Comparative study of the binary icosahedral quasicrystal $Cd_{5.7}Yb$ and its crystalline approximant Cd_6Yb by low-temperature ultrahigh-resolution photoemission spectroscopy

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Low-temperature ultrahigh-resolution photoemission (PE) spectroscopy of the recently discovered binary icosahedral (*i*) $Cd_{5.7}Yb$ and its 1/1-cubic approximant Cd_6Yb has commonly revealed a sharp Fermi edge with a marked spectral intensity decrease towards the Fermi level (E_F), indicating the presence of a dip near E_F which is consistent with the recent result of electronic structure calculations [Y. Ishii and T. Fujiwara, Phys. Rev. Lett. **87**, 206408 (2001)], and the dip at E_F is found to be much deeper in *i*-$Cd_{5.7}Yb$ than in 1/1-Cd_6Yb. Moreover, surface core-level shifts (SCS's) are clearly observed in the quasicrystal and the approximant, and the SCS's are found to be substantially different between these two compounds of different long-range orders.

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I. INTRODUCTION

The existence of a pseudogap at the Fermi level (E_F)[1–3] and the spiky density of states (DOS) of a typical energy scale of 10-50 meV[1,4] were predicted for icosahedral (*i*) quasicrystals by electronic structure calculations on their crystalline analogs, the so-called approximants. In order to verify these features unambiguously, photoemission (PE) spectroscopy studies have been performed in a number of ternary stable *i* phases.[5] Among these a PE spectroscopy experiment with ultrahigh energy resolutions as low as 5 meV at low temperatures down to 12 K, performed by Stadnik and co-workers,[6,7] clearly showed a sharp Fermi cutoff and a marked intensity decrease toward E_F, the latter of which is consistent with the existence of the predicted pseudogap near E_F. However, no indication of the predicted spiky structure was obtained with such a high resolution. A recent PE study on single-grain *i*-AlPdMn also revealed no sign of the spiky features in the DOS, indicating that the absence is not a consequence of the existence of different crystallographic orientations at the surfaces of the polyquasicrystalline alloys.[8] The reason for the absence of the fine structures was mainly attributed to two possible cases[6]: (i) the presence of topological or chemical disorder which is unavoidable even in the samples of highest perfection, and (ii) the possibility that the predicted spiky feature is an artifact of the calculations. In this view, the recent results of Zijlstra and Janssen[9] support the latter case, which showed that in the case of the three-dimensional Penrose tiling model the fine structure seen in the low-order approximants cannot survive in the quasicrystalline limit. However, no decisive conclusion has been drawn for the existence of the spikes in the DOS of the real quasicrystals.

The recently discovered stable binary $Cd_{5.7}Yb$ quasicrystal[10,11] is of particular interest from the view of PE spectroscopy: First, there exists a cubic crystalline approximant[12,13] in the vicinity of the composition of the *i* phase, thus enabling us to investigate the influence of quasiperiodicity on the electronic structure, since it is believed that the difference between the two phases exists only in the long-range order. Second, it is a binary stoichiometric compound whose single-phase region is considerably narrow compared with the ternary quasicrystals, and thus is expected to contain much less chemical disorder. This is also suggested from the structural analysis on its approximant Cd_6Yb, showing that there are no sites occupied statistically by Cd and Yb atoms,[13] which is in striking contrast with the case of the ternary approximants such as α-AlMnSi (Ref. 14) and $Mg_{32}(Al,Zn)_{49}$,[15] where some sites are considered to be chemically disordered. Third, since it contains a rare-earth element whose $4f$ states lie close to E_F,[16] and such well localized $4f$ states are likely to produce sharp final-state multiplet structures in the PE spectrum, we expect that a surface-sensitive PE technique allows us to investigate changes of the electronic structure in the surface region of the solid with high resolution.

In this paper we show a PE study of the binary icosahedral quasicrystal $Cd_{5.7}Yb$ and its cubic approximant Cd_6Yb, together with direct experimental evidence of the surface states in the quasicrystal as well as in the approximant. A comparison will be made in detail between the two compounds of different long-range orders, and the result for the quasicrystal will be also discussed in view of the predicted spikiness in the DOS.

