



## Cooling rate dependence of polymorph selection during rapid solidification of liquid metal zinc

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**Abstract:** The polymorph selection during rapid solidification of zinc melt was investigated by molecular dynamics simulation. Several methods including  $g(r)$ , energy, CNS, basic cluster and visualization were used to analyze the results. The results reveal that the cooling rate has no observable effect on the microstructure as  $T > T_c$  ( $T_c$  is the onset temperature of crystallization); and at the first stage of crystallization, although microstructures are different, the morphologies of nucleus are similar, which are composed of HCP and FCC layers; the polymorph selection of cooling rate finally takes place at the second stage of crystallization: at a high cooling rate, the rapid increase of FCC atoms leads to a FCC crystal mixed with less HCP structures; while at a low cooling rate, HCP atoms grow at the expense of FCC atoms, resulting in an almost perfect HCP phase. The results reveal that the cooling rate is one of the important factors for polymorph selection.

**Key words:** polymorph selection; crystal structure; rapid solidification; metal zinc; molecular dynamics simulation

### 1 Introduction

Polymorphs have different physical properties [1], e.g., materials solidified into different polymorphs will result in different macro-properties. Therefore, controlling polymorph form is crucial for many applications, and it is also a great technological importance in making of drugs and pigments as well food. So, controlling and designing the polymorphism of crystals have attracted a great deal of attention in various fields [2–5]. The structure of a crystal is developed from the nuclei which often consist of different polymorphic structures. While the nucleation and growth are a very complex process, in which the structure of polymorph is affected by several factors such as impurities, cooling rates and boundary condition. Thus, the control of polymorph selection during crystallization is still a mysterious problem, which demands further explorations [5,6].

Polymorph selection is a complex phenomenon mainly resulted from the competition of kinetics and thermodynamics [7,8]. Much attention has been paid on this issue and great progress was achieved in the past. Both experiment and simulation have shown that nucleation stage is important for controlling polymorph selection [9,10]. In the very recent work of ZHANG et al [4], the Lennard–Jones system often evolves into a polymorphic crystal with either fivefold-symmetric stacking faults or single-direction stacking faults, and such an evolution depends on the configuration of FCC/HCP concomitance in the nucleation stage. For spherical particle system and Lennard–Jones particle system, the polymorphism can be controlled by varying the conditions of crystallization (e.g., the value of the dimensionless screening parameter, the pressure at fixed supercooling) [11,12]. However, experiments have suggested that seeding with the desired polymorph in nucleation stage is not sufficient to ensure the growth of a desired polymorph [10]. Therefore, the polymorphism

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control remains a long standing and challenging issue and efforts are still urgently needed to make a comprehensive understanding of this phenomenon.

In this work, we focus on the effect of cooling rate on the polymorph selection during rapid solidification. The molecular dynamics (MD) simulations for the rapid solidification of liquid zinc have been performed at two cooling rates. And several analysis methods including the cluster type index method (CTIM) [13–17] and visual analysis have been adopted to detect the structure evolution during solidification. It is found that via cross nucleation of different layers, the cooling rate plays a critical role in polymorph selection that begins to work at the second stage of crystallization.

## 2 Computation details

We use the effective pair potential function of the generalized nonlocal model-pseudopotential (GNMP) to model the interactions between atoms [18,19]. The potential is defined as

$$V(r) = (Z_{\text{eff}}^2/r) \left[ 1 - \left( \frac{2}{\pi} \right) \int_0^\infty F(q) \sin(rq) dq / q \right] \quad (1)$$

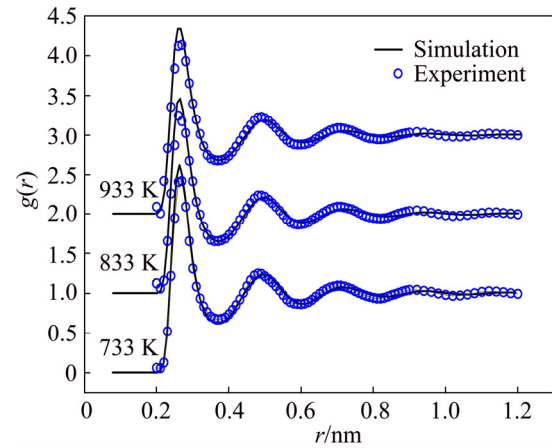
where  $Z_{\text{eff}}$  is the effective ionic valence and  $F(q)$  is the normalized energy wave number characteristic, and both of them were defined in detail in Refs. [18] and [19]. The reliability of the potential for metal zinc has been demonstrated by computing its liquid structure [20]. The pair potential is cut off at 20 a.u., and the time step is 5 fs.

