Experimental Evidence for the *p*-*d* Hybridization in the Cd-Ca Quasicrystal: Origin of the Pseudogap

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Ca $2p$-$3d$ resonant photoemission spectroscopy of a Cd_6Ca crystalline approximant unambiguously demonstrates that the low-lying unoccupied $3d$ levels of calcium are lowered below the Fermi energy by the formation of the approximant, as suggested from electronic structure calculations [Y. Ishii and T. Fujiwara, Phys. Rev. Lett. **87**, 206408 (2001)]. Moreover, the Ca $3d$ partial density of states (DOS) obtained near the Fermi energy is in reasonable agreement with theoretical Ca $3d$ DOS. These results verify the unconventional picture that the origin of the pseudogap in the Cd-based quasicrystals is due to *hybridization* of the Ca $3d$ band with the Cd $5p$ band.

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It has been widely believed that the pseudogap in the density of states (DOS) of quasicrystals (QC) is a consequence of the Hume-Rothery mechanism, where the Fermi-sphere–quasi-Brillouin zone interaction of s, p states energetically pushes down the electronic states near the Fermi level (E_F), resulting in a depression of DOS at E_F, i.e., a pseudogap [1,2]. This Hume-Rothery picture has been further exploited by Sato *et al.* [3], based on a band structure calculation using an experimentally derived structure of the Al-Mg-Zn approximant, where the pseudogap is understood as a result of the lifting of degenerate states at high symmetry points of the Brillouin zone.

On the other hand, Ishii and Fujiwara have recently invoked a different picture that the element of low-lying unoccupied d states is essential for the pseudogap formation in the case of Cd-based approximants, hence, of the Cd-based QC [4]. They have predicted that unoccupied d states in atomic Ca and Yb are lowered by alloy formation, as a consequence of hybridization with Cd $5p$ states. This p-d hybridization produces bonding orbitals just below E_F, resulting in a shallow pseudogap above E_F. According to their calculations, E_F is not located at the bottom of the pseudogap, but is pinned at the shoulder of the occupied band, and the electron occupation of the bonding states mainly accounts for the cohesion of the Cd-based compounds. Such an important role played by d states was also suggested for Al-based compounds by Trambly de Laissardière *et al.* [5], who have shown, based on calculations, that both the Hume-Rothery mechanism and the sp-d hybridization work simultaneously to form a pseudogap in Al-based Hume-Rothery alloys containing transition elements.

The binary Cd-Ca and Cd-Yb QC [6,7] are of a particular interest for a spectroscopic study since they are composed of only two elements, simplifying the interpretation of experimental spectra. Among the two, the Cd-Ca system is more advantageous for the purpose of studying the sp-d hybridization since the valence band spectrum is predominantly made of strong $4f$ derived peaks in the case of the Cd-Yb system [8], obscuring a subtle contribution of d states that might exist. In this Letter, the electronic structure of Cd_6Ca [9] is investigated in detail using high-resolution ultraviolet photoemission spectroscopy (UPS) and Ca $2p$-$3d$ resonant photoemission spectroscopy (RPES) at low temperatures in order to probe the theoretically predicted p-d hybridization in the close vicinity of E_F. We also present Ca $3d$-partial DOS in terms of an on-resonance minus off-resonance spectrum. Direct comparisons of the experimental DOS with theoretical DOS including Ca $3d$-partial DOS and Cd $5p$-local DOS are made at near-E_F region, providing experimental evidence for the p-d hybridization in the Cd_6Ca approximant.

Flakes of the high purity elements of Cd (99.9999%) and Ca (99.99%) with the compositions of Cd_6Ca and $Cd_{5.7}Ca$ were wrapped tightly inside molybdenum foil and sealed in a quartz tube under argon atmosphere. The elements were heated to 973 K to react with each other, then annealed at 773 K for 50 h, and quenched into chilly water to obtain a homogeneous, equilibrium phase. The characterization of the samples was performed by powder x-ray diffraction measurements with Cu $K\alpha$ radiation. He I UPS measurements with 20 meV energy resolution were performed for both the Cd_6Ca approximant and the $Cd_{5.7}Ca$ QC in the Institute for Solid State Physics, the University of Tokyo. X-ray absorption spectroscopy (XAS) and RPES measurements with 80 meV energy resolution were performed for Cd_6Ca using incident photon energies of $h\nu = 345$–352 eV near the Ca $L_{2,3}$ edge at the beamline BL25SU in SPring-8, Hyogo, Japan. In both measurements, GAMMADATA-SICENTA SES2002 hemispherical analyzer was utilized and clean surfaces were obtained by cleaving samples under ultrahigh vacuum with base pressures better than 10^{-11} and 10^{-10} Torr, respectively.

