

Observation of metal–insulator transition in Al–Pd–Re quasicrystals by x-ray absorption and photoemission spectroscopy

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Using x-ray absorption and valence-band photoelectron spectroscopy (PES) we investigated the electronic structures of icosahedral (*i*)-Al₇₀Pd_{22.5}Re_{7.5} quasicrystals (QCs) with a 4.2 K/300 K resistivity ratio, r , ranging from 8.3 to 107 obtained under various annealing conditions. Our Al K - and Pd L_3 -edge x-ray absorption results show that the density of states, $N(E)$, near the Fermi level, E_F , jumps to a larger value when r decreases down to below about 20.6. The valence-band PES results show that $N(E)$ near E_F is greatly reduced in *i*-Al₇₀Pd_{22.5}Re_{7.5} QCs relative to that of the pure metal, which confirms the existence of the pseudogap. The PES spectrum has a sharp cutoff at E_F for $r=8.3$ QC, while it decreases smoothly down to zero at E_F for larger r 's. The combined results suggest the occurrence of metal–insulator transition at an r between 13 and 20.6. © 2003 American Institute of Physics. [DOI: 10.1063/1.1565183]

Quasicrystalline alloys have received increasing interest owing to their unusual physical properties.^{1,2} For example, icosahedral (*i*) phases of Al-based quasicrystals (QCs) have high electrical resistivity (ρ) and a negative temperature coefficient of resistivity.^{3,4} The stability or metastability of QCs was attributed to the Hume–Rothery effect, which causes the formation of a pseudogap in the electronic density of states, $N(E)$, at the Fermi level (E_F).^{3,5,6} Low-temperature photoemission studies of Stadnik *et al.* demonstrated that the pseudogap plays an important role in determining the stability of QCs, though it was argued not to be the major cause of the observed high ρ in QCs.⁷ Recent studies of *i*-Al–Pd–Re QCs also revealed that these QCs have the highest ρ at 4.2 K and the evidence of a metal–insulator transition (MIT) at a critical resistivity ratio $r=\rho(4.2\text{ K})/\rho(300\text{ K})$ obtained under some appropriate annealing condition.^{4,8,9} Studies using soft x-ray emission and absorption spectroscopy provided further insight into the electronic structures of quasicrystalline Al–Pd–Mn¹⁰ and *i*-Al–Pd–Re^{7,11,12} alloys. In this study we have performed a systematic investigation of the electronic structures of both occupied and unoccupied valence states as functions of r for *i*-Al–Pd–Re QCs using Al K -, Pd and Re L_3 -edges x-ray absorption near edge structure (XANES) and valence-band photoelectron spectroscopy (PES) measurements.

XANES and PES spectra were obtained at the Synchrotron Radiation Research Center, Hsinchu, Taiwan. For all samples, the Al K -edge XANES spectra were obtained from high-energy spherical grating monochromator beamline using the fluorescence yield method, while the Pd and

Re L_3 -edges XANES spectra were obtained using the double crystal monochromator and wiggler-C beamlines by the sample drain current and fluorescence methods, respectively. Valence-band PES measurements were performed using the low-energy spherical grating monochromator beamline. The fabrication and characterization of the samples are described elsewhere.¹³

Figure 1 shows the Al K -edge XANES spectra of the various *i*-Al₇₀Pd_{22.5}Re_{7.5} QC samples and pure Al. The spectra were normalized using the incident beam intensity, I_0 , keeping fixed the area under the spectra in an energy range between 1605 and 1627 eV (not fully shown in the figure). The leading near-edge feature was argued to be due to strong hybridization between Al p and Pd/Re d orbitals.^{14,15} For $r=107, 75.6, 52,$ and 20.6 samples the leading feature as indicated by the position of the maximum intensity, which is marked by an arrow, in these spectra consistently shifts to lower energies when r decreases from 107 to 20.6 as shown in Fig. 1. For pure Al, $r<1$ because the electric resistivity increases with the temperature for a metal. Thus, the leading feature in the spectra of $r=13$ and 8.3 and pure Al samples also consistently show a shift to lower energy when r is decreased. There is a discontinuity in the shift of the leading feature between $r=20.6$ and $r=13$, which indicates a sudden change (or transition) of the electronic property. All spectra extend up to about 30 eV above the edge in agreement with the finding of Tamura *et al.*¹⁶ The enlarged near edge features shown in the inset of Fig. 1 are obtained by subtracting an arc tangent type background (represented by the dotted curve) from the measured spectra. The inset of Fig. 1 shows that the near edge spectra, which reflect the density of unoccupied Al $3p$ -derived states, of the QCs with $r=13$ and 20.6 have the largest and smallest intensities, respectively.

