Supplementary information

Central role of *d*-band energy level in Cu-based intermetallic alloys

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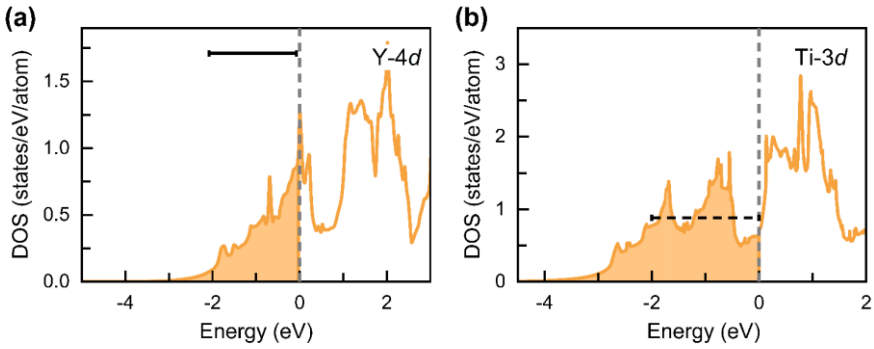
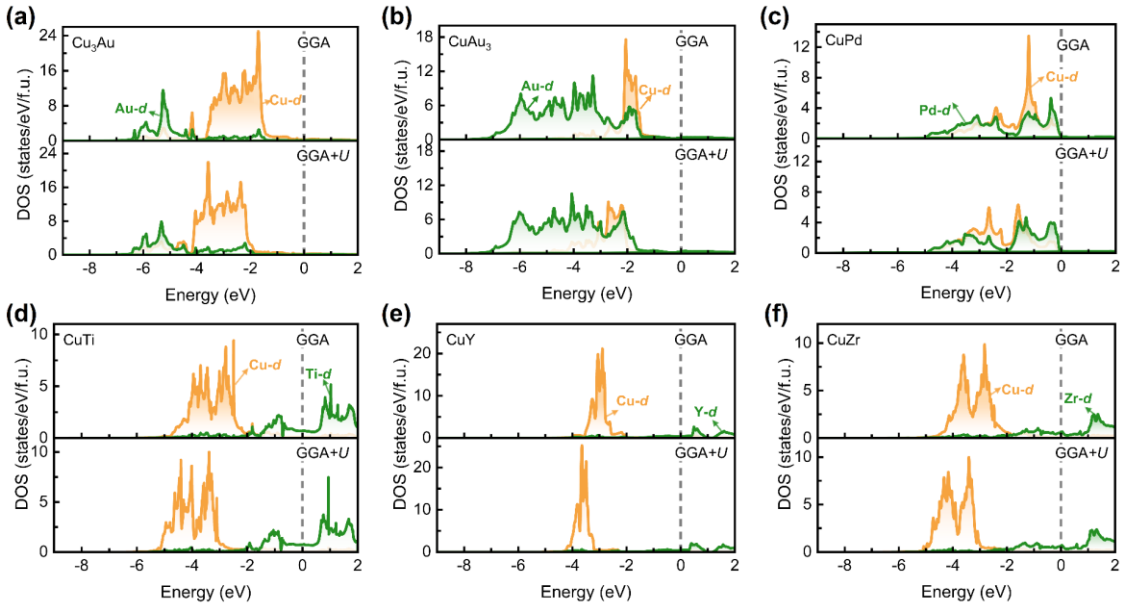
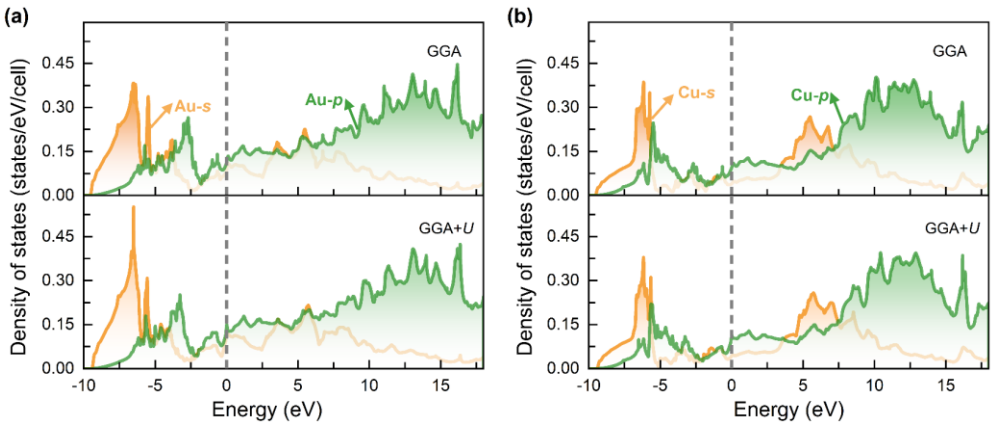


Supplementary Figure 1. Density of states (DOS) of transition metals. DOS of (**a**) Y-4*d* orbital and (**b**) Ti-3*d* orbital, and the vertical dashed line is the Fermi level. The horizontal black solid line in (**a**) indicates experimentally reported *d*-band ranges and the horizontal dashed line in (**b**) indicates the range of experimentally measured *d*-band width at ½ maximum, both are based on the photoemission spectra[1,2].



Supplementary Figure 2. DOS of Cu-TM intermetallic compounds. Calculated density of states of *d*-bands using GGA (up panel) and GGA+*U* (down panel) of Cu-based transition metals. In (**a-f**), the dashed vertical lines show the Fermi energy level.



