

## Narrow Photoemission Peak at the Fermi Level in Fe/Cu(111)

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We have studied electronic states of Fe adatoms deposited on Cu(111) by photoemission spectroscopy and have found a narrow peak at the Fermi level in the Fe 3*d* spectral function. The Fe 3*d* spectral function would be consistent with the Anderson impurity model, which has been widely used for the interpretation of bulk Ce and Yb compounds. This result indicates a strong reduction of hybridization between the Fe 3*d* state and the conduction-band states and an enhancement of effective Coulomb interaction for the Fe 3*d* electrons in an Fe adatom on Cu(111).

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Photoemission spectroscopy (PES) of correlated electron systems including Mott insulators, heavy fermions, and high-temperature superconductors has revealed a variety of sharp spectroscopic structures near the Fermi level ( $E_F$ ), which correspond to their anomalous transport and thermodynamic properties. Among these photoemission features, a very narrow peak at  $E_F$  observed in some Ce and Yb compounds is one of the most intriguing structures revealed by high-energy-resolution PES [1]. The narrow peak at  $E_F$  is consistent with the Anderson impurity model (AIM) [2], which contains the conduction-band states and the single-impurity 4*f* state with energy  $\epsilon_0$  and on-site Coulomb interaction  $U$ . According to AIM, in addition to the atomiclike excitation peaks at  $\sim\epsilon_0$  ( $\ll E_F$ ) and at  $\sim\epsilon_0 + U$  ( $\gg E_F$ ), a sharp Kondo resonance peak may appear at  $E_F$  in the 4*f* spectral function due to weak hybridization ( $<U$ ) between the 4*f* state and the continuum with Fermi cutoff even if the bare 4*f* level  $\epsilon_0$  is fairly far below  $E_F$  [3].

Recently, several groups have performed a scanning tunneling spectroscopy (STS) study for magnetic adatoms deposited on noble-metal surfaces [4–8] and have found a narrow dip, which is asymmetric with respect to  $E_F$ . The observed dip in the STS spectra shows modulation of the tunneling current to the conduction-band states induced by the magnetic adatom. The dip structure has been well reproduced based on AIM with the magnetic adatom treated as the Anderson impurity whose 3*d* or 4*f* electrons nearly maintain their atomic character. The STS spectrum of Co/Au(111) [5] has been further analyzed by Schiller and Hershfield [9] and Újsághy *et al.* [10] with AIM. In addition to reproducing the dip structure observed by STS, they calculated the Co 3*d* spectral function of Co/Au(111) and found a very sharp Kondo resonance peak at  $E_F$ . In a correlated electron system, its spectral function deviates remarkably from the ground-state density of states (DOS). In the case of Co/Au(111), the Co 3*d* spectral peak at  $E_F$  is narrower than the ground-state 3*d* DOS calculated with the local spin density approximation (LSDA) [10,11] by 2 orders of magnitude. This situation indicates that for the 3*d* transition-metal adatom (i) hybridization between the adatom and the host metal is much reduced and (ii) the

effective 3*d* Coulomb interaction is enhanced due to poorer screening in comparison with those in the embedded impurity system. Consequently, the 3*d* spectral function of the transition-metal adatom might be similar to the 4*f* spectral function of *bulk* Ce or Yb compounds, which have been widely studied experimentally and theoretically. Therefore, it is quite challenging to observe directly such an unusual 3*d* spectral function of adatom systems by PES with an ultraviolet (UV) excitation photon, where its photoionization cross section for the 3*d* orbital is relatively large [12]. To this end, we have made a PES study of a dilute Fe adsorbate deposited on a Cu(111) surface. In the low coverage limit, the result should be representative of the electronic properties of single Fe atoms adsorbed on the surface. We have used a Cu(111) substrate since it does not show any reconstruction: Macroscopic PES measurement of adatoms on a reconstructed surface, e.g., Au(111) surface, would yield complicated results since the adatoms at different adsorption positions may give different photoemission signals.

A Cu(111) single crystalline substrate was cleaned by Ar-ion sputtering and annealing cycles. Finally we observed the threefold LEED patterns and the well-known surface state at  $\sim 0.4$  eV [13,14] in the normal-emission UV photoemission spectrum. A small amount of Fe was deposited onto the Cu(111) substrate by electron-bombardment heating. At deposition we held the substrate at  $\sim 95$  K in order to reduce diffusion and formation of dimers or larger nuclei of Fe. X-ray and UV PES spectra were measured using an Omicron EA 125 hemispherical analyzer. The sample can be rotated around two axes while the analyzer and the photon sources are fixed. The polar rotation axis was in the  $(\bar{1}\bar{1}2)$  direction and perpendicular to the plane defined by the UV incidence and the electron emission. The angle between the UV incidence and the electron emission was fixed to be  $60^\circ$ . The acceptance angle of the analyzer  $\Delta$  was  $\pm 8^\circ$  or  $\pm 1^\circ$ . X-ray photoemission spectra were measured at the polar angle  $\theta = 0^\circ$  (normal emission) with  $\Delta = \pm 8^\circ$ . UV photoemission measurements were performed at  $\theta = 0^\circ$  with  $\Delta = \pm 1^\circ$  (angle-resolved mode) or at  $\theta = 25^\circ$  with  $\Delta = \pm 8^\circ$  (partially angle-integrated mode). From the

