Vol 18 No 11, November 2009
1674-1056/2009/18(11)/4949-06

Chinese Physics B

© 2009 Chin. Phys. Soc.
and IOP Publishing Ltd

Reverse Monte Carlo study on structural order in liquid and glassy AlFe alloys*

Zhang Jing-Xiang(张景祥)[a)b)†], Li Hui(李 辉)[a)], Zhang Jie(张 洁)[a)], Song Xi-Gui(宋西贵)[a)], and Bian Xiu-Fang(边秀房)[a)]

[a)] *Key Lab of Liquid Structure and Heredity of Materials, Ministry of Education, School of Materials Science and Engineering, Shandong University, Jinan* 250061, *China*

[b)] *School of Information Science and Engineering, University of Jinan, Jinan* 250022, *China*

(Received 15 December 2008; revised manuscript received 6 March 2009)

This paper reports that anomalous local order in liquid and glassy AlFeCe alloy has been detected by x-ray diffraction measurements. The addition of the element Ce has a great effect on this local structural order. The element Ce favours interpenetration of the icosahedra by sharing a common face and edges. It argues that frustration between this short-range order and the long-range crystalline order controls the glass-forming ability of these liquids. The obtained results suggest that a system having a stronger tendency to show local icosahedral order should be a better glass-former. This scenario also naturally explains the close relationship between the local icosahedral order in a liquid, glass-forming ability, and the nucleation barrier. Such topological local order has also been analysed directly using the reverse Monte Carlo method. It also estimated the fraction of local ordered and disordered structural units in a glassy AlFeCe alloy.

Keywords: reverse Monte Carlo, x-ray diffraction (XRD), liquid metal, metallic glass
PACC: 6125M, 7215C

1. Introduction

The nature of the short-range structure of metallic liquids and glasses is a long-standing problem,[1−4] but is much less well understood than long-range crystalline order. Frank[5] first suggested that large supercooled liquids might be due to local icosahedral order in the liquid phase. He justified this suggestion by pointing out that for a 13-atom Lennard–Jones cluster, the icosahedron was significantly lower in energy than the fcc cuboctahedron.[5] Direct experimental proof of five-fold symmetric structures in bulk undercooled melt has been reported.[6] Recently, Liu *et al* [4] reported an icosahedral short-range order (ISRO) in pure supercooled liquid transition metals using an electromagnetic levitation technique. However, since the measured structure factor is an angular averaged quantity, most experimental evidence is limited to the pair correlation function (PCF). It is rather difficult to directly image the ISRO in supercooled liquid and glass by experimental methods. Several molecular dynamics simulations have been applied to study the ISRO.[7,8] However, the information on the ISRO obtained by computer simulation has relied heavily on empirical potentials.[9] Despite numerous experimental and theoretical attempts to investigate the ISRO in liquid and glass, no satisfactory understanding has been reached.

For several decades, AlFe alloys have attracted the interest of many researchers.[10,11] Most of this interest is motivated by the glass-forming ability of those materials.[12,13] Unfortunately, the identification between the bonding type and the structure of liquid and amorphous AlFe alloy is not clear, as only a statistical average of the structure via neutron or x-ray measurement exists.[14] The structural characteristics of liquid-quenched amorphous AlFe alloys lead to a number of remarkable mechanical, magnetic and corrosion properties.[15] These alloys have high strength, high ductility, low density and high resistance to corrosion. A fundamental understanding of the atomic

*Project supported partially by the National Natural Science Foundation of China (Grant Nos 50831003 and 50871062), New Century Excellent Talent Program of Ministry of Education of China (Grant No NCET-05-0599), the National Basic Research Program of China (Grant No 2007CB613901), the National Science Foundation for Distinguished Young Scholars of China (Grant No 50625101), the Scientific Research Foundation for Returned Overseas Chinese Scholars, Ministry of Education of China (Grant No JIAO WAI SI LIU2007–1108) and the National Science Foundation for Distinguished Young Scholars of Shandong Province, China (Grant No JQ200817).

