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1999 J. Phys.: Condens. Matter 11 L569

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## LETTER TO THE EDITOR

**The structure of supercooled elemental liquids**Shankar Krishnan<sup>†</sup> and Stuart Ansell<sup>‡</sup><sup>†</sup> Containerless Research, Inc., Evanston, IL 60201, USA<sup>‡</sup> ESRF, Grenoble, France

Received 8 October 1999, in final form 9 November 1999

**Abstract.** Recent measurements of the atomic structure of supercooled liquid B, Ni, Si and Zr show a short-range structure similar to that of the nucleating crystalline phases. As the liquids are supercooled, the coordination numbers and interatomic distances increase, decrease or remain essentially constant to approach the values characteristic of the crystals that nucleate from the liquid. Further support for the present observations comes from prior results on Ga, Ge and Pd. This observed correlation between supercooled liquid and crystalline structures provides new insight into nucleation phenomena. The trends in the experimental results and the relationship between the short-range structural properties of supercooled elemental liquids and their crystalline counterparts are discussed.

The earliest model for the structure of liquid metals was proposed by Frank [6] who suggested that monatomic liquids, including most liquid metals, contained icosahedral (12-fold coordination) order. The structure of liquids in the supercooled state is of considerable interest in connection with classical nucleation theory [7]. Our recent results [1–5] clearly show that the first-shell coordination and interatomic distances in the supercooled liquid approach the corresponding values of the nucleating solid at the nucleation temperature. In this letter, we summarize and discuss these new liquid structure results.

The structural measurements on supercooled liquids were obtained by integrating an apparatus for levitation of liquid samples with an x-ray synchrotron radiation scattering facility [1]. Deep undercooling of the liquid was achieved in the containerless conditions. Structure factors,  $S(Q)$ , and pair distribution functions,  $g(r)$ , were calculated from the scattering measurements, from which nearest-neighbour distances and coordination numbers were derived. Table 1 summarizes the coordination numbers and nearest-neighbour distances for the liquids. The table includes melting temperatures and short-range structural data for amorphous and crystalline phases.

The results for liquid silicon [2] show that, as the liquid is supercooled, the sub-peak located between the two main peaks in the  $g(r)$  splits into two weak features. This is accompanied by a reduction in the coordination number for the first shell from  $6.4 \pm 0.5$  at 1829 K (143 K above the melting point) to  $5.6 \pm 0.5$  at 1560 K (130 K below the melting point). Extrapolation of this trend to the homogeneous nucleation limit ( $\approx 330$  K below the melting point) yields a mean first-shell coordination of  $4.6 \pm 0.5$ , similar to the value of 4 for covalently bonded solid silicon. A reduction in coordination with supercooling has been predicted from recent molecular dynamics (MD) simulations [8]. The mean nearest-neighbour distance for liquid Si also decreases with supercooling to approach the interatomic distance values for crystalline silicon (table 1).

**Table 1.** Short-range structural properties of liquids, supercooled liquids, nucleating crystals and amorphous phases.

Element and phases	Temperature (K)	Coordination number	Interatomic distance (Å)	References	
Si	liquid	1829	$6.4 \pm 0.5$	$2.46 \pm 0.01$	[2]
	supercooled liquid	1560	$5.6 \pm 0.5$	$2.41 \pm 0.01$	[2]
	crystal	1686 <sup>a</sup>	4	2.35	[10]
	amorphous		3.6–3.9	2.41	[11]
B	liquid	2580	$5.8 \pm 0.5$	$1.76 \pm 0.01$	[3]
	supercooled liquid	2070	$6.2 \pm 0.5$	$1.78 \pm 0.01$	[3]
	crystal	2360 <sup>a</sup>	6.6	1.833	[12, 13]
	amorphous		6.4	1.803	[12]
Zr	liquid	2600	$12.5 \pm 1$	$3.19 \pm 0.01$	[4]
	supercooled liquid	2000	$9.75 \pm 1$	$3.11 \pm 0.01$	[4]
	crystal	2125 <sup>a</sup>	8	3.20	[10]
	amorphous		12	3.125	[14]
Ni	liquid	2000	$11.8 \pm 0.5$	$2.54 \pm 0.01$	[5]
	supercooled liquid	1550	$11.9 \pm 0.5$	$2.52 \pm 0.01$	[5]
	crystal	1726 <sup>a</sup>	12	2.505	[10]
	amorphous		12	2.492	[15, 16]

<sup>a</sup> Melting temperatures.

Results on crystalline and amorphous materials are at room temperature.

Supercooling of liquid boron also results in structural changes [3]. Recent *ab initio* MD simulations [9] for the high-temperature liquid are in excellent agreement with the present experimental results. As the liquid is supercooled, there is considerable sharpening of the two main peaks and shifts in their relative position in the  $g(r)$ . The mean first-shell coordination number increases slightly from  $5.8 \pm 0.5$  in the normal liquid to  $6.2 \pm 0.5$  in the supercooled liquid, approaching the value of 6.6 for  $\beta$ -rhombohedral boron. In addition, the mean interatomic spacing increases with supercooling to approach values observed in crystalline boron.

