

## Shoulder-peak formation in the process of quenching

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(Received 1 May 2003; published 31 July 2003)

The shoulder peak in liquid with medium range order (MRO) is first reported and its origin is analyzed by molecular dynamics calculation in this paper. Convincing evidence is presented that this structural order, manifested by a shoulder peak in the pair correlation function, can be interpreted as entanglement and interpenetration of ideal and defective icosahedra sharing common vertexes and faces. The bond energy which are directly related to chemical ordering, together with the geometrical constraint, play important roles in the local structure formation. It is concluded that liquid is able to sustain the presence of its predominantly icosahedral local order due to quick cooling. The present result thus indicated that shoulder peak induced medium range order should be a common feature of icosahedrally ordered liquids.

DOI: 10.1103/PhysRevB.68.024210

PACS number(s): 61.25.Mv, 71.15.Pd

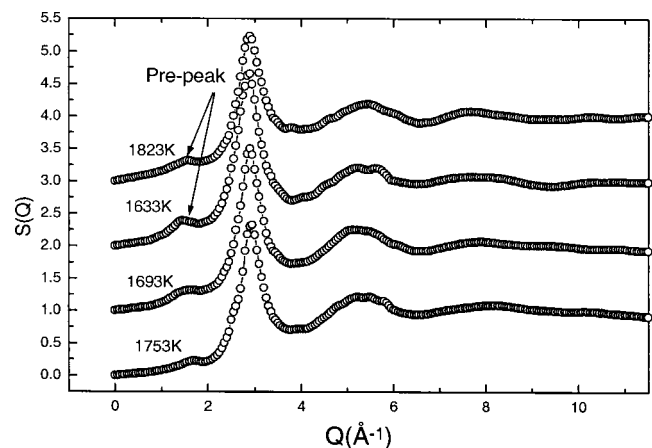
The discovery of medium range order with a polyhedral system has aroused interest in the study of the relationship between medium range order in liquid alloys or metallic glasses and the long range order in this new state of matter.<sup>1-3</sup> Previously, the idea that structures of liquid metals could be based on packing of icosahedral units was suggested by Frank in order to explain supercooling effects.<sup>4</sup> Even though this property was later confirmed by molecular dynamics simulations of supercooled liquids,<sup>5</sup> experimental proof is still required. Several researchers<sup>6-8</sup> first attempted to describe the Al-Mn structure by icosahedral glass models which display long range orientational order, but only short-range translational order is observed. From several diffraction studies for Al-Fe-Cu, it was shown that both orientational order and long range quasiperiodic translational order occur in this stable phases.<sup>9,10</sup> Most structural models involve packing of various icosahedral clusters with a large number of atoms, such as Mackay clusters.<sup>11-12</sup> Clusters are not only a convenient geometrical description of these complex phases but indeed play a role in their properties.<sup>13-15</sup> Although the results of previous studies on liquid<sup>16-19</sup> suggest the presence of local icosahedral order in these liquid states, no direct comparison has yet been made with the local order in the solid state.

Amorphous materials are characterized by disorder or structural randomness. Generally, glass is viewed as a "frozen liquid," however, there is much controversy regarding the underlying mechanisms.<sup>20,21</sup> Some important questions on about freezing have remained unanswered. Especially, medium range order (MRO) in liquids and glass solid is a subject of much current interest.<sup>22,23</sup> This notion refers to structural ordering occurring at length scales beyond that characteristic of short range order (SRO) and associated with the nearest-neighbor environment. It is interesting to study the cooling process of the MRO system. However, until now, results in this research field have been insufficient. In this paper, a shoulder peak is reported. The main purpose of this paper is to investigate the origin of shoulder peak observed in Al-Fe liquid simulated by molecular dynamics. The results

presented below provide convincing account for a shoulder peak of this liquid manifesting the presence of MRO.

As shown in Fig. 1, the structure factor  $S(Q)$  of Fe-Al liquid features a well defined prepeaks at around  $Q=1.8$ , a clear signature of the presence of MRO, distinguishing this liquid from all the known simple monatomic liquids. It is difficult to derive unambiguous information on the nature and extent of MRO in noncrystalline materials from experimental structural measurements. However, one celebrated structural feature often taken to be a signature of MRO is the first sharp diffraction peak in the structure factor in certain classes of amorphous solids. It occurs at a value of  $Q$  smaller than the position of main peak of structure factor  $S(Q)$ . The chemical order effects may contribute to the first sharp diffraction peak. The prepeak has a different origin than the long-range periodicity which gives rise to the Bragg peaks, but it cannot be an effect of system size. The observation of MRO in Fe-Al liquid further enables us to investigate its cooling process. What would happen when cooling?

