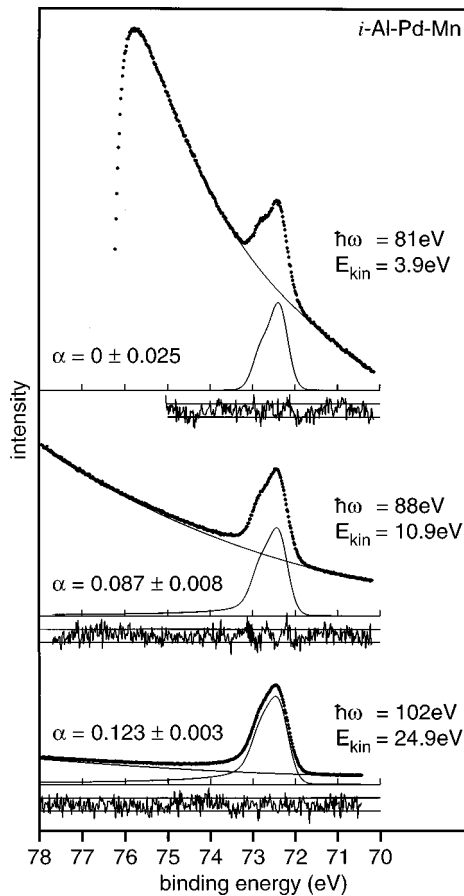
FIG. 3. Al $2p$ core-level spectra at different excitation and thus kinetic energies. Also shown are fits of Doniach-Šunjić doublets with third-order polynomial background. The residuum is normalized to the Poisson statistic indicated by the upper and lower bound at $\pm\sqrt{N}$. With rising energy the spectra become more surface sensitive and the effective singularity index α increases as indicated.

FIG. 4. Lower part: Asymmetry parameter α of Al $2p$ from fits to spectra recorded with different kinetic energies. Filled symbols are used for i-Al-Pd-Mn spectra, different symbols pertain to different cleaves. Results for fcc-Al (Ref. 12) are shown as crosses. Upper part: Surface to bulk intensity ratio of Al(100) Al $2p$ core level spectra from Ref. 12. Note the similarity between decreasing surface sensitivity and decreasing α. Inset: sample spectrum of clean Al(111),[9,12] recorded at a photon energy of 86 eV. Note the clear separation of the spin-orbit components, and the small linewidth.

these only the polynomial background may affect the determination of α as discussed below. The Gaussian width σ is found to be about 450 meV, which suggests that several lines contribute to the overall peak shape; the narrow Al $2p$ lines from an Al(111) single-crystal surface, recorded under similar experimental conditions,[9,12] are shown in the inset of Fig. 4 for comparison. For a quasicrystal this distribution of core levels is not surprising, since its constituent elements experience a multitude of local chemical environments throughout the crystal. Modeling these different contributions by a single broadened line is a realistic approach which does not adversely affect the results for the asymmetry parameter, since its magnitude depends almost entirely on the shape of the curve beyond about 0.7 eV higher binding energy than the peak. All 40 spectra recorded over a wide range of photon energies from six different cleaved surfaces were consistently described by the same model function.

In the spectra at higher energies an appreciable asymmetry in the core-level line was found. This can be seen by eye from the shape of the high binding energy tail of the $\hbar\omega$ = 88 eV and $\hbar\omega$ = 102 eV core-level spectra. This observation, together with the good overall agreement between the spectra and the model functions as judged by the residual shown below each curve, already has important implications. The Doniach-Sunjic model implicitly assumes a constant
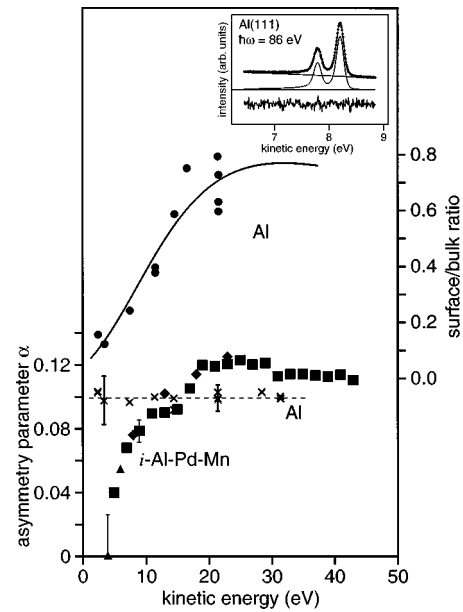
spectrum of low-energy excitations across E_F,[10,11] a requirement which is only met if the DOS near E_F is only weakly structured. Since the model describes the spectra well this indicates that there is a smooth DOS without sharp features near E_F in i-Al-Pd-Mn, supporting our valence level DOS reconstruction in Fig. 2.

