

First X-Ray Scattering Studies on Electrostatically Levitated Metallic Liquids: Demonstrated Influence of Local Icosahedral Order on the Nucleation Barrier

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To explain the unusual stability of undercooled liquids against crystallization, Frank hypothesized that the local structures of undercooled liquids contain a significant degree of icosahedral short-range order, which is incompatible with long-range periodicity. We present here the first direct experimental demonstration of Frank's complete hypothesis, showing a correlation between the nucleation barrier and a growing icosahedral short-range order with decreasing temperature in a $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ liquid. A new experimental facility, BESL (Beamline Electrostatic Levitation), was developed to enable the synchrotron x-ray structural studies on deeply undercooled, reactive liquids.

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Below their equilibrium melting temperatures, T_m , liquids transform to ordered phases having lower free energies. Because of the frequent abundance of sites that catalyze the nucleation of the new phase, such as container walls and impurities in the liquid, this crystallization generally occurs very near to T_m . If this heterogeneous nucleation can be bypassed, it becomes possible to probe the homogeneous nucleation mechanism, proceeding by spontaneous fluctuations within the parent phase. Over 50 years ago Turnbull demonstrated that metallic liquids can be cooled far below their equilibrium melting temperatures (undercooled) without crystallization [1], signaling a large barrier to the formation of the ordered phase. Since Fahrenheit it was known that this was possible in liquids such as water [2], but given their similar densities and properties, the barrier separating the liquid and crystal phases in metals and alloys was assumed to be small. To explain those surprising results, Frank hypothesized that the local structures of undercooled metallic liquids are actually quite different from those of crystal phases, containing a significant degree of icosahedral order that is incompatible with the extended periodicity of the crystal [3]. Such structural differences must create a barrier to the formation of crystal phases, explaining the observed undercooling behavior. Here, we present the first data that directly link nucleation with growing icosahedral order in the undercooled liquid, proving this hypothesis.

Several previous experimental and theoretical studies are consistent with Frank's hypothesis, but do not provide a direct proof. Icosahedral short-range order (ISRO) is often favored in small clusters, as was observed recently in liquid Pb close to a (001) surface of Si, for example [4]. The perturbing influence of the surface on the liquid structure, however, is unclear. Although icosahedral order is incompatible with the translational periodicity of a

lattice, many crystalline phases (e.g., crystal approximants, C14 Laves phase, etc.) show a varying degree of ISRO, while icosahedral quasicrystals have extended icosahedral order [5]. Measurements for a series of Al-Cu-Fe and Al-Cu-Co liquids using electromagnetic levitation [6] and Ti-Zr-Ni liquids using electrostatic levitation (ESL) [7] show an increase in the maximum undercooling before crystallization with a decreasing ISRO of the crystallized phase, consistent with Frank's hypothesis. Direct observations of ISRO in the undercooled liquids, however, were not made. Recently, ISRO was reported in undercooled Ni, Fe, and Zr [8]. While those results do confirm Frank's hypothesis of ISRO in undercooled liquids, the link between ISRO and the nucleation barrier for the solid phase was not experimentally established.

To confirm Frank's hypothesis, ISRO in the liquid must be observed directly and coupled with the nucleation barrier for crystallization. That is demonstrated in this Letter. An increasing ISRO in a Ti-Zr-Ni liquid with undercooling is measured using a recently developed technique [Beamline Electrostatic Levitation (BESL)] that allows *in situ* x-ray diffraction studies on electrostatically levitated droplets. Further, we show that this increasing ISRO is responsible for the nucleation of a metastable Ti-Zr-Ni icosahedral quasicrystal phase (*i* phase) from the undercooled liquid instead of the stable polytetrahedral C14 Laves phase, which also tends to nucleate easily over a wide composition range (see [9] for the Ti-Zr-Ni phase diagram containing the C14 phase; the structure of the C14 phase is presented in [10]). Since the driving free energy for nucleation is larger for the C14 phase, the preferred nucleation of the *i* phase signals a smaller nucleation barrier [11], indicating that the short-range order of the liquid is more similar to that of the *i* phase than to the tetrahedral structure of the C14 phase. These data demonstrate the connection between the local

