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Competition between fcc and icosahedral short-range orders in pure and samarium-doped liquid aluminum from first principles

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Development of structural order in liquid aluminum upon rapid cooling is studied by *ab initio* molecular-dynamics simulations and the recently developed atomistic cluster alignment method. We show that there is a strong competition between icosahedral and fcc short-range orders (SROs) in the system. Although the liquid eventually crystallizes into fcc structure when $T \leqslant 800$ K, the icosahedral short-range order (ISRO) is found to be much stronger than the fcc SRO in the liquid. Doping of Sm in Al liquid can hinder the fcc crystallization and enhance the ISRO.

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I. INTRODUCTION

Although metallic liquids look homogeneous macroscopically, they exhibit short-range order (SRO) at the atomistic scale, which is believed to play an important role in dictating the structural transformations in the liquid upon rapid cooling. In many metallic systems, geometrical frustration caused by icosahedral short-range order (ISRO) has been often considered as the origin of the liquid-glass transition.[1–6] Since icosahedral clusters cannot achieve a global periodic packing, such geometrical frustration will lead to glass formation.[7] Indeed, recent experiments have shown a correlation between the increase of nucleation barriers of crystalline phases and enhancement of ISRO with undercooling in bulk metallic glass forming systems.[4,5] However, the fact that the strong ISRO in liquid may not necessarily lead to good glass formability often has been overlooked. This is the case for liquid Al as will be discussed in this paper. We show that although ISRO is strong in liquid Al, crystallization of the fcc structure can take place rapidly when the system is cooled well below the melting temperature. However, minor doping of rare-earth element Sm can suppress the development of fcc nucleation in the undercooled liquid and help ISRO to win over the fcc order and hence can lead to glass formation under rapid cooling conditions.

II. SIMULATION DETAILS

Ab initio molecular-dynamics simulation of Al was performed within the framework of plane-wave-based density-functional theory (DFT) as implemented in VASP.[8] A plane-wave basis set with an energy cutoff of 240 eV was used. The electron-ion interaction was described by the projected augmented-wave method,[9] and both the local-density approximation (LDA)[10] and the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form for the exchange-correlation energy were investigated. Only the Γ point was used and the N-V-T ensemble (constant number of particles, constant volume, and constant temperature) with Nose thermostats was simulated. A typical time step of 3 fs was used with the Verlet algorithm to integrate Newton's equations of motion. A cubic unit cell with periodic boundary conditions containing 108 atoms was used in the simulation. The liquid samples were first prepared at 1500 K to reach thermal equilibrium (well above the melting temperature of 937 K), followed by cooling to 1200, 1100, 1000, 900, and 800 K successively with a rate of 3.3×10^{13} K/s. After the system was thermally equilibrated and the pressure tuned to be essentially zero through the adjustment of the size of the simulation cell at each temperature, an additional 16 000 molecular-dynamic (MD) steps at each temperature were followed for statistical sampling. We also performed the MD simulation using a 256-atom unit cell at 1000 K and the results of pair-correlation functions from both 108-atom and 256-atom unit cells are essentially identical. As shown in Fig. 1, the pair-correlation function (PCF) of liquid Al around 1000 K obtained from our simulations using both LDA and GGA agrees well with that from previous *ab initio* simulation.[11] The average bond length (the position of the main peak of pair-correlation function) in the liquid from the *ab initio* simulations using LDA is slightly (about 1%) shorter than that from the experimental x-ray-diffraction measurement.[12] Despite this small discrepancy in the bond length, the first-principles LDA and GGA calculations have been proven to be accurate for structural and other properties of Al. Therefore the liquid structure obtained from the *ab initio* simulations should be reliable for our purpose of polyhedral short-range-order analysis as we discuss below.

III. RESULTS AND DISCUSSION

A. Cluster alignment analysis of pure liquid Al

Since the widely used Voronoi tessellation method for local structure analysis[13] is not suitable for fcc SRO (which is very crucial in the Al system) because of the well-known geometry degeneracy problem,[14] a cluster alignment method[15] recently developed by us is used in this paper to investigate the competition between icosahedral and fcc SROs in Al- and Sm-doped Al systems. Clusters up to the size of first atomic shell are defined for each atom in the sample. The "order" characteristics of these clusters are measured by their alignment to the "ideal" 13-atom icosahedral or fcc templates. Each cluster is rotated and translated with respect to the

