PHYSICAL REVIEW B **81**, 140202(R) (2010)

Structural and dynamic evolution in liquid Au-Si eutectic alloy by *ab initio* molecular dynamics

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(Received 8 March 2010; published 19 April 2010)

We report the results of first-principles molecular-dynamics simulations for liquid and undercooled eutectic $Au_{81}Si_{19}$ alloys at various temperatures. Through comparisons between $Au_{81}Si_{19}$ and Au liquids, we show the strong effects of Si alloying on the atomic-scale structure, namely the occurrence of a well-defined chemical short-range order and the slowing of the formation of icosahedral local motifs as a function of temperature. Such a behavior may explain the stability of the liquid phase at the eutectic composition by an enhancement of AuSi interactions. In examining the dynamic properties of both systems, we demonstrate a strong interplay between these structural changes and the evolution of diffusivity at low temperatures. All these results yield a possible scenario for the occurrence of such an unusual deep eutectic point.

DOI: 10.1103/PhysRevB.81.140202 PACS number(s): 61.25.Mv, 61.20.Ja, 66.10.−x

Undercooling phenomena of metallic liquids have challenged thermodynamics, crystal nucleation theory, and the physics of liquids since their first observation.[1] To explain the large undercooling observed in some metallic alloys, Frank was the first to suggest that the internal structure of the liquid itself must be responsible for the metastable behavior.[2] Icosahedral clusters were supposed to form in the liquid, which increases the nucleation barrier for crystallization. These clusters, models of icosahedral short-range order (ISRO), are now widely accepted as the origin of undercooling and as basic structural elements of liquid and amorphous metallic systems.[3] The presence of ISRO in metallic systems has been proven experimentally[4,5] and by *ab initio* molecular dynamics simulations (AIMD).[6]

By contrast, the undercooling behavior of metal-semiconductor alloys is not well understood although eutectic compositions in these systems can easily form glasses with rapid cooling, such as the AuSi eutectic alloy that was the first discovered metallic glass.[7] Metal-semiconductor eutectic alloys are also very important for the electronics industry. For instance, the binary metal-semiconductor liquids are at the heart of the catalytic growth of semiconductor nanowires by the vapor-liquid-solid process[8] since their liquid phase guarantees a very high mobility of the semiconductor atoms at relatively low temperatures.

For AuSi, the eutectic temperature (359 °C) is many hundreds of degrees below the melting points of Au (1063 °C) and Si (1412 °C). The reasons for such an unusual deep eutectic point remain puzzling and attract therefore considerable attention. The deep eutectic point has been speculated to be related to the high stability of the liquid phase that exhibits bonding behavior distinct from the solid phase,[9,10] contrary to a commonly held assumption. Despite the large amount of research in this system, remarkably little is known about the properties of the liquid AuSi eutectic alloy, in particular, about atomic structures and diffusion properties. Very recently, Takeda *et al.*[11] proposed a structural investigation of liquid AuSi and AuGe alloys around the eutectic region by coupling x-ray diffraction measurements with reverse Monte Carlo simulations. The reproduced atomic arrangements around the eutectic region are discussed only in terms of local coordinations. They exhibit a substitutional-type structure where the dense random packing of Au atoms is preserved and Si or Ge atoms occupy the Au sites randomly.

Molecular dynamics simulations offer an alternate possibility to reveal the complete details of the local structure in liquids and their dynamic properties not available from experiments. However, an accurate simulation of the properties of liquid AuSi alloys is still a challenging problem since bonding in the liquid phase are not well described by currently available pair and embedded-atom potentials[12] and have to be captured from first principles within the density functional theory (DFT).

To further address the important question of the local structure in connection with the stability and the fluidity in the liquid eutectic alloys, we have performed a series of full *ab initio* molecular dynamics simulations within the DFT of the pure Au liquid and liquid AuSi eutectic alloy in the stable and undercooled states. These calculations allow us to resolve their structure and dynamics from first principles. We examine the evolution of the local ordering as a function of the Si-alloying effect and temperature as well as the atomic diffusion in order to understand the presence of the deep eutectic point in this system. For the eutectic alloy, our findings show that the local structure is characterized by a strong AuSi affinity, which disfavor the occurrence of the ISRO. Using pure Au liquid as the reference system, we obtain an amount of icosahedral ordering in AuSi that is a factor of two smaller than that of Au at its melting temperature. Moreover, we clearly demonstrate that the slowing of formation of icosahedral motifs as a function of temperature explains the exceptional diffusivity of the eutectic alloy at low temperatures.

