Rev. Adv. Mater. Sci. 36 (2014) 21-28

RESEARCH PROGRESS OF FIVE-FOLD SYMMETRY CLUSTERS

G.F. Li, X.Y. Shu and J.W Liu

School of Material Science and Engineering, Nanchang Hangkong University, Jiangxi 330063, China

Received: June 06, 2013

Abstract. Since 1984, Shechtman *et al.* published a paper which marked the discovery of quasicrystals. The local five fold symmetry (LFFS) structure is becoming an unsocial hero, who walks a muricated way against classical crystallography. As well known, the LFFS clusters have largely potential application prospect in catalysis, in recomposing physical, mechanical and thermal performance of bulk metallic glasses, in composing "super atom" materials, in some creative manufacture technologies of crystal metal from amorphous straightly. In this paper, we summarize the ubiquitous existence, particularity, performance and research progress of LFFS clusters in metallic glasses, and put forward some urgent problems.

1. INTRODUCTION

Although the elastic modulus E of bulk metallic glasses (BMG) is linear relationship with its solvent component's E in solute-solvent model [1] (Fig. 1), and the density of BMG can somewhat indicate the glass formation ability (GFA) [2], otherwise the ratio of peak positions normalized to the first peak of radial distribution function is constant [3], the microstructure of BMG remains mysterious at present. The mathematics models of BMG have been explored as Bernal's dense random packing model [4], Geskel's short-range ordered model [5], and "solute-centred quasi-equivalent cluster" model put forward by Sheng [6], furthermore criterions to evaluate GFA have been designed by maximum cross section thickness D_m, glass transition temperature T_g, temperature rate T_{rg}($T_{rg}=T_g/T_l$, where T_l is the liquidus phase temperature), supercooled liquid region ΔT_x($\Delta T_x = T_x - T_g$, where T_x is onset crystallization) and parameter γ($\gamma=T_x/(T_g+T_l)$), but only few methods have usefulness to design the GFA of BMG. In engineering, though some experiential techniques are practiced to estimate GFA for some certain metallic system, the reasons why there is largely different GFA for some BMGs only with little component changed are still undiscovered originated from lacking microstructure information of BMG's formation process.

Prevenient papers indicated the icosahedron clusters [12-15], which had dense topological packing structure and low energy in thermal state with local five-fold symmetry (LFFS), were treated as the unit cell for liquidus alloy and BMG. Nevertheless, some BMGs don't have such particular structures [16]. Thereby it is unacceptable to consider it as a unit cell in amorphous materials. Recently, scientists reported that there was another omnipresent primitive cells in metallic glasses—symmetry units, especially the LFFS clusters or polyhedron, which played a vital role in GFA, mechanical property and special manufacture technology of BMG [12,17,18]. Thus, in order to study the microstructure, mechanical property and GFA of metallic glasses, it is imperative to anatomize the LFFS clusters, especially to reveal the formation process and growth capability of such short range order(SRO) structures [10,12,17,19].However, the focus on LFFS clusters is only in their topological

Corresponding author: G.F. Li, e- mail: lgf_918@126.com

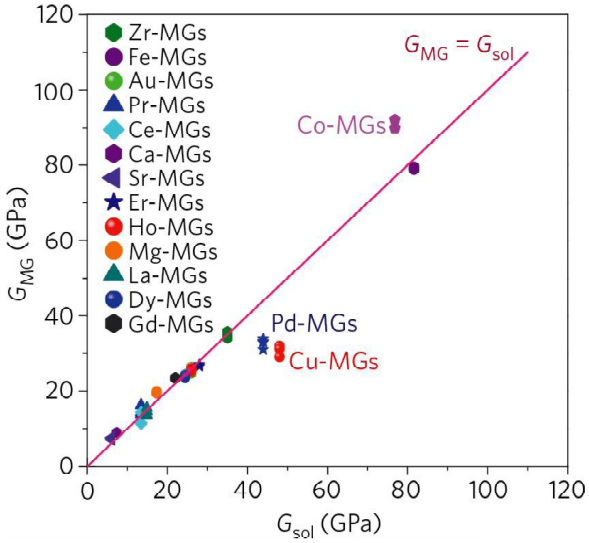

Fig. 1. The average ratio of shear modulus for various metallic glasses(G_{MG}) and their solvents(G_{sol}) is close to 1 [1] (Reproduced by the kind permission of Nature Publishing Group).