†Corresponding author. E-mail: zhangjxedu@163.com

structure and electronic nature of these alloys is essential to explore the origin of their properties.[14] Glass is one of the most common materials, but its physics and especially its dynamics are still poorly understood. Recently, local atomic structural order in liquid and glass has attracted considerable attention since it is believed that the local structure has a strong influence on the nucleation mechanism.[16] However, few efforts have focused on the relationship between local order and glass-forming ability. In this paper, we present x-ray diffraction (XRD) data from liquid and glassy AlFe and AlFeCe alloys. The results exhibit an anomalous local order developed in liquid AlFeCe alloy as temperature decreases. To further explain the experimental data, the ISRO is obtained directly by reverse Monte Carlo (RMC) simulation. The influence of the element Ce on the local order and glass-forming ability is also discussed in this paper.

2. Experimental method and RMC details

Ingots of $Al_{90}Fe_{10}$ and $Al_{90}Fe_5Ce_5$ (both in atomic percentage) were prepared by melting of high purity constituents (Al 99.999 wt% and Fe 99.9 wt%) in a Al_2O_3 crucible under argon atmosphere. Measurements were performed at constant temperatures of 1818, 1718, 1578, 1448 and 1338 K with an accuracy of ± 5 K. The liquid and amorphous alloys were investigated with a high-temperature x-ray diffractometer made in Ukraine (model DPAZHM). The scattering experiment was performed on a diffractometer equipped with Mo Kα radiation and a bent graphite monochromator. The intensity measurements were carried out by the $\theta - \theta$ step scanning method in an angular range of $5^\circ \leq 2\theta \leq 90^\circ$, which corresponds to a Q range of $7.7 \leq Q \leq 125$ nm^{-1}. The scattering intensity measured in arbitrary units can be converted into the coherent scattering intensity per atom in electron units, using the generalized Krogh–Moe–Norman method[17] with an atomic scattering factor including an anomalous dispersion factor. Compton scattering was also adjusted by using the values given by Cromer and Mann. The total structure factor $S(Q)$ was then obtained through the scattering intensity, where $Q = (4\pi/\lambda)\sin\theta$ is the magnitude of the scattering vector, and λ is the wavelength.

Amorphous ribbons were prepared by a single roller melt-spinning technique under a partial argon atmosphere. The diameter of the copper roller was 35 cm with a typical circumferential velocity of 40 m/s. The ribbons were about 2 mm in width and 25 μm in thickness. The alloys were melted in an arc furnace and spouted at temperatures of 1338, 1400, 1600 and 1700 K respectively.

A successful method for quantitative analysis of highly disordered structures is RMC refinement,[18] which can be applied simultaneously to diffraction data, allowing the construction of a 3-dimensional model of disordered systems. The cubic atomic configurations of amorphous AlFe and AlFeCe were therefore constructed by using RMC simulations of XRD spectrums. The advantage of this method is that by way of statistical matching between theoretical and experimental spectra under constraints, it can calculate atomic positions directly from experimental data without any hypothetical structural model. As a result, it avoids the traditional structural search by trial and error, where the features observed in PCFs or structure factors out of scattering data are compared with model predictions based on assumed packing geometries. With the RMC, the information drawn from the experiments can be expanded from one to three dimensions. In this paper, a random atomic configuration in a cubic box of 500 atoms was constructed for AlFeCe and AlFe with periodic boundary conditions. The scale of the simulation box was determined by the XRD and the closest distance between the atoms was based on the PCFs. The structure was iteratively improved by reducing the normalized fit residua between the simulated and experimental spectra. The RMC simulation is implemented by using the Metropolis algorithm.

