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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 $a_i = (4\pi\epsilon_0\hbar^2/m_0e^2Z)\sqrt{1-(v_i/c)^2}$ will shrink, especially for the high-speed inner electrons. For $1s$ electrons in the nonrelativistic limit[7] the average speed v_{1s} is Z a.u.. Thus, for Au, $v_{1s}/c = 79/137 = 0.5766$, implying a $1s$ orbital shrinkage of 18.3%. This relativistic contraction does not occur for the d electrons which experience a large centrifugal force $l(l+1)/r^2$. The relativistic s-orbital contraction has long been associated[8] with the ‘‘inert pair effect’’ in coordination chemistry, whereby the tightly bound $6s^2$ electrons become chemically inert (unoxidized) in compounds of Tl, Pb, and Bi which consequently have effective chemical valences of 1, 2, and 3, respectively, rather than 3, 4, and 5 implied by their outer electron configuration s^2p^1, s^2p^2, and s^2p^3 (like the corresponding elements Ga, Ge, and As, higher up in the Periodic Table column). Now the relativistic contraction of the s orbitals lowers their orbital energies. At the same time, this contraction better screens the nucleus, causing the outer d electrons to experience lesser binding, and therefore a larger spatial extent. In *elemental* forms of the late $5d$ metals (bulk, surface, and chains), bonding is supplied by the s band at the Fermi energy ε_F, and by the deeper lying d band. The relativistic lowering of the energy of the s band, and the associated raising of the energy of the d band brings the s band closer to the d band. This enhances the s-d hybridization and leads in low-coordination structures to the formation of strong bonds, favoring surface reconstruction[1–3] and atomic chain formation[4–6] in Ir, Pt, and Au, but not in Rh, Pd, and Ag. The opposing relativistic shifts in the energies of the $6s$ and $5d$ orbitals have also been implicated[9] in the colors of Au and Ag: while the $5d \rightarrow \epsilon_F(s)$ absorption onset (2.4 eV) in Au renders it a gold color, in Ag the relativistic lowering of the s band and the raising of the d band are much smaller, so the $4d \rightarrow \epsilon_F(s)$ onset (3.7 eV) is in the ultraviolet, making Ag white.

The above discussions pertain to $4d$ and $5d$ *elements*. Here we discuss relativistic effects on *compounds*. Although it is well known at the level of standard chemistry[10] that the main chemical difference between pairs of $4d$ and $5d$ transition elements from Nb/Ta through Ag/Au is the relativistic contraction of the valence s and p states relative to the d and f states, here we provide a quantitative, electronic structure analysis of this effect, and demonstrate its consequences on phase stability. We show, via first-principles calculations, that in binary *compounds* of late $3d$-$5d$ intermetallics, the *intersublattice* $3d$-$5d$ coupling is dominant. This effect results from the relativistic upshift of the $5d$ band, which brings it closer to the $3d$ band of the *other* element, significantly enhancing $3d$-$5d$ bonding. In addition, the relativistic s orbital contraction significantly reduces the lattice constant of the $5d$ element, thus lowering the size mismatch with the $3d$ element.[11] This reduces the strain energy associated with packing $3d$ and $5d$ atoms of dissimilar sizes onto a given lattice.[2,3] Both the enhanced d-d chemical bonding and the reduced packing strain are larger in $3d$-$5d$ intermetallics than in $3d$-$4d$. This explains the long standing[12] puzzle of why the $3d$-$5d$ compounds CuAu and NiPt have negative formation enthalpies[13] $(\Delta H < 0)$, and thus form stable ordered compounds,[14] whereas the analogous isovalent $3d$-$4d$ compounds CuAg and NiPd, made of elements from the same columns in the periodic table, have[13,15] $\Delta H > 0$ and thus phase separate.[14] Simple arguments, such as atomic size-mismatch or electronegativity differences, do not explain this puzzle: The constituent elements in the stable $(\Delta H < 0)$ NiPt and CuAu compounds have *larger* atomic size mismatch than the unstable $(\Delta H > 0)$ NiPd and CuAg. Likewise, the stable NiPt has a *smaller* (Batsanov[16]) electronegativity difference than unstable CuAg. Furthermore, the *ab initio* calculated charge density of NiPt and NiPd (the upper panels of Fig. 1) are extremely similar, giving no hint why NiPt is stable, whereas NiPd is not.

