

# Free-atom-like *d*-states in single atom alloy catalysts

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## Abstract

Electronic structure governs catalytic properties. Alloying provides a means of tuning electronic structure to tailor a metal's catalytic performance. However, mean-field behavior in metals imposes limits. To access unprecedented catalytic behavior, materials must exhibit emergent properties that are not simply interpolations of the constituent components' properties. Here we show an emergent electronic structure in single-atom alloys, whereby weak wavefunction mixing between minority and majority elements results in a free-atom-like electronic structure on the minority element. This unusual electronic structure alters the minority element's adsorption properties such that bonding with adsorbates resembles bonding in molecular metal complexes. We demonstrate this phenomenon with AgCu alloys, dilute in Cu, where the Cu *d*-states are nearly unperturbed from their free-atom state. *In-situ* electron spectroscopy demonstrates this unusual electronic structure persists in reaction conditions and exhibits a 0.1 eV smaller activation barrier than bulk Cu in methanol reforming. Theory predicts several other dilute alloys exhibit this phenomenon offering a design approach that may lead to alloys with unprecedented catalytic properties.

## Introduction

The ability to design an optimal catalyst for a given reaction is one of the major goals of catalysis research. Homogeneous catalysts can exhibit exceptional product selectivities due to the fine control of chemical bonding that is possible through the narrow electronic states of molecular complexes. However, industrial processes more commonly use heterogeneous metal catalysts due to less-demanding product separation. Mean-field behavior often dominates the adsorption properties of heterogeneous catalysts because of their broad electronic band structures. Consequently, heterogeneous catalysts generally follow scaling relationships.<sup>1, 2, 3, 4, 5, 6, 7, 8</sup> These relationships place fundamental limitations on the achievable catalytic performance. For instance, technologically important reactions such as the oxygen evolution reaction in water splitting,<sup>9</sup> ammonia synthesis<sup>8</sup> and electrochemical CO<sub>2</sub> reduction<sup>8</sup> cannot be catalyzed at the thermodynamics optimum, due to scaling relationships. In order to make such highly desirable reactions as water splitting and CO<sub>2</sub> reduction economically viable using renewable energy inputs, researchers are seeking means to circumvent known scaling relationships.

A useful way of tuning a metal catalyst's properties is via alloying.<sup>10</sup> Alloys generally follow scaling relationships. However, a recently introduced design concept for alloys could potentially provide a way to circumvent scaling relationships. The concept is that of single atom alloys (SAAs).<sup>11, 12</sup> SAA's consist of a noble metal matrix, with active metal atoms dispersed across the surface, such that no bonds between neighboring active sites form. Such an approach could combine the best properties of heterogeneous and homogeneous catalysts.<sup>13, 14, 15</sup> Microscopic studies of such alloys reveal that reactant activation can occur at single-atom sites, followed by spillover onto the matrix surface.<sup>13</sup> The spillover effect results in a separation of adsorption and desorption sites, thereby preventing over-binding of adsorbates. In principle, the effect of site isolation in SAA's could breach the known limits of scaling relationships.

There are several examples in the scientific literature demonstrating enhanced catalytic properties of SAA's via isolating activation and desorption steps.<sup>16</sup> The unique bonding geometry of SAA's could potentially also give rise to changes in the solute atom's electronic structure.<sup>17</sup> Electronic structure changes typically observed on alloying involve a shift in the *d*-band position relative to the

Fermi level. Such alloys exhibit mean-field behavior. In contrast, cases have been predicted where the dilute addition of a foreign metal into a host can result in band narrowing and adsorption properties that are not calculated from linear interpolation of the constituent element properties.<sup>18</sup>

Here we report on the experimental finding that certain SAA's exhibit an electronic structure in which the *d*-band of the solute becomes atomically narrow. We demonstrate this property for AgCu alloys, containing dilute Cu concentrations, using valence photoemission spectroscopy to provide a direct measure of the SAA's DOS. These measurements show that the Cu 3*d* states are five times narrower than those of bulk Cu (i.e. 0.5 eV for Cu in AgCu compared to 2.5 eV for bulk Cu). Projected density of states (pDOS) calculations show that the solute's *d*-states resemble those of a free-atom, whereby the *d*-electron orbitals are nearly degenerate. A series of computational experiments reveals that this phenomenon arises when solutes in dilute concentrations (i.e. in the absence of solute-solute bonding) exhibit weak interaction with the electronic states of the matrix element. This effect arises due to minimal energetic and spatial overlap between solute and matrix atoms. Although the electronic structure is free-atom-like in terms of its energy distribution, equilibration of electron chemical potentials with the surrounding matrix gives the free-atom-like states an anionic character, as apparent from X-ray photoemission spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) measurements and density function theory (DFT) calculations.

Calculated adsorbate bonding energies demonstrate that these localized charge centers can bind to adsorbates in a manner akin to molecular metal complexes, for instance the narrowness of the Cu 3*d* states results in  $\pi$ -bonding to adsorbed oxygen, increasing its overall bond strength compared to bulk copper. Calculated adsorption energies for other main-group elements reveal that the free-atom-like electronic structure can also weaken adsorbate bonding, depending on adsorbate electronegativity and valence electron population. The observed bonding trends result from two main contributions: ionic and covalent bonding. The increased negative charge density on the impurity ion influences the ionic contribution, while the extreme narrowness of the *d*-band influences the covalent contribution. These parameters can guide the design of such SAA's.