Figures 2 and 3 show the normalized Pd and Re L_3 -edges

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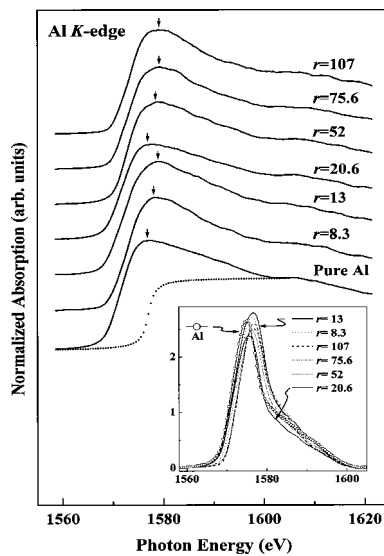


FIG. 1. Normalized Al K -edge x-ray absorption spectra of i -Al₇₀Pd_{22.5}Re_{7.5} QCs and pure Al. The lower inset shows the enlarged near edge features after background subtraction.

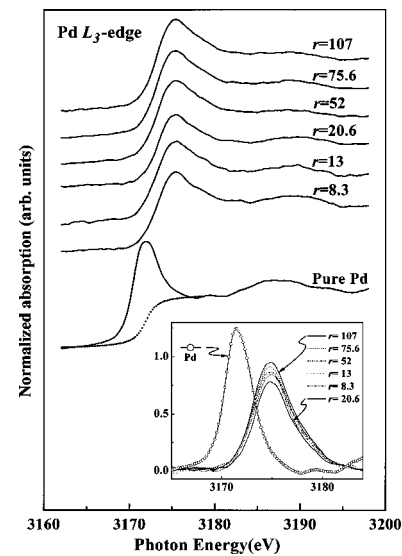


FIG. 2. Normalized Pd L_3 -edge x-ray absorption spectra of i -Al₇₀Pd_{22.5}Re_{7.5} QCs and pure Pd. The lower inset shows the enlarged near edge features after background subtraction.

x-ray absorption spectra of i -Al₇₀Pd_{22.5}Re_{7.5} QCs and reference Pd and Re metals. In the insets of Figs. 2 and 3 the spectra have been subtracted with an arctangent type background as shown by the dotted curves to better illustrate the contributions from unoccupied Pd $4d$ and Re $5d$ derived states in QCs and pure Pd and Re metals. In contrast to the Al K -edge XANES spectra, the near edge features in the Pd L_3 -edge spectra of QCs and reference Pd are more symmetric and narrower, which suggest that these features are dominantly contributed by unoccupied Pd $4d$ orbitals because a free Pd atom has a $4d^{10}$ configuration without $6s$ electrons.¹⁷ The Re L_3 -edge spectrum of the Re metal as shown in Fig. 3 has two features located about 10538 and 10552 eV. The occurrence of two prominent features shows that this spectrum is an overlapping of two unoccupied Re $5d$ subbands split by the crystal field. Re L_3 -edge spectra extend to about 30 eV similar to Al K -edge spectra, while the Pd L_3 -edge spectra extend only up to about 10 eV. The Pd and Re L_3 -edge XANES spectra of QCs are also shifted by ~ 3.5 and ~ 0.8 eV, respectively, toward the higher energy side and the near edge features are broader than those of corresponding Pd and Re metals. The intensities of the near edge features for QCs are reduced relative to that for the pure metal for Pd, while they are enhanced for Re. The observed large Pd L_3 -edge shift was attributed to the large work function difference between QCs and pure Pd.¹⁸ The reduction of the numbers of unoccupied Pd $4d$ -derived states in QCs can be understood by a much larger electronegativity for Pd (2.2)¹⁷ than for Al (1.61),¹⁷ which causes a transfer of electrons from Al to Pd and reduces the number of unoccupied Pd $4d$ states. Since Re also has a larger electronegativity (1.9),¹⁷ the enhancement of unoccupied Re $5d$ -derived states may be due to the increase of electrostatic potential given rise by electron transfer from Al to the Re $6s$ -derived states.

The near edge features in the Al K - and Pd and Re L_3 -edges spectra were integrated between 1560.3 and 1602.3 eV, 3170.7 and 3181.9 eV, and 10510 and 10566 eV, respectively, as shown in Fig. 4. For a semiconductor/insulator with an energy gap, the increase of the concentra-

tions of electron and hole carriers is proportional to an exponential function of the temperature, which greatly outweighs the increase of resistive electron-phonon interactions. Thus, ρ (300 K) is much less than ρ (4.2 K) and $r \gg 1$ if the energy gap is not too large (if the energy gap is too large, ρ is still very large at 300 K). For metals without an energy gap, the concentration of electron carriers does not increase with temperature as rapidly as that of the semiconductor/insulator, so that r is greatly reduced. Since QCs are composed of metal atoms, $N(E)$ is not expected to have a real energy gap, so that the large r values of QCs was interpreted as the existence of a pseudogap.^{7,11,12} The pseudogap manifests itself as a diminishing $N(E)$ or depletion of states near E_F and was argued as one of the factors responsible for the anomalously low electrical conductivity of i -Al-Pd-Re QCs.^{3,5,6} Thus, an increase of r means that a greater number of states near E_F are depleted, which will be

