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Sodium–gold binaries: novel structures for ionic compounds from an *ab initio* structural search

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Abstract. Intermetallic compounds made of alkali metals and gold have intriguing electronic and structural properties that have not been extensively explored. We perform a systematic study of the phase diagram of one binary system belonging to this family, namely $\text{Na}_x\text{Au}_{1-x}$, using the *ab initio* minima hopping structural prediction method. We discover that the most stable composition is NaAu_2 , in agreement with available experimental data. We also confirm the crystal structures of NaAu_2 and Na_2Au , that were fully characterized in experiments, and identify a candidate ground-state structure for the experimental stoichiometry NaAu . Moreover, we obtain three other stoichiometries, namely Na_3Au_2 , Na_3Au and Na_5Au , that could be thermodynamically


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stable. We do not find any evidence for the existence of the experimentally proposed composition NaAu_5 . Finally, we perform phonon calculations to check the dynamical stability of all reported phases and we simulate x-ray diffraction spectra for comparison with future experimental data.

 Online supplementary data available from stacks.iop.org/NJP/15/115007/mmedia

Unusual and intriguing electronic properties have been found in the binary phases of alkali metals and gold [1–4]. Proceeding through the alkali metal series from LiAu to CsAu , a metal–insulator transition occurs from KAu to RbAu . All compounds have an ionic character, with gold being the anion. The structural properties of these binaries are also peculiar: while RbAu and CsAu adopt an octo-coordinated CsCl structure, analogous to that of CsBr and CsI ionic crystals, the structures of the metallic NaAu and KAu compounds are more complicated and still not fully characterized. A new three-dimensional icosahedral quasi-crystal has recently been discovered by exploring the ternary Na–Au–Ga system [5].

Experimental studies on NaAu solid compounds date back to the beginning of the 20th century. Zintl *et al* [6] obtained a black deposit from an ammonia solution of sodium by adding Au , which they claimed to be a NaAu compound. Since then, three other stoichiometric compounds were obtained from the melts of Na and Au , namely Na_2Au , NaAu_2 and NaAu_5 [2, 7]. While the crystal structures of Na_2Au and NaAu_2 have been fully characterized, no definitive structure is given in the literature for NaAu or NaAu_5 [2, 8–10]. Also, Na_3Au has recently been synthesized under pressure [4].

As gold is a highly electronegative element, while alkali metals are electropositive, one expects some ionic character for alkali metal–gold compounds. The negative oxidation state of gold is the focus of intensive studies, as summarized in recent review papers [11, 12]. Note that by changing x in the $\text{Na}_x\text{Au}_{1-x}$ compound one can in principle change the charge of gold from 0 at $x = 1$ to -1 at $x = 0.5$, and to even more exotic charges by further increasing x . This is relevant in situations where the charge of gold is important, such as for catalysis.

A further motivation to study NaAu binary systems comes from the fact that previous results on clusters and thin-films [1, 3, 13–15] hint at the existence of very different stoichiometries and coordinations. From the theoretical side, there are very few *ab initio* investigations of this family of compounds [16] and almost all the published calculations are devoted to NaAu clusters [3, 14, 15].

Determining from first principles the phase diagram of a solid starting solely from its elemental composition is one of the most fundamental problems in materials science. The phase diagram of a binary compound represents the thermodynamic equilibrium of phases of a two-component system and it reveals useful insights into fundamental thermodynamic properties. However, the experimental determination of a phase diagram is an extremely time-consuming process, that requires careful synthesis and characterization of all possible phases. Accurate *ab initio* computational tools can significantly accelerate the construction of phase diagrams at zero temperature and zero pressure. Furthermore, it is straightforward to include the effects of pressure and temperature.

The theoretical problem of determining a binary phase-diagram can be reduced to the problem of finding the lowest-energy structures for the different possible binary compositions.

The best way to search for new crystal structures is to perform a systematic survey of the enthalpy surface using some sophisticated crystal-structure prediction method. In this context, we use the minima hopping method (MHM) [17, 18], which employs a very efficient algorithm to identify the global minimum on the enthalpy surface while gradually exploring low-lying structures. This method is here coupled to *ab initio* density functional theory (DFT).