II. EXPERIMENT

Pure elements of Cd($6N$) and Yb($3N$) with nominal compositions $Cd_{5.7}Yb$ and Cd_6Yb were melted in a molybdenum foil sealed in a quartz tube under argon atmosphere. The ingots were subsequently annealed at 673 K for 24 h to obtain a homogeneous, equilibrium phase. The samples were confirmed to be a single phase of the icosahedral quasicrystal or the cubic approximant by x-ray-diffraction spectroscopy with Cu $K\alpha$ radiation. PE measurements were performed on a spectrometer built using a Scienta SES2002 electron analyzer, a monochromatic He I source(GAMMADATA), and a thermally shielded sample holder with a flowing liquid He cryostat. The highest energy resolution (including analyzer and light) of the instrument is 1.4 meV, and the resolution was intentionally set to 20 or 7 meV for the present study in

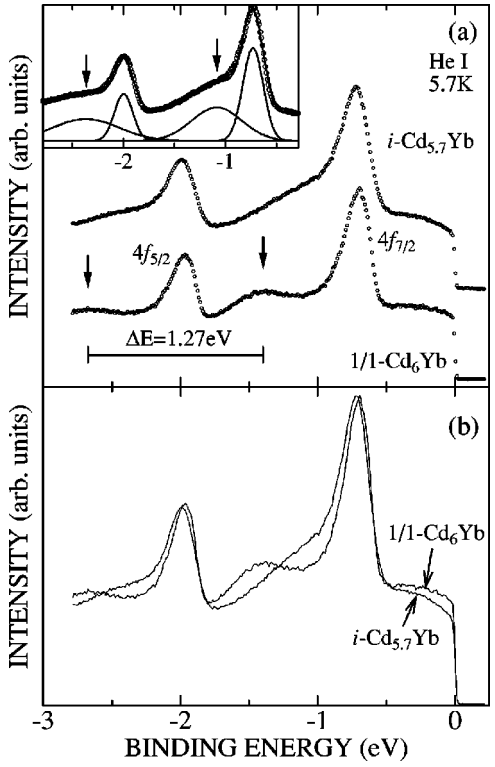

FIG. 1. (a) Low-temperature He-I PE spectra of i-$Cd_{5.7}Yb$ and 1/1-Cd_6Yb with an energy resolution of 20 meV. The inset shows the deconvolution of the i-$Cd_{5.7}Yb$ spectrum as described in the text. (b) The same spectra superimposed on one another for a better comparison.

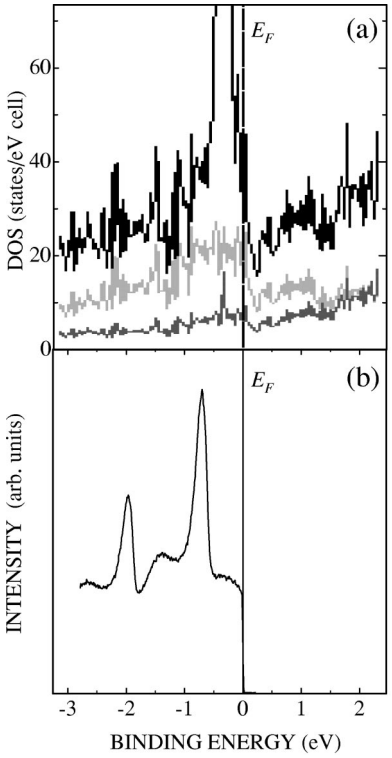

FIG. 2. Comparison between (a) the theoretical DOS from Ref. 16 and (b) the present He-I PE spectra for Cd_6Yb. In (a), the black, light gray, and dark gray curves represent the total and partial (Cd $5p$ and Yb $5d$) DOS's respectively.

order to obtain reasonable count rates. Samples were mounted on the thermally shielded sample holder, and the sample temperature was measured using a calibrated silicon diode sensor to an accuracy of ± 0.5 K. The base pressure of the spectrometer was better than 5×10^{-11} Torr. Clean surfaces were obtained by fracturing the samples *in situ*. The measurements were performed in a couple of minutes after fracturing and oxidization of the surfaces was monitored by the time evolution of spectra. The intrinsic surface signals were found to disappear in an hour or two after fracturing due to oxidization of the surfaces. By measuring two samples for each compound, we confirmed that all the results shown in this paper are reproducible and hence we conclude that the observed spectra represent intrinsic electronic structures. E_F of the samples was referenced to that of a gold film evaporated onto the sample substrate, and its accuracy is estimated to be better than ± 0.05 meV.