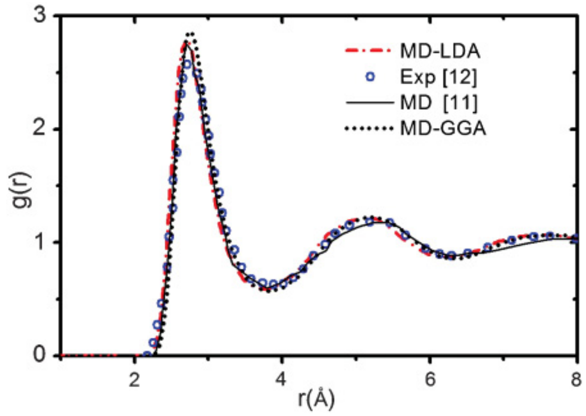

FIG. 1. (Color online) The pair-correlation functions of liquid Al from *ab initio* MD simulations using both GGA and LDA are compared with previous simulation (Ref. 11) and experimental data (Ref. 12).

two templates respectively to minimize the mean-square pair distances between its "best" 13 atoms and the corresponding 13 atoms in the templates. If the root-mean-square distances between the cluster and template after the alignment is less than 20% of the average bond length in the template (which is about the width at half height of the first peak of pair-correlation functions of the liquids), the cluster is classified as having the same SRO as that of the template.

Figure 2(a) shows the population of icosahedral and fcc clusters in a pure Al sample at different temperatures obtained from our cluster alignment analysis. Both icosahedral and fcc SROs are found to develop during the cooling process, but the ISRO is always stronger than the fcc SRO when the temperature is above the melting point, as one can see from Fig. 2(a). Even below the melting point and before crystallization at 800 K, the population of the icosahedral clusters is still larger than that of fcc clusters. The results from LDA and GGA simulations are very similar except that the orders in the simulation using GGA are lightly stronger. This result is consistent with our previous study that the energy of the icosahedral cluster is slightly lower than that of the fcc cluster when the clusters are embedded in Al liquid.[16] At 800 K, crystallization takes place rapidly and the whole MD simulation cell transforms to a fcc crystal within 4 ps in our LDA simulation. Such "catastrophe crystallization" due to a small simulation cell has also been reported in the earlier MD studies based on empirical potentials.[17] We note that Celino *et al.* suggested that icosahedral clusters (both perfect and defective) play an important role in preventing the crystallization in liquid Cu.[18] In our present work, we show that although ISRO is stronger than the fcc order in pure liquid Al above the melting temperature, the system is still crystallized into a fcc structure rapidly below the melting point. It should be noted that the common-neighbor analysis used in Ref. 18 provides information only about a fragment of the polyhedral clusters in the liquid. By contrast, our cluster alignment approach can give a more comprehensive and accurate description of local polyhedral order in the liquid.

Although the crystallization in a larger unit cell may take a longer time, the analysis of the local structure evolution from the present simulation can provide useful insights into the crystallization nucleation process. It is interesting to note that at 800 K the fraction of fcc clusters fluctuate between 1% and about 5% before the rapid crystallization, as shown in the inset at the upper left corner of Fig. 3. This observation indicates that the critical nucleation size of the fcc phase is about five to six interpenetrating fcc clusters, which consist of about 20 atoms. Below this critical size, the ISRO still prevails. However, the fcc crystallization takes over quickly as long as the critical nucleation size is reached, as shown in Figs. 4(a)–4(i). We can see that the fcc clusters (larger (brown) balls) are rare and quite separated in Figs. 4(a) and 4(b). These fcc clusters are fluctuating with a short lifetime. When the population of the fcc clusters increases, they tend to pack together and a small fcc fragment emerged, as shown in Figs. 4(c) and 4(d) [from

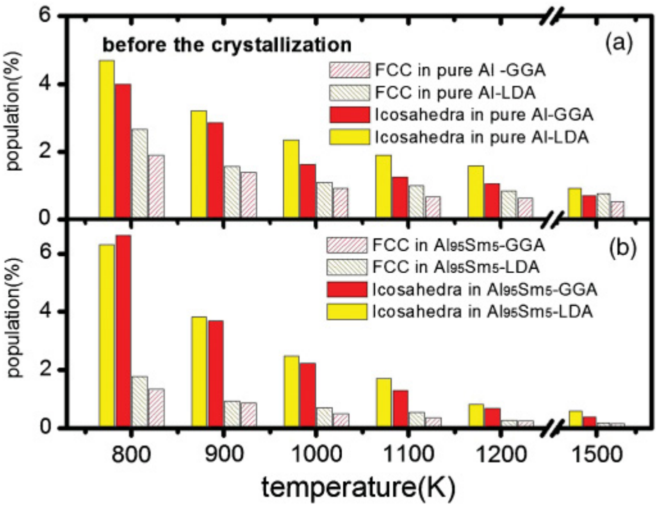

FIG. 2. (Color online) The population of fcc and icosahedral clusters in (a) pure Al system and (b) $Al_{95}Sm_5$ binary system from 1500 to 800 K. The population in (a) is analyzed before the fcc crystallization at 800 K. The result from both GGA and LDA simulations are shown for comparison.

