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Structure of eutectic alloys of Au with Si and Ge

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Abstract

Au–Si and Au–Ge alloy systems have a deep eutectic point in the Au-rich concentration region where the melting point falls down to 633 K. In order to investigate the liquid structure in relation to the glass-forming tendency of these alloys, high-energy X-ray diffraction measurements have been carried out at the eutectic composition and at compositions with excess amounts of Au or IVb element. The nearest neighbor correlations in the eutectic liquids are intense and sharp in the pair distribution function and exhibit a rather small temperature dependence in comparison with those alloys of other than the eutectic composition. Structural models for these liquid alloys are proposed with the aid of reverse Monte Carlo simulation. The reproduced atomic arrangements around the eutectic region exhibit a substitutional-type structure where the dense random packing of Au atoms is preserved and Si or Ge atoms occupy the Au-sites at random.

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1. Introduction

The Au–Si alloy system has a deep eutectic around the composition of 19 at.% Si, where the melting point falls down to 636 K, although each pure elemental material has a high melting temperature (Si 1683 K, Au 1338 K [1]). This is also the case for the Au–Ge, where it also falls down to 629 K at 28 at.% Ge being far below the melting temperature of pure Ge [1]. Au–Si is well known as the leading material related to the discovery of metallic glasses since for the quenched material at the composition of 25 at.% Si a hallow diffraction pattern was firstly observed for metallic alloys [2]. After this discovery, Mangin et al.[3] reported the structure of vapour deposited amorphous Au–Si films by electron diffraction. The prominent sharp main peak was observed around $Q = 2.78$ Å^{-1}, however, the pre-peak which had been observed at 1.55 Å^{-1} in the pioneer work [2] was out of the accessible range of Q. From the density measurements, they concluded that in the Au-rich region of less than 40 at.% Si the number density was roughly constant within several atomic percent. The value was less than that of crystalline Au which suggested that amorphous Au–Si alloys have a close-packed structure and the additional Si atoms occupy preferably the substitutional positions in this particular range of composition [3]. It has been pointed out that there exists some association tendency between Au and Si atoms in the liquid state [4], which is controversial to the discription of amorphous alloys given by Mangin et al. [3]. This might be because the previous structural studies on Au–Si alloys were to some extent unreliable due to the heavy absorption of both X-ray and neutron beams by Au atoms in the diffraction experiments. It is interesting to investigate the relation between the glassy state, which does not generate any long range order, and the local structure of the eutectic liquid.

It is worth noting that the temperature coefficient of atomic or electronic transport properties in the eutectic liquid region show deviations from those at higher temperatures. The deviation of the diffusion coefficient of liquid $Au_{81}Si_{19}$ occurs at around 1073 K [5] and that of the electrical resistivity is observed at around 973 K [6]. The electrical resistivity of liquid Au–Si alloys as well as that for amorphous alloys [3] show the negative temperature coefficients in this particular range [6].

In the eutectic region of liquid Au–Ge alloys, the structure factors obtained by X-ray diffraction have small pre-peaks [7]

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at around $Q = 1.5\,Å^{-1}$ in accordance with the earlier study in a restricted range of Q [4], which suggested some associations of Au_4Ge in the eutectic liquid [7]. However, it still remains unclear whether the obtained structure factors actually reflect the liquid structure of bulk state or not.

The purpose of this paper is to study the temperature dependence of the structure factors of liquid Au–Si and Au–Ge alloys around the eutectic region by X-ray diffraction measurements using extremely high-energy incident beams and to invesitgate why the eutectic liquid is stabilized down to such a low temperature. From the observed structure factors and pair correlation functions, the partial pair correlations and the atomic arrangements are derived through the reverse Monte Carlo analysis [8]. The temperature dependence of atomic arrangements in liquid Au–Si and Au–Ge alloys around the eutectic compositions will be discussed in detail.