III. RESULTS AND DISCUSSION

Figure 1(a) presents low-temperature PE spectra for i-$Cd_{5.7}Yb$ and 1/1-Cd_6Yb measured at 5.7 K, and in Fig. 1(b) we show the same spectra superimposed on one another in order to clarify the difference between the two compounds. First of all, a common feature is observed in both spectra of i-$Cd_{5.7}Yb$ and 1/1-Cd_6Yb: Two distinct peaks appear around binding energies of -0.7 and -2.0 eV. Comparing with the theoretical DOS,[16] as shown in Fig. 2, where a narrow peak due to the Yb $4f$ states lie just below E_F, the observed peaks can be readily assigned to the Yb $4f$ states. This is further confirmed by the fact that the estimated energy separation of 1.27 eV between the peaks corresponds exactly to the atomic spin-orbit energy 1.27 eV, and hence we conclude that the peaks are due to the $4f_{7/2}$- and $4f_{5/2}$-derived states as appropriate. In Fig. 1(b), we note that the peak positions of the Yb $4f$ doublet are deeper for the i phase than for the approximant, by about 25 ± 5 meV. This implies that the electronic system around Yb atoms is more stable in the i phase than in the approximant. Also, as clearly seen from Fig. 2, some difference in the Yb $4f$ peak positions is noticed between the theoretical DOS and the PE spectrum; the $4f$ states of the theoretical DOS lie at somewhat lower binding energies compared with the observation. The reason for such a difference is most probably attributed to the atomic sphere approximation employed in the calculation.

A striking feature in the PE spectra in Fig. 1 is the existence of two humps on the higher binding-energy side of the corresponding $4f$ peaks, as clearly seen at around binding energies at -1.4 and -2.7 eV for the approximant, while they are mixed with the doublet of the $4f$ states for the quasicrystal. The locations of the humps for 1/1-Cd_6Yb were determined to be -1.40 ± 0.01 and -2.68 ± 0.01 eV from the positions of the intensity maxima of the humps. In the case of i-$Cd_{5.7}Yb$, since the humps are not separated from the bulk $4f$ peaks, a deconvolution of the spectrum by using

Gaussian functions and assuming a linear background has been performed in order to determine their locations. The result of the least-squares fit is shown in the inset of Fig. 1(a) and the locations of the humps were determined to be -1.08 ± 0.05 and -2.37 ± 0.05 eV. In rare-earth-metal compounds, such extra humps in the vicinity of well-localized states such as the $4f$ states are well known for core-level shifts at the surface. [the so-called surface core-level shift, (SCS)],[17,18] which reflect changes of the electronic structure in the surface region. The energy separation of the humps is about 1.3 eV for both compounds, and agrees well with the $4f$ splitting energy of the bulk states, confirming that they are due to the $4f$-derived states. We note that the presence of the surface peaks in turn verifies that the two main features in the PE spectra are *indeed* the bulk $4f$ spin-orbit doublet. The lowering of the binding energy at the surface indicates that the binding energies of surface atoms are higher than those of bulk atoms. The surface components are shifted to higher binding energies by 0.68 ± 0.01 eV for 1/1-Cd_6Yb and by 0.36 ± 0.05 eV for i-$Cd_{5.7}Yb$. Interestingly, the SCS's of 1/1-Cd_6Yb fall in the range of those reported in a number of Yb compounds including a Yb metal,[17] while they are considerably smaller for i-$Cd_{5.7}Yb$. The small SCS's in the quasicrystal mean that the local environment around the Yb atoms at the surface is quite similar to that in the bulk. Taking into account that all the Yb atoms participate in 12 Yb icosahedral clusters in 1/1-Cd_6Yb, and that this also seems to be the case for i-$Cd_{5.7}Yb$, the result may be taken as an indication that for i-$Cd_{5.7}Yb$ the icosahedral clusters composed of 12 Yb atoms persist even at the surface. Such a conjecture for the *i* phase is consistent with the result of scanning tunneling microscopy observations where the fractured surfaces of the single-grain *i*-AlPdMn are not atomically flat but made up of clusters 8-10 Å in diameter.[19] In addition, the surface peaks are substantially broader than the bulk peaks in both phases, possibly due to contributions from more than one surface layer and to surfaces of different crystallographic orientations. The present paper reports an observation of the SCS's in the quasicrystal as well as in the approximant. The existence of the SCS's themselves unambiguously verifies that as in many Yb compounds the electronic structure at the surface is also different from that in the bulk in the case of the quasicrystal and the approximant. Although there have been a number of indications which could be interpreted as evidence that the electronic structure at the surface differs from that of the bulk in quasicrystals,[20,21] to our knowledge the present experiment is the first *direct* observation of the surface states in the quasicrystal and the approximant. Furthermore, from the results we conjecture that the surface sensitive measurement such as the tunneling spectroscopy, which probes the surface DOS only, cannot draw a decisive conclusion on the bulk electronic states of the quasicrystals.

