Comparison of the electronic structure of AlPd and $Al_{70}Pd_{20}Mn_{10}$

M. Zurkirch, M. De Crescenzi,[*] M. Erbudak, and M. Hochstrasser

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Zürich, Switzerland

A. R. Kortan

AT&T Bell Laboratories, Murray Hill, New Jersey 07974
(Received 1 November 1996)

The electronic structure of crystalline AlPd and quasicrystalline $Al_{70}Pd_{20}Mn_{10}$ has been investigated by x-ray photoelectron and electron energy-loss spectroscopy. The spectral shape of the Pd-derived $4d$ states in the valence-band region and the $3d$ core-level shifts are identical in both alloys, suggesting similar local environments for Pd atoms, both chemically and structurally. Although the macroscopic crystal structure is essentially different, these alloys have remarkably similar electronic properties determined by the Al-Pd interaction. In both materials, the spectra display a satellite at an energy of approximately 20 eV, accompanying all excitations, which is localized at the Pd site, whereas plasmon losses characteristic of pure Al are strongly suppressed. The Al-Mn interaction in the quasicrystal causes minor changes in the Al core levels and in the valence band by increasing the density of states at the Fermi level. [S0163-1829(97)02014-6]

$Al_{70}Pd_{20}Mn_{10}$ (AlPdMn) is a quasicrystal with an atomic structure possessing local icosahedral point-group symmetry and perfect aperiodic long-range order, which was determined using transmission electron microscopy[1] and secondary-electron imaging (SEI).[2,3] Its electronic properties have been investigated, and the element-specific, orbital-momentum resolved density of states (DOS) in the valence band has been determined.[4,5] A certain similarity between the valence band of crystalline AlPd and quasicrystalline AlPdMn has already been recognized.[6,7] In a recent study on AlPdMn, core-level shifts with respect to pure metals as well as single-electron and collective excitations have been determined.[7] It was found that plasmon excitations are strongly damped, suggesting that Al $3sp$ electrons are not quasifree in the quasicrystal as in the pure metal, but localized as a result of hybridization with Pd $4d$ states. Yet, the metallic appearance of the DOS in several quasicrystals has recently been established in high-resolution photoemission experiments.[8]

In this work we present comparative results of electron spectroscopy, obtained on an icosahedral AlPdMn and a crystalline AlPd alloy sample in the CsCl structure, in order to show that the samples have strikingly similar electronic properties, i.e., energy shifts of Pd core level and valence-band shapes, as well as strongly damped plasmon losses. It is found that the DOS at the Fermi level, E_F, is higher for AlPdMn than AlPd, owing to the Mn $3d$ electrons. The results indicate that not the long-range crystalline structure, but the short-range properties, in particular those of Pd atoms, have a crucial impact on the electronic properties of such alloys. Moreover, differences in core-level shifts of Al in the investigated samples are attributed to an additional interaction of Al with Mn in the quasicrystal. It is recognized that no features in the electronic structure can exclusively be related to the quasicrystalline structure. Hence, the so-called pseudogap[4] is *not* a property that is specific to quasicrystals.

X-ray photoelectron (XPS) and electron-energy-loss spectroscopy (EELS) experiments were performed in an ultrahigh vacuum chamber with a total pressure in the 10^{-9} Pa region. The macroscopic-sized samples, i.e., 10×7 mm^2 for the crystalline AlPd and 6×4 mm^2 for the quasicrystalline AlPdMn, were grown by conventional techniques.[9] The surfaces were cleaned by sputtering with Ar$^+$ and subsequently heat treated at 700 K. The atomic structure of the surfaces was investigated by means of low-energy electron diffraction (LEED) and SEI. The details of the apparatus as well as the principles of the SEI technique can be found elsewhere.[2,7] The electron gun used for EELS and SEI delivered a beam in a wide energy range, and focused on the specimen to a spot size of 0.3 mm. The total energy resolutions for XPS and EELS were 1.0 and 0.7 eV, respectively.

