

Nonlocal First-Principles Calculations in Cu-Au and Other Intermetallic Alloys

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Cu-Au is the prototypical alloy system used to exemplify ordering and compound formation, and it serves as a testbed for all new alloy theory methods. Yet, despite the importance of this system, conventional density functional theory (DFT) calculations with semilocal approximations have two dramatic failures in describing the energies of this system: (1) DFT formation energies of the observed Cu_3Au and CuAu compounds are nearly a factor of 2 smaller in magnitude than experimental values, and (2) DFT predicts incorrect ordered ground states for Au-rich compositions. Here, we show how modern extensions of DFT based on nonlocal interactions can rectify both of these failures. Our corrections shed light on improving the theoretical predictions for alloy systems to determine accurate formation energies, order-disorder critical temperatures, phase diagrams, and high-throughput computations.

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Metallic alloy systems exhibit a remarkable variety and complexity of phase diagrams. Cu, Ag, and Au are noble transition metals along the same column in the periodic table with filled $3d$, $4d$, and $5d$ bands. Binary mixtures between these three elements exhibit significantly different phase stability: Experimental phase diagrams [1–5] show that the Cu-Au, Ag-Au, and Cu-Ag binary systems exhibit ordered structures, complete miscibility, and phase separation, respectively. The binary Cu-Au system [2,3] has long been considered the classic paradigm [6] for alloy theory, and hence most new developments in theoretical techniques for phase stability have been tested in this system: the cluster variation method [7], the cluster expansion method to describe atomic configurations [8], the mixed-space cluster expansion method including strain effects [9], the coupling between configurational and vibrational thermodynamics [9], and calculation of phase diagrams (CALPHAD) methods [10]. Cu-Au is known experimentally to form intermetallic compounds [2–5] at $x_{\text{Au}} = 0.25$ (Cu_3Au) and 0.5 (CuAu), and the crystal structures are well established to be $L1_2$ and $L1_0$, respectively. Although the structure of the ordered phase in Au-rich Cu-Au is not as well established, it has been suggested that the stable Au-rich low- T phase is CuAu_3 in the $L1_2$ structure [2–5]. The experimentally determined heats of formation (at 320 K) [1] of ordered Cu-Au compounds at $x_{\text{Au}} = 0.25$ (Cu_3Au), 0.5 (CuAu), and 0.75 (not-fully-ordered CuAu_3) are -74 , -93 , and -39 meV/atom, respectively [Fig. 1(a)].

First-principles density-functional theory (DFT) based on (semi)local exchange-correlation (XC) functionals [such as the local density approximation (LDA) and generalized gradient approximation (GGA)] has been used to successfully predict a wide range of solid properties. However, although Cu-Au is such an important alloy system, currently

all DFT (LDA or GGA) calculations have two dramatic failures in describing the energies of this system. (1) There exists a large discrepancy between DFT (LDA or GGA) formation energies and experimental values. DFT-calculated formation energies in Cu-Au [9,11–15] are approximately half of the experimental values [the DFT-GGA(LDA) values are -44 (-37) and -56 (-48) meV/atom in Cu_3Au and CuAu , respectively, whereas the experimental formation energies are -74 and -93 meV/atom. See Table I]. The inclusion of vibrational thermodynamic contributions does not significantly change these energies: The theoretically calculated formation energies at a finite temperature (300 K) are only slightly different (< 1 meV/atom based on our phonon calculations) from those without phonon contributions. (2) DFT (LDA or GGA) calculations predict experimentally unobserved ground state structures for the Au-rich portion of the Cu-Au phase. Using the cluster expansion method and DFT calculations, Ozoliņš *et al.* [9] found a stable Au-rich phase ($x_{\text{Au}} = 0.667$), $\text{CuAu}_2\text{-}\beta_2$, which is not observed experimentally, and predicted that the ordered CuAu_3 phase with the $L1_2$ structure is not stable (not only above the tie line connecting CuAu_2 and Au, but also above the tie line connecting CuAu and Au). The source of such a large formation energy discrepancy and incorrect ordered ground states ground state line at the Au-rich side in Cu-Au has been an unanswered question for many years. In the present Letter, we show that both of these discrepancies can be corrected by the inclusion of medium-range exchange interactions in the exchange-correlation energy functional. Here, we adopt a hybrid functional that mixes exact exchange with a semilocal exchange-correlation functional. We have further validated the extent of our conclusion by testing hybrid functionals on intermetallic systems in which a semilocal XC already describes the formation energies well (i.e., systems for which the discrepancies of Cu-Au do

