Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Pressure-induced Na-Au compounds with novel structural units and unique charge transfer

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Index **Page**

1. Computational details……2
2. Calculated Birch-Murnaghan equation of states for *Cmcm*-structured Na_3Au……4
3. Calculated formation enthalpies per f.u. of stable Na-Au compounds……5
4. Phonon dispersion curves for stable Na-Au compounds……6
5. Electronic band structures calculated by the PBE hybrid functional……7
6. PDOS calculated by the PBE hybrid functional for stable Na-Au compounds……8
7. The PDOS of Au in *Cmmm* Na_0Au and solid Au at 50 GPa……9
8. Superconductive properties of Na_2Au……9
9. Calculated ELF of stable Na-Au compounds……10
10. Structural information of predicted stable Na-Au compounds……11
11. References……13

Computational Details

Our structural prediction approach is based on a global minimization of free energy surfaces merging *ab initio* total-energy calculations with CALYPSO (Crystal structure AnaLYsis by Particle Swarm Optimization) methodology as implemented in the CALYPSO code [1,2]. The structures of stoichiometry Na_xAu_y (x =1-6 and y = 1; x =1 and y = 2; x =3 and y = 2) were searched with simulation cell sizes of 1-4 formula units (f.u.) at 0, 50, and 100 GPa. In the first step, random structures with certain symmetry are constructed in which atomic coordinates are generated by the crystallographic symmetry operations. Local optimizations using the VASP code [3] were done with the conjugate gradients method and stopped when total energy changes became smaller than 1×10^{-5} eV per cell. After processing the first generation structures, 60% of them with lower enthalpies are selected to construct the next generation structures by PSO (Particle Swarm Optimization). 40% of the structures in the new generation are randomly generated. A structure fingerprinting technique of bond characterization matrix is applied to the generated structures, so that identical structures are strictly forbidden. These procedures significantly enhance the diversity of the structures, which is crucial for structural global search efficiency. The structural searching simulations for each stoichiometry were stopped after generating 2000 ~ 2400 structures (e.g., about 20 ~ 30 generations).

To further analyze the structures with higher accuracy, we select a number of structures with lower enthalpies and perform structural optimization using density functional theory within the generalized gradient approximation [4] as implemented in the VASP code. The cut-off energy for the expansion of wavefunctions into plane waves is set to 1000 eV in all calculations, and the Monkhorst–Pack *k*-mesh with a maximum spacing of $2\pi \times 0.02$ Å^{-1} was individually adjusted in reciprocal space with respect to the size of each computational cell. This usually gives total energy well converged within ~1 meV/atom. The electron-ion interaction was described by means of projector augmented wave with $2s^2 2p^6 3s^1$ and $5d^{10} 6s^1$ electrons as valence for Na and Au atoms, respectively.

The phonon spectra and electron-phonon coupling calculations are carried out with the density functional perturbation (linear response) theory as implemented in the QUANTUM ESPRESSO package [5]. We employ the ultrasoft pseudopotentials with $2s^22p^63s^1$ and $5d^{10}6s^1$ as valence electrons for Na and Au atoms, respectively. The kinetic energy cutoff for wave-function expansion is chosen as 70 Ry. To reliably calculate electron-phonon coupling in metallic systems, we need to sample dense k-meshes for electronic Brillouin zone integration and enough q-meshes for evaluating average contributions from the phonon modes. We have calculated the superconducting T_c of metallic Na_xAu_y (x =1-6 and y = 1; x =1 and y = 2; x =3 and y = 2) as estimated from the McMillan-Allen-Dynes formula [6-8]:

$$T_C = \frac{\omega_{\log}}{1.2k_B}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right].$$

Here, k_B is the Boltzmann constant and μ^* is the Coulomb pseudopotential ($\mu^* = 0.1$). The electron-phonon coupling constant, λ, and the logarithmic average phonon frequency, $\omega_{\log}$, are calculated by the Eliashberg spectral function for electron-phonon interaction:

$$\alpha^2F(\omega) = \frac{1}{N(E_F)}\sum_{kq,v}\left|g_{k,k+q,v}\right|^2\delta(\varepsilon_k)\delta(\varepsilon_{k+q})\delta(\omega-\omega_{q,v})$$

where $\lambda = 2\int d\omega\frac{\alpha^2F(\omega)}{\omega}$; $\omega_{\log} = \exp\left[\frac{2}{\lambda}\int\frac{d\omega}{\omega}\alpha^2F(\omega)\ln(\omega)\right]$. Herein, $N(E_F)$ is the electronic density of states at the Fermi level, $\omega_{q,v}$ is the phonon frequency of mode v and wave vector q, and $|g_{k,k+q,v}|$ is the electron-phonon matrix element between two electronic states with momenta k and $k+q$ at the Fermi level [9,10].