The polycrystalline AlPd sample consisted of grains that were large enough for LEED as well as SEI patterns to be observed. Figure 1(a) shows an SEI pattern obtained from one such grain, the center of which is obliterated by the shadow of the electron gun. The main symmetry directions are clearly discernible as bright patches, e.g., the (100) direction on the upper right-hand side, the (101) direction just below the electron gun, and the (111) direction on the left-hand side of the pattern. Figure 1(b) displays a computational reproduction, generated by using central projection, of the pattern from a body-centered cubic lattice on the same scale and orientation as the experimental pattern. The agreement between the experimental and computational results confirms that the sample was in its high-temperature β phase, that is in the CsCl structure, supporting the observations of x-ray diffraction during crystal growth. The surface composition was determined to be that of bulk AlPd by comparing the ratios of the Pd $3d$ and the Al $2p$ XPS emission intensities for the pure metals with those in the alloy. For AlPdMn, on the other hand, it was found that the concentration of Pd in the surface region is higher than expected with respect to the bulk concentration. The Pd enrichment is caused by preferential sputtering of surfaces[7] that partly remained even after annealing at 700 K.
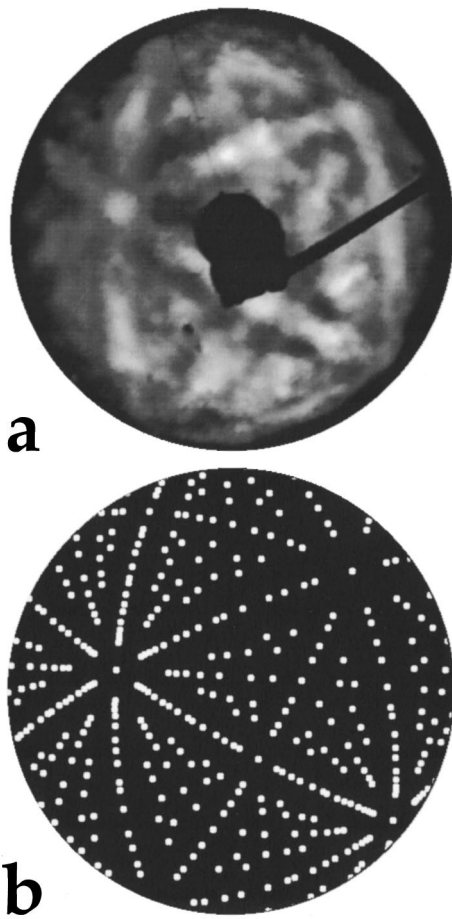
a

b

FIG. 1. (a) A secondary-electron pattern obtained from a poly-crystalline AlPd alloy at a primary-electron energy of 2000 eV. The central part of the pattern is obliterated by the shadow of the electron gun used for the excitation. (b) Central projection of a body-centered cubic lattice, drawn on the same angular scale and the same orientation as the experimental pattern to furnish a direct comparison.

The SEI patterns obtained from the single quasicrystal of AlPdMn, on the other hand, can be reconciled with the $(\overline{5}\,\overline{3}m)$ point-group symmetry of the icosahedron.[2,3,10] This observation is in agreement with the structure models based on the analysis of neutron and x-ray diffraction data, proposing that at least 60% of the atoms in the unit formula are situated in the so-called pseudo-Mackay clusters composed of two shells: a small icosahedron and a larger icosidodecahedron.[11]

