




## Doping-stabilized Au-N compounds via lithium atoms at high pressure

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As a powerful tool, pressure can effectively tune the electronic structure of elements, such as gold (Au), to react with other elements and form a material that is inaccessible at atmospheric pressure. However, current knowledge shows that Au cannot form stable compounds with nitrogen (N) even under extreme compression, and it is thus of fundamental interest to hunt stable compounds with Au-N bonds in the fields of physics and chemistry. Here, we perform extensive swarm-intelligence structure searching simulations on the Au-N system under high pressure by introducing the additional element of lithium (Li). Remarkably, a variety of ternary Au-N-Li structures with archetypal Au-N bonds features are proposed to be stable under high pressure, becoming an example of stable compounds with Au-N bonds, where Li plays a key role in providing electrons and improving the stability of the Au-N system. These results establish the theoretical stability of the compressed ternary Au-N-Li system, and more importantly, highlight the importance of lithium as the electron donor in tuning the structures of Au-bearing compounds.

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### I. INTRODUCTION

Gold (Au), a noble element on the periodic table, is one of the most frequently used elements in basic science and practical applications today, exhibiting many attractive physicochemical properties due to its extreme inertness under ambient conditions [1–4]. Its unique features, different from the other elements of the same group such as silver (Ag) and copper (Cu), lie in the strong attraction to valence electrons that prevents Au from losing the outermost electrons, which can be understood with the relativistic effect [1,3,4]. Nevertheless, Au can still be oxidized to common Au<sup>3+</sup> by forming stable simple compounds with strong oxidants, such as archetype fluorine and oxygen [3,5,6]. Nitrogen, as a neighbor of fluorine and oxygen in the periodic table, its Au-bearing compound has gradually attracted attention owing to the excellent performance of metal nitrides in high energy density [7,8], superhard material [9,10], electron field emitters [11–14], and catalysts [15,16].

Driven by the potential properties of Au-N compounds, concerted efforts have been devoted to their syntheses for several decades. For example, it was not until 2002 that the Au-N bonds were observed in a film [17–23], while these

compounds were found to be unstable by the fact that they decompose when heated to 200 °C [24]. Moreover, in another experiment, the characteristic peak of the Au-N bonds in the experiment of X-ray gradually disappeared with the measurement time running [25]. To date, these experiments all show that currently known Au-N compounds are likely to become unstable in the laboratory. Therefore, the stabilization of a compound with Au-N bonds is still a compelling open question and remains challenging.

It has been commonly accepted that compression can dramatically regulate the basic physical and chemical behavior of elements, by shortening interatomic distances, raising the energy of the ground state, and finally leading to the formation of unusual stoichiometries or unprecedented compounds [26–29]. More specifically, several new oxidation states of Au have been proposed under high pressures, which are completely infeasible at atmospheric condition. For example, Au-O can form an unexpected AuO<sub>2</sub> structure with the new-fangled Au<sup>4+</sup> [5]; AuF<sub>6</sub> is calculated to be stable, where the Au ions should adopt a higher oxidation state of 6<sup>+</sup> with the aid of high pressure [3,6]; and even Au with negative valence state is anticipated to show a *p*-block characteristic in the binary Li-Au and Na-Au alloys [1,30]. Even though high-pressure means are a powerful tool, we have not yet found any stable signs of binary Au-N structures. Moreover, a previous theoretical study reported a way of stabilizing ternary gold hydrides [31], in which the electronic structure of the original system is affected by forming stable Au-H bonds with alkaline or alkaline-earth metals. Inspired by this pioneering train of thought, it is of great interest to explore the possibility of achieving stable Au-N bonds in an appropriate compressed ternary stable system by introducing