While this electronic structure can exist under vacuum conditions, alloy catalysts often restructure when exposed to reactive atmospheres, potentially resulting in clustering of solute atoms and phase segregation.<sup>19</sup> *In-situ* XPS of the alloy in methanol reforming demonstrates that this SAA can retain its free-atom-like electronic structure under reaction conditions. In this reaction, AgCu exhibits an effective activation energy for H<sub>2</sub> formation 0.1 eV lower than bulk Cu. Calculations of the rate-limiting step in methanol reforming reveal that the lower activation energy on the SAA is a result of stronger bonding between Cu and H in the transition state on the SAA.

Using an SAA strategy where solute atoms perform reactant activation, one could use a narrow *d*-band to increase adsorbate binding, thereby increasing overall activity, which is particularly important when active sites are necessarily present in low concentrations. However, to take advantage of this phenomenon in catalysts design, one must judiciously match the electronic structure of the alloy with the desired adsorbate. By computationally screening several other Ag-based alloys, we have found the free-atom-like electronic structure occurs in several other dilute alloys. With these alternative compositions, one has flexibility in matching the position of the free-atom-like *d*-state with the adsorbate of interest. This strategy could potentially achieve catalytic properties that are not possible through conventional alloy compositions.

## Results & Discussion

### Free-atom-like Electronic Structure in a Bulk Metal

Valence photoemission spectra, as in Figure 1 a), reveal a striking feature in the electronic structure of dilute AgCu alloys: The *d*-band of copper is extremely narrow. Such spectra are an experimental measure of density of states, and show that the 3*d*-band of copper in AgCu (the peak at 2-3 eV) is one-fifth the width of the *d*-band in bulk copper, as seen in Figure 1 b). The Ag 4*d* band (the broad feature between 3.5-8.0 eV) is unchanged in the alloy relative to pure silver. The sample is a chemically reduced, single-phase AgCu alloy (0.3 at % Cu), measured at the Cooper minimum of Ag 4*d* ( $h\nu=150$  eV) to increase the sensitivity to Cu 3*d* states (Supplementary Figures 2, 3).<sup>20</sup>

Density-of-states calculations accurately reproduce the narrow Cu  $d$ -band of the dilute AgCu alloy. The calculated Cu pDOS of Ag<sub>31</sub>Cu<sub>1</sub> in Figure 1 c) shows that the Cu 3d line-shape in dilute AgCu is nearly symmetric. This line-shape implies that the Cu 3d states do not strongly hybridize with its coordination environment (Supplementary Figure 5). In contrast, the line-shape of the Cu 3d band in bulk Cu is irregular, as shown in Figure 1 d). Its irregular line-shape reflects the broadening of electronic states in solids due to translational symmetry and wave-function hybridization between neighboring atoms.

The symmetry-resolved pDOS of Ag<sub>31</sub>Cu<sub>1</sub> show that the  $e_g$  and  $t_{2g}$  states of Cu in AgCu are nearly degenerate, as is evident by the overlapping  $t_{2g}$  and  $e_g$  pDOS in Figure 1 b). In contrast, the  $e_g$  and  $t_{2g}$  states in bulk Cu are split by the strong interaction with their coordination environment, as expected. This observation indicates a nearly uniform coordination field for the Cu 3d states in Ag<sub>31</sub>Cu<sub>1</sub>, implying free-atom-like Cu  $d$ -states in the alloy. The free-atom nature of these states becomes even clearer when one looks at the spatial distribution of Cu 3d wavefunctions, which very closely resemble the  $d$ -states of the free atom, both in terms of shape and spatial extent (Supplementary Figure 6).

These electronic structure characteristics reveal a fundamental difference in the Ag-Cu and Cu-Cu interactions. In dilute AgCu, no Cu-Cu interactions are present. Cu atoms are isolated from one another, and surrounded by a matrix of Ag atoms (because AgCu is a substitutional alloy).<sup>21</sup> Although the Ag-Cu bond of the alloy is longer than the Cu-Cu bond of bulk copper (2.89 Å and 2.59 Å, respectively), bond length in this case is not the main factor influencing  $d$ -bandwidth, as seen from calculations of the compressed lattice (Supplementary Figure 7). Strong hybridization requires wave-functions to spatially and energetically overlap. Figure 1 a) shows that the Cu 3d states do not overlap energetically with the Ag 4d band. We conclude that energy mismatch between Ag 4d and Cu 3d states is the main contributor to the sharpness and degeneracy of the Cu 3d states.