Fermi edge of the Cu(111) substrate, the Fermi level of the UV PES spectra was determined and the energy resolution was estimated to be  $\sim 25$  meV. The energy reference of the x-ray photoemission spectra is Cu  $2p_{3/2}$  core level (932.66 eV). Before measurement of each sample, we eliminated completely the deposited Fe adatoms of the previous sample by Ar-ion sputtering. The base pressure of the measurement chamber was  $\sim 2 \times 10^{-10}$  Torr. All the procedures including substrate cleaning, Fe evaporation, and photoemission measurement were done in a single chamber.

Figure 1(a) shows representative Fe  $2p_{3/2}$  core-level spectra of Fe/Cu(111), where the amount of Fe adatoms decreases from the top to the bottom. Since photoemission intensity for the thinnest and the second thinnest samples (two curves from the bottom) is very weak, we show the sums of the spectra measured for three independent samples with similar depositions. We have estimated small Fe coverage of the samples from the Cu  $2p$  and Fe  $2p$  photoemission intensity,  $I(\text{Cu } 2p)$  and  $I(\text{Fe } 2p)$  [15]. Assuming  $E_{\text{kin}}^{-1}$  form for the efficiency of the hemispherical analyzer, we can deduce the Fe thickness  $a$  as

$$a \approx A / \left( 1 + \frac{A}{\lambda^*} \right), \quad (1)$$

where

$$A \equiv \frac{I(\text{Fe } 2p)}{I(\text{Cu } 2p)} \frac{\sigma(\text{Cu } 2p)}{\sigma(\text{Fe } 2p)} \frac{E_{\text{kin}}(\text{Fe } 2p)}{E_{\text{kin}}(\text{Cu } 2p)} \lambda.$$

Here,  $\sigma$  is the photoionization cross section [12],  $E_{\text{kin}}$  is the kinetic energy of the photoelectron,  $\lambda$  and  $\lambda^*$  are the escape depth of a Cu  $2p$  electron passing through Cu and through Fe [17], respectively. The second term of the denominator in Eq. (1) originates from an exponential decay of the Cu  $2p$  photoelectron penetrating the Fe thin films [18]. To quote the coverages below, we have converted angstroms into monolayers (ML) according to the relation  $1 \text{ ML} = 2.08 \text{ \AA}$ , which has been determined by the LEED analysis of the pseudomorphic fcc Fe film on Cu(111) [16]. As the Fe coverage decreases from 0.81 to 0.03 ML, the Fe  $2p_{3/2}$  peak position shifts by  $\sim 0.4$  eV to the higher binding energy side. Since Ushida *et al.* reported that the Fe  $2p$  level of a sputter-deposited Fe film was shifted to the lower binding energy side about 0.3 eV by annealing [19], the observed shift in Fe/Cu(111) would be attributed to a decrease in the number of atoms neighboring the Fe adatom for thinner samples.

The valence band of Fe/Cu(111) has been studied with the photon energy of 21.2 eV, as shown in Fig. 1(b). The angle-resolved normal-emission spectrum of Cu(111) is shown at the bottom of the figure. It shows sharp structures of the Cu  $3d$  band between 2 and 4 eV and a small peak of the Shockley surface state at 0.4 eV, as reported by many authors [13,14]. Since this paper focuses on the  $3d$  spectral

