Photoemission study of $Al_{70}Pd_{20}Mn_{10}$ quasicrystal

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Abstract

Measurements with photoemission spectroscopy in the photon-energy range 35–150 eV have been used to measure the valence band of the stable icosahedral $Al_{70}Pd_{20}Fe_{10}$. The maxima of the Pd 4d- and Mn 3d-derived states are respectively at 3.6 and 0.7 eV below the Fermi level. The strong decrease of intensity towards the Fermi level suggests the presence of a pseudogap at the Fermi level. No unusual features in the valence band of icosahedral $Al_{70}Pd_{20}Mn_{10}$, which could be ascribed to its quasiperiodic nature, are observed within the resolution of the experiment.

1. Introduction

The dramatic discovery of an icosahedral Al–Mn alloy by Shechtman et al. [1] extended the dichotomous division of solids into either crystalline or amorphous by introducing the notion of quasicrystals (QCs). This new form of matter has long-range *quasiperiodic* order and long-range orientational order of crystallographically forbidden (five-fold, eight-fold, ten-fold, and 12-fold) symmetries [2]. A central problem in solid-state physics is to determine whether this new quasiperiodic structure leads to the expected novel physical properties which are found neither in crystalline nor in amorphous materials.

Prior to 1987, all known QCs were thermodynamically *metastable*. They exhibited significant structural disorder as manifested in the broadening of the X-ray diffraction lines. It was argued that this disorder might inhibit detecting possible novel intrinsic physical properties. It was therefore of great impor-

tance when the first thermodynamically *stable* icosahedral (i) alloys Al–Cu–M (M=Fe, Ru, Os) were discovered [3] as they posses a high degree of structural perfection comparable to that found in the best periodic alloys. These new i-alloys indeed exhibit some unusual behaviour [4]. Their most striking characteristics is an unusually high resistivity (up to 30000 μΩ cm in Al–Cu–Ru systems at 4.2 K [4]) and a temperature coefficient which is generally negative. This puts them at the border of the metal–insulator transition. Other anomalies in transport properties have been also observed [4].

Recently, a new stable i-phase has been found in the Al–Pd–Mn system [5]. It differs from other stable i-phases in that the samples are free of atomic disorder and phason strains even in the rapidly solidified state [6]. Furthermore, this phase forms in a wide composition range. Structural studies with different techniques show that this phase forms in a perfect i-state [7]. Therefore this system is ideal for

studies of its possible unusual physical properties.

Most of the studies performed so far are related to the structural characteristics of the i-Al–Pd–Mn alloys [7,8]. A few investigations of their physical properties are summarized below. The first magnetic measurements [9] indicated distinct differences in the magnetic properties between i and corresponding amorphous alloys in the i-Al–Pd–Mn system. Spin-glass behaviour was observed and the data were interpreted in terms of magnetic and nonmagnetic Mn atoms [9]. Furthermore, the concept of a giant magnetic moment on the Mn atoms was invoked [9], which is also known to exist in crystalline alloys of transition metals in a Pd matrix. Recent magnetic studies of the i-Al–Pd–Mn alloys [10] show the presence of both diamagnetic and paramagnetic susceptibilities. The alloys seem to become more diamagnetic as their resistivity increases [10].

NMR measurements [11] were interpreted in terms of two classes of Mn sites invoked earlier to explain magnetic measurements [9,10]. Thermal neutron energy-loss scattering experiments [12] indicate the presence of some fine structures in the generalized vibrational density of states which were not found previously in other stable i-alloys.

Resistivities of up to $10000 \, \mu\Omega$ cm were found at low temperatures in the i-Al–Pd–Mn alloys [10,13]. It was also noted that the resistivity strongly depends on the composition and the structural quality of the samples used [10]. The high values of resistivity were interpreted as evidence for the presence of a pseudogap in the electronic density of states at the Fermi level, DOS(E_F) [10,13].