Next we focus on the structure in the vicinity of E_F in the PE spectra. As seen from Fig. 1(a), a decrease of the spectral intensity towards E_F which is well distinguished from the Fermi cutoff is observed for both phases, and this trend becomes enhanced near E_F. Moreover, the intensity depression at E_F is found to be considerably stronger for the *i* phase

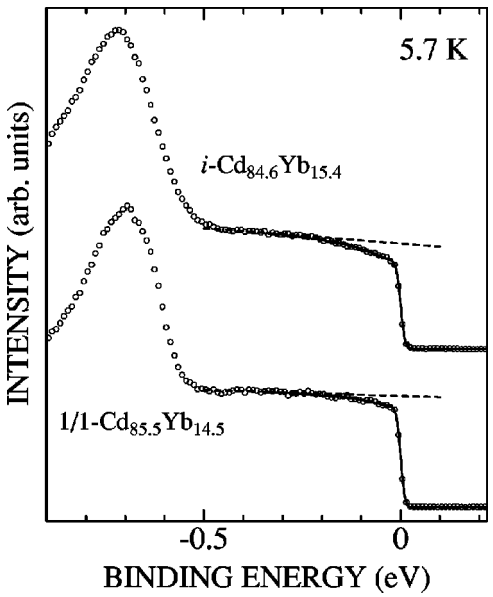

FIG. 3. He-I PE spectra of i-$Cd_{5.7}Yb$ and 1/1-Cd_6Yb in the vicinity of E_F, enlarged from Fig. 1. The broken lines and the solid curves represent the normal DOS extrapolated from the BE range between -0.45 and -0.25 eV and the fits to the model as described in the text, respectively.

than for the approximant [Fig. 1(b)], which clearly shows that the dip at E_F is deeper in the quasicrystal than in the cubic approximant. The stronger intensity decrease near E_F, i.e., less occupied states in the vicinity of E_F in i-$Cd_{5.7}Yb$, directly indicates a larger energy gain due to the dip formation in the *i* phase than in the approximant. In order to estimate the DOS depression at E_F quantitatively, a simple phenomenological model, proposed by Mori *et al.*[22] and adopted in a number of papers,[5] is also used to fit the present data, which approximately describe the depression of the DOS at E_F by a Lorentzian function centered around E_F, i.e., $[1-C\Gamma^2/\{(E-E_F)^2+\Gamma^2\}]$, multiplied by the Fermi-Dirac function at 5.7 K and convoluted with a Gaussian describing the instrumental broadening of the FWHM of 20 meV. Although the position of E_F is not expected to coincide with the minimum of the dip,[16] it suffices for a comparison of the