Supplementary Figures

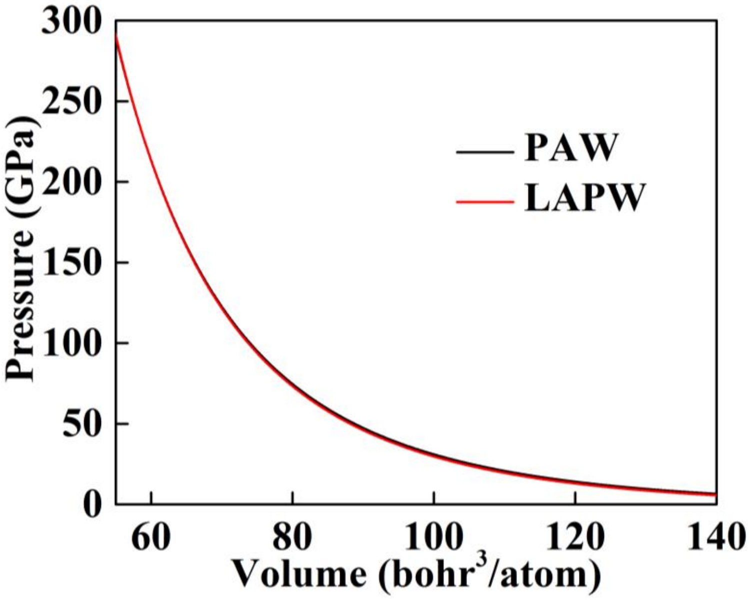

Figure S0. Comparison of the fitted Birch-Murnaghan equation of states for Na_3Au with *Cmcm* symmetry by using the calculated results from the PAW pseudopotentials and the full-potential LAPW methods.