characters [10,20-22], such as space distribution, transitional or spherical symmetry, relative radius distribution function, packed density and connection ability with other crystal polyhedron clusters(as Bernal polyhedron). But the problems why the component with little change altered the GFA [10] and how clusters connected with each other to form solid [13] couldn't be not illuminated only by their topological structures character. In the near future, it was found that the transformation of multiple phases [23], such as vitreous phase to crystal [24], plasticity to brittleness of BMG [25], has relation with the electronic structure of local clusters. So what is the structural character of local clusters? How does the local environment influence? What about the research progress? In the following parts, we will analyse them deeply.

2. INFLUENCE ON MATERIALS PROPERTY

As well known, ductile metals, such as low-carbon steels, have special high fracture toughness (more than 200 MPa $m^{1/2}$), but a low plastic yield strength (less than 500 MPa), which are originated from their internal microstructure of periodicity and defects as dislocation [32]. On the opposite, traditional inorganic glasses, *i.e.* oxide glasses of silicates, have very high estimated yield strengths (up to 3 GPa) but lack any intrinsical toughness (less than 1 MPa $m^{1/2}$), and consequently their failure is accommodated by brittle fracture occurring well below the theoretical yield strength (less than 100 MPa). However, the fracture toughness values of metallic glasses range from about 0.5 GPa (for weak rare-earth metal glasses) [33] to as high as 5 GPa (for strong ferrous metal glasses) [34]. Then it could be seen that the difference among crystal metal, inorganic glass and metallic glass only derives from their microstructures, especially from their atomic clusters either with spherical periodic symmetry or translational symmetry.

Recently, it is found that the mechanical property [26-28], thermodynamics [29], and GFA [20-21,30-31]of metallic glasses have a relationship with their microstructure, especially with their LFFS clusters. Wang *et al.* [26] reported that plastic deformation of local structures came from the small degree region of LFFS. Shintani *et al.* [29] found that the same thermal conductivity curves of different BMGs at low temperatures also were caused by LFFS structure. Royall *et al.* [12] discovered the colloid gel couldn't crystallize because of embarrassing from LFFS icosahedron structures. Clusters, which are the primitive cell in glasses, play a vital role in catalyst technology [35] and nano materials [36]. Many scientists researched metallic clusters [37,38], C_{60} [39], metallic-metalloid clusters [40], and illuminated their geometric stability, chemical property and microscopic mechanics, especially paying attention on icosahedron clusters for its performance, character, manufacture and so on.

3. THE PERFORMANC OF LFFS CLUSTER

As well known, icosahedron cluster with LFFS, which is also called "super atom" [41] (Fig. 2), is an excellent catalyst material. Gong *et al.* [42] deduced that 58 Aurum atoms can form a distorted cage with LFFS by first principle calculation. Bergeron *et al.* [41] found amount of $Al_{13}I_n^-$ clusters acting as super atoms in the chemical reaction between Al_n^- and CH_3I solution. Wherein the number of atoms *n* of $Al_{13}I_n^-$ clusters are at even value [43]. Based on such super clusters, Gong *et al.* [44] and Khanna *et al.* [45] constructed a suppositional super crystal comprised by $Al_{12}C$ cluster called as 'super atom'. But analyzing its electronic structure and energy state, they found such super materials can't steadily exist not only from analyzing their geometry property but also from the Gibbs free energy. Somewhere, Pang *et al.* [46] and Smekal *et al.* [47] revealed the icosahedron and double-five pyramid structures would have low energy when the total atoms of cluster are small. In experiments, it was found the

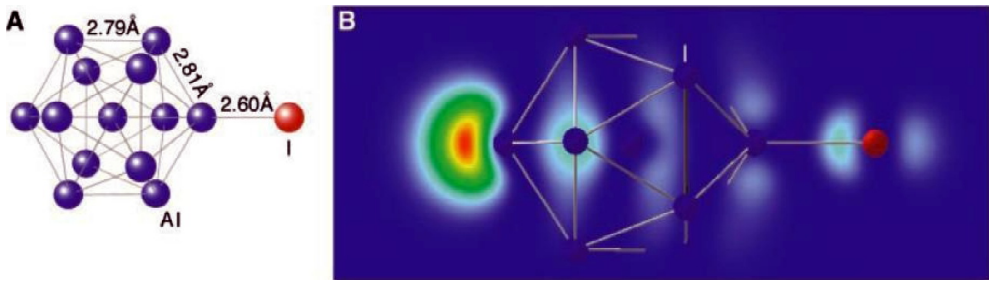

Fig. 2. Super atom $Al_{13}I^-$ and its charge density map [41] (Reproduced by the kind permission of Elsevier Publishing Group).