The MD simulation was carried out in a cubic box with 10000 zinc atoms under ambient pressure and three dimensional periodic boundary conditions. In this simulation, the damped force method (also called the Gaussian thermostat) [21,22] is adopted to control the temperature of the system. Subjected to the Maxwell distribution law, the position and velocity of each atom are initialized randomly at 973 K (much higher than the melting point of zinc (692 K)). First of all, let the system run 50000 time steps to obtain equilibrium liquid state determined by the energy change of the system; then, the system is quenched to 73 K at two cooling rates of  $Q_1=5 \times 10^{11}$  K/s and  $Q_2=1 \times 10^{11}$  K/s. Finally, the microstructural evolution is analyzed by means of the common neighbor sub-cluster (CNS), the enhanced cluster-type index method (CTIM-2) [13,14] and 3D graph technique.

## 3 Results and discussion

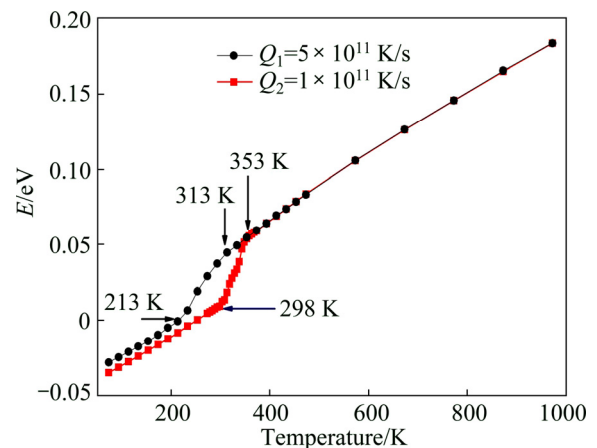
As well known, the pair distribution function (PDF or  $g(r)$ ) can be obtained by Fourier transformation of X-ray diffraction factor  $S(q)$ , so the current simulation

can be verified by comparing the calculated  $g(r)$  curves with the experimental results obtained by WASEDA [23], as shown in Fig. 1. Obviously, the calculated results are perfectly in agreement with the experiment data. This demonstrates that the effective pair potential function adopted here is successful in describing the interactions among zinc atoms.



**Fig. 1** Comparisons of simulation  $g(r)$  curves (solid lines) with experimental data (circles) for zinc at different temperatures

Figure 2 shows the evolution of average energy  $E$  per atom with the decrease of temperature at two cooling rates. The slopes of both curves have twice steep jumps, which implies that the solidifications experience first-order phase transitions. And the initial temperatures ( $T_c$ ) of crystallization can be evaluated to be about 313 K and 353 K at  $Q_1$  and  $Q_2$ , respectively. And the end temperatures ( $T_e$ ) of the phase transition are respectively 213 K and 298 K. Obviously, with the decrease of the cooling rate,  $T_c$  increases, while  $\Delta T$  ( $T_c - T_e$ ) decreases. This is because under a slower cooling rate, for a certain temperature decrease, it needs more time to relax the system. In other words, the slower the cooling rate is, the closer the system is to the equilibrium state at any



**Fig. 2** Relationship between total energy per atom and temperature at different cooling rates

temperature. This will result in a higher  $T_c$  and a smaller  $\Delta T$ . For convenience, we call crystallization completing at  $T_c$ , although structure transformation may still occur at  $T < T_c$ .

In order to monitor the local structure in the system during rapid solidification, we first consider a kind of structure (called as common neighbor sub-cluster, CNS) that is composed of a pair of atoms (called as root pair or reference pair) and their common near neighbors (CNNs). This technique was earlier generalized by HONEYCUTT and ANDERSON [24], and recently has been enhanced by TIAN et al [25], which has been widely used to analyze liquid, glass, crystal, and particle systems [26–29]. In this technique, if a pair of atoms depart less than a pre-set distance  $r_c$  (that is usually determined by the first valley of the PDF curve), they are bonded, and four integers  $ijkl$  (a CNS-index) are used to describe a CNS. If the reference pair is bonded,  $i$  is 1; otherwise,  $i$  is 2.  $j$  represents the number of CNNs.  $k$  is the number of bonds among CNNs. And the last index  $l$  is the number of bonds in the longest continuous chain formed by the  $k$  bonds. When the microstructures are described by CNS, the 1555, 1544 and 1433 are the characteristic ones for liquid and amorphous states; 1444 and 1666 (with ratio of 6:8) for BCC crystal; 1421 for FCC crystal; and 1421 and 1422 (with ratio of 6:6) for HCP crystal.

