

PARTIAL AND TOTAL DENSITIES OF STATES IN ICOSAHEDRAL $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$

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ABSTRACT

Measurements with synchrotron-radiation-based photoemission spectroscopy have been used to determine the Mn 3*d* and Pd 4*d* empirical partial density of states and the empirical total density of states in the stable icosahedral alloy $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ of high structural quality. Good agreement has been found between these densities and the theoretical predictions for the 8/5 approximant of the icosahedral Al-Pd-Mn phase. No unusual features in the empirical density of states of icosahedral $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$, which could be ascribed to its quasiperiodic nature, have been observed within the resolution of the experiment. It has been demonstrated that to detect the theoretically predicted minimum of the density of states at the Fermi level and its spikiness, high-energy-resolution photoemission experiments are indispensable.

1. Introduction

Conventional, valence-band photoemission spectroscopy (PES) is one of the most direct probes of the total electronic density of states (DOS) below the Fermi level E_F . The availability of synchrotron radiation as a tunable source of photon energy $h\nu$ now also makes it possible to determine the partial density of states (PDOS) of the *d* or *f* character, which has been traditionally obtained by using the soft x-ray emission (SXE) technique. It is both the total DOS and the PDOS which are essential for a complete characterization of the electronic structure of a given material.

In a previous article,¹ we reported on an investigation of the valence band of the icosahedral (*i*) alloy $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$. In this paper, we present the first determination of the experimental Mn 3*d* and Pd 4*d* PDOS's in *i*- $\text{Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ with the PES technique, which are then compared with the corresponding PDOS's determined from the SXE experiments.² We discuss these Mn 3*d* and Pd 4*d* PDOS's and the experimental total DOS in relation to recent theoretical calculations of the electronic structure of the approximants of the *i*-Al-Pd-Mn alloy.³

2. Experimental

The details of the sample preparation were described elsewhere.¹ The x-ray diffraction study showed that the sample was essentially single phase and exhibited resolution-limited Bragg-peak widths.¹

Photoemission spectra were collected at room temperature on beam line U14A at the National Synchrotron Light Source at the Brookhaven National Laboratory. The spectra were corrected for various instrumental factors.¹ They can be thus compared not only with respect to their shape but also in terms of their intensities. The overall (photon and electron) energy resolution was 0.4 eV. Other experimental details were described elsewhere.¹

3. Results and Discussion

In order to determine the experimental Mn 3d and Pd 4d PDOS's, the PES spectra measured for $h\nu$ values close to the Pd 4d Cooper minimum¹ were used since these spectra exhibit the strongest variation in intensity caused by the large change in the photoionization cross section of the Pd 4d orbital. By taking the difference between the $h\nu=100$ eV and 120 eV valence bands, which have been scaled either to the height of the Pd 4d or to the height of the Mn 3d peak, one obtains respectively the PDOS's of the Mn 3d and Pd 4d character. As the difference spectra have some scatter, they were smoothed to allow a better comparison with theory (Figs. 1 and 2). It should be stressed that, apart from expected minor differences, the same shapes for the experimental Mn 3d and Pd 4d PDOS's are obtained from the valence bands measured for other $h\nu$ values close to the Cooper minimum. However, the above subtraction method may lead to some artifacts for the absolute values of binding energies (BE's) larger than about 5 eV. This is mainly due to the uncertainties associated with the correction of the raw PES spectra for the secondary-electron background which sharply increases¹ for BE's with the absolute values larger than about 5 eV.

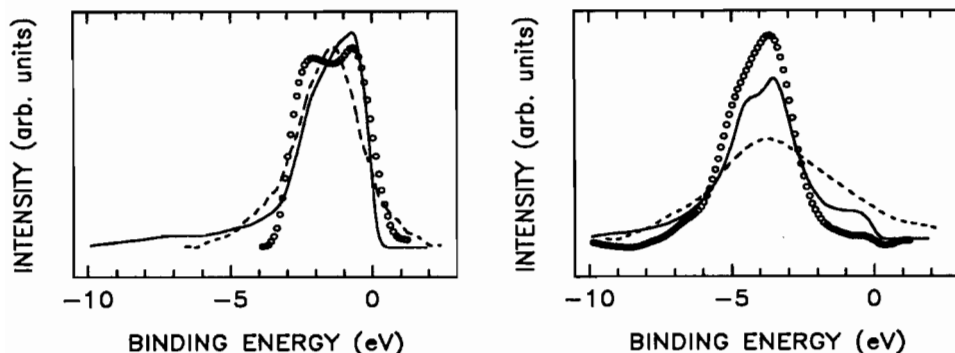


Fig. 1 (left): Comparison of the partial DOS of the Mn 3d character in the ϵ -Al-Pd-Mn alloy obtained from the PES spectra (open circles) and from the SXE measurements (dashed line, Ref. 2) with the corresponding broadened theoretical partial DOS (solid line, Ref. 3), as described in the text.