3. Results and discussion

In Fig.1, shoulder peaks of PCF curves can be observed at $r = 3.5$ Å (1 Å=0.1 nm) (shown by an arrow), a signature of polytetrahedra in closepacked structures. This provides evidence for abnormal ordered structural characteristics of liquids. It is noticeable that when the liquid possesses a stronger medium range concentration fluctuation, the main peak in the PCF is almost symmetric in the liquid AlFe alloy (as shown in Fig.2). But when 5 at% Fe is substituted by Ce, the case is remarkably different. The PCF assumes asymmetric form with a right-hand shoulder in the liquid AlFeCe at low temperatures (as shown in Fig.1). The clear development of a shoulder on the right side of the main peak is observed in these x-ray

studies as temperature decreases. It is often assumed that local structures in liquids can be described by tightly bound, noninteracting and close-packed clusters. The presence of a shoulder on the right side of the main peak is generally indicative of anomalous local structural order in the liquid. As temperature decreases, the shoulder becomes more distinct. This demonstrates that the local order in the liquid becomes better defined and more pronounced at lower temperature. That confirms the predictions made by Steinhardt and Nelson.[19] This shoulder is a consequence of local icosahedral order. In contrast, no shoulder peak is observed in the PCF of the liquid AlFe alloy (shown in Fig.2). The results show that the local atomic structures in the liquid AlFe alloy are not the same as those in the liquid AlFeCe alloy. We suggest that the shoulder is due to the existence of double icosahedra and double defective icosahedra.[11,20] The difference of the PCF between liquid AlFe and AlFeCe alloys shows further that the addition of Ce results in the shoulder. The addition of Ce can improve the interaction between atoms and help the formation of icosahedral structures. We suggest that this feature should be more pronounced for a supercooled liquid. In order to clarify the origin of the shoulder peak, RMC simulation has been done to obtain the local atomic structures in liquid AlFe and AlFeCe alloys. A lot of transition-metal-aluminium (TM-Al) alloys usually exhibit at least some degree of medium-range order (MRO). Experiments of small-angle scattering have revealed that the structure of liquids is not entirely homogeneous but contains structural fluctuations, sometimes even on different length scales.[19] Interaction potential gives rise to such a network structure which manifests the presence of the MRO.

A comparison between RMC simulations and experimental spectra is shown in Figs.1 and 2. A good match of the PCFs was achieved between the results from experimental x-ray data and the RMC configuration. Therefore, the RMC liquid configuration reproduced the correct XRD experiments and also the proper clusters, which serve as dominant building blocks for the liquid structure. This means that RMC is capable of providing information about the geometrical arrangement of the XRD. The RMC curve reproduces almost exactly the overall shape of the PCFs and also the shoulder peak. The short-range shape of the PCF by RMC is accurately reconstructed due to the unique sensitivity of the x-ray signal.

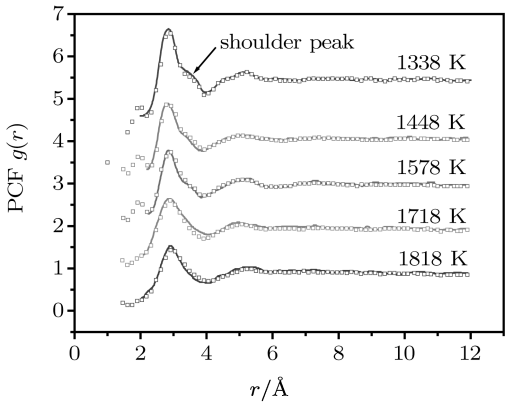


Fig.1. Shoulder peaks (indicated by an arrow) on pair correlation functions (PCFs) of liquid AlFeCe alloy (square symbols for experimental results and solid lines for RMC simulations).

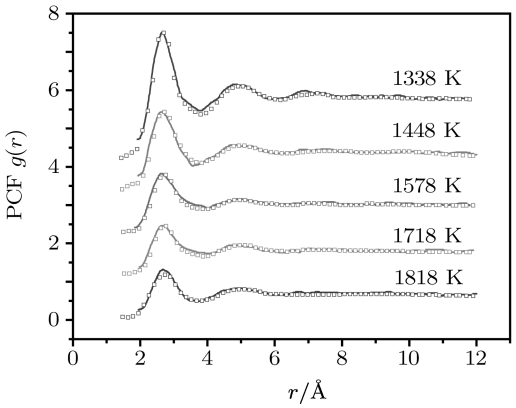


Fig.2. PCFs for experimental and RMC simulations of liquid AlFe alloy (square symbols for experimental results and solid lines for RMC simulations).