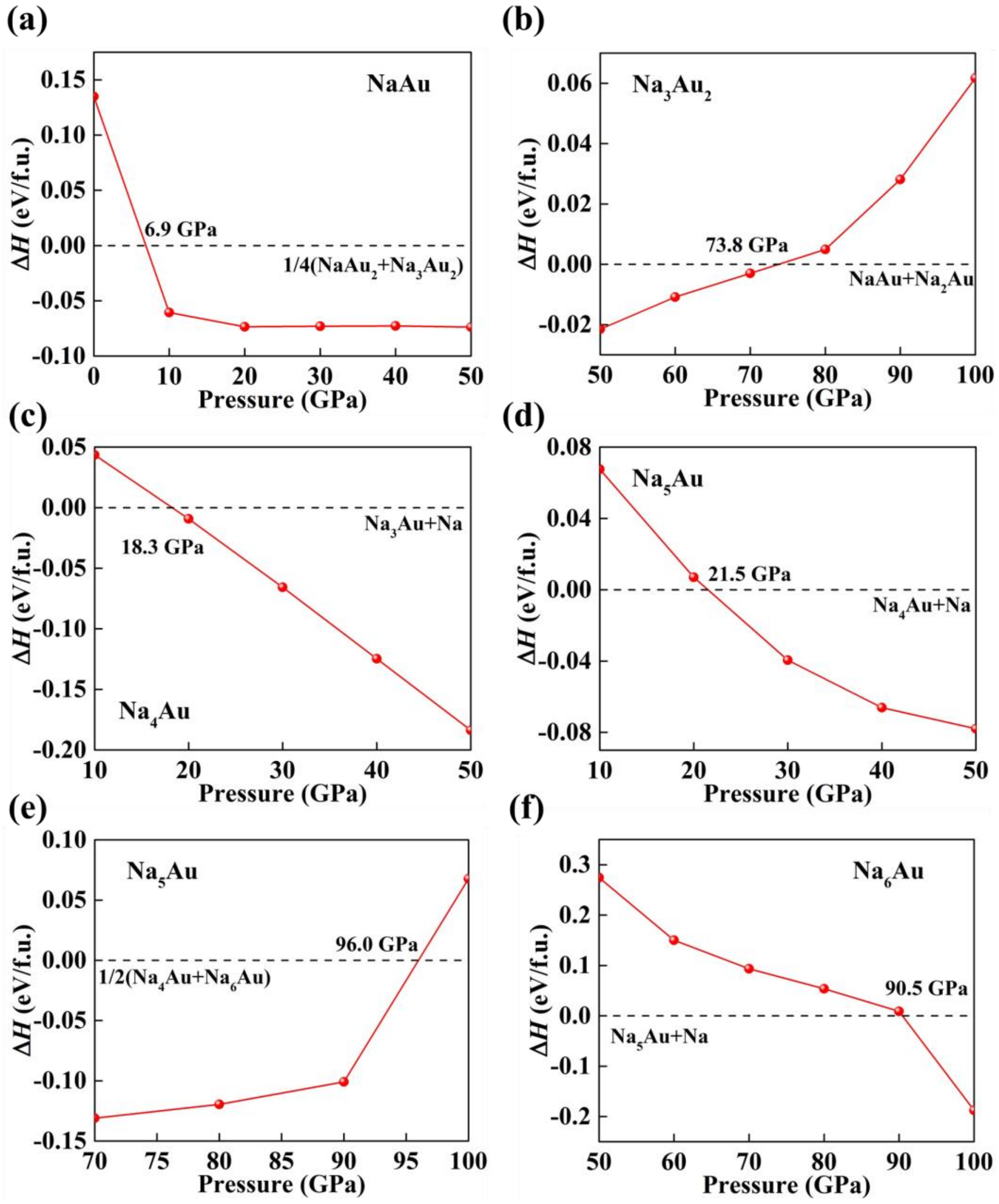

Figure S1. (a) Calculated formation enthalpy per formula unit of $P4/mmm$ NaAu relative to Fd-3m $NaAu_2$ plus $C2/c$ Na_3Au_2 as a function of pressure. (b) Calculated formation enthalpy per formula unit of $Cmmm$ Na_3Au_2 relative to $Cmmm$ NaAu plus Fd-3m Na_2Au as a function of pressure. (c) Calculated formation enthalpy per formula unit of R-3m Na_4Au relative to $P6_3cm$ Na_3Au plus Na as a function of pressure. (d) Calculated formation enthalpy per formula unit of $C2/c$ Na_5Au relative to R-3m Na_4Au plus Na and (e) $C2/m$ Na_4Au plus $C2/c$ Na_6Au as a function of pressure. (f) Calculated formation enthalpy per formula unit of $C2/c$ Na_6Au relative to $C2/c$ Na_5Au plus Na as a function of pressure.

