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The effect of the Mn constituent on the electronic structures of $\text{Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ quasicrystals studied by x-ray absorption and photoemission spectroscopy

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Abstract

X-ray absorption near-edge fine structure (XANES) and valence-band photoelectron spectroscopy (PES) measurements were performed to elucidate the effect of the Mn constituent on the electronic structures of icosahedral (i)- $\text{Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ quasicrystals (QCs). Pd and Re L_3 -edge and Al K-edge XANES spectra reveal that the unoccupied Pd 4d, Re 5d and Al 3p states are insensitive to the Mn doping. The valence-band PES and resonant photoemission analysis indicate a marked Mn 3d contribution within ~ 5 eV of the Fermi level, suggesting that the Mn doping increases the conductivity of i-Al–Pd–Re–Mn QCs.

1. Introduction

Icosahedral quasicrystals (i-QCs) have attracted much attention because they have unusual physical properties [1, 2]. For instance, they have a much higher electrical resistivity, ρ , than their constituent metals and have a negative temperature coefficient of resistivity [3, 4]. A number of studies have found the presence of a pseudo-gap in the electronic density of states (DOS) near/at the Fermi level (E_f) for i-QCs [4–7]. Recent investigations on i-Al–Pd–Re

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Table 1. The composition, r -value and the expected conductive behaviour (ecb) of the $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QC samples.

x	$r = \rho(4.2 \text{ K})/\rho(300 \text{ K})$	ecb
0.0	8.3	Metal/semimetal
0.0	52	Insulator/semiconductor
0.1	38.7	Insulator/semiconductor
0.2	7.4	Metal/semimetal

QCs have revealed evidence of a metal–insulator transition (MIT) at a critical resistivity ratio $r = \rho(4.2 \text{ K})/\rho(300 \text{ K})$ under a suitable annealing condition [8–12]. They also demonstrated that the MIT generally occurs in the range $r = 20\text{--}30$. Furthermore, the conductivity of $i\text{-Al}\text{-Pd}\text{-Re}\text{-Mn}$ [13, 14] and $i\text{-Al}\text{-Pd}\text{-Mn}$ [15, 16] QCs increased with the Mn concentration. In other words, the Mn-doped QCs become less resistive, i.e. the metallicity of the quasicrystalline alloy increases, with the increase of the Mn content. The knowledge of the electronic structures of Mn-doped QCs is important in understanding the effect of the Mn constituent on the transport properties of these materials. Thus, a systematic study of the electronic and atomic structure of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs as a function of the Mn concentration using Al K-edge and Pd, Re and Mn L_3 -edge x-ray absorption near-edge structure (XANES), Mn K-edge extended x-ray absorption fine structure (EXAFS) and valence-band photoelectron spectroscopy (PES) has been performed. The metallicity and electronic structures will be elucidated in terms of the occupied and unoccupied valence states in $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs for various Mn contents.

2. Experiment

Pd and Re L_3 -edge and Al K-edge XANES and Mn K-edge EXAFS spectra were obtained from double-crystal monochromator-15B, wiggler-17C and Dragon-11A beamlines using fluorescence mode, respectively, at the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. The Mn L_3 -edge XANES spectra were obtained at the Advanced Light Source (ALS) from the beamline-7.0.1, which has a spherical grating monochromator, using sample current mode. Valence-band PES measurements were also performed using the low-energy spherical grating monochromator-08A beamline at NSRRC, at a base pressure of $\sim 5 \times 10^{-10}$ Torr with an EAC-125 hemispherical electron energy analyser. The samples were cleaned by repeated cycles of argon-ion bombardment before annealing (up to $\sim 350^\circ\text{C}$). Ingots of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ ($x = 0.0, 0.1$ and 0.2) alloys with various r -values were formed by arc melting of a mixture of high-purity Al (99.99 wt%), Pd (99.99 wt%), Re (99.99 wt%) and Mn (99.99 wt%) metals in a purified argon atmosphere, under a suitable annealing condition. In general, the QCs were prepared by annealing these ingots in a vacuum at $960\text{--}980^\circ\text{C}$ for 24 h. That of the $x = 0.0$ sample was further annealed at 600°C for 1–2 h in order to increase the value of r (the r -value varies from 8.3 to 52). Table 1 lists the composition, r -value and the expected conductive behaviour of the $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QC samples. The fabrication and characterization of the samples are described elsewhere [9, 13].

