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Existence of a stable compound in the Au-Ge alloy system

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First-principles electronic structure calculations predict the existence of a crystalline compound in the Au-Ge system. The structure is found by matching the theoretically determined local atomic structure in the liquid state with that for experimentally known crystal structures in other alloys. Subsequently, the best matching crystalline structures were structurally optimized using first-principles methods. Surprisingly, although Au-Ge is known as a non-compound-forming system, a crystal structure was found to be more stable than the terminal phases by about 6 meV/atom at $T=0$ K. Possibly, this structure can be prepared by a suitably chosen substrate such as Pt_5P_2.

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Eutectic Au-Ge alloys are among the most unknown ubiquitous materials around—they form an essential ingredient in semiconductor interconnects as testified by more than 20 000 patents that explicitly mention them. The eutectic alloys are of great interest also for nanoscience applications such as growing Ge nanowires.[1]

In many aspects Au-Ge appears similar to Au-Si: both systems feature deep eutectics, lack well-defined experimentally observed compounds, and both are among the earliest known metallic glasses.[2,3] Recent experimental studies have shown marked differences between the two systems, however. Whereas eutectic Au-Si exhibits a liquid surface structure with strong Si surface enrichment and planar ordering,[4] this is not observed in eutectic Au-Ge.[5] The coordinations in the eutectics also show differences.[6]

Recently, it was predicted that a compound Au_4Si could exist in Au-Si (Ref. 7) in spite of it being known as a non-compound-forming system.[8] This makes relevant the question whether a similar compound exists in Au-Ge in view of long-term phase stability and time evolution of physical properties of interconnects of semiconductor and other devices. It should be mentioned that we are interested in stable compounds at ambient pressure and we are not concerned with the high-pressure hcp phase $Au_{0.75}Ge_{0.25}$ (Ref. 9) or with metastable compounds.[3]

Here, we shall apply the same methodology as in Ref. 7. First, the local atomic coordinations are determined via first-principles molecular-dynamics modeling of the eutectic alloy, followed by a matching of the local atomic environment with all known experimental crystal structures as compiled in the Pauling File Binaries database.[10,11] The structures that match best and are compositionally close to the eutectic are selected for detailed study. They are structurally refined and their stabilities with respect to the elemental ground states are determined. This methodology does not guarantee that there is not a lower-energy structure. After all, only the set of observed crystal structures are used for the match, and quite possibly as yet an unknown crystal structure could occur. However, if only one structure is found to be stable, it does prove the alloy to be a compound-former and more sophisticated and computationally demanding methods can be applied to find even more stable compounds.[12–15]

Using the local atomic structure in the liquid state to search for crystal structures might appear unlikely to succeed because metallic melts usually feature icosahedral clusters[16] which are not seen in the stable crystal structures. In Au-Ge the situation is a little different however: icosahedral order is not prominent, the local atomic structure in the liquid is very stable with respect to temperature, and this structure persists down to the eutectic temperature (634 K) which is about half of the melting point of the pure elements (Au: 1337 K; Ge: 1216 K).[6,17,18] The thermal stability implies that local atomic structures in the liquid are strongly bonded and not much affected by thermal excitations. Thus the spectrum of atomic environments in the liquid can reasonably be expected to give a shortlist of the most likely crystal structures. Here, we use the coordination number (CN) distribution in the liquid as the only descriptor of local atomic structure for matching with crystal structures although other local atomic structure descriptors, such as common neighbor analysis and (partial) structure factors, can be used also. It should be mentioned that in spite of its thermal stability the local atomic structure in the liquid is not kinetically locked because our calculations give diffusivities characteristic of a liquid phase.[19]

The local structure of the liquid eutectic alloy was determined through *Ab Initio* Molecular Dynamics (AIMD) simulations[20–24] with the same settings as in Ref. 7. All the dynamical simulations were carried out in the NVT ensemble by means of a Nosé thermostat to control temperature. Newton's equations of motion were integrated using the Verlet algorithm with a time step of 3 fs. We have considered systems of 256 atoms in a cubic box with periodic boundary conditions. The initial structure is obtained by adding silicon atoms to a pure gold liquid structure up to the eutectic composition. Only the Γ point was considered for integrations over the supercell Brillouin zone. For each temperature, runs involved 3 ps of equilibration followed by 27 ps during which 2000 configurations were sampled to obtain averaged structural quantities. The partial pair-correlation functions for each type of pair were evaluated for the positions of their extrema to define the coordination shells. More particularly, the Au and Ge coordination numbers were determined by