The AIMD simulations were carried out using the DFT as implemented in the Vienna *ab initio* simulation package.[13] Projected augmented plane waves[14] (PAWs) with the Perdew-Wang exchange-correlation potentials have been adopted. The valence state of each element has been defined previously in the provided PAW potentials and the plane-wave cutoff is 245 eV. All the dynamical simulations were carried out in the canonical ensemble by means of a Nosé thermostat to control temperature. Newton' s equations of motion were integrated using the Verlet algorithm in the velocity form with a time step of 3 fs (see Ref. 15 for a comprehensive textbook). We have considered a system of 256 atoms in a cubic box with periodic conditions. Only the Γ point was considered to sample the supercell Brillouin zone. For $Au_{81}Si_{19}$ alloy, the initial configuration was taken from the well-equilibrated liquid Au system in which some Au atoms were randomly substituted with Si atoms. For both Au and $Au_{81}Si_{19}$ systems, the volume of the cell was fixed to reproduce the experimental densities.[16] Each system is equilibrated at $T=1400$ K for 3 ps, the run was continued for 30 ps. Then for $Au_{81}Si_{19}$, the system is quenched successively to $T=1200$, 1000, and 700 K, mentioning that the same equilibration protocol at 1400 K was used for each temperature. The procedure is repeated in the undercooled region for $T=600$, 500, and 400 K. For pure Au, the undercooled region is defined by $T=1200$ and 1000 K. We take advantage of the large cooling rate provided by AIMD simulations, 5×10^{12} K s^{-1}, to explore the metastable undercooled state. More specifically, it is experimentally known that the equilibrium eutectic mixture is formed when the alloy is slowly cooled ($<10^{3}$ K s^{-1}) while amorphous phases are obtained for cooling rates larger than 10^{6} K s^{-1}. For each system and temperature, 2000 configurations were used to produce averaged structural quantities such as the partial pair-correlation functions. Among these configurations, ten were selected at regularly spaced time intervals to extract their inherent structures.[17]

We first examine the evolution of the local structure throughout the temperature range during cooling of $Au_{81}Si_{19}$ liquid. In Fig. 1, the partial pair-correlation functions $g_{ij}(r)$ are displayed. Upon undercooling, the evolution is small with only a weak increase in the first peak and an enhancement of a shoulder in the second peak of the three partials. The main feature is the relative height of the first peaks of AuSi and SiSi partials. It is a clear indication that the liquid phase is characterized by strong intermixing between Au and Si atoms, namely, a strong chemical short-range order (CSRO). The calculated Warren CSRO parameter as well as the negative heat of mixing indicates also a preferred association of unlike atoms in the liquid phase.[18] The main consequence of this effect is the existence of close packing in the liquid alloy that accommodates Si atoms like "solute" atoms. This result is not dissimilar to the model proposed initially by Hume-Rothery and Anderson for eutectic alloys.[9] Such a behavior contrasts with the known thermodynamically stable solid made of two separate phases and may largely account for the sharp low-lying eutectic in this system as discussed by Chen and Turnbull.[10] The high stability of the liquid phase can be also related to the recent discovery of a new crystalline ground state at the eutectic composition. Tasci *et al.*[19] predict the occurrence of a new crystalline ground state using the liquid structure as a guide for phase stability on the solid state. More particularly, the Pd_4Se prototype structure is computed to be stable by about 10 meV/atom relative to the terminal fcc Au and diamond Si phases at 0 K.

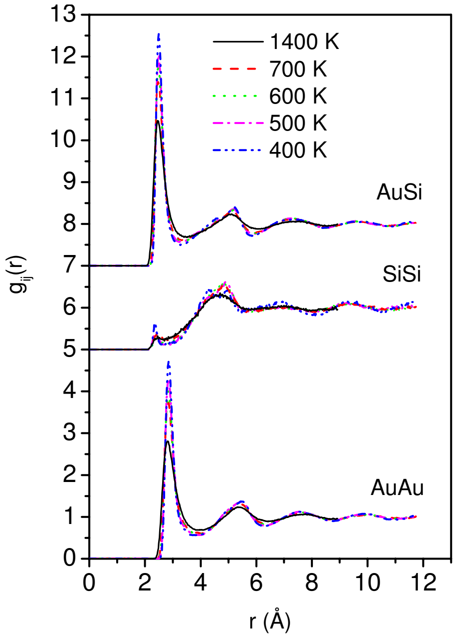

FIG. 1. (Color online) Partial pair-correlation functions of $Au_{81}Si_{19}$ as a function of temperature. The curves for SiSi and AuSi partials are shifted by an amount of 5 and 7, respectively.