3. Results and discussion

Figure 1 and the upper and lower insets show the normalized Pd and Re L_3 -edge and Al K-edge XANES spectra of the $x = 0.0, 0.1$ and 0.2 $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs. The

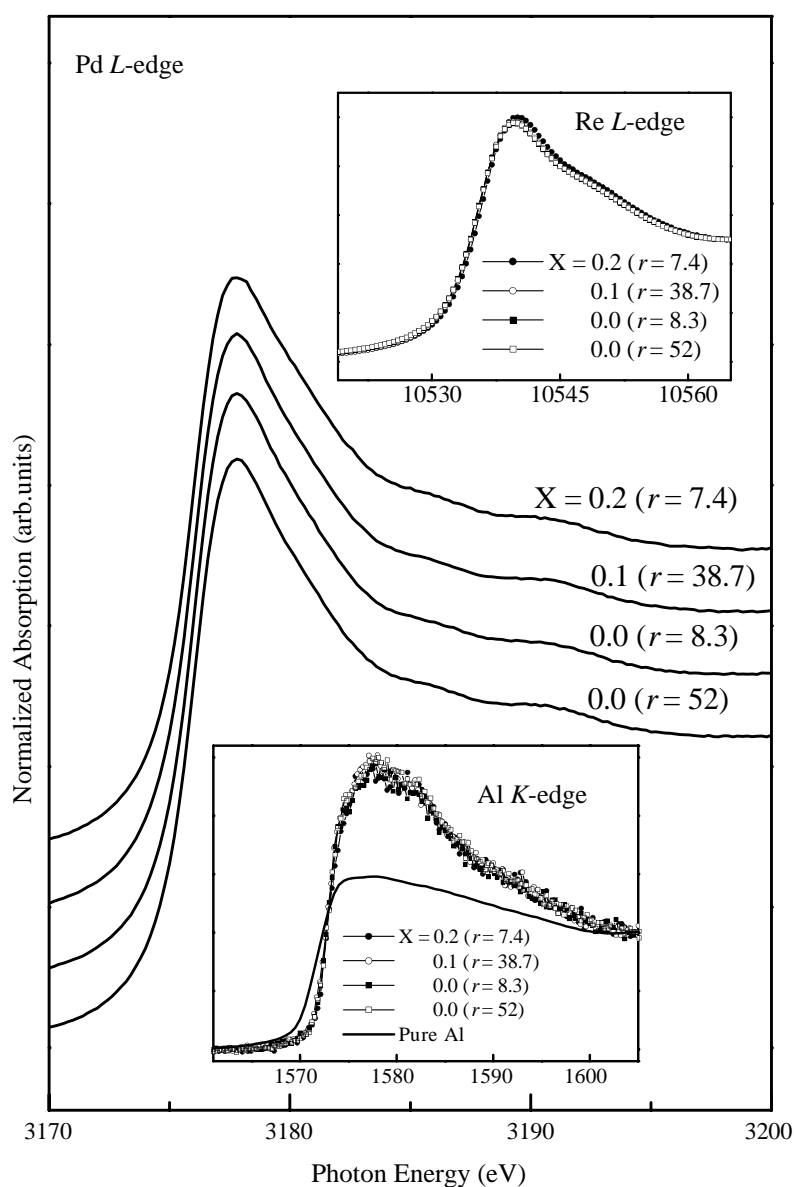


Figure 1. This figure and the upper and lower insets present the normalized Pd and Re L_3 -edge and Al K-edge XANES spectra of the $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ ($x = 0.0, 0.1$ and 0.2) QC samples.

leading near-edge features are attributable to unoccupied Pd 4d, Re 5d and Al 3p derived states, respectively [17, 18]. The general line-shapes and intensities of the Pd and Re L_3 -edge and Al K-edge XANES spectra of the $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ samples are almost identical, regardless of the increase of the Mn content from $x = 0.0$ to 0.2 with $r = 7.4$ ($x = 0.2$), 8.3 ($x = 0.0$), 38.7 ($x = 0.1$) and 52 ($x = 0.0$). As stated previously, r has been used to determine the metallic or insulating nature of $i\text{-Al-Pd-Re}$ QCs. Using this rule, the $r = 7.4$ ($x = 0.2$) and 8.3 ($x = 0.0$) $i\text{-Al-Pd-Re}$ QC samples will be metals and the $r = 38.7$