### Anionic Nature of Cu in AgCu

Despite the lack of wave-function overlap between Ag and Cu in the alloy, charge density transfers between Ag and Cu. From the electron chemical potentials of Ag and Cu, it is not immediately clear in which direction, if any, one should expect electrons to move. One can estimate electron chemical potentials from work functions (for solids) and electronegativities (for atoms). The work function of Ag has been reported between 4.26 and 4.70 eV,<sup>22</sup> and that of Cu at 4.65 eV,<sup>23</sup> while the electronegativities of Cu and Ag are 4.48 eV and 4.44 eV, respectively.<sup>24</sup>

Although one cannot reliably predict charge transfer from reported work functions or electronegativities, XPS spectra of the AgCu alloy in Figure 2 a) show direct evidence of charge transfer from Ag to Cu. There is a shift in the Cu 2p<sub>3/2</sub> peak by -0.23 eV ± 0.05 eV (towards lower binding energy relative to bulk metallic Cu). A negative chemical shift in XPS does not necessarily imply an increase in electron density. Screening of the core-hole (i.e. final-state effects) can dominate measured chemical shifts in binary metal alloys.<sup>25, 26</sup> A well-screened core-hole results in lower measured binding energies, compared to poorly-screened core-holes.<sup>27</sup> To assess the change in core-hole screening between Cu and AgCu, we calculated the energy of Ag<sub>31</sub>Cu<sub>1</sub> with and without valence relaxation. We find that the initial-state shift is -0.5 eV (relative to pure Cu) and the initial-state plus final-state shift is -0.4 eV (relative to pure Cu). Thus, the main contribution to the observed binding energy shift is the initial-state, namely the increased charge on the Cu center.

The Cu L<sub>3</sub> NEXAFS (Figure 2) provides additional evidence of the charge transfer to Cu. The measured spectra exhibit an absorption edge shift toward lower excitation energy by 0.3 eV, in agreement with the observed XPS shift. Furthermore, the decrease in the intensities of the absorption peaks of the alloy-labeled β and γ in Figure 2—indicate a filling of unoccupied states. Calculated NEXAFS and unoccupied pDOS (Supplementary Figure 8) show that the features labeled β and γ in Figure 2 reflect transitions into unoccupied Cu 3d states of  $t_{2g}$  and  $e_g$  symmetry, respectively. The feature labeled α is due to transitions into the Cu 3d states just above the Fermi level. Thus, the decrease of the Cu L<sub>3</sub> features indicates an increased electron density in the  $d$ -states in the alloy. It must be noted that the Cu L<sub>3</sub> edge is insensitive to the Cu 4s unoccupied states,<sup>28</sup> so we could not assess experimentally the filling of 4s states in the alloy. However, due to mixing of  $s$ ,  $p$  and  $d$  states, it is likely that all states increase in occupation.

In addition to the evidence provided by XPS and NEXAFS measurements, analysis of the Löwdin charges on Cu centers confirms that they have higher electron count in AgCu than elemental Cu (Supplementary Table 1). Voronoi population analysis also confirms an increased charge on the Cu in the alloy, with Cu centers of Ag<sub>31</sub>Cu<sub>1</sub> having 0.4 electrons more than in elemental Cu,

accommodated by the *s*, *p* and *d* states. Charge-density difference plots show the spatial distribution of the additional charge around the Cu centers (Supplementary Figure 9).

## Adsorbate Bonding Model

When considering standard models of adsorbate bonding to metal surfaces, such as the Newns-Anderson-Grimley model—one expects this unusual electronic structure to significantly alter adsorption. The Newns-Anderson-Grimley model is an analytical model for describing hybridization between adsorbate molecules and electronic band structures of metal surfaces.<sup>29, 30, 31, 32</sup> Its greatest merits are in its conceptual simplicity and ability to enable interpretation of adsorbate-surface bonding. The model shows that when adsorbates hybridize with broad metal valence bands (such as an *s*-band), a broadened adsorbate state results (Figure 3 a). In contrast, when adsorbates hybridize with narrow valences bands (such as a *d*-band) the adsorbate state can split into localized, bonding and anti-bonding states (Figure 3 b). The largest metal bandwidth for which adsorbate state splitting occurs is dictated by the energetic alignment between the adsorbate state and the metal band, as well as the interaction strength between the metal band and adsorbate state. In general, band narrowing gives rise to increased interaction strength.

To determine whether splitting or broadening occurs upon adsorption, it is helpful to examine the graphical solutions to the Newns-Anderson-Grimley model, as shown in Figure 3 c-d). To do so, we can approximate the metal's DOS using a semi-ellipse. The dashed blue line in Figure 3 c-d) is called the adsorption function, and has the form  $(\epsilon - \epsilon_a)/V^2$ .  $\epsilon_a$  is the energy of the adsorbate electron state, and scales with adsorbate electronegativity.  $V^2$  is the coupling strength, and depends on the spatial overlap between adsorbate and metal states.

By taking the Hilbert transform of the *d*-band DOS (orange curve), and finding the intersections with the adsorption function, one can determine whether adsorbate state splitting or broadening occurs.<sup>29, 30, 33</sup> If the adsorption function only intersects the Hilbert transform once, as in Figure 3 c), then broadening occurs. If the adsorption function intersects the Hilbert transform more than once, as in Figure 3 d), then adsorbate state splitting occurs. The energetic position of the re-hybridized adsorbate states are indicated by the filled blue dots in Figure 3 c-d). The third intersection between the adsorption function and the Hilbert transform gives rise to a virtual state, that is non-localized and of much lower density than the localized bonding and anti-bonding states.