The atomic structure of liquid $Au_{81}Si_{19}$ is therefore largely different from the like-atom clustering observed in the solid phase. More insight into the structural changes is gained by analyzing the inherent structures and characterizing the local environment surrounding each atomic pair that contributes to the first peaks of $g_{ij}(r)$ in terms of the number and properties of common nearest neighbors of the pair under consideration.[20] We considered bonded pairs for which the root pair has at least one Au atom in $Au_{81}Si_{19}$ and temperature evolution is compared to that of bonded pairs in pure Au liquid. In Fig. 2, we report the most abundant bonded pairs, i.e., 142x (sum of 1422 and 1421), 1431 and 15xx pairs found in both systems. The number of 15xx bonded pairs is a direct measure of the degree of icosahedral ordering including both perfect and distorted icosahedral motifs while 142x bonded pairs are characteristic of close packed structures. The 1431 pairs either can be considered as

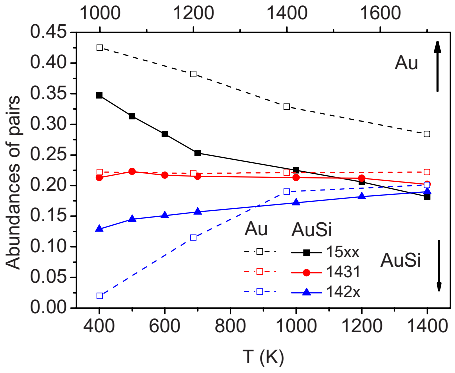

FIG. 2. (Color online) Evolution of the most important bonded pairs for Au and $Au_{81}Si_{19}$ as a function of temperature. See text for more details.

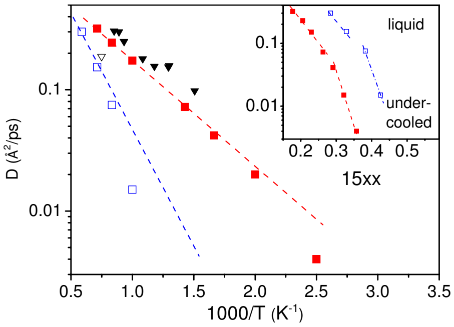

FIG. 3. (Color online) Evolution of the self-diffusion coefficients for Au (open squares) and $Au_{81}Si_{19}$ (full squares) as a function of temperature. The open triangle corresponds to the experimental value of liquid Au at the melting point inferred from the viscosity data of Ref. 24 and the full triangles are the experimental data of Ref. 23 of $Au_{81}Si_{19}$ in the liquid state. Inset: evolution as a function of the abundance of bonded icosahedral pairs.

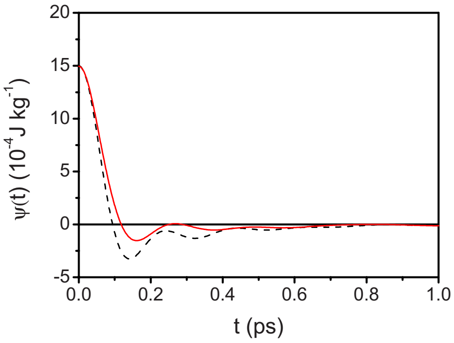

FIG. 4. (Color online) Velocity-autocorrelation function for Au (dashed line) and Au in $Au_{81}Si_{19}$ (solid line) at $T=1200$ K.

distorted icosahedra or distorted close-packed structures.[6] As they are similar in both systems and hold steady with temperature, they are not considered to be responsible for differences between both systems and/or as a function of temperature. For both systems, the fraction of 15xx is already present in the liquid phase and grows rapidly as the temperature drops in their undercooled liquid regions. At the same time, we note a decrease of 142x pairs. The interesting result is that the fraction of 15xx in the liquid phase decreases dramatically after the Si alloying. Indeed, at the melting temperature of Au, the fraction of 15xx in liquid Au is two times greater than that found in the $Au_{81}Si_{19}$ liquid. In comparison, the doubling of the fraction of 15xx in the $Au_{81}Si_{19}$ liquid occurs only around the eutectic temperature, 704 °C lower in temperature. At still lower temperatures, the development of icosahedral motifs slows down in the $Au_{81}Si_{19}$ liquid. Such a situation is quite opposite to what is observed in binary Cu-Zr alloys that can be vitrified in bulk metallic glasses since alloying effects in these alloys lead to an enhancement of the icosahedral local symmetry.[21] As we will demonstrate in this Rapid Communication, the evolution of the local structure as a function of the Si-alloying effect and temperature is crucial in understanding dynamic properties of the liquid phase at the eutectic composition.