order of the liquid and the nucleation barrier. That the development of regions of short-range order (SRO) in the liquid is critical for the nucleation of ordered phases with similar SRO blurs the distinction between homogeneous and heterogeneous nucleation in these cases and indicates that fluctuations of the local order parameter (as well as the global one) are important and must be considered in nucleation theories.

Containerless processing methods are required to study the crystallization and structure of the highly reactive $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ liquids. Undercooling studies were made on samples 2.3–2.5 mm diameter that were levitated using the ESL facility located at NASA/Marshall Space Flight Center [12]. The samples were positively charged with ultraviolet light and levitated in vacuum ($\approx 10^{-7}$ Torr) between electrostatic plates as described elsewhere [13]. Samples were melted using a YAG laser. The decoupling between heating and positioning in the ESL is an improvement over electromagnetic levitation techniques, allowing undercooling studies on a wider range of materials such as the high density, low melting temperature Ti-Zr-Ni alloys of interest. Optical pyrometers with a 1.2 to 1.4 μm wavelength range were used to measure the sample temperature to a relative accuracy of ± 1 K.

The ESL-based x-ray diffraction facility (BESL), central to the results reported here, was recently developed through a joint collaboration between researchers from Washington University, NASA Marshall Space Flight Center, and μ -CAT (beamline 6ID-D) at the Advanced Photon Source (APS) located at Argonne National Laboratory, to obtain x-ray structural data for equilibrium and metastable liquids and solids [14]. Two separate Be windows (2.5 in. diameter, 0.015 in. thick) were installed in the ESL chamber at diametrically opposite ends of the chamber for the entrance of the incident x ray and exit of the diffracted beam. The diffracted beam was detected over a large q range in less than 1 s using a MAR3450 image plate, allowing studies of the metastable liquid in the deeply undercooled state as well as the structural identification of transient solid phases that form during nucleation. Given the restricted range of scattering angles with the Be windows used, high energy x rays (125 keV, 0.099 Å) were used to provide a scattering range of $0 \leq q \leq 9 \text{ \AA}^{-1}$; sample absorption and multiple scattering were also negligible at these energies.

Figure 1(a) shows the sample temperature as a function of time for a small (≈ 2.5 mm diameter) electrostatically levitated liquid droplet of $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ alloy during free radiation cooling from far above the liquidus temperature of 1093 K. The high atomic mobility in liquids permits rapid crystal growth, producing the sharp rise observed in sample temperature due to the evolved heat of fusion during solidification, a process called recalescence. The reduced undercooling, $\Delta T_r = (T_L - T_r)/T_L$, where T_L is the liquidus temperature and T_r is the tem-

perature at the start of recalescence, provides a measure of the barrier to nucleation, i.e., how difficult it is to form the first stable region of the new phase. Two recalescence events are observed, the first with a rise in temperature from 953 to 1058 K, followed within a few seconds by a second rise to 1083 K. This behavior is reproducible, observed over many different thermal cycles of the same sample, as well as for different samples of similar composition. *In situ* x-ray diffraction patterns [Fig. 1(b)] show that during the primary recalescence from 953 K [Fig. 1(a)] a metastable *i* phase nucleates and grows. This *i* phase subsequently transforms within a few seconds to the stable C14 Laves phase during the second recalescence from 1058 to 1083 K, the equilibrium solidus temperature. BESL made the identification of such a short-lived metastable phase possible.

