# Difference in Icosahedral Short-Range Order in Early and Late Transition Metal Liquids

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New short-range order data are presented for equilibrium and undercooled liquids of Ti and Ni. These were obtained from *in situ* synchrotron x-ray diffraction measurements of electrostatically levitated droplets. While the short-range order of liquid Ni is icosahedral, consistent with Frank's hypothesis, significantly distorted icosahedral order is observed in liquid Ti. This is the first experimental observation of distorted icosahedral short-range order in any liquid, although this has been predicted by theoretical studies on atomic clusters.

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While lacking the long-range translationally periodic order of a crystalline solid, liquids contain a significant amount of short-range order. The first successful models of liquid structures, based on a dense random packing (DRP) of hard-spherelike atoms [1], were reasonably adequate for closed-shell inert gas systems. However, the atomic interactions in metallic or covalently bonded liquids make the structures too complicated to be described by such a simple model. A theoretical understanding of the structures of liquid transition metals [2], for example, is still incomplete three decades after the first systematic experimental data were obtained [3]. Liquid structures from molecular dynamics (MD) simulations using the pair potentials of Wills and Harrison (WH) [4], and from an analytic solution of the hypernetted chain theory using a more accurate pair potential derived from the embedded-atom-method [2], agree reasonably well with the experimental results for the late transition metals (LTM). However, they fail for the early (Sc, Ti, V) transition metals (ETM), where the theory cannot even reproduce the correct peak positions of the structure factor, $S(q)$. To clarify whether these failures point to an inadequacy in the theories or the experimental data [2–4], more precise experiments are necessary [2].

Here we present x-ray diffraction data from the equilibrium and undercooled (i.e., metastable liquids below their melting temperature) liquids of an early (Ti) and a late (Ni) transition metal. These data show the development of icosahedral short-range order (ISRO) with increasing undercooling in liquid Ni, consistent with the results of recent neutron diffraction studies on electromagnetically levitated liquids [5], and the half-century-old prediction of Frank [6]. To explain the experimental data for Ti, however, the ISRO must be distorted. Although distorted icosahedral order, resulting from a competition between structural (maximum number of bonds) and electronic (Jahn-Teller effect) contributions to the energy, has been predicted in atomic cluster studies [7–10], to our knowledge, the present results are the first experimental observations of such distortions.

Measurements of the liquid structures of high melting temperature materials (e.g., transition metals) are often plagued by contamination from container materials, oxidation, etc. These problems can be avoided by using recently developed containerless processing techniques such as aerodynamic [11], electromagnetic (EML) [5], or electrostatic (ESL) [12] levitation. The number of potential heterogeneous nucleation sites is also decreased due to the absence of container walls and the high vacuum ($10^{-7}$ Torr in ESL) or inert gas environment (aerodynamic and EML), allowing structural studies to be made of undercooled, as well as equilibrium liquids. The data presented here were obtained using the recently developed BESL technique [12] (acronym for beam line ESL). Small spheres (2.2–2.5 mm diameter) of high purity Ti (99.995%) and Ni (99.995%), prepared by arc melting in a high-purity argon atmosphere, were levitated in an ESL and melted using 30 W diode and 30 W $CO_2$ lasers. Diffraction data were obtained on the MU-CAT (beam line 6ID-D) at the Advanced Photon Source (APS) located at Argonne National Laboratory using a MAR3450 image plate, as described elsewhere [12,13].

The structure factor data for equilibrium and undercooled Ni liquids are shown in Fig. 1(a). These are in good agreement with recently reported EML-based neutron diffraction results [5], as shown by a comparison between the EML data at 1465 K (closed circles) and the ESL data at $T = 1490$ K (connected open circles). Considering that the two data sets were obtained by two completely different levitation (ESL vs EML) and diffraction (x-ray vs neutron) techniques, the agreement is remarkable. While first-principle theoretical calculations of $S(q)$ for Ni (dashed line) [2] are in qualitative agreement with the experimental data, one important point is missing. The