In Figure 3 c), where the metal band is broader than the interaction strength (i.e.  $W > V^2$ ), the adsorption function can only intersect the Hilbert transform once, and a broadened re-hybridized adsorbate state results. In Figure 3 d), where the metal band is narrower than the interaction strength (i.e.  $W < V^2$ ), bonding and anti-bonding re-hybridized states result. The consequence of re-hybridization to adsorbate bond-strength depends on the position of the bonding and anti-bonding states relative to the Fermi level. States below the Fermi level will be filled, while those above the Fermi level will be empty. Filled bonding states increase bond strength between adsorbate and surface, while filled anti-bonding states decrease bond strength.

## Activating New Adsorbate Bonds on AgCu

In the case of dilute AgCu, the Cu *d*-band is much narrower than any pure metal. The *d*-band widths of transition metals range from ca. 2.5 to 11.5 eV,<sup>31</sup> while the width of the Cu *d*-band in AgCu is only 0.5 eV. Given this extreme narrowness, it should be capable of a strong interaction with adsorbate orbitals that are otherwise inaccessible. To illustrate this point we compare the calculated pDOS of O bound to bulk Cu and AgCu. The very narrow *d*-band effectively increases the interaction strength with the O *2p* levels, such that the *2p<sub>x</sub>* and *2p<sub>y</sub>* orbitals become involved in bonding, giving rise  $\pi$ -bonds between O and the Cu center of AgCu.

Figure 4 a) and d) show the calculated pDOS of Cu *3d* and O *2p* for O adsorbed to Cu<sub>36</sub> and Ag<sub>35</sub>Cu<sub>1</sub> surfaces, respectively. In the case of O bound to Cu<sub>36</sub>, the O *2p<sub>z</sub>* state splits into bonding and anti-bonding orbitals because the *z*-axis points toward the surface, thus there is substantial spatial overlap between the O *2p<sub>z</sub>* and Cu *3d* states. In contrast, the O *2p<sub>x</sub>* and *2p<sub>y</sub>* states—which lie parallel to the surface and have limited spatial overlap with the Cu *d*-states—remain un-split, resulting in broadened non-bonding states. Figure 4 b) depicts an energy-level diagram of this scenario. On Ag<sub>35</sub>Cu<sub>1</sub>, the narrow *d*-band couples strongly with the O states. Here the coupling strength with the O *2p<sub>x</sub>* and *2p<sub>y</sub>* states is strong enough to split them into bonding and anti-bonding states despite limited spatial overlap. As shown schematically in Figure 4 e), this interaction results in  $\pi$ -bonding between O and the Cu center.

From the graphical solutions to the Newns-Anderson-Grimley model, shown in Figure 4 c) and f), one can see why the narrow  $d$ -band gives rise to the formation of  $\pi$ -bonds. First, it is important to note that each of an adsorbate's electronic states has its own  $(\epsilon-\epsilon_a)/V^2$  line in graphical solution presented here. The slope of the line reflects the state's interaction strength. A steeper slope indicates a weaker coupling strength. Furthermore, the  $2p_x$ ,  $2p_y$  and  $2p_z$  states are degenerate (in the isolated atom) as reflected by them intersecting the  $x$ -axis at the same value (i.e. identical  $\epsilon_a$  values). From Figure 4 c) and f) one can see that, for  $p_x$  and  $p_y$  states on elemental copper, the  $(\epsilon-\epsilon_a)/V^2$  line only intersects the Hilbert transform at one point, indicating a weak interaction. In contrast, for the narrow  $d$ -band of AgCu, the  $(\epsilon-\epsilon_a)/V^2$  line of the  $p_x$  and  $p_y$  states intersects the Hilbert transform thrice, indicating the formation of localized bonding and anti-bonding states.

The wavefunctions of the  $\sigma$  and  $\pi$  bonding and anti-bonding states that are highlighted in the pDOS of Figure 4 d), are shown in Figure 4 g). Here one can clearly identify the states as  $\sigma$  and  $\pi$ , based on the symmetry of the wavefunctions, as bonding or anti-bonding, based on the phase change of the wavefunctions across the bond axis. The formation of the  $\pi$ -bond for O adsorbed to AgCu, and the incomplete filling of the  $\pi^*$ -bond, results in a large increase in bond strength (i.e. 0.3 eV stronger than on elemental copper). Several other adsorbates (S, Se, Te, Cl, Br, and I) exhibit similar enhanced bonding on AgCu.

## General Adsorbate Bonding Trends

The bonding of other elements to the narrow  $d$ -band reveals some general bonding trends. We have calculated adsorption energies of the  $s$ - and  $p$ -block elements adsorbed on top of the Cu site in the dilute AgCu alloy. We compared these values with the respective adsorption energies on elemental Cu. Figure 5 shows the difference in adsorption energy between adsorbates bound to elemental copper and to copper sites of the alloy (i.e.  $E_{ads}(Cu)-E_{ads}(AgCu)$ ) plotted against the difference in electronegativity between Cu and the respective adsorbates. Here one can see that the narrow  $d$ -band does not always give rise to an increase in bond strength relative to bulk Cu. The adsorbates in the top-left quadrant bond weaker to AgCu than to Cu, and the adsorbates in the bottom right quadrant bond more strongly to AgCu.