The most used technique for the theoretical determination of phase diagrams is cluster expansion [19, 20], which offers a computationally tractable link between accurate first-principles calculations of total energies and statistical mechanics techniques for multicomponent solids. Other *ab initio* structural search methods, such as genetic algorithms [21, 22] and random search [23], have been recently employed to study binary systems and theoretically determine the convex hull. High-throughput *ab initio* computation and data mining were also used for the structural prediction of binary alloys [24].

In this work, we use the MHM for the first time to investigate the phase diagram of binary compounds. The MHM explores the ground-state energy surface by performing short molecular dynamics escape steps followed by local geometry relaxations, taking into account both atomic and cell variables. The initial velocities for the dynamics are aligned preferably along soft-mode directions in order to favor the escape through lower barriers to low-enthalpy structures. Revisiting already known structures is avoided by a feedback mechanism. The MHM has been used for structural prediction in a wide range of materials with remarkable results [25–29].

In this paper we apply the MHM to study the phase diagram of $\text{Na}_x\text{Au}_{1-x}$. For a given stoichiometry, the initial geometries for the MHM runs were obtained randomly, ensuring only that the minimal distance between the atoms was at least equal to the sum of the covalent radii. We used cells containing up to 12 atoms, which, depending on the stoichiometry, corresponds to 1–4 formula units. During the structural search runs, forces and energies were obtained in the framework of DFT using the all-electron projector augmented wave method as implemented in vasp [30]. The Perdew–Burke–Ernzerhof approximation [31] to the exchange–correlation functional was used together with a plane-wave cutoff of 287.4 eV and a number of k -points in direction α given by $|b_\alpha|/(0.03 \times 2\pi)$, where b_α is the reciprocal lattice vector. The resulting structures were then reoptimized by ensuring numerical convergence to less than 2 meV atom⁻¹ by using automatically determined dense k -point grids (see supplementary data (available from stacks.iop.org/NJP/15/115007/mmedia)).

We studied 19 different stoichiometries of $\text{Na}_x\text{Au}_{1-x}$, ranging from pure gold to pure sodium. As discussed above, excluding the pure elemental crystals, five compositions were reported experimentally [32]: Na_3Au [4], Na_2Au [2, 8], NaAu_2 [2, 9], NaAu [2, 6] and NaAu_5 [2]. Na_3Au was recently produced under pressure, and seems to crystallize in a hexagonal ($P6_3cm$) or trigonal ($P-3c1$) lattice [4]. The structures of Na_2Au and NaAu_2 are well characterized. A sample of Na_2Au of overall composition 69.95 at.% at 25 °C Na was indexed as belonging to the $I4/mcm$ space group, crystallizing in a CuAl_2 -type structure [2] with $a = 0.7417$ nm and $c = 0.5522$ nm. On the other hand, NaAu_2 has $Fd\bar{3}m$ symmetry, and crystallizes in a MgCu_2 -type structure [2] with $a = 0.7818$ nm (averaging on three compositions between 33 and 38 at.% at 25 °C). NaAu has been reported to be a complex structure and no crystallographic data are given [2]. Finally, there exists some experimental evidence of the production of NaAu_5 at 775 °C [2], that unfortunately has not yet been confirmed.

Figure 1 shows the convex hull of NaAu binaries, calculated considering all the lowest-energy structures resulting from the MHM simulations for the different compositions $x = \text{Na}/(\text{Na} + \text{Au})$. In this figure, low-energy structures are indicated by crosses, while