Figure 2 shows the results of XPS measurements in the valence-band region obtained from AlPd and AlPdMn. The spectra fully overlap, apart from the contribution at a binding energy (E_B) of 0.7 eV in AlPdMn, which is due to the Mn-derived $3d$ states.[5,6] In order to emphasize this additional emission in the quasicrystal, the difference between the two energy-distribution curves is shown in the same figure. Obviously, the quasicrystalline sample even has a higher DOS at the E_F than the crystalline AlPd. The Pd $4d$-derived states in both alloys are centered at $E_B = 4.1$ eV. This resemblance of the valence bands has already been recognized and taken as an indication for similar electronic structures.[6,7]
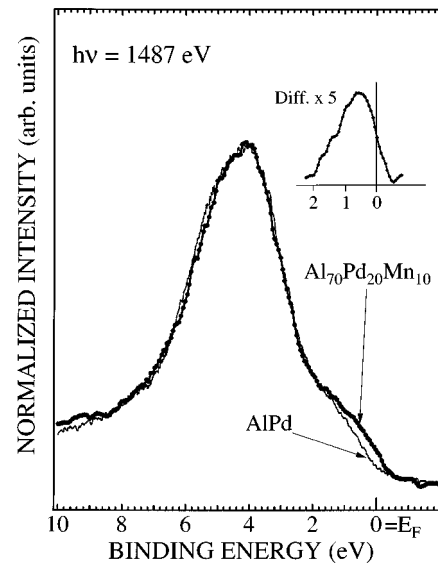

FIG. 2. X-ray photoelectron spectra at a photon energy of $h\nu = 1486.6$ eV from the valence bands of icosahedral $Al_{70}Pd_{20}Mn_{10}$ and polycrystalline AlPd. The binding energy is referred to the E_F. The inset shows, five-times magnified, the additional emission in the quasicrystal due to Mn $3d$ electrons.

Figure 3 (top) illustrates XPS measurements of the valence bands in an extended energy region in order to display the satellite structure accompanying the Pd $4d$ levels. The energy zero is placed at the binding energy of the Pd $4d$ states to facilitate a direct comparison with the EELS spectra (bottom) recorded at an electron energy of 1500 eV, so that the inelastic cross section is similar to that of the photoelec-
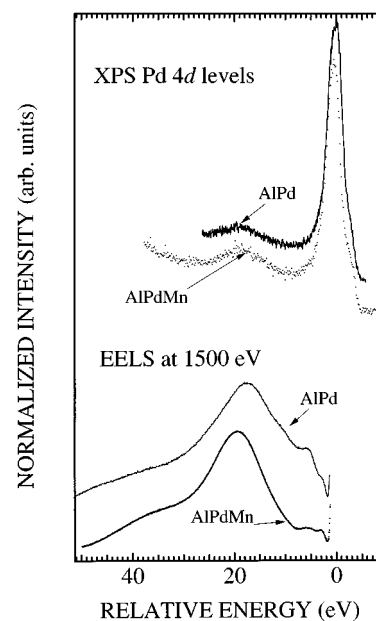

FIG. 3. XPS spectra from the valence bands of AlPd and $Al_{70}Pd_{20}Mn_{10}$ (upper curves) compared with EELS spectra taken at 1500 eV (lower curves). The abscissa represents the relative energy, i.e., zero is placed at the centeroid of the Pd $4d$ states for the XPS curves and at the primary-electron energy of 1500 eV for the EELS results.

trons considered here. The energy zero is placed at the primary energy. The emission from Pd $4d$ states is accompanied by a broad satellite at an energy of approximately 20 eV.[12] Similarly, a broad loss channel is detected at a loss energy of 20 eV in EELS. The fact that the Pd $3d$ core levels are equally accompanied by such a loss[7] leads to the conjecture that this loss channel represents an excitation localized at the Pd site. In order to shed light onto such a transition, tight-binding linear-muffin-tin-orbital method (TB-LMTO) calculations for AlPd have been performed.[13] Therein, the Pd p- and f-derived unoccupied DOS shows a distinct feature at 16.5 eV above the E_F. According to this calculation, a Pd $4d \rightarrow p$ or f transition has an energy of approximately 20.5 eV, which agrees with the observed satellite energy. Moreover, bremsstrahlung-isochromat spectroscopy (BIS) measurements on pure Pd exhibit a feature at 22 eV.[14] Taking into account a shift of approximately 2 eV of all the Pd core levels in AlPd with respect to pure Pd,[7,15] a loss of 20 eV results. Optical experiments on pure Pd metal have shown a salient energy-loss channel at 20.4 eV,[16] which is in agreement with theoretical band-structure calculations attributing this loss to transitions into unoccupied final states.[17] Therefore, we can conclude that the energy loss observed in our spectra reflects $d \rightarrow f$ transitions localized at the Pd atoms in the alloys considered.