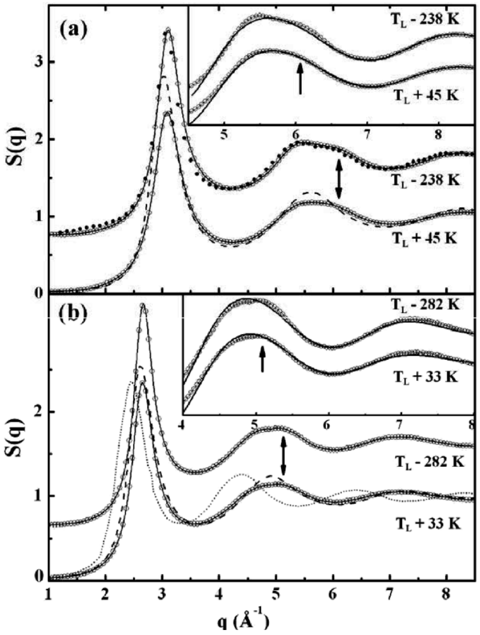

FIG. 1. X-ray structure factor for liquid Ni (liquidus temperature, $T_L = 1728$ K) (a) and Ti ($T_L = 1940$ K) (b) as a function of temperature (connected open circles); the curves are displaced vertically for clarity. Dashed lines are from theory [2]. Selected (for clarity) neutron diffraction data from EML experiments [5] for Ni are shown as closed circles in (a) and the x-ray data from earlier work on Ti [3] are shown by the dotted line in (b). Insets show the fit of the experimental data (connected open circles) to a 13-atom icosahedron (solid lines), above and below the melting temperatures. The fitting parameters for Ni are $r_0 = 2.37$ Å and $\langle \delta r_0^2 \rangle = 0.028$ Å$^2$ for $T_L - 238$ K, and $r_0 = 2.35$ Å and $\langle dr_0^2 \rangle = 0.034$ Å$^2$ for $T_L + 45$ K; for Ti, the parameters are $r_0 = 2.74$ Å and $\langle dr_0^2 \rangle = 0.049$ Å$^2$ for $T_L - 282$ K, and $r_0 = 2.72$ Å and $\langle dr_0^2 \rangle = 0.058$ Å$^2$ for $T_L + 33$ K.

clear development of a shoulder on the high-$q$ side of the second peak (shown by the arrow) with increasing undercooling in these ESL studies and in the EML experiments [5], is absent in the theoretical $S(q)$. The measured $S(q)$ for equilibrium and undercooled liquids of Ti, along with the earlier data by Waseda (dotted line) [3] and more recent theoretical calculations (dashed line) [2], are shown in Fig. 1(b). The peak positions in the $S(q)$ obtained here are significantly different from those found in the earlier studies [3], but are in much better agreement with the theoretical results obtained by the embedded atom method [2]. Again, however, there is a significant shoulder on the high-$q$ side of the second peak in the experimental data, which is even more intense than the second peak [inset of Fig. 1(b)]. Moreover, unlike Ni, the relative intensity and shapes of the second peak and shoulder change little with increasing undercooling (decreasing temperature).

It is often assumed that the local structures in liquids can be described by tightly bound, noninteracting, close-packed, clusters [5,6,12,14]. The presence of a shoulder on the high-$q$ side of the second peak is generally indicative of icosahedral short-range order (ISRO) in the liquid. For Ni, the ratios of the peak positions in $S(q)$, determined by fitting two overlapping Gaussian peaks, are $q(\text{2nd})/q(\text{1st}) = 1.74 \pm 0.01$ and $q(\text{shoulder})/q(\text{1st}) = 1.95 \pm 0.01$, in reasonable agreement with those expected for a perfect icosahedron (1.71 and 2.04, respectively) [15]. Recently, the local structures of liquid Ni [5] and Ti-Zr-Ni (which crystallizes to an icosahedral quasicrystal [12]) have been successfully described by icosahedral clusters. The present results are, therefore, consistent with Frank's hypothesis [6], suggested to explain why liquid metals could be frequently retained in a metastable (undercooled) state below their equilibrium melting temperature [16]. For atoms interacting by a Lennard-Jones (LJ) potential, an increasing degree of ISRO over cubic ordering in the undercooled liquid was demonstrated in molecular dynamics simulation studies [17]. One important difference between the experimental results presented here and the MD calculations, however, is that the ISRO vanishes above the melting temperature in the simulation studies [17], whereas it persists up to the highest measurement temperature (~100 K above $T_L$) for liquid Ni. This likely reflects the difference between the LJ central-potential and the true Ni potential, which retains some angular dependence. ISRO has been inferred for a number of amorphous metallic alloys both in experimental [18] and theoretical studies, based on dense random packing (DRP) of hard sphere models [1]. However, direct experimental observation of ISRO in metal [5] and alloy liquids [12] was possible only recently, due to the vastly improved measurement techniques.