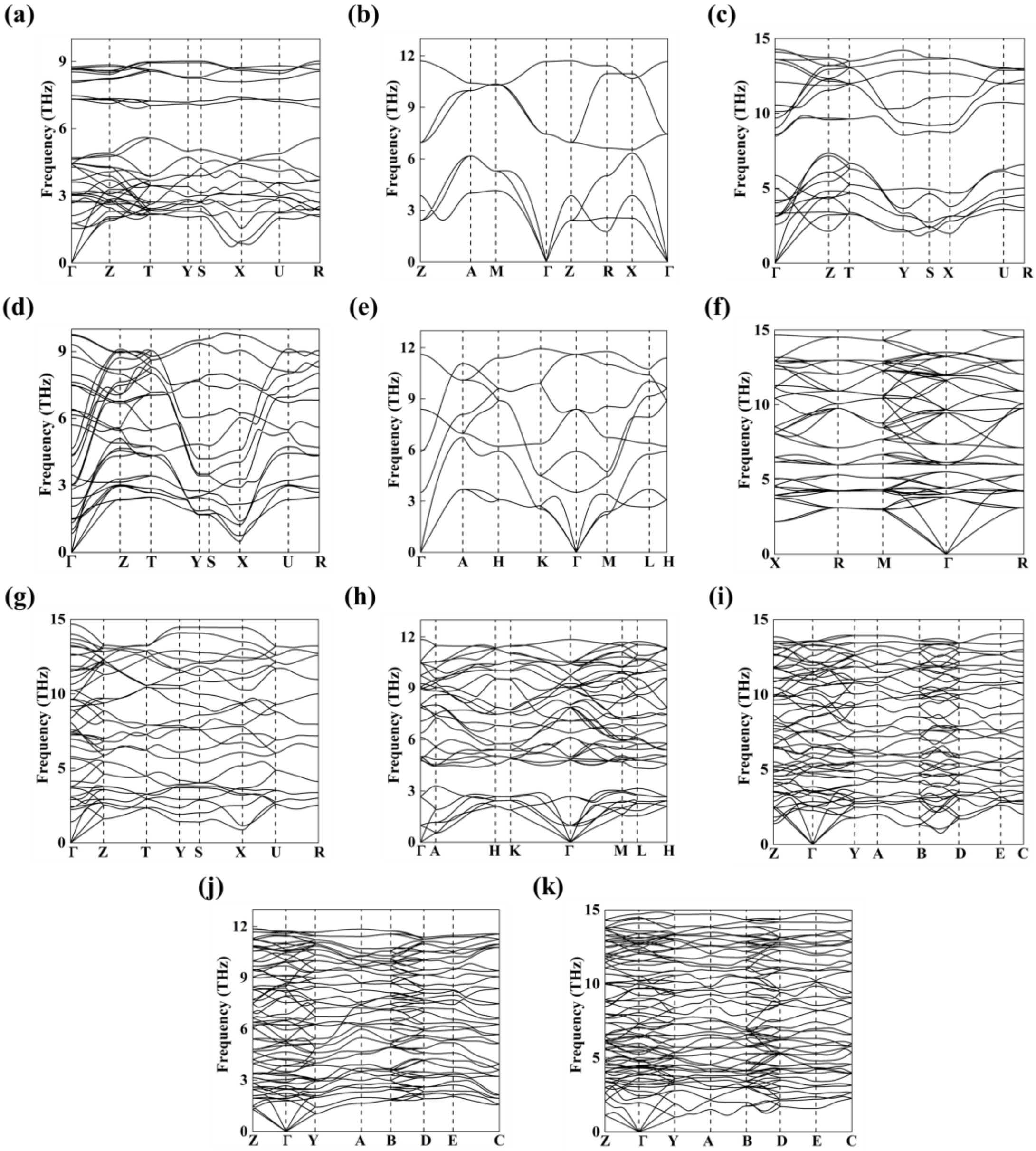

Figure S2. Phonon dispersion curves for (a) *Cmmm* $NaAu_2$ at 50 GPa. (b) *P*4/*mmm* NaAu at 50 GPa. (c) *Cmmm* NaAu at 100 GPa. (d) *Cmmm* Na_3Au_2 at 50 GPa. (e) *P*6/*mmm* Na_2Au at 50 GPa. (f) *Fd*-3*m* Na_2Au at 100 GPa. (g) *Cmcm* Na_3Au at 100 GPa. (h) *R*-3*m* Na_4Au at 50 GPa. (i) *C*2/*m* Na_4Au at 100 GPa. (j) *C*2/*c* Na_5Au at 50 GPa. (k) *C*2/*c* Na_6Au at 100 GPa.