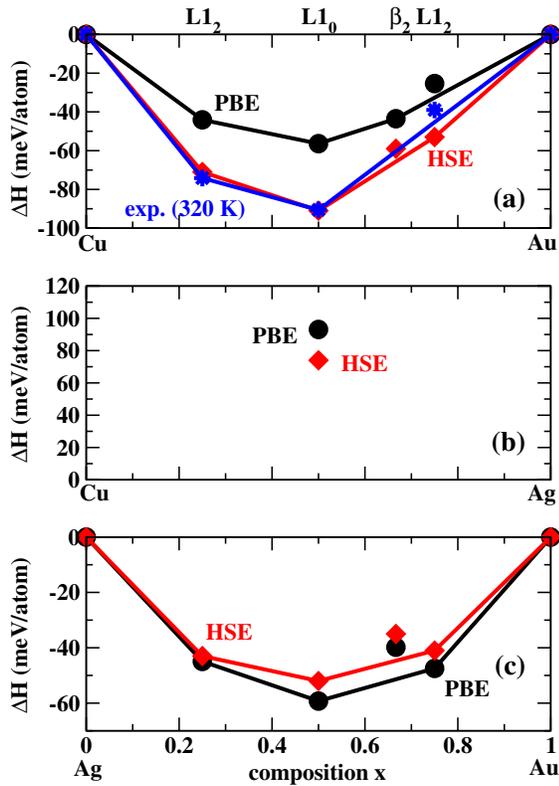


FIG. 1 (color online). Formation energy (ΔH) convex hulls of three alloy systems [Cu-Au (a), Cu-Ag (b), and Ag-Au (c)] using different methodologies (PBE and HSE). The filled black circle and red diamond and lines represent DFT calculations using PBE and HSE, respectively. The blue star line is the experimental formation energy of ordered Cu-Au at 320 K [1].

not exist). We find a strong validation of our conclusion by testing the alloy systems Ag-Au, Cu-Ag, Al_2Ca , and CuPd, in which nonlocal DFT calculations result in similar formation energies as those using semilocal calculations.

In this Letter, we use DFT to study several different alloy systems: Cu-Au, Ag-Au, Cu-Ag, Al-Ca, and Cu-Pd. For Cu-Au, Ag-Au, and Cu-Ag, we investigate alloy compounds at $x = 0.25, 0.5, 0.667,$ and 0.75 with structures $L1_2, L1_0, \beta_2,$ and $L1_2$, respectively. (For Cu-Ag, we only

study the $L1_0$ structure as a prototypical ordered phase since the system is actually observed to phase separate.) We perform DFT calculations using the Vienna *Ab Initio* Simulation Package (VASP) code with the projector-augmented wave (PAW) scheme [16]. We employ the PAW potentials with projectors above the vacuum level, since these are the most accurate potentials presently distributed with VASP (labeled GW). We systematically use different approximations to treat the electronic XC energy: the semilocal GGA of Perdew, Burke, and Ernzerhof (PBE) [17], and the hybrid XC developed by Heyd, Scuseria, and Ernzerhof (HSE06 or HSE for simplicity) [18]. The energy cutoff for the plane wave expansion of the electronic orbitals is 600 eV. The Brillouin zones are sampled by Monkhorst-Pack [19] k point meshes to yield energies converged to within 2 meV/atom. Atomic positions and lattice parameters are both relaxed until all the forces and components of the stress tensor are below 0.01 eV/Å and 0.2 kbar, respectively.