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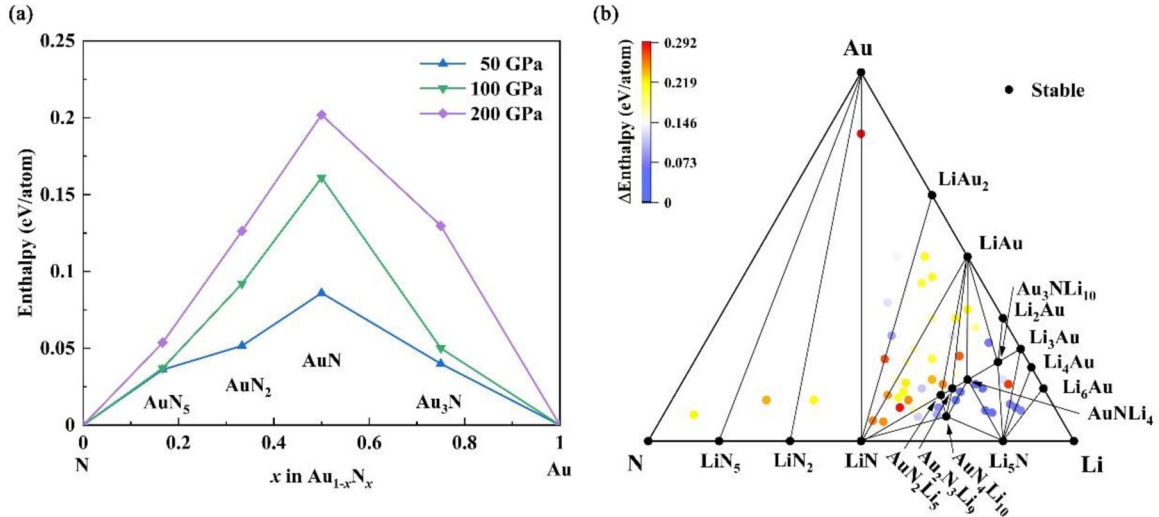


FIG. 1. (a) Convex hull for various Au-N compounds at 50, 100, and 200 GPa. (b) Phase stabilities of various  $Au_xN_yLi_z$  compounds with respect to elemental Au, N, and Li, binary Li-Au, and Li-N systems at 0 K and 100 GPa. The black dots represent thermodynamically stable structures. The unstable structures are marked by color dots, and different colors imply the level of enthalpy exceeding the convex hull in the unit of eV/atom.

additional free electrons from doped elements, such as lithium.

In this work, therefore, we have performed extensive structure searches on ternary  $Au_xN_yLi_z$  ( $x$ : 1–5;  $y$ : 1–5;  $z$ : 1–10) system under high pressure. At megabar pressure, we propose several stable compounds of  $Au_2N_3Li_9$ ,  $AuNLi_4$ ,  $AuN_2Li_5$ , and  $AuN_4Li_{10}$  as typical representatives, in which the Au-N bonds are validated based on electronic structure simulations. The current findings not only establish the ground-state structures of the Au-N-Li system but also shed light on a way of searching for “impossible” aurides combined with compression and electron doping.

## II. COMPUTATIONAL DETAILS

The crystal structure predictions of the binary Au-N and ternary Au-N-Li systems with maximum 30 atoms per cell were based on the particle swarm optimization technique implemented in our developed CALYPSO code [32,33]. First-principles calculations were performed under the framework of the density-functional theory [34] using the Vienna *Ab initio* Simulation Package (VASP) [35] code within the generalized gradient approximation. Taking both the amount of calculation and efficiency of calculation into consideration, we adopted the Perdew-Burke-Ernzerhof [36] exchange-correlation functional. The electron-ion interaction is described by pseudopotentials built within the scalar relativistic projector augmented-wave approximation [37] with  $5d^{10}6s^1$ ,  $2s^22p^3$ , and  $2s^1$  valence electrons for Au, N, and Li atoms, respectively. The cutoff energy was set to 600 eV, and appropriate Monkhorst-Pack  $k$  meshes were used to ensure that total energy calculations converged to less than 1 meV/atom. The dynamical stability of predicted structures was calculated by using the linear response theory as implemented in the PHONOPY code [38]. A  $3 \times 3 \times 1$  supercell containing 126 atoms and a  $1 \times 3 \times 2$  supercell containing 144 atoms were used in the phonon calculations

for  $Au_2N_3Li_9$  and  $AuNLi_4$ , respectively. For  $AuN_2Li_5$  and  $AuN_4Li_{10}$  compound, we chose a  $4 \times 2 \times 1$  supercell containing 256 atoms and a  $3 \times 2 \times 2$  supercell containing 180 atoms for the phonon calculations, respectively. The thermodynamic stability of Au-N-Li compounds was estimated with respect to the precursors of elemental Au, N, Li solids and stable binary compounds. Furthermore, the crystal orbital Hamilton population (COHP) and the integrated COHP (ICOHP) [39,40].