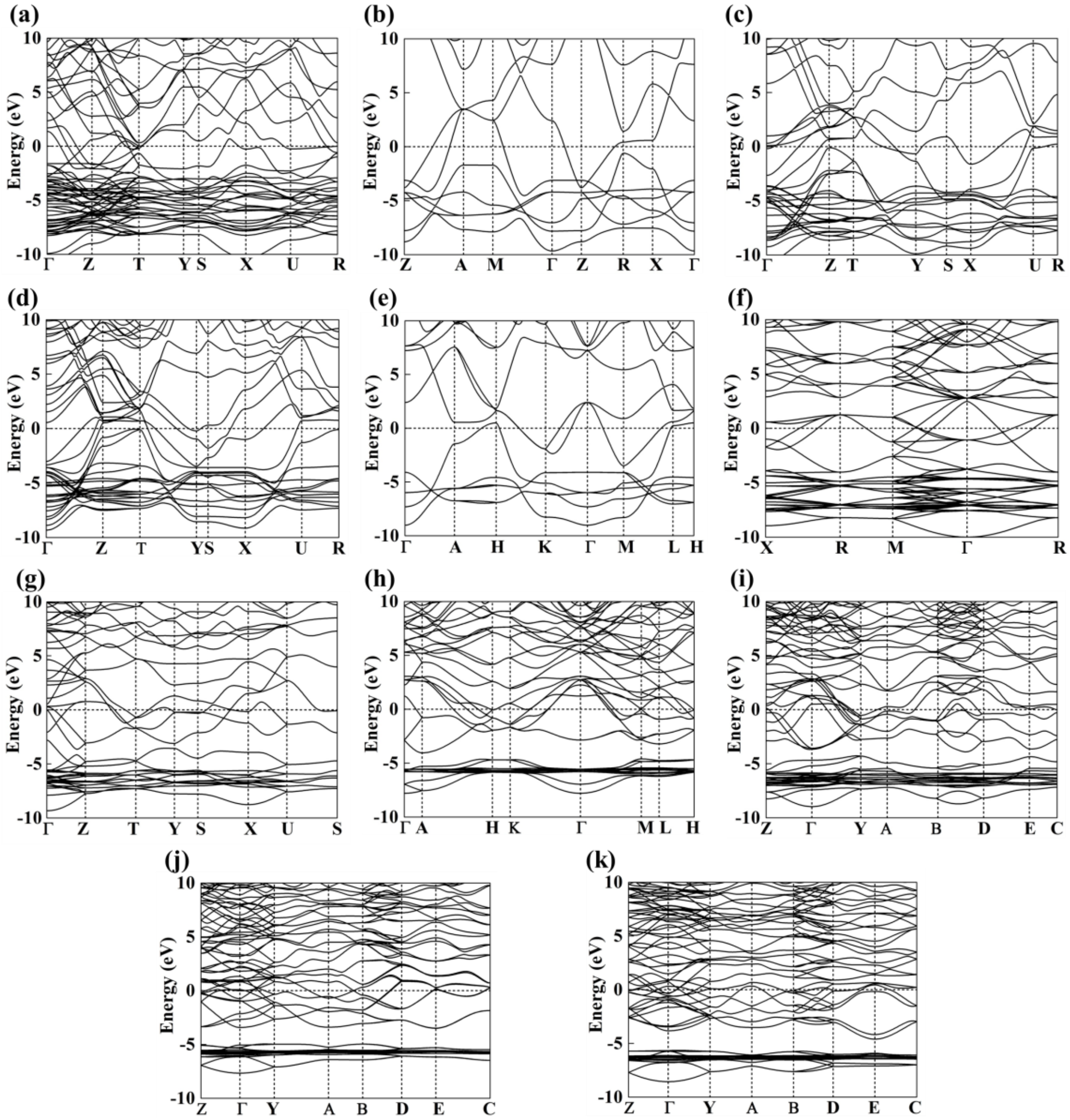

Figure S3. Electronic band structures calculated by the PBE hybrid functional for (a) *Cmmm* $NaAu_2$ at 50 GPa, (b) *P*4/*mmm* NaAu at 50 GPa, (c) *Cmmm* NaAu at 100 GPa, (d) *Cmmm* Na_3Au_2 at 50 GPa, (e) *P*6/*mmm* Na_2Au at 50 GPa, (f) *Fd*-3*m* Na_2Au at 100 GPa, (g) *Cmcm* Na_3Au at 100 GPa, (h) *R*-3*m* Na_4Au at 50 GPa, (i) *C*2/*m* Na_4Au at 100 GPa, (j) *C*2/*c* Na_5Au at 50 GPa, and (k) *C*2/*c* Na_6Au at 100 GPa.

