Scripta Materialia 143 (2018) 86–89

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Regular article

Structural connection between gallium crystals and near-T_m liquids under ambient pressure

F. Zhang [a,*], Y. Sun [a], X.D. Wang [b], Q.P. Cao [b], J.Z. Jiang [b], C.Z. Wang [a], K.M. Ho [a,c,d]

[a] Ames Laboratory, US Department of Energy, Ames, IA 50011, USA
[b] International Center for New-Structured Materials (ICNSM), Laboratory of New-Structured Materials, State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou, 310027, People's Republic of China
[c] Department of Physics, Iowa State University, Ames, IA 50011, USA
[d] Hefei National Laboratory for Physical Sciences at the Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

ARTICLE INFO

Article history:
Received 6 June 2017
Received in revised form 23 August 2017
Accepted 12 September 2017

Keywords:
Liquids
Short-range ordering
Crystallization
Genetic algorithm
Molecular dynamics

ABSTRACT

We study the short-range structural order in liquid gallium prepared by ab initio molecular dynamics simulations. We found that at 400 K, which is close to the melting point (Tm) of Ga, the dominant motif in the liquid phase is identical to that in the stable solid phase Ga-I. Strong directional bonding in this motif prevents it from nucleation in the liquid phase. Meanwhile, a newly identified motif, topologically distinct from yet related to those in β-Ga and Ga-III phases, is also abundant in Ga liquid. This new motif could serve as precursors for β-Ga or Ga-III during crystallization.

Published by Elsevier Ltd on behalf of Acta Materialia Inc.

Gallium is an element that exhibits profound complexity in both liquid and crystalline phases. Under ambient pressure, Ga has a stable orthorhombic phase Ga-I [1] that has hybrid covalent and metallic bonding characters according to *ab initio* calculations [2,3]. Ga-I has a very low melting temperature (T_m) of 303 K, and the liquid phase shows anomalous features in the structure factor, which can also be attributed to partial covalent bonding [4–6]. When Ga liquid is cooled below T_m, it does not necessarily crystallize into the stable Ga-I phase; instead, a series of metastable phases can be accessed [7]. In particular, highly supercooled Ga liquid droplets have a clear tendency to form a triclinic metastable β-Ga phase [8] before finally transforming into Ga-I [9]. In our current *ab initio* molecular dynamics (AIMD) simulations, under an ultrafast cooling rate of 3.3×10^{15} K/s, the liquid sample crystallizes into the body-centered tetragonal (bct) Ga-III phase, which is metastable at ambient pressure and can be stabilized at high pressure and high temperature [7].

Knowledge about the liquid structure is necessary to understand the complex phase selection. While apparently lacking long-range translational symmetry, liquids have clear short-range order (SRO), which is usually characterized by typical local clusters up to the first atomic shell. Such structural order can have a large impact on crystallization or vitrification processes upon fast quenching [10–12]. Earlier work used the Honeycutt-Anderson (HA) common-neighbor analysis [13] to study the ordering in Ga liquids [5,14]. However, since HA index only reveals a fragment of a local cluster [15], such analysis can hardly give a complete picture of the dominant SRO in the liquid phase. Recently, it was demonstrated that typical undercooled metallic liquids or glasses share the same SRO, which was called "crystal genes", with a series of crystalline structures in glass forming binary alloys Cu-Zr and Al-Sm [16]. It is intriguing to examine whether the concept of crystal genes persists in the single-elemental Ga liquid with complicated chemical bonding.

Since the crystal genes may not exist in known crystalline phases of Ga, we performed a systematic genetic-algorithm (GA) search [17,18] for more low-energy crystalline structures containing up to 50 atoms per unit cell. To facilitate the search, a semi-empirical Tersoff potential [19] was used for energy calculations during the search. Then, 100 structures with the lowest Tersoff energy in the converged GA pool were collected for relaxations using more accurate density-functional theory (DFT), as implemented in the VASP code [20]. The projected augmented-wave (PAW) method [21] is used to describe the electron-ion interaction, and the generalized gradient approximation (GGA) in the Predew-Burke-Ernzerhof (PBE) form [22] is employed for the exchange-correlation energy functional. An energy cutoff of 168.35 eV was used for the plane-wave basis set. A dense *k*-point mesh generated using the automatic scheme [23] the length parameter $l = 25$ Å, to guarantee the *k*-points are evenly distributed in the Brillouin zone.

