Anomalies in liquid structure of Ni$_3$Al alloys during a rapid cooling process

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Molecular dynamics simulations on the structure of liquid Ni$_3$Al are carried out at constant pressure for different temperatures. Thereby, it is demonstrated that such anomalies as those present in the observed pair correlation functions for Ni$_3$Al liquid are not due to the effect of system size, but are a consequence of the occurrence of particular clusters (or local ordering units) during quick cooling conditions.

I. INTRODUCTION

In recent years there has been an upsurge of interest[1–9] in understanding metallic glasses or amorphous solids. A quick survey of many of the metallic glasses prepared in laboratories reveals that glasses with transition metals as one (or both) of the components constitute quite a large family. Therefore, to understand the physical or structural properties of glasses, theoretically, it is perhaps simpler to first understand the amorphous states of their transition metal constituents. In the process of glass formation, a supercooled liquid is a key step. The dynamics of supercooled liquids is an active area of current experimental and theoretical interest. Neutron scattering techniques have made tremendous progress in enriching our knowledge of the variety of relaxation phenomena prevailing in many glass-forming materials.[10–12] Mode-coupling theory,[13,14] which is a formal generalization of the kinetic theory of an equilibrium liquid and of Vlasov plasma theory, has in recent years received considerable attention. In the structural aspect of glasses, the pair correlation function (PCF) is no doubt of unquestioned value. It yields central information about the short-range order and serves as a key test for different structural models. To study theoretically the pair correlation function, molecular dynamics and Monte Carlo methods are most frequently employed.

Since the discovery of the quasicrystalline phase in AlMn alloys,[15] icosahedral order in liquid alloys has generated renewed interest. Frank[16] was first to suggest that the structure of liquid metals could be based on icosahedral packing, in order to explain supercooling effects. Thirty years later, this description has been confirmed by molecular dynamics simulation of supercooled liquids.[17] Recently, medium-range order (MRO)[18–22] has raised interest in the study of the relationship between liquid and glass. Many researchers have focused attention on the study of topological and structural order in liquid and glass Al$_{80}$Ni$_{20}$ alloys.[23] It is well known experimentally and theoretically that the dominance of icosahedral order increases when approaching the glass transition. However, this is not the case for Ni$_3$Al alloys, because this alloy is one of the few metals that have anomalies in liquid and glass under rapid cooling conditions. In this paper, a shoulder peak is reported on. And the main purpose of this paper is to investigate the origin of this shoulder peak observed in Ni-Al liquid simulated by molecular dynamics. The results presented below provide a convincing account for a shoulder peak of this liquid manifesting the presence of MRO.

II. SIMULATION PROCESS

The quality of a computer simulation depends on two essential features: the accuracy of the interatomic potential and the particle number in the microscopic ensemble used to describe macroscopic materials. A suitable interatomic potential of metals is the foundation of molecular dynamics simulation. Bhuiyan, Silbert, and Stott used an embedded atom method to study the structure and thermodynamic properties of liquid transition metals, their calculated results are in good agreement with the experimental results.[24] Molecular dynamics simulation can generate realistic structural models for materials and provide information about the dynamics of glass formation. Here we report the results of extensive simulation of the cooling of Ni-Al systems at constant pressure. The systems consisted of 500 atoms subject to periodic boundary conditions. A two component system with 75% Ni and 25% Al atoms is 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 particle velocities to a final temperature of 300 K at quenching rate equal to 4.5 $\times 10^{13}$ K/s. The system is subsequently allowed to evolve at constant temperature for 5×10^6 time steps. Our simulation studies are based on the tight binding potential (TB-SMA).[25]

To analyze the structural changes accompanying freezing, we adopt a common technique used by Honeycutt and Anderson.[26,27] The structures are analyzed by 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 (*A-A*, *A-B*, *B-B*). Such atoms are referred to as neighbors or, equivalently, are considered to form a bond. The first index is 1 if the pair is bonded and 2 otherwise. 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 an ambiguity about the arrangement of the bonds and to resolve this a fourth index is added. This method is able to distinguish various local structures between fcc, hcp, bcc, and the icosahedral structures. The different types of bond pairs are associated with the different types of local order. For example, the fcc
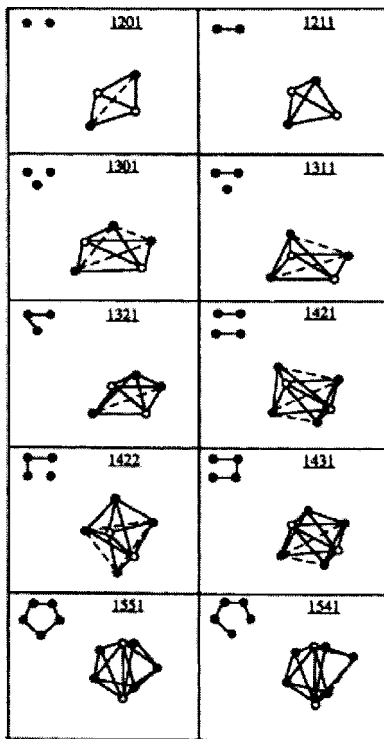
FIG. 1. Schematic diagram for some clusters in dense atomic systems.