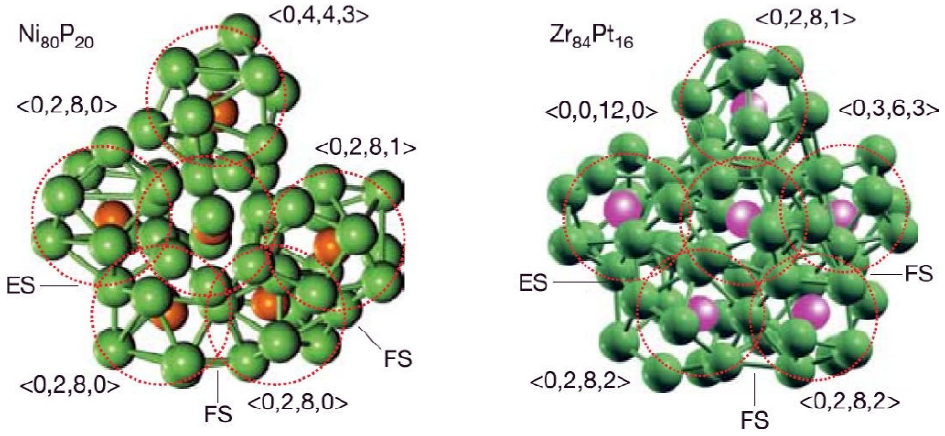

Fig. 3. The packing of the solute-centred quasi-equivalent cluster connections with fivefold symmetry [6] (Reproduced by the kind permission of Nature Publishing Group).

metallic clusters were only in pentagon, icosahedron and hexagon configurations in insert gas condensation method of deposited on substrate surface. And electron and diffraction microscope analysis showed stable metallic clusters could be regarded as multiply twinned particles of face-centered cubic structure [48]; furthermore such twinned particles were easily transformed into single crystal [48]. Thereby the icosahedron clusters have the highest stability and excellent catalyst property, but their structural stability is influenced by different local environments they were surrounded in. So the icosahedron clusters with LFFS are the key to manufacturing excellent catalyst and super materials.

4. LFFS CLUSTER IN LIQUID METAL

In fact, the solidification process of liquid metal is practically considered as the competition process between crystal and noncrystal nucleation respectively [31]. Clusters, which are regarded as the basical component unit, are very important in the primal stage of liquid metal solidification process. So it has significant implication to investigate the growth model of different clusters in liquidus/solid coexisting phase [49], and establishing some perspicuous and effective rules to instruct designing detailed component of metal glasses so as to good GFA. Royall *et al.* [32] proposed the reason why colloid gel particles couldn't crystallize is originated from the existence of LFFS icosahedron cluster by advanced microscope. In the past fifty years ago, Frank [50] pointed out the icosahedron clusters were the essential factors to generate super-cooling state for liquidus alloy. Gibson [51] showed it was significant to develop crystallization dynamics by revealing the structure and formation course of critical nucleation for amorphous materials. Many experiments [20] indicated that the crystal clusters, such as with four- or six-fold symmetry structure, and noncrystal clusters with LFFS could coexist together in the initial nucleation stage. However, because of its internal defect of LFFS structures, it couldn't overspread geometrical space only by repeating themselves one and another. So different clusters phagocytized each other on their skin interfaces, then resulting in forming crystal or glasses founded on their stability and growth capability [17]. Simulation experiments showed Voronoi pentagon configuration holds particularity position in quenching treatment process [52]. It is found the formation rate of LFFS clusters is faster