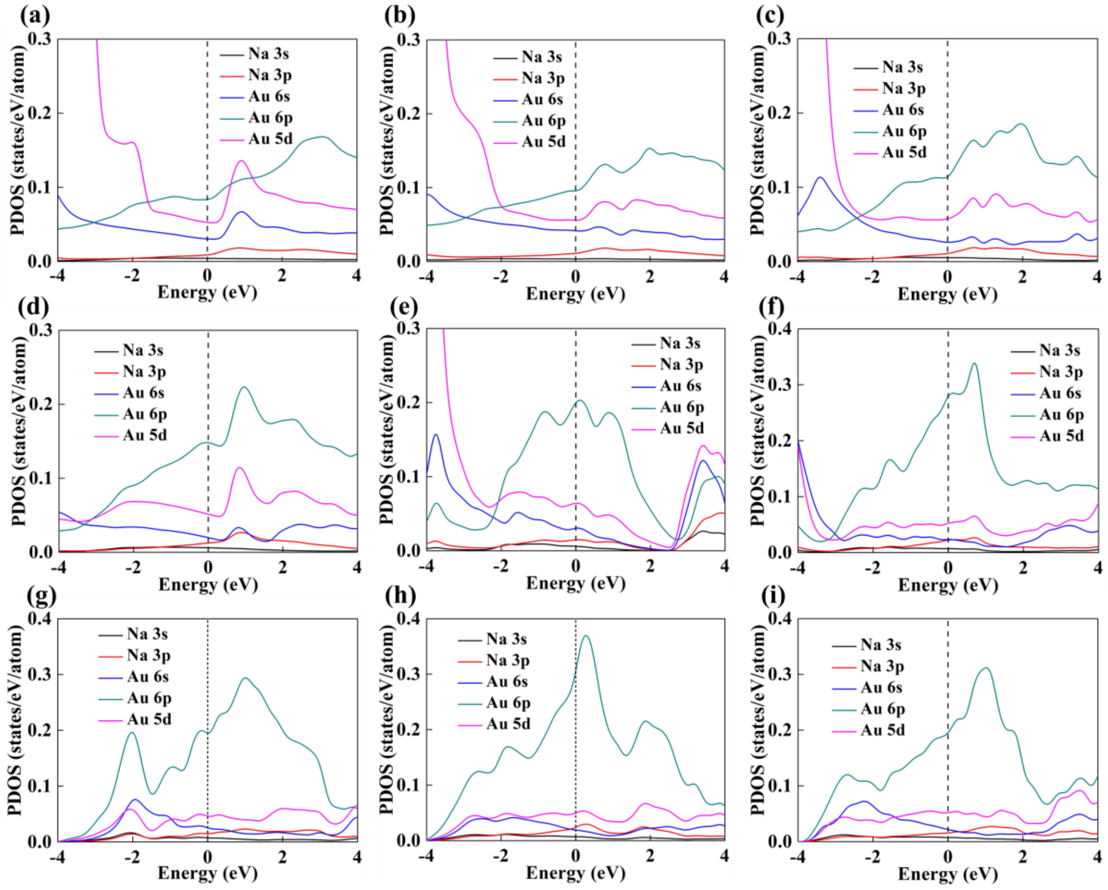

Figure S4. PDOS calculated by the PBE hybrid functional for (a) *P*4/*mmm* NaAu at 50 GPa, (b) *Cmmm* NaAu at 100 GPa, (c) *Cmmm* Na_3Au_2 at 50 GPa, (d) *P*6/*mmm* Na_2Au at 50 GPa, (e) *Fd*-3*m* Na_2Au at 100 GPa, (f) *Cmcm* Na_3Au at 100 GPa, (g) *R*-3*m* Na_4Au at 50 GPa, (h) *C*2/*m* Na_4Au at 100 GPa, and (i) *C*2/*c* Na_5Au at 50 GPa.

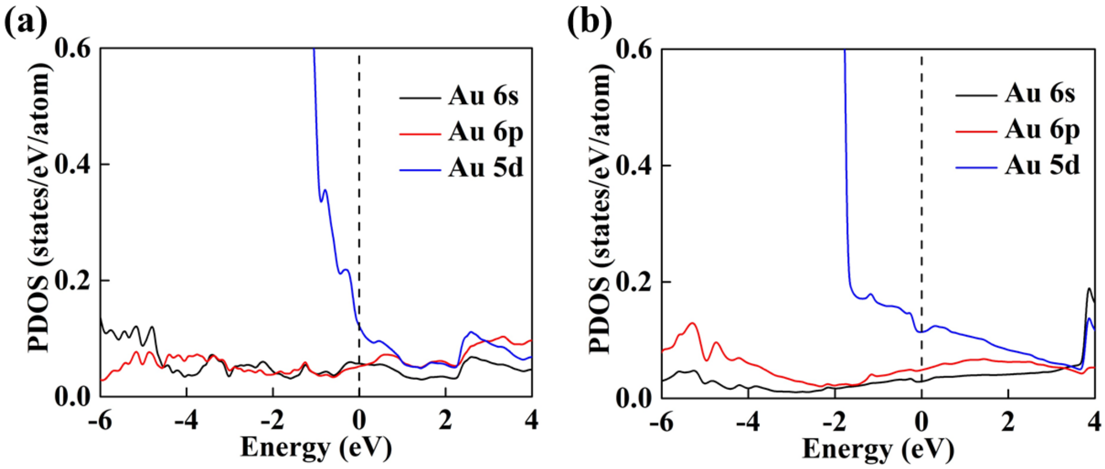

Figure S5. The PDOS of (a) Au in *Cmmm* Na_0Au and (b) solid Au at 50 GPa.