Supplementary Figure 3. DOS of Au-*s*, Au-*p*, Cu-*s* and Cu-*p* orbitals in CuAu intermetallic alloy. DOS of (**a**) Au and (**b**) Cu in CuAu calculated based on the GGA (up panel) and GGA+*U* (down panel). The dashed vertical lines show the Fermi energy level. Applying *U* values to Cu-3*d* has marginal effects on other orbitals (*s* and *p*) in the alloy.

Supplementary Table 1. Formation energies of Cu-TM intermetallic alloys using GGA and GGA+*U*. Additionally, we give the experimentally determined formation energies of ordered structures of CuY[3], CuSc[4], CuTi[5,6], CuZr[6], CuAu[7], CuZn[8], CuPd[8] and Cu_2Cd[8]. (Units: meV/atom).

	CuY	CuSc	CuTi	CuZr	CuAu	CuZn	CuPd	Cu_2Cd
GGA	-254	-278	-133	-138	-56	-92	-120	8
GGA+*U*	-205	-215	-83	-96	-93	-114	-139	-12
Experiment	-200	-217	-100	-94	-93	-124	-140	-26
	CuV	CuCr	CuMn	CuFe	CuCo	Cu_8Ni	CuNb	CuMo
GGA	135	314	581	142	140	-0.5	196	345
GGA+*U*	201	358	636	173	148	2.6	236	386
Experiment	--	--	--	--	--	--	--	--
	CuTc	CuRu	CuRh	CuAg				
GGA	267	297	65	98				
GGA+*U*	301	320	70	94				
Experiment	--	--	--	--				

Supplementary Table 2. GGA and GGA+*U* calculated band centers of Cu-3*d* and TMs-*d* in CuTM intermetallic alloys.

	CuAu		Cu_3Au		$CuAu_3$		CuPd	
	Cu-3*d*	Au-5*d*	Cu-3*d*	Au-5*d*	Cu-3*d*	Au-5*d*	Cu-3*d*	Pd-4*d*
GGA	-2.48	-4.33	-2.63	-4.59	-2.22	-4.14	-1.82	-2.14
GGA+*U*	-3.13	-4.33	-3.28	-4.55	-2.88	-4.15	-2.32	-2.01
	CuSc		CuTi		CuY		CuZr	
	Cu-3*d*	Sc-3*d*	Cu-3*d*	Ti-3*d*	Cu-3*d*	Y-4*d*	Cu-3*d*	Zr-4*d*
GGA	-3.12	-1.86	-3.22	-1.52	-2.95	-1.86	-3.16	-1.68
GGA+*U*	-3.71	-1.84	-3.85	-1.51	-3.55	-1.80	-3.79	-1.68
	CuZn		Cu_2Cd					
	Cu-3*d*	Zn-3*d*	Cu-3*d*	Cd-4*d*				
GGA	-3.18	-7.19	-2.75	-8.57				
GGA+*U*	-3.94	-9.48	-3.45	-10.65				

d-band center is calculated by using the following formula:

$$E_d = \frac{\int_{-\infty}^{0} x\,\rho_x dx}{\int_{-\infty}^{0} \rho_x dx}$$

Here, x is the energy and ρ_x is the density of states of *d*-band in compounds.

Supplementary Discussion

The cohesive energies of Cu-Au intermetallic alloys

The cohesive energies (E_{coh}) of a material M with *n* atoms can be defined as[9,10],

$$E_{coh} = \frac{1}{n}\left(E_M - \sum_{a}^{n} E_a\right) \quad (1)$$

where E_M is the total energy of the bulk material at equilibrium and E_a denotes the corresponding energy of the constituent atoms.

Supplementary Table 3 lists the E_{coh} as obtained from GGA, GGA+*U*, and HSE06. The mean absolute error (MAE) and mean absolute percentage error (MAPE) are calculated with respect to the experimental data[11,12]. It is clear from Supplementary Table 3 that the GGA-calculated E_{coh} of Cu_3Au (-3.420 eV/atom), CuAu (-3.320 eV/atom), and $CuAu_3$ (-3.174 eV/atom) are closer to the experimental measurements [Cu_3Au (-3.650 eV/atom), CuAu (-3.751 eV/atom), and $CuAu_3$ (-3.801 eV/atom)] than the GGA+*U* and HSE06 results. The overall description of the E_{coh} of the Cu-Au systems is best at the GGA level, with a MAPE (MAE) of 11.43 % (0.429 eV/atom), compared to 15.73 % (0.589 eV/atom) and 18.20 % (0.681 eV/atom) for the GGA+*U* and HSE06 results, respectively.

Supplementary Table 3. The cohesive energies (in eV/atom) of Cu_3Au, CuAu and $CuAu_3$ using different DFT approaches (GGA, GGA+*U* and HSE06). The experimental cohesive energies are obtained using Refs. [5,6].

	Cu_3Au	CuAu	$CuAu_3$	MAE (eV/atom)	MAPE (%)
GGA	-3.420	-3.320	-3.174	0.429	11.43
GGA+*U*	-3.163	-3.166	-3.107	0.589	15.73
HSE06	-3.097	-3.074	-2.988	0.681	18.20
Experiment	-3.650	-3.751	-3.801		

Supplementary Table 4. The Millikan charge in the GGA+*U* framework.

	s	*p*	*d*
Cu	0.25	1.06	9.69
Au	0.44	1.04	9.50
Cu in CuAu alloy	0.12	1.19	9.75
Au in CuAu alloy	0.30	1.19	9.45

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