We employ in our calculations the full-potential linearized augmented plane wave method[17,18] and the exchange-

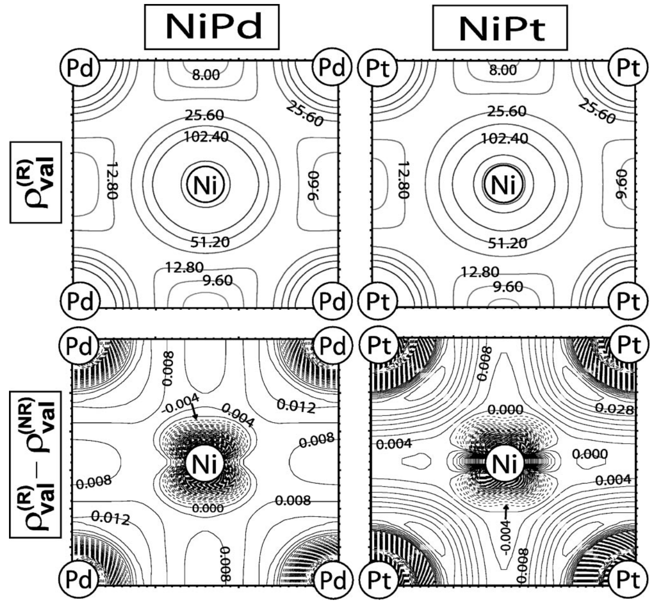

FIG. 1. Upper panels: The valence charge density for NiPd and NiPt, calculated relativistically, showing no discernible differences. Lower panels: Showing that relativity strongly enhances the bonding charge density in NiPt, but not in NiPd. The contour step for the charge density difference $\rho_{\mathrm{val}}^{(\mathrm{R})}(r)-\rho_{\mathrm{val}}^{(\mathrm{NR})}(r)$ in the lower panels is $0.004e/\text{Å}^3$.

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.

To gain better insight into those trends, we have decomposed[11] the total formation energies $\Delta H=\Delta H_{\mathrm{chem}}+\Delta H_{\mathrm{elast}}$ into "chemical" (chem) and "elastic" (elast) parts, as follows: The "elastic energy of formation" is the energy needed to deform the elemental solids A and B from their respective equilibrium lattice constants a_{A}^0 and a_{B}^0, to the lattice constants $\bar{a}$ of the final AB compound (here, $L1_0$):

$$\Delta H_{\mathrm{elast}}=x[E_A(\bar{a})-E_A(a_A^0)]+(1-x)[E_B(\bar{a})-E_B(a_B^0)]. \tag{1}$$

Since a deformation of equilibrium structures is involved, $\Delta H_{\mathrm{elast}}>0$. The "chemical energy of formation" is simply the difference between the (fully relaxed) total energy $E(A_xB_{1-x};\bar{a})$ of the compound, and the energies of the deformed constituents,

$$\Delta H_{\mathrm{chem}}=E(A_xB_{1-x};\bar{a})-xE_A(\bar{a})-(1-x)E_B(\bar{a}). \tag{2}$$

Thus $\Delta H_{\mathrm{elast}}$ is a volume-deformation energy of the constituents, whereas ΔH_{chem} is the constant-volume energy change between the "prepared" constituents and the compound, and consists of any chemical effect such as hybridization, charge-transfer, altered band occupation, etc. Clearly, the sum $\Delta H_{\mathrm{chem}}+\Delta H_{\mathrm{elast}}$ gives the conventional definition of compound formation energy.

Table I shows that the relativistic effect significantly *reduces* the "elastic energy of formation" of $3d$-$5d$ compounds (e.g., from $+549.2$ to $+404.5$ in NiPt, and from $+477.8$ to $+373.1$ in CuAu). This effect is much smaller in the $3d$-$4d$ compounds (e.g. from $+286.3$ to $+269.7$ in NiPd, and from $+267.4$ to $+254.8$ in CuAg). The reason for this can be appreciated by inspecting the nonrelativistically- and relativistically-calculated equilibrium lattice constants of the fcc elements, given in Table I: Relativity significantly reduces a_{Au}^0 and a_{Pt}^0 (by 5.2% and 4.2%), but does not change a_{Cu}^0 and a_{Ni}^0 much. Consequently, the strain $\epsilon=2(a_A^0$

TABLE I. Calculated $L1_0$ formation energies (in meV/atom) and equilibrium lattice constants (in a.u.) of the elemental solids and compounds with or without the relativistic effect. Note how relativity reduces the lattice constants, especially of the heavy element B, and its compound.