The semilocal PBE functional is a widely used exchange-correlation approximation in solid system simulations and successfully predicts a wide range of properties. Therefore, as a baseline for semilocal DFT, we use PBE to predict the energetics of Cu-Au. For the Cu-Au alloy, our PBE formation energies [the black circle/line in Fig. 1(a), Table I] are very similar to the LDA results in Ref. [9]: We find similar formation energies, specifically, an unstable CuAu_3 phase and a stable CuAu_2 phase. The PBE-calculated formation energies of Cu_3Au and CuAu are ~ 40 meV/atom higher (more positive) or roughly a factor of 2 smaller in magnitude than experimental values of ordered phases at 320 K. Different basis sets [9] (such as the linearized augmented plane wave method) to construct the orbitals have been used in Cu-Au theoretical calculations (Table I), but none of them result in Cu-Au formation energies in quantitative agreement with the experimental values. Therefore, the large formation energy discrepancy appears to be caused by the semilocal PBE exchange-correlation approximation. We hypothesize that a more accurate XC functional (e.g., including the nonlocal exchange interactions) is necessary for quantitatively accurate energetics in the Cu-Au system.

TABLE I. Formation energies of three alloy systems (Cu-Au, Ag-Au, and Cu-Ag) using different DFT approaches (LDA, PBE, or HSE) on ordered structures. The LDA results [9] are using linearized augmented plane wave basis sets. Additionally, we give the experimentally determined formation energies of ordered structures of Cu-Au (320 K) [1]. (The formation energy of CuAu_3 is from a not-fully-ordered experimental structure [1].) (units: meV/atom).

	Cu_3Au	CuAu	CuAu_2	CuAu_3	CuAg	Ag_3Au	AgAu	AgAu_2	AgAu_3
Ordered	$L1_2$	$L1_0$	β_2	$L1_2$	$L1_0$	$L1_2$	$L1_0$	β_2	$L1_2$
Experiment (ordered) [1]	-74	-93	...	-39
LDA [9]	-37	-48	-41	-17					
PBE	-44	-56	-44	-25	93	-45	-59	-40	-47
HSE	-71	-91	-59	-53	74	-43	-52	-37	-41

We turn to the HSE hybrid functional calculations to include these nonlocal exchange interactions. We perform the HSE hybrid calculations self-consistently, and fully relax all cell-internal and -external degrees of freedom. For the Cu-Au alloy, the HSE formation energies (Table I) of Cu_3Au (-71 meV/atom) and CuAu (-91 meV/atom) are significantly more negative than those using PBE, and are in excellent agreement with the experimentally measured values [1] (-74 and -93 meV/atom for Cu_3Au and CuAu). The HSE theoretical ground state line [the red diamond/lines in Fig. 1(a)] contains $\text{Cu}_3\text{Au}-L1_2$, $\text{CuAu}-L1_0$, and CuAu_3-L1_2 . It is specifically noteworthy that the Au-rich compound suggested by experimental reports, CuAu_3-L1_2 , is a stable phase in the HSE calculations (but not PBE), whereas the $\text{CuAu}_2-\beta_2$ compound is unstable in HSE calculations (but erroneously predicted to be stable by PBE). The HSE formation energy of the perfectly stoichiometric ordered CuAu_3-L1_2 structure is -53 meV/atom, slightly lower than the experimentally measured -39 meV/atom. Some of this small difference with experiment could be due to the lack of complete order in the experimental CuAu_3 phase, which would raise its formation energy [1]. The good agreement between theoretical calculations and experimental measurements in Cu-Au confirms our hypothesis that the nonlocal exchange interactions in the exchange-correlation functionals play an important role in formation energies in Cu-Au. We also investigate the effect of the HSE calculations on lattice constants. The lattice constants of Cu, Cu_3Au , CuAu , CuAu_3 , Au, and Ag using PBE are overestimated compared to the experimental values [5,20] (Fig. 2), typical of the PBE functional. Including the nonlocal interactions in HSE results in lattice constants much closer to experimental values (Fig. 2).

To understand the physical contributions of nonlocal exchange interactions in the formation energy calculations, we plot the electronic density of states (eDOS) of the d band of Cu($3d$), Ag($4d$), Au($5d$), and CuAu ($3d + 5d$) (we only show the eDOS of CuAu as an example) using PBE and HSE (Fig. 3). The PBE eDOS of the fcc Cu, Ag, and Au (the black lines in Fig. 3) are in good agreement with previous theoretical work [21]. We estimate the width of the