Our GA search successfully identified the Ga-I as the ground state phase at 0 K and under ambient pressure. The next two lowest-energy

---

* Corresponding author.
E-mail address: fzhang@ameslab.gov (F. Zhang).

http://dx.doi.org/10.1016/j.scriptamat.2017.09.019
1359-6462/Published by Elsevier Ltd on behalf of Acta Materialia Inc.

structures in the GA pool are Ga-III and β-Ga, respectively. Other structures in the GA pool have not been observed in experiments. We then analyze the clusters surrounding each Ga atom up to the first atomic shell. Interestingly, all the clusters collected from the 10 lowest-energy structures can be classified by only 4 different motifs, suggesting energetic stability of these 4 motifs. The atomic configurations of these 4 motifs are shown in Fig. 1 and their presence in the l0 lowest-energy structures in the GA search is summarized in Table 1. In Fig. 1, M1 and M2 have a low coordination number of 7, as compared with 12 in close-packing fcc or hcp structures. There are dimer-like Ga—Ga bonds with short bond-lengths of ~2.5 Å in both M1 and M2 motifs, showing significant covalent bonding characters. The coordination number is increased to 8 and 12 in M3 and M4, respectively. The minimal bond length is also increased to 2.80 Å and 2.95 Å in M3 and M4, respectively. These facts indicate increasing metallic bonding characters in M3 and M4. Especially, the ideal M4 motif, collected from the Ga-III phase [7], has a bct structure with $c/a = 1.49$ in our DFT calculations. Ga-III can be considered as a deformed fcc phase, since fcc can also be viewed as bct with $c/a = \sqrt{2}$. Indeed, a phase transition from bct (Ga-III) to fcc (Ga-IV) can occur under high pressure of ~150 GPa [24]. Motifs M2–M4 also share a similar “boat”-like substructure, as shown by the red atoms in Fig. 1. However, due to the different bond lengths and shape of the “boat”, together with the differences in other parts as highlighted by the green atoms in Fig. 1, these three motifs are clearly distinguishable. Later, we will demonstrate that the relation in these motifs might play an important role in phase selection during crystallization of Ga liquids.

We have performed AIMD simulations to prepare the liquid sample. In AIMD, we used Nosé-Hoover thermostat [25] to control the temperature, and a time interval of 3 fs to integrate Newton's equations of motion. A smaller energy cutoff of 134.68 eV, compared with structural relaxation, was used for the plane-wave basis in AIMD to accelerate the calculation. Only the Γ point was used to sample the Brillouin zone since the simulation box was sufficiently large. A cubic box with periodic boundary conditions, containing 216 Ga atoms, was fully melted at 2000 K to remove the crystalline symmetry and reach thermal equilibrium, followed by step-wise cooling to 400 K with a rate of 0.1 K per MD step. The internal pressure was maintained almost zero by adjusting the box size during the cooling process. After that, the sample was annealed at 400 K for additional 12,000 steps. In a recent publication, we have reported that the AIMD samples clearly display liquid behavior at $T = 400$ K and above with a profound change of the liquid structure at around 1000 K [26]. Here, we focus on a near-T_m temperature: 400 K.

Table 1
Energy and motifs of 10 lowest-energy structures identified in Ga search. Energy is referenced to the ground state Ga-I.

No.	1 (Ga-I)	2 (Ga-III)	3 (β-Ga)	4	5
Energy (meV/atom)	0	1.6	6.3	8.0	9.2
Motifs	M1	M4	M3	M3	M4
No.	6	7	8	9	10
Energy (meV/atom)	9.8	11.2	13.3	16.8	27.1
Motifs	M3	M3	M4	M1, M2	M2, M3