The most salient feature of Figure 5 is the general trend between bonding strength to AgCu and adsorbate electronegativity. In particular, adsorbates that have electronegativities less than that of Cu tend to bond weaker to the alloy than to elemental copper, while adsorbates with larger electronegativities than Cu tend to bond stronger to the alloy than to elemental copper.<sup>34</sup> This trend is a reflection of the increased electron density on the Cu center in the alloy, and results in an ionic contribution to adsorbate bonding.

In addition to the ionic component, a covalent component also contributes to bonding. The covalent bonding trend is played out in a more complex manner, and requires consideration of the Newns-Anderson-Grimley model. At first glance, there appears to be significant scatter in the plot of Figure 5. However, one resolves a hidden pattern in the scatter by grouping the data points according to the adsorbates' valence electron configurations. The data points in Figure 5 have been labeled according to their groups in the periodic table. They are plotted in order of increasing electronegativity from left to right (i.e. group 1: Cs, Rb, K, Na, Li; group 2: Ba, Sr, Ca, Mg, Be; group 4: Sn, Ge, Si, C; group 5: Sb, As, P, N; group 6: Te, Se, S, O; group 7: I, Br, Cl, F).<sup>34</sup> Within a given group, the adsorption energy difference scales with electronegativity. As elaborated in detail in the supplementary material (Supplementary Figure 11), the difference between groups arises due to differences in covalent bonding, and are a consequence of the positions of the re-hybridized adsorbate states relative to the Fermi level.

## The $d$ -State's Role in Catalysis

The predicted influence of the free-atom-like  $d$ -states on adsorbate bonding begs the question of how such states behave catalytically. First, one must wonder whether such states can even exist under reaction conditions. To answer this question, we employed *in-situ* XPS, whereby one can measure the valence density of states under catalytically active conditions. The reaction chosen here is methanol reforming (i.e.  $CH_3OH + H_2O \rightarrow H_2 + CO_2$ ). As shown in Figure 6 (a), the free-atom-like Cu  $d$ -states are retained under reforming conditions (i.e. 1:1  $CH_3OH:H_2O$ , at 0.5 mbar and 300°C) with simultaneous detection of  $H_2$  activity. To compare the catalytic properties of Cu in the dilute alloy with those of bulk Cu, we determined activation energies using Arrhenius plots, Figure 6 (b). These yielded effective activation energies of  $0.72 \pm 0.05$  eV and  $0.62 \pm 0.04$  eV for Cu and AgCu, respectively. These values are based on eight independent measurements (four per material), with error bars representing three-times the standard deviation. The samples were in the form of pressed alloy powders, as described in the methods section.

To understand how the AgCu alloy gives rise to this difference in activation energy, we have performed a series of minimum-energy pathway (MEP) calculations and examined the transition state of the rate-determining step. We must point out that modern computational methods suitable for large metallic slabs cannot resolve an activation energy as small as 0.1 eV, thus one cannot interpret quantitative differences in predicted activation energy smaller than 0.1 eV. Nonetheless, one can still rely on qualitative behavior. The MEP calculations yielded nearly identical values for activation barrier, indicating that the experimental values are within the error bar of the MEP calculations and there is no significant discrepancy.

The most interesting aspect of the MEP calculations is the geometries of the transition states. The rate-determining step for methanol reforming is H-abstraction from a methoxy group.<sup>35</sup> As shown in Figure 6 c) and d), the abstracted H atom in the transition state on bulk Cu sits in a bridge site, while on AgCu the H atom sits in a nearly top-site geometry. Simple bond counting indicates that the Cu-H bond in AgCu must be significantly stronger than the Cu-H bond in bulk Cu. In both cases, to go from the initial state to the transition state, one Cu-O bond and one C-H bond were broken. In the case of bulk Cu, two Cu-H bonds form, while in the case of AgCu only one Cu-H bond forms. Nonetheless, the difference in energies between initial state and transition state is equal within 0.1 eV. This implies that the bond to H is nearly twice as strong on AgCu than on bulk Cu. This interpretation was verified by calculating the binding energy of H<sup>+</sup> on Cu and AgCu (Supplementary Figure 12).

### Alternative Narrow *d*-Band Alloys

While the narrow *d*-band exhibits enhanced catalytic activity for the particular reaction examined here, as Figure 5 suggests, not all adsorbates behave the same. Thus to achieve catalytic improvements, one must judiciously match the adsorbate with the *d*-band. One cannot freely change the position of the Cu *d*-band; however, by changing the solute and solvent of the alloy, one can retain the free-atom-like narrowness and obtain alternative positions of the *d*-state relative to the Fermi level. We have screened several other solutes in a silver host to search for similar materials (Au, Ni, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, Fe, W, Mn, Re, Co, Rh, Ir, Pd, Cd, Zn, Pt and Os). Among these alloys we have found only four solutes that give rise to such extremely narrow *d*-bands, namely AgNi, AgPd, AgMn and AgCr (Figure 7). These findings are in agreement with the results recently presented by Thirumalai and Kitchin.<sup>17</sup> Interestingly, in the cases of AgMn and AgCr, the impurity state is magnetic, while in AgNi and AgPd it is not. This occurs when the *d*-states of the impurity comes within the on-site *dd* Coulomb repulsion energy (*U*) of the Fermi level, and the system lowers its energy by filling only one spin-polarized state to form a localized magnetic state.<sup>29</sup> This observation is essentially the same phenomenon discovered in the 1960's, when it was found that impurities in metals can become magnetic when present in very dilute concentrations.<sup>36</sup> The physics behind this phenomenon was developed shortly thereafter by P. W. Anderson et. al.,<sup>29</sup> and is essentially the same physical process behind the state localization demonstrated here. Magnetic moment localization has been demonstrated for a number of dilute alloys. These physics principles could be applied to catalysis on a broader scale to obtain alloys that potentially do not exhibit mean-field behavior.