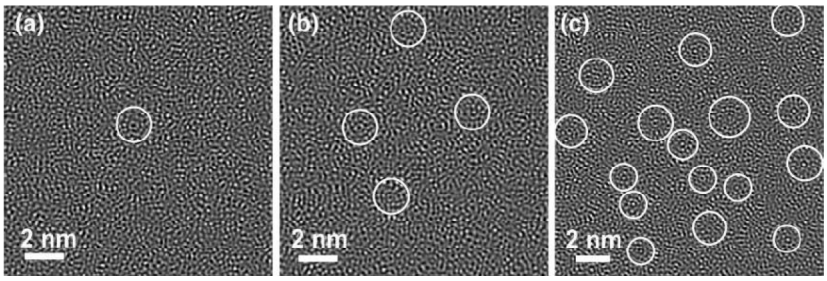

Fig. 4. The typical icosahedronlike atomic ordering in the ZrTiCuNiBe BMG after isothermally annealing [18] (Reproduced by the kind permission of American Institute of Physics).

than the crystal nucleation [6] (Fig. 3). Albeit single LFFS clusters disappeared rapidly, they could complect together to form as a network in the center of the polymer, leading to form a local particles system with higher density and lower energy. Consequently, a larger network of medium range order with LFFS formed easily, which then blocked crystallization instead of enhancing glasses appearing [14]. Then we can see the energy difference between metastable glasses structure and stable crystal structure could be deduced by amorphous materials themselves through optimizing their interaction of SRO structures. So the essence of improving GFA is to increase the existing ability of LFFS clusters.

5. LFFS CLUSTERS IN METALLIC GLASSES

Because of lacking defects (such as dislocation, twin crystal) in microstructure, metallic glasses perform low plasticity, high yield strength and low fracture toughness. Though their plasticity and toughness could be improved by adjusting component, the microscopic mechanics for these performances didn't be unveiled [52]. Based on molecular dynamics, Wang *et al.* [53] analyzed microstructure information of CuZr BMGs in the plastic deformation process. It was showed that plastic deformation of local structures came from the small degree region of LFFS in metallic glasses. Along with additional plastic deformation, regional intensity of low LFFS became much dense then the local plastic strain extended to some other compact LFFS region, such process leading to brittleness fracture. In view of omnipresent existence of LFFS structure in vitreous materials, Liu *et al.* [54] proposed a new way to produce crystal particles, such as twin crystal or nano crystal, and improve the plasticity of BMG by reducing LFFS structural density to enhance the rate of crystal clusters through several special heat treatment technologies.

As monotonous symmetry clusters were unusual in BMG, experimental results from XRD, HRTEM and neutron diffraction analysis showed that because of large packed density and low thermodynamics energy, the isocaheron clusters were ubiquitous in liquid metal and BMG. For examples, in Al-Cu-Ni-Zr alloy [55], the primary crystal was fcc-NiZr2 structure, but there also emerged Ni4Zr9 icosahedron clusters. Otherwise there were icosahedron clusters in Laves phases of the cubic structure of AlNiZr(Cu2Mg) alloy and hexagon structure of Al2Zr(MgZn2) alloy. Wang *et al.* [18] probed the crystallized technology of BMG in several annealing processes by HRTEM and MD method (Fig.4). The results revealed that icosahedron clusters and crystal clusters were coexisting and there was a clear interface between them when the annealing temperature was low; following with additional temperature, the density of nanocrystal particles and icosahedron particles were increasing, which exhibited a wonderful growth competition to form crystal or BMG. Hwang *et al.* [56] also elaborated that the crystal clusters with four- or six-fold symmetry and noncrystal clusters with LFFS could be found in the slow cooling process of CuZrAl liquid metal.

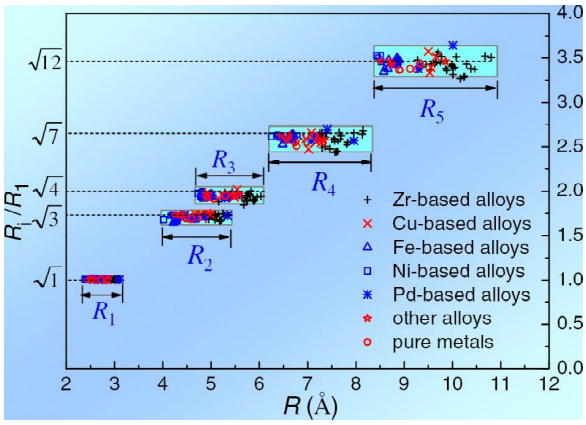

Fig. 5. Ratio of peak positions normalized to the first peak Ri/R1 for 64 MGs [22] (Reproduced by the kind permission of American Institute of Physics).

