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Icosahedral order and defects in metallic liquids and glasses

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Molecular-dynamics simulations of 500 particles have been performed to study the icosahedral order and the defects in the supercooled liquid and glass states of metallic Mg_3Ca_7. Not only are Frank-Kasper polyhedra and Bernal "hole" polyhedra detected, but also a variety of defective icosahedra. Especially, the number of the type of defective icosahedron defined by eight 1551 bonds, two 1661 bonds, and two 1441 bonds is much greater than the number of any kind of Frank-Kasper and Bernal polyhedra. This strongly supports the physical picture of liquids and glasses being a disordered, entangled array of $+72°$ and $-72°$ disclination lines in an icosahedral medium.

During the cooling process there exists a competition between a local preference for icosahedral structure and the global requirement of filling space, and therefore the system exhibits a growth of short-range icosahedral order until it is limited near the glass transition by frustration effects. The frustration comes from the difficulty in close packing with perfect tetrahedra in flat three-dimensional (3D) space. Although all bonds in the ideal tessellation of $S3$ of a four-dimensional sphere are associated with five-fold symmetrical bipyramid,[1] composed of perfect tetrahedra, in a 3D flat space liquids and glasses cannot be composed of only fivefold symmetry bonds; there should be $-72°$ and $+72°$ disclination lines, which are associated with sixfold and fourfold bipyramids. The canonical Kasper polyhedra, being nodes for $-72°$ lines, and the Bernal canonical "hole" polyhedra formed from links of $+72°$ disclination lines are believed by Nelson and other authors[1-3] to be present in significant numbers in supercooled liquids and glasses. However, until now, the defective icosahedra of disclination lines have not been reported as being found directly and quantitatively in liquids and glasses.

The main purpose of this work is to identify the icosahedra and the variety of defective icosahedra, which could be associated with the disclination lines, in a real binary metallic system. This can be done only through a computer experiment, not in a laboratory experiment.

The computer liquids and glasses of Mg_3Ca_7 are simulated by molecular-dynamics (MD) techniques using the damped force method. MD is carried out in a cubic box subject to the widely used periodic boundary conditions with 150 Mg particles and 350 Ca particles. The effective pair potential[4] obtained from the generalized nonlocal model pseudopotential theory[5] is used. This pair potential is cut off at 20.0 a.u. The density is held at 0.003 602 3 particles per volume a.u. throughout all simulations. The time unit is 0.6766×10^{-12} sec and the time step is chosen at 10^{-15} sec. In order to get a melting liquid state, the simulations are started at 1100 K, which is 70 K higher than the melting temperature. First, at this temperature, the system is run for 30 000 time steps to guarantee an equilibrium liquid state. Next, the damped force method[6] is adopted to decrease the temperature with the cooling rate at 4×10^{13} K/sec by forcing the bath temperature to decrease linearly at every time step. The configurations are recorded at particular temperatures during the quenching process. For each of the recorded configurations, another run of 4000 time steps at the given temperature is performed in order to determine the thermodynamic quantities. During each of these runs, 20 configurations are saved, one at each 200 time steps, and then the steepest descent energy minimization procedure with the conjugate gradient method, suggested by Stillinger and co-workers,[7] is imposed on each of these configurations to extract their inherent configurations, in which atoms are brought to a local minimum on the potential-energy surface. This procedure has been used extensively as a very powerful means of analyzing the structure of liquids, amorphous solids, and even crystals.[8,9] It is presumed that the analysis of the inherent structure of a material can provide a clearer picture of its structure because the inherent structure does not contain instantaneous high-energy fluctuations that are present in the actual dynamical state and obscure our observation.

The structural analyses of liquids and glasses are performed by using the pair analysis technique and index of Honeycutt and Andersen[10] in a separate program. All the results of structural analysis are obtained by averaging over the 20 inherent configurations. If the distance of two atoms (a pair) is smaller than a given cutoff distance, chosen to equal the position of the first minimum in the appropriate pair distribution function (Mg-Mg, Ca-Mg,

Ca-Ca), then, such atoms are referred to as neighbors or, equivalently, are considered to form a bond. With the Honeycutt-Andersen pair analysis technique, the fivefold symmetry bonds plus other different kinds of bonds, which describe precisely the microscopic local structure, can be seen easily at the atomic level by computer. The 1551 bond represents the two neighboring atoms with five common neighbors that form a pentagon of near-neighbor contacts. The 1551 bond is situated in a fivefold symmetry environment. The number of 1551 bonds is a direct measurement of the degree of icosahedral ordering. Figure 1 shows the relative number of different kinds of bonds as a function of temperature on cooling. It is clear that the number of 1551 bonds increases on cooling. Also, we have calculated the local parameter[12] W_6, defined for an individual atom. Its behavior is the same as the curve 1551 of Fig. 1. It is reasonable to say that the nature of order parameter W_6 and the number of the 1551 bonds is the same. Furthermore, 18 and 39 icosahedra, defined as in Ref. 8, are found in the system at $T = 1100$ and 100 K, respectively. 165 atoms are in the icosahedra at $T = 1100$ K, whereas 301 atoms, of the 500, are in icosahedra at $T = 100$ K. Each icosahedron interpenetrates 1.54 others and shares a face with 0.54 other icosahedra.