The details of the seven major CNSs mentioned above in the two simulated processes are shown in Fig. 3. One can see that the crystallization behavior depends on the cooling rate. In particular, before crystallization (as  $T > T_c$ ), the evolution of seven CNSs is almost not related to the cooling rate: the percentages of 1555 (much more rapid) and 1666 increase and simultaneously get the maxima at  $T_c$ , while that of 1433 decreases (see Figs. 3(b) and (d)), and others (1444, 1544, 1421, and 1422) have almost no change. As  $T_c < T < T_e$ , the percentages of 1421 and 1422 increase (see Figs. 3(a) and (c)) at the expense of 1555, 1544 and 1433 (Figs. 3(b) and (d)). The increase rate of 1421 is similar at  $Q_1$  and  $Q_2$ ; however, the increase rate of 1422 is much larger at  $Q_2$  than that at  $Q_1$ . Other five CNSs decrease to almost zero at  $T_e$  at the end of the phase transition. The most obvious difference happens after the phase transition. As  $T < T_e$ , at  $Q_1$ , the percentage of 1421 has a small increase, while that of 1422 has a tiny decrease; at  $Q_2$ , the percentage of 1421 has a distinct decrease, whereas that of 1422 has a higher increase, and finally they have the same percentage of 50% as  $T < 213$  K. Thus, at  $Q_1$ , the system results in a final state ( $T = 150$  K) composed of 1421 (75%), some 1422 (15%) and little other CNSs; While at  $Q_2$ , it is with the same amount of 1421 and 1422 (should be an HCP crystal).

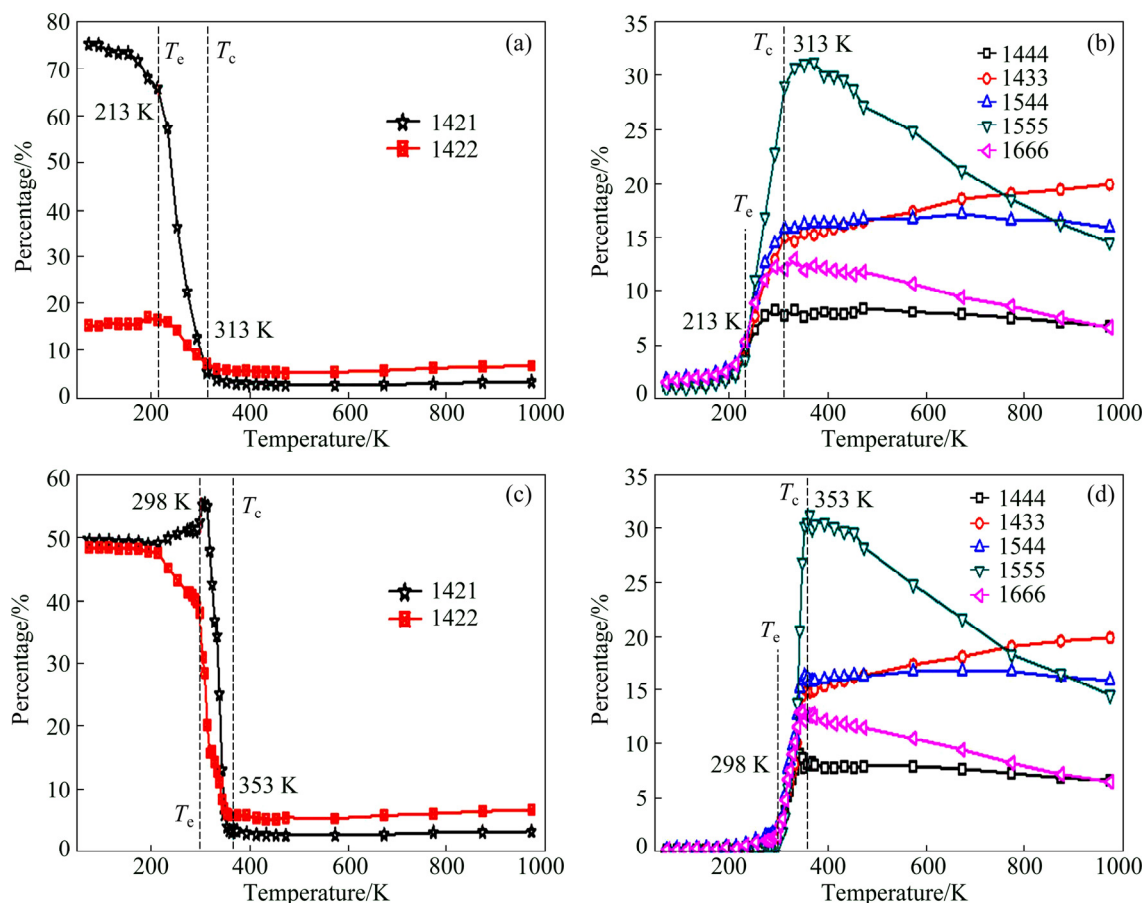
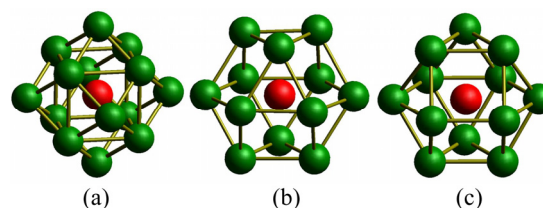