($x = 0.1$) and 52 ($x = 0.0$) samples will be insulators. However, the similarity of the general line-shape and features in the Pd and Re L_3 -edge and Al K-edge XANES spectra of all the four samples suggests otherwise. The Al K-edge XANES spectrum of the pure Al metal is also given in figure 1, which shows that the leading edges of the Al K-edge XANES spectra of QC samples shift slightly to higher binding energies relative to that of the pure Al metal. Alternatively, this can be interpreted as a depletion/reduction of the Al 3p partial DOSs at E_f . The depletion/reduction of the Al DOSs at E_f was described as an existence of pseudo-gap and was correlated with a higher resistance [5, 19, 20].

Figure 2 presents the normalized Mn L_3 -edge XANES spectra of the i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} ($x = 0.1$ and 0.2) samples. According to dipole-transition selection rules, the dominant transition is from Mn 2p_{3/2} to unoccupied Mn 3d states. The area beneath the white-line feature in the Mn L_3 -edge spectra is mainly a convolution of the absolute square of the transition matrix element and the unoccupied DOSs of Mn 3d character. In figure 2, the general line-shapes of the Mn L_3 -edge XANES spectra of the $x = 0.1$ and 0.2 QCs are similar to each other. However, the intensities of the white-line features of the $x = 0.2$ sample markedly exceed those of the $x = 0.1$ sample, which suggests that the variation of r of i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs is related to the Mn 3d-derived states. The inset of figure 2 displays Fourier transform (FT) amplitudes of EXAFS $k^3\chi$ data and their corresponding oscillation at the Mn K-edge of the $x = 0.1$ and 0.2 QCs, which show that the Mn K-edge FT spectra overall are very similar for those two samples. This result suggests that Mn atoms in the i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs have similar local atomic structures irrespective of the r -values.

Figure 3 presents the valence-band PES spectra of i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs with an incident photon energy of 80 eV. Comparing the spectra of i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs between -1 eV and E_f (0) and that of the pure Re metal displayed in the inset (a) of figure 3, the spectra of the three i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs with $x = 0.1$ ($r = 38.7$), $x = 0.2$ ($r = 7.4$) and $x = 0.0$ ($r = 8.3$) show clear E_f cutoff, which indicates that these three samples are metallic or semi-metallic. The spectrum of the $x = 0.0$ ($r = 52$) sample also shows an E_f cutoff, although the cutoff edge is not as sharp as others, which led Lay *et al* to propose the existence of a pseudo-gap near/at E_f in the DOSs of i-Al-Pd-Re QCs [11]. According to the general rule of the r -value, the $x = 0.1$ ($r = 38.7$) QC sample should be an insulator, which is not compatible with the present PES result. Thus, the use of the r -value to determine whether Mn-doped i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QC is metallic or insulating is not reliable. The conductivity is proportional to the product of the carrier density and the effective relaxation time and inverse proportional to the effective mass of carriers [21]. The carrier density in turn depends on the details of the DOS within about $k_B T$ of E_f for metals or semimetals, which do not have an energy gap at E_f . In this case, if the DOS increases rapidly immediately above/near E_f , so that the carrier density increases with temperature sharply and outweighs the decrease of the effective relaxation time due to carrier-phonon interactions, the conductivity (resistivity) may increase (decrease) with temperature such that $r = \rho(4.2 \text{ K})/\rho(300 \text{ K}) \gg 1$ like a semiconductor or insulator. In contrast, the carrier density in an intrinsic semiconductor/insulator is due to thermal excitation from the states near the valence-band maximum across the energy gap to the states near the conduction-band minimum, which increases exponentially with the temperature.

The overall PES spectra of i-Al₇₀Pd_{22.5}(Re_{1-x}Mn_x)_{7.5} QCs can be roughly divided into two regions: (-3 eV, E_f) and (-14 eV, -3 eV). The (-3 eV, E_f) region is enlarged in the inset (b) of figure 3. In this region, there is a shallow feature centred at about -2.3 eV. This feature is enhanced for the Mn-doped samples, which suggests that occupied Mn 3d states contribute to this feature, as already noticed by Zhang *et al* [22] and Wu *et al* [23]. In the (-14 eV,