While energy-loss spectra of pure Al predominantly show plasmon excitations,[18] all loss features in AlPd due to Al plasmons are missing. Instead, the EELS spectra for both AlPd and AlPdMn show two distinct losses at approximately 3 and 6 eV,[19] in agreement with previous optical studies.[20] Furthermore, core excitations from Al $2p$ levels at a loss energy of around 72 eV could be identified for both AlPd and AlPdMn.[7] In pure Al metal, this energy-loss region is overwhelmed by plasmon losses. Therefore, the observation of $2p$ losses is a further confirmation of the absence of strong plasmon excitations in these alloys.

In order to obtain additional information about electronic excitations at the Al site, Al $2s$ XPS spectra were recorded.[7] The Al $2p$ peak is not suitable because of the Pd $4s$ levels with $E_B = 87.1$ eV, which obscure the $2p$ emission in the extended energy region where plasmon losses are expected. Figure 4 compares the results on AlPd (top) and AlPdMn (bottom). While the Al $2s$ core level is shifted by 0.2 eV in the quasicrystal with respect to pure Al,[6,7] a shift of approximately 1 eV is observed for AlPd. As the core-level shifts of Pd are nearly the same in both alloys,[7,15] the difference for Al can be attributed to an additional Al interaction with the Mn atoms. In the alloys considered here, the satellites accompanying the core levels are markedly different from those of the pure Al at 15.5 eV.[7] They have an energy of approximately 19 eV with a significantly lower intensity. Certainly, this energy does not correspond to the plasmon energy of Al because this would require an increase in the number of quasifree electrons at the Al site. In order to account for the presence of a minor increase in the intensity at 19 eV, different loss channels have to be taken into account. There is certainly a contribution by the strongly damped plasmons of Al, together with the $3sp \rightarrow d$ transition with an energy of approximately 16 eV as predicted by the TB-
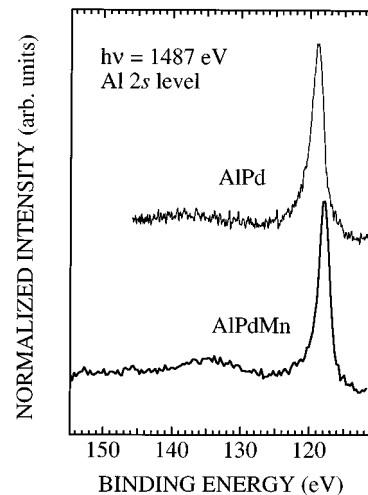

FIG. 4. Al $2s$ core-level XPS spectra obtained from AlPd (top) and $Al_{70}Pd_{20}Mn_{10}$ (bottom).

LMTO calculations.[13] BIS measurements on pure Al are similarly in good agreement with such a transition.[21] Moreover, the Pd $4d \rightarrow f$ transition induced by electrons emanating from the Al site may still have a contribution to the Al $2s$ spectrum in this energy region. Hence, it is difficult to make a conjecture about the origin of this insignificant signal in the measured spectra.

In summary, two alloys with totally different long-range structural properties, i.e., AlPdMn consisting of pseudo-Mackay clusters distributed in a perfect quasiperiodic matrix and AlPd in its β phase having a CsCl structure, have been compared with respect to their electronic properties. Both XPS and EELS spectra are very similar for the two samples. Thus, no specific influence of the quasicrystalline structure on the electronic properties could be detected. It has been found that the DOS at the E_F is even lower in AlPd than that in the AlPdMn. Consequently, the quasigap, i.e., the relative dip in the DOS, is more pronounced in the crystalline AlPd than in the quasicrystalline sample. Hence, it is not a property exclusive to and characteristic of quasicrystals. The loss channel at 20 eV which occurs in EELS as well as in XPS was established to be a Pd $4d \rightarrow f$ transition. Theoretical results,[13,17] BIS measurements,[14] and optical data[16] on pure Pd confirm this transition.