It thus seems that very high resistivities and diamagnetism are characteristic features of all stable i-alloys of high structural quality. This in turn implies very low values of DOS(E_F), i.e., the presence of a pseudogap at E_F. The existence of such a pseudogap has been suggested by the electronic structure calculations performed for some approximants of QCs [14].

To determine any possible unusual features in the DOS of i-alloys, and in particular the presence of a pseudogap in the DOS(E_F), one needs information not only on the DOS(E_F), which is inferred *indirectly* from the specific heat or resistivity measurements, but also on the DOS below and above E_F. Therefore, studies using spectroscopic techniques

which probe DOS at energies in the vicinity of E_F are extremely useful. Here we present the results of the photoemission spectroscopy (PES) measurements of the high structural quality, stable i-$Al_{70}Pd_{20}Mn_{10}$ alloy.

2. Experimental procedure

An alloy of composition $Al_{70}Pd_{20}Mn_{10}$ was produced by arc melting in argon of high-purity elemental constituents. It was annealed between 1123 and 1173 K for 10 h in vacuum, and then cut into slices suitable for PES measurements. The details of the sample preparation are described elsewhere [5]. All the peaks in the X-ray diffraction spectra could be indexed to the icosahedral phase [5].

Photoemission spectra were collected on beamline U14A at the National Synchrotron Light Source at Brookhaven National Laboratory. Photon energies between 35 and 150 eV were selected with two plane grating monochromators and the electrons were analyzed at near-normal emission with a PHI 15-255 precision electron energy analyzer. The resulting overall resolution was 0.4–0.5 eV. The sample was cleaned in the experimental vacuum chamber either by Ar-ion bombardment or by mechanical abrasion using an alumina scraper. No differences between the PES spectra corresponding to these two surface-treatment methods could be detected. This is consistent with the observation that no significant change of the composition of the surface-region, with respect to that of the bulk, occurs in Pd-containing alloys during Ar-ion bombardment [15]. The surface cleanliness of the sample was frequently checked by monitoring the appearance of the oxide features in the Al 2p line and/or in the valence band [16]. The base pressure in the experimental chamber was in the high 10^{-11} Torr range.

All the spectra presented in this work were obtained from at least two different regions of the sample studied, and turned out to be indistinguishable within the resolution of the experiment. The position of the Fermi level was determined by measuring the Fermi edge and/or the Al 2p line (for photon energies larger than 100 eV) of an adjacent Al sample. It was additionally verified by a linear extrapolation of the leading edge of the valence band of the measured

spectra. The accuracy of the E_F calibration is 0.10 eV. All the PES spectra presented here were corrected first for the energy dependence of the electron transmission of the electron energy analyzer. Next, they were normalized for the photon-flux, and the secondary-electron contribution was subtracted in the usual way [17] by assuming that secondary-electron background intensity at each binding energy (BE) is proportional to the total integrated signal at lower binding energies. The first two corrections slightly change the shape of the original spectrum, whereas the third one produces the largest changes. The importance of these corrections is illustrated in Fig. 1. It can be seen that they have no significant influence on the shape of the spectrum close to E_F, but change the spectrum substantially at higher binding energies (the negative value of BE in Fig. 1 indicates the energy scale below E_F). The PES spectra corrected in such a way can be compared not only with respect to the shape but also in terms of their intensities.

3. Results and discussion

The structure of the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ (Fig. 1) consists of two broad features: a peak at BE$= -3.6$ eV and another one at BE$= -0.7$ eV. The

BE$= -3.6$ eV feature has a shoulder on the higher BE side. In order to identify the origin of these two features, photoemission spectra were measured at different photon energies $h\nu$.