	Relativistic							Nonrelativistic						
	ΔH	ΔH_{chem}	$\Delta H_{\mathrm{elast}}$	a_A	a_B	a_{L1_0}	c/a	ΔH	ΔH_{chem}	$\Delta H_{\mathrm{elast}}$	a_A	a_B	a_{L1_0}	c/a
NiPd	+49.3	−220.4	+269.7	6.508	7.278	7.111	0.924	+84.6	−201.7	+286.3	6.544	7.388	7.192	0.922
NiPt	−85.1	−489.6	+404.5	6.508	7.384	7.175	0.927	+111.1	−438.1	+549.2	6.544	7.703	7.389	0.913
CuAg	+102.1	−152.7	+254.8	6.663	7.573	7.363	0.924	+127.1	−140.3	+267.4	6.712	7.726	7.472	0.924
CuAu	−49.5	−422.6	+373.1	6.663	7.659	7.413	0.918	+165.4	−312.4	+477.8	6.712	8.064	7.678	0.917

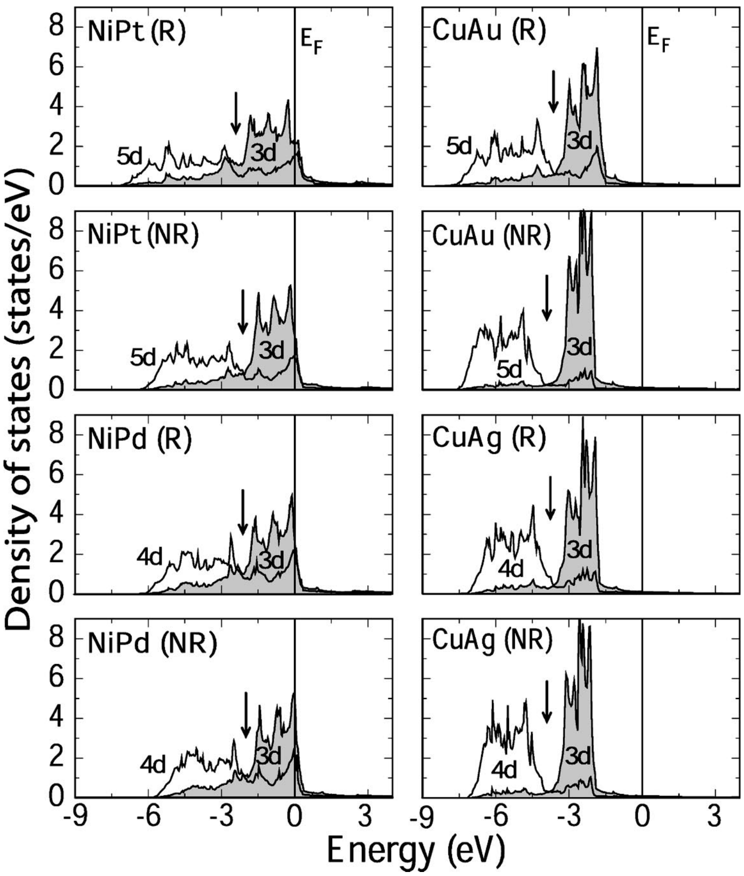

FIG. 2. The atom-projected local density of states (DOS) of the *d* bands.

$-a_B^0)/(a_A^0+a_B^0)$ 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 $3d$-$4d$ case, relativity reduces the strain only from 14.1% to 12.8% in CuAg, and from 12.1% to 11.2% in NiPd. Note that the *stable* compounds NiPt and CuAu have a larger strain energy and atomic size-mismatch than the unstable NiPd and CuAg, respectively.

In addition to reduction in the (positive) ‘‘elastic energy of formation,’’ Table I shows that relativity enhances the (negative) ‘‘chemical energy of formation’’ (e.g., from -438.1 to -489.6 in NiPt, and from -312.4 to -422.6 in CuAu). This effect is much smaller in $3d$-$4d$ compounds (e.g., from -201.7 to -220.4 in NiPd, and from -140.3 to -152.7 in CuAg). We find two effects that explain this relativistic chemical stabilization: First, the relativistic raising of the energy of the $5d$ state reduces the $3d$-$5d$ energy difference and thus improve the $3d$-$5d$ bonding; second, the relativistic lowering the *s* and *p* bands and raising of the *d* band leads to an increased occupation of the *bonding* *s* and *p*

TABLE II. Integrated number of electrons of each angular momentum type within the atomic spheres of Ni, Cu, Pd, Ag, Pt, and Au with radii $R_{\mathrm{Ni}}=R_{\mathrm{Cu}}=2.2a_0$, $R_{\mathrm{Pd}}=R_{\mathrm{Pt}}=2.3a_0$, and $R_{\mathrm{Ag}}=R_{\mathrm{Au}}=2.4a_0$, respectively. ‘‘tot’’ represents total valence electrons in the atomic sphere.

