Local Order of Liquid and Supercooled Zirconium by *Ab Initio* Molecular Dynamics

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(Received 8 April 2003; published 3 November 2003)

It has been suggested that icosahedral short-range order (SRO) occurs in deeply undercooled melts of pure metallic elements. We report results of first-principles molecular dynamics simulations for stable and undercooled zirconium liquids. Our results emphasize the occurrence of a local order more complex than the icosahedral one. For stable liquid, the local order is interpreted on the basis of a competition between a polytetrahedral SRO and a bcc-type SRO. We also demonstrate that a bcc-type SRO increases with the degree of undercooling.

DOI: 10.1103/PhysRevLett.91.195501 PACS numbers: 61.20.–p, 61.25.–f

Satisfactory understanding of the structural properties of the stable and undercooled melts is a fundamental problem since it is believed that the local structure of melts has a strong influence on the nucleation mechanism [1]. Frank [2] was the first to suggest that the local structure could be based on icosahedral packing which is incompatible with the long-range periodicity of the crystalline solid. The same arguments were used to explain the experimentally observed deep undercooling in some pure liquid metals. Thirty years later, this description was confirmed by molecular dynamics simulations of supercooled liquids using Lennard-Jones (LJ) potentials to describe atomic interactions [3].

Very recently, Schenk *et al.* [4] reported a neutron scattering experiment on pure supercooled liquid transition metals, namely, Fe, Ni, and Zr, using an electromagnetic levitation technique. For all three elements, they argued that an icosahedral short-range order (ISRO) occurs in the stable liquid and increases in the supercooled state, using limited structural information since the measured structure factor is an angular averaged quantity. However, their conclusions are only in partial agreement with Frank's arguments and the well-known behavior obtained by several molecular dynamics (MD) simulations for the LJ system [3,5,6], since they pointed out [4] that larger polytetrahedral structures than icosahedron give a better description of the measured structure factor. Moreover a quite pronounced ISRO is revealed already above the melting temperature.

In the present Letter, we address the important question of the short-range order (SRO) in liquid metals and its evolution in the supercooled region by performing a series of first-principles MD simulations of liquid Zr as a function of temperatures. In the absence of direct experimental observations, the use of predictive *ab initio* techniques is crucial to determine the local structure in undercooled metallic melts. First-principles calculations differ substantially from those based on LJ potentials as it is known that the density functional theory (DFT) provides an accurate description of chemical directional bonding in noble metals [7] as well as in transition metals having an incomplete d shell such as Zr [8,9].

As a correct description of a liquid demands that a time evolution is taken into account, *ab initio* MD simulations have been performed using the VASP code [10]. We used the Perdew-Wang exchange and correlation potential [11] and the projector augmented-wave (PAW) method [12] in the implementation of Kresse and Joubert [13]. In the present PAW potential, the $5s$, $4d$ orbitals as well as the semicore $4s$ and $4p$ orbitals are treated as valence orbitals with a plane-wave cutoff of 300 eV. Only the Γ k point has been considered to sample the supercell Brillouin zone. The simulations were carried out in the NVT ensemble, using a Nosé thermostat [14], with a cubic cell containing $N = 108$ atoms subject to standard periodic boundary conditions. Four temperatures were considered, namely, $T = 2500$, 2200, 2000, and 1850 K, and the volume of the cell has been fixed to reproduce the experimental densities [15]. The two former temperatures are in the stable liquid, above the experimental melting temperature of 2123 K, while the two latter are in the supercooled region. The typical durations of the runs are 3 ps with a time step of 1 fs. The procedure of the simulations is the following: starting at 2500 K from a well-equilibrated state, the system is quenched instantaneously to 2200 K at constant volume and, after 3 ps time, the system is compressed to the experimental density. This procedure is repeated for the subsequent temperatures. After an equilibration period of 2 ps, a number of 100 configurations at each temperature were extracted to produce averaged structural quantities. The total energy remained essentially constant during each run, attesting that the system was not subject to a phase transition, such as crystallization.

In Fig. 1, the pair-correlation functions, $g(r)$, were displayed for the temperatures considered in this work. Going from the stable liquid at 2500 K to the supercooled