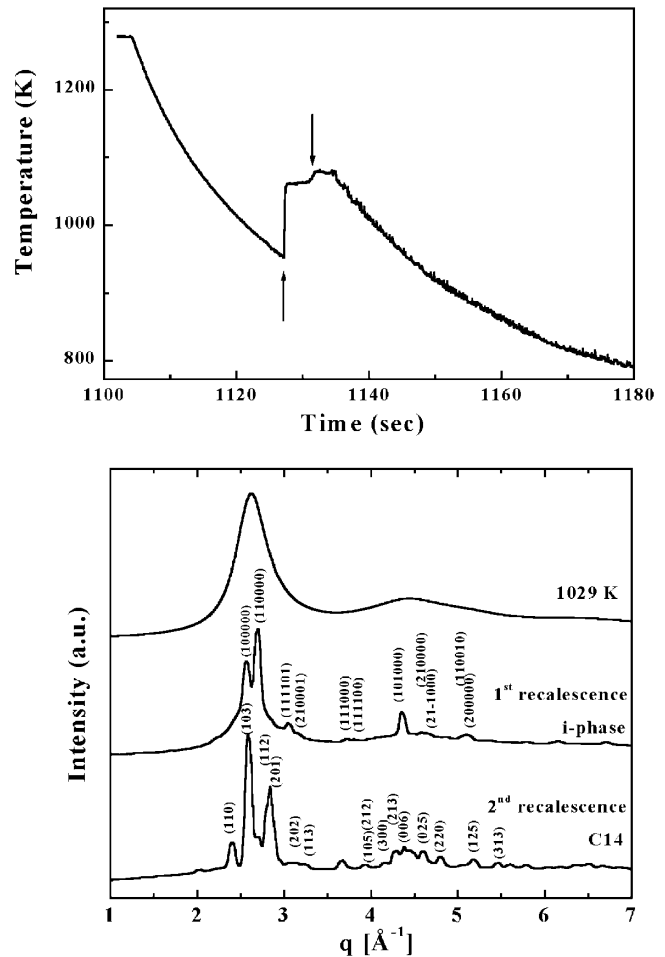


FIG. 1. (a) Cooling curves for electrostatically levitated 2.5 mm droplet of $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ as a function of temperature showing two recalescence events (indicated by arrows). (b) X-ray diffraction pattern as a function of momentum transfer, q ($= 4\pi \sin\theta/\lambda$), for the undercooled $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ alloy liquid at 1029 K, during the 1st recalescence to the *i* phase, and during the 2nd recalescence to the C14 phase.

The *i* phase is metastable above 843 K [9]. It is therefore surprising that the metastable *i* phase nucleates before the C14 polytetrahedral phase, which is often presumed to have similar short-range order to the liquid [15] and is known to nucleate easily over a wide composition range. Therefore, the nucleation barrier of the *i* phase must be lower than for crystallographic phases, even those with local polytetrahedral order.

Figure 2 shows the x-ray structure factors extracted from the scattering data for the $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ liquid as a function of undercooling. The data were corrected for contributions from the Be window, air scattering, and Compton scattering [16]. The most interesting aspect of the data is the enhancement of a shoulder (more clearly visible in Fig. 3) on the high- q side of the second peak in $S(q)$ with increasing undercooling, in the same temperature range where nucleation of the *i* phase becomes favorable. This shoulder, also observed in many different thermal cycles on this sample and for samples of similar composition, is consistent with local icosahedral order [17]. The increasing distinction of the shoulder with decreasing temperature demonstrates that the order in the liquid becomes better defined and more pronounced at lower temperature (see Fig. 3), confirming predictions made earlier by Steinhardt *et al.* [18]. The relative locations of the first two peaks in $S(q)$, $q_2/q_1 = 1.72$, and the location of the shoulder on the second peak, $q_{\text{shoulder}}/q_1 = 1.97$, are in good agreement with those expected for a perfect icosahedron [17], $q_2/q_1 = 1.71$ and $q_{\text{shoulder}}/q_1 = 2.04$, indicating little distortion in the icosahedral order of the liquid. While shown here for alloy liquids, the development of the high- q shoulder on the second peak has also been observed in x-ray [7] and neutron diffrac-