By taking advantage of the Cooper minimum in the Pd 4d photoelectron cross section, which is calculated to be at $h\nu = 115$ eV for pure Pd [18], but which occurs in Pd-alloys at $h\nu \approx 130$ eV [15], one can determine the Pd 4d-derived features in a valence band. An inspection of Fig. 2 shows that as $h\nu$ increases, the relative contribution of the BE$= -3.6$ eV feature with respect to the BE$= -0.7$ eV feature first decreases, reaches a minimum at $h\nu \approx 130$ eV, and then starts to increase. To present this behaviour in a more quantitative way, the intensity ratio of the BE$= -3.6$ and -0.7 eV peaks as a function of $h\nu$ is plotted in Fig. 3. Note that there is a steep decrease of this ratio for photon energies up to about 127 eV, and then a moderate increase at higher photon energies, which is in agreement with the theoretical Pd 4d photoelectron cross section dependence upon photon energy around the Cooper minimum [18]. It is thus concluded that the BE$= -3.6$ eV feature is predominantly due to the Pd 4d-derived states.

In order to identify the main features in a valence band due to Mn 3d states, a resonant photoemission effect can be employed. In this effect the ionization

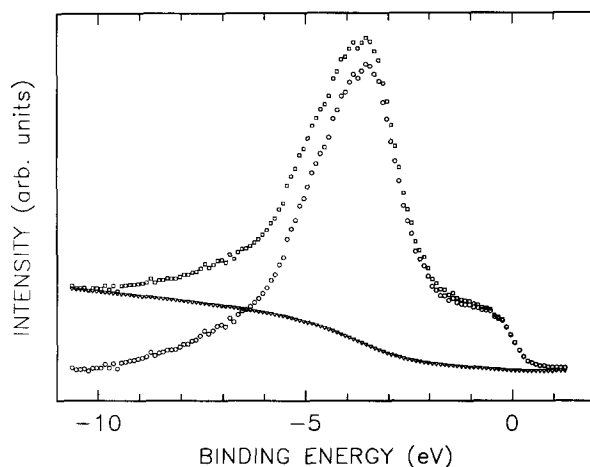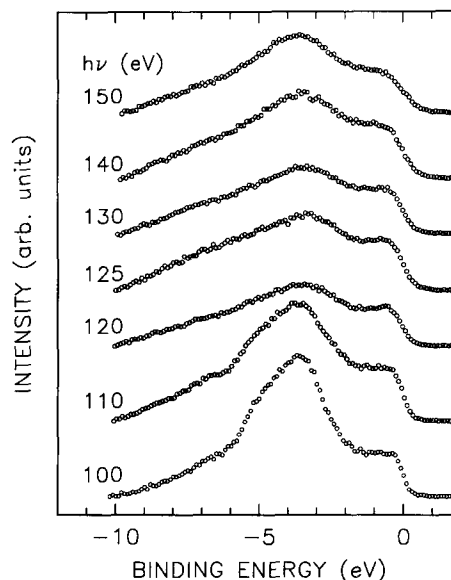Fig. 1. Effect of the secondary-electron contribution on the valence-band spectrum of i-$Al_{70}Pd_{20}Mn_{10}$ measured with a photon energy $h\nu = 50$ eV. ($\square$) Original spectrum, (∇) secondary-electron contribution to the analyzer- and flux-corrected original spectrum, ($\bigcirc$) resultant spectrum after subtraction of the secondary-electron contribution.

Fig. 2. Valence-band spectra of i-$Al_{70}Pd_{20}Mn_{10}$ for different photon energies $h\nu$ in the vicinity of the Pd 4d Cooper minimum.
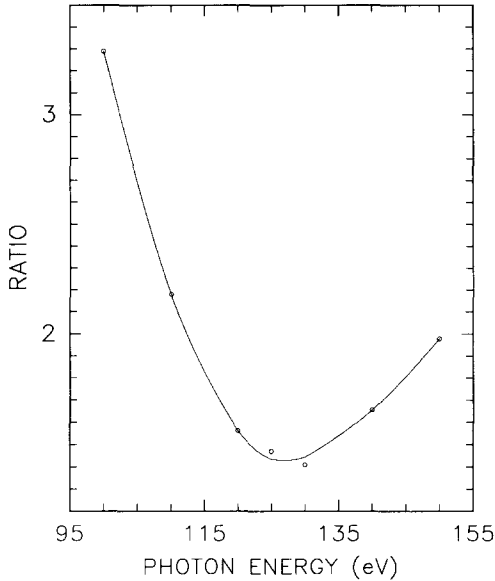
Fig. 3. Intensity ratio of the two features in Fig. 2 at the binding energies −3.6 and −0.7 eV as a function of photon energy. The solid line is a guide for the eye.