Fig. 3 Relationship between percentage of CNSs and temperature at two cooling rates: (a, b)  $Q_1 = 5 \times 10^{11}$  K/s; (c, d)  $Q_2 = 1 \times 10^{11}$  K/s

As for 1444 and 1666 that can be the building block of BCC crystals (with ratio of 6:8), at  $T < T_c$ , their amount no longer increases, but decreases rapidly to nearly zero at the end of crystallization. It suggests that the liquid zinc does not experience a metastable BCC phase, but directly crystallizes into the final state of HCP crystal or the mixture of HCP and less FCC structures. Thus, zinc is different from simple liquids, where metastable BCC structures are the crystalline precursor on the way from liquid-like atoms to FCC (or HCP) crystals [30–32]. And the FCC–HCP coexisting scenario for zinc makes sense because the FCC and HCP phases are structurally compatible and have almost equivalent free energies [33,34]. The cohesive interaction in zinc is so strong that a small energy fluctuation in supercooled liquid will yield the more energetically and kinetically favorable HCP and FCC crystalline structures, and hence the BCC nucleus is usually bypassed. This scenario is similar to the simulation result for the crystallization process of supercooled liquid aluminum [8,35].

The local configuration revealed by a CNS is shared by a group atom, but does not belong to any single one. In order to clearly detect the local configuration around single atoms, the cluster-type index method (CTIM) [13,14,30,36] has been proposed based on the work of QI and WANG [37]. In the CTIM, a basic cluster is composed of an atom and all near neighbors are in a spherical region with a radius of  $r_c$ . The deficiency of this method caused by a fixed  $r_c$  has been overcome by introducing the topologic criterion proposed in Ref. [25]. In the enhanced CTIM (called as CTIM-2) [13,14,30,36], six integers ( $n, n_1, n_2, n_3, n_4, n_5$ ) are used to describe such a basic cluster. The first integer  $n$  represents the total number of neighbor atoms of the central atom (namely, the coordination number of the central atom), and  $n_1, n_2, n_3, n_4$ , and  $n_5$  are respectively the numbers of the 1444, 1555, 1666, 1421 and 1422 CNSs in which the central atom is one of the reference-pair atoms.

In CTIM-2, the BCC, HCP and FCC basic clusters can be expressed as (14 6 0 8 0 0), (12 0 0 0 6 6) and (12 0 0 0 12 0), respectively, as shown in Fig. 4. Take the BCC basic cluster as an example, (14 6 0 8 0 0) means that the central atom has 14 near neighbors, six of which are connected with the central atom by 1444 CNS and other eight are 1666 CNS. Accordingly, the BCC, HCP and FCC atoms are identified as the centre of BCC, HCP and FCC basic clusters, respectively. Based on the CTIM-2, the larger clusters consisting of different types of basic clusters can be clearly described. Aforementioned analysis reveals that 1421 and 1422 play the key role in crystallization, whereas all others including 1444 and 1666 are negligible. Thus, the change of the number of HCP and FCC basic clusters (composed of 1421 and 1422) in the system with temperature is