One can now ask where the other atoms are? What kinds of local structure do they have? To answer these questions we note that the links of $+72°$ and $-72°$ disclination lines are associated with fourfold and sixfold symmetrical bipyramids, respectively. The fourfold symmetrical bipyramid can be represented by a 1441 pair, which has four neighboring atoms (with four bonds between them) in common with the pair. The sixfold symmetrical bipyramid may be designated by a 1661 pair, which has six neighboring atoms (with six bonds between

them) in common with the pair. The 1441 and 1661 bonds (pairs) are viewed as the segments of the disclination lines. It is not surprising that the creation of 1551 bonds and the annihilation of 1661 and 1441 bonds are observed on cooling as shown in Fig. 1.

All canonical Frank-Kasper (FK) polyhedra[13] and a number of defective icosahedra are detected and counted in a computer glass for the first time, to our knowledge. The Honeycutt-Andersen index gives us an opportunity to precisely define FK, Bernal, and other defective icosahedra in a very simple way. For example, if and only if the central atom has fourteen neighboring atoms, twelve of which are joined to the central atom by twelve 1551 bonds and two of which are joined to the central atom by two 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 bonds is called a defective icosahedron. We note that all the following results are for the glass state at $T = 100$ K. Eight FK polyhedra, composed of twelve 1551 bonds and two 1661 bonds, 7.8 FK polyhedra, made of twelve 1551 bonds and three 1661 bonds, and 0.65 FK polyhedra, composed of twelve 1551 bonds and four 1661 bonds, are detected. 3.5 Bernal[14] canonical "hole" polyhedra, composed of eight 1551 bonds and two 1441 bonds, are found. 9.9 defective icosahedra, characterized by ten 1551 bonds and one 1441 bond interposed between two 1661 bonds, and 9.7 defective icosahedra, having eight 1551 bonds together with a 1661 bond interposed between two 1441 bonds, are observed. Not a single polyhedron prohibited by the combining law, such as a polyhedron consisting of twelve 1551 bonds and one 1661 bond or of eleven 1551 bonds and one 1441 bond, was found. Nineteen other different kinds of defective icosahedra, which are nodes of the links of $+72°$ and $-72°$ disclination lines and are not yet discussed by other authors, are also found. In particular, 18.2 defective icosahedra, packed by two 1441 bonds, eight 1551 bonds, and two 1661 bonds, are found. The $+72°$ and $-72°$ disclination lines are completely paired in this kind of defective icosahedra. It is worth noting that the number of this kind of defective icosahedra is the greatest among all defective icosahedra, being next only to the number of icosahedra. This kind of polyhedra can be viewed as an important type of defective icosahedron, which are due to dislocations. The population of FK polyhedra with coordination number $Z = 14$ and with $Z = 15$ only ranks eighth and ninth, respectively. The population of Bernal canonical hole polyhedra with $Z = 10$ ranks thirteenth. That of FK polyhedra with $Z = 16$ ranks twenty-fifth, next to the last one in Table I. 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. The three indices are enough because 1331 and 1771 bonds are rarely found in the defective icosahedra.

One point should be noted. Only 1551 bonds, but not 1541 bonds, are regarded as fivefold symmetry by us. Although a 1541 bond (pair) has five neighbors (fivefold) in common, these five neighbors have only four bonds, the
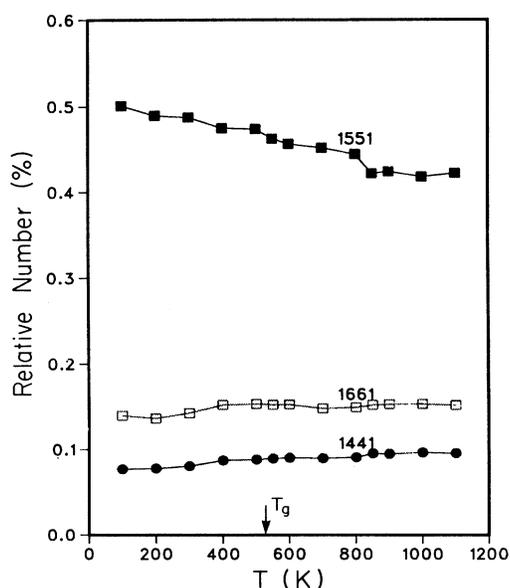

FIG. 1. Relative number of different types of bonds in the inherent configurations as a function of temperature on cooling. The glass transition temperature T_g noted here is determined as in Ref. 11.

