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A. K. Gangopadhyay[1], G. W. Lee[1], J. R. Rogers[2], T. J. Rathz[3], A. I. Goldman[4], D. S. Robinson[4], R. W. Hyers[5], K. F. Kelton[1]

[1]Department of Physics, Washington University, St. Louis, MO 63130; [2]NASA Marshall Space Flight Center, Huntsville, AL 35812; [3]University of Alabama, Huntsville, AL 35801; [4]Ames Laboratory USDOE and the Department of Physics and Astronomy, Iowa State University, Ames IA 50011; [5]University of Massachusetts, Amherst, MA 01003

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Introduction

The local structural order in liquids, and the similarity of that to the order in crystal phases that form from the liquid during freezing, are questions of fundamental interest. In 2002, we developed a new technique (BESL, Beamline Electrostatic Levitation) that enabled high-energy x-ray diffraction studies to be made on liquid and solid samples that were levitated in an electrostatic field (ESL). We measured the structures of equilibrium and supercooled Ti-Zr-Ni liquids and correlated this with the phase formation sequence during solidification. An observed growing icosahedral order led to the preferential nucleation of a metastable icosahedral quasicrystal, demonstrating a half-century-old hypothesis connecting the local order in the liquid to a nucleation barrier (a barrier to the formation of the ordered phase) [1]. We subsequently discovered that icosahedral order is present even in some pure liquid 3d transition metals, such as Ni, but it becomes distorted as the angular dependence of the interatomic potential becomes dominant, as in Ti [2].

Our initial measurements were intended to serve only as a proof-of-concept; the results greatly exceeded expectations. In 2003, the structures of a variety of elemental and alloy liquids were measured to address questions raised by the initial studies.

Methods and Materials

A large range of equilibrium and supercooled liquids were studied, including elemental Si, Ni, Pd, Ti, and Zr, and alloys of Ti-Zr, Ti-Zr-Ni, Ti-Zr-Ni-Ag, Ti-Zr-Ni-Pt, Ti-Hf-Ni, Ti-Zr-Hf-Ni, Zr-Pd, Zr-Nb-Cu-Ni-Al, Zr-Ti-CuAl-Ni, Ti-Fe- Ti-Fe-Si, and Ti-Fe-Si-O. All samples were processed in BESL, in which samples are processed by electrostatic levitation (ESL), which has significant advantages over other levitation methods. Sample heating is completely decoupled from sample levitation, supercooling studies are made in high vacuum (~ 10^{-8} torr), the samples that can be studied are not limited by their electrical conductivity, and sample position can be maintained to within better than 100 μm. The samples were heated using one or more lasers to temperatures that could far exceed the melting temperatures.

A schematic diagram for BESL is shown in figure 1. Two separate Be windows were installed in the ESL chamber at diametrically opposite ends of the chamber for the entrance of the incident x-ray and the exit of the diffracted beam. High energy x-rays (125 keV) were used to allow measurements at high q; sample absorption and multiple scattering were also small at these energies. In the original version of BESL, scattering data could only be obtained to q ~ 8.5 $Å^{-1}$, limited by the diameter of the Be exit window. This was increased to ~ 14 $Å^{-1}$ for the measurements made in 2003, although background effects hindered quantitative interpretations for q > 11 $Å^{-1}$. Diffraction patterns were collected in less than one second using a MAR3450 area detector and at continuous rates of up to 30 patterns per second using a GE Revolution 41-rt area detector.

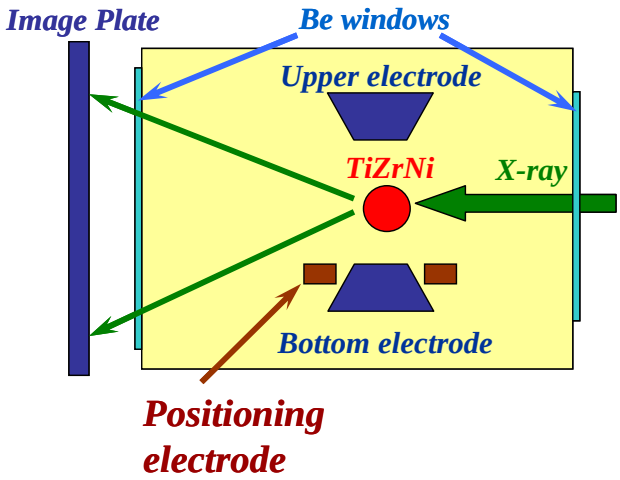

FIG 1 –A schematic diagram of BESL, showing the position of the sample, levitation electrodes, and the diffraction geometry.

