

## Covalent interaction of H with the $d$ electrons at the (111) surface of Ag

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The interaction of H with the Ag(111) surface has been investigated using angle-resolved-photoemission spectroscopy with synchrotron radiation. The bonding and antibonding states of a covalent interaction of Ag  $4d$  bands with the H  $1s$  level are clearly observed. The occupation of the antibonding state accounts for the low chemisorption energy of H on the Ag(111) surface.

Chemisorption of hydrogen on metal surfaces used as a simple prototype system for the study of the interaction of an atom or a small molecule with a surface.<sup>1</sup> These many studies have established that for transition metals, a strong chemical bond is formed between the H atom and the metal surface, and that both  $s$  and  $d$  electrons participate in the interaction.<sup>2-5</sup> The relative contribution of the  $d$  and  $s$  substrate electrons in the H-metal bond has been debated until a unifying picture emerged.<sup>6</sup> According to this picture, this interaction can be considered in two steps. First, the H  $1s$  orbital interacts with metal  $s$  electrons forming a H  $1s$  bonding state (or resonance). The bond formed between the H  $1s$  and the metal  $s$  electrons accounts for most or all of the H-metal bond energy. For transition and noble metals,  $d$  electrons also participate in bonding through a covalent coupling with the H  $1s$  bonding state or resonance. This results in the bonding and the antibonding states, as schematically illustrated in Fig. 1. The antibonding orbital, which is split off from the top of the  $d$  bands, is empty (transition metals) or filled (noble metals) depending on the position of the Fermi level relative to the  $d$  bands. Therefore, the H  $1s$ -metal  $d$  interaction further strengthens the H-metal bond for transition metals but weakens it for noble metals.

Experimentally, the H-metal bond has been extensively investigated. A large body of experimental data has been accumulated for transition metals,<sup>7</sup> and the trends within the  $3d$  and  $4d$  series has been reproduced by theoretical calculations.<sup>8,9</sup> For noble metals, where dissociation is activated, the chemisorption energies have also been determined indirectly by the combination of adsorption and desorption studies.<sup>10-14</sup> Compared to transition metals, the H-metal bond on Cu(111) and Ag(111) is much weaker.<sup>15</sup> In particular, the weak H-Ag bond leads to a chemisorption state of atomic H that is metastable relative to the recombinative desorption into molecular hydrogen.<sup>14</sup>

This paper reports on angle-resolved photoemission spectroscopy (ARPES) measurement on the H-adsorbed Ag(111) surface. The H  $1s$ -Ag  $4d$  bonding and antibonding states located below and above the Ag  $4d$  bands, respectively, are observed. In particular, the observation of the *occupied* antibonding state provides direct spectroscopic evidence for the theoretical picture presented above. The occupation of the H

$1s$ -metal  $d$  antibonding state is responsible for the weak H-metal bond on noble metals compared to those on transition metals.

The ARPES measurements were conducted using synchrotron radiation on the National Synchrotron Light Source (NSLS) VUV beamline U-12 at Brookhaven National Laboratory (Upton, New York). The energy analyzer has an angular resolution of  $\sim 2^\circ$  and the overall energy resolution of the system (electrons plus photons) was 0.12 eV at  $h\nu=30$  eV and 0.17 eV at  $h\nu=45$  eV. A clean Ag(111) surface was prepared by repeated cycles of sputtering with Ne ions and annealing to  $\sim 720$  K. Sample cleanliness was checked by the appearance and the intensity of the surface state-peak near  $E_F$  in normal-emission spectra of a clean Ag(111) surface. Atomic H was dosed on the surface by predissociating hydrogen using a hot tungsten wire located  $\sim 3$  cm in front of the sample held at 100 K. The H adsorption on the Ag(111) surface has been reported to induce a  $2\times 2$  low-energy electron-diffraction (LEED) pattern at 0.5 ML coverage.<sup>15,16</sup> All the spectra reported here were taken with exposures which produced good  $2\times 2$  LEED patterns (near  $\Theta\sim 0.5$