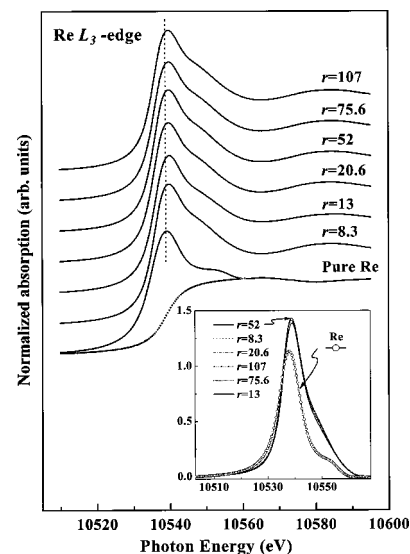


FIG. 3. Normalized Re L_3 -edge x-ray absorption spectra of i -Al₇₀Pd_{22.5}Re_{7.5} QCs and pure Re. The lower inset shows the enlarged near edge features after background subtraction.

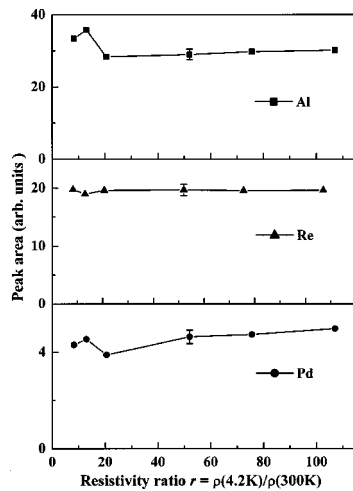


FIG. 4. Integrated intensities of the near edge features in the Al K - and Pd and Re L_{3} -edge XANES spectra as functions of r for i -Al₇₀Pd_{22.5}Re_{7.5} QCs.

accompanied by an enhancement of unoccupied states and the peak area of the near edge feature in the XANES spectrum will increase monotonically with the increase of r . Though Fig. 4 shows that the peak area of the Re $5d$ feature is nearly a constant, both the peak areas of Al $3p$ and Pd $4d$ features increase monotonically with r for an r greater than about 20.6 just like we have discussed. In the region of r between 8.3 and 20.6, the peak areas of the Al $3p$ and Pd $4d$ near edge features jump to significantly higher values, which suggests a significant change in the electronic structure near E_F . The sudden increase of the near edge XANES feature means an increase of $N(E)$ near and above E_F . For a gapless electronic structure near E_F , this property implies an increase of $N(E)$ near and below E_F . Thus, our XANES results suggest that in the region $r < 20.6$ QCs are metallic and QC has a MIT around $r = 20.6$. This finding supports the low-temperature conductivity and magnetoconductivity measurements for i -Al₇₀Pd_{22.5}Re_{7.5} QCs.^{9,19}

Figure 5 presents the valence-band PES spectra of QCs for $r = 8.3, 20.6,$ and 107 with an incident photon energy of 80 eV. The maximum intensity was normalized to unity for comparison. An interesting property of these spectra is that they rise slowly from E_F (0 eV) down to about -3 eV and then rise sharply to form the prominent feature at ~ -6 eV. The PES spectra of QCs can be divided into $(-3$ eV, $E_F)$ and $(-14, -3$ eV) two regions, which were attributed primarily to the Re $5d$ - and Pd $4d$ -derived states, respectively.^{7,11,12,20} The spectra were also pointed out to contain contributions from Al $3p$ and $3s-d$ states distributed between -14 and -3 eV.¹⁰ One can also expect significant contribution from Re $6s$ states to the PES spectrum because an isolated Re atom has a $6s^25d^5$ electron configuration.¹⁷ The feature between -3 eV and E_F is in sharp contrast to that of the pure Re metal shown in the inset (a) of Fig. 5. The section of the PES spectra of QCs between -3.5 eV and E_F has been enlarged in the inset (b) of Fig. 5, which shows a markedly lower spectral intensity of the $r = 20.6$ sample than those of the $r = 8.3$ and 107 samples. This result is consistent with the absorption spectra shown in Fig. 4, in which Al $3p$ and Pd $4d$ near edge features have the lowest intensities around $r = 20.6$. The $r = 8.3$ sample exhibits a distinctive sharp Fermi