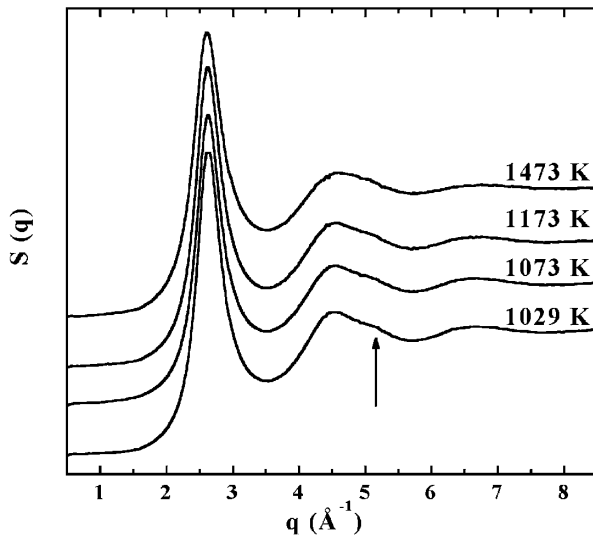


FIG. 2. $S(q)$ for the $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ liquid as a function of temperature. An increase in the intensity of the shoulder on the second peak (indicated by the arrow) is observed as the temperature is lowered below the liquidus temperature (1083 K).

tion [8] studies on pure Ni, further indicating that it reflects growing icosahedral *topological* order.

In a liquid, it may be assumed that tightly bound, close-packed, clusters dominate the scattering at large q , allowing further investigations of the diffraction results. This is illustrated in Fig. 3 at two different temperatures, showing the fit to a 13-atom icosahedral cluster with Ni at the center and Ti atoms on the 12 vertices, consistent with a structural model for the Ti-Zr-Ni quasicrystal [19]. The shoulder, prominent in the experimental data, is reproduced in the $S(q)$ calculated from this cluster, if no thermal effect is considered. When the Debye-Waller (DW) factors, computed following the method used by [20], are included to account for the temperature dependence, the shoulder becomes less prominent, particularly at lower temperatures (lower curve, Fig. 3), contrary to experimental results. This indicates that the DW factors are overestimated and are possibly anisotropic, as has been reported recently for Al-based quasicrystals [21]. The locations and the intensities of the second and third peaks in $S(q)$ fit well, however. In this method, the atom positions are scaled to a fundamental length scale, the icosahedral center to vertex distance [$r_0 = 2.88 \text{ \AA}$ (1473 K) and 2.92 \AA (1029 K)]; the fit thermal deviations are $\langle(\delta r_0)^2\rangle = 0.081 \text{ \AA}^2$ (1473 K) and 0.064 \AA^2 (1029 K).

All thermodynamic models for nucleation predict that clusters of the new phase in the liquid must reach a specific size (the critical size) before they are biased to grow rather than dissolve; the critical size is inversely proportional to the driving free energy, e.g., the undercooling, ΔT , in this case [11]. Since the data in Fig. 2