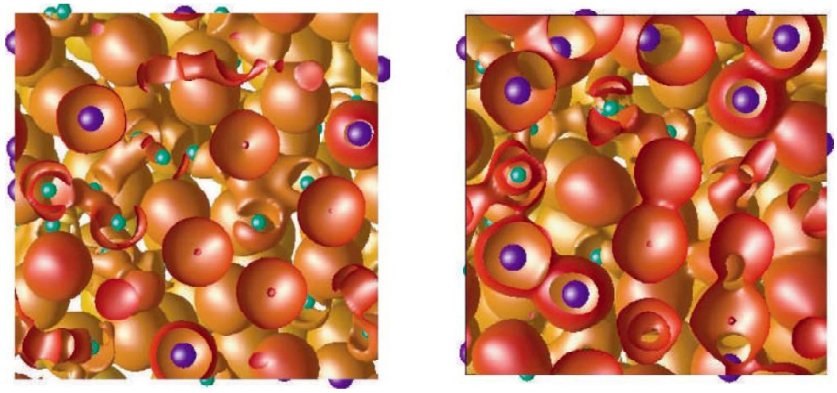

Fig. 6. The strong bonding between Ce-Ce is apparent in the *f*-electron delocalized glass by LDA calculation [23] (Reproduced by the kind permission of Nature Publishing Group).

However, owing to small nucleation ratio of icosahedron clusters, the interfaces between crystal/noncrystal clusters disappeared slowly in annealing treatment, as a result to form crystal materials. Jiang et al. [24] studied the transformation mechanism of crystal state from the amorphous structure of Ce75Al25 by imposing external superpressure. The results showed there appeared surprising long-rang FCC topological order structure in Ce75Al25 BMG, then deducing the LFFS clusters could be forced to translate into crystal if the atomic movement was small and the chemical explanation of such phenomenas may be through the localization of *f* orbit electrons of Cerium element [23]. Liu *et al.* [22] (Fig. 5)compared the structural symmetry distribution of 64 BMGs and found the structural symmetry transforming degree of translational symmetry from spherical-periodic symmetry as LFFS was increasing along with the solidification of liquid metal into solid BMG. So probing LFFS can help bring forward creative thoughts and explore methods to manufacture new materials.

6. SIMULATINO STUDY OF LFFS CLUSTER

Presently, perfecting noncrystal solidification theory need to supervise and track the supercooled solidification process of liquid metal. However, it is impossible to reproduce the detailed microstructures in nonequilibrium solidification process in present experimental techniques. So many problems, *i.e.* what is the evolution of microstructures of BMG, the formation process of SRO structures, the transformation between SRO and MRO clusters and the baffling mechanism of crystallization by local clusters, are not explained distinguishingly for us. Then theory simulation experiments are the only way to scrutinize the solidification process of liquid metal. At present, the main method is molecular dynamics(MD) simulation. By setting some characteristic atomic distance [57], it seems accurate to forecast the structural character of BMG by MD simulation. But how and what does the growth process of BMG? How to design BMG by adjusting its component? All of these are not answered by MD.

Whereas it becomes more and more complicated in researching microstructure of BMG: (1) although it could similarly exhibit and predict the mechanical performance of BMG by "solute-centred quasi-equivalent cluster" model [6] , many BMGs are ternary or multicomponent solid alloy [58], so it is hard to distinguish which constitute is solvent or solute [59]; (2) the experimental measurement can only give 2D microstructure picture, where the 3D figuration information of atomic aggregation is difficult to exhibit by reverse Monte-Carlo method for multicomponenet BMG [5]; (3) at present, atomic information of BMG is ubiquitous described by statistic method, however it is not accurate. Though Wang *et al.* [1] showed the elastic modulus of BMG is linear relationship with that of its solvent component by comparing 13 kinds of amorphous materials, and Inoue *et al.* [8] put forward three rules to design BMG; Dong *et al.* [60] established 'e/a-variant criterion' to schematize BMG, who first quantize to constitute the component of vitreous solid; the mathematics models of BMG have been explored as Bernal's dense random packing model [4], Geskel's short-range ordered model [5].Li *et al.* [61-63] had studied the transition state of clusters in growth evolution of crystal to or from noncrystal nucleation by first principle calculation or in simulating the rapid solidification process of liquid metal by MD method. Several parameters, such as electronic structure, thermal dynamics situation and

bonding state and so on, had been utilized to characterize and analyze the stability, the formation and growth capability of clusters. The results showed that it was difficult for non-crystal configurations with LFFS to be synthesized by means of crystal clusters, but the reverse process may be easy happened. Till then the microstructure of BMG seems to be more and more distinct. But the reason why there is largely different GFA of BMG in homologous elements only with little change of component content is still undiscovered [9-11].