Figure 1 presents near-E_F PE spectra of Cd_6Ca at photon energies of 21.2 and 350 eV measured at 5.7 and 20 K, respectively, and the inset shows near-E_F PE spectra of both the Cd_6Ca approximant and the $Cd_{5.7}Ca$ QC at 5.7 K for comparison. Two narrow peaks were observed in Cd_6Ca at 11.3 and 10.4 eV (not shown), and they are assigned as Cd $4d_{3/2}$ and $4d_{5/2}$-derived states, respectively, since the binding energies as well as their splitting energy agree well with those of Cd $4d_{3/2}$ (11.7 eV) and Cd $4d_{5/2}$ (10.7 eV) of the Cd metal. These fully occupied Cd $4d$ states apparently do not contribute to cohesion. On the other hand, as seen in the near-E_F PE spectra of Fig. 1, a peak structure with a width of about 1 eV is observed just below E_F, and E_F is located, i.e.,"pinned," at the shoulder of the peak, not at the minimum of the DOS, in agreement with the theoretical calculations [4]. Thus, the result suggests that E_F is situated at the edge of the pseudogap. Here, we note that the extremely sharp Fermi cutoff is clearly separated from the structure near E_F owing to the high resolutions and the low temperatures of the measurements. A similar peak structure is also observed in the near-E_F PE spectrum of the $Cd_{5.7}Ca$ QC, and we have found that the positions of the peak maxima are exactly the same for the two compounds, i.e., 0.36 ± 0.01 eV, indicating that they are because of the same origin, i.e., the common local structure. From the figure, we also notice that the peak structure is more pronounced in the QC than in the approximant, and this point is addressed later in this Letter. Another significant feature here is that the structure near E_F is greatly enhanced at the photon energy of 21.2 eV compared with that at 350 eV. This is understood from the difference in the photoionization cross section among Cd $5s$, $5p$, and Ca $3d$ states: Taking into consideration that the contributions from Cd $5p$ and Ca $3d$ states are mostly enhanced when reducing the photon energy from 350 to 21.2 eV, the enhancement is taken as evidence that the structure is composed of the Cd $5p$ and/or Ca $3d$ states. This suggests that the observed feature is due to hybridization between Cd $5p$ and Ca $3d$ states.

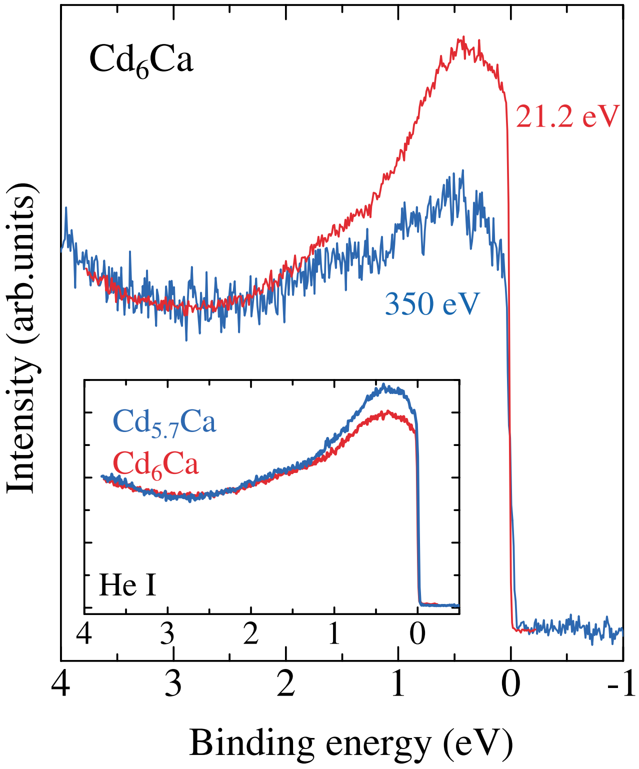

FIG. 1 (color). Near-E_F PE spectra of Cd_6Ca at different photon energies of 21.2 (red) and 350 eV (blue) measured at 5.7 and 20 K, respectively. The inset shows He I PE spectra of the Cd_6Ca approximant (red) and the $Cd_{5.7}Ca$ QC (blue) measured at 5.7 K.