2. Experimental procedure

X-ray diffraction measurements on liquid $Au_{81}Si_{19}$ and $Au_{69}Si_{31}$ were carried out using the two-axis diffractomator of BL04B2 in SPring-8. The incident X-ray beam was 113.26 keV in energy and 0.1093 Å in wavelength obtained from a Si(1 1 1) monochromator with the third harmonic reflection. The disk sample with a thickness of 0.2 mm was put into a quartz glass container and inserted into the gap between two X-ray windows polished to a 0.3 mm thickness. The extremely high-energy X-ray beam allowed us to use samples in transmission geometry which is proper not only for the exact measurement of the absolute intensity in the small scattering angle region but also for measuring reliable diffraction data of the bulk liquid. The sample in the quartz container was located together with an inner heater in a chamber optimized for this kind of X-ray scattering measurements by an easy set-up of heating elements, easy centering of sample cell, wide available scattering angles accomplished with a wide Kapton-window. High temperatures were achieved by Mo-resistance heating wire of 0.5 mm diameter. The measurements were carried out under He atmosphere at a pressure of 1 bar. For liquid Au and Au–Ge alloys, the diffraction measurements were carried out using the two-axis diffractometer at BL08W in SPring-8. The incident X-ray beam was 181.0 keV in energy and 0.0685 Å in wavelength. In this case the disk sample had a thickness of 0.5–0.7 mm.

The structure factors were obtained after conventional corrections such as subtraction of the scattering contribution from the container, correction of X-ray absorption and polarization factor, subtraction of Compton-scatterings and normalization by the atomic form factor. The structure factors were deduced by Faber-Ziman type formulae.

3. Experimental results

Fig. 1 shows the structure factors, $S(Q)$, of liquid Au–Si alloys together with those of liquid Si and Au. In the structure factor of liquid $Au_{81}Si_{19}$, clear oscillations are observed up to $20\,Å^{-1}$ even at the highest temperature of 1073 K. The position of first peak in $S(Q)$ locates at $2.70\,Å^{-1}$ at 653 K and shifts slightly to $2.73\,Å^{-1}$ with increasing temperature. The peak heights at 653 K is about 3.0, which is much higher than that of pure liquid Au at 1423 K, and becomes lower to 2.4 with increasing temperature at 1073 K. The pre-peak, which has been obtained around $1.55\,Å^{-1}$ by X-ray diffraction for the metallic glassy state [2] was not observed in present structure factors. Although at 823 K the structure factor of liquid $Au_{69}Si_{31}$ has also the sharp first peak and clear oscillations, we cannot exclude the possibility of solidification of the sample due to the closeness to the liquidus curve. The shape of the first peak in $S(Q)$ at 1123 K looks broad and round on the low-Q side, which is quite different from that at 823 K. The oscillations in high-Q region are considerably damped at 1123 K in comparison with that at 823 K and also with those of the eutectic liquids. However, the profiles of the structure factors of liquid $Au_{81}Si_{19}$, $Au_{75}Si_{25}$ and $Au_{69}Si_{31}$ preserve the feature of liquid pure Au rather than that of liquid Si. For a liquid alloy with a large difference between the two atomic form factors, the structure factor can be negative for small Q value.

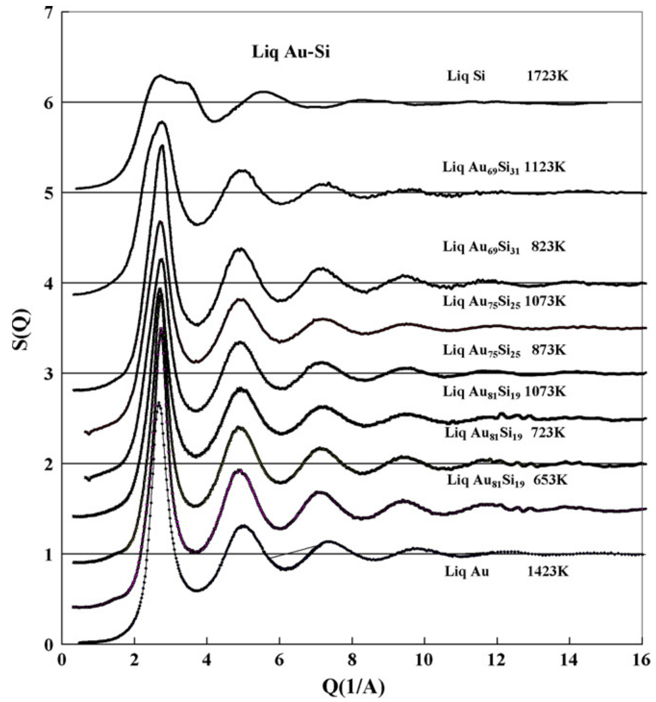

Fig. 1. Total structure factors of liquid Au–Si alloys.