7. CHEMICAL EFFECT OF LFFS CLUSTERS

Currently, it is impossible to explain why "there is largely different GFA of BMG in homologous elements only with little change of component" only by atomic configuration difference [11]. Some papers reported that the supercooled velocity of Zr-BMG would decrease sharply with minim addition of Al impurity [64]. The geometric microstructure of such amorphous metal showed the polygon clusters with LFFS which centered around Cu atom could be increased by addition of Al element about 7% percent, resulting in identifying local clusters polymers, decreasing thermal energy and enhancing their stability [65]. Furthermore the electronic structure researches showed the Al-Cu bond would be shortened because of *sp* hybridization, and the Cu and Zr atoms around Al element increased slowly then to drive chemical and topological effect, so the GFA of Cu46Zr47Al7 alloy improved obviously by addition little aluminum compared to Cu46Zr54 BMG [65]. A research of the calculated electronic structures demonstrated the strong chemical affinity between the transitional metal (TM) and metalloid, resulting from the partial covalent nature of the bonding that was still mostly non-directional. In the TM–TM glasses, it often unveiled non-additive pair interaction, originating from the charge transfer and screening of *d* electrons. Chemical SRO was well known in these transitional metal BMG systems, and was usually one of the prerequisites for the easy formation of BMGs [6]. Researching on CeAl BMG, Sheng *et al.* [23,24] pointed out such glasses could be forced to translate into another dense crystal [24] or noncrystal [23] materials due to their *f* orbital electrons localized (Fig. 6), bond distance shortened and the difference of volume and electronegativity for Ce and Al elements. Whereas the structural alloying effect is originated from topological or chemical difference is still unknown. Some experience rules revealed several uncertain relationship between the physical property and GFA of BMG, but only few rules have implication to forecast GFA[66]. So it is a challenge to design and predict GFA only by its component information.

8. CHALLENGES

Recently, studying the electronic structure and illuminating the relationship between component and microstructure of BMG is an innovation way to improve GFA and design new BMGs. Secondly, it needs to elucidate the intrinsical performance of LFFS clusters in different situations, such as vacuum, surface or interface of solid, so as to produce much stable super icosahedron clusters and super materials comprised by super atom. Thirdly, to liquid metal, the internal mechanism of probing how clusters conjoined as network to form dense vitreous materials is to decipher the netting ability of different symmetry clusters. Fourthly, if we want to solve the puzzle of designing excellent clusters, metallic glasses and nanocrystal only by theory method, the competition on the interface of noncrystal/crystal nucleastion may be the key point to be cared about. Fifthly, the way to obtain BMG and super atom is to research the chemical effect between local atomic structures and component. By virtue of simulating electronic, energy and translational microstructure, it can establish some stable rules among local atomic structure, component and GFA in devising BMG.

ACKNOWLEDGEMENTS

We would like to thank our anonymous reviewers for extremely helpful comments. We acknowledge the support from the National Natural Science Foundation of China (Grant No. 51071065), Natural Science Foundation of Jiangxi Province (20132BAB216012)

REFERENCES

[1] W.H.Wang // *Nature Mater.* **11** (2012) 275.
[2] Y.Li, Q.Guo, J.A.Kalb and C.V.Thompson // *Science* **322** (2008) 1816.
[3] X.J.Liu, Y.Xu, Z.P.Lu, X.Hui, G.L.Chen, G.P.Zheng and C.T.Liu // *Acta Mater*. **59** (2011) 6480.
[4] J.D.Berna // *Nature* **185** (1960) 68.
[5] P.H.Gaskell // *Nature* **276** (1978) 484.
[6] H.W.Sheng, W.K.Luo, F.M.Alamgir, J.M.Bai and E.Ma // *Nature* **439** (2006) 419.