FIG. 2. Prepeak in experimental structural factors $S(Q)$.

structure has the type of 1421 bond pair, whereas the hcp crystal has the equal number of 1421 and 1422 bond pairs. The difference between 1421 and 1422 bond pairs is the topological arrangement of the two bonds between the four neighbors. The bond pair 1551, corresponding to a pentagonal bipyramid, is the characteristic of icosahedral order. The 1321 and 1311 bond pairs represent the rhombus symmetrical features of short-range order. Figure 1 shows some atomic bond pairs that appeared in the system.

In this paper, the pair correlation function (PCF)[28] is applied to detect the structural evolution in a melt. If a new structure occurs, the PCF shows some relevant changes.

III. RESULTS AND DISCUSSIONS

As shown in Fig. 2, the structure factor $S(Q)$ of Ni-Al liquid features a well defined prepeak at around $Q=1.9$, 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. The prepeak 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, it is not due to system size but it is a consequence of chemical order. Figure 2 shows the effect of temperature on the prepeak is large. The height of the prepeak lowers with temperature increase. This implies that high temperature weakens medium range order. The observation of
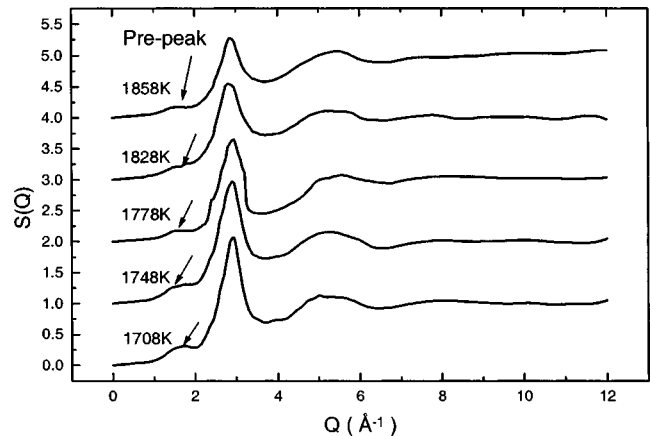
MRO in Ni-Al liquid further piques our interest in studying its cooling process. What would happen if the Ni-Al liquid would be quenched during the rapid cooling conditions?

Figure 3 shows the results for the partial pair correlation function. We immediately notice the Ni-Al partial pair correlation function has a large value. This shows that the local order in Ni-Al glasses is dominated by the strong covalent Ni-Al bond. This indicates that each Ni atom is surrounded by a few Al atoms and has no direct Al-Al neighbors, the distribution of Ni and Al atoms around Ni 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 Ni-Ni, Ni-Al, and tot correlation function, we find a shoulder peak around $R=3.158, 4.212, 3.205$, respectively. Also, the second peak of Al-Al correlation function is beyond the first peak. Interestingly, with decreasing temperature, the height of the peak increases. The shoulder peak incidentally becomes more pronounced and at temperature $T=300$ K it becomes a clearly independent peak. Moreover, the shoulder peak in Ni-Ni, Tot correlation function is very close to the major peak, but the shoulder peak in Ni-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 prevalent. However, the potential is in second place. So the local order is destroyed, the shoulder peak can not 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 the liquid. The MRO would be screened by the chemical ordering of different atomic species and medium range order of Ni-Al system results in a shoulder peak appearing in the pair correlation function. Chemical bond energy and local geometrical structure are responsible for the shoulder peak of pair correlation function. In order to confirm this hypothesis, we try in this paper to analyze local cluster and polyhedra in liquids.