To analyse the structural changes of liquid and glass we adopt a common technique used by Anderson and co-workers.[21] In this scheme, two atoms are said to be near neighbours if they are within a specified cutoff distance of each other. Honeycutt and Andersen used four integers *ijkl* to characterize clusters in a liquid system. The first integer, either 1 or 2, indicates the diagram type, that is, whether or not the atoms composing the root pair are near neighbours. The second integer represents the number of near neighbours shared by the root pair. The third integer denotes the number of bonds between the shared neighbours. A fourth integer, whose value is arbitrary as long as it is used consistently, is added to provide a unique correspondence between the number and the diagram. Each of the various phases of a dense bulk system has its own signature in the diagrams that characterize its local structures. The 1421 and 1422 pairs are less abundant in a random close-packed glass system. The 1551 and 1541 pairs, which are not present

in perfect fcc or hcp crystals, are relatively numerous in supercooled liquid and glasses. Mackay icosahedra contain some 1551 pairs, not present in either fcc or hcp crystals. A large Mackay icosahedron is, however, composed of twinned and distorted fcc tetrahedra. Types of pairs not found in fcc systems can appear only where these tetrahedra meet together. In fact, the 1551 cluster is a decahedron. It is necessary to point out that the 1551 and 1541 clusters are used to directly measure the icosahedral order in the liquid. The 1421 cluster is a typical pair of an fcc crystal. The 1661 and 1441 clusters are characteristic pairs of a bcc crystal. The 1421 and 1422 clusters are related to the hcp crystal. The 1201 and 1311 clusters represent the rhombus symmetrical features of the short-range position order. Scatter plots of these indices for liquid AlFe and AlFeCe are shown in Fig.3. The plots clearly show that liquid AlFeCe has a larger proportion of polytetrahedral pairs and fewer close-packed environments. The short-range order of the liquid state is dominated by icosahedral and distorted icosahedral inherent structures since the 1551 bonded pairs are preponderant. However, although the 1551 pairs are relatively numerous, the absence of the 1661 and 1441 is a strong indication that the liquid is characterized by a short-range order which is more complex than what is found in the 13-atom icosahedron. The 1441 and 1661 pairs are also of importance; when associated with the 1551 bond pairs, they are in favour of Frank–Kasper (FK) polyhedra of high coordination, namely, Z14, Z15 and Z16.[22] As temperature decreases, the competition between five-fold structures and crystalline units becomes prominent and will eventually control the final evolution of the system. If the five-fold structural units dominate, the system will become amorphous and quasicrystal. Nelson[23] has shown that disclination lines should be introduced in the transformation of regular polytetrahedral packing from curved to Euclidean space. If these disclination lines are arrayed periodically one obtains crystalline structures called (FK) phases.[24] If the disclination lines have a disordered arrangement it has been suggested that one obtains structures typical of liquids and glasses. The disclination lines are associated with 1441 and 1661 bond pairs. The 1441 bond pairs are the four-fold symmetrical structure and the 1661 bond the six-fold structure. FK phases are sometimes referred to as tetrahedrally close-packed for their polytetrahedral nature is closely related to many icosahedral quasicrystals.[25] The Honeycutt–Anderson index gives us an opportunity to precisely define icosahedra, FK, Bernal, and other defective icosahedra in a very simple way. For convenience, Qi and Wang[26] use a signature to represent those defective icosahedra. 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 neighbouring 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. In the same way, other polyhedra can be defined. On the basis of the work of Qi and Wang, Liu *et al* [27] developed a new cluster-type index method, which was used to characterize complex cluster structures. Figure 4 shows the numbers of different kinds of polyhedra in the inherent structures as a function of temperature. As for liquid AlFeCe alloy, icosahedra and double icosahedra show significant changes as temperature varies. We therefore conclude that icosahedral structures are predominant in liquid systems. The structural transition temperature is identical to the temperature where the shoulder peak forms (see Fig.1). A polyhedron consisting of some 1551, 1661 and/or 1441 clusters is called a defective icosahedron. As shown in Fig.4 some defective icosahedra are also found in our system. About 12 icosahedra were detected in the sample of 500 atoms. That gives a percentage of 15% in atomic number. 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 a macroscopic system. All icosahedra and defective icosahedra interpenetrate and share faces and vertexes with other icosahedron and defective icosahedron to construct double icosahedra and double defective icosahedra. Table 1 gives the number of various polyhedra and defective polyhedra at 1338 K. We suggest that the double icosahedra and double defective icosahedra are the origin of the shoulder. Interestingly, the polyhedra in liquid AlFe are much fewer than those in the liquid AlFeCe alloy. Because fewer icosahedra exist in the liquid AlFe alloy, the shoulder on the right side of the main peak shrinks and is then not observed on the PCF curve of the liquid AlFe alloy.