Fig. 2 shows the total pair correlation function, $g(r)$, of liquid Au–Si alloys. The nearest neighbor distances in liquid Au–Si alloys are ranged from 2.80 to 2.82 Å and are slightly larger than that of pure liquid Au (∼2.72 Å). The temperature dependence of liquid $Au_{81}Si_{19}$ appears to be smaller than that of liquid $Au_{69}Si_{31}$ and the second peak of $Au_{81}Si_{19}$ is split at 653 K. The splitting of the second peak in the correlation function suggests that with respect to the second nearest neighbors at least two types of preferred local structure or orientation appear at low temperatures. The average coordination numbers in both liquids increase with decreasing temperature. The oscillation in the structure factor of liquid $Au_{69}Si_{31}$ is damped with increasing temperature suggesting the large fluctuations of the atomic arrangement in the liquid state.

Fig. 3 shows the structure factors of liquid Au–Ge alloys together with those of liquid Au and Ge. The structure factors of liquid $Au_{80}Ge_{20}$ and $Au_{72}Ge_{28}$ are similar to that of pure liquid Au. The first peak in $S(Q)$ of the eutectic liquid $Au_{72}Ge_{28}$ is broader than that of the eutectic liquid $Au_{81}Si_{19}$ and its height shows a small temperature dependence. The oscillations in the $S(Q)$ for $Au_{72}Ge_{28}$ can be clearly seen up to almost $20\,Å^{-1}$ at all temperatures even up to 1173 K. The pre-peak, observed at

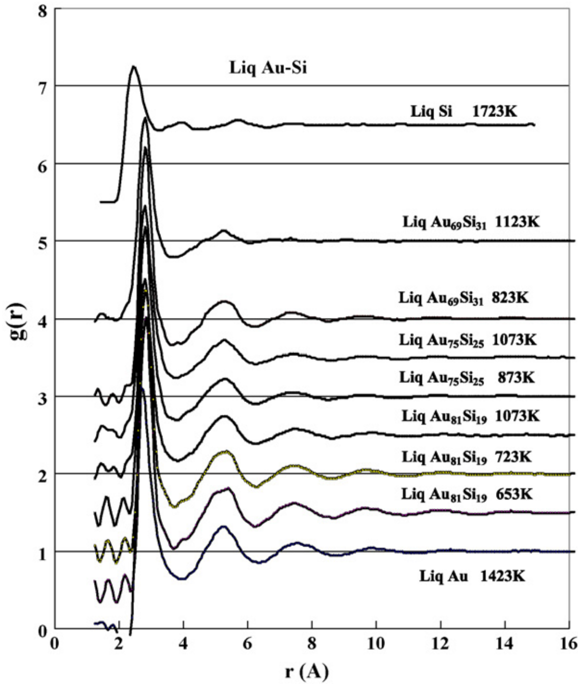

Fig. 2. Total pair correlation functions of Au–Si alloys.

around 1.5 Å^{-1}, which has been reported in the previous results [7], was not observed. For the structure factors with excess Ge beyond the eutectic composition, the shape of the first peak in the $S(Q)$ appears deformed.

Fig. 4 shows the total pair correlation functions of liquid Au–Ge alloys. The temperature dependence of $g(r)$ in liquid Au$_{72}$Ge$_{28}$ is considerable and the peak height decreases with increasing temperature. However, the peak position does not change with temperature. This suggests that the nearest neighbor atoms are restricted to certain positions with some order. Unlike the case of liquid Au$_{81}$Si$_{19}$, the second peak of liquid Au$_{72}$Ge$_{28}$ does not show the splitting even at the lowest temperature. With adding excess Ge beyond the eutectic composition, the correlation in $g(r)$ decreases rapidly and tends to disappear at the distance around 6 Å. This feature is similar to the case of liquid Au–Si alloys and suggests large fluctuations of the atomic configuration.