For this purpose, we have monitored dynamic properties of Au and $Au_{81}Si_{19}$ by first evaluating the mean-square displacement (MSD) to determine the self-diffusion coefficients, D, as well as their evolution as a function of temperature shown in Fig. 3. In order to get the equilibrium solid phase, atoms have to diffuse rather large distances while the formation of metastable phases should be limited by diffusion processes in both liquid and solid phases. Therefore, diffusion processes are also important factors to explain the occurrence of stable or metastable solid phases at the eutectic composition. In the liquid state, the ballistic regime in the MSD is directly followed by a diffusive regime at long times from which D is extracted. At lower temperatures corresponding to the undercooled region, a well-known caging effect[22] takes place after the ballistic motion, delays the diffusive regime and gives rise to the non-Arrhenius dramatic slowdown of D. This is expected at least qualitatively by the mode coupling theory,[22] describing an evolution between a homogeneous viscous flow at high temperatures to a heterogeneous dynamics driven more and more by thermally activated events as the temperature is lowered, and dominated by cage effects that will be analyzed below in terms of backscattering. As shown in Fig. 3, for $Au_{81}Si_{19}$ the values of D are in good agreement with the experimental data[23] in the liquid state and display the same evolution with temperature. For pure Au at the melting point, the value of D is close that inferred from the viscosity measurements[24] by using the Stokes-Einstein relation. Note that the self-diffusion coefficients of Au and Si species in the alloy are very similar and then the self-diffusion coefficient of the alloy gives direct information about the Si-alloying effect on the diffusivity of Au atoms.

At the temperature corresponding to the melting of pure Au, the diffusivity of the $Au_{81}Si_{19}$ liquid is found to be twice that of pure liquid Au. At the eutectic temperature, $Au_{81}Si_{19}$ still displays a diffusivity characteristic of a liquid phase, which is not the case for pure Au. Such an increase in the diffusivity by the Si-alloying effect can be related to dynamical correlations. Because of their high density, the backscattering regime is predominant for pure Au and $Au_{81}Si_{19}$ liquids. The backflow induced by a moving atom increases the probability of an atom to jump back toward its initial position. It is characterized by a well-pronounced minimum in the velocity autocorrelation function which is very sensitive to the local liquid density. From Fig. 4, it can be seen that this minimum is more important for pure Au than for $Au_{81}Si_{19}$ at the melting temperature of Au. This variation is due to the strong chemical short-range order in $Au_{81}Si_{19}$, which has two main effects: the first one is to decrease the local gold density around a given gold atom while the second one is to slow down the occurrence of the icosahedral motifs, as discussed below, which are known to be the most compact local structures. Consequently, the backscattering is less pronounced in the alloy and the diffusivity is higher.

We come now to the discussion of the evolution of diffusivity as a function of temperature, shown in Fig. 3. While it is Arrhenius for $Au_{81}Si_{19}$ in the liquid state, in accordance with experiment, it becomes non-Arrhenius below the eutectic point, with a more rapid decrease in D. Such an evolution also holds for pure Au with a lower diffusivity. As mentioned above, below the melting or eutectic point, a rapid increase in the 15xx bonded pairs is seen in both systems. It is worth mentioning that such a rapid increase in the icosahedral ordering associated to a non-Arrhenius evolution of the diffusivity is a characteristic feature of fragile liquids.[25,26] Clearly, the development of a icosahedral ordering in the undercooled regime leads to a more pronounced backscattering effect and then is directly responsible for the slowdown of the dynamics in the undercooled liquid. Such a joint evolution is a strong indication that a correlation between the icosahedral local structure and the diffusivity might exist, as emphasized in the Inset of Fig. 3. This correlation, revealing a behavior in the stable liquid which is distinctive from that of the undercooled liquid, give the possibility to distinguish the two regimes. It explains also the ability of this alloy to form amorphous phases because metallic amorphous phases are known to be stabilized due to the slow dynamics induced by the icosahedral ordering in the supercooled liquid.[6]

In summary, the results presented here enable us to identify the Si-alloying effect on the local structure as a fundamental process underlying the peculiar properties of the eutectic liquid $Au_{81}Si_{19}$ alloy. The local structure of the eutectic alloy shows a well-defined CSRO that enhances AuSi interactions in contrast with the solid mixture and may explain the high stability of the liquid phase on the basis of preferential AuSi bonds. By computing dynamic properties, namely, the self-diffusion coefficients and velocity autocorrelation functions of both systems, we demonstrate that the other consequence of the Si-alloying effect is to lower the icosahedral ordering and then to boost the atomic mobility with self-diffusion coefficients characteristic of the liquid state down to the eutectic temperature. Moreover, the rapid icosahedral increase occurs only below the eutectic temperature, in the undercooled region, and is responsible for the non-Arrhenius slowing down the dynamics. We believe that the existence of the very deep eutectic in this system arises from these unusual bonding properties.

We acknowledge the CINES and IDRIS under Project No. INP2227/72914 as well as PHYNUM CIMENT for computational resources. The ANR is gratefully acknowledged for financial support under Grant No. ANR:BLAN06-3_138079.

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