Figure 2(a) shows XAS spectrum of Cd_6Ca in the vicinity of Ca $L_{2,3}$ absorption edge. The XAS spectrum displays the local unoccupied Ca $4s$ and $3d$ states due to the dipole selection rules of the x-ray absorption process. It is composed of two peaks at photon energies 348.2 and 351.6 eV with an additional weak structure at the onset. The peaks are mainly ascribed to $2p^6 3d^0 \rightarrow 2p^5 3d^1$ transitions and their splitting energy (3.4 eV) coincides well with the spin-orbit splitting (3.5 eV) of the Ca $2p$ core level. Here, the weak structure at about 346 eV is attributed to the L_3 ($2p_{3/2} \rightarrow E_F$) edge since the energy corresponds well to the L_3 edge (346.2 eV) of Ca metal. Figure 2(b) shows RPES spectra of Cd_6Ca at photon energies ranging from 345 to 352 eV. Here, features marked by a solid triangle are observed at constant kinetic energy, i.e., around 345.5 eV, and can be assigned as Ca $L_3M_{4,5}M_{4,5}$ Auger. The spectra at 348 and 352 eV correspond to on-resonance [see Fig. 2(a)]. It is clearly seen that the RPES intensity is appreciably enhanced in the close vicinity of E_F for the on-resonant spectra. This means that Ca $3d$ states *do* exist at E_F, in agreement with the theoretical calculations [4].

In order to more clearly see the Ca $3d$ contribution to the valence band of Cd_6Ca, the off-resonant spectrum at 346 eV was subtracted from the on-resonant spectrum at 352 eV as shown in Fig. 3(a), which gives Ca $3d$ partial DOS. We note that the photoionization cross sections of the Cd $5s$, $5p$, and Ca $3d$ states should show a smooth variation with the incident photon energy at around 350 eV, which justifies subtraction of two spectra at different photon energies within only several eV. As a result, we have found that there exists an appreciable contribution of d states near E_F, especially in the close vicinity of E_F. This experimental d DOS clearly demonstrates that the Ca $3d$ states, which are unoccupied in Ca metal, are lowered below E_F by formation of the crystalline approximant. In Fig. 3(b) is presented theoretical d DOS of Cd_6Ca calculated with the tight-binding linear muffin-tin orbitals (LMTO) method in the atomic sphere