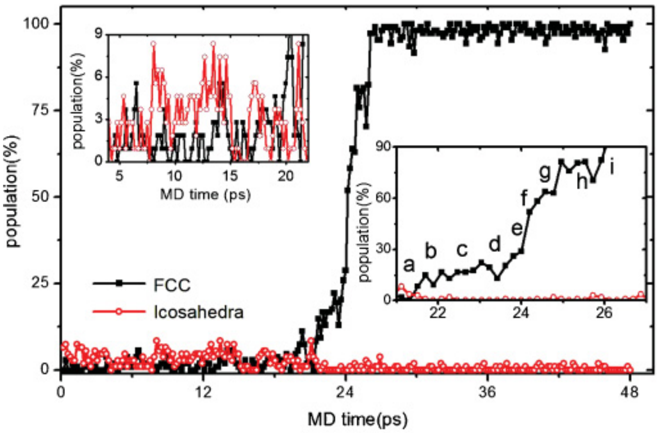

FIG. 3. (Color online) Populations of the fcc and icosahedral clusters in the pure Al sample as a function of MD simulation time at 800 K. The inset at the upper-left corner shows the populations before the crystallization and the inset at the lower-right corner shows the populations at the snapshots corresponding to Figs. 4(a)–4(i) as indicated. The results are from the DFT-LDA simulations.

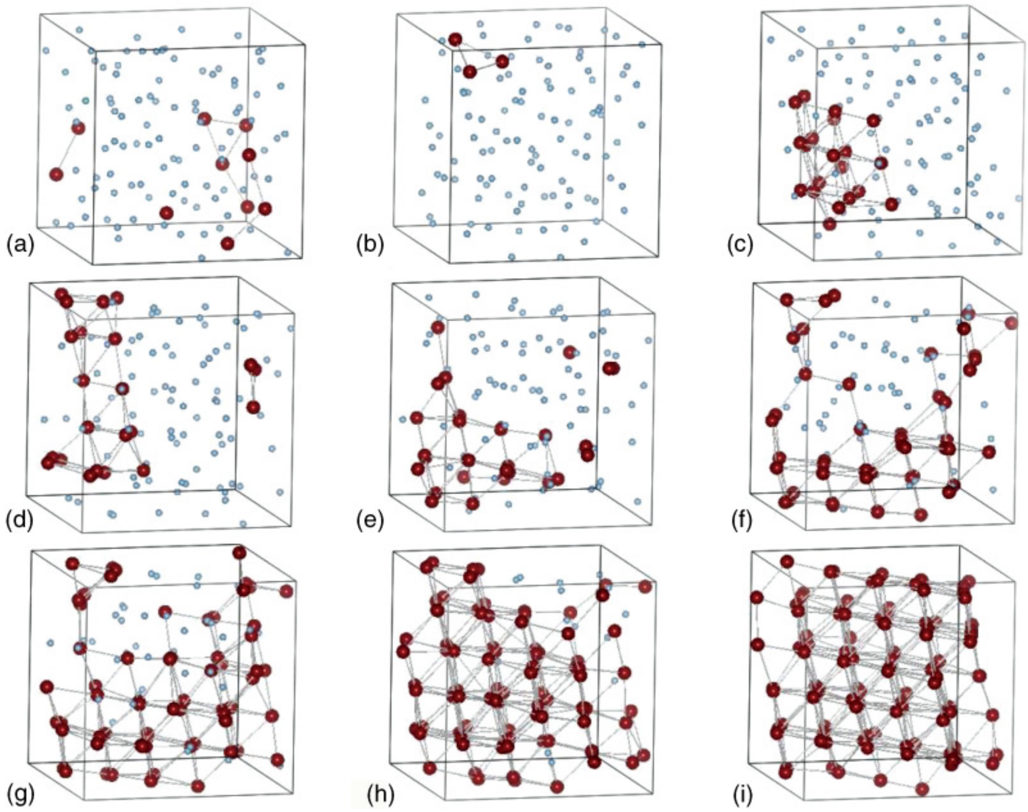

FIG. 4. (Color online) The fcc crystallization process in pure Al system at 800 K from our *ab initio* LDA-MD simulations. (a)–(f) Snapshots in the MD simulation at 21.17, 21.56, 22.73, 23.67, 23.97, 24.15, 24.3, 25.5, and 26.25 ps, respectively. Larger (brown) balls are Al atoms with fcc type SRO.