## III. RESULTS AND DISCUSSION

### A. Stability of binary Au-N and ternary Au-N-Li systems

In an attempt to investigate the stability of the Au-N system under high pressure, we have performed structural searches on stoichiometric  $AuN_5$ ,  $AuN_2$ ,  $AuN$ , and  $Au_3N$  at 50, 100, and 200 GPa. Unfortunately, the formation enthalpy at 0 K and selected pressure with respect to elemental Au and N of these candidate structures are positive [Fig. 1(a)], which means that all the selected Au-N compounds are thermodynamically unstable up to at least 200 GPa. Moreover, under elevating pressure, the tendency towards decomposition becomes more pronounced. Thus, these results allow us to judge that even the powerful tool of pressure could not modify the stability of Au-N compounds.

Beside the tool of pressure, electron doping strategy could also help to tune the stability of Au-N compounds by introducing the element of Li as the electron doner. At megabar pressure and zero temperature, a variety of stoichiometries of Au-N-Li have been systematically investigated with the crystal structure prediction method in this study. The cubic structure ( $Fm-3m$ ) of Au [41], the  $Cmca-24$  structure of Li [42–45], and the  $I2_13$  phase of solid  $N_2$  [46,47] were adopted to estimate the formation enthalpy. The stabilities of Li-Au [1] and Li-N [48,49] systems have been examined by previous theoretical studies, and thus, in this work, the ground-state structure of each stoichiometry at corresponding pressures was employed as mentioned in references directly. As shown

TABLE I. Selection of formation routes to Au-N-Li compounds at 100 GPa. The right column provides corresponding calculated enthalpies of formation. Enthalpy is given in eV/f.u. for reaction as written.

	$\Delta E$ (eV/f.u.)
$2\text{LiAu} + 3\text{LiN} + 4\text{Li} \rightarrow \text{Au}_2\text{N}_3\text{Li}_9$	-8.1
$2\text{LiAu} + 2\text{LiN} + \text{Li}_5\text{N} \rightarrow \text{Au}_2\text{N}_3\text{Li}_9$	-3.5
$\text{LiN} + \text{Li}_3\text{Au} \rightarrow \text{AuNLi}_4$	-2.4
$\text{LiAu} + \frac{1}{2}\text{LiN} + \frac{1}{2}\text{Li}_5\text{N} \rightarrow \text{AuNLi}_4$	-1.3
$\text{LiAu} + 2\text{LiN} + 2\text{Li} \rightarrow \text{AuN}_2\text{Li}_5$	-4.4
$2\text{LiN} + \text{Li}_3\text{Au} \rightarrow \text{AuN}_2\text{Li}_5$	-2.9
$\text{Li}_3\text{Au} + 4\text{LiN} + 3\text{Li} \rightarrow \text{AuN}_4\text{Li}_{10}$	-9.2
$\text{Li}_5\text{N} + \text{LiAu} + 3\text{LiN} + \text{Li} \rightarrow \text{AuN}_4\text{Li}_{10}$	-5.5

in the ternary phase diagram [Fig. 1(b)], the colored dots should decompose into elemental or Li-N or Li-Au systems or any other ternary compounds; conversely, five black dots represent thermodynamically stable Au-N-Li stoichiometries of  $\text{Au}_2\text{N}_3\text{Li}_9$ ,  $\text{AuNLi}_4$ ,  $\text{AuN}_2\text{Li}_5$ ,  $\text{AuN}_4\text{Li}_{10}$ , and  $\text{Au}_3\text{NLi}_{10}$ . Structural parameters of these stable compounds are listed in Table S1 [50]. Since  $\text{Au}_3\text{NLi}_{10}$  does not contain any Au-N bond, our study thus focused on the investigation of  $\text{Au}_2\text{N}_3\text{Li}_9$ ,  $\text{AuNLi}_4$ ,  $\text{AuN}_2\text{Li}_5$ , and  $\text{AuN}_4\text{Li}_{10}$ . Owing to the extraordinarily complexity of a ternary system with a higher degree of freedom, we cannot fully rule out the possibility for the existence of other stoichiometric Au-N-Li or large-size structures with lower energy that have not yet been considered here. However, our simulations indicate that the introduction of additional lithium is a reliable way to stabilize ternary Au-N-Li compounds with Au-N bonds at high pressure.