TABLE I. Number of the icosahedra and the variety of defective icosahedra in the glass state at $T = 100$ K.

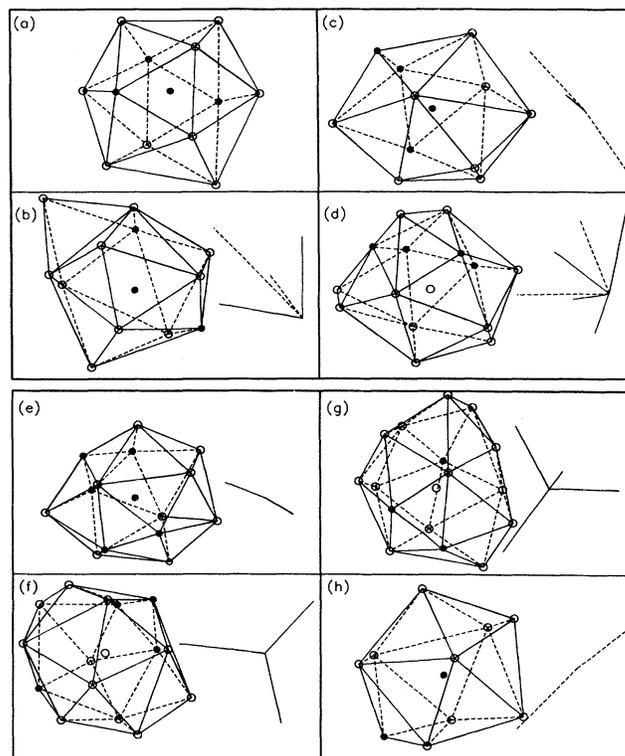| Signature	Coordination No.	No. of polyhedra
(0,12,0)	12	39
(2,8,2)	12	18.2
(2,8,1)	12	10.95
(2,8,4)	14	10.0
(1,10,2)	13	9.9
(3,6,4)	13	9.25
(1,10,4)	15	8.35
(0,12,2)	14	8.00
(0,12,3)	15	7.80
(2,8,5)	15	6.85
(1,10,3)	14	5.8
(1,10,5)	16	4.10
(2,8,0)	10	3.50
(2,8,3)	13	2.85
(3,6,5)	14	2.80
(2,8,7)	17	2.00
(4,4,6)	14	1.85
(3,6,3)	12	1.70
(2,8,6)	16	1.35
(3,6,2)	11	0.80
(3,6,6)	14	0.80
(3,6,1)	10	0.70
(3,6,7)	15	0.70
(4,4,3)	11	0.70
(0,12,4)	16	0.65
(4,4,4)	12	0.55

FIG. 2. Important defective icosahedra found in the inherent configuration from MD simulation. The open and solid circles represent Ca and Mg atoms, respectively. The left sides of the figures are representations of defective icosahedra as links of disclination lines, dashed lines are $+72°$ disclination lines, solid lines are $-72°$ lines. (a) icosahedron; (b) (2,8,2) polyhedron; (c) (2,8,1); (d) (2,8,4); (e)–(g) are FK polyhedra with $Z = 14$–16, or (0,12,2), (0,12,3), and (0,12,4); (h) Bernal polyhedron with $Z = 10$, or (2,8,0).

distance between two of the five neighbors always being beyond the cutoff distance of the first shell of the central atom, which leads to an asymmetrical environment for the 1541 bond. The same applies to other four, five, and sixfold bonds. However, the Voronoi statistics using a simple number of the face cannot distinguish the difference between the 1551 and 1541 bonds.

The number of icosahedra and defective icosahedra is shown in Table I. Representative pictures of the top three defective icosahedra, as well as the FK and Bernal polyhedra, together with their representation as links of disclination lines, taken from a single inherent configuration, are shown in Fig. 2. We have the pictures for all defective icosahedra, which are not presented here because of text length limits and which are available on request. Although hole defective icosahedron (3, 6, 0) and (3, 5, 0) are allowed, they are difficult to find in the glass state, because their coordination number is far from the average coordination number $Z = 13.41$, which is slightly bigger than the value $Z = 13.397$ for an ideal glass.[1] 301 atoms are in 39 icosahedra and 486 atoms are counted in the icosahedra and the defective icosahedra. In other words, we may say that 185 atoms are distributed in 120.15 defective icosahedra for a 500 particle sample. However, all icosahedra and defective icosahedra interpenetrate and share faces with other icosahedron and defective icosahedron.