Figs. 4(c) to 4(d) takes about 1 ps]. In a very short time the fcc region extends to nearly the whole simulation cell, as shown in Figs. 4(h)–4(i), and a sudden jump in the population of fcc clusters can also been seen from Fig. 3. The populations of the icosahedral and fcc clusters at the snapshots corresponding to those shown in Figs. 4(a)–4(i) are also plotted in the inset at the lower-right corner of Fig. 3.

B. Cluster alignment analysis of Sm-doped liquid Al

The results for the pure Al system discussed above suggest that the strong tendency of crystallization below the melting temperature is due to the aggregation of fcc clusters in the undercooled liquid, which helps fcc SRO win over the ISRO. If we can disrupt the growth and aggregation of the fcc clusters in the undercooled liquid by doping of other elements, it would be possible to prevent the easy crystallization and promote the glass formation. In order to verify this idea, we have performed *ab initio* MD simulations for Sm-doped liquid Al and compared the results with those from the pure Al systems. The Sm-doped Al is chosen because it is a glass-forming alloy with optimal Sm composition of 12%.[19] In our study, a composition of 95 Al atoms and 5 Sm atoms is chosen and the atomic coordinates used in the analysis is prepared with the same procedure and at the same temperatures as for pure Al systems.

The population of Al-centered icosahedral and fcc clusters from 1500 to 800 K in the $Al_{95}Sm_5$ liquid obtained from our cluster alignment analysis is shown in Fig. 2(b) in comparison with that in the pure Al system shown in Fig. 2(a). We see a systematic suppression of fcc SRO in Sm-doped liquid Al near or above the melting temperatures (937 K). The ISRO is also suppressed at high temperatures but enhanced strongly upon cooling to low temperatures near or below the melting point. The results from LDA and GGA simulations are again very similar.

The results shown in Fig. 2 indicate that the doped Sm atoms have a significant effect on the competition between icosahedral and fcc SROs in liquid Al. As shown in Fig. 5(a), the average number of Sm atoms in the first shell of the fcc clusters at low temperatures is smaller than that expected from a random distribution of Sm atoms in the liquid [dotted line in Fig. 5(a)], implying that the fcc clusters tend to avoid Sm atoms because fcc SRO is suppressed by the presence of doped Sm atoms. On the other hand, the average number of Sm atoms in the first shell of the icosahedral clusters is larger than the value from a random distribution, indicating that the icosahedral clusters are further stabilized by the presence of Sm atoms. This result provides some clues to understanding why the glass formability of liquid Al is improved dramatically with small doping of Sm (the glass forming composition range is 8–16 at. % of Sm in experiments). In order to address the seemingly promotion effect of Sm atoms on the ISRO in liquid $Al_{95}Sm_5$, we further analyzed the distribution of icosahedral clusters with a different number of Sm atoms on their first shell. Figure 5(b) shows the relative population of the Al-centered