[7] Y.Q.Cheng and E.Ma // *Progress in Mater. Sci.* **56** (2011) 379.
[8] A.Inoue // *Acta Mater.* **48** (2000) 279.
[9] Y.Q.Cheng, H.W.Sheng and E.Ma // *Phys.Rev.B* **78** (2008) 014207.
[10] D.H.Xu, G.Duan and W.L.Johnson // *Phys.Rev.Lett*. **92** (2004) 245504.
[11] A.L.Geer and E.Ma // *MRS Bull*. **32** (2007) 611.
[12] C.P.Royall, S.R.Williams, T.Ohtsuka and H.Tanaka // *Nature Mater*. **7** (2008) 556.
[13] A.Hirata, P.F.Guan, T.Fujita, Y.Hirotsu, A.Inoue, A.R.Yavari, T.Sakurai and M.W.Chen // *Nature Mater*. **10** (2011) 28.
[14] A.R.Yavari // *Nature* **439** (2006) 405.
[15] J.Ding, Y.Q.Cheng, H.W.Sheng and E.Ma // *Phys.Rev.B* **85** (2012) 060201.
[16] L.Huang, C.Z.Wang, S.G.Hao, M.J.Kramer and K.M.Ho // *Phys.Rev.B* **81** (2010) 014108.
[17] H.L.Peng, M.Z.Li, W.H.Wang, C.Z.Wang and K.M.Ho // *Appl.Phys.Lett*. **96** (2010) 021901.
[18] Q.Wang, C.T.Liu, Y.Yang, Y.D.Dong and J.Lu // *Phys.Rev.Lett*. **106** (2011) 215505.
[19] D.Ma, A.D.Stoica, X.L.Wang, Z.P.Lu, M.Xu and M.Kramer // *Phys Rev B* **80** (2009) 014202.
[20] W.H.Wang, Q.Wei and S.Friedrich // *Phys.Rev.B* **57** (1998) 8211.
[21] L.Yang, G.Q.Guo, L.Y.Chen, S.H.Wei, J.Z.Jiang and X.D.Wang // *Scripta Mater*. **63** (2010) 879.
[22] X.J.Liu, Y.Xu, X.Hui, Z.P.Lu, F.Li, G.L.Chen, J.Lu and C.T.Liu // *Phys.Rev.Lett*. **105** (2010) 155501.
[23] H.W.Sheng, H.Z.Liu, Y.Q.Cheng, J.Wen, P.L.Lee, W.K.Luo, S.D.Shastri and E.Ma // *Nature Mater*. **6** (2007) 192.
[24] Q.S.Zeng, H.W.Sheng, Y.Ding, L.Wang, W.G.Yang, J.Z.Jiang, W.L.Mao and H.K.Mao // *Science* **332** (2011) 1404.
[25] H.J.Wang, X.J.Gu, S.J.Poon and G.J.Shiflet // *Phys.Rev.B* **77** (2008) 014204.
[26] H.L.Peng, M.Z.Li and W.H.Wang // *Phys.Rev.Lett*. **106** (2011) 135503.
[27] S.Pauly, S.Gorantla, G.Wang, U.Kuhn and J.Eckert // *Nature Mater.* **9** (2010) 473.
[28] Y.Q.Cheng, A.J.Cao, H.W.Sheng and E.Ma // *Acta Mater*. **56** (2008) 5263.
[29] H.Shintani and H.Tanaka // *Nature Mater.* **7** (2008) 870.
[30] X.D.Hui, X.J.Liu, R.Gao, H.Y.Hou, H.Z.Fang, Z.K.Liu and G.L.Chen // *Science in China Series G* **51** (2008) 400.
[31] U.Agarwal and A.E.Fernando // *Nature Mater.* **10** (2011) 230.
[32] M.E.Launey and R.O.Ritchie // *Adv.Mater.* **21** (2009) 2103.
[33] X.K.Xi, D.Q.Zhao, M.X.Pan, W.H.Wang and J.J.Lewandowski // *Phys.Rev.Lett*. **94** (2005) 125510.
[34] A.Inoue // *Nature Mater*. **2** (2003) 661.
[35] M.Turner, V.B.Golovko, O.P.Vaughan, P.Abdulkin, M.A.Berenguer, M.S.Tikhov, B.F.Johnson and R.M.Lambert // *Nature* **454** (2008) 981.
[36] M.Valden, X.Lai and D.W.Goodman // *Science* **281** (1998) 1647.
[37] D.E.Bergeron, A.W.Castleman, T.Morisato and S.N.Khanna // *Science* **304** (2004) 84.
[38] M.D.Hughes, Y.J.Xu P.Jenkins, P.Mcmorn, P.Landon, D.I.Enache, A.F.Carley, G.A.Attard, G.J.Hutchings, F.King, E.H.Stitt, P.Johnston, K.Griffin and C.J.Kiely // *Nature* **437** (2005) 1132.
[39] R.Taylor and R.M.Walton // *Nature* **363** (1993) 685.
[40] S.F.Li and X.G.Gong // *Phys.Rev.B* **70** (2004) 075404.
[41] D.E.Bergeron and A.W.Castleman // *Chem. Phys. Lett.* **371** (2003) 189.
[42] C.D.Dong and X.G.Gong // *J.Chem.Phys.* **132** (2010) 104301.
[43] D.E.Bergeron, P.J.Roach, A.W.Castleman, N.O.Jones and S.N.Khanna // *Science* **307** (2005) 231.
[44] X G.Gong // *Phys. Rev. B* **56** (1997) 1091.
[45] S.N.Khanna and P.Jena // *Phys. Rev. Lett.* **69** (1992) 1664.
[46] J.Z.Pang, G.H.Wang, L.Dou and C.D.Gong // *Phys. Lett. A* **117** (1986) 115.
[47] L.Smekal, M.Ghiotti and A.G.Williams // *Phys. Rev. B* **78** (2008) 085016.
[48] H.Q.Zhang, M.Han, Q.Wang and G.H.Wang // *Surf. Rev. Lett.* **3** (1996) 1195.
[49] C.G.Tang and P.Harrowell // *Nature materials* **12** (2013) 507.
[50] F.C.Frank // *Proc.R.Soc.Lond.A* **215** (1952) 43.
[51] J.M.Gibson // *Science* **13** (2009) 942.
[52] M.Wakeda, Y.Shibutani, S.Ogata and J.Y.Park // *Intermetallics* **15** (2007) 139.
[53] W.H.Wang, C.Dong and C.H.Shek // *Mater.Sci.Eng.R* **44** (2004) 45.
[54] X.J.Liu, G.L.Chen, F.Li, X.D.Hui, Z.P.Lu, F.Ye and C.T.Liu // *Intermetallics* **18** (2010) 2333.