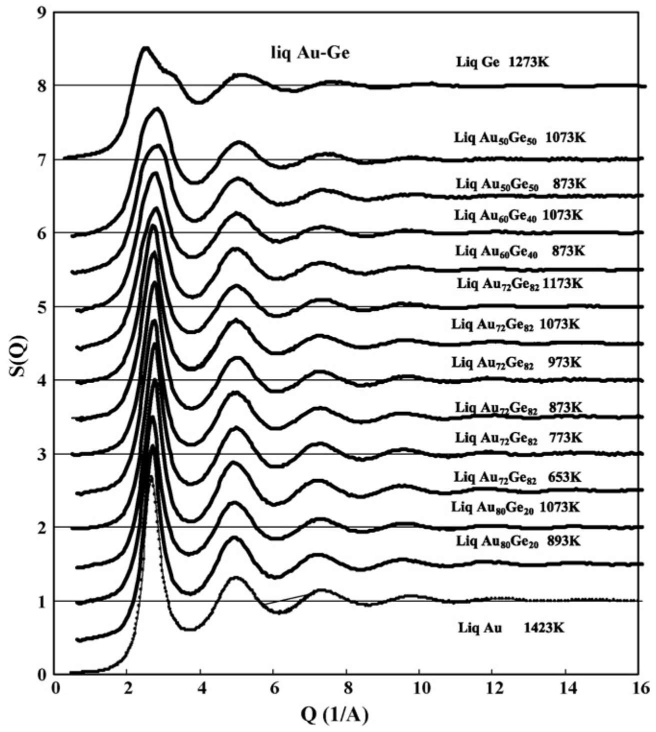

Fig. 3. Total structure factors of liquid Au–Ge alloys.

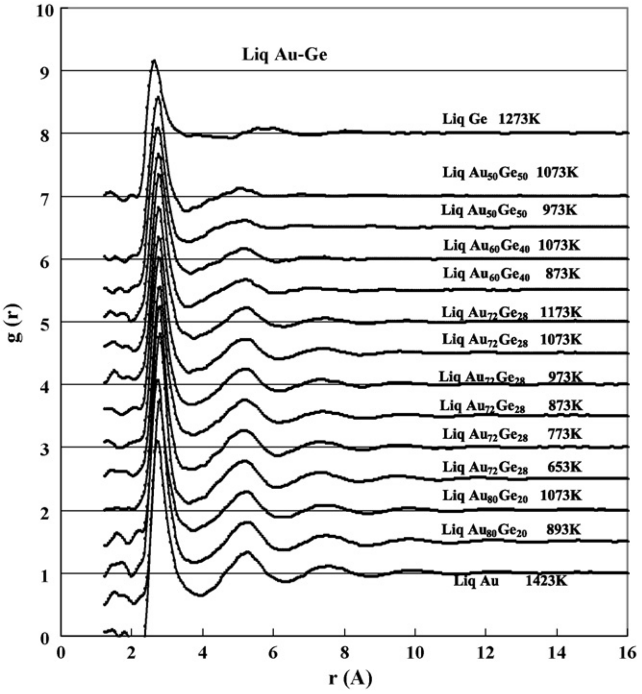

Fig. 4. Total pair correlation functions of Au–Ge alloys.

4. Structural model from the RMC method

In order to obtain the atomic arrangement of these liquids in detail the Reverse Monte Carlo structural modeling (RMC) developed by McGreevy and Pusztai [8] has been applied. The conditions in the structural modeling procedure for liquid Au$_{81}$Si$_{19}$ at 653 K, are as follows. The number of atoms was 5000 (Au 4050, Si 950), and the number density was 0.056 Å^{-3} which corresponds to the side length of cubic simulation box of 44.62 Å. The cut off lengths were 2.2, 2.0, and 1.8 Å for Au–Au, Au–Si and Si–Si atomic pairs, respectively.

Fig. 5 shows the distribution of the calculated partial pair coordination numbers in liquid Au$_{81}$Si$_{19}$ at 1073 and 653 K compared with that of pure liquid Au at 1423 K. The average coordination number in liquid Au is evaluated as 12.1. For liquid Au$_{81}$Si$_{19}$, the average coordination number of Au atoms around an Au atom increases from 9.9 to 10.3 with decreasing temperature from 1073 to 653 K and that of Si atoms around an Au atom varies from 2.24 to 2.32. The total coordination number of an Au atom is 12.3 at 1073 K which is slightly larger than that of pure liquid Au and increases to 12.6 at 653 K. The figure