For the stable compounds with Au-N bonds, we also propose a great number of possible reaction routes to synthesize these predicted structures for experiment, as shown in Table I. (I)  $2\text{LiAu} + 2\text{LiN} + \text{Li}_5\text{N} \rightarrow \text{Au}_2\text{N}_3\text{Li}_9$ , (II)  $\text{LiN} + \text{Li}_3\text{Au} \rightarrow \text{AuNLi}_4$ , (III)  $2\text{LiN} + \text{Li}_3\text{Au} \rightarrow \text{AuN}_2\text{Li}_5$ , and (IV)  $\text{Li}_3\text{Au} + 4\text{LiN} + 3\text{Li} \rightarrow \text{AuN}_4\text{Li}_{10}$ , with relative formation enthalpies of  $-0.25$ ,  $-0.39$ ,  $-0.36$ , and  $-0.61$  eV/atom, respectively, at 100 GPa. We further focused on the minimum stable pressure region for the future synthesis, as the phase diagram shown in Fig. 2. It is clearly seen that the  $\text{AuN}_2\text{Li}_5$  structure is thermodynamically stable at a pressure range of 60–100 GPa.

We also performed phonon dispersion curves for investigating the dynamic stability of these thermodynamically stable compounds. The dynamic stability of these predicted structures is confirmed by the absence of any imaginary frequency in the whole Brillouin zone as shown in Fig. 3.

### B. Crystal structures of Au-N-Li compounds

The predicted stable phases with Au-N bonds are shown in Fig. 4. It is worth mentioning that despite the difference in composition and symmetry, crystal structures of ternary Au-N-Li structures exhibit quite similar Li-N bonding patterns. To better understand the structural characteristic for different stoichiometries, we analyze the Au-N-Li compounds with Au-N bonds at 100 GPa. The  $P\bar{4}m2$ - $\text{Au}_2\text{N}_3\text{Li}_9$ ,  $C2/m$ - $\text{AuNLi}_4$ , and  $P6_3/mmc$ - $\text{AuN}_2\text{Li}_5$  are crystallized in layered structure of

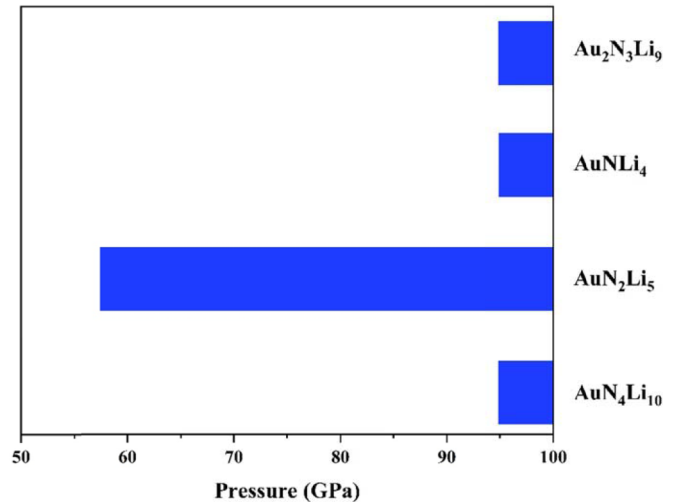


FIG. 2. Pressure-composition phase diagram of the Au-N-Li system from 50 to 100 GPa. The stable phases are shown in blue line. The gold atom maintains the phase of  $Fm\bar{3}m$  in this pressure interval. The ground-state structure of nitrogen transfers from  $R\bar{3}c$ -N to  $cg$ -N above 50 GPa, and in this pressure interval lithium undergoes phase transition with a sequence of  $I\bar{4}3d \rightarrow Aba2-40 \rightarrow Cmca-24$  at 60 and 80 GPa, separately. For binary Li-N compounds, the structures were taken from the phase diagrams which have been mentioned in former studies. For binary Li-Au systems, we choose the structure with low energy as the ground-state structure at the target pressure.

Li-N units, where Au atoms placed between layers are connected to N atoms with Au-N bond lengths of 2.38, 2.21, and 2.03 Å at 100 GPa, respectively. The Li-N layer in  $\text{Au}_2\text{N}_3\text{Li}_9$  consists of  $\text{LiN}_4$  and  $\text{LiN}_5$  units, while the Li-N layer in  $\text{AuNLi}_4$  is folded and consists of edge-sharing  $\text{LiN}_3$  and  $\text{Li}_2\text{N}_3$ . The Li-N layer in  $\text{AuN}_2\text{Li}_5$  consists of face-sharing  $\text{LiN}_4$  and  $\text{LiN}_6$  units. Meanwhile, for the predicted  $\text{AuN}_4\text{Li}_{10}$  that adopts a  $I4/m$  space group, Li and N atoms form a three-dimensional network structure with  $\text{LiN}_4$  and  $\text{LiN}_5$  units as shown in Fig. 4(d). Each Au atom in the tubes has a coordination number of 4, connecting to the surrounding nitrogen atoms with a tetrahedral configuration, and forming  $\text{AuN}_4$  units in tubular structure with Au-N bonds lengths of 2.10 Å at 100 GPa, which implies that this unit is formed via  $sp^3$  hybridization of Au as shown in Fig. 4(d). This result is also similar to that in the Li-Au-P system [51].