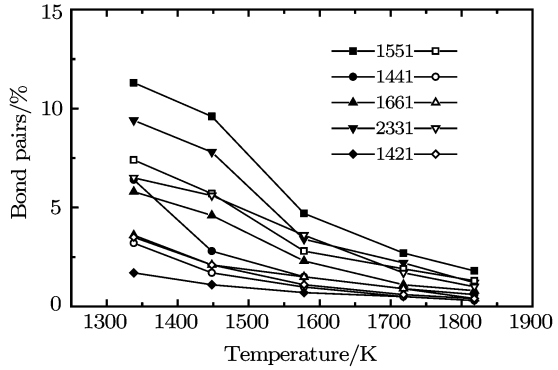


Fig.3. Density numbers of bonded pairs in liquid AlFe and AlFeCe calculated from the RMC configurations of liquid AlFe and AlFeCe alloys (solid symbols for AlFeCe and open symbols for AlFe).

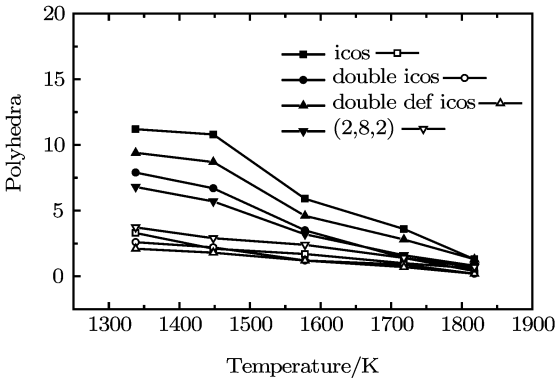


Fig.4. Various defective icosahedra and perfect icosahedra at different temperatures (solid symbols for AlFeCe and open symbols for AlFe).

Table 1. The number of various polyhedra at 1338 K.

signature	coordination number	polyhedra number
(2,8,2)	12	11.2
(0,12,0)	12	31
(2,8,1)	11	9.6
(2,8,4)	14	7.8
(1,10,2)	13	6.4
(3,6,4)	13	3.5
(1,10,4)	15	5.4
(0,12,2)	14	3.8
(0,12,3)	15	4.4
(2,8,5)	15	3.2
(1,10,3)	14	3.4
(1,10,5)	16	2.1
(2,8,0)	10	1.7
(2,8,3)	13	1.3
(3,6,5)	14	1.1
(2,8,7)	17	1.5
(4,4,6)	14	1.5
(3,6,3)	12	1.5
(2,8,6)	16	1.7

Why is the glass-forming ability of liquid AlFeCe alloy much better than that of liquid AlFe? As can be seen in Figs.1, 3 and 4, icosahedral order still exists even above liquid temperature, at least in this alloy. The geometrical structures and their compatibility are important for their nucleation. From a geometrical point of view, bcc, fcc and hcp structural units are not easy to pack around the icosahedral unit to reach a specific critical size of the nucleus. This incompatibility of the icosahedra with the bcc, fcc and hcp structural units will lead to a barrier for nucleation. In fact, the inherent structure of liquid AlFeCe at low temperatures is one with icosahedral structural units.[28] This structure favours the formation of quasicrystal and glass structures rather than crystalline structures.