Molecular dynamics simulation can generate realistic structural models for materials and provide information about the dynamics of the glass formation. Here we report

FIG. 1. Prepeak in experimental structural factors  $S(Q)$ .

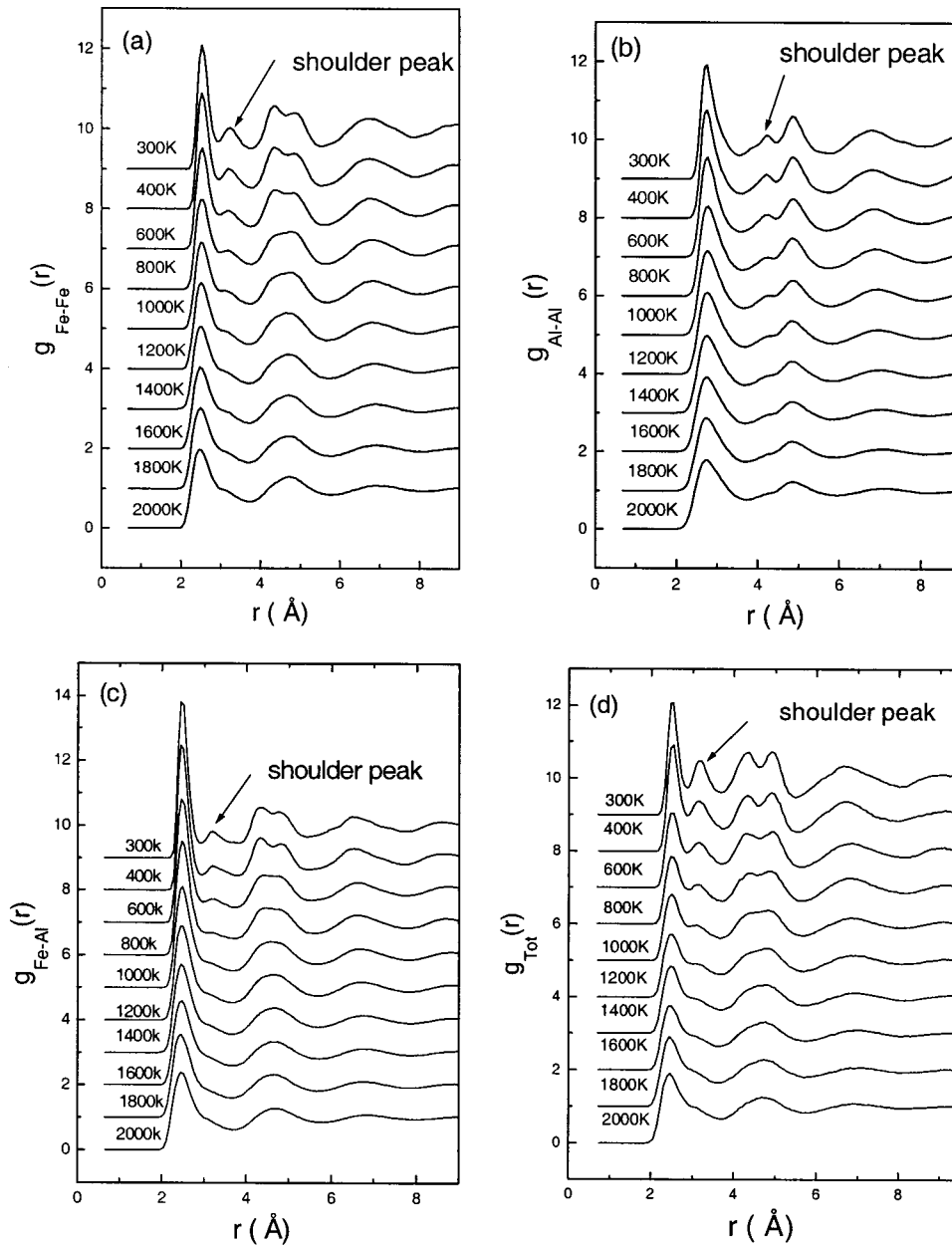


FIG. 2. Shoulder peaks in pair correlation functions on cooling (a)  $g_{\text{Fe-Fe}}(r)$ , (b)  $g_{\text{Al-Al}}(r)$ , (c)  $g_{\text{Fe-Al}}(r)$ ,  $g_{\text{tot}}(r)$ .