Results and Discussions

A detailed analysis of the diffraction data is not yet complete. The results already obtained, however, provide new information on the structures of supercooled liquids, critique theoretical predictions of liquid-liquid phase transitions, allow an examination of some proposed reasons for metallic glass formation, and constitute a proof of concept for a new method for the rapid and accurate determination of phase diagrams and the phase formation sequence in high temperature alloys. Two case studies that are being prepared for publication are briefly mentioned here.

A. Structural Studies of Supercooled Liquid Silicon

Aptekar first predicated a liquid-liquid phase transition in Si[3]. Computer simulations indicate that the occurrence and nature of these transitions are sensitive to the form of the assumed interatomic potential[4-8]

Recently, containerless processing techniques were used to investigation these questions. Results from X-ray studies of liquid Si, made using conical nozzle levitation (CNL) [9,10] and electromagnetic levitation (EML) [11], indicate no discontinuous liquid-liquid transition with supercooling. While a change in the

coordination number was reported in both studies, in once case it decreased (6.3 at 1767 K to about 5.65 at 1458 K) [9,10] while in the other case it increased (4.9 at 1893 K to 6.1 at 1403 K) [11].

X-ray diffraction measurements were made as a function of temperature in BESL using the GE Revolution 41-rt area detector, obtaining structural information of liquid Si at the deepest supercooling yet attained. Figure 2 shows S(q) as a function of temperature for liquid Si; complete diffraction patterns were obtained each second. While there is little change in the peak positions, the intensity of the high-q shoulder on the first peak continuously increases relative to the low-q shoulder with decreasing supercooling, indicating ordering in the liquid. Interestingly, no discontinuous change was observed, as might be expected for a liquid-liquid phase transition.

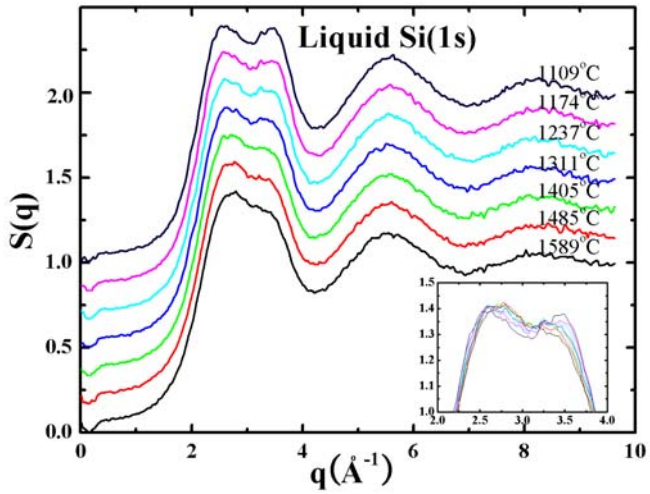

FIG 2: S(q) for liquid Si as a function of temperature; the inset shows the first peak.

Figure 3 shows S(q) measured at a rate of 10 Hz, allowing structural studies to be made down to recalescence, where the liquid nucleates the crystal phase, demonstrating that the structural changes are continuous.

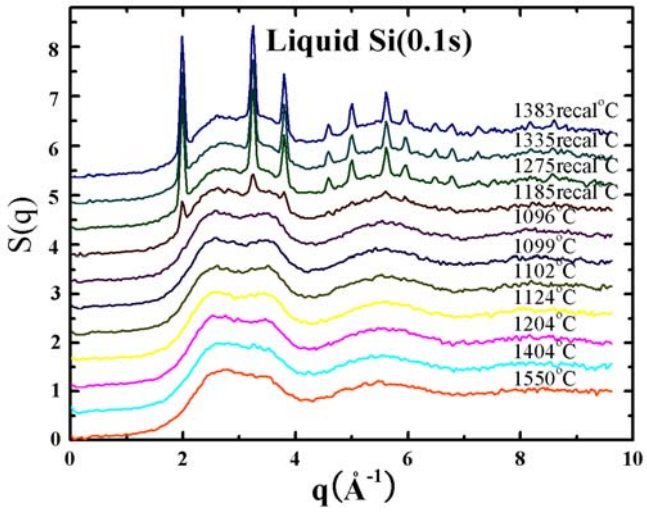

FIG 3: S(q) from diffraction patterns taken at a rate of 10 Hz. The samples nucleates the crystal phase at 1185C.