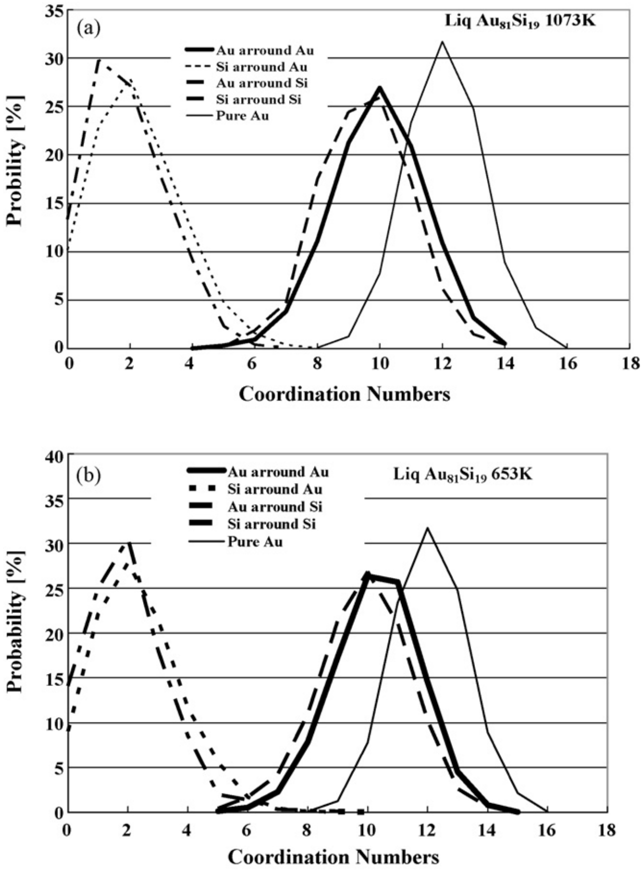

Fig. 5. Distributions of the coordination numbers in liquid Au$_{81}$Si$_{19}$ at: (a) 1073 K and (b) 653 K.

shows that the partial coordination around an Au atom is almost similar to that around a Si atom at both temperatures.

From the atomic arrangement generated by RMC structural modeling, the bond angle distribution among Au–Au–Au atoms were calculated and shown in Fig. 6. The regular icosahedron has two bond angles of 60° and 120° which is the local environmental model of dense random packing. The bond angle distribution of Au–Au–Au atoms of pure liquid Au exhibits two maxima at around 55° and 108°, which is a signature of typical random packing, because bond angle tends to lower when the bond length is distributed within the nearest neighboring shell in the liquid state. The bond angle distribution among Au–Au–Au triplet for liquid Au$_{81}$Si$_{19}$ also has a high peak around 55° and the value slightly increases to 58° with decreasing temperature. This feature means that the eutectic liquid at the lowest temperature is much more dense and tight compared with those at higher temperature and that of pure liquid Au. The results of the coordination number and the bond angle distribution analysis lead us to the interpretation that the addition of Si into pure liquid Au is replaced by Si from Au, and the temperature dependence of the structure of the eutectic liquid results from the densification with decreasing temperature. The split of the second peak in the total $g(r)$ of liquid Au$_{81}$Si$_{19}$ at the lowest temperature results from the separation in the second peak position between Au–Au and Au–Si partial correlations.

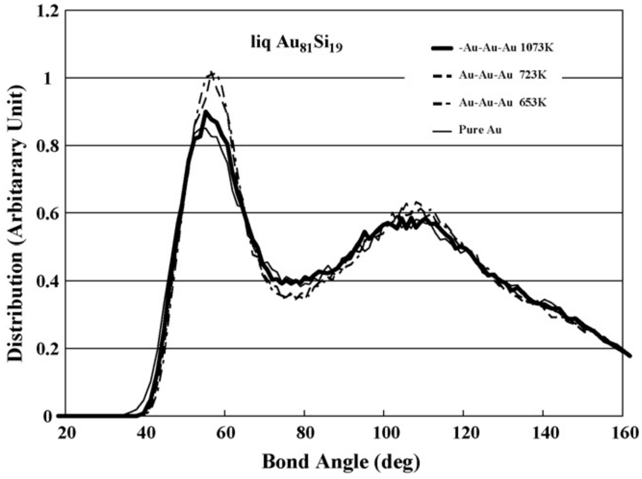

Fig. 6. Bond angle distribution of Au–Au–Au in liquid Au$_{81}$Si$_{19}$.