[55] U.Koster, D.Zander and R.Janlewing // *Mater.Sci.Forum* **386-388** (2002) 89.
[56] J.Hwang, Z.H.Melgarejo, Y.E.Kalay, I.Kalay, M.J.Kramer, D.S.Stone and P.M.Voyles // *Phys.Rev.Lett.* **108** (2012) 195505.
[57] G.L.Chen, X.J.Liu, X.D.Hui, H.Y.Hou, K.F.Yao, C.T.Liu and J.Wadsworth // *Appl.Phys.Lett*. **88** (2006) 203115.
[58] A.L.Greer and E.Ma // *MRS Bull* **32** (2007) 611.
[59] Z.W.Zhu, H.F.Zhang, W.S.Sun, B.Z.Ding and Z.Q.Hu // *Scripta Mater.* **54** (2006) 1145.
[60] X.Cheng, Q.Wang, W.R.Chen and C.Dong // *Science in China Series G* **51** (2008) 421.
[61] P.Peng, G.F.Li, C.X.Zheng, S.C.Han and R.S.Liu // *Science in China Series E* **49** (2006) 385.
[62] G.F.Li, P.Peng, D.W.Zhou and S.C.Han // *Comput. Mater. Sci.* **47** (2009) 302.
[63] P.Peng, G.F.Li, Z.A.Tian, K.J.Dong and R.S.Liu // *Comput. Mater. Sci.* **44** (2009) 881.
[64] P.Yu, H.Y.Bai, M.B.Tang and W.L.Wang // *J.Noncryst.Solids* **351** (2005) 1328.
[65] X.K.Xi, L.L.Li, B.Zhang, W.H.Wang and Y.Wu // *Phys.Rev.Lett.* **99** (2007) 095501.
[66] Z.P.Lu and C.T.Liu // *Mater.Trans*. **48** (2007) 2476.