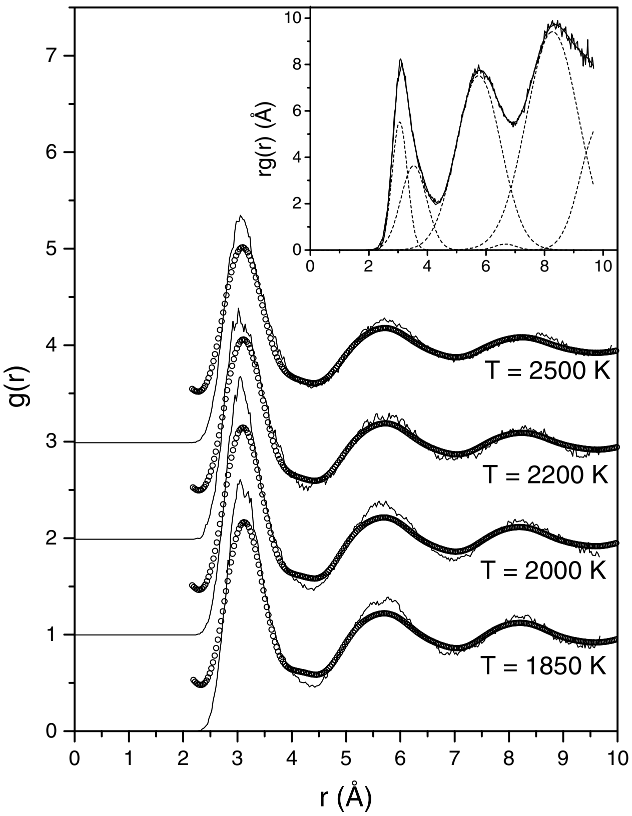

FIG. 1. Pair-correlation function $g(r)$ for the four temperatures. The solid lines correspond to the MD simulations and the open circles belong to the experimental data of Schenk *et al.* [4]. The curves are shifted upwards by an amount of 1, 2, and 3 for 2000, 2200, and 2500 K, respectively. The inset shows the calculated $rg(r)$ at 2000 K, its analysis in Gaussian peaks (solid line), and the different Gaussian peaks (dashed curves).

states at 1850 K, the first peak and subsequent oscillations narrow and their height increases, which shows that the supercooled liquid becomes more structured. It should be noted that a remarkable agreement is found with the recent experimental $g(r)$ of Schenk *et al.* [4], both for the stable and the undercooled liquids, albeit the peaks are somewhat higher.

The first coordination shell is defined by a cutoff distance r_c, which is taken to be the first minimum of $g(r)$. We have found that $r_c = 4.3$ Å whatever the temperature, and this value will be kept throughout this study for the analysis of the structural properties. An increase of N_c between 13.2 and 13.9 occurs with decreasing temperature in agreement with those obtained by Schenk *et al.* They are slightly higher than the experimental ones but remain in the experimental error bars and are also consistent with the coordination numbers calculated for other metallic systems [8].

Such an evolution of the coordination number in the supercooled regime brings us to analyze the pair-correlation function in more detail. As the first peak of $g(r)$ appears to be asymmetric, it might be composed of more than one atomic shell. Following Kita *et al.* [16], we have performed a decomposition using Gaussian peaks of the function $rg(r)$, which was applied successfully to liquid Si as well as to liquid Ni, Fe, and Cu. The inset of Fig. 1 shows the decomposition of $rg(r)$ at 2000 K in six Gaussian peaks. All 18 parameters were allowed to vary freely and were optimized by a least-squares method. Indeed, the first peak is composed of two Gaussian peaks situated at R_a and R_b, and the ratio R_a/R_b decreases from 1.178 to 1.153 as T is lowered. Interesting enough, upon supercooling, the ratio R_b/R_a becomes close to that of the two first nearest-neighbor distances for a bcc lattice $2/\sqrt{3} = 1.1547$. The high value of the coordination number and the possibility to decompose the first peak of $g(r)$ into two subpeaks is an indication that the SRO of liquid and supercooled Zr is more complex than the one given by a simple icosahedral ordering, as was also pointed out by Schenk *et al.* [4]

The fact that the topological SRO is modified as T is lowered is also confirmed by the bond-angle distribution functions, as seen in Fig. 2, for $T = 2500$ K in the stable liquid and $T = 2000$ K in the supercooled region. For both temperatures, the calculated distribution shows a prominent peak near $\theta = 55°$, a broad maximum near $\theta = 110°$, and a rather flat maximum around $\theta = 150°$. The separation between the two first peaks is more pronounced as T is lowered, which confirms that the supercooled liquid becomes more structured. The location of the first two peaks may indicate some preference for bcc-type order with respect to the icosahedron symmetry (icosahedral bond angles are $\theta = 63.5°$ and $116.5°$) but the shoulder locates around 150° which indicates in the first place a complex polytetrahedral order.

To obtain a more detailed three-dimensional description of the local atomic configuration, we use the common-neighbor analysis [5,17] in which the first two

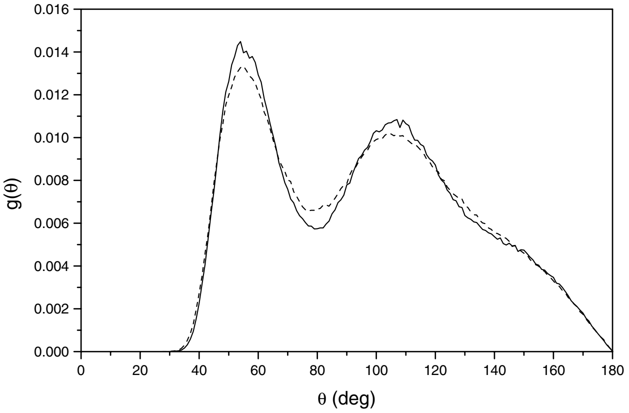

FIG. 2. Bond-angle distribution at $T = 2500$ K (dashed line) and $T = 2000$ K (solid line).

peaks of the pair-correlation function are decomposed. This method is able to characterize the local environment surrounding each atomic pair that contributes to the peaks of $g(r)$, in terms of the number and properties of common nearest neighbors of the pair under consideration. Such an analysis is performed on inherent structures in which the atoms are brought to local minima of the potential energy surface by applying a technique similar to the steepest-descent minimization proposed by Stillinger and Weber [18]. For each temperature, namely, $T = 2500$ K and $T = 2000$ K, height selected configurations are used to generate the inherent structures.