The overall features of partial structure analysis of liquid Au$_{72}$Ge$_{28}$ are similar to those of liquid Au$_{81}$Si$_{19}$. The distributions of the partial coordination numbers are shown in Fig. 7. At 653 K, the local environment around an Au atom is quite similar to that around a Ge atom. The mean coordination number of Au atoms around a central Au atom is 8.24 and that of Ge atoms around an Au atom is 3.07. The total coordination number around an Au atom is a little smaller than that for liquid Au$_{81}$Si$_{19}$, reflecting the fact that Ge atoms have a larger atomic size than that of Si. With increasing temperature from 653 to 1073 K, the partial coordination number of Au atoms around a

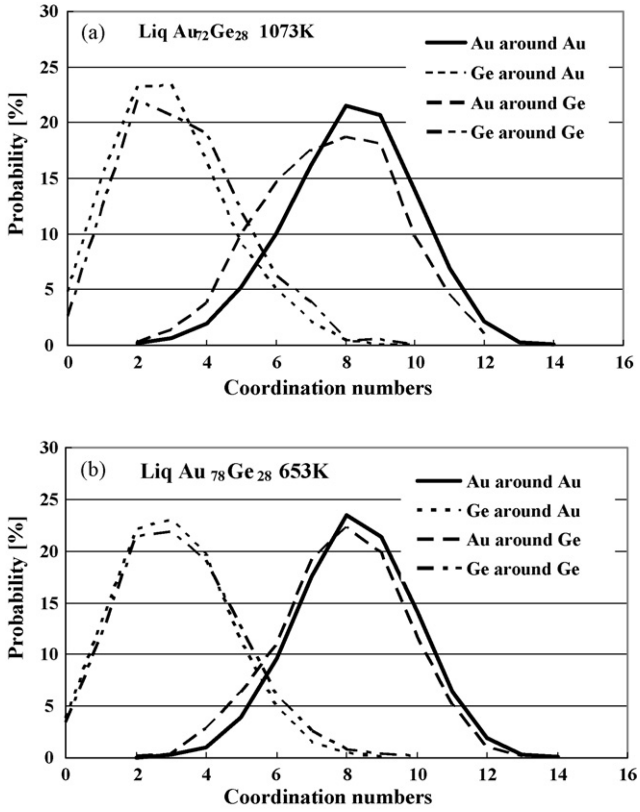

Fig. 7. Distributions of the coordination numbers in liquid Au$_{72}$Ge$_{28}$ at: (a) 1073 K and (b) 653 K.

central Ge atom decreases from 7.89 to 7.55. The distribution becomes broader at higher temperature and deviates from the right and regular position around a central Au atom. It may be interpreted as a tendency to the preference of like pairs at high temperature.

In contrast to the case of liquid $Au_{81}Si_{19}$, a splitting of the second peak in $g(r)$ of liquid $Au_{72}Ge_{28}$ has not been clearly observed. The position of the second peak in the partial pair correlation for Au–Ge coincides with that of Au–Au in liquid $Au_{72}Ge_{28}$, where this might also result from the atomic size difference between Ge and Si.

According to the RMC analysis of liquid $Au_{50}Ge_{50}$ all distribution functions of partial coordination of Au–Au, Au–Ge, Ge–Au and Ge–Ge are quite similar to each other. The mean partial coordination number is around 5 for each partial and the deviation is very large. This means that liquid $Au_{50}Ge_{50}$ has a completely random, and still substitutional-type structure.

The eutectic composition of Au–Si or Au–Ge seems to correlate with the difference atomic size of Si and Ge, and this composition may correspond to the threshold of percolation of Si or Ge atoms in the metallic medium of Au.

5. Conclusions

The structure factors of liquid Au–Si and Au–Ge alloys around the eutectic composition have been measured as a function of temperature, and a structural model has been proposed by the reverse Monte Carlo technique. The analysis of the partial coordination numbers and the detailed atomic arrangements at the eutectic compositions suggest that Si and Ge atoms locate at the substitutional positions of the Au atoms, and much dense liquid is generated with decreasing the temperature at the eutectic composition. The liquid around the eutectic composition becomes a densely packed liquid just above the liquidus curve. Liquid $Au_{81}Si_{19}$ has a split second peak in the pair correlation function at the lowest temperature of 653 K which results from the separation of the second neighbor distance of Au–Si and Au–Au correlations. On the other hand, the second neighbor distribution of Au–Ge pairs almost coincides with that of Au–Au pairs in eutectic $Au_{72}Ge_{28}$ even at the lowest temperature. The liquid containing an excess of Si or Ge beyond the eutectic composition may have some loose or free space in the structure and fluctuation appears in the liquid state.

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