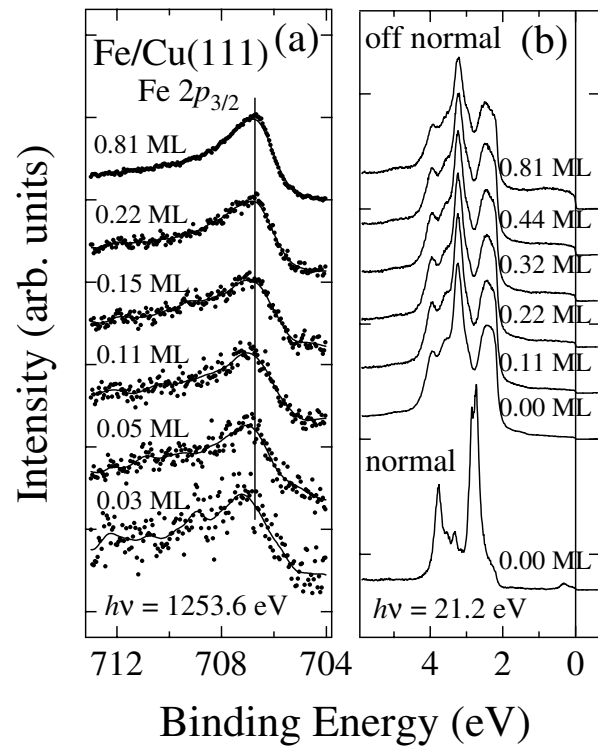


FIG. 1. (a) Typical Fe  $2p_{3/2}$  photoemission spectra of Fe/Cu(111) taken with  $h\nu = 1253.6$  eV. Smoothed data curves are also shown in addition to the experimental data points. The Fe coverage decreases from the top to the bottom. The vertical bar indicates the peak position for the thickest sample (0.81 ML). (b) Typical off-normal-emission valence-band spectra of Fe/Cu(111). A normal-emission spectrum is also shown for Cu(111).

function of the Fe adsorbate near  $E_F$ , we measured the photoemission spectra of Fe-deposited samples with the polar angle  $\theta = 25^\circ$ , where the photoemission spectrum of Cu(111) is relatively flat from  $E_F$  down to  $\sim 2$  eV, as visible in the figure. We set the acceptance angle  $\Delta = \pm 8^\circ$  for the efficiency of intensity. From the bottom to the top, the Fe amount increases as noted in the figure. The spectra are normalized in intensity between  $\sim 1.7$  and  $\sim 4.6$  eV, where the Cu  $3d$  band is dominant. The spectral intensity just below  $E_F$ , which corresponds to the Fe  $3d$  spectral function, evolves as the amount of Fe increases.

In Fig. 2 we show typical valence-band spectra of Fe/Cu(111) in the energy region between  $E_F$  and the top of the Cu  $3d$  band, where Fe  $3d$  and Cu  $4s$  orbitals contribute to the spectra. We note that the ratio of the photoionization cross section [12]  $\sigma(\text{Fe } 3d)/\sigma(\text{Cu } 4s)$  is 22 for the excitation photon energy of 21.2 eV. Since the spectra have been normalized to the intensity of the Cu  $3d$  band as in Fig. 1(b), the spectrum of Cu(111) in the figure (bottom curve) would show the Cu  $4s$  contribution of the Cu(111) substrate in the spectra of the deposited samples. Actually, the difference spectrum between the spectrum of the 0.81 ML sample and that of the Cu(111) substrate, presented by dots in the figure, is almost the

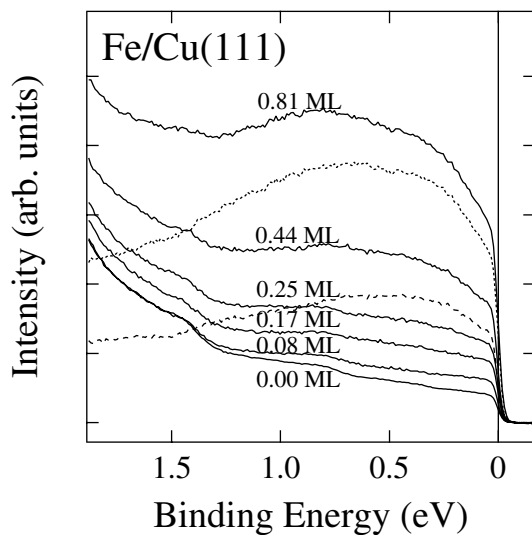


FIG. 2. Representative valence-band spectra of Fe/Cu(111) near  $E_F$ . The normalization condition is the same as in Fig. 1(b). The difference spectra between Fe/Cu(111) and Cu(111) are shown by dots for the 0.81 ML sample and by a dashed curve for the 0.44 ML sample.

same as the spectrum of polycrystalline Fe measured with the photon energy of 21.2 eV [20]. The energy position of the intensity maximum is  $\sim 0.65$  eV both in the present difference spectrum and in the spectrum of bulk Fe, indicating that interaction between the Fe adatoms is dominant even in this sample, where the Fe coverage is  $\sim 1$  ML. The difference spectrum between the spectrum of the 0.44 ML sample and that of the substrate is also shown by a dashed curve in the figure. As the Fe amount decreases, the position of the Fe  $3d$  intensity maximum is shifted to  $E_F$ , the opposite direction of the shift observed in the Fe  $2p$  core level shown in Fig. 1(b). Here, the electronic structure of an ultrathin Fe film down to  $\sim 0.25$  ML has already been studied at room temperature on Cu(111) [21,22] and on polycrystalline Cu [23]. The shifts in the Fe  $2p$  and  $3d$  levels to the opposite directions with varying coverage have also been observed in the photoemission spectra of Fe adsorbate on polycrystalline Cu [23]. Such deposition dependence cannot be explained within a simple shift in  $E_F$  accompanied by the contact of different metals but might indicate that the electronic states of Fe adatoms are significantly different from those of bulk Fe. As the Fe amount further decreases, the broad peak structure disappears, whereas the spectral weight in the vicinity of  $E_F$  remains relatively large.