		Relativistic (R)				Nonrelativistic (NR)				R vs NR difference			
		s	*p*	*d*	tot	*s*	*p*	*d*	tot	*s*	*p*	*d*	tot
NiPt	Ni	0.35	0.35	8.17	8.86	0.33	0.28	8.20	8.81	0.02	0.07	−0.03	0.05
	Pt	0.42	0.30	7.11	7.83	0.24	0.21	7.45	7.91	0.18	0.09	−0.34	−0.08
NiPd	Ni	0.37	0.32	8.13	8.82	0.35	0.28	8.19	8.82	0.02	0.04	−0.06	0.00
	Pd	0.33	0.28	7.77	8.37	0.27	0.24	7.88	8.39	0.06	0.04	−0.11	−0.02
CuAu	Cu	0.36	0.30	9.13	9.78	0.35	0.24	9.20	9.78	0.01	0.06	−0.07	0.00
	Au	0.44	0.27	8.09	8.81	0.25	0.20	8.39	8.84	0.19	0.07	−0.30	−0.03
CuAg	Cu	0.38	0.28	9.12	9.78	0.36	0.25	9.16	9.78	0.02	0.03	−0.04	0.00
	Ag	0.34	0.26	8.71	9.31	0.29	0.23	8.84	9.36	0.05	0.03	−0.13	0.05

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 $5d$ and $3d$ bands are closer to each other in the relativistic limit than in the nonrelativistic limit: Nonrelativistic CuAu has a largest separation between the $5d$ and $3d$ 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 ΔH, 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 $3d$-$4d$ cases. The larger $3d$-$5d$ overlap in NiPt than in CuAu may also explain the more negative formation energy in NiPt than in CuAu. Therefore, we conclude that the d-d interaction from different sublattices in late d compounds plays a key role.

The second effect is that relativity results in lowering of the energy of the *s* and *p* bands and raising of the energy of the *d* band, which leads to an increased occupation of the *bonding s* and *p* bands and a depletion of the *antibonding* edge of the *d* band in the $5d$ elements. Indeed, from Table II we see that the $5d$ elements Pt and Au gain significant sp occupation ($+0.27e$ in NiPt and $+0.26e$ in CuAu) and lose d occupation ($-0.34e$ in NiPt and -0.30 in CuAu) due to the relativistic effect. The opposing trends in sp and d charge arrangement leads to a small net change in the total charge (noted as the "charge compensation effect"[24]). Since the *bonding* sp band increases its occupation, whereas the upper *antibonding* edge of the d band is depleted, these relativistic effects increase the stability of NiPt and CuAu. In contrast, the relativistic gain in sp occupation and loss of d occupation in the $4d$ elements Pd and Ag is much smaller (Table II). The relativistically-enhanced chemical bonding is illustrated in the lower panels of Fig. 1, which show the difference $\rho_{\mathrm{val}}^{(\mathrm{R})}(r)-\rho_{\mathrm{val}}^{(\mathrm{NR})}(r)$ between the relativistically-calculated and nonrelativistic valence charge densities. We see that relativity results in a strong accumulation of bonding charge on the Ni-Pt bonds, but not on the Ni-Pd bonds. Therefore, relativity enhances strongly the bonding between the $3d$ and $5d$ atoms, but not between the $3d$ and $4d$ atoms.

In summary, we explain the puzzle of why the $3d$-$5d$ late transition metal intermetallics CuAu and NiPt are stable, whereas the isovalent CuAg and NiPd are not, as a *relativistic effect*, and find that the relativistic effect reduces strongly the elastic strain energy in the $3d$-$5d$ compounds due to the reduction of the $3d$ and $5d$ atomic size-mismatch, whereas this effect is much smaller in the $3d$-$4d$ compounds. Furthermore, relativity results in the raising of the energy of the $5d$ band (bringing the $5d$ band closer to the $3d$ band) and in a large charge-transfer from the antibonding edge of the $5d$ band to the bonding $6s,p$ bands, enhancing the chemical stability of the $3d$-$5d$ compounds.

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