**Fig. 4** 3D graphs for three typical basic clusters of BCC, FCC and HCP (for clarity, bonds between centre atoms and near neighbors are omitted): (a) BCC (14 6 0 8 0 0); (b) FCC (12 0 0 0 12 0); (c) HCP (12 0 0 0 6 6)

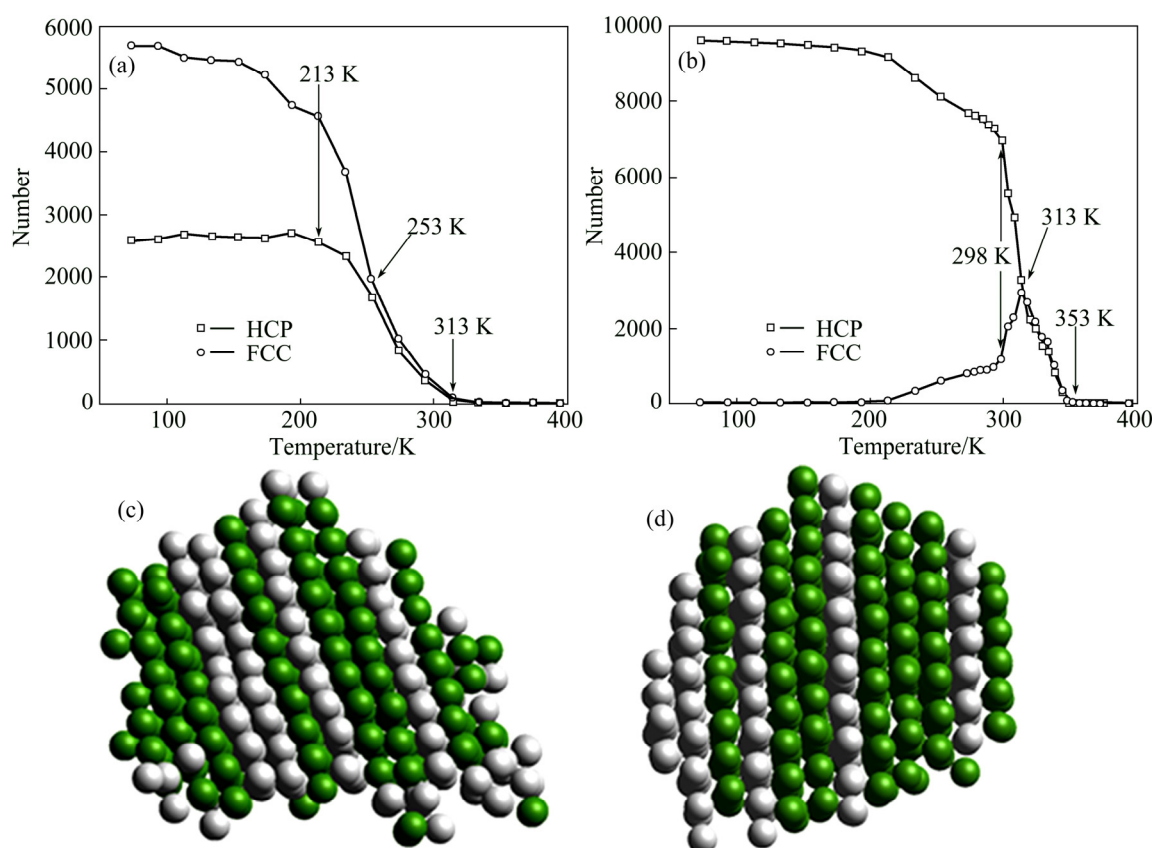
depicted in Fig. 5, while the BCC cluster is not presented here.

We now pay attention to the evolution of clusters in the crystallization at different cooling rates. Figure 5 shows that the numbers of FCC and HCP clusters begin to have difference when  $T < 253$  K at  $Q_1$  and  $T < 313$  K at  $Q_2$ . Thus, for convenience, each crystallization process is divided into two stages. The first stage is  $253 \text{ K} < T < 313 \text{ K}$  at  $Q_1$  and  $313 \text{ K} < T < 353 \text{ K}$  at  $Q_2$ , and the second stage is  $213 \text{ K} < T < 253 \text{ K}$  at  $Q_1$  and  $298 \text{ K} < T < 313 \text{ K}$  at  $Q_2$ . Figure 5 demonstrates that at the first stage, both HCP and FCC clusters grow concomitantly. And according to the configuration of nuclei shown in Figs. 5(c) and (d), the nucleation and growth processes occur through the successive formation of HCP and FCC atoms in layer distribution, that is, it is a cross nucleation. This is different from the results of O'MALLEY and SNOOK [38] and LEYSSALE et al [39], in which the HCP- and FCC-type atoms in the nucleus show a great tendency for blocks-like distribution, or the case in a random mixture of the two types of atoms [40].