The coordination number as a function of temperature, computed from the g(r) calculated from the S(q) data in figures 2 and 3 is constant, 6 ± 0.1, in contradiction with previous experimental studies and theoretical predictions. These more accurate data, then, indicate the absence of a liquid-liquid phase transition in supercooled Si, down to the recalescence point.

B. Rapid Identification of Phase Formation Sequence in High Temperature Alloys

High reactivity with container materials and the environment are major obstacles in the study of high temperature materials. BESL provides an opportunity for *in-situ* structural studies of stable and metastable phases of a large variety of materials at any temperature of practical interest. This is illustrated in figure 4, showing the phase formation sequence of a Ti-Fe-Si-O alloy studied by BESL from above the liquidus temperature, T_l, down to room temperature. These data were obtained in only a few minutes of experimental time, using the GE Revolution 41-rt area detector.. The levitated sample was superheated approximately 180 K above T_l and the droplet was allowed to cool by turning off the laser power; the containerless environment and high vacuum ensured free radiative cooling. The temperature was measured every 60 ms and X-ray diffraction data were collected at 1 pattern/s during cooling.

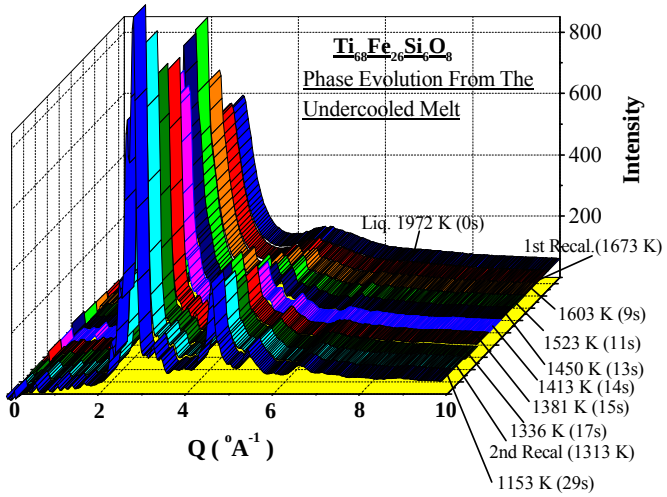

FIG 4: Nucleation and growth of different solid phases from a supercooled liquid droplet of $Ti_{68}Fe_{26}Si_6O_8$ during free radiative cooling in BESL [36].

The solid that nucleated after the first recalescence at 1584 K, changed little except for an increase in fraction until the second recalescence occurred at 1460 K. The first nucleating solid was identified as a hexagonal phase (a = 3.0| Å, c = 4.89 Å), similar to the oxygen stabilized α-Ti phase. At the second recalescence temperature of 1460 K, another solid, identified as a bcc 1/1 crystal approximant phase (13.19 Å) nucleated. A close examination of the diffraction pattern between 2 – 6 $Å^{-1}$ shows clear changes over this temperature range. The α-Ti and some liquid phase still remained after the second recalescence. On further cooling, the 1/1 approximant phase started growing at the expense of the α-Ti, consuming the remainder of the liquid. Finally, below approximately 1300 K, the entire sample solidified to the 1/1 approximant phase. This clearly shows that the 1/1 approximant

phase forms by a peritectic reaction of the α-Ti with the liquid. Interestingly, the as-cast alloy showed only the 1/1 approximant phase with a small amount of TiFe. Therefore, without *in-situ* studies, it would have been extremely difficult to identify the intermediate solid (α-Ti) and the formation mechanism of the 1/1 approximant phase. The whole experiment lasted for only about 40 s, demonstrating the speed and power of this newly developed technique

Conclusion

The data presented clearly demonstrate the capabilities of BESL for fundamental studies of liquid structures and phase formation sequences for high temperature materials. Coupled with ESL measurements of the thermophysical properties, new insight is emerging of the impact of structure on liquid stability, phase transitions, and glass formation.

Acknowledgements

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