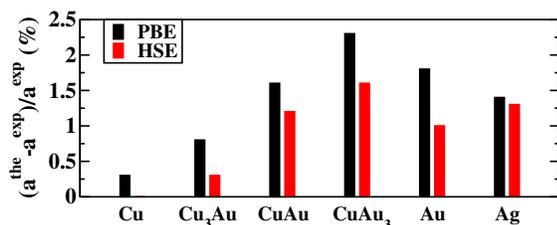


FIG. 2 (color online). Lattice constant differences between theoretical predictions and experimental determinations in Cu-fcc, $\text{Cu}_3\text{Au}-L1_2$, $\text{CuAu}-L1_0$, CuAu_3-L1_2 , Au-fcc, and Ag-fcc. The black and red bars represent DFT calculations using PBE and HSE, respectively. HSE predicts the same Cu-fcc lattice constant as the experimental determinations.

d band by I^d/A_{eDOS}^d , where I^d is the integral over energy of the d -band eDOS and A_{eDOS}^d is the average value of the d -band eDOS. The PBE-calculated d -band widths (the black lines in Fig. 3) of Cu (3.5 eV) and Ag (3.5 eV) are similar to experimental measurements [Cu ($\sim 3-4$ eV) [22,23] and Ag (~ 3.5) [22]], but the d -band widths of Au (5.2 eV) and CuAu (5.4 eV) are ~ 0.8 and ~ 0.6 eV smaller than the experimental value (~ 6 eV) [22,24], respectively. The PBE-calculated d -band edges of Cu, Ag, Au, and CuAu are significantly different from the experimental measurements (the grey regions in Fig. 3), and the theoretically calculated d bands using PBE are shifted towards the Fermi level. Using the HSE functional with nonlocal exchange interactions, the theoretically calculated d bands (the red lines in Fig. 3) shift towards lower energies compared to PBE. This d -band shift makes the HSE theoretical d -band edges nearly the same as those from experimental measurements (the grey regions in Fig. 3). Furthermore, we find that the HSE calculated widths of the d band of Cu (3.9 eV), Au (5.6 eV) and CuAu (5.7 eV) are broadened compared to those using PBE, which leads to a good agreement with the experimentally measured d -band widths (the grey regions in Fig. 3). For Ag, the width of HSE d band is 3.6 eV, which is similar to the experimental and PBE calculated value. The observed changes are in full agreement with our expectations. Nonlocal Hartree-Fock-like exchange always lowers fully occupied shells, in this case the d states, and concomitantly spatially contracts the

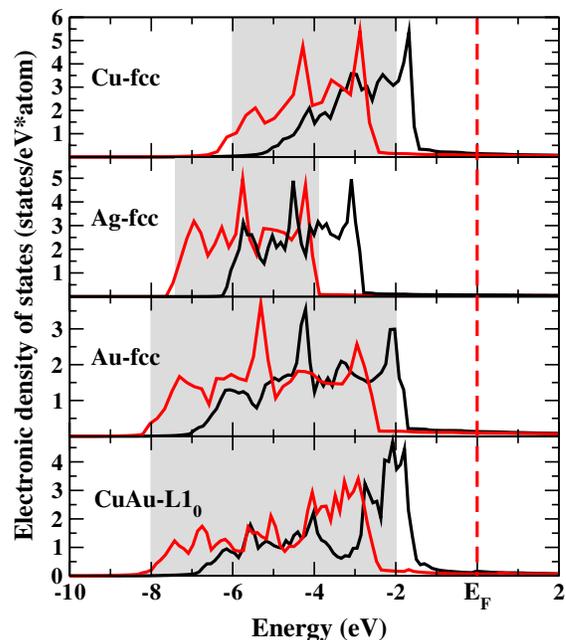


FIG. 3 (color online). Theoretically calculated electronic density of states of d -band [from top to bottom: Cu-fcc($3d$), Ag-fcc($4d$), Au-fcc($5d$), and $\text{CuAu}-L1_0$ ($3d + 5d$)] using PBE (black lines) and HSE (red lines). The red dashed line is the Fermi level and the grey regions are the experimentally determined d -band ranges [22–24].

orbitals. This results in a reduced Pauli repulsion between the d states, decreasing the lattice constants and increasing the formation energies, exactly paralleling our modeling results. Our results clearly demonstrate that the inaccurate description of d orbitals in PBE is a serious issue for the accurate description of intermetallic compounds involving Cu, Ag, and Au.