An evaluation of the asymmetry parameter α from spectra of different photon energies yields the surprising result that α increases from 0 to 0.125 in going from very low to high kinetic energies as shown by the filled symbols in the lower part of Fig. 4. Within the sudden approximation, the singularity index α is independent of excitation energy; however, to our knowledge this dependence, or rather the lack of it, has not yet been systematically studied in the literature. Thus we have examined the asymmetry in the shape of the Al $2p$ line from Al(111) and Al(100) single-crystal data[12] as a function of excitation energy. These data are shown in Fig. 4 as crosses; note also the asymmetry in the sample Al(111) spectrum, recorded at low kinetic energies, in the inset of Fig. 4. Within the experimental uncertainty α in Al(111) and (100) remains constant over the investigated energy range.

An increase of the excitation energy from the photoemission threshold upwards changes the kinetic energy of the Al $2p$ photoelectrons, which causes the sampling depth of the photoemission experiment to decrease, by virtue of enhanced inelastic electron scattering. This decrease, often described by the so-called ''universal curve'' of electron escape depths,[12] can be measured independently through the relative intensity of surface and bulk core-level emission from Al(100), where a distinct surface component is found. In the

top half of Fig. 4 the ratios of surface and bulk Al $2p$ core-level intensities measured from an Al(100) surface[12] are displayed by open circles. The continuous line is calculated from an inelastic mean-free-path formula by simple geometric attenuation arguments. The formula was assumed in the form given as the ''universal curve'' by Seah and Dench[13] with empirical parameters adjusted to reproduce the Al(100) data shown. It is found that the escape depth of photoelectrons varies from over 10 to about 2 Å in this energy range, kinetic energies around 35 eV being most surface sensitive. As the escape depth decreases, indicated by a rising surface-to-bulk ratio, core levels of near-surface atoms receive a higher weight within the line shape. The values for α derived from a fit to the spectra of i-A-Pd-Mn are shown in Fig. 4 as diamonds and squares. They exhibit a trend of decreasing α with decreasing kinetic energy. Since α remains constant in the spectra from Al metal, we interpret the the trend in α, which mirrors that of the escape depth, to mean that the asymmetry parameter for atoms near the surface in i-Al-Pd-Mn is larger than for those probed in the bulk, where α seems to be close to zero.

The specific choice of a model for the secondary electron background has implications for the exact determination of α from the fits. A step is found in the background under the core level for Al $2p$ spectra taken at higher kinetic energies. Intensity drawn from an *underestimated* step could lead to an overestimation of α. However, in spectra with an essentially flat background above 25 eV kinetic energy we find the third-order polynomial background in our model function to provide this step. In regions of highly curved background below 20 eV kinetic energy no step is seen in the polynomial, indicating that either no step is present or a possible step is underestimated, leading to a potential overestimation of α. Thus, the finding that α decreases with increasing escape depth is not affected by our choice of the background function. In order to make sure that a correlation between the background parameters and the asymmetry parameters in the line-shape analysis does not adversely affect our conclusions concerning the trend in α with kinetic energy, we have carried out several tests. First, the correlation coefficients[14] between the third-order polynomial parameters and α were determined for each of the spectra where α deviates from its high-energy value, based on the inverse of the error matrix which is calculated in the Levenberg-Marquardt algorithm. These indicated a low correlation between these two parameters, and in fact between all parameters that could somehow influence our determination of α. However, in order to more fully investigate correlation between parameters which might interfere with the determination of α, we show in Fig. 5 a contour plot of the value of the reduced χ^2 as a function of the third-order polynomial coefficient c_3 and the α parameter for the spectrum at 8 eV kinetic energy. These were evaluated by a fit run over each of a grid of more than 900 values for α and the polynomial coefficient. The axes are centered around the optimum parameter value, and scaled in terms of the confidence interval for each parameter, i.e., the inverse of the square root of the respective diagonal element of the error matrix.[14] The optimum parameters have a χ^2 slightly below 1 (cross in the center of the plot). The confidence interval for an increase of the reduced χ^2 by 1, 2, and 3 standard deviations σ are indicated on the respective con-
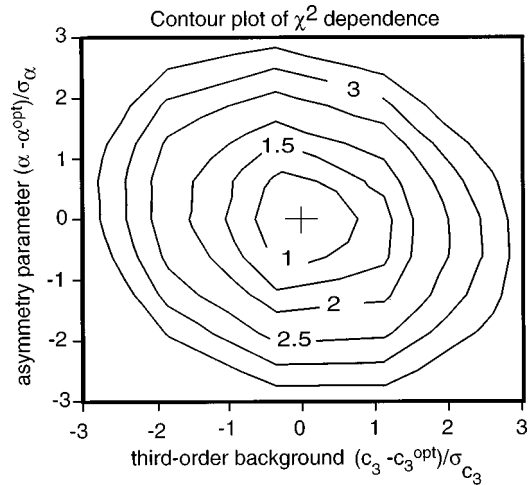