### Conclusion

Cu 3*d* states in dilute AgCu alloys exhibit a free-atom-like electronic structure, where the Cu *d*-states are extremely narrow due to minimal wave-function mixing with Ag valence states, and result in a localized negative charge on the Cu centers. This electronic structure results in different adsorbate bonding to AgCu compared to elemental Cu, due to from two main contributions: 1) an ionic and 2) a covalent contribution. The ionic contribution is influenced by the increased negative charge density on the Cu center in AgCu, and results in stronger bonding to electronegative elements, and weaker bonding to electropositive elements (compared to elemental copper). The covalent contribution depends on the valency and energetic position of the adsorbates relative to the Cu 3*d* states and the Fermi level. In general, the narrowness of the Cu 3*d* state gives rise to strong coupling to adsorbates, and can give rise to the formation of new covalent bonds. *In-situ* XPS measurements show that this electronic structure can exist under reaction conditions. Activation energy measurements demonstrate AgCu to have a 0.1 eV lower effective activation energy than Cu for H<sub>2</sub> formation in methanol reforming. The difference in activation energy is a result of enhanced H-bonding to the free-atom-like Cu center in the transition state on AgCu. We predict similar free-atom-like electronic structures to exist in other Ag-based alloys, such as AgPd, AgNi, AgMn and AgCr.

### Methods

AgCu alloys were prepared by melting Ag (5N) and Cu (5N) in a graphite crucible, and casting into an 8 mm diameter disk. Photoemission measurements were performed at the "Innovative Station for In-Situ Spectroscopy" beamline at the Helmholtz-Zentrum Berlin's BESSY II synchrotron facility, using a Specs GmbH Phoibos 150 analyzer. Alloy surfaces and reference samples (Ag and Cu) were sputtering for 30 min (1.5 kV at  $2 \times 10^{-4}$  mbar Ar), followed by annealing in H<sub>2</sub> ( $p = 0.5$  mbar) at 650 °C. Cleanliness was confirmed by XPS survey measured at  $h\nu = 1486.7$  eV and 355 eV. Cu  $2p_{3/2}$  spectra were measured at  $h\nu = 1486.7$  eV. Valence photoemission spectra were measured at  $h\nu = 100$  eV, 150 eV and 700 eV. NEXAFS spectra were measured in partial electron yield mode by measuring the Cu *LMM* emission line at kinetic energy of 900 eV with a hemispherical analyzer, while sweeping the photon energy across the Cu  $L_3$ -edge. X-ray powder diffraction patterns were measured on a Bruker D8 Advance (LynxEye Detector) in Bragg Brentano geometry (Cu radiation).

Alloy powders used for Arrhenius plots were synthesized by precipitating Copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , 0.0397 mmol,  $\geq 99\%$  p.a. ACS, Carl Roth) with silver powder (4.612 mmol, 99.999%, -22 mesh, Premion), in ultrapure water from a Millipore treatment system (Milli-Q), to achieve a Cu at 0.5 atomic percent. The resulting powder was thermally dried at 110 °C for 12h in synthetic air. Calcination in synthetic air at 350 °C for 3h yielded the final  $\text{Ag}_{0.95}\text{Cu}_{0.05}$  sample. The powder was reduced in tube furnace under a continuous flow 5% H<sub>2</sub> in Ar, at 600 °C for 48 hours. The resulting powder was loosely pressed into a pellet. The Cu samples were pellets pressed from high purity Cu powder (99.999%, purchased from American Elements, -325 mesh).

The Quantum ESPRESSO (QE) package<sup>37</sup> was employed for DFT calculations using the Perdew, Burke, and Ernzerhof (PBE)<sup>38</sup> exchange and correlation potential and ultrasoft pseudopotentials. Complete details of our approach are available elsewhere.<sup>39, 40</sup> Briefly, a planewave basis set with a kinetic energy cutoff of 30 Ry for wavefunctions (300 Ry for charge density) was used along with a  $k$ -point mesh, equivalent to  $(30 \times 30 \times 30)$  for the primitive Cu unit cell. Marzari-Vanderbilt<sup>41</sup> cold smearing was used with a 0.02 Ry smearing parameter. In the pure metals the lattice parameters were optimized. In the alloys the ions were also allowed to relax. Core level shifts were calculated in both the initial state approximation and with the  $\Delta$ SCF method to capture final state effects.<sup>42</sup>