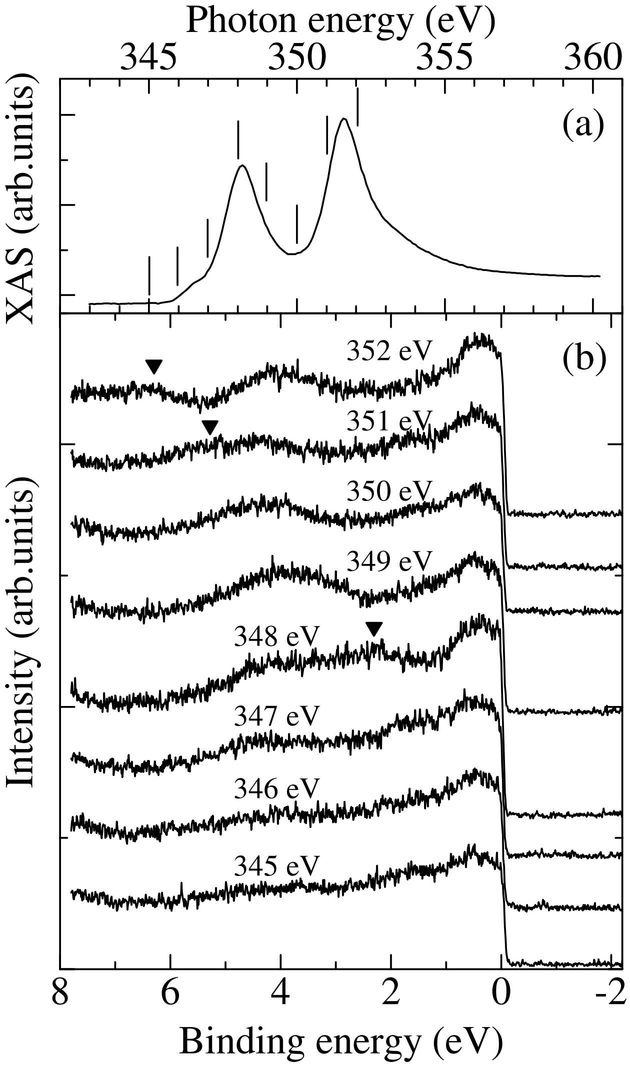

FIG. 2. (a) XAS spectrum of Cd_6Ca in the vicinity of Ca $L_{2,3}$ absorption edge. Vertical bars correspond to the photon energies at which photoemission measurements were performed. (b) Resonant photoemission spectra of Cd_6Ca with incident photon energies $h\nu = 345$–352 eV at 20 K. The spectra at 348 and 352 eV correspond to on-resonance. Features denoted by a solid triangle appear at constant kinetic energy and are assigned as Ca $L_3M_{4,5}M_{4,5}$ Auger.

approximation (ASA) [4] for comparison. It is found that the experimental d DOS shows reasonable agreement with the theoretical d-DOS, in particular, in the close vicinity of E_F where both the d DOS steeply increase as E_F is approached. The agreement between the experimental and the theoretical d DOS indicates that the existence of the Ca $3d$ states near E_F is a consequence of the p-d hybridization predicted by the theoretical calculations.

A close examination of the crystal structure of Cd_6Ca [9] reveals three types of Cd neighbors around the Ca site (S3 site), which belongs to the third shell of the 66-atom icosahedral cluster; one belongs to the second shell (S2 site), i.e., Cd_{20} dodecahedron, another belongs to the fourth shell (S4 site), i.e., Cd_{30} icosidodecahedron, and the other is so-called glue Cd atoms (S5 site) [6]. In order to obtain insight into which Cd atoms of the three types are responsible for the observed p-d hybridization, comparison of an experimental PE spectrum with theoretical local p DOS at the S2, S4, and S5 sites [10] are made as shown in Fig. 4. Here, the He I PE spectrum is compared since it is most predominantly composed of the Cd $5p$ and Ca $3d$ states compared with the other spectra following the discussion of Fig. 1. From the figure it is obvious that the local p DOS at the S2, S4, and S5 sites all exhibit a similar peak structure in the close vicinity of E_F, i.e., within 1 eV below E_F. This means that the Cd $5p$ states at all these sites contribute to the peak structure near E_F of the total DOS, suggesting that they are hybridized with Ca $3d$ states. By examining the crystal structure of Cd_6Ca it is found that the Cd atoms at the S2 and S4 sites bind Ca atoms up into a Ca_{12} icosahedron giving rise to the stability of the cluster and, on the other hand, the glue Cd atoms at the S5 site connect a Ca_{12} icosahedron with its neighbors along [111] and [100] directions stabilizing the cluster packing in the approximant structure. Henceforth, we are reasonably led to conjecture that the