Now we turn to clarify the above aspects. For this, the pair-analysis technique is applied to the atomic configura-
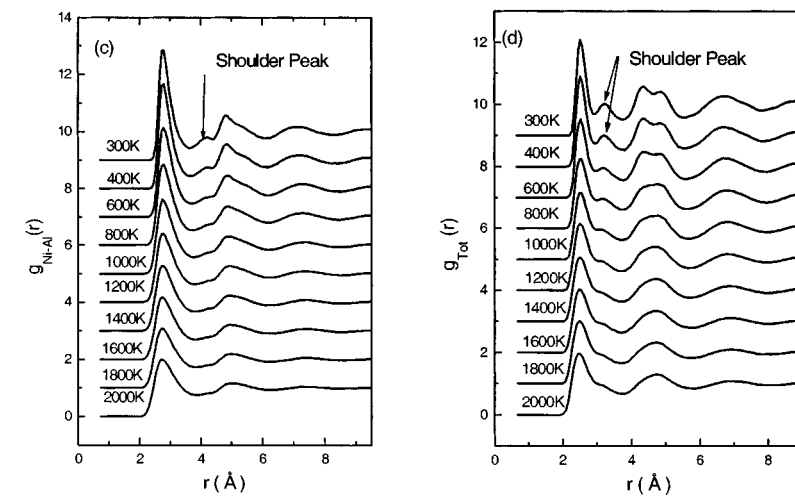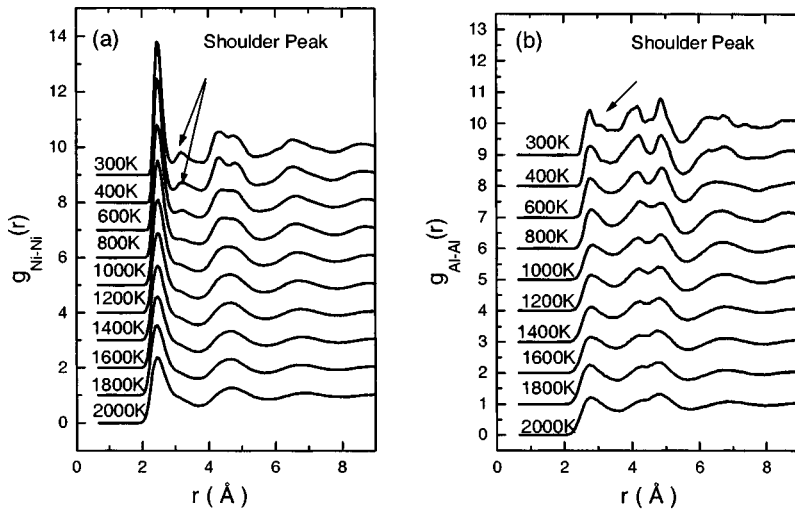
FIG. 3. Shoulder peaks in pair correlation functions on cooling (a) $g_{Ni-Ni}(r)$, (b) $g_{Al-Al}(r)$, (c) $g_{Ni-Al}(r)$, $g_{tot}(r)$.
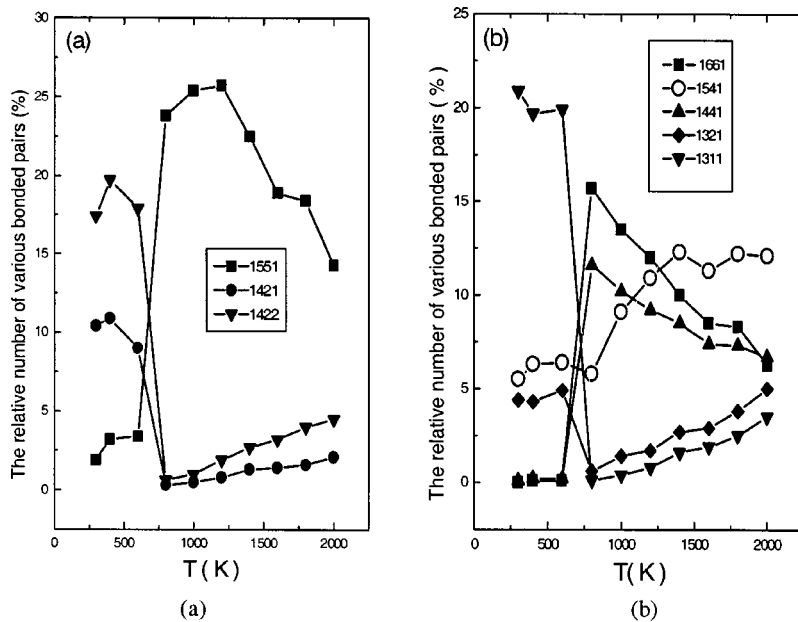

FIG. 4. Some relative numbers of bond pairs on cooling of the 500-atom system. (a) 1551, 1421, 1422; (b) 1661, 1541, 1441, 1301, 1311.