The calculated $S(q)$ from an ensemble of 13-atom icosahedral clusters fit the experimental data for Ni reasonably well when the Debye-Waller (DW) factors for atomic vibration within the cluster [5,12,14] are taken into account [inset in Fig. 1(a)]. However, the experimentally observed distinct shoulder on the second peak in the undercooled state is not reproduced; instead an asymmetric second peak is predicted. Similar problems were also encountered in fits to the neutron diffraction studies for Ni [5]. They likely reflect an overestimation of the DW factor in the undercooled state, considered to be isotropic. The decreasing quality of the fit to experimental data with decreasing temperature [inset of Fig. 1(a)] suggests that the DW factor becomes increasingly anisotropic with increasing undercooling. An anisotropic DW factor has been observed in Al-based quasicrystals [19]. A better fit to the experimental liquid data will require a more detailed knowledge of the vibrational modes of the icosahedral clusters for undercooled liquids. Because of the overestimated temperature dependence, the $S(q)$ calculated without the DW factor better reflects the essential features of short-range order in undercooled liquids.

In contrast, the experimental data for Ti fit poorly to a 13 atom icosahedral cluster model, even above the melting temperature [inset of Fig. 1(b), and Fig. 3]. The coordination number estimated from the radial distribution function constructed from the scattering data for Ti was 12 ± 1, consistent with a close-packed cluster. The temperature dependence of the second peak and the shoulder is smaller than that observed for Ni. The ratios of the peak positions ($q^{2\text{nd}}/q^{1\text{st}} = 1.76 \pm 0.01$ and $q^{\text{shoulder}}/q^{1\text{st}} = 1.92 \pm 0.01$) also differ slightly more than do the Ni data from the ideal values for an icosahedral cluster (1.71 and 2.04, respectively) [15]. But, more importantly, the intensity of what was a high-$q$ shoulder of the second peak in the Ni data, is now larger than the intensity of the second peak itself, even above the melting temperature. This is surprising, since the calculated $S(q)$ for a *monatomic* icosahedral cluster never shows such reversed peak intensities, irrespective of the cluster size; neither can it be explained by other closed packed structures such as bcc, fcc, and hcp, or a 15-atom Frank-Kasper cluster (often considered to represent short-range order in glasses).

To understand the difference in the liquid structures of Ni and Ti, we recall that $s$ and $d$ electron interactions dominate the bonding in transition metals. The $d$ electrons are more delocalized in ETM, making $s$-$d$ hybridization effects more important than in LTM. Changes in the nature of the atomic interactions on traversing the transition metal series largely contribute to the systematic changes in their bulk [20] as well as small atomic cluster properties [21]. Comparing measured liquid structure factors with predictions from hard sphere models, Waseda [3] found that the atomic packing becomes more central-potential-like in liquids on progressing from Ti to Ni across the 3$d$ transition metal series, and from Ce to Yb in the 4$f$ series. The greater angular dependence of the interatomic potentials for early transition metals than for the late transition metals is consistent with the observation that the ISRO is more distorted in Ti than in Ni. Consistent with this, distorted ISRO has been reported in theoretical studies of Ti clusters [8].

The calculated $S(q)$ for clusters with differing degrees of distortion along the twofold, threefold, and fivefold axes of an icosahedron, as suggested in Ref. [8], however, showed no appreciable change in the relative intensity of the shoulder and the second peak from the undistorted icosahedron as will be discussed later (see inset in Fig. 3). This indicates that the clusters in liquid Ti may be even more severely distorted. Theoretical calculations of Al and Ga show that distorted decahedral clusters, produced by the rotation of one pentagonal cap of an icosahedron along the fivefold axis with respect to the opposite pentagonal cap, have lower energies than perfect icosahedral clusters [9], and similar energies to distorted icosahedral clusters [10]. Similar clusters might characterize the distortion evident in the $S(q)$ data for Ti.

Figure 2 shows that the relative intensities and positions of the 2nd peak and high-$q$ shoulder are sensitive to the rotation angle of one pentagonal cap with respect to the other along the fivefold axis, $\phi$, and the angle, $\theta$, between the fivefold axis and the center to pentagonal atom bonds. The rotation directions for the distortion, $\phi$ and $\theta$ are determined following Refs. [8–10]. For a rotation angle, $\phi$, of 36°, i.e., a perfect decahedron, the intensity of the shoulder is higher than the second peak. For an icosahedral cluster, the nearest and next nearest neighbor bonds and the number of bonds for the surface atoms make the primary contributions to the second peak and the shoulder, respectively. A change in $\theta$ affects the next nearest neighbor bond lengths of the surface atoms and, therefore, has a more dramatic effect on the second peak than does a rotation in $\phi$. A change of $-5°$ in $\theta$ reverses the ratio of the second peak and the shoulder [Fig. 2(b)]. For the combined distortion $\theta = -6°$ and $\phi = 10°$, the calculated $S(q)$ reproduces the most important feature of the experimental data (thick solid line in the inset of Fig. 3), i.e., the higher intensity of the shoulder compared to the second peak. When the DW factor is included in the simulation of the distorted cluster, as shown in Fig. 3, the overall agreement for a distorted icosahedron (thick line) is significantly better than for an undistorted icosahedron (thin line). The peaks become less distinct (thick line in Fig. 3) due to the overestimation of the DW factor as discussed earlier in the case of Ni; the calculated data still maintain the shape of the peaks (slower rise at lower $q$ than for a undistorted icosahedron), however. Without the DW factor, the calculated structure factors for different type of distortions are shown in the inset of Fig. 3. Again, the second peak and the shoulder are better reproduced by the above