The main conclusion, however, is that plasmon excitations due to Al sp electrons are not only strongly damped in AlPdMn but also in a periodic structure like AlPd. Whereas in AlPd only a strong interaction of Pd $4d$ and Al $3sp$ electrons are responsible for a localization of these otherwise quasifree electrons, it is the additional Mn $3d$ electrons in the quasicrystal, which induce an electronic interaction with the rest of the electron gas. Hence, plasmon excitations in AlPd alloys seem not to depend as much on the macroscopic structure as on the local Pd environment.

*Permanent address: Dipartimento di Matematica e Fisica, Università di Camerino, I-62032 Camerino, Italy.

[1] A. P. Tsai, A. Inoue, and T. Masumoto, Jpn. J. Appl. Phys. **26**, L1505 (1987).

[2] M. Erbudak, H.-U. Nissen, E. Wetli, M. Hochstrasser, and S. Ritsch, Phys. Rev. Lett. **72**, 3037 (1994).

[3] M. Zurkirch, M. Erbudak, H.-U. Nissen, M. Hochstrasser, E. Wetli, and S. Ritsch, Philos. Mag. Lett. **72**, 199 (1995).

[4] E. Belin and Z. Danhkazi, J. Non-Cryst. Solids **153/154**, 298 (1993).

[5] G. W. Zhang, Z. M. Stadnik, A.-P. Tsai, and A. Inoue, Phys. Lett. A **186**, 345 (1994).

[6] G. W. Zhang, Z. M. Stadnik, A.-P. Tsai, and A. Inoue, Phys. Rev. B **50**, 6696 (1994).

[7] M. Zurkirch, A. Atrei, M. Hochstrasser, M. Erbudak, and A. R. Kortan, J. Electron Spectrosc. **77**, 233 (1996).

[8] Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa, and S. Takeuchi, Phys. Rev. Lett. **77**, 1777 (1996).

[9] A. R. Kortan, F. A. Thiel, H. S. Chen, A. P. Tsai, A. Inoue, and T. Masumoto, Phys. Rev. B **40**, 9397 (1989).

[10] M. Zurkirch, A. Atrei, M. Erbudak and M. Hochstrasser, Philos. Mag. Lett. **73**, 107 (1995).

[11] M. Boudard, M. de Boissieu, C. Janot, G. Herger, C. Beeli, H.-U. Nissen, H. Vincent, R. Ibberson, M. Audier, and J. M. Dubois, J. Phys. Condens. Matter **4**, 10 149 (1992).

[12] Due to the broadness of the peaks, the energy position could only be determined within an accuracy of ± 1 eV.

[13] R. Monnier (unpublished).

[14] W. Speier, R. Zeller, and J. C. Fuggle, Phys. Rev. B **32**, 3597 (1985).

[15] F. U. Hillebrecht, J. C. Fuggle, P. A. Bennett, Z. Zołnierek, and Ch. Freiburg, Phys. Rev. B **27**, 2179 (1983).

[16] J. H. Weaver, Phys. Rev. B **11**, 1416 (1975), and references therein.

[17] R. Lässer and N. V. Smith, Phys. Rev. B **25**, 806 (1982).

[18] J. Geiger and K. Wittmack, Z. Phys. **195**, 44 (1966).

[19] A comprehensive analysis of electron-energy-loss spectra in terms of optical constants is in preparation.

[20] L. Digiorgi, M. A. Chernikov, C. Beeli, and H. R. Ott, Solid State Commun. **87**, 721 (1993).

[21] H. J. W. M. Hoekstra, W. Speier, R. Zeller, and J. C. Fuggle, Phys. Rev. B **34**, 5177 (1986).