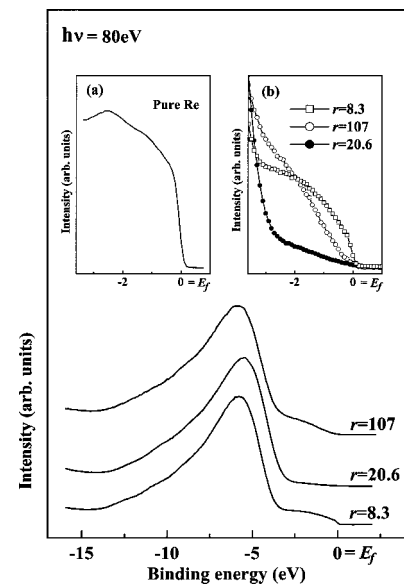


FIG. 5. Representative valence-band PES spectra of $r = 8.3, 20.6,$ and 107 QC samples for an incident photon energy of 80 eV. The insets (a) and (b) show the enlarged spectra near E_F for the reference Re metal and i -Al₇₀Pd_{22.5}Re_{7.5} QCs, respectively.

edge cutoff, which shows that this sample is metallic. In contrast, the PES spectra of the $r = 20.6$ and 107 samples decrease smoothly down to zero at E_F , which is a characteristic of an insulator. Thus, we have observed MIT in i -Al₇₀Pd_{22.5}Re_{7.5} QCs.

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- ¹D. Shechtman, I. Blech, D. Gratias, and J. W. Cahn, Phys. Rev. Lett. **53**, 1951 (1984).
- ²See, *From Quasicrystals to More Complex Systems*, edited by F. Axel, F. Dénoyer, and J. P. Gazeau (EDP Science, Les Ulis, 2000).
- ³B. D. Biggs, S. J. Poon, and N. R. Munirathnam, Phys. Rev. Lett. **65**, 2700 (1990).
- ⁴F. S. Pierce, Q. Guo, and S. J. Poon, Phys. Rev. Lett. **73**, 2220 (1994).
- ⁵P. A. Bancel and P. A. Heiney, Phys. Rev. B **33**, 7917 (1986).
- ⁶T. Fujiwara and T. Yokokawa, Phys. Rev. Lett. **66**, 333 (1991).
- ⁷Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa, S. Takeuchi, and K. H. J. Buschow, Phys. Rev. B **55**, 10938 (1997).
- ⁸Q. Guo, F. S. Pierce, and S. J. Poon, Phys. Rev. B **52**, 3286 (1995).
- ⁹C. R. Wang, H. S. Kuan, S. T. Lin, and Y. Y. Chen, J. Phys. Soc. Jpn. **67**, 2383 (1998); C. R. Wang and S. T. Lin, *ibid.* **68**, 3988 (1999).
- ¹⁰E. Berlin, Z. Dankházi, A. Sadoc, and J. M. Dubois, J. Phys.: Condens. Matter **6**, 8771 (1994).
- ¹¹Z. M. Stadnik, D. Purdie, M. Garnier, Y. Baer, A.-P. Tsai, A. Inoue, K. Edagawa, and S. Takeuchi, Phys. Rev. Lett. **77**, 1777 (1996).
- ¹²T. Schaub, J. Delahaye, C. Berger, H. Guyot, R. Belkhou, A. Taleb-Ibrahim, and Y. Calvayrac, Eur. Phys. J. B **20**, 183 (2001).
- ¹³C. R. Lin, S. T. Lin, C. R. Wang, S. L. Chou, H. E. Horng, J. M. Cheng, Y. D. Yao, and S. C. Lai, J. Phys.: Condens. Matter **9**, 1509 (1997).
- ¹⁴M. Springborg and R. Fischer, J. Phys.: Condens. Matter **10**, 701 (1998).
- ¹⁵M. Weinert and R. E. Watson, Phys. Rev. B **58**, 9732 (1998).
- ¹⁶E. Tamura, J. van Ek, M. Fröba, and J. Wong, Phys. Rev. Lett. **74**, 4899 (1995).
- ¹⁷*Table of Periodic Properties of the Elements* (Sargent-Welch Scientific Company, Skokie, IL, 1980).
- ¹⁸M. Zurkirch, A. Atrei, M. Hochstrasser, M. Erbudak, and A. R. Kortan, J. Electron Spectrosc. Relat. Phenom. **77**, 233 (1996).
- ¹⁹J. Delahaye and C. Berger, Phys. Rev. B **64**, 94203 (2001).
- ²⁰D. Naumović, P. Aebi, L. Schlapbach, C. Beeli, T. A. Lograsso, and D. W. Delaney, Phys. Rev. B **60**, R16330 (1999).