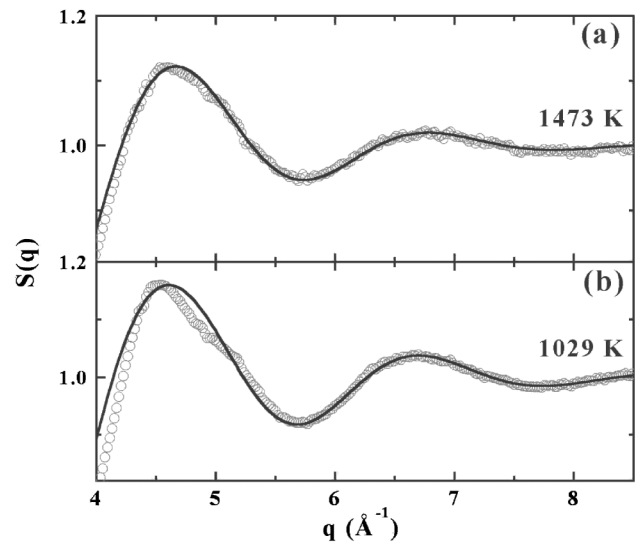


FIG. 3. Comparison between the experimental data (circles) for $S(q)$ for a $\text{Ti}_{39.5}\text{Zr}_{39.5}\text{Ni}_{21}$ alloy liquid at 1473 (a) and 1029 K (b), and the fit to a 13 atom icosahedral cluster decorated by a Ni atom at the center and Ti atoms at the 12 vertices (solid line). Such short-range order is reflected in the second peak (shown), and higher order peaks (not shown).

demonstrate that, at least in this alloy, icosahedral order already exists above the liquidus temperature, the relative length scales of the critical cluster size and the coherence length of the order in the liquid must be important. At equilibrium or near equilibrium conditions (when held isothermally at $\Delta T \leq 30$ K) the stable C14 phase is the primary nucleating phase in the $\text{Ti}_{37}\text{Zr}_{42}\text{Ni}_{21}$ liquid after a long time (not shown here), due to the small driving free energy and the relatively small nucleation barrier arising from the icosahedral short-range order in the liquid. As the temperature of the liquid is decreased, the nucleation of the metastable i phase becomes possible below its metastable liquidus temperature, due to a growing coherence length in the liquid and a decreasing critical size for the i phase (due to an increasing driving free energy). From the classical theory of nucleation [11], the diameter of the critical nucleus is calculated to be approximately 3.5 nm at the recalescence temperature (953 K). The interfacial free energy (0.061 J/m^2), required for such estimates, was obtained from our measured maximum undercooling and the heat of fusion and viscosity data [$\Delta H_f = 8.1 \text{ kJ/mol}$, $\eta = 0.00718 \exp[697/(T - 791)]$ Pascal, unpublished results]. The coherence length estimated from the width of the first peak is approximately 2.1 nm at 1029 K, the lowest temperature for which $S(q)$ could be measured. The coherence length is expected to increase further as the nucleation temperature is approached. While the liquid/cluster interface is certainly more diffuse than assumed within the classical theory [11], such similar length scales clearly suggest that the structural fluctuations in the liquid act as a template, decreasing the barrier for the nucleation of the icosahedral quasicrystal, and blurring the distinction between homogeneous and heterogeneous nucleation of ordered phases with local or extended icosahedral symmetry. Within the classical theory of nucleation (CNT), the nucleation barrier is described by an interfacial free energy between small clusters of the crystal phase and the liquid phase [11]. A correspondence between local order in the liquid and the interfacial energy gives quantitative agreement with experimental undercooling data [22]. While not inconsistent with Frank's hypothesis, the identification of local order with interfacial energy is not required. A formalism (such as an extended density functional approach) that is based on the local order parameter would be more applicable than the CNT for discussions of the nucleation of ordered phases having a local structure that is like that of the liquid.

To summarize, we have demonstrated an enhanced icosahedral short-range order with undercooling in Ti-Zr-Ni liquids that form icosahedral quasicrystals, decreasing the barrier for the nucleation of the metastable i phase, even over the formation of stable polytetrahedral crystal phases. This verifies Frank's hypothesis that the origin of the barrier to nucleation of crystallographic phases is the formation of local icosahedral

order in the liquid. The data presented demonstrate that the *local* order in the liquid strongly influences the nucleation of specific phases. While it is not surprising that the local structures of strongly bonded liquids or polymers influence the phases that form, these results demonstrate that the same is true in metallic liquids, although the atomic interactions are weaker and more isotropic. The influence of preexisting local order in the liquid, then, is an important ingredient in the liquid/solid phase transition that should be considered in theoretical treatments of nucleation.

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