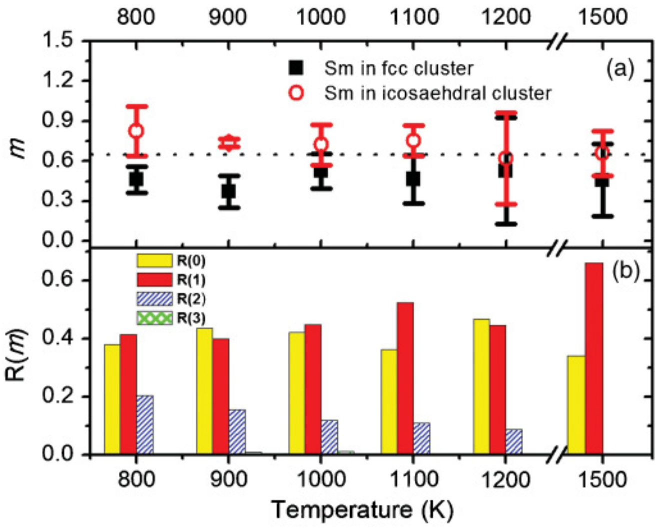

FIG. 5. (Color online) (a) Number of Sm atoms (m) in Al-centered icosahedral and fcc clusters in $Al_{95}Sm_5$ alloy from 1500 to 800 K. The dashed line is the average number of Sm in an Al-centered cluster assuming a random distribution of Sm. (b) Relative population $R(m)$ ($m = 0, 1, 2, 3$ is the number of Sm atoms in the clusters) of the Al-centered icosahedral clusters as the function of temperature. $R(m)$ is defined as $R(m) = n_{\rm ico}^{\rm Sm=m}/n_{\rm ico}$, where $n_{\rm ico}$ is the total number of Al-centered icosahedral clusters and $n_{\rm ico}^{\rm Sm=m}$ is the number of Al-centered icosahedral clusters that have m Sm atoms on their first neighbor shells.

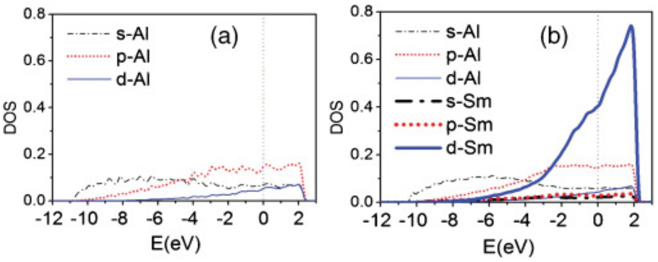

FIG. 6. (Color online) Projected local partial density of states (DOS) of both the Al and Sm atoms with s, p, and d characters in (a) pure liquid Al at 800 K and (b) liquid $Al_{95}Sm_5$ at 800 K liquids, respectively. The DOS is normalized to one atom. The Fermi energy is at zero (dash line).

icosahedral clusters that have m Sm atoms ($m = 0, 1, 2, 3$) in their first neighbor shell. We can see from the plot that while the relative population of the icosahedral clusters with zero and one Sm atom is dominated, it decreases as the temperature is lowered. By contrast, the relative population of the icosahedral clusters with two Sm atoms increases systematically in the quench. Icosahedral clusters with three or more Sm atoms are negligible. These results suggest that two Sm atoms should be the optimal doping concentration for the 13-atom icosahedral clusters. The high population of icosahedral clusters with zero and one Sm atom in liquid $Al_{95}Sm_5$ occurs because there are not enough Sm atoms available for the icosahedral clusters at this composition. As Sm concentration increases, more and more icosahedral clusters will be stabilized by replacing two Al atoms on their first shell with two Sm atoms. It is interesting to note that two Sm atoms in a 13-atom icosahedral cluster correspond to a composition of 15% Sm, which is within the range of good glass-formation composition in the Sm-Al alloy system.

C. Effects of Sm doping

From a geometrical packing point of view, fcc packing is favored when the size of the center atom is the same as its neighboring atoms, i.e., $P = r_c/r_n = 1.0$ where r_c and r_n are the radius of the center and neighboring atoms, respectively. The influence of Sm doping on the fcc clusters can be partially explained by the packing effect because the metallic radius of Al (1.43 Å) is quite different from that of Sm (1.81 Å). For an ideal 13-atom icosahedral cluster, the radius ratio P is 0.90.[20,21] Since the size of Sm is larger than that of Al, replacing Al atoms on the first shell of an icosahedral cluster by Sm atoms will reduce the radius ratio P from 1.0 and thus promote the stability of the icosahedral cluster. However, if the packing effect is the only factor that stabilizes the icosahedral cluster, the number of Sm atom in the first shell of the Al-centered icosahedral clusters should be larger than 2, which is inconsistent with our observation discussed above. Therefore electronic structure should also play an important role in the Sm-doped liquid Al in addition to the packing effects.

