Why are the 3*d*-5*d* compounds CuAu and NiPt stable, whereas the 3*d*-4*d* compounds CuAg and NiPd are not

L. G. Wang and Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401
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We show that the existence of stable, ordered $3d$-$5d$ intermetallics CuAu and NiPt, as opposed to the unstable $3d$-$4d$ isovalent analogs CuAg and NiPd, results from relativity. First, in shrinking the equilibrium volume of the $5d$ element, relativity reduces the atomic size mismatch with respect to the $3d$ element, thus lowering the elastic packing strain. Second, in lowering the energy of the bonding $6s,p$ bands and raising the energy of the $5d$ band, relativity enhances ~diminishes! the occupation of the bonding ~antibonding! bands. The raising of the energy of the $5d$ band also brings it closer to the energy of the $3d$ band, improving the $3d$-$5d$ bonding.

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Remarkable differences were recently noted between the physical properties of the late $5d$ elements Ir, Pt, and Au and the corresponding isovalent $4d$ elements Rh, Pd, and Ag. For example, whereas the surfaces[1–3] of these $5d$ metals reconstruct, those of the $4d$ metals do not. Similarly, nanowires[4–6] of these $5d$ elements evolve spontaneously into remarkably stable single-atom chains, whereas $4d$ wires do not. Both phenomena were explained[2,3,5] in terms of the relativistic effects in low-coordination $5d$ elements: Due to the relativistic mass increase $m_i = m_0/\sqrt{1-(v_i/c)^2}$ ~where m_0 is the rest mass and v_i is the speed of electron in orbital i!, the orbital radius $a_i = (4\pi\epsilon_0\hbar^2/m_0e^2Z)\sqrt{1-(v_i$

correlation functional of Ceperley and Alder,[19] parametrized by Perdew and Zunger.[20] ~We have checked the effect of exchange-correlation by comparing the formation energy of $L1_0$ CuAu using the generalized gradient approximation exchange-correlation functional[21] giving $\Delta H = -49.4$ meV/atom, and the local density apprpximation[19,20] functional giving $\Delta H = -49.5$ meV/atom.! The plane wave basis used had a cutoff energy of 16 Ry, whereas the cutoff for charge density and potential was 82 Ry. A **k** mesh equivalent[22] to the 60 special points of the $8\times8\times8$ fcc mesh was used in the evaluation of Brillouin zone integrals. The muffin-tin radii were set to $R_{\mathrm{Ni}}=R_{\mathrm{Cu}}=2.2a_0$, $R_{\mathrm{Pd}}=R_{\mathrm{Pt}}=2.3a_0$, and $R_{\mathrm{Ag}}=R_{\mathrm{Au}}=2.4a_0$, where a_0 is the Bohr radius. With these parameters ΔH was converged to within 2 meV/atom.

Table I gives the calculated formation energies of the $L1_0$ structure of NiPd, NiPt, CuAg, and CuAu calculated relativistically ~R! as well as nonrelativistically ~NR!. In our calculation, the core states are treated fully relativistically whereas the valence states are calculated scalar-relativistically ~without spin-orbit coupling!. This treatment is reasonable because the spin-orbit interaction only plays a trivial role in stabilizing long-range order phases.[23] The relativistically calculated formation energies ~in meV/atom! are $+49.3$, -85.1, $+102.08$, and -49.53, for NiPd, NiPt, CuAg, and CuAu. We see the clear compound-forming trend of CuAu and NiPt ($\Delta H<0$), as contrasted with the phase-separating trend ($\Delta H>0$) of CuAg and NiPd.

$-a_B^0)/(a_A^0+a_B^0)$ associated with lattice packing is reduced from 18.3% and 16.3% for nonrelativistic CuAu and NiPt, to 13.9% and 12.6%, respectively, in the relativistic limit. In contrast, in the $3d$-$4d$

bands and a decreased occupation of the *antibonding d* band. These effects can be appreciated by inspecting the calculated atom-projected *d*-band density of states ~Fig. 2! and the integrated orbital charges in Table II. Indeed, from Fig. 2 we can see that the 5*d* and 3*d* bands are closer to each other in the relativistic limit than in the nonrelativistic limit: Nonrelativistic CuAu has a largest separation between the 5*d* and 3*d* bands, the next is nonrelativistic CuAg, then is relativistic CuAg, and the last is relativistic CuAu ~see the arrows in Fig. 2, which mark the valley between two *d* bands!. This order coincides with the decreasing order of formation energies D*H*, 165.4, 127.1, 102.1, and -49.5 meV/atom, respectively. We find the same trend for NiPt~NR!, NiPd~NR!, NiPd~R!, and NiPt~R!. Also, for NiPt~R! and CuAu~R!, which have negative formation energies, the *d* bands are much wider ~resulting in better overlap! than in the nonrelativistic limit and with respect to the corresponding 3*d*-4*d* cases. The larger 3*d*-5*d* [illegible] (limirb131n-4)r.b 22.5285 0 TD (d)1(thn)-3tF11 1 1 1teF1