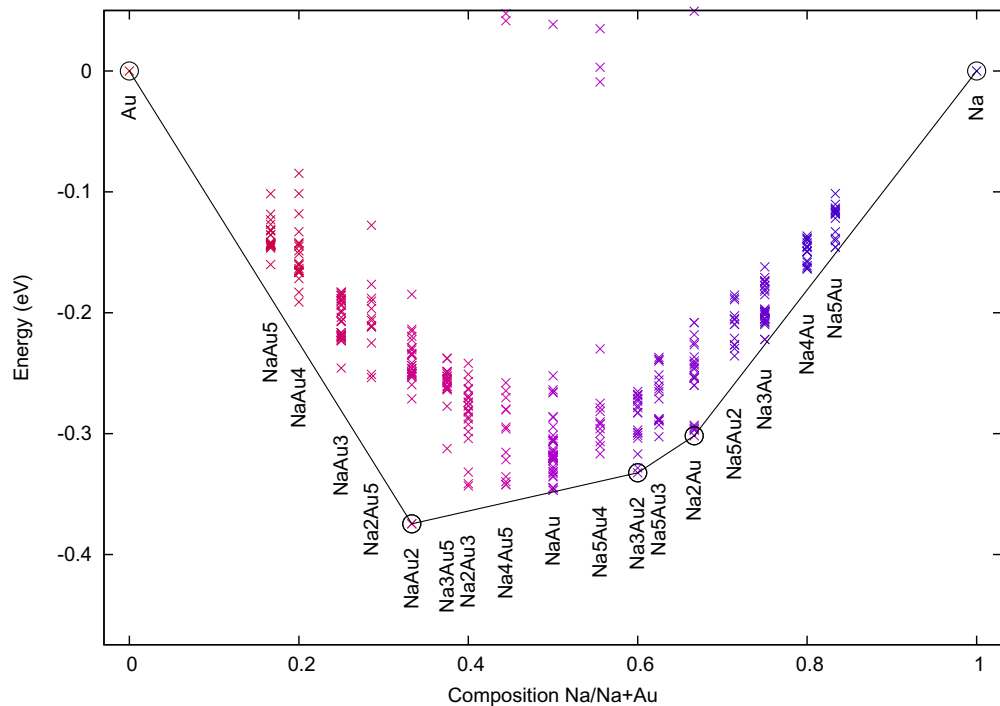


Figure 1. Convex hull of the sodium–gold binary system obtained from *ab initio* MHM calculations. Every cross corresponds to a different metastable structure. The thermodynamically stable compositions are indicated by circles.

thermodynamically stable compositions are marked with a circle. The position of a structure with respect to the convex hull gives the primary criterion for its stability: all phases corresponding to points on top of the line are stable, and those above are unstable. There are, however, two details that we have to keep in mind: (i) there is always an error in the estimation of the formation energy inherent to our theoretical method. Therefore, structures that are ‘unstable’ but close to the convex hull can be stable experimentally, and the inverse can also be true. Of course, a definitive answer regarding the (non)existence of any material can only be given by experiment. (ii) Structures that are close to the stability line can sometimes be stabilized by temperature, pressure, doping or even intrinsic defects.

Based on these rules, we selected our lowest-energy phases which form the convex hull or that are very close to it for further theoretical characterization. The selected crystal structures are presented in figure 2. Further information is contained in the supplementary data (available from stacks.iop.org/NJP/15/115007/mmedia).

We remark that our structural prediction yields the correct ground-state for both pure sodium ($P6_3/mmc$ structure with $a = 0.377$ nm and $c = 0.615$ nm) and gold ($Fm\bar{3}m$ structure with $a = 0.408$ nm). Furthermore, we also obtained the experimentally known structures for the Na_2Au and NaAu_2 phases. The theoretical lattice parameters of Na_2Au are $a = 0.738$ nm and $c = 0.563$ nm, and for NaAu_2 we find $a = 0.795$ nm, in very good agreement with the experimental values [2].

The proximity of the lowest energy structure of NaAu to the convex hull line suggests that this is a good candidate for the NaAu experimental samples. The NaAu structure has $R\bar{3}m$ symmetry, with $a = 0.565$ nm and $c = 1.43$ nm. Of course, we cannot exclude that even more