We have analyzed the electronic structures of the pure Al and $Al_{95}Sm_5$ liquids by calculating the projected local partial density of states (DOS) with s, p, and d characters, respectively, for the Al and Sm atoms in the liquids. The results presented

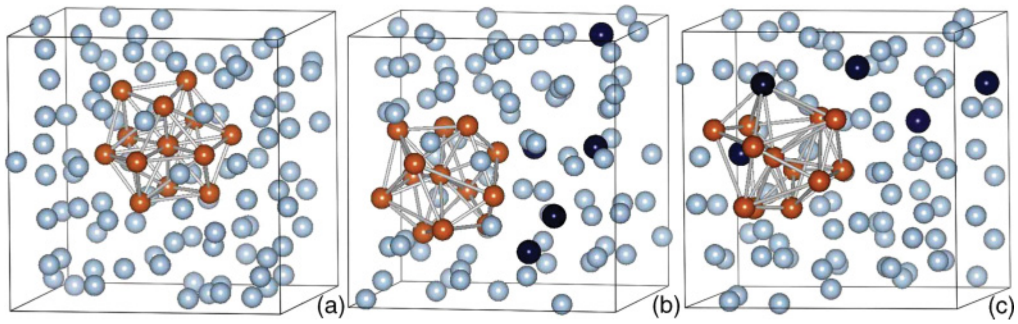

FIG. 7. (Color online) Representative structure of fcc and icosahedral clusters in pure Al and $Al_{95}Sm_5$ liquids at 800 K. (a) A fcc cluster in pure liquid Al; (b) an all-Al icosahedral cluster in $Al_{95}Sm_5$ liquid; (c) a Sm-doped icosahedral cluster in $Al_{95}Sm_5$ liquid. The light blue atoms are Al atoms not in the cluster. The yellow atoms are Al atoms in the cluster. The dark blue atoms are Sm atoms.

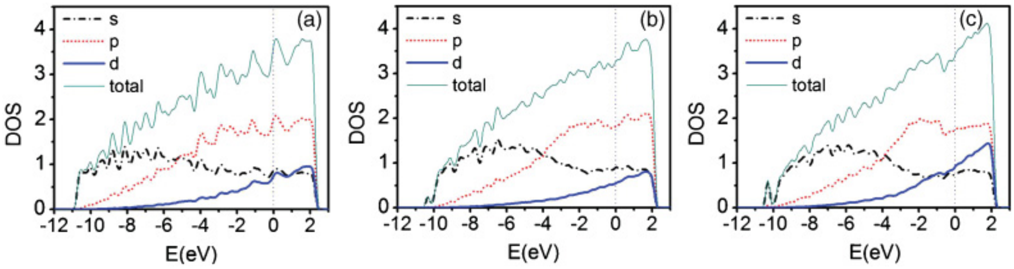

FIG. 8. (Color online) Projected local partial density of states (DOS) with *s*, *p*, and *d* characters, respectively, for different types of clusters as shown in Fig. 7. (a) DOS of a fcc cluster in pure liquid Al; (b) DOS of an all-Al icosahedral cluster in $Al_{95}Sm_5$ liquid; (c) DOS of a Sm-doped icosahedral cluster in liquid $Al_{95}Sm_5$. The Fermi energy is at zero (dash line).

in Fig. 6 are obtained by averaging over the DOS generated from ten snapshots taken from the MD trajectories over 3 ps of simulation time. As one can see from Fig. 6, Sm atoms exhibit much stronger *d*-bonding character in comparison with Al atoms. We have also calculated the DOS for different types of clusters in the liquids at 800 K, i.e., fcc cluster in pure liquid Al, pure Al icosahedral cluster in liquid $Al_{95}Sm_5$, and Sm-doped icosahedral cluster in liquid $Al_{95}Sm_5$, respectively, as shown in Fig. 7. The results of DOS as shown in Fig. 8 also indicate that the clusters with Sm atoms exhibit stronger *d*-bonding characters. Because of the stronger *d*-bonding character of Sm, the icosahedral clusters with the number of Sm atoms less than or equal to 2 in the Sm-doped liquid Al can be stabilized even though these clusters are not closely packed.

IV. SUMMARY

In summary, we have investigated the competition between icosahedral and fcc SROs in pure Al and minor Sm-doped Al alloy in liquid and undercooled liquid by *ab initio* MD simulations and cluster alignment analysis. The crystallization process of liquid Al upon cooling is also investigated. We show that although fcc SRO is weaker than ISRO in pure liquid Al, it develops quickly below the melting point leading to rapid crystallization. We also show that doping of Sm exhibits significant effects on the phase selection pathway of the liquid Al upon rapid cooling. The fcc SRO is suppressed and crystallization does not occur in Sm-doped liquid, and ISRO is enhanced in favor of glass formation. The large size and the strong *d*-bonding character of Sm atoms in doped-Al systems are the important factors that affect the development of SRO in the liquid.

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