For calculating  $L$ -edge spectra we employed a Bethe-Salpeter Equation (BSE) approach.<sup>43</sup> These calculations were carried out on the relaxed structures by combining the Kohn-Sham wavefunctions from QE with the NIST core-level BSE solver (NBSE)<sup>44</sup> through the OCEAN package.<sup>45, 46</sup> We used norm conserving pseudopotentials generated with the FHI98PP package<sup>47</sup> where the exchange and correlation was treated with the local density approximation (LDA).<sup>48</sup> A kinetic energy cutoff of 200 Ry (800 Ry) was used for wavefunctions (charge density). Ground and final state calculations were performed with a  $k$ -point mesh equivalent to  $(12 \times 12 \times 12)$  for the primitive unit cell and Methfessel-Paxton smearing<sup>49</sup> was used with a width of 0.002 Ry. Screening calculations were performed including bands up to 100 eV above the Fermi energy and a  $(4 \times 4 \times 4)$   $k$ -point mesh. Spectra were broadened with a 0.6 eV wide Lorentzian, the natural line width<sup>50</sup>, and were aligned relative to one another using the corresponding  $\Delta$ SCF binding energy.

For partial density of states calculations we first computed the pDOS of  $\text{Ag}_{255}\text{Cu}_1$  with the single copper atom in place of a silver atom in a  $(4 \times 4 \times 4)$  crystallographic cell of FCC silver in order to model the 0.3 at% alloy. Because there were no significant differences in the pDOS of  $\text{Ag}_{255}\text{Cu}_1$  and  $\text{Ag}_{31}\text{Cu}_1$  we used the  $\text{Ag}_{31}\text{Cu}_1$  system for computational efficiency for the Cu  $L$ -edge calculations.

Adsorbate binding energies were calculated using a  $(3 \times 3)$  surface alloy– $\text{CuAg}_8$ , where one Ag atom from  $\text{Ag}_9$  was replaced with a Cu atom—on top of three layers of bulk silver with 20 Å of vacuum separating periodic images. The atomic positions in the slab were optimized first (without the adsorbate present). Then the adsorbate was placed on a top site and its geometry relaxed while constraining slab atoms. Voronoi and Löwdin charge integrations were performed according to references <sup>51</sup> and <sup>52</sup>.

## Competing Interests

The authors declare no competing financial and non-financial interest.

## Data Availability Statement

All raw data used in this work are available on request from the authors.

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## Author Contributions

M.G. and T.J. conceived, designed and planned the project. M.G. measured and analyzed the photoemission spectra as well as activation energies. T.J. performed the theoretical calculations. R.S., S.P. and A.K. provided direction, guidance and assistance in data interpretation. S.B. assisted in photoemission measurements. L.Z. synthesized the samples used for activity measurements. M.A. synthesized the bulk metal samples. M.S. and F.G. measured and analyzed the X-ray diffraction data. M.G. and T.J. wrote the manuscript. All authors provided input and advice while writing manuscript drafts. M.G. and T.J. contributed to this work equally.

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## Figure Captions

**Figure 1** - Density of states plots show the free-atom-like nature of the Cu 3d states in AgCu. (a) The Measured valence photoemission spectra ( $h\nu = 150$  eV) of an AgCu alloy containing 0.3 at. % Cu (red curve), and metallic Ag (blue curve) reveal the narrow Cu 3d states at binding energy  $\sim 2.5$  eV. (b) Difference spectrum of AgCu and Ag, plotted with a Cu reference spectrum demonstrate that the Cu 3d states in AgCu are one fifth the width they are in bulk Cu. (c) Calculated Cu-based pDOS of  $Ag_{31}Cu_1$  (d) and pure bulk Cu show that the Cu 3d states of AgCu are nearly degenerate, while they are heavily split in bulk Cu. The near degeneracy in AgCu indicates a very weak interaction between Cu 3d states and the surrounding Ag matrix.

**Figure 2** - Evidence of charge transfer. (a) Cu  $2p_{3/2}$  XPS spectra of elemental copper (red, solid dots) and AgCu (blue, hollow dots) reveal a shift in Cu  $2p_{3/2}$  binding energy for AgCu. After excluding final-state effects as the cause of this shift (see main text), the binding energy shift indicates a higher electron density on the Cu centers in AgCu, compared to bulk Cu. Note, for an accurate binding energy measurement we carefully calibrated the spectrometer's energy scale directly after the measurement of the alloy (with Au  $4f_{7/2}$  of sputter-cleaned Au at 83.98 eV, and Cu  $2p_{3/2}$  at 932.67 eV). (b) The measured Cu  $L_3$  absorption spectra of elemental Cu (red, solid dots) and 0.3 % AgCu (blue, hollow dots) show likewise an edge shift in AgCu, and also signs of higher electron occupation on Cu in AgCu, as evident by the decrease in features  $\beta$  and  $\gamma$ . (c) The calculated Cu  $L_3$  spectra of bulk Cu (red, solid line) and  $Ag_{31}Cu_1$  (blue, dashed line) confirm the observed spectra and indicate that the decrease in features  $\beta$  and  $\gamma$  reflects a filling of Cu 3d  $t_{2g}$  and  $e_g$  states, respectively.