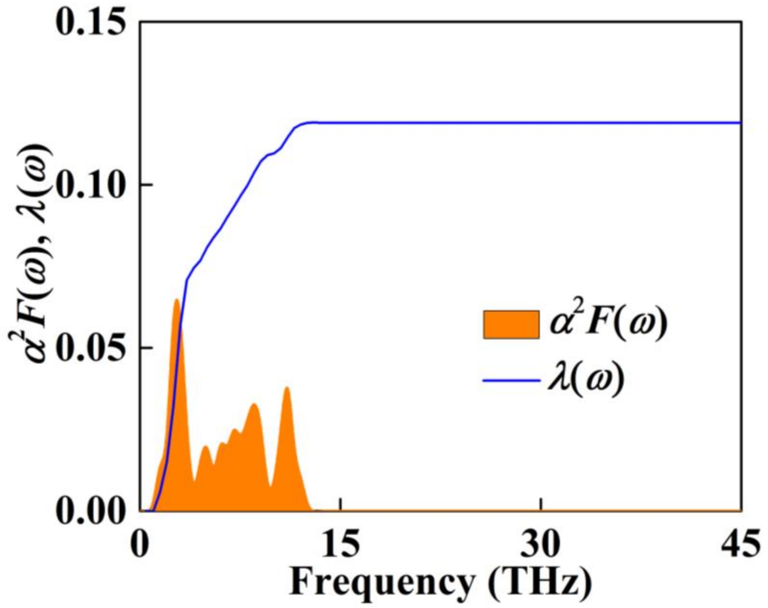

Figure S6. The Eliashberg spectral function $\alpha^2F(\omega)$ and integrated electron-phonon coupling parameters $\lambda(\omega)$ of Na_2Au. And the calculated superconducting transition temperature (T_c) of Na_2Au is 0 K.

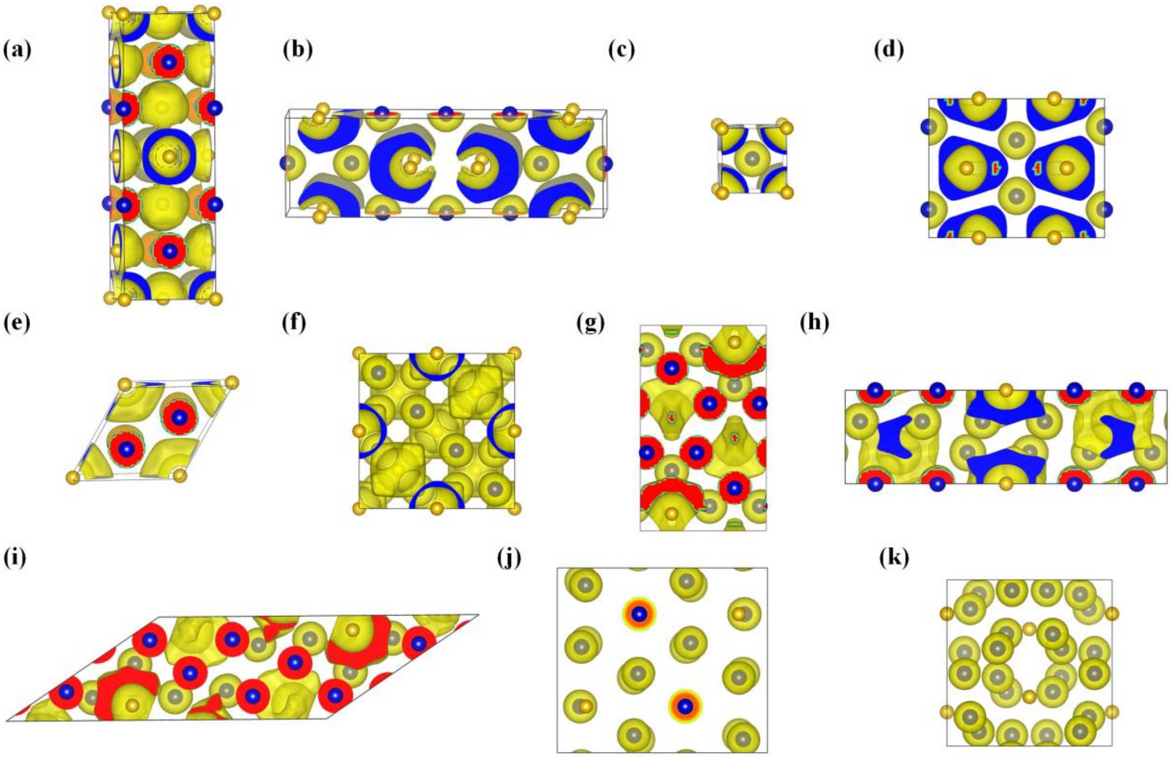

Figure S7. ELF of stable Na-Au compounds. (a) *Cmmm* $NaAu_2$ at 50 GPa, (b) *P*4/*mmm* NaAu at 50 GPa. (c) *Cmmm* NaAu at 100 GPa. (d) *Cmmm* Na_3Au_2 at 50 GPa. (e) *P*6/*mmm* Na_2Au at 50 GPa. (f) *Fd*-3*m* Na_2Au at 100 GPa. (g) *Cmcm* Na_3Au at 100 GPa. (h) *R*-3*m* Na_4Au at 50 GPa. (i) *C*2/*m* Na_4Au at 100 GPa. (j) *C*2/*c* Na_5Au at 50 GPa. (k) *C*2/*c* Na_6Au at 100 GPa. For all Na-Au compounds, no electrons sit at the interstitial regions.