### C. Stabilization mechanism of compounds and Au-N bonds

In order to understand the role of Au-N bonds in the Au-N-Li system, we further analyzed the electronic characteristics of Au-N bonds in these stable compounds. The electron localization functions (ELF) for each structure with Au-N bonds are plotted as shown in Fig. 5. It is clearly seen that the ELF values correspond to the obvious electronic localization between the Au and N atoms, as illustrated in Fig. 5. The large ELF value between Au and N atoms corresponds to the Au-N bonds and Li atoms act as the electron donor. In the  $\text{Au}_2\text{N}_3\text{Li}_9$  and  $\text{AuN}_2\text{Li}_5$ , each gold atom is connected with two nitrogen atoms. In the  $\text{AuN}_4\text{Li}_{10}$ , it is obvious that Au atoms are connected with four N atoms nearby by forming  $\text{AuN}_4$

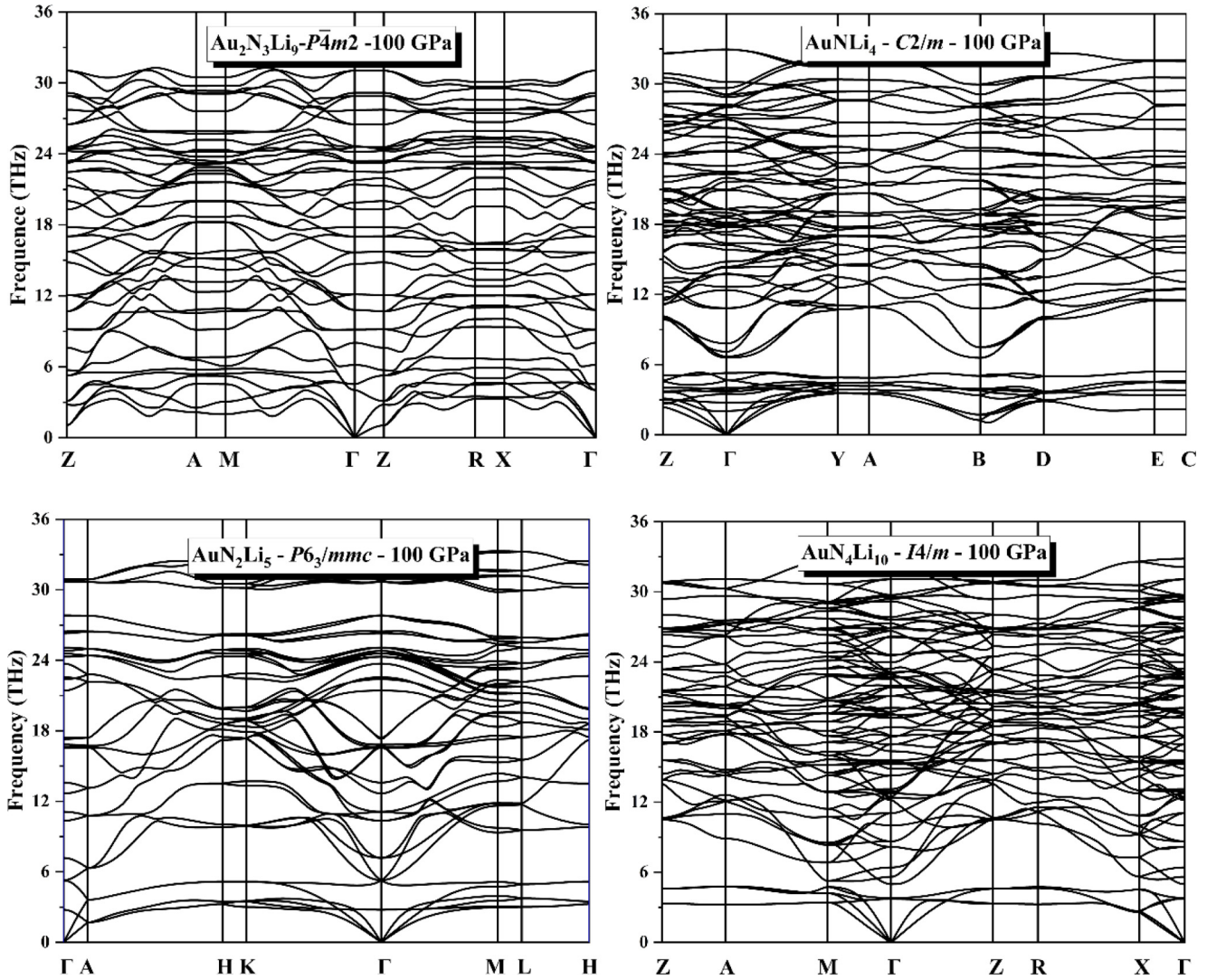


FIG. 3. Calculated phonon spectra for various Au-N-Li compounds with Au-N bonds at 100 GPa. There are no imaginary modes for these structures, which indicates dynamical stability of these predicted structures.

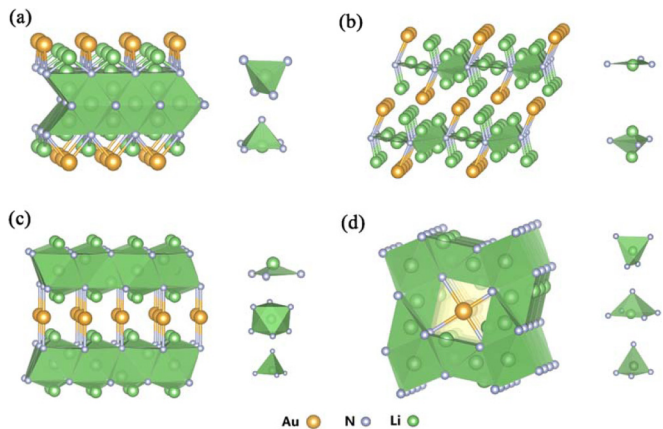


FIG. 4. Stable structures of  $Au_xN_yLi_z$  at 100 GPa; the Au-N and Li-N frameworks are shown. (a)  $Au_2N_3Li_9$  in  $P\bar{4}m2$  structure. (b)  $AuNLi_4$  in  $C2/m$  structure. (c)  $AuN_2Li_5$  in  $P6_3/mmc$  structure. (d)  $AuN_4Li_{10}$  in  $I4/m$  structure.