Enhanced ISRO would cause viscosity to increase with decreasing temperature and make a liquid less fragile. A liquid with stronger ISRO would suffer from a stronger frustration effect. Thus, the distance of cooperativity among clusters would increase with increasing ISRO. Positive correlation among the ISRO has been confirmed by our results. Enhanced ISRO results in a better glass-forming ability and makes the liquid stronger. As long as the primary crystallization of the supercooled liquid belongs to the formation of intermetallic crystals, local icosahedral structures will act as random fields against the crystallization. The formation of local icosahedral structures reduces the Gibbs free-energy difference between supercooled liquid and crystal and also increases the interface tension, which makes crystallization difficult.[29] For a deeper supercooled liquid, on the other hand, local structures of the liquid with shoulder peaks are more similar to those of a quasicrystal.[30,31] The symmetry of local icosahedral structures is consistent with that of a quasicrystal. Thus quasicrystal formation is easier there.[29,30] If the tendency to icosahedral chemical order is strong, a liquid may become stable against crystallization, which leads to a better glass-forming ability. As for the relationship between glass and quasicrystal formation, it is worth mentioning a newly emerging paradigm for quasicrystal. Quasicrystal is a state of close packing of single locally favoured structures. Quasicrystal order is a kind of unconventional positional and orientational order of locally favoured structures which allow overlapping with each other. Here, quasicrystal is regarded as a state that maximizes icosahedral chemical order or hierarchical order of the locally favoured structures.[30] We suggest that

local icosahedral chemical order in a liquid is a prerequisite for quasicrystal order.

Now, a new question is put forward: can the shoulder peak of the PCF which appeared in liquid AlFeCe be observed in glassy AlFeCe alloy? Figure 5 shows the results for the experimental PCF of glassy AlFeCe ribbons. The obvious splitting of the second peak is noticed in the PCF, indicating the existence of the glassy units in the system.[32] The splitting second peaks of the PCF, a common feature of supercooled liquids and glasses, have also been shown to be a consequence of polytetrahedral order.[33] Even more dramatically, on the right-hand side of the main peak in the PCF, we also found a shoulder peak around $r = 0.31$ nm. Interestingly, with decreasing temperature, the height of the shoulder peak increases. The shoulder peak is very similar to the ones seen in liquid AlFeCe alloy in Fig.2. This result further confirms our hypothesis that liquid AlFeCe possesses an abnormal structural order, and this abnormal structural order can exist in its glassy states. All FK polyhedra and a number of defective icosahedra are detected and counted based on the configurations obtained by RMC simulations as shown in Table 1. In the glassy AlFeCe alloy system, a perfect icosahedron is observed. The cluster (0,12,2) is a kind of FK polyhedra whose structure is very close to the perfect icosahedron.[33] It is also found in glassy AlFeCe alloy. In this paper, defective icosahedra (2,8,1) and (2,8,2) have also been detected respectively. Glass is composed of both perfect icosahedra and defective icosahedra. This result coincides with the above analysis on bond pairs.

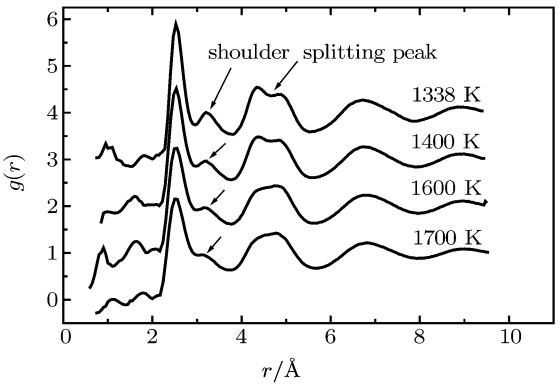


Fig.5. Shoulder peaks appearing in experimental pair correlation functions of glassy AlFeCe ribbons at different pouring temperatures.