**Figure 3** – Newns-Anderson-Grimley adsorption model. (a) This schematic DOS of an adsorbate bonding to a broad metal band, illustrates how the interaction leads to a broadened adsorbate state. (b) This schematic DOS of an adsorbate bonding to a narrow metal band illustrates how the adsorbate state splits into bonding and anti-bonding states. (c)-(d) The graphical solution to the

Newns-Anderson-Grimley model allows one to identify when adsorbate state broadening and splitting occur. The red semi-ellipses represent the metal DOS, the orange curve is the Hilbert transform of the DOS. The dotted blue line is the adsorption function and the solid blue dots indicate the energy position of the re-hybridized adsorbate states. (c) In the case of a broad metal band, the adsorption function intersects the Hilbert transform only once, indicating that a broad re-hybridized adsorbate state forms. (d) In the case of a narrow metal band, the adsorption function intersects the Hilbert transform three times, indicating that the re-hybridized adsorbate state splits into bonding and anti-bonding orbitals. The two bracketing intersection points indicate the energetic positions of the bonding and anti-bonding orbitals.

**Figure 4** - Formation of new bonds. (a) The pDOS of O adsorbed to Cu and (d) to the Cu site of  $\text{Ag}_{35}\text{Cu}_1$  reveal an important difference in the way the narrow d-band interacts with adsorbates. They show that additional  $\pi$ -bonds can form between the adsorbate and the narrow d-states. The dashed red line indicates the Cu 3d pDOS of the unperturbed metal. The solid blue line represents the pDOS of O 2p states. The filled Gaussian shapes are shown for illustrative purposes to indicate the bonding type of the given pDOS features. (b), (e) Schematic energy-level diagrams of the O 2p states as an O atom adsorbs to the Cu and AgCu surfaces, respectively, illustrate that on bulk Cu, the O  $2p_x$  and  $2p_y$  states do not bond with the Cu 3d band, while on AgCu these state hybridize with the narrow Cu 3d states to form  $\pi$  bonds. (c), (f) Graphical solutions to the Newns-Anderson model for O  $2p_z$  and O  $2p_{x,y}$  illustrate that the reason for the different bonding situations for the broad Cu 3d band and narrow Cu 3d state is the stronger interaction strength of the narrow d-states. The calculated wavefunctions for the states labeled in as  $\sigma$ ,  $\pi$ ,  $\pi^*$  and  $\sigma^*$  illustrate the real-space bonding formed between O and Cu in AgCu.

**Figure 5** – Adsorption energy trends. This plot shows the difference in adsorption energy between adsorbates on bulk copper and the copper center of  $\text{Ag}_{35}\text{Cu}_1$  versus adsorbate electronegativity (relative to electronegativity of copper) for adsorbates of the s- and p-blocks. The dashed grey line indicates cases where there is no difference in covalent bonding between adsorption to Cu and to AgCu. The plot reveals a general trend between bond strength on AgCu and adsorbate electronegativity, where electronegative elements tend to bond stronger to the narrow d-band of AgCu than the broad d-band of Cu. Scatter in the plot can be resolved by separating adsorbates according to group. Symbols are colored according to group and proceed from left to right in the order listed here. Red squares: Group 1 (Cs, Rb, K, Na, Li); Green triangles: Group 2 (Ba, Sr, Ca, Mg, Be); Purple dots: Group 4: (Sn, Ge, Si, C); Orange circles: Group 5 (Sb, As, P, N); Grey cross: Group 6 (Te, Se, S, O); Blue diamonds: Group 7 (I, Br, Cl, F). Energies were calculated using DFT for on-top adsorption geometry.

**Figure 6** – Free-atom-like state in reaction conditions. (a) A valence photoemission spectrum of  $\text{Ag}_{99.5}\text{Cu}_{0.5}$  measured under methanol reforming conditions (0.5 mbar, 1:1  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$ ,  $300^\circ\text{C}$ ) reveals that the narrow Cu 3d band of AgCu can survive reative conditions. (b) Catalytic activity measurements under these conditions yield Arrhenius plots of  $\text{H}_2$  production from  $\text{Ag}_{99.5}\text{Cu}_{0.5}$  (red dots) and Cu (blue dots), and show that the effective activation energy for  $\text{H}_2$  production on AgCu is 0.1 eV lower than on bulk Cu. The error bars in (b) represent three times the standard deviation from four independent replicates. (c),(d) The calculated structures of the transition states of the rate-limiting step for methanol reforming on Cu and  $\text{Ag}_{31}\text{Cu}_1$ , respectively, give insight to why the AgCu exhibits a smaller activation energy. The single bond to H on AgCu, compared to the two bonds to H on bulk Cu indicate that the H-Cu bond on AgCu is much stronger than on bulk Cu. The orange, grey, black, red and white spheres represent Cu, Ag, C, O and H, respectively.

**Figure 7** – Alternative narrow d-band alloys. Calculated pDOS of several Ag-based alloys show that narrow d-bands can exist in other alloy compositions. Among all the transition metal solutes in Ag-based alloys, the only others found to exhibit such strong d-band narrowing were (a) AgNi, (b) AgPd, (c) AgMn and (d) AgCr. The top two alloys exhibit spin degeneracy, while the bottom two exhibit spin splitting. The spin-split cases could play a role in mechanisms involving a magnetic transition state.