tions obtained from the present MD simulation to determine the microstructure of the presently considered rapid quenching in metals. Figure 4 shows the relative numbers of different kinds of bonded pairs of atoms in the inherent structures as function of temperature on cooling. All of the types of pairs show significant changes as the temperature decreases. When $T > 800$ K, we therefore find a substantial increase in three types of pairs, the 1551, 1441, 1661. But the 1421, 1422, 1311, 1321 bond pairs decrease with temperature decrease. When $T < 800$ K, the 1551, 1661, and 1441 bond pairs decrease with temperature decrease; however, the 1421, 1422, 1311, 1321 bond pairs increase as temperature decreases. The structural transition temperature is identical to the temperature of shoulder peak formation in Fig. 3. The occurrence of the shoulder peak results from the sudden changes of bond pairs. The points of the obtained results that merit emphasis are as follows. (1) At low temperature, the relative number of 1551 atomic bonded pairs (which are characteristic of icosahedral structure) are so small that no icosahedra are present in the present MD simulation. This is contrary to the results of conventional rapidly quenched metals,[28] each containing many icosahedra (corresponding to a large number of 1551 atomic bond pairs). This metal contains so many other bond pairs that a shoulder peak is present on the right side of the first peak of PCF for Ni_3Al metal. (2) Of the various atomic bonded pairs, the numbers of 1311 and 1321 atomic bonded pairs (which appear in rhombohedral structure) are the most prevalent in the present simulation. The above description of the bond pairs may now be used to illustrate the presence of a shoulder on the right side of principal peak of PCF at low temperature because the corresponding relative number of 1311 and 1321 bonded pairs are found to be non-negligible. In addition, the same MD simulation has been carried out for pure cobalt metal.[29] It is found that the corresponding relative number N_{1311} and N_{1321} is negligible and that, as also demonstrated in Ref. 29, the corresponding PCF does not exhibit any shoulder, this being consistent with observation. [See Fig. 4(a) of Ref. 29 for details]. This simply implies that the shoulder in question is closely associated with those clusters, each of which consists of 1311 and 1321 atomic bond pairs shown in Fig. 4.

The above interpretation of the small shoulder peak may now be extended to illustrate by the number of polyhedra in liquid Ni_3Al. 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
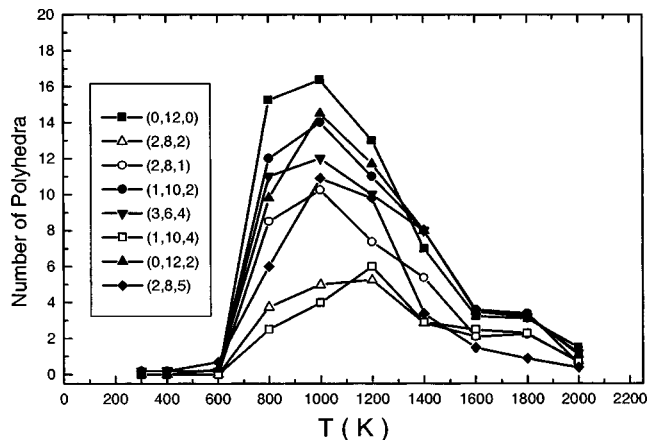

FIG. 5. Various defective icosahedra and ideal icosahedron on cooling.

polyhedron consisting of some 1551, 1661, and/or 1441 clusters is called a defective icosahedron. As shown in Fig. 5, (0,12,0), (2,8,2), (2,8,1), (1,10,2), (3,6,4), (1,10,4), (0,12,2), (2,8,5) polyhedra (composed of 1441, 1551, and 1661 bond pairs) has a sudden change as the temperature drops. This result is consistent with the evolution of bond pairs. The decrease of the 1441, 1551, and 1661 bond pairs result in the decrease of the number of complete icosahedron and defective icosahedra at low temperatures. With temperature decrease, the complete icosahedra and defective icosahedra would decompose to the 1311 and 1321 bond pairs which results in the shoulder peaks on PCF.

IV. SUMMARY

This simulation may have implications for our understanding of a origin of the shoulder peak. Chemical ordering and geometrical constraints result in the formation of bond pairs on a rapid time scale. The above analysis tells us that the 1321 and 1331 bond pairs are the most prevalent in the supercooled liquid and glass Ni_3Al. The shoulder peak results from the occurrence of the 1311 and the 1321 bond pairs. The anomaly of PCF, as noted in Fig. 3, is common for these rapidly quenched metals. The shoulder on the right side of the principal peak of a PCF arises from the effects of the clusters and becomes a small obvious peak in the normal-liquid to supercooled-liquid transition because more clusters of this type appear to affect the PCF in this case. This is not the case at all for conventional rapidly quenched metals for which no shoulder appears on the PCF, this being due to the effects of many icosahedra on atomic structure.

ACKNOWLEDGMENTS

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