Fig. 4. Valence-band spectra of i-$Al_{70}Pd_{20}Mn_{10}$ for different photon energies $h\nu$ around the Mn 3p→3d transition. A, B, and C identify features for which CIS spectra were measured (Fig. 5).

cross section of an outer-shell electron is enhanced as the excitation energy exceeds the threshold of an inner excitation. Resonant PES was used in previous work to determine the Fe 3d-derived features in the valence bands of i-Al–Cu–Fe alloys [16,19]. For transition-metal elements the resonance occurs at excitation energies near the 3p threshold, which for the Mn 3p→3d transition occurs at about 47 eV. As the photon energy increases (Fig. 4), the intensity of the BE = −0.7 eV feature is slightly suppressed at $h\nu = 47$ eV. This indicates that this feature may be predominantly due to the Mn 3d-derived states.

More convincing evidence for ascribing the BE = −0.7 eV feature to the predominantly Mn 3d-derived states can be obtained by performing a resonance photoemission experiment in the so-called constant-initial-state (CIS) mode [20]. The photoemission intensity in this mode is measured as a function of photon energies for selected valence-band positions identified by their initial energy E_i. Such CIS spectra for the E_i values corresponding to the features denoted by A, B, and C in Fig. 4 are shown in Fig. 5. One can clearly see the presence of resonances for photon energies around 47 eV. The line shape of the resonance, $I(h\nu)$, can be characterized by the Fano profile [21]
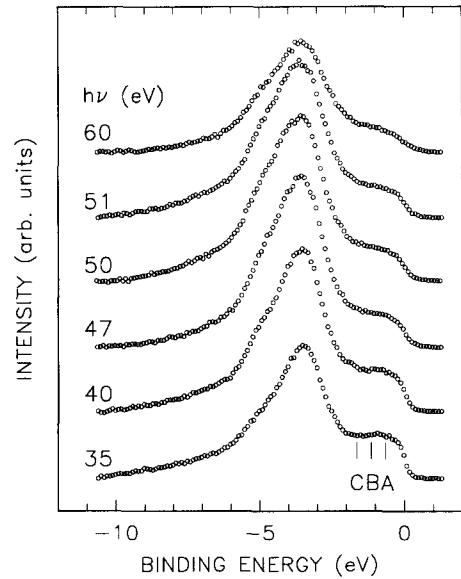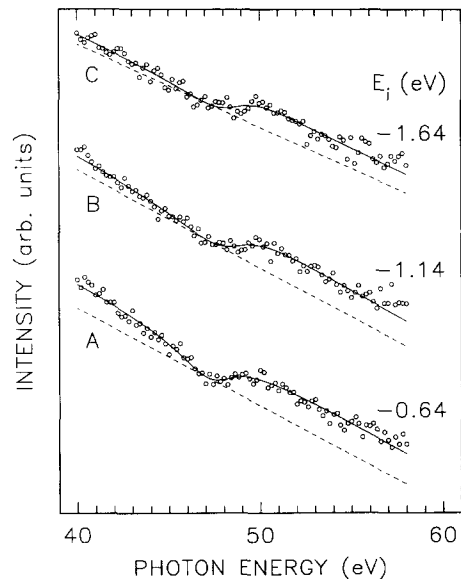

Fig. 5. Constant-initial-state (CIS) spectra for the valence-band features A, B, and C in Fig. 4 that are identified here by the same letters and by their corresponding initial energies E_i. The solid line is a fit to the Fano profile and a linear background (shown by a broken line), as described in the text.