units. To illustrate the charge transfer between Au, N, and Li, we performed the Bader charge calculations. In general, the Au/N atoms gain electrons from Li atoms. The Bader charge analysis demonstrates that N atoms in  $Au_2N_3Li_9$ ,  $AuNLi_4$ ,  $AuN_2Li_5$ , and  $AuN_4Li_{10}$  gain 1.84, 1.86, 1.75, and 1.79  $e$ , respectively. In  $Au_2N_3Li_9$ , each Au gains 0.33  $e$  from Li atoms. However, the calculated Au charge of  $-1.01 e$  in  $AuNLi_4$  is much higher than the charge transfer of Au in other compounds, which indicates the  $5d^{10} 6s^2$  configuration of Au. In  $AuN_2Li_5$  and  $AuN_4Li_{10}$ , every Au atom accepts about 0.11  $e$  from Li atoms.

To evaluate the bonding intensity of those structures, we calculated the electronic projected density of states (PDOS) and projected crystal orbital Hamiltonian population (pCOHP) that measures weighted population of wave functions on two atomic orbitals of a pair of selected atoms. The results shown in Fig. 6 indicate considerable Au-N bonding interactions. For these structures at 100 GPa, especially for the  $Au_2N_3Li_9$  and  $AuN_2Li_5$ , the states around the Fermi level are mainly contributed by the hybridizations of Au 5d and N 2p orbitals which indicate strong Au-N bonding interactions.