For both temperatures, Table I contains the relative abundance of selected pairs, averaged over the height inherent configurations. A set of four indices is associated with each of them [5]: (i) the first index denotes to what peak of $g(r)$ the pair under consideration belongs, i.e., the root pair; (ii) the second index represents the number of near neighbors shared by the root pair; (iii) the third index is for the number of nearest-neighbor bonds among the shared neighbors; (iv) a fourth index is used to distinguish configurations with the same first three indices but with a different topology. This method is able to distinguish between various local structures like fcc, hcp, bcc, and icosahedral environments. For example, four bonded pairs are represented in a bulk fcc crystal: 1421, 2101, 2211, and 2441. A bulk hcp contains the same pairs but not with the same weight and additional pairs like 1422 and 2331 pairs. The 1441, 1661, 2101, 2211, and 2441 are typical pairs of the bulk bcc crystals. On the other hand, the pair 1551, corresponding to a pentagonal bipyramid, is characteristic of icosahedral order. For instance, local order built on a 13-atom icosahedron leads to the occurrence of 1551, 1321, and 2331 pairs [19].

TABLE I. Analysis of the simulations in bonded pairs for $T = 2500$ K (liquid) and $T = 2000$ K (supercooled). The absolute error bars of the abundances are 0.01.

Bonded pairs	Liquid	Supercooled
1551	0.32	0.27
1541	0.16	0.10
1421	0.01	0.00
1422	0.01	0.01
1431	0.11	0.14
1201	0.00	0.00
1211	0.00	0.00
1301	0.00	0.00
1311	0.00	0.00
1321	0.01	0.01
1331	0.01	0.01
1661	0.16	0.23
1441	0.10	0.14
1771	0.00	0.00
2211	0.96	1.03
2101	0.89	0.72
2441	0.31	0.41
2331	0.90	0.82
2321	0.04	0.15

The microscopic analysis emerging from the data of Table I indicates that the short-range order of the liquid state is dominated by icosahedral and distorted icosahedral inherent structures since the 1551 and 1541 bonded pairs are preponderant. However, although the 2331 pairs are relatively numerous, the absence of the 1321 pairs and the high value of the 2101 ones is a strong indication that the liquid is characterized by a SRO that is more complex than the one found in the 13-atom icosahedron. The 1441 and 1661 pairs are also of importance. When associated with the 1551 and 2331 bonded pairs, they are in favor of Frank-Kasper (FK) [20] polyhedra of high coordination, namely, $Z14$, $Z15$, and $Z16$ (see, for example, Ref. [21] for a detailed description). However, as discussed above, these two pairs may contribute also to a bcc-type local structure since the 2101, 2211, and 2441 bonded pairs have a non-negligible weight [22].

Upon supercooling, the competition between fivefold and the bcc-type symmetries is reinforced since the number of 1551 and 1541 bonded pairs decreases while the number of 1441 and 1661 pairs increases. Thus these two variations support the occurrence of a more pronounced bcc-type structure as well as an increasing complexity of the Frank-Kasper based-polytetrahedral symmetry in the supercooled regime.

To summarize, we have performed *ab initio* MD simulations of liquid Zr in order to analyze the local order and its evolution upon supercooling. The structure of the liquid and undercooled states, characterized through their $g(r)$, was found to be in very good agreement with the very recent measurements of Schenk *et al.* [4]. A more refined structural analysis, using a method to classify inherent structures, allows one to gain additional insight into the atomic configurations characterizing the SRO found in the liquid and undercooled states. In the undercooled state, the classification of inherent structures clearly points out two major changes with respect to the liquid states: (i) a polytetrahedral SRO that consists of more numerous FK polyhedra larger than the icosahedron, such as $Z14$, $Z15$, and $Z16$; (ii) a reinforcement of the bcc-type SRO, which is the symmetry of the high temperature crystalline phase of Zr. This competition is guided by the interactions, calculated accurately within the DFT, which lead to a short-range order more complex than the icosahedral SRO obtained on the basis of geometrical arguments [2].

The authors gratefully acknowledge V. Simonet, T. Schenk, and R. Bellissent for fruitful discussions and for giving experimental data of $g(r)$, as well as D. L. Price for useful comments and S. K. Lai for technical details concerning the common-neighbor analysis. We acknowledge PHYNUM-CIMENT-UJF at LPMMC for computational resources on the PC cluster.

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