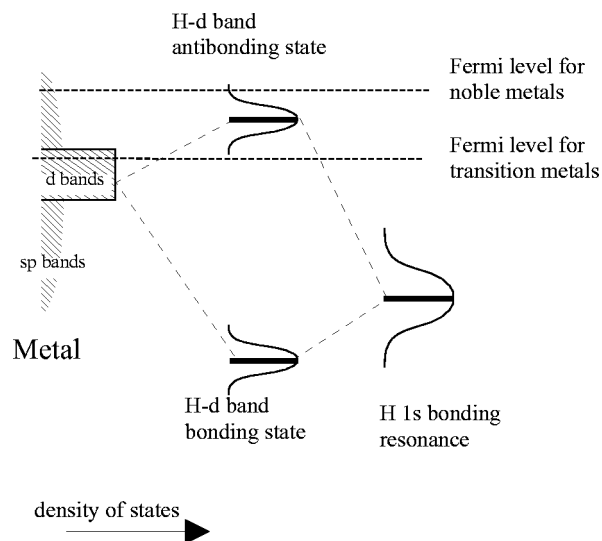


FIG. 1. Schematic illustration of the covalent interaction of H atom with transition metal and noble metal surfaces (modified from Fig. 2 of Ref. 6).

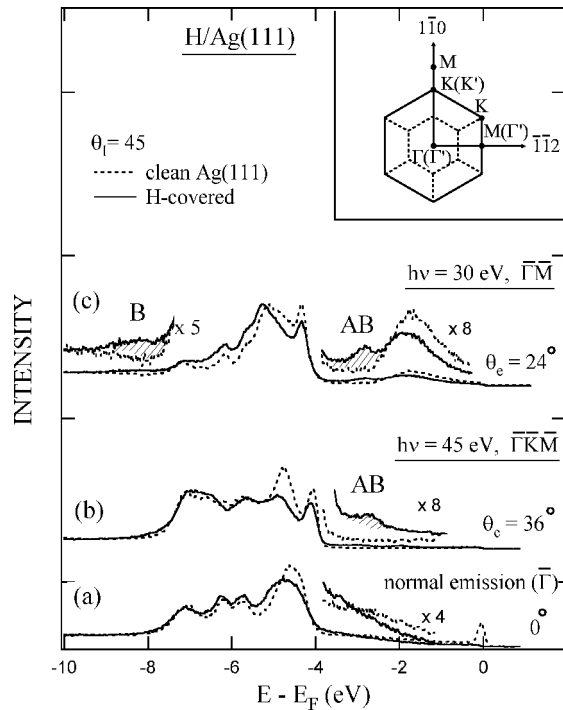


FIG. 2. Photoemission spectra for the clean and the H-covered (near 0.5 ML) Ag(111) surfaces at 100 K. AB and B denote H-induced features *below* and *above* the *d* bands, respectively. The SBZs of the (1×1) (solid line) and (2×2) (broken line) structures are drawn in the inset.  $\bar{\Gamma}$ ,  $\bar{K}$ , and  $\bar{M}$  ( $\bar{\Gamma}'$ ,  $\bar{K}'$ ,  $\bar{M}'$ ) are the high-symmetry points in the (1×1)[(2×2)] SBZ.

ML). The details of the coverage dependence will be presented elsewhere.<sup>17</sup>

Figure 2 displays three sets of angle-resolved photoemission spectra for clean (dotted lines) and H-covered (solid lines) Ag(111) surfaces at 100 K. The coverage in each case is  $\sim 0.5$  ML H coverage producing a 2×2 LEED pattern. Like other noble metals, the normal-emission [ $\bar{\Gamma}$  in the surface Brillouin zone (SBZ)] spectrum of the clean Ag(111) surface [Fig. 2(a)] shows an intense surface state near  $E_F$ .<sup>18</sup> Adsorption of H on the surface completely quenches this peak. No new H-induced features are observable in the normal-emission spectrum [see blowup of *s*-band region in Fig. 2(a)], except for slight changes in relative intensity within the *d*-band region (4–7.5 eV below  $E_F$ ). In the off-normal emission spectra [Figs. 2(b) and 2(c)], new H-induced peaks appear both above and below the *d* bands. There are also quite pronounced changes within the *d* bands. The H-induced peak above the *d* bands at  $-2.5$  eV initial-state energy (labeled as AB) appears in both the  $\bar{\Gamma}\bar{K}\bar{M}$  and the  $\bar{\Gamma}\bar{M}$  directions. Below the *d* bands, a broad feature (labeled as B) is visible at  $-8.5$  eV initial state energy in the  $\bar{\Gamma}\bar{M}$  direction. This feature is not visible in the  $\bar{\Gamma}\bar{K}\bar{M}$  direction.