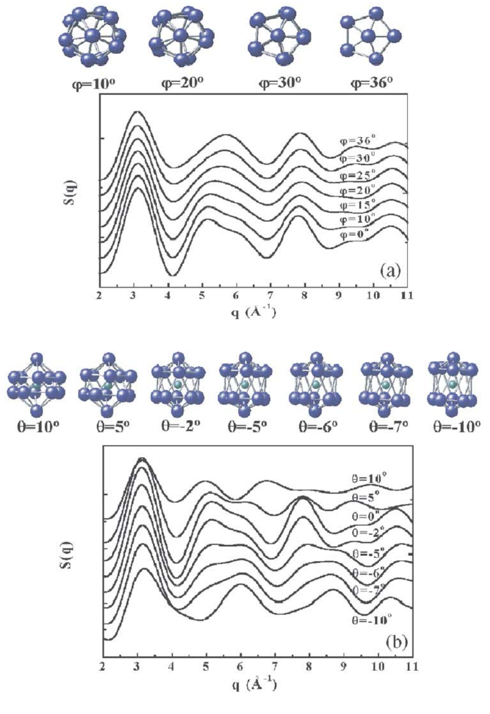

FIG. 2 (color online). Calculated x-ray structure factors for icosahedra with different amounts of distortions in $\varphi$ (a) and $\theta$ (b).

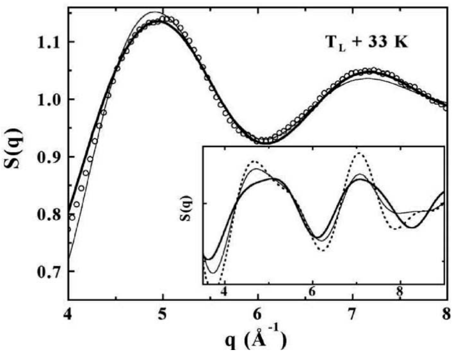

FIG. 3. Comparison of the experimental data (open circles) with the calculated structure factors for Ti for an undistorted (thin line) and distorted (thick line) icosahedron ($\theta = -6°$ and $\varphi = 10°$) including the DW factor ($r_0 = 2.871$ Å and $\langle dr_0^2 \rangle = 0.034$ Å$^2$). The inset shows the calculated structure factors for different degrees of distortion without DW factor; the solid line is calculated for the above distortions, and the dotted and thin lines are for $D_{3d}$ (threefold) and $D_{2d}$ (twofold) [8] distortions, respectively.

distortions than distortions along twofold and threefold axes [8].

The highly distorted icosahedral clusters in liquid Ti compared to the relatively undistorted ones in Ni, and the weaker temperature dependence of the structure factor for Ti [Figs. 1(a) and 1(b)] are therefore, all consistent with their atomic bonding properties. Accordingly, distorted icosahedral (or decahedral) short-range order is also expected in other early transition metal (e.g., Sc, V, and Zr) liquids. Of course, the connection between the local order of the liquid and the nucleation barrier, proposed by Frank, remains essentially unchanged. While the nucleation barrier for crystal phases will be little affected by the degree of perfection of ISRO, it could have a dramatic effect on the nucleation of ordered phases with icosahedral short-range order, such as the icosahedral quasicrystal.

In summary, using the recently developed BESL technique on the Advance Photon Source, the structure factors for liquid Ti and Ni were determined for equilibrium and undercooled liquids. In particular, more precise structure factor data for liquid Ti, which are consistent with theoretical predictions [2], were obtained, which has been lacking for more than 25 years. Nearly perfect icosahedral short-range order was observed in Ni; in Ti this was significantly distorted. To our knowledge, this is the first direct experimental evidence for a distorted icosahedral (or decahedral) short-range order in a liquid metal and the first time that the degree of distortion has been correlated with the atomic interaction. In addition, although distortions in atomic clusters have been predicted in a number of theoretical studies [7–10], they have never been observed experimentally. Similar distorted icosahedral order is anticipated in other early transition metal liquids. Although simplistic, the single cluster model presented here effectively captures the essential features of the local liquid structure. More elaborate *ab initio* theoretical and molecular dynamics simulations of liquid structures are needed, however. It is our hope that the results presented here will stimulate these studies.

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