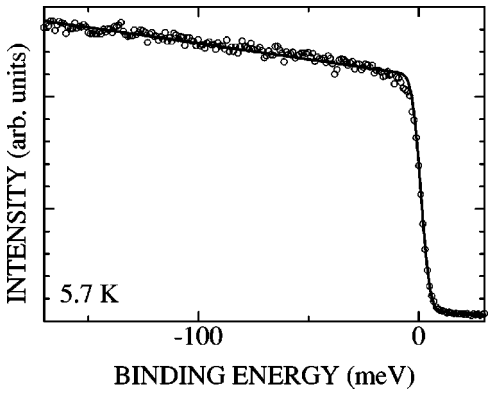

FIG. 4. Low-temperature He-I PE spectrum of i-$Cd_{5.7}Yb$, with an energy resolution of 7.2 meV.

dip depth between the two compounds. Here the energy range for the linear extrapolation describing the DOS without the dip was set the same for both phases at binding-energies (BE's) between -0.45 and -0.25 eV. In the formula, C and Γ denote the depth and width of the dip, respectively. The results of the fitting are shown in Fig. 3. The values obtained from the fits are $C=18.8\%$ and $\Gamma=96$ meV for i-$Cd_{5.7}Yb$, and $C=11.1\%$ and $\Gamma=94$ meV for 1/1-Cd_6Yb. Thus the depression of the DOS at E_F is estimated to be deeper in the quasicrystal by a factor of 1.7. A similar trend was reported in several ternary systems,[23,24] and interpreted to be due to the Hume-Rothery mechanism, i.e., almost spherical contacts of the Fermi surface with the Jones zone of the quasicrystals.[25] However, concerning the stability of the *i* phase, we should recall that the existence of the pseudogap in 1/1-Cd_6Yb is not due to the Hume-Rothery mechanism but to the hybridization of the Cd $5p$ and Yb $5d$ states.[16] Therefore, we reasonably speculate that the pronounced dip at E_F in the quasicrystal is also due to the same mechanism with a stronger p-d hybridization effect, possibly enhanced by its quasiperiodic order.

Figure 4 presents the PE spectrum of i-$Cd_{5.7}Yb$ with an energy resolution of 7.2 meV at the low temperature of 5.7 K in the vicinity of E_F, where the lifetime broadening effect is negligible.[5] The solid line in Fig. 4 represents a fit to a linearly decreasing intensity multiplied by the Fermi-Dirac function at 5.7 K and convoluted with a Gaussian with a FWHM of 7.2 meV. First of all, a marked intensity decrease toward E_F is clearly seen, which is well distinguished from the Fermi cutoff owing to the ultrahigh resolution and the low temperature of the measurement. The sharp Fermi cutoff suggests that i-$Cd_{5.7}Yb$ is basically a metal at the low temperature despite the observed unusual electronic properties.[26] Second, the observed spectrum is smooth and varies monotonically against the binding energy with the present experimental resolution of 7.2 meV. Hence we cannot extract any appreciable sign of spiky feature in the DOS for the binary *i* phase, although it is expected to contain less chemical disorder as described in the text.

IV. CONCLUSIONS

A comparative study of the recently discovered binary icosahedral $Cd_{5.7}Yb$ and its cubic approximant Cd_6Yb has been performed using ultrahigh-resolution photoemission spectroscopy at the low temperature of 5.7 K. The PE spectra of both compounds revealed a sharp Fermi edge and a marked spectral intensity decrease toward E_F, the latter of which indicates the presence of a pronounced dip near E_F, in agreement with the theoretical DOS of 1/1-Cd_6Yb. The depression of the DOS at E_F is substantially deeper in i-$Cd_{5.7}Yb$ than in its approximant Cd_6Yb, by a factor of 1.7 according to the simple model, giving rise to the stability of the *i* phase relative to the approximant. In addition, no indication of a spiky structure was obtained for i-$Cd_{5.7}Yb$, which is a stoichiometric compound with considerably less chemical disorder. Finally, surface core-level shifts due to differences in the electronic states at the surface are clearly seen in the quasicrystal and the approximant, and the shifts are found to be substantially different between the two compounds. The result may imply that the surface sensitive measurement such as the tunneling spectroscopy cannot draw a decisive conclusion on the bulk electronic states of the quasicrystals.

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