Figure 3 focuses on the energy region *above* the *d* bands, displaying the changes as a function of collection angle or momentum in the  $\bar{\Gamma}\bar{M}$  [Fig. 3(a)] and the  $\bar{\Gamma}\bar{K}\bar{M}$  [Fig. 3(b)] directions. In both directions, the spectra are dominated by broad and highly dispersing bulk *sp* bands of Ag (peaks marked by open circles). The H-induced peak (tic mark) appears between the peaks from the bulk *sp* and *d* bands of Ag.

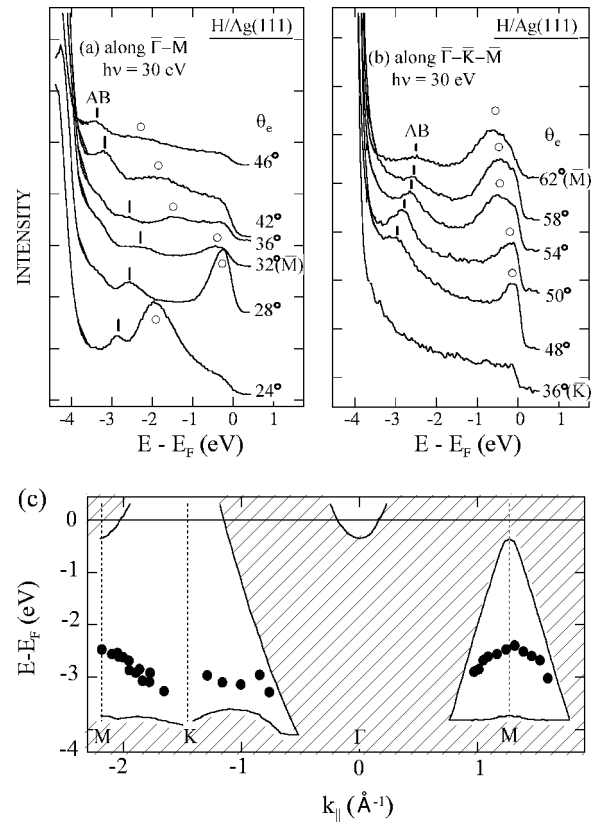


FIG. 3. Dispersion of the H-induced “AB” peak in the region *above* the *d* bands: photoemission spectra as a function of the electron emission angles in the  $\bar{\Gamma}\bar{M}$  direction (a), in the  $\bar{\Gamma}\bar{K}\bar{M}$  direction (b), and a plot of energy vs momentum ( $k_{||}$ ) parallel to the surface (c). The shaded area is a calculated projection of the part of the bulk Ag bands onto the (111) surface (Ref. 19).

These peaks are quite narrow [full width at half maximum (FWHM)  $\sim 0.5$  eV] and disperse forming a two-dimensional band. The measured dispersion of this H-induced band is shown in Fig. 3(c) for the  $\bar{\Gamma}\bar{M}$  and  $\bar{\Gamma}\bar{K}\bar{M}$  directions on the (111) surface. The shaded area is the projection of the bulk bands<sup>19</sup> onto the SBZ of the clean (1×1) structure. The H-induced extrinsic surface state exists within the *s*-*d* gaps at  $\bar{M}$  and  $\bar{K}$  in the SBZ of the clean surface. The measured dispersion is quite small ( $\sim 0.6$  eV) given the limited range of the SBZ where the H-induced state exists. This band is attributed to a H 1*s*-Ag 4*d* antibonding state, split off from the top of the bulk *d* bands.

Figure 4(a) presents the spectra showing the electron distribution curves from the bonding band (B) *below* the Ag *d* bands as a function of the emission angle in the  $\bar{\Gamma}\bar{M}$  direction. The presence of a H-induced peak below the bottom of the *d* bands is evident for the emission angles between 20° and 30°, which correspond to the wave vectors about half-way between the  $\bar{\Gamma}$  and  $\bar{M}$  point in the SBZ. This is the zone boundary ( $\bar{M}'$ ) of the new (2×2) H-induced surface structure. The dispersion of the H-bonding band is shown in Fig. 4(b). This band is the H 1*s*-derived *bonding* state, split off from the bottom of bulk bands due to the covalent coupling to Ag bands. Its position in energy ( $\sim 8.5$  eV binding energy) and the peak width (FWHM  $\sim 1$  eV) are consistent with the characteristics of the H-metal bonding states; characterized