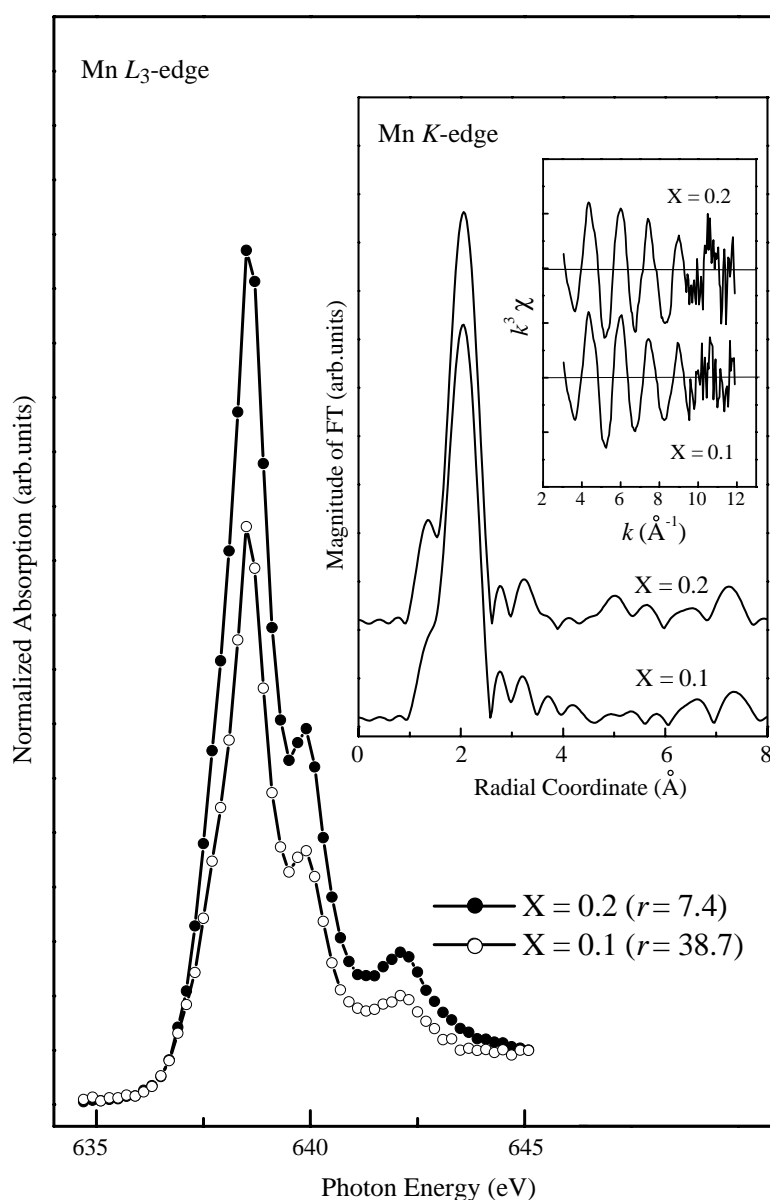


Figure 2. Normalized Mn L_3 -edge x-ray absorption spectra of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ ($x = 0.1$ and 0.2) QC samples. The inset displays FT amplitudes of EXAFS $k^3\chi$ data from $k = 3.5$ to 10.5 \AA^{-1} and their corresponding oscillations at the Mn K-edge.

-3 eV) region, there is a prominent feature centred at about -5.7 eV , which was attributed primarily to the Re 5d- and Pd 4d-derived states [6, 7, 11, 24]. The spectra were also noted to include contributions from Al 3p and 3s-d states distributed between -14 and -3 eV [19].

Figure 4 displays valence-band PES spectra of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs ($x = 0.1$ and 0.2) obtained at various photon energies from $h\nu = 48$ to 58 eV to elucidate the contribution of Mn 3d states near/below E_f by Mn core-state-3d resonance. Subtracting the *off-resonance*