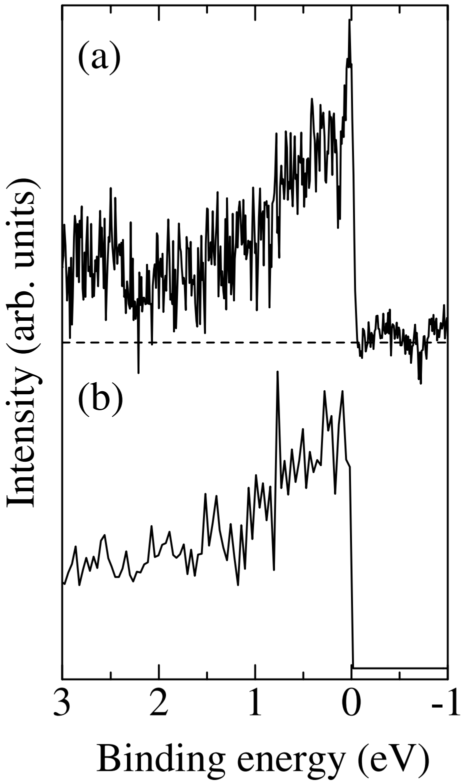

FIG. 3. (a) On-resonance minus off-resonance spectrum of Cd_6Ca. The off-resonant spectrum at 346 eV was subtracted from the on-resonant spectrum at 352 eV (see Fig. 2). (b) Theoretical Ca $3d$ DOS of Cd_6Ca calculated with the LMTO-ASA method [4]. In the theoretical $3d$ DOS, the DOS above E_F has been cut off in order to set the condition the same as the experiment.

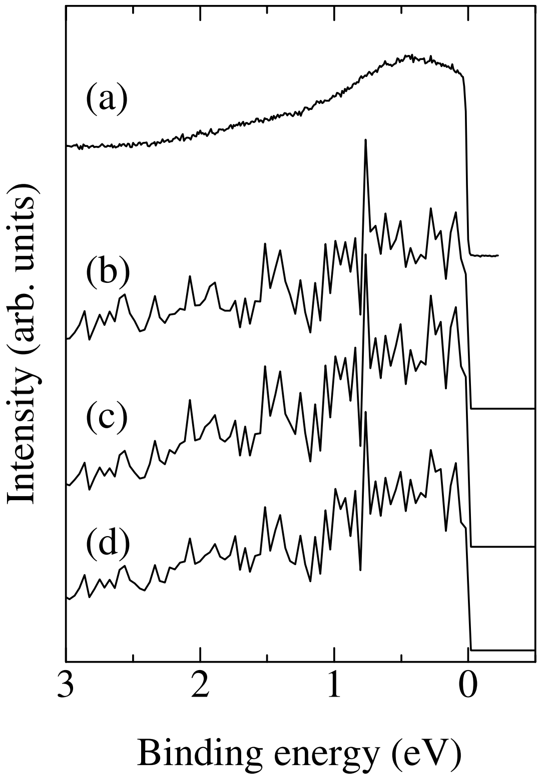

FIG. 4. Comparisons of (a) the experimental He I PE spectrum with theoretical local p DOS at (b) S2, (c) S4, and (d) S5 sites calculated with the LMTO-ASA method [10]. In the theoretical local p-DOS, the DOS above E_F is cut off in order to set the condition the same as the experiment.

observed structure in the near-E_F PE spectrum is a consequence of the enhanced chemical bonding both inside and outside the Ca_{12} cluster, giving rise to the stability of the cluster by itself and cluster packing as well. Finally, we speculate that the same mechanism also works in the case of $Cd_{5.7}Ca$ QC since the same feature is observed in the near-E_F PE spectrum and, in addition, the local atomic structure would be similar for the two compounds. More importantly, similar partial d DOS has been observed for the $Cd_{5.7}Ca$ QC, indicating that the d states do exist below E_F also for the QC [11]. Since the pseudogap is formed by the p-d hybridization between Cd and Ca atoms, the density of Cd-Ca pairs seems to play a crucial role in the relative stability of the QC and the approximant. In this respect, the higher Ca concentration of the $Cd_{5.7}Ca$ QC implies higher density of Cd-Ca pairs and, hence, the stability due to the p-d hybridization should be more remarkable for the QC than for the approximant. This may be the origin of the stability of the binary QC relative to the approximant. It might be of interest to note that the peak structure of the QC is more enhanced than that of the approximant, which is consistent with this scenario.

In conclusion, this Letter reports experimental evidence that the hybridized Ca $3d$ states do exist below the Fermi energy, indicating that the unoccupied $3d$ levels of calcium are lowered below the Fermi energy as a consequence of formation of the crystalline approximant Cd_6Ca. In addition, the obtained partial d DOS shows reasonable agreement with the theoretical d DOS. These results verify the unconventional picture that the origin of the pseudogap in the Cd-based QC is because of hybridization between the d and p states.

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