Thirty-one central atoms of icosahedra are Mg, whereas only 8 central atoms of icosahedra are Ca. This proves that the small atoms prefer to locate at the central of icosahedras. It is easy to understand this because it is well known that the distance between surface neighbor atoms is about 5% larger than the distance between surface atoms and the central atom for a perfect icosahedron. The small Mg atoms and big Ca atoms can fit this case easily. Therefore a suitable proportion of the number of small to big atoms is an important factor for the glass forming ability.

FK (Ref. 13) 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 bipyramid. Larger distortions are required for other types of bonds. To investigate how the required distortion and energies of the different type of bonds affect their population, we have calculated the populations and energies for all types of bonds. The bond energy for two atoms i and j connected by a bond of type l is defined by

$$V_l = V(r_{ij}) + \sum_{\substack{k=1 \\ (k \neq i,j)}}^{N} V(r_{ik}) + \sum_{\substack{m=1 \\ (m \neq i,j)}}^{N} V(r_{jm}) . \qquad (1)$$

This is then averaged over all bonds of type l in the inherent configurations of the system at a given temperature. The total energy of the system is not simply equal to the sum over all of the bond energies defined above.

The summation of the number of 1551, 1661, and 1441 bonds is about 74% of the total number of all types of bonds. Results show that the 1551 bond has the lowest energy, -0.0645 a.u., and the percentage of the 1551 bonds is 50%, which is largest among all types of bonds. Both favorable energy and the smallest tetrahedral distortion required for the 1551 bond result in its having the largest population. While the energy of the 1441 bond, being -0.0638 a.u., is lower than the energy of the 1661 bond, which is -0.0628 a.u., the percentage of the 1441 bonds at 7.7%, is lower than that of the 1661 bonds at 13.9%. This illustrates that the interplay between favorable energy and unfavorable distortion required for 1441 bond and unfavorable energy and favorable distortion for 1661 bond determinates their respective percentages. The energy of the 1331 bond is -0.0586 a.u., thus both energy and distortion unfavorability for 1331 bonds lead to its population, only 0.11%, being much less than that of the 1551, 1441, and 1661 bonds. Similarly, 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 short-range order, together with the geometrical constraint play very important roles in the local structure of glasses and liquids.

We firmly conclude from our simulation results that the physical picture of the structure of metallic glasses and liquids being a disordered, entangled array of disclination lines in an icosahedra medium is realistic.

[1]D. R. Nelson, Phys. Rev. B **28**, 5515 (1983).

[2]J. F. Sadoc, J. Phys. (Paris) Colloq. **41**, C8-326 (1980); D. R. Nelson and M. Widom, Nucl. Phys. **B240**, 113 (1984); S. Sachdev and D. R. Nelson, Phys. Rev. Lett. **53**, 1947 (1984).

[3]F. Spaepen, in *Rapidly Quenched Metals,* edited by B. Cantor (The Metals Society, London, 1979).

[4]S. Wang and S. K. Lai, J. Phys. F **10**, 2717 (1980).

[5]D. H. Li, X. R. Li, and S. Wang, J. Phys. F **18**, 307 (1986).

[6]W. G. Hoover, A. J. C. Ladd, and B. Moran, Phys. Rev. Lett. **48**, 1818 (1982); D. J. Evans, J. Chem. Phys. **78**, 3297 (1983); D. Brown and J. H. R. Clarke, Mol. Phys. **51**, 1243 (1984).

[7]F. H. Stillinger and T. A. Weber, Phys. Rev. A **25**, 978 (1982); F. H. Stillinger and R. A. LaViolette, Phys. Rev. B **34**, 5136

(1986).

[8]H. Jónsson and H. C. Andersen, Phys. Rev. Lett. **60**, 2295 (1988).

[9]W. C. Swope and H. C. Andersen, Phys. Rev. B **41**, 7042 (1990).

[10]J. D. Honeycutt and H. C. Andersen, J. Chem. Phys. **91**, 4950 (1987).

[11]H. R. Wendt and F. F. Abraham, Phys. Rev. Lett. **41**, 1244 (1978).

[12]P. J. Steinhardt, D. R. Nelson, and M. Ronchetti, Phys. Rev. B **28**, 784 (1983).

[13]F. C. Frank and J. S. Kasper, Acta Crystallogr. **11**, 184 (1958); **12**, 483 (1959).

[14]J. D. Bernal, Proc. R. Soc. London Ser. A **280**, 299 (1964).