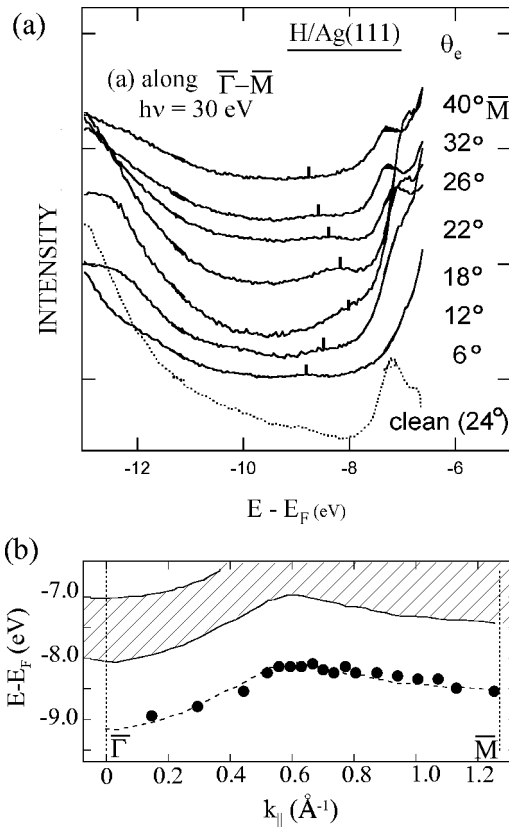


FIG. 4. Dispersion of the H-induced “B” peak in the region below the  $d$  bands: photoemission spectra as a function of the electron emission angles in the  $\bar{\Gamma}-\bar{M}$  direction (a), and a plot of energy vs momentum ( $k_{\parallel}$ ) parallel to the surface along with the calculated projection of the part of the bulk Ag bands onto the (111) surface (shaded area).

by a broad peak in the energy range of 6–9 eV below  $E_F$ .<sup>20,21</sup> In the  $\bar{\Gamma}-\bar{K}-\bar{M}$  direction, the bonding state is not observed, presumably because of very small intensity in this direction. Previously, an angle-integrated photoemission study reported that the H-bonding state of H/Ag(111) was located  $-7.3$  eV below the Fermi level.<sup>12</sup> The disparity in energy ( $\sim 1$  eV) is rather too large, considering the small dispersion of this state. We believe that the previous result based on the difference analysis of the angle-integrated photoemission spectra was erroneous.

The measured dispersion of both the bonding [Fig. 4(b)] and antibonding bands [Fig. 3(c)] presents an enormous puzzle. The dispersion is characteristic of the bulk  $1\times 1$  structure, not the surface  $(2\times 2)$  structure. The measured dispersion of the H  $1s$ -derived bonding state in Fig. 4(b) does not exhibit the  $(2\times 2)$  symmetry observed with LEED.<sup>16</sup> The  $\bar{M}$  point in the SBZ of the  $(1\times 1)$  (see inset in Fig. 2) is the  $\bar{\Gamma}'$  point in the  $(2\times 2)$  zone. Therefore, the dispersion shown in Fig. 4(b) should be symmetric. Interestingly, it appears to follow the band edge of Ag(111) in the  $\bar{\Gamma}-\bar{M}$  direction (the dashed line). The lack of the correct dispersion is less obvious for the antibonding states, but what is totally missing is the H-induced state at  $\bar{\Gamma}$  in the SBZ. The  $\bar{M}$  point in the  $(1\times 1)$  SBZ is equivalent to the  $\bar{\Gamma}'$  point in the  $(2\times 2)$  zone. There is absolutely no sign of this

H-induced state in normal emission [Fig. 2(c)]. The  $(1\times 1)$  periodicity of the H  $1s$  bonding state has been commonly observed for many other H-adsorbed metals, including Ni(111), Pd(111), Pt(111),<sup>20</sup> and Cu(111).<sup>21</sup> They all exhibited a simple  $(1\times 1)$  periodicity, independent of the surface structure indicated by LEED [e.g., H/Ni(111)- $2\times 2$ ].<sup>22</sup> There is no adequate explanation of this observation. Obviously, the H-induced bonding and antibonding states have more bulk  $(1\times 1)$  character than surface  $(2\times 2)$  character.