In order to show the Fe  $3d$  spectral function clearly, we present a series of difference spectra  $I(\text{Fe/Cu}(111)) - I(\text{Cu}(111))$  in Fig. 3. As already stated, we have prepared three independent samples for the thinnest (0.03 ML) and the second thinnest (0.05 ML) films and have confirmed the reproducibility of these difference spectra. The two curves from the bottom of the figure are again the sums of the spectra measured for the three independent samples. The Fe  $3d$  spectral function of 0.03 ML Fe adatoms shows

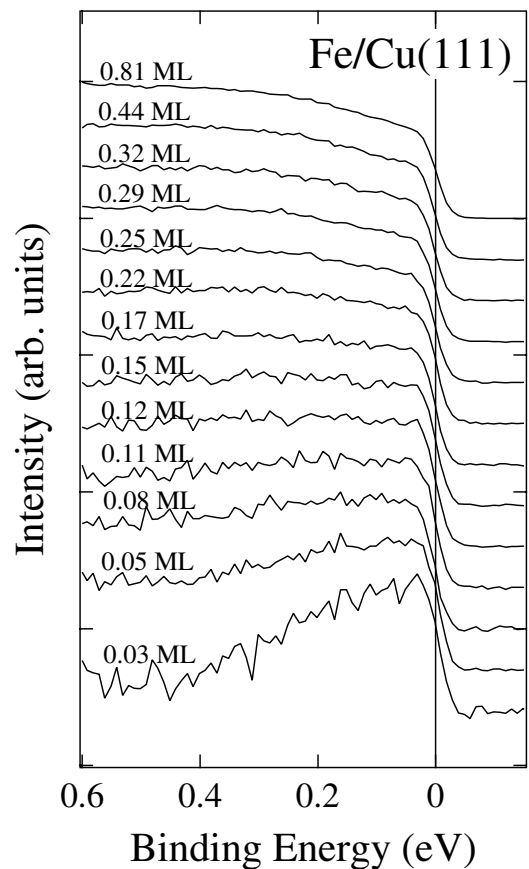


FIG. 3. Difference spectra in the vicinity of  $E_F$  between Fe/Cu(111) and Cu(111).

a narrow peak at  $E_F$ , qualitatively different from that of the 0.81 ML films. Since a photoemission spectrum is the spectral function multiplied by the Fermi-Dirac function, it is not clear whether the maximum position of the Fe  $3d$  spectral function is below  $E_F$  or above  $E_F$  in the present spectrum. Focusing on this narrow peak at  $E_F$  in the Fe  $3d$  spectral function, its line shape would be consistently interpreted within AIM on the condition of the weak  $3d$ -continuum hybridization [24]. Here, for the Co adatom on Au(111), the width of the peak at  $E_F$  in the  $3d$  spectral function [10] is calculated to be only a few meV, while that of the ground-state LSDA DOS is several hundred meV [10,11]. The width of the Fe  $3d$  spectral peak observed in this paper of Fe/Cu(111) is a few hundred meV, much broader than that of the  $3d$  spectral function of Co/Au(111) and rather close to that of the ground state DOS. We should note here that the Fe  $3d$  line shape in Fig. 3 strongly depends on the Fe deposition amount in going from 0.05 to 0.03 ML, implying that the effect of the interaction between the adatoms still appears in the spectrum for 0.03 ML samples and that the width of the  $3d$  spectral peak would be much narrower for an individual Fe adatom. Nevertheless the observed line shape of the Fe  $3d$  spectral function near  $E_F$  is still very sharp compared with that of bulk Fe alloys or compounds. Since the width of the  $4f$  spectral peak observed at  $E_F$  is on the order

of 100 meV [1] for some bulk Ce or Yb compounds, the present result would mean that for the Fe adatom the hybridization between the Fe  $3d$  state and the host metal is strongly reduced and that the effective Fe  $3d$  Coulomb interaction is enhanced.

To conclude, we have studied the electronic structure of the Fe adatom deposited on Cu(111) by x-ray and UV PES. We have found a narrow  $3d$  spectral peak at  $E_F$ , which would be consistent with the recent STS studies and the AIM analysis. The result has revealed the similarity between the  $3d$  electron of a surface adatom and the  $4f$  electron in some bulk Ce or Yb compounds in the vicinity of  $E_F$ .

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