The cooling rate dependence of the polymorph selection presents at the second stage of the phase transition. At the first stage, morphologies of nuclei obtained at  $Q_1$  and  $Q_2$  are essentially similar: the amounts of FCC and HCP atoms are always equal, as shown in Figs. 5(c) and (d), i.e., polymorph selection does not occur at this stage. At the second stage, polymorph selection begins to work, and still continues after the phase transition. At the cooling rate of  $Q_1$ , as  $T < 253 \text{ K}$ , the number of HCP atoms levels off, while that of FCC atoms still grows. And the system finally becomes a mixture (at 73 K) where the HCP (56.98%) and FCC (26.00%) crystal structures coexist, together with little others. While at the slower cooling rate of  $Q_2$ , as  $T < 313 \text{ K}$ , the FCC atoms continually transform into HCP atoms; finally, the system results in a rather perfect HCP crystal with 96.08% of HCP atoms, 0.70% FCC atoms and 3.22% of other structures at 73 K.

The final structures solidified at different cooling rates have also been checked by comparing the calculated  $g(r)$  with perfect spectra of FCC and HCP

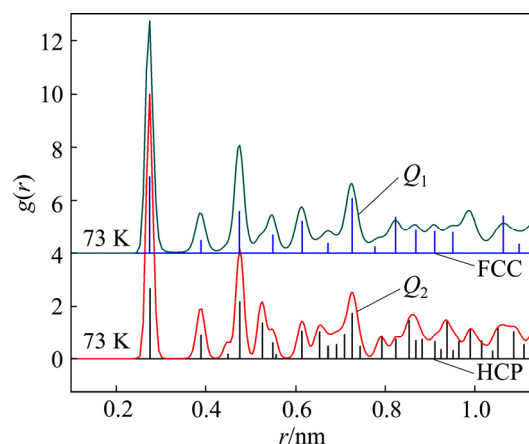




**Fig. 5** Relationship between number of FCC and HCP basic clusters with temperature at cooling rate of  $Q_1=5 \times 10^{11}$  K/s (a) and  $Q_2=1 \times 10^{11}$  K/s (b); and snapshots of nuclei at 293 K,  $Q_1$  (c) and 338 K,  $Q_2$  (d) (Green is for HCP atoms and gray is for FCC ones)

crystals, as shown in Fig. 6. The curves for  $Q_1$  and  $Q_2$  are highly consistent with the perfect  $g(r)$  spectra for FCC and HCP, respectively. Relative to the perfect FCC spectrum, the extra peak at about 1.0 nm on the  $g(r)$  curve obtained at  $Q_1$  just aligns with a line for HCP crystals, strongly indicating the existence of HCP structures in the FCC dominant mixture. Thus, the  $g(r)$  analysis result is precisely consistent with that of CTIM-2.

This result demonstrates that the cooling rate plays a key role in the polymorph selection for zinc and it begins to work at the second stage of the phase transition. Polymorph selection is a complex process resulted from the interplay between thermodynamics and kinetics [5]. Among several mechanisms proposed for polymorph selection, the cross nucleation is a kinetic phenomenon associated with a free energy barrier of activation [38,39], usually proceeded via heterogeneous nucleation one polymorph on another. For two polymorphs that have equivalent free energies, the free-energy barrier of cross-nucleation is much lower than that of homogeneous nucleation and can be easily overcome by the collective fluctuations in the fluid [41]. For zinc, FCC and HCP have almost equivalent free energies [33,34] and structurally compatible surface that can