The identification of the H-induced peak above the  $d$  bands in the photoemission spectra as the antibonding state relies on the theoretical picture of the interaction of H with metal surfaces shown in Fig. 1. At present, there is no calculation of an electronic structure of H/Ag(111) with which this work can be directly compared. However, the assignment of the H  $1s$ -Ag  $4d$  antibonding state can be justified by the comparison with the calculations existing for other noble metals, Cu and Au, and transition metals, Ni and Pt.<sup>6</sup> For all these metals, the H  $1s$ - $d$  antibonding states appear above the  $d$  bands in the calculated density of one-electron states (DOS) for chemisorbed H on the (111) surface. For Cu and Au, they are located below the Fermi level while they are above the Fermi level for Ni and Pt.

Our observation of the H  $1s$ -Ag  $4d$  bonding and antibonding states provides strong experimental evidence supporting the theoretical picture of the interaction of H with transition and noble metal surfaces,<sup>6</sup> which claims that the  $d$  bands participate in H-metal bonding through a covalent coupling with a H  $1s$ -derived resonance. In particular, the occupation of the antibonding state is consistent with the low chemisorption energy of H on the Ag surface.<sup>12–14</sup> The existence of the H  $1s$ -metal  $d$  antibonding state has been the object of many experimental investigations, especially for transition metals. For example, Reimer *et al.*<sup>23</sup> reported a weak feature at 1.3 eV above  $E_F$  in the inverse-photoemission spectra of H/Ni(100), attributing it to the H  $1s$ -Ni  $3d$  antibonding state.<sup>24</sup> Another example is H/Ti(0001).<sup>25</sup> An occupied H-induced state was observed within the  $d$ - $d$  band gap, as well as a H  $1s$ -derived state below the Ti  $3d$  bands, in the photoemission spectra. Theoretical analysis of its orbital revealed an antibonding character of H  $1s$ -Ti  $3d$  interaction. The occupation of this state, however, does not lead to the weakening of the H-Ti bond because of its position in energy. H/Cu(111) was also previously examined using ARPES.<sup>21</sup> While a H  $1s$  bonding state was observed, no extra H-induced spectral features were found above the  $d$  band. In contrast to Cu, our ARPES study of H/Ag(111) clearly demonstrates the existence and the occupation of the H  $1s$ -Ag  $4d$  antibonding state above the  $d$  bands.

The difference between the photoemission spectra of H/Cu(111) and H/Ag(111) can be explained from the theory. According to the theoretical picture, the coupling strength between H  $1s$  and the metal  $d$  electrons depends on the orbital overlap, i.e., the size of the  $d$  orbitals of the metal.<sup>6</sup> Since the  $d$  orbital of Cu is more localized than that of Ag, H  $1s$ -Cu  $3d$  coupling is smaller than H  $1s$ -Ag  $4d$  coupling. This results in the antibonding state of H/Cu being poorly split off from the bulk Cu  $d$  bands, making the observation in PES more difficult than that of H/Ag. Another possibility is that even if the H-Cu antibonding state is well separated

from the bulk  $d$  bands, its observation is limited to a narrower range of  $k_{\parallel}$  in the SBZ. While both Cu(111) and Ag(111) have gaps between the  $d$  bands and the Fermi level at zone boundaries, Cu(111) has a smaller gap than Ag(111).

The difference in the chemisorption energy between H/Cu and H/Ag is also qualitatively explained with the same reasoning. Because of either the smaller orbital overlap or the lower degree of filling of the antibonding state,<sup>26</sup> the repulsive contribution of H  $1s$ -Cu  $3d$  coupling in the H-metal interaction is smaller than that of H  $1s$ -Ag  $4d$ . This is also consistent with the experimental fact that the H chemisorption energy on Cu(111) is larger than on Ag(111).

In summary, the surface electronic structure of H/Ag(111)

has been investigated using the angle-resolved PES. In the spectra, both a bonding and an antibonding states of the H  $1s$ -Ag  $4d$  covalent interaction were found below and above the bulk bands, respectively. The observation of the occupied antibonding state split off from the top of the Ag  $4d$  bands supports the picture of the covalent interaction between H  $1s$  and metal  $d$  electrons of the transition and the noble metals. The weak H-metal bond on the noble-metal surfaces, as compared to on the transition-metal surfaces, can be explained by the occupation of this antibonding state.

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