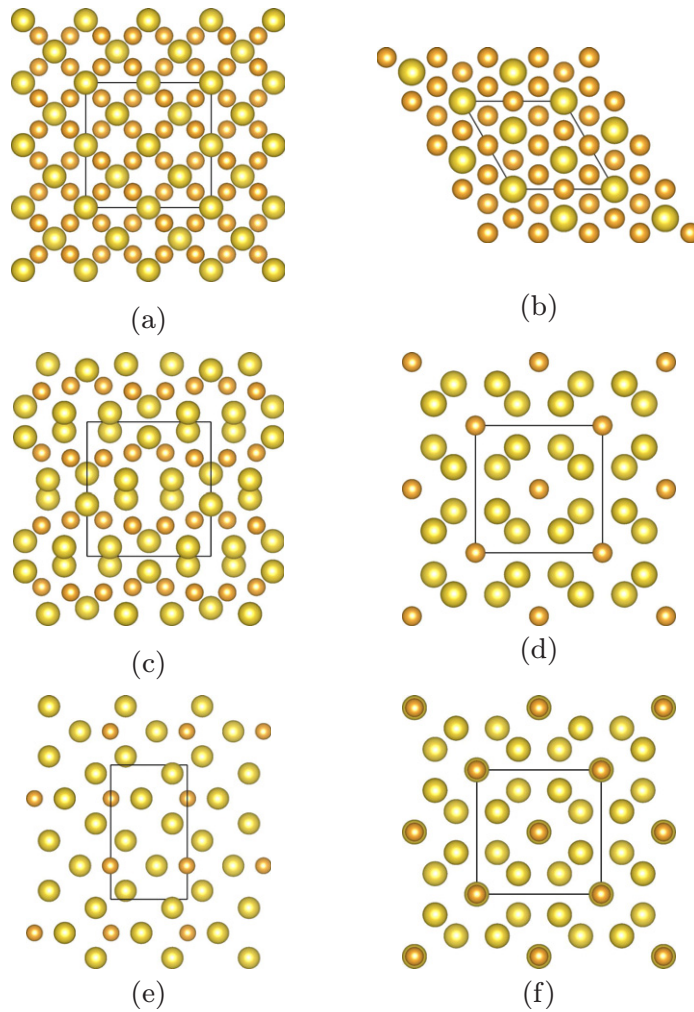


Figure 2. Crystal structures of the lowest-energy phases of $\text{Na}_x\text{Au}_{1-x}$: (a) NaAu_2 (cubic, $Fd\bar{3}m$); (b) NaAu (rhombohedral, $R\bar{3}m$); (c) Na_3Au_2 (monoclinic, $C2/c$); (d) Na_2Au (tetragonal, $I4/mcm$); (e) Na_3Au (monoclinic, $P2_1/m$); and (f) Na_5Au (tetragonal, $P4/nbm$). Sodium atoms are represented by large yellow spheres, while gold atoms are the small orange spheres.

stable structures may be found using larger supercells for the structural search. Despite our extensive search, we could not find any stable structure for the other possible experimental stoichiometry, NaAu_5 . Also in this case, more formula units per cell may be needed to identify a stable geometry. However, our lowest-energy structure of NaAu_5 is very far from the convex hull, inferring that this stoichiometry might not be stable at all. Indeed, the single reported experimental observation has not yet been verified.

We also found three other structures on top or very close to the convex hull which were not reported experimentally: Na_3Au_2 , Na_3Au and Na_5Au . Na_3Au_2 crystallizes in a monoclinic $C2/c$ structure with $a = 0.786$ nm, $b = 0.851$ nm and $c = 0.704$ nm. Na_3Au has a monoclinic $P2_1/m$ space group with $a = 0.573$ nm, $b = 0.926$ nm and $c = 0.458$ nm. Finally, Na_5Au has a tetragonal $P4/nbm$ structure with $a = 0.763$ nm and $c = 0.624$ nm.

We remark that our structure for Na_3Au is different from the one found experimentally under pressure [4]. As the experimental structure has 24 atoms in the unit cell, it would not show up in our simulations that, in this case, were limited to 3 formula units (12 atoms). We compared the experimental structure to those obtained through our MHM runs and we found: (i) at 0 GPa our $P2_1/m$ structure is 4 meV atom^{-1} more stable than the experimental atomic arrangements; (ii) the experimentally determined $P6_3cm$ and $P-3c1$ structures have essentially the same energy (to less than 1 meV atom^{-1}); (iii) the experimental unit cells have a smaller volume per atom than our $P2_1/m$ phase (27.13 versus 27.91 \AA^3) so that it is understandable that the former can be stabilized by pressure. In our calculations Na_3Au lies slightly above the convex hull in agreement with the experimental observation of a reversible transformation to Na_2Au upon release of pressure [4].