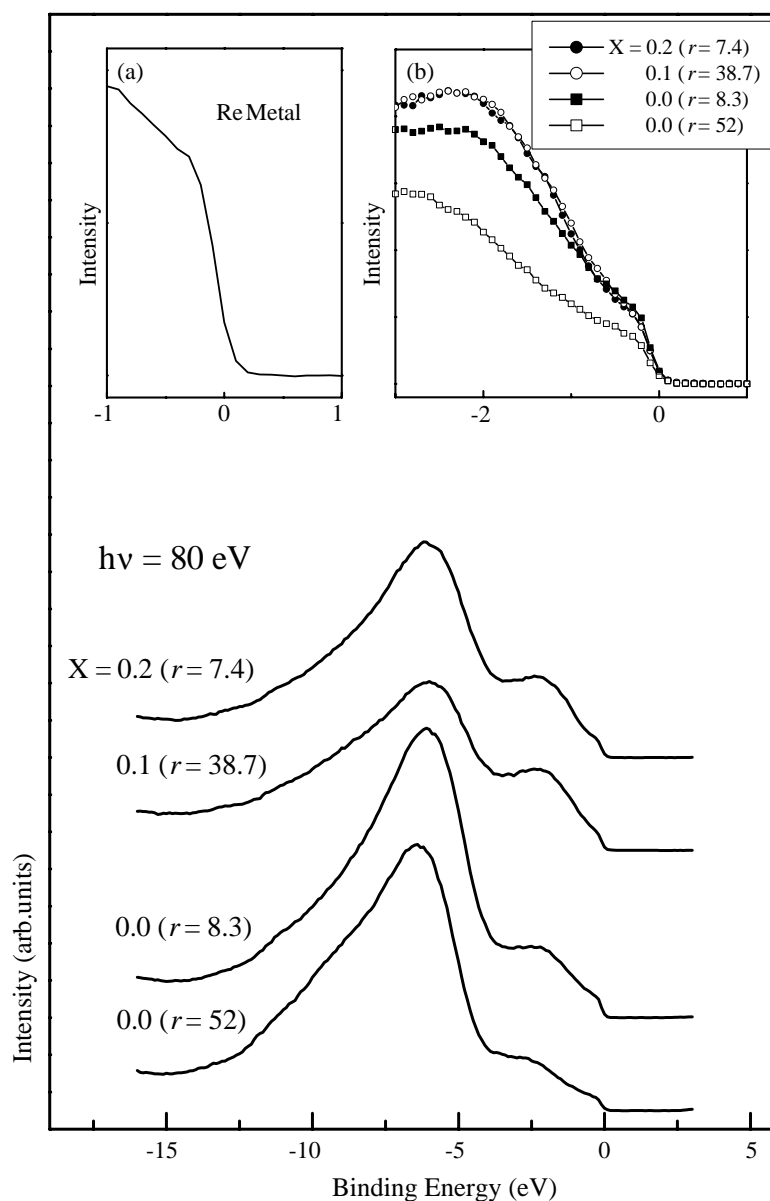


Figure 3. Valence-band PES spectra of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs with an incident photon energy of 80 eV. Insets (a) and (b) display the enlarged spectra near E_F for the reference Re metal and $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs, respectively.

($h\nu = 48$ eV) spectrum from the *on-resonance* (54 eV) spectrum yielded the bottom figure in figure 4. Happo *et al* [25] and Sato *et al* [26] attributed resonant photoemission to the interference between the direct excitation of Mn 3d electrons and the Mn 3p–3d core-excitation process, followed by a super-Coster–Kronig decay. When the photon energy is larger than the Mn 3p–3d energy difference, Mn 3p core electrons can be excited to unoccupied Mn 3d states to become Mn 3d electrons, which resonantly enhances the photoionization cross section