4. Conclusions

In this paper, the origin of the shoulder peak of the PCF has been investigated by experimental and theoretical methods. An increasing ISRO in AlFeCe liquid can be manifested by shoulder peaks. Further, we suggest that liquid AlFeCe with stronger ISRO is a better glass-former than a liquid AlFe alloy. These results demonstrate that local atomic structural order is important and considerable in nucleation theories.

References

[1] Du X H and Huang J C 2008 *Chin. Phys.* B **17** 0249
[2] Wang G H, Pan H, Ke F J, Xia M F and Bai Y L 2008 *Chin. Phys.* B **17** 0259
[3] Li H and Pederiva F 2003 *Phys. Rev.* B **68** 054210
[4] Liu H R, Liu R S, Zhang A L, Hou Z Y, Wang X and Tian Z A 2007 *Chin. Phys.* **16** 3747
[5] Frank F C 1952 *Proc. R. Soc.* A **215** 43
[6] Reichert H, Klein O, Dosch H, Denk M, Honkimäki V, Lippmann T and Reiter G 2000 *Nature* **408** 839
[7] Doye J P K and Wales D J 1996 *Science* **271** 484
[8] Clarke A S and Jonsson H 1993 *Phys. Rev.* E **47** 3975
[9] Cozzini S and Ronchetti M 1996 *Phys. Rev.* B **53** 12040
[10] Asta M, Ozolins V, Hoyt J J and van Schifgaarde M 2001 *Phys. Rev.* B **64** 020201
[11] Li H 2003 *Phys. Rev.* B **68** 024210
[12] Avali A, Lozovoi A Y and Finnis M W 1999 *Phys. Rev. Lett.* **83** 979
[13] Spaczer M, Caro A and Victoria M 1995 *Phys. Rev.* B **52** 7171
[14] Maret M, Pomme T, Pasturel A and Chieux P 1990 *Phys. Rev.* B **42** 1598
[15] Mansour A N, Dmitrienko A and Soldatov A V 1997 *Phys. Rev.* B **55** 15531
[16] Fayos R, Bermejo F J, Dawidowski J, Fischer H E and Gonzalez M A 1996 *Phys. Rev. Lett.* **77** 3823
[17] Elliott S R 1991 *Phys. Rev. Lett.* **67** 711
[18] McGreevy R L 2001 *J. Phys.: Condens. Matter* **13** R877
[19] Steinhardt P J and Nelson D K 1984 *Phys. Rev. Lett.* **53** 1947
[20] Salmon P S 1994 *Proc. R. Soc.* A **445** 351
[21] Honeycutt J D and Andersen H C 1987 *J. Phys. Chem.* **91** 4590
[22] Hafner J 1985 *J. Phys. Colloques* **46** C9-69
[23] Nelson D R 1983 *Phys. Rev. Lett.* **50** 982
[24] Frank F C and Kasper J S 1958 *Acta Cryst.* **11** 184
[25] Henley C L and Elser V 1986 *Phil. Mag.* B **53** L59
[26] Qi D W and Wang S 1991 *Phys. Rev.* B **44** 884
[27] Tian Z A, Liu R S, Zheng C X Liu H R, Hou Z Y and Peng P 2008 *J. Phys. Chem.* A **112** 12326
[28] Zhang L, Wu Y S, Bian X F, Li H, Wang W M, Li J G and Lun N 1999 *J. Phys.: Condens. Matter* **11** 7959
[29] Tanaka H 2003 *J. Phys.: Condens. Matter* **15** L491
[30] Lee G W Gangopadhyay A K, Kelton K F, Hyers R W, Rathz T J, Rogers J R and Robinson D S 2004 *Phys. Rev. Lett.* **93** 037802
[31] Luo W K, Sheng H W, Alamgir F M, Bai J M, He J H and Ma E 2004 *Phys. Rev. Lett.* **92** 145502
[32] Li H, Zhao J J and Wang G H 2002 *J. Chem. Phys.* **116** 10809
[33] Li H and Pederivade F 2003 *J. Chem. Phys.* **118** 10707