In order to further evaluate the stability of the new phases found with the MHM we calculated their phonon spectra. In fact, the existence of imaginary frequencies in the spectra indicates dynamical instability, i.e. that the structure is not a minimum and that the correct structure contains a larger number of atoms in the unit-cell. Note that this is not a proof that the structure is the absolute minimum, but only indicates that it is a valid (meta-)stable phase. Our phonon calculations were performed with density-functional perturbation theory as implemented in the ABINIT [33] DFT software package with a norm-conserving set of pseudopotentials as found in the ABINIT web page. We note that structures reoptimized with ABINIT were very close to the ones obtained with VASP. For the six structures shown in figure 2 we used a cutoff energy of 40 Ha, a $2 \times 2 \times 2$ q -grid and a $4 \times 4 \times 4$ (for Na_5Au and Na_3Au_2) or a $8 \times 8 \times 8$ (for the others) k -point grid.

Figure 3 shows the phonon bandstructures for the new phases that are not experimentally known (the other phonon band structures can be found in the supplementary data (available from stacks.iop.org/NJP/15/115007/mmedia)). We can observe that, as expected, acoustic frequencies go to zero at Γ and no unstable modes are present, clearly showing the dynamical stability of these phases. Furthermore, the maximum phonon frequencies range from 160 to 190 cm^{-1} . These values are larger than their counterparts for pure sodium ($\sim 120 \text{ cm}^{-1}$ [34]) and pure gold ($\sim 150 \text{ cm}^{-1}$ [34], [35]), indicating a stronger (ionic) bonding in the alloys. The analysis of the electronic band structures (also shown in the supplementary data) confirms that all the different phases are metallic.

The metallic character of these compounds and their larger phonon frequencies raises the question of superconductivity in $\text{Na}_x\text{Au}_{1-x}$. According to the strong-coupling theory of electron–phonon mediated superconductivity, the transition temperature is proportional to an average phonon frequency. It is well known that neither sodium nor gold is superconducting at ambient pressure, but it is unclear if the increased phonon frequencies in Na–Au alloys is enough to yield superconductivity. To investigate this matter we performed linear-response calculations of the electron–phonon coupling with ABINIT. Our results indicate that these alloys are very likely superconductors, but with transition temperatures as low as 2 K due to the relatively small value of the electron–phonon coupling constant λ .

In table 1 we report the Bader charges on the crystallographically non-equivalent atoms for the lowest-energy structures of each stoichiometry. We can clearly see that the negative charge on gold increases monotonically by increasing the sodium content. In particular, it reaches the remarkable value of -2.25 for Na_5Au , showing that the NaAu binary system is a perfect playground to study how gold behaves in very different chemical environments.

Table 1. Stoichiometry, Bader charge on Na inequivalent atoms and on Au inequivalent atoms for the lowest-energy structures found. The Bader charges are given in elementary charge units.

Stoichiometry	Charge on Na	Charge on Au
NaAu ₂	0.81	-0.40
NaAu	0.70, 0.74	-0.72
Na ₃ Au ₂	0.71	-1.06
Na ₂ Au	0.63	-1.25
Na ₃ Au	0.60, 0.66	-1.85
Na ₅ Au	0.18, 0.52	-2.25