FIG. 5. Contour plot of the value of χ^2 as a function of the asymmetry parameter α and the third-order polynomial coefficient, scaled in terms of the confidence interval for each parameter and related to the optimum parameter value as determined from the fit. The contours give an increase of the reduced χ^2 in units of its standard deviation, where the minimum of χ^2 is approximately 1. The absence of a strong valley along the diagonal demonstrates that the two parameters are not correlated; hence no adverse effect on the determination of α occurs.

tours. The most important finding is that the contour of χ^2 does not exhibit a diagonal valley, showing that there is almost no correlation between these fit parameters. Similar plots were derived for all spectra near the photoemission threshold, and for different sets of parameters. Thus the background does not have a detrimental effect on our determination of α, and the trend in α clearly is due to a physical process as described in detail above.

The value of α reflects the efficiency of screening of the core hole by the valence charges. It is thus determined by the orbital symmetry and the DOS near E_F. Both high angular momentum and low DOS near E_F lead to a diminished screening and thus a low value of α.[15] In our experiment the singularity index of the Al $2p$ line of i-Al-Pd-Mn measured near the surface is found to be close to that of pure Al metal, while it vanishes for the highest bulk sensitivity. This cannot be assigned to a difference in the orbital character of the valence charge. It is obvious that the state density at E_F is severely affected. This view is corroborated by that fact that in the extremely surface sensitive surface tunneling spectra of cleaved i-Al-Pd-Mn quasicrystals only metallic signatures are observed.[16]

One of the frequently employed explanations for the reduced density of states is based on band-structure effects due to the high symmetry of the quasicrystal.[17] If its electronic structure is viewed in a free-electron picture, the DOS will be proportional to $\sqrt{E}$, altered by van Hove singularities which arise from gaps generated by the pseudopotentials of the atoms. The magnitude of these singularities, and thus of the deviations imposed on the DOS, depends on the multiplicity of the reciprocal-lattice vector associated with the gap. Since quasicrystal reciprocal-lattice vectors have large multiplicities,[18] the deviations can become quite large and introduce gaps in the state density. If these gaps occur near E_F, the Fermi surface can be altered significantly. If this

leads to a decrease in the Fermi volume, the band-structure energy could be lowered, thus enhancing the stability of the phase by the Hume-Rothery argument.[17] Lowering the symmetry of the quasicrystal by introducing a surface will affect the states in its vicinity. Fewer directions of the quasicrystalline lattice will be equivalent and the effective multiplicities of the reciprocal-lattice vectors will be reduced. Thus dips in the DOS are reduced as well. This might lead to an increased DOS at E_F near the surface as shown by the present experiments.

A different model for the reduced density of states at E_F in i-Al-Pd-Mn considers the structure of icosahedral quasicrystals as a self-similar hierarchic ordering of clusters called pseudo-Mackay icosahedra (PMI).[18,19] The electronic structure can be evaluated treating every PMI as a spherical well potential.[20] The total state density derived from this model is a superposition of the DOS of successive inflated PMI. With increasing energy—as E_F is approached—the states stem from increasingly bigger cluster formations. Introducing a surface will affect the large clusters and thus the states near E_F more readily. A perturbation of the hierarchic order of clusters deemed responsible for the reduced density of states near E_F then explains our above experimental results.

The conclusion that icosahedral quasicrystals have a high density of states at E_F near the surface serves to solve the apparent discrepancy between both the theoretical indications for the existence of a pseudogap at E_F, and the structureless and sizeable DOS at E_F as observed in surface-sensitive photoelectron spectroscopy (cf. Refs. 3, 6, and Fig. 2). We show that the electronic structure at the surface of i-Al-Pd-Mn differs from that of the bulk, since it exhibits a continuous DOS, observed directly in the valence-band spectra and indirectly in the screening of the core hole. In the bulk the DOS has a pseudogap, which is reflected in the vanishing asymmetry of the bulk sensitively measured core line.

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