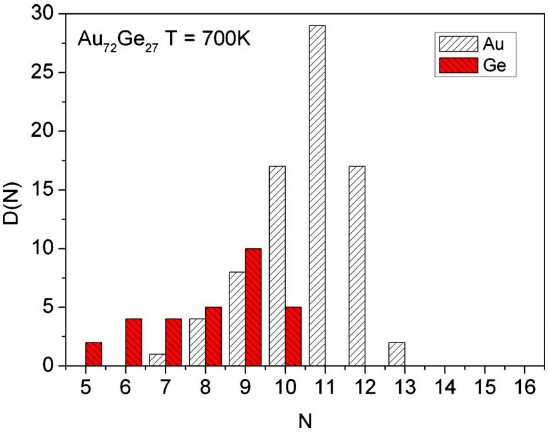

FIG. 1. (Color online) AIMD computed coordination number distribution of Au and Ge for liquid $Au_{72}Ge_{28}$ alloy at 700K.

counting the number of atoms in the first coordination shells directly from the configurations. The first coordination shells have radii corresponding to the first minimum of the partial pair-correlation functions $g_{ij}(r)$ $(i,j=\text{Au and Ge})$ of the liquid. Consequently the CN for each atom results from the sum of Au and Ge atoms being inside the shells. This method has the advantage of providing the CN around individual Au or Ge atoms, and therefore gives access to their distributions. We have verified that the CNs averaged over the configurations, i.e., $CN_i=CN_{ii}+CN_{ij}$, are the same as those obtained from the integration of the radial distribution functions $RDF_{ij}(r)=c_j 4\pi\rho r^2 g_{ij}(r)$, where ρ is the atomic density and c_j the concentration of the type j atom. The values of the average CNs are not very sensitive to the variation in the cut-off distances. The resulting total coordination number takes a value of 10.3 at 700 K, in good agreement with the experimental value of 10.4.[18]

Figure 1 shows the AIMD calculated CN distributions in the $Au_{72}Ge_{28}$ alloy at 700 K. It features two CN ranges with Au (Ge) atoms in the CN range of 7–13 (5–10) in good agreement with the experimental findings.[18] The database was then searched for all structures that had one atomic species with CNs 7–13 and another atomic species with CNs 5–10. Additionally we imposed that the species with the smaller CN have a concentration within the interval 24–32 at.% (Ref. 25) and we excluded structures with partially occupied sites. A database[10,11] with about 30.000 structures, belonging to 2634 prototypes, yielded just 11 candidate structures.

TABLE I. DFT computed formation enthalpy ΔH and the excess volume ΔV for Au-Ge prototype structures.

Composition	Prototype structure	ΔV (Å^3/atom)	ΔH (meV/atom)
Au	Au,cF4, 225	0.00	0.0
$Au_{0.75}Ge_{0.25}$	Cu_3As, cI64, 220	−0.15	30.2
$Au_{0.75}Ge_{0.25}$	Mg_3Hg, hR72, 155	−0.53	80.7
$Au_{0.75}Ge_{0.25}$	Mn_3As, oS16, 63	−0.38	67.4
$Au_{0.75}Ge_{0.25}$	PH_3, cP16, 201	7.77	271.3
$Au_{0.71}Ge_{0.29}$	Mg_2Ga_5, tI28, 139	−0.29	111.0
$Au_{0.71}Ge_{0.29}$	Nd_2Te_5, oS28, 63	−0.82	45.6
$Au_{0.71}Ge_{0.29}$	Ni_5Sb_2, mS28, 5	−0.61	37.0
$Au_{0.71}Ge_{0.29}$	$Pt_{12}Si_5$, tP68, 85	−0.43	28.1
$Au_{0.71}Ge_{0.29}$	Pt_5P_2, mS28, 15	−0.41	−6.1
$Au_{0.70}Ge_{0.30}$	Gd_3Sn_7, oS20, 65	−1.41	70.4
$Au_{0.69}Ge_{0.31}$	Sm_9Ga_4, tI26, 87	−1.48	73.6
Ge	C,cF8, 227	0.00	0.0