$$I(h\nu) = I_0(\nu) \frac{(\epsilon + q)^2}{1 + \epsilon^2} + I_{nr}(\nu) ,$$

where $I_0(\nu)$ is the nonresonant Mn 3d emission, $I_{nr}(\nu)$ is a noninterfering background contribution, q is the Fano asymmetry parameter, and $\epsilon = 2(h\nu - E_R)/\Gamma$ is the reduced energy expressed in terms of the energy, E_R, and width, Γ (FWHM), of the resonance. A linear background was assumed in the fit (broken line in Fig. 5). The detail analysis of the fitted parameters is given elsewhere [22]. Here we only notice that the resonance amplitude decreases with the increase of E_i (Fig. 5). This means that the peak of the Mn 3d-derived states is at about 0.7 eV below E_F and that the Mn 3d states spread throughout the region a few eV below E_F, probably as a result of hybridization with the Al sp and Pd 4d states.

Our result for the position of the maximum of the Pd 4d-derived states agrees well with the value of -3.5 eV obtained in a recent soft X-ray emission (SXE) study [23] of i-$Al_{71}Pd_{19}Mn_9$ (Fig. 2 in Ref. [23]). However, the peak of the Mn 3d-derived states at -1.3 eV (Fig. 2 in Ref. [23]) differs from our value of -0.7 eV. This may be related to the large uncertainty ± 0.3 eV in determining the position of the Fermi level in the SXE study [23].

It is well established from experiments in the XPS and UPS photon-energy range that in pure Pd [24] and Mn [25] there is a high $DOS(E_F)$. The observed broad peak in the valence band of Pd lies in the range 1.3–2.3 eV below E_F, depending on the photon energy used [24]. For pure Mn, two features at about 0.5–1.0 and 3.0 eV below E_F are present in the valence band [25]. The Pd 4d peak at -3.6 eV observed in the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ (Figs. 1, 2, and 4) clearly indicates the shift of the Pd 4d-derived states away from E_F, which should lead to the decrease in the Pd 4d-contribution to the $DOS(E_F)$. Such a shift is less obvious for the Mn 3d-derived states. The strong depression of intensity towards E_F observed in the valence-band spectra of i-$Al_{70}Pd_{20}Mn_{10}$ (Figs. 1, 2, and 4) is mostly due to the Fermi level cut off broadened by the instrumental resolution. It may be also due to the part of the pseudogap at E_F predicted by theory [14] and is consistent with transport data of stable i-alloys [4,10,13,16] and the SXE measurements [23]. However, to clearly

separate these two sources of the decrease of the photoemission intensity toward the E_F, high energy-resolution PES experiments are required. To prove unambiguously the presence of such a pseudogap, the region directly above E_F, where an increase in intensity is expected, would have to be measured by inverse PES which is sensitive to the unoccupied DOS. Inverse PES experiments performed on i-$Al_{55}Li_{35.8}Cu_{9.2}$ [26] revealed indeed the opening of a pseudogap just above E_F.

Theoretical calculations [14] suggest the presence of many spikes in the DOS of QCs. The existence of such rapidly varying DOS has been also suggested [27] to explain the unusual temperature dependence of resistivity and thermoelectric power in α-Al–Mn–Si approximant. The valence bands of i-$Al_{70}Pd_{20}Mn_{10}$ presented here show no evidence for spikes within the energy resolution of our experiment. If such spikiness indeed occurs in QCs, it must be at an energy level much smaller than 0.4 eV.

4. Conclusions

The structure of the valence band of i-$Al_{70}Pd_{20}Mn_{10}$ consists of two main features at about 0.7 and 3.6 eV below E_F. The first feature was shown to be due to the Mn 3d-derived states, whereas the other was shown to result from the predominantly Pd 4d-derived states. The strong decrease of intensity towards E_F was interpreted as an indication of the presence of the minimum of the DOS at E_F. No unusual features in the valence band, which could be associated with the quasiperiodic nature of the sample studied, were found within the energy resolution of the experiment.

Acknowledgement

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