the results of extensive simulation of the cooling of Fe-Al systems at constant pressure (0.132 Mpa). The systems consisted of 500 atoms subject to periodic boundary conditions. Two component system with 50% Fe and 50% Al atoms are studied. Our aim here is to study the nonequilibrium properties of this well characterized model. Our strategy is the following. Starting from an equilibrium system at initial temperature 2000 K, we instantaneously quench the system by rescaling particles velocities to a final temperature 300 K at a quenching rate equal to  $2.5 \times 10^{13}$  K/s. The system is subsequently allowed to evolve at constant temperature for  $5 \times 10^6$  time steps. This paper will make use of the  $n$ -body potential developed by Besson.<sup>24</sup>

Figure 2 shows the results for the partial pair correlation function. We immediately notice that the Fe-Al partial pair correlation function has a maximum among three partial pair correlation function. This shows that the local order in Fe-Al

glasses is dominated by the strong covalent Fe-Al bond. This indicates that each Fe atom is surrounded by a few Al atoms and no direct Al-Al neighbors, the distribution of Fe and Al atoms around Fe sites changes essentially as expected in a chemically random alloy. The obvious splitting of the second peak of  $g(r)$  gives strong evidence for an amorphous structure. Even more dramatic, on the right hand of the major peak in the Fe-Fe, Fe-Al, and tot. correlation functions, we find a shoulder peak around  $R = 3.238, 4.181, 3.19$ , respectively. Also, on the left of the second peak of Al-Al correlation function, a little shoulder is observed. Interestingly, with the decreasing temperature, the height of the peak increases. As for the Fe-Al alloy, the melting point is about 1650 K. With the temperature decreases, the shoulder peak incidentally becomes more pronounced and at the temperature  $T = 300$  K it becomes a clearly independent peak. Moreover, the shoulder peak in the Fe-Fe, Fe-Al, and tot. correlation

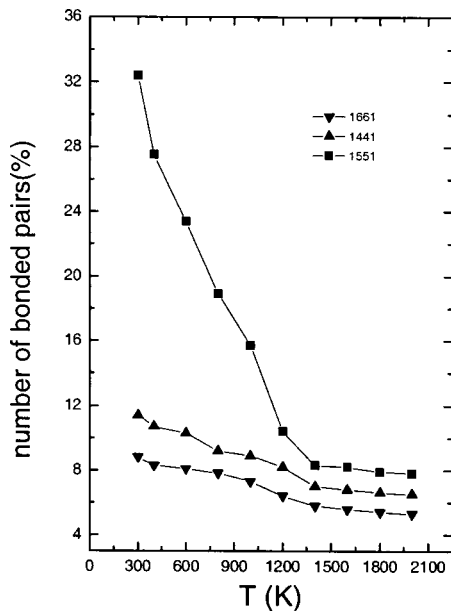


FIG. 3. Some relative numbers of bond pairs on cooling of the 500-atoms system.

functions is very close to the major peak, but the shoulder peak in the Al-Al correlation function is very close to the second peak. It is worth noticing that, during the cooling process, the kinetic energy and the potential energy are two competing tendencies, at high temperature, kinetic energy is in the predominate position, and the potential is in second place, local order is destroyed, so the shoulder peak cannot be observed; with the temperature lowering, the potential energy is in first place, chemical order results in the local structure formation, so the shoulder peak occurs. The great shoulder peak found in the PCF led us to assume the presence of a new strong local order in liquid. The MRO would be screened by the chemical ordering of different atomic species and medium range order of Fe-Al system results in a shoulder peak appearing in the pair correlation function. Chemical bond energy and the local geometrical structure are responsible for the shoulder peak of the pair correlation function. In order to ascertain this hypothesis, we try in this paper to analyze the local cluster and polyhedra in liquids.

To analyze the structural changes accompanying freezing, we adopt a common technique used by Honeycutt and Anderson.<sup>25,26</sup> The first indicates pairs of atoms with four indices. The first indicates whether the pair of atoms is closer than a given cutoff distance, chosen to equal the position of the first minimum in the appropriate pair correlation function. Such atoms are referred to as neighbors or, equivalently, are considered to form a bond. The second index is the number of neighbors common to the two atoms, and the third is the number of bonds between the common neighbors. Sometimes there is ambiguity about the arrangement of the bonds and to resolve this a fourth index is added.