In order to further validate our findings, we next turn to other alloy systems (Cu-Ag, Ag-Au, Al_2Ca , and CuPd) which seemingly do not have the same discrepancy between experiment and semilocal DFT calculations. For the Cu-Ag alloy, formation energies calculated both by semilocal PBE [the black circle in Fig. 1(b) and Table I] and nonlocal HSE [the red circle in Fig. 1(b) and Table I] of the ordered CuAg-L1_0 structure are significantly positive, which agrees with the phase separation tendencies experimentally observed in the Cu-Ag phase diagram. For the Ag-Au system, the experimental phase diagram shows complete miscibility across the entire composition range [3–5]. For computational efficiency, we perform calculations of small-unit-cell ordered compounds ($\text{Ag}_3\text{Au-L1}_2$, AgAu-L1_0 , $\text{AgAu}_2\text{-}\beta_2$, and $\text{AgAu}_3\text{-L1}_2$) rather than the observed disordered solid solution phases. Both PBE and HSE give similar Ag-Au formation energies of ordered crystal structures (Table I). Constructing the ground-state convex hulls [Fig. 1(c)] from our PBE- and HSE-calculated energies (Table I), we find Ag_3Au , AgAu , and AgAu_3 are stable (but not AgAu_2), in agreement with previous LDA calculations in Ref. [9].

We further test the accuracy of hybrid functionals for intermetallic compounds by examining two well-known compounds, Al_2Ca and CuPd [3]. We choose these two compounds because they have experimentally well-established values of the formation energies, -304 ± 9 [25] and -140 ± 21 meV/atom [3], respectively. The PBE-calculated formation energies (-334 and -120 meV/atom for Al_2Ca and CuPd) are in good agreement with the experimental values. HSE calculations give an Al_2Ca formation energy of -310 meV/atom, which is in excellent agreement with the experimental value; the CuPd formation energy is -170 meV/atom, which is close to the experimental value. In both cases, corrections from nonlocal exchange are towards the experimental values (although somewhat “overcorrecting” in the CuPd case). All of these calculations demonstrate that even in intermetallic systems which are well described by the semilocal PBE functional (Cu-Ag, Ag-Au, Al_2Ca , and CuPd), the nonlocal HSE functional shows reasonable or better results. These results strongly validate the improvement in accuracy when using HSE for intermetallics.

The results of the current Letter have significant implications for intermetallic systems beyond just the Cu-Au system. In a recent high-throughput DFT study, Curtarolo *et al.* [26] surveyed the ordering tendencies of a large number (435) of d -electron binary intermetallics using

(semilocal) DFT and found 20% of the calculated formation energies did not even qualitatively agree with the sign of the experimental measurements. Our results suggest that nonlocal DFT calculations could possibly reconcile many of these discrepancies. For example, experimentalists observe that the mixing of Cu and Cd can yield ordered phases, such as Cu_2Cd (the experimentally determined formation energy is -26 meV/atom) [3]. But the semilocal PBE predicts no mixing of Cu and Cd (the PBE-calculated formation energy of Cu_2Cd is $+5$ meV/atom). In an attempt to solve this controversy, we carried out nonlocal HSE calculations of Cu_2Cd , and find a formation energy of -18 meV/atom, which is the opposite sign from PBE results, and is in good agreement with the experimental measurements. Thus, we suggest that the formation energies, lattice parameters, and other properties of a wide range of intermetallic compounds could be improved by using the nonlocal HSE functional.

Our work clearly demonstrates the importance of the nonlocal exchange in intermetallic compounds, whereas conventional wisdom assumes that the nonlocal exchange is only of relevance for insulators and semiconductors. Nonlocal interactions significantly influence the electronic structures of Cu and Au. Using the nonlocal HSE functional, we have rectified the failures in the Cu-Au system: The formation energies and ordered ground state line are in excellent agreement with the experimental measurements, and the experimentally suggested $\text{CuAu}_3\text{-L1}_2$ structure is a stable phase. (For other alloys such as Ag-Au, Cu-Ag, Al_2Ca , and CuPd, both HSE and PBE give similar results.) Our corrections in the Cu-Au system shed light on improving the theoretical performance in alloy systems to determine correct formation energies, order-disorder critical temperatures, phase diagrams, high-throughput computations, and so forth.

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