Supplementary Table

Table S1. Structural information of predicted stable Na-Au compounds.

Phase	Pressure (GPa)	Lattice Parameters (Å, °)	Atoms	Wyckoff Positions (fractional)		
				x	***y***	***z***
Cmmm **NaAu$_2$**	50	a = 3.713	Na(4i)	0.5000	0.8312	-0.0000
		b = 11.526	Au(2c)	0.5000	0.0000	0.5000
		c = 3.9035	Au(2a)	0.0000	0.0000	0.0000
		$\alpha = \beta = \gamma$ = 90.0000	Au(4j)	-0.0000	0.1687	0.5000
P4/mmm **NaAu**	50	$a = b$ = 2.671	Na(1d)	0.5000	0.5000	0.5000
		c = 3.797	Au(1a)	0.0000	0.0000	0.0000
		$\alpha = \beta = \gamma$ = 90.0000				
Cmmm **NaAu**	100	a = 6.6789 b = 5.3166	Na(4j)	0.0000	0.79768	0.5000
		c = 2.599	Au(4g)	0.7149	-0.0000	-0.0000
		$\alpha = \beta = \gamma$ = 90.0000				
Cmmm **Na$_3$Au$_2$**	50	a = 3.9951	Na(2c)	0.5000	-0.0000	0.5000
		b = 12.7262	Na(4j)	0.5000	0.7984	0.5000
		c = 2.6214	Au(4i)	0.0000	0.8934	-0.0000
		$\alpha = \beta = \gamma$ = 90.0000				
P6/mmm **Na$_2$Au**	50	$a = b$ = 4.1578	Na(2c)	0.6667	0.3333	-0.0000
		c = 2.633	Au(1b)	-0.0000	0.0000	0.5000
		$\alpha = \beta$ = 90.0000				
		γ = 120.0000				
Fd-3m **Na$_2$Au**	100	$a = b = c$ = 6.3585	Na(16c)	0.6250	0.3750	0.8750
		$\alpha = \beta = \gamma$ = 90.0000	Au(8b)	0.7500	0.2500	0.2500

***Cmcm* Na$_3$Au**	100	$a = 3.9229$	Na(4c)	0.0000	0.2075	1.2500
		$b = 8.4118$	Na(8f)	0.5000	0.1197	1.0513
		$c = 5.1283$	Au(4c)	0.5000	0.4177	1.2500
		$\alpha = \beta = \gamma = 90.0000$				
***R*-3*m* Na$_4$Au**	50	$a = b = 4.2491$	Na(6c)	-0.0000	-0.0000	0.7129
		$c = 12.6022$	Na(6c)	-0.0000	-0.0000	0.90635
		$\alpha = \beta = 90.0000$	Au(3b)	-0.0000	0.0000	0.5000
		$\gamma = 120.0000$				
***C*2/*m* Na$_4$Au**	100	$a = 12.9363$	Na(4i)	0.0790	-0.0000	0.2245
		$b = 3.9027$	Na(4i)	0.9452	-0.0000	0.2801
		$c = 7.4706$	Na(4i)	0.6639	-0.0000	0.7770
		$\alpha = \gamma = 90.0000$	Na(4i)	0.1407	0.5000	0.4513
		$\beta = 146.0666$	Au(4i)	0.8268	0.5000	0.8578
***C*2/*c* Na$_5$Au**	50	$a = 5.2357$	Na(8f)	0.3063	0.6348	1.4061
		$b = 8.2804$	Na(8f)	0.7811	0.6152	1.4278
		$c = 7.3007$	Na(4e)	0.5000	0.8907	1.2500
		$\alpha = \gamma = 90.0000$	Au(4e)	-0.0000	0.8639	1.2500
		$\beta = 90.3426$				
***C*2/*c* Na$_6$Au**	100	$a = 6.5402$	Na(8f)	0.6064	0.0637	-0.3728
		$b = 6.5242$	Na(8f)	0.1927	0.9132	-0.4056
		$c = 6.9143$	Na(8f)	0.8591	0.1740	0.0996
		$\alpha = \gamma = 90.0000$	Au(4e)	-0.0000	0.7959	0.2500
		$\beta = 97.3864$				

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