Figure 3 shows the relative numbers of different kinds of bonded pairs of atoms in the inherent structures as function of temperature on cooling. None of the types of pairs shows any significant change as the temperature is varied in the range  $T > 1400$  K. We therefore find that the structure have

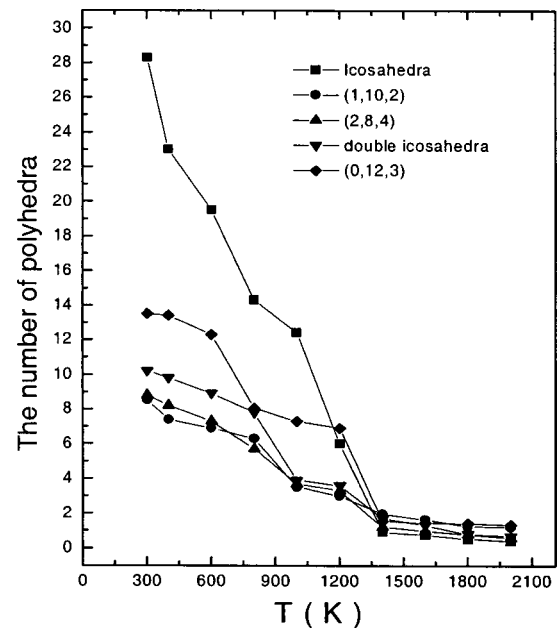


FIG. 4. Various defective icosahedra and ideal icosahedron on cooling.

no big changes with temperature at high temperature. At low temperatures, however, there is a substantial increase in three types of pairs, the 1551, 1441, 1661. The 1551 pairs correspond to two neighboring atoms with five common neighbors that form a pentagon of near neighbor contacts. The 1551 pair is characteristic of icosahedral ordering. The structural transition temperature is identical to the temperature of shoulder peak formation in Fig. 2.

All canonical Frank-Kasper (FK)<sup>26</sup> polyhedra and a number of defective icosahedra are detected and counted in a simulated liquid. The Honeycutt-Anderson index gives us an opportunity to precisely define icosahedron, FK, Bernal, and other defective icosahedra in a very simple way. For convenience, we use a signature to represent those defective icosahedra by us. The first index in the signature is the number of 1441 bonds, the second index is the number of 1551 bonds, the third index is the number of 1661 bonds. For example, if and only if the central atom has 14 neighboring atoms, 12 of which are joined to the central atom by 1551 bonds and two of which are joined to the central atom by 1661 bonds, then they define a FK polyhedron with coordination number  $Z = 14$ . In the same way, other polyhedron can be defined. A polyhedron consisting of some 1551, 1661, and/or 1441 clusters is called a defective icosahedron. As shown in Fig. 4, (0,12,3) polyhedra, made of twelve 1551 bonds and three 1661 bonds, and (0,12,4) polyhedra, composed of twelve 1551 bonds and four 1661 bonds, are detected. (2,8,4) Bernal canonical hole polyhedra, composed of eight 1551 bonds, two 1441 bonds, and four 1661 bonds are found. (1,10,2) defect icosahedra, characterized by ten 1551 bonds and one 1441 bond interposed between two 1661 bonds, are observed in system. The structure of the Fe-Al component glass is predominantly icosahedra. We found 28 icosahedra in a sample of 500 atoms, with 60% of the atoms in icosahedra. On average, each icosahedron interpenetrates 2.1 and shares

a face with 1.9 other icosahedra. This suggests that the tendency to form icosahedral structures would be even greater in macroscopic system. Not only ideal icosahedra detected but also a variety of defective icosahedra. All icosahedra and defective icosahedra interpenetrate and share faces and vertexes with other icosahedron and defective icosahedron. The novel shoulder peaks result from the interpenetration of icosahedra and defective icosahedra. During the cooling process, crystal nucleation and icosahedral ordering are two competing tendencies with a smaller time scale in the two component liquids, and we find clear anticorrelation between the crystal pairs and the icosahedral pairs in low temperature configurations obtained.