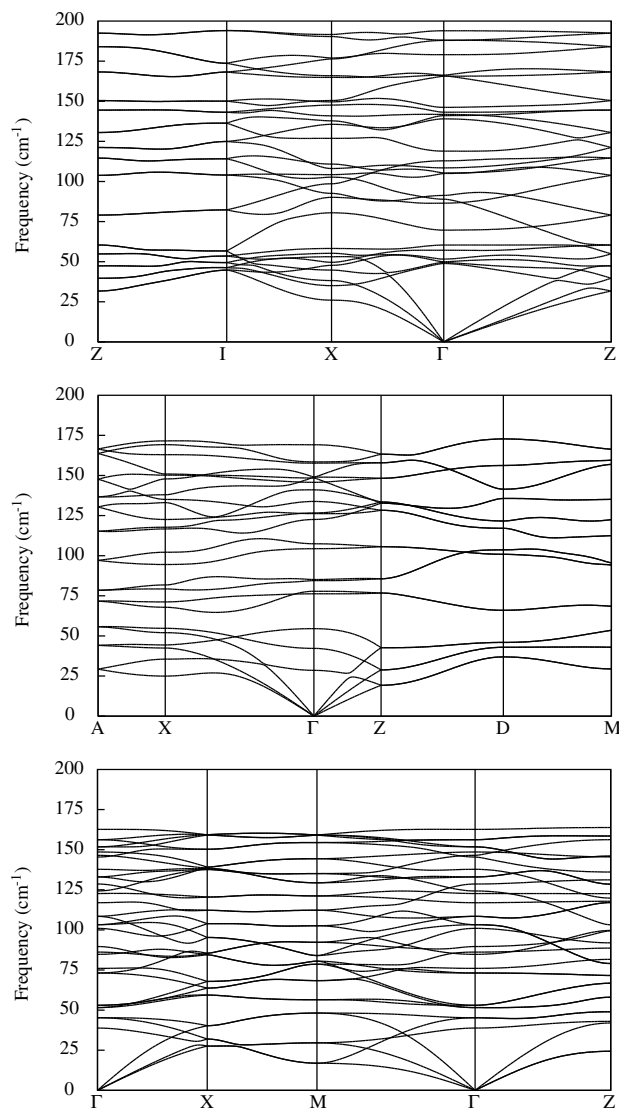


Figure 3. Phonon band structures. From top to the bottom: Na₃Au₂, Na₃Au and Na₅Au.

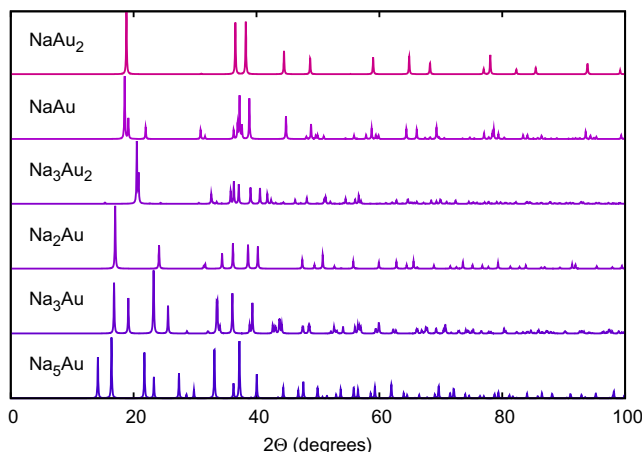


Figure 4. Simulated x-ray diffraction spectrum with Cu $K\alpha$ radiation $\lambda = 1.54178 \text{ \AA}$.

Finally, in figure 4 we provide simulated x-ray diffraction spectra for the lowest-energy structures of the six stable compositions. Comparing with the experimental reported spectrum for NaAu_2 in [36], it is notable that both NaAu_2 and NaAu agree well with experiments (despite the large amount of noise present in the experimental data): the peak around $2\theta = 10^\circ$ and the two peaks near $2\theta = 20^\circ$ and 40° are present in both spectra.

In summary, using the MHM we found two already known and four novel structures of $\text{Na}_x\text{Au}_{1-x}$ that are expected to be thermodynamically stable. In the cases of Na_2Au and NaAu_2 our minima hopping runs converged to the reported experimental geometries. We found a likely candidate for the crystal structure of NaAu , which was reported experimentally but not fully characterized. We also found for the first time a tetragonal Na_5Au phase, and monoclinic phases for Na_3Au_2 and Na_3Au . We calculated phonon band structures for the lowest-energy phases and we found that all of them are dynamically stable. Of course, the methodology presented here to study thermodynamic phase diagrams is absolutely general, and can be used for any other binary system.

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