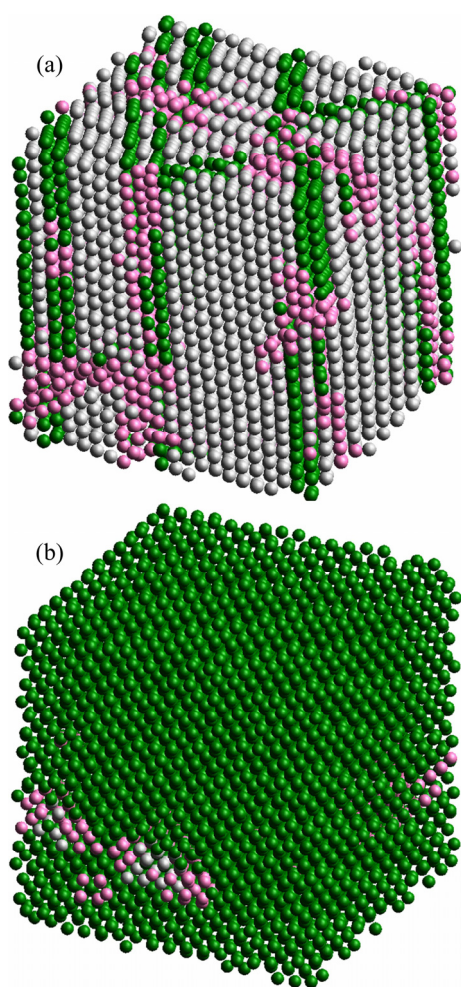


**Fig. 6**  $g(r)$  curves of system at 73 K (The blue spectrum is for perfect FCC crystal and the black one is for perfect HCP crystal)

further lower the free-energy barrier of nucleation. Thus, the cross-nucleation of HCP layers can take place on the structurally compatible (111) surface of the FCC nucleus, and vice versa. This is just the case of our simulations reported here. However, if the cooling is too rapid, the kinetics is suppressed and the cross-nucleation will not be evoked. In this case, the FCC and HCP blocks will randomly distribute in the final solid, as shown by the

previous studies [42–44].

However, the final morph is not determined by whether the cross-nucleation occurs. As illustrated in the present work, at both cooling rates, the cross-nucleation takes place at the beginning of the phase transition, while the morph of the final solid is different. In the present work, the higher cooling rate results in a mixture of HCP and FCC layers as well as less other structures (Fig. 7(a)); while the lower cooling rate leads to an almost perfect HCP crystal (Fig. 7(b)). Thus, the cooling rate plays a critical role in determining the morph of the solid obtained by solidification. In brief, our result indicates that the cooling rate is also one of the important factors for polymorph selection.



**Fig. 7** 3D views for final state of atoms at 73 K obtained at different cooling rates (Color configuration: green represents HCP atom, gray represents FCC atom, and purple represents others): (a) High cooling rate; (b) Low cooling rate

## 4 Conclusions

1) The cooling rate does not exert observable effect on the microstructure of the simulated system before the beginning of crystallization.

2) In the initial stage of crystallization, the microstructures begin to get difference, while in both systems, the nucleus is composed of HCP and FCC layers, i.e., the cooling rate has no influence on the polymorph selection.

3) While in the second stage of crystallization and after the phase transition, the cooling rate dependence of the polymorph selection occurs: at higher cooling rates with no change of HCP atoms, FCC atoms keeps increasing, resulting in a mixture of HCP and FCC crystal structures; while at lower cooling rates, HCP atoms grow at the expense of FCC atoms and an almost perfect HCP phase is obtained at last.

4) The cooling rate is an important factor for polymorph selection.

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## 液态金属锌快速凝固过程中 冷速对多晶形选择的影响

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**摘 要:** 采用分子动力学模拟方法研究液态金属锌快速凝固过程中多晶形选择。并采用多种方法如  $g(r)$  函数, 能量、CNS、基本团簇法和三维可视化对结果进行分析。结果表明, 当  $T > T_c$  ( $T_c$  为晶化起始温度) 时, 冷速对微观结构没有明显的影响; 在晶化的第一阶段, 尽管不同冷速下系统的显微组织不同, 但晶核的形态相似, 都是由层状分布的 FCC 和 HCP 结构组成; 冷速对多晶形选择的影响在晶化的第二个阶段开始凸显出来: 在较高冷速下, FCC 原子的快速增加导致最后形成 FCC 和 HCP 共存的晶体结构; 而在较低冷速下, HCP 原子以 FCC 原子减少为代价快速增加, 系统最终形成完美的 HCP 晶相。对于多晶形选择, 冷速是一个非常重要的因素。

**关键词:** 多晶形选择; 晶体结构; 快速凝固; 金属锌; 分子动力学模拟

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