Then, the clusters extracted from the liquid sample are compared with the GA-identified motifs in Fig. 1, following a cluster-alignment method [15]. An alignment score, quantitatively describing how an as-extracted cluster deviates from a template motif, is defined as

$$f = \min_{0.80 \le \alpha \le 1.2} \left(\frac{1}{N} \sum_{i=1}^{N} \frac{(\mathbf{r}_{ic} - \alpha \mathbf{r}_{it})^2}{(\alpha \mathbf{r}_{it})^2} \right)^{1/2}, \quad (1)$$

where N is the number of atoms in the template motif; $\mathbf{r}_{ic}$ and $\mathbf{r}_{it}$ are the atom positions in the cluster and template after the alignment, respectively; and α is a coeffient to adapt the template's bond length in order to achieve an optimal alignment. The smaller the alignment score is, the more similar the cluster is to the template. We show in Fig. 2(a) the distribution of the alignment score obtained by aligning the clusters in the AIMD sample at $T = 400$ K with all the cluster motifs given in Fig. 1, from which one can see that the popularity of M1-M4 decreases in the liquid sample as the peak position moves to larger values. For comparison purpose, we also show in Fig. 1(a) the score distribution for aligning clusters in Ga liquids with the icosahedron (ICO) motif, one of the most commonly seen structural order in liquids [27], *e.g.*, in Al liquids that belongs to the same group as Ga in the periodic table [15]. In contrast, the icosahedron motif is the least favored among all examined

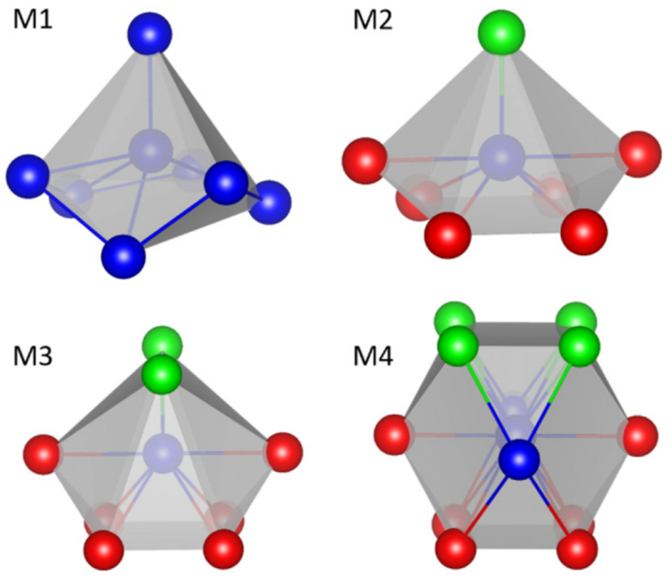

Fig. 1. Most popular first-shell cluster motifs in low-energy structures found by a GA search. M1 exists in Ga-I, M3 in β-Ga, and M4 in Ga III. M2 is not seen in previously known Ga phases. Atoms of all colors represent Ga. In M2, M3 and M4, red atoms show a similar “boat-like” substructure, while the green atoms highlight the difference in these motifs.

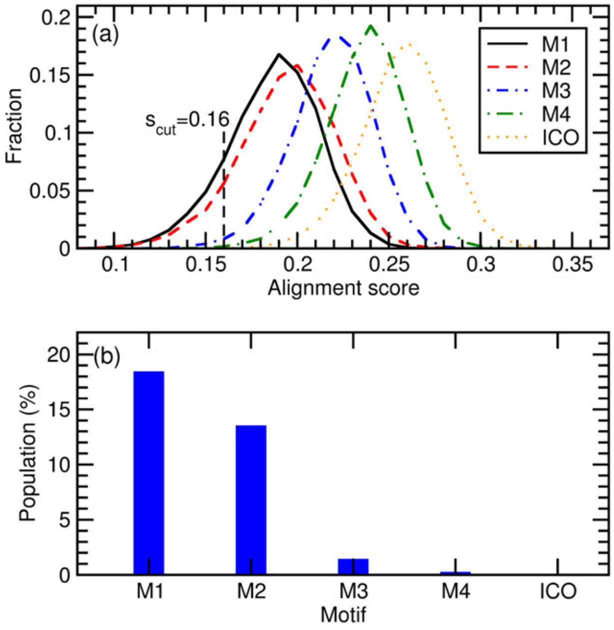

Fig. 2. (a) Distribution of the alignment score and (b) population for clusters extracted from the AIMD sample at $T = 400$ K aligned with the cluster motifs given in Fig. 1, as well as the icosahedron motif.