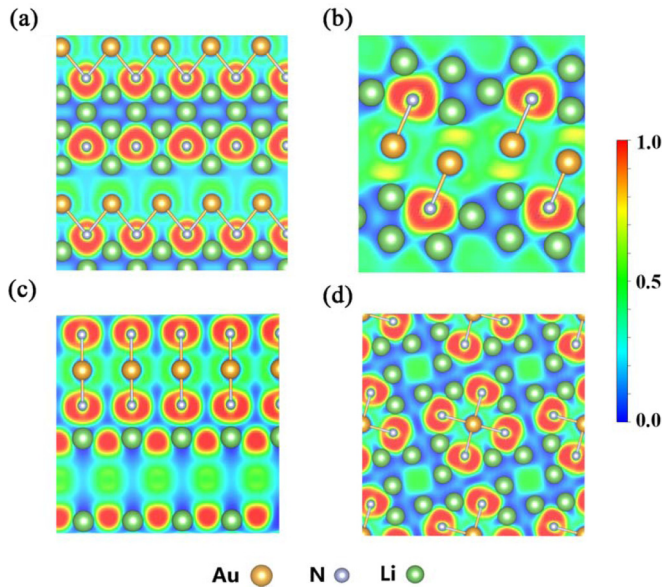


FIG. 5. Calculated electron localization functions of (a)  $\text{Au}_2\text{N}_3\text{Li}_9$ , (b)  $\text{AuNLi}_4$ , (c)  $\text{AuN}_2\text{Li}_5$ , and (d)  $\text{AuN}_4\text{Li}_{10}$ .

Moreover, the  $\text{Au}_2\text{N}_3\text{Li}_9$  compound is a semiconductor with the energy band gap of about 0.87 eV, as shown in Fig. 6(a) and Fig. S1 [50]. The results in Figs. 6(b), 6(d), 6(f), and 6(h) also reveal characteristic Au-N bonding as indicated by the features of low-energy bonding states while part of the antibonding states is occupied below the Fermi level. The calculated ICOHP values for the Au-N bonds at Fermi energy are  $-0.321$  eV/pair in  $\text{Au}_2\text{N}_3\text{Li}_9$  and  $-0.766$  eV/pair in  $\text{AuNLi}_4$ , and  $-2.027$  eV/pair in  $\text{AuN}_2\text{Li}_5$  and  $-1.601$  eV/pair in  $\text{AuN}_4\text{Li}_{10}$ , accordingly. These results also prove that Au and N have a strong interaction in these stable structures, in sharp contrast to previously discovered Au-N compounds.

The key questions lie in the fact of why can the binary Au-N compounds be unstable at high pressure, and how does the Li atom reverse the situation. We learned from the previous studies of Au-H and P-H systems [52] that the introduced lithium atoms would provide electrons to the system which would combine with Au or P and form ion compounds. We found that the contribution of the electron donor in this system is not as same as the previous works and thus requires further analysis. To figure out how the electron donor dominates the