The 11 prototype structures were relaxed through first-principles calculations with the same approximations as used for the AIMD simulations. The atomic species in the candidate prototype structures were substituted by Au and Ge atoms, with respect to their CNs and compositions. Brillouin-zone integrations used a Gamma point centered grid with at least 5000/(number of atoms in unit cell) uniformly distributed **k** points. Precision was set to "accurate" and the convergence criterion for the energy was 0.1 meV. A cut-off kinetic energy of 400 eV was used. The system was optimized first over volume only, next over cell shape, followed by optimization over internal coordinates, and finally over all crystallographic degrees of freedom simultaneously, in order to assure retention of the original structure type. In the structural optimizations, the Methfessel-Paxton scheme[26] was employed, but for the final static evaluation of the total energy we used the tetrahedron scheme with Blöchl corrections.[27]

After structural optimization, the formation enthalpy ΔH and the excess volume ΔV per atom are obtained through the following equations:

$$\Delta H(Au_nGe_m) = [H(Au_nGe_m) - nH(Au) - mH(Ge)]/(n+m), \tag{1}$$

$$\Delta V(Au_nGe_m) = [V(Au_nGe_m) - nV(Au) - mV(Ge)]/(n+m), \tag{2}$$

reference system for pure Au (Ge) being the face centered cubic structure (diamond structure). Table I lists all prototype structures considered as Au-Ge compounds. In addition to the prototype, the Pearson classification and space group label are shown also.[10] Clearly Au-Ge is not very similar to Au-Si because only three of the 11 prototype structures correspond with those previously generated for Au-Si. With the exception of PH_3 prototype $Au_{0.75}Ge_{0.25}$, all candidate struc-

TABLE II. DFT computed structural properties of Au_5Ge_2, mS28, 15. Column labeled "Wyck." represents site multiplicity and the Wyckoff symbol.

Lattice	$a=11.365$ Å; $b=6.261$ Å; $c=7.675$ Å			
Parameters	$\gamma=90.3°$			
Sites	Wyck.	x	y	z
Au1	8*f*	0.87031	0.77888	0.43442
Au2	8*f*	0.87132	0.77507	0.06544
Au3	4*e*	0	0.11784	0.25
Ge	8*f*	0.17158	0.40862	0.24989

tures yield low formation enthalpies and small volume contractions. Among the candidate structures Au_5Ge_2, structural properties given in Table II, with the Pt_5P_2 prototype structure is found to be stable by about 6 meV/atom relative to the terminal Au and Ge phases at 0 K.

The Au_5Ge_2 compound is stable also when other exchange-correlation functionals are considered: the generalized gradient approximation of Perdew-Burke-Ernzerhof[28] gives ΔH as -4.7 meV/atom and ΔV as -0.43 Å^3/atom while local density approximation[29] gives ΔH as -10.5 meV/atom and ΔV as -0.45 Å^3/atom.

The Au_5Ge_2 compound is characterized by strong Au-Ge interactions as evidenced by Ge being fully coordinated by 6 Au atoms, and Au atoms having CNs of 9 and 10, with the 2 and 3 shortest bondlengths involving Ge neighbors. Strong Au-Ge interaction was surmised previously in the liquid phase[17] and the amorphous state.[30] This finding contradicts the common understanding of Au-Ge as a non-compound-forming system with mutually insoluble terminal phases. Recently, some of the authors proved the existence of a compound in the Au-Si system also,[7] but note that the Au_5Ge_2 structure and the Au_4Si structure (Pd_4Se prototype[7]) are not similar and have distinct CNs and confirming that Au-Si and Au-Ge are only superficially similar.

The Au_5Ge_2 structure can possibly be prepared by low temperature annealing of Au-Ge deposited on a suitable lattice-matched substrate, the (010) plane of the Pt_5P_2 might be a candidate for this purpose.

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[25] We limited the composition range because the local atomic structure in the liquid is composition dependent.[6,18] This is evident also when considering that pure Au has CN=12 and pure Ge has CN=4. Expanding the composition range to 20–34 at. % Ge did generate more structures, but none of these were more stable than those found in the 24–32 interval.

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