Fig. 2 (right): Comparison of the partial DOS of the Pd 4d character in the ϵ -Al-Pd-Mn alloy obtained from the PES spectra (open circles) and from the SXE measurements (dashed line, Ref. 2) with the corresponding broadened theoretical partial DOS (solid line, Ref. 3), as described in the text.

A comparison between the Mn 3d and Pd 4d PDOS's obtained from the PES spectra and those measured with the SXE spectroscopy (Figs. 1 and 2), both of which were normalized to the same area, reveals that the former exhibit more structure than the latter. This is perhaps not surprising in view of the lifetime broadening effects, which are much more severe for the SXE technique than for the PES method.^{4,5}

In a recent theoretical study³ the electronic structure of several rational approximants of the ϵ -Al-Pd-Mn phase was calculated. In order to make a meaningful comparison between the theoretical and experimental PDOS's, the former have to be appropriately broadened to account for the lifetime broadening effects inherent to the PES technique and for the finite resolution of a PES experiment.^{5,6} The theoretical Mn 3d and Pd 4d PDOS's of the 8/5 approximant³ were first multiplied by the Fermi-Dirac function at room temperature, then convoluted with a Lorentzian to account for the lifetime broadening, and finally convoluted

with a Gaussian to account for the instrumental broadening. The Lorentzian full width at half maximum (FWHM) was taken in the form^{5,6} $\Gamma_L^0(|BE| - E_F)^2$, with $\Gamma_L^0 = 0.02 \text{ eV}^{-1}$. The Gaussian FWHM was set to 0.4 eV. A reasonable agreement is obtained between such broadened theoretical PDOS's and the corresponding experimental ones derived from the PES spectra (Figs. 1 and 2). In particular, the humps at the left sides of the main theoretical Mn 3d and Pd 4d peaks are observed in the corresponding PES PDOS's.

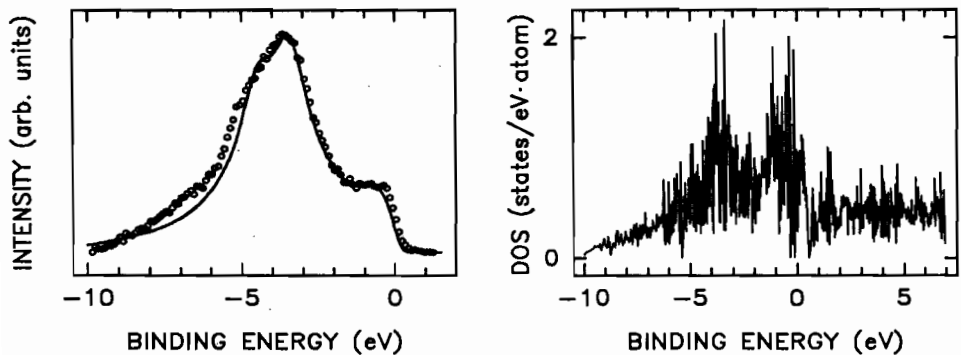


Fig. 3 (left): Comparison of the valence band of the $i\text{-Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ alloy measured at $h\nu=100 \text{ eV}$ (open circles, Ref. 1) with the broadened theoretical DOS for the 8/5 approximant of the $i\text{-Al-Pd-Mn}$ alloy (solid line, Ref. 3), as described in the text.

Fig. 4 (right): Theoretical DOS for the 1/1 approximant of the $i\text{-Al-Pd-Mn}$ alloy (model M2 from Ref. 3).