FK has shown that, from a geometrical point of view, the required distortion of tetrahedron around the 1551 bonds in a 3D space is the smallest among all tetrahedra in different bipyramids. The distortion of the tetrahedron in sixfold symmetrical bipyramid 1661 is smaller than in fourfold and threefold symmetrical pyramids. Large distortions required for other types of bonds. To investigate how the required distortion and energies of different type of bonds affect their population, we have calculated the populations and energies for all types of bonds. It can be calculated that 1551 cluster has the lowest energy  $-0.0647$  a.u. and the percentage of the 1551 bonds is 32% which is the largest among all types of clusters. Both favorable energy and the smallest distortion required for the 1551 bond result in its having the largest population. While the energy of the 1441 bond, being  $-0.0637$  a.u., is lower than the energy of the 1661 bond, which is  $-0.0629$  a.u., the percentage of the 1661 bonds at 8.8%, is lower than that of the 1441 bonds at 11.4%. This illustrates that the interplay between favorable energy and unfavorable distortion required for 1441 bond and unfavorable energy and favorable distortion for 1661 bond determines their respective percentage. Similarity, the population of other type of bonds can also be explained by this rule. The above analysis indicates that the bond energies, which are directly related to chemical ordering, together with the geometrical constraint play very important roles in the local ordering of glass.

One can now ask what is the relationship between shoulder peak and the MRO? And is the shoulder observed in the PCF of other liquid pure metals related to icosahedral order? During the cooling process there exists a competition between the local preference for icosahedral structure and the global requirement of filling up the space. Although icosahedral clusters cannot fill space by themselves, one might imagine that the icosahedral clusters aggregate in an orderly fashion, until structural frustration produced by aggregation builds up to suppress aggregation itself. Two icosahedral clusters would connect or interlock in two ways: one is by sharing a triangle face, therefore sharing three nearest-neighbor atoms; the other is the interconnection where one of the vertices of a cluster lies on the center of the other cluster, and the clusters share a pentagonal bipyramid or a heptatope

cluster. When the temperature drops, the icosahedral clusters would produce a big structure with medium range order by aggregation in these two interlocking manners. Note that one of the two interlocking icosahedral clusters in either case cannot be superimposed on the other by translation, but they are related by mirror symmetry. However, interlocking of icosahedral clusters is dependence on the interaction between atoms. It can be seen that the interaction of Fe-Al alloy exhibits a rather complex feature, it displays a strong attractive force between Fe and Al atoms, and a weak attractive between Al and Al atoms. This complex interaction must be playing a subtle and delicate role in the liquid structures of the Fe-Al alloy. Indeed, as shown in Fig. 2, the pair correlation functions are quite different from many commonly observed monatomic systems. Shoulder peak exhibits an anomalous ordered structure in system. Medium-range order is reflected by a prepeak in the structure factor. This prepeak result from the complex interaction between the atoms. But, if the system would produce shoulder in PCF, it would meet two conditions, one is suitable quick cooling rate, the other is complex interaction between atoms. In fact, the shoulder peak also exhibits complex interaction between atoms in system. Based on this point of view, we think the shoulder peak is a new signature of MRO. As for the pure liquid metals, for example, Al and Pb, we do not observe the shoulder in the PCF in the rapid cooling conditions. Because its interactions are not complex, some icosahedral clusters and other clusters would not produce complex structure. Ga is a very special metal. Maybe we can observe the shoulder in the PCF of liquid Ga under the quick cooling conditions. Some researcher proved that the interaction of Ga is rather complex.<sup>27</sup>

The simulation may have implications for our understanding of the origin of the shoulder peak, medium range order, and growth of the icosahedral phase. Chemical ordering and geometrical constraint results in the formation of the icosahedra and defective icosahedra on a rapid time scale. The above analysis tells us that the physical picture of the structure of metallic is a disordered entanglement with a lot of icosahedra. The shoulder peak results from interpenetration of ideal and defective icosahedra sharing common vertexes and faces. The main accomplishment of the present paper is the study of the quick cooling simulation of liquid Fe-Al alloy with medium-range order and the shoulder peak is observed in PCF under quick cooling conditions. Both the quick cooling rate and the complex interaction potential result in the shoulder-peak formation during the quick cooling process. The shoulder peak exhibits anomalous order in supercooled liquid and glassy Fe-Al systems.

This work was supported by the National Natural Science Foundation (NSF), Grant Nos. 29890210, 50071028, 50231040 and this work is also supported in part by Natural Science Foundation (NSF) of Shandong province, Grant No. L2000F01.

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