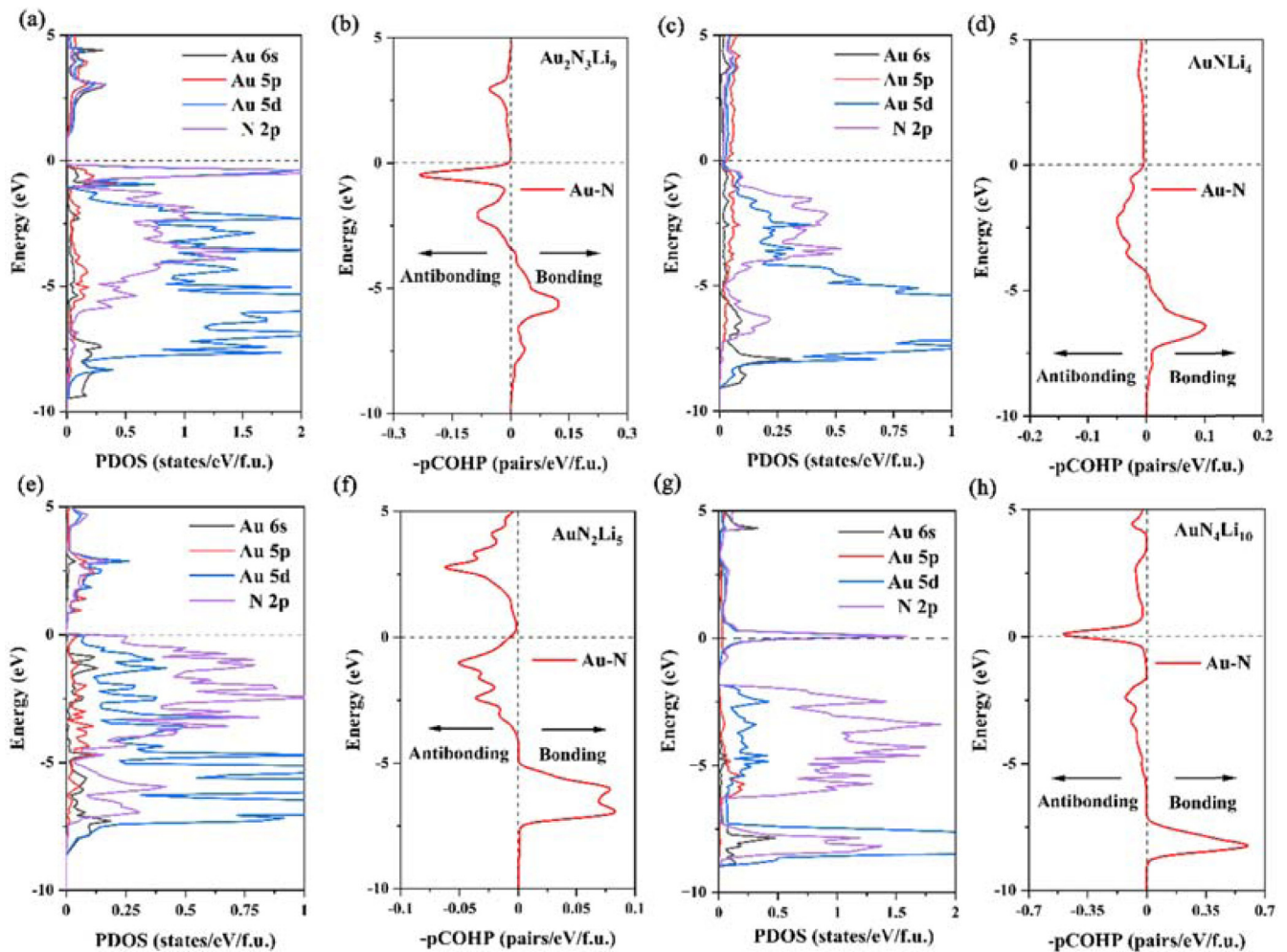


FIG. 6. Electronic properties of the four stable Au-N-Li compounds at 100 GPa. The Fermi energy is set to zero of the energy. (a), (c), (e), (g) PDOS of Au-6s, Au-5p, Au-5d, and N-2p orbitals in the predicted compounds  $\text{Au}_2\text{N}_3\text{Li}_9$ ,  $\text{AuNLi}_4$ ,  $\text{AuN}_2\text{Li}_5$ , and  $\text{AuN}_4\text{Li}_{10}$ , respectively. (b), (d), (f), (h) Projected crystal orbital Hamiltonian population ( $-\text{pCOHP}$ ) of  $\text{Au}_2\text{N}_3\text{Li}_9$ ,  $\text{AuNLi}_4$ ,  $\text{AuN}_2\text{Li}_5$ , and  $\text{AuN}_4\text{Li}_{10}$ , successively. The values of  $-\text{pCOHP} > 0$  signify bonding states and the values of  $-\text{pCOHP} < 0$  signify antibonding states.

stability of the compounds, we removed all the Li or Au atoms of stable structures, respectively. We calculated their energy relative to the elemental. It was found that the Au-N compounds became extremely unstable in energy after the Li atoms had been removed. However, once removing Au atoms, all structures were still thermodynamically stable. For example, the energy of AuN<sub>4</sub>Li under convex hull was reduced from  $-0.275$  to  $-0.330$  eV/atom, which reveals that the stability of this compound benefits from Li-N units.

#### IV. CONCLUSIONS

In summary, we explored the structure of Au-N and Au-N-Li ternary compounds at high pressures through ternary structure prediction methods, by which we have found five stable compounds (Au<sub>2</sub>N<sub>3</sub>Li<sub>9</sub>, AuN<sub>4</sub>Li, AuN<sub>2</sub>Li<sub>5</sub>, AuN<sub>4</sub>Li<sub>10</sub>, and Au<sub>3</sub>N<sub>4</sub>Li<sub>10</sub>) at 100 GPa. COHP and charge analysis clearly show the Au-N bonds in four of these stable compounds, as the example of stable Au-N compounds. Further analy-

ses prove that the stable mechanism of Au-N-Li compounds originates from introducing the electron donor (Li atoms) which react with N and form stable compounds. Our current results highlight the key role of Li in stabilizing the Au-N compounds.

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