In order to compare the theoretical total DOS calculated for the 8/5 approximant of the $i\text{-Al-Pd-Mn}$ alloy³ with the valence band of $i\text{-Al}_{70}\text{Pd}_{20}\text{Mn}_{10}$ measured¹ at a given $h\nu$, the theoretical Al, Pd, and Mn PDOS's have to be first multiplied^{5,6} by the corresponding photoionization cross sections at that $h\nu$. Since these cross sections are expected to differ in the studied alloy from their atomic values, the ratio of the photoionization cross sections corresponding to the Mn 3d and Pd 4d orbitals had to be varied to get the best agreement between theory and experiment. The sum of the products of the theoretical PDOS's and the corresponding cross sections was broadened in the same way as described before. Good agreement is obtained (Fig. 3) between the valence band measured at $h\nu=100 \text{ eV}$ and the broadened theoretical DOS. It is thus concluded that the main features of the theoretical Mn 3d and Pd 4d PDOS's and of the total DOS calculated for the 8/5 approximant of the $i\text{-Al-Pd-Mn}$ alloy are observed in the corresponding experimental PES spectra.

The theoretical calculations predict the existence of a structure-induced pseudogap in the DOS around E_F for higher-order approximants of the $i\text{-Al-Pd-Mn}$ alloy.³ Furthermore, the DOS is predicted to have a fine structure in the form of many spiked peaks (Fig. 4). Neither the minimum of the DOS(E_F) nor the DOS spikiness have been observed in the PES spectra within the resolution of the experiment. There can be several reasons for this. First, in a hypothetical case of the absence of the lifetime broadening effects, an energy resolution better than about 0.1 eV is required to detect possible pseudogaps and spikiness in the DOS (Fig. 5). In a real PES experiment, the lifetime broadening effects smear out the fine DOS structure, especially for BE's far from E_F (Fig. 6). Thus, the highest possible energy resolution (better than about 20 meV) is essential to investigate the possible existence of the predicted DOS(E_F) minimum and the DOS spikiness. Second, there is some degree of chemical and topological disorder even in the quasicrystals which are regarded

as "perfect" from the structural point of view.^{5,6} Chemical disorder is associated with the fact that all known stable quasicrystals are ternary alloys.^{5,6} Topological disorder results from the very nature of quasiperiodicity which implies that no two crystallographic sites of a given atom are exactly the same. These two types of disorder, which are clearly observed with the experimental local probes,^{5,6} may significantly influence the electronic properties of quasicrystals; in particular, they may smear out the DOS spikiness and the $DOS(E_F)$ minimum.

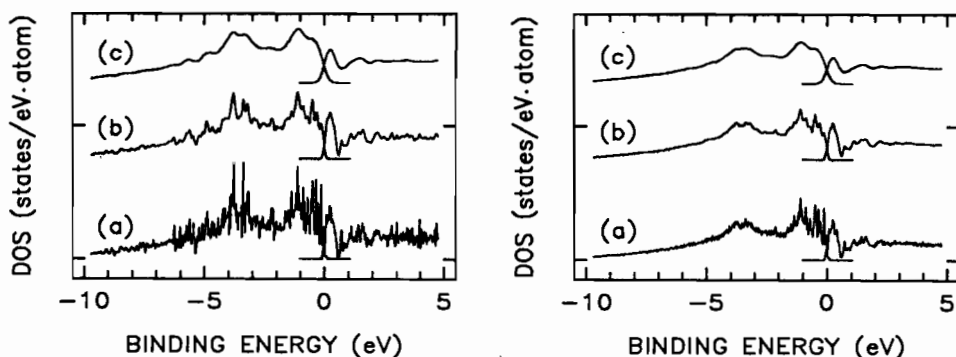


Fig. 5 (left): Theoretical DOS from Fig. 4 multiplied by the Fermi-Dirac function at room temperature and convoluted with a Gaussian of the FWHM equal to (a) 0.02 eV, (b) 0.1 eV, and (c) 0.4 eV. The separation between the two ticks on the ordinate scale corresponds to 2 states/eV·atom.

Fig. 6 (right): Theoretical DOS from Fig. 4 multiplied by the Fermi-Dirac function at room temperature and convoluted with a Lorentzian of the FWHM equal to $\Gamma_L^0(|BE| - E_F)^2$, where $\Gamma_L^0 = 0.02$ eV⁻¹, and with a Gaussian of the FWHM equal to (a) 0.02 eV, (b) 0.1 eV, and (c) 0.4 eV. The separation between the two ticks on the ordinate scale corresponds to 2 states/eV·atom.

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