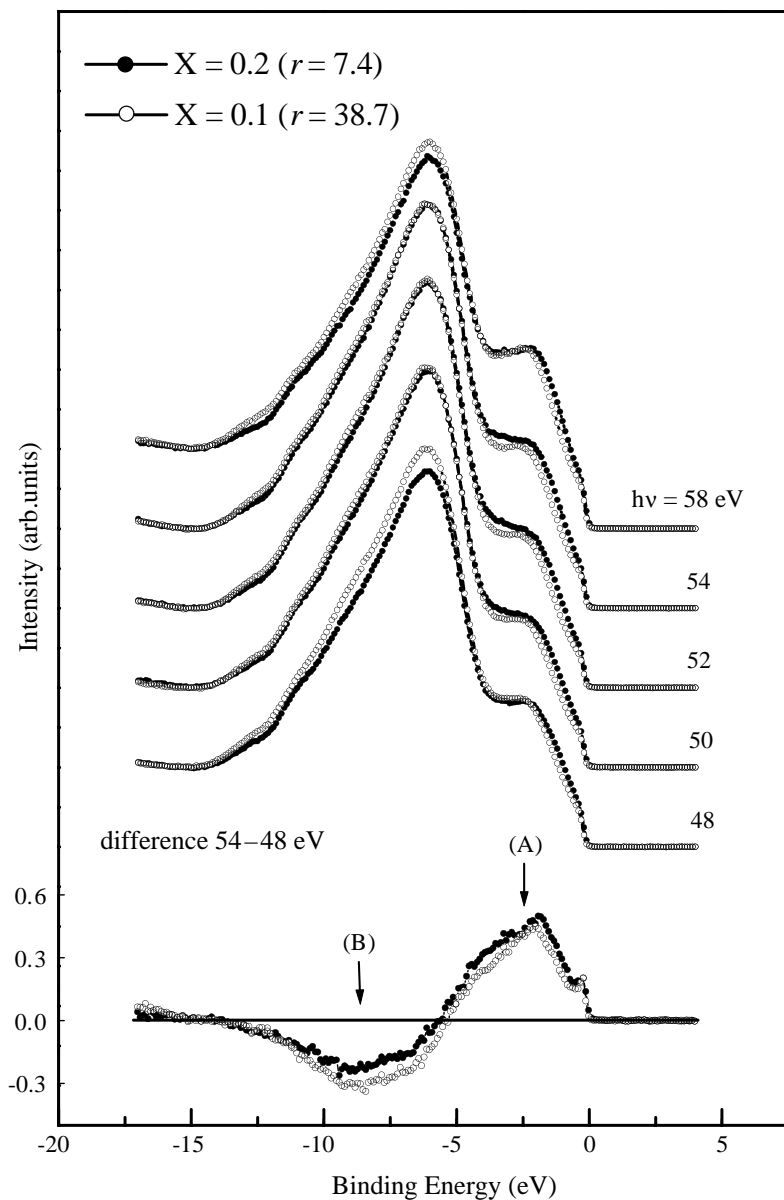


Figure 4. Valence-band PES of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs ($x = 0.1$ and 0.2) obtained at various photon energies from $h\nu = 48$ to 58 eV. The bottom panel presents difference spectra between *on-resonance* ($h\nu = 54$ eV) and *off-resonance* ($h\nu = 48$ eV) spectra for $x = 0.1$ and 0.2 samples.

of Mn 3d electrons. The difference valence-band spectra for both $x = 0.1$ and 0.2 QCs show that the intensities of features A and B are enhanced and reduced, respectively. The clear enhancement of feature A indicates that occupied Mn 3d states contribute significantly to feature A, which is within ~ 5 eV of E_f (note the Re core excitation to 5d *resonance* is not in this photon energy region [27]). In contrast, the reduced intensity of feature B is

primarily due to the fact that Pd 4d and Al 3p contribute significantly to feature B and the photoionization cross sections of Pd 4d and Al 3p states for $h\nu = 58$ eV are smaller than those for $h\nu = 48$ [27]. The result that Mn 3d contributes significantly to the top ~ 5 eV near/below the E_f in the valence band of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs is consistent with that obtained in earlier studies [22, 23]. As stated above, $i\text{-Al-Pd-Re-Mn}$ and $i\text{-Al-Pd-Mn}$ QCs become less resistive, i.e. the metallicity is increased, as the Mn content increases, which strongly correlates with the significant enhancement of the partial DOS of Mn 3d contribution near/below the E_f .

4. Conclusion

In summary, Pd and Re L_3 -edge and Al K-edge XANES spectra demonstrate that the unoccupied Pd 4d, Re 5d and Al 3p states are insensitive to the Mn doping in the $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QC samples. The intensities of the white-line features at the Mn L_3 -edge increase with the Mn concentration, suggesting that the variation of the conductivity or metallicity of $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs is related to Mn 3d-derived states. The Mn K-edge EXAFS result suggests that Mn atoms in the $x = 0.1$ and 0.2 $i\text{-Al}_{70}\text{Pd}_{22.5}(\text{Re}_{1-x}\text{Mn}_x)_{7.5}$ QCs have similar local atomic structures irrespective of the value of r . The valence-band PES and resonant photoemission analysis revealed a marked Mn 3d contribution to the valence band within ~ 5 eV of E_f . The resistivity ratio, i.e. the r -value, is found not reliable to determine whether a Mn-doped QC sample is a metal or an insulator.

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