The mean first-shell coordination for liquid zirconium *increases* with increasing temperature [4]. At low temperatures ( $T \approx 2000$  K) in the supercooled melt, the first shell coordination is  $9.8 \pm 0.5$ . As the temperature of the melt increases, a rapid change in first-shell coordination is observed to  $12.6 \pm 0.5$  at 2600 K. Solid zirconium has two crystalline modifications, the low-temperature  $\alpha$ -hcp and the high temperature  $\beta$ -bcc phase. The solid phase that forms from the supercooled liquid has the bcc structure which undergoes a martensitic transformation to the  $\alpha$ -hcp structure at a temperature of about 1000 K when the solid is cooled to room temperature. The mean interatomic spacing values decrease in the supercooled liquid and approach the crystalline values.

Liquid nickel [5] shows no significant change in the structure with supercooling. The mean first-shell coordination remains at  $11.9 \pm 0.5$  over a 600 K temperature range, including 200 K in the supercooled regime. The stable solid phase of nickel has the fcc structure with a first-shell coordination of 12. The interatomic spacing values do not change appreciably with supercooling, and it can be seen that the liquid values are essentially the same as the amorphous and crystalline values.

Table 1 shows that each of the four elements has similar short-range structural parameters in the deeply supercooled liquid, amorphous and crystalline phases. The larger coordination in amorphous Zr relative to the liquid should not be considered an exception since the supercooled liquid is similar to the higher-temperature eight-coordinated solid phase and the amorphous

material is deposited at lower temperatures where the solid is 12 coordinated. The similarity between the amorphous and crystalline phases is well known and has been discussed in the literature [15, 16]. However the idea that the supercooled liquid and crystalline solid exhibit similar short-range order near the nucleation temperature is new.

Some further results in the literature support the present observations. X-ray absorption measurements on normal and supercooled liquid gallium [17] show that the liquid structure is essentially similar to that of  $\beta$ -Ga, which is the crystal that nucleates from the deeply supercooled liquid. A neutron diffraction study on supercooled Ga [18] gave a first-shell coordination of 10.2 at moderate supercooling, similar to the coordination of  $\beta$ -Ga, and quite different from a value of seven for the stable  $\alpha$ -Ga. The  $S(Q)$  for supercooled liquid Ga exhibited a pronounced shoulder on the high- $Q$  side of the first peak [18, 19] similar to that for  $\beta$ -Ga. The  $\beta$ -Ga-like features appear to increase in strength with deeper supercooling and the similarities between the supercooled liquid and crystalline phases were discussed [19]. Considering that there are four possible crystalline forms of Ga, the tendency for the liquid structure to assume the short-range structure of the nucleating crystal provides further support for our correlation. The similarity between supercooled and nucleating crystal structures has also been suggested for supercooled Bi and Hg [19].

Filliponi and Di Cicco [20] measured the EXAFS spectrum of Ge in the 950–1610 K temperature range including the supercooled liquid state. They reported a continuous decrease in the location of the first peak maximum in the  $g(r)$  and a reduction in first-shell coordination with supercooling, similar to the results on silicon. The change in coordination in liquid Ge is also predicted by the *ab initio* MD simulations of Kresse and Hafner [21]. A recent experimental study of supercooled Pd [22] shows well defined structural differences between the normal and supercooled liquid Pd. In addition, the results show a slight increase in the Pd–Pd nearest-neighbour distance and a slight increase in coordination with supercooling. Further measurements nearer the supercooling limit are needed to assess if the short-range structure begins to resemble the nucleating crystalline phase.

It is noted that the supercooled liquid results presented here were obtained in each case at temperatures somewhat greater than their supercooling limits. It is well known that most liquids can be supercooled to approximately 80% of their melting temperatures. For example, bulk supercoolings of 330 K for Si [23], 350 K for Ni [24], 350 K for Zr [25] and 280 K for B [3] have been achieved in containerless experiments. We predict further changes in the liquid structure that minimize the differences in the short-range structure between the liquid and the nucleating crystalline phases as the supercooling limit is approached.

Frank's model [6] of 12-fold (icosahedral) coordination is generally accepted to describe monatomic, close-packed liquids. The results on liquid nickel and zirconium and those of Waseda [26] on several other liquid metals show 12-fold coordination at temperatures above the melting point, in support of this model. However, it is also demonstrated that the coordination can change with temperature in the supercooled state even for zirconium which is 12 coordinated at higher temperatures. The low coordination numbers for liquid B and Si arise from the presence of directional bonding and open packing, and these liquids are not suggested as tests of the Frank model [6]. However they do show the same trend that is observed in all cases for which structural data are available for supercooled liquids, that coordination and nearest-neighbour distances in the liquid approach those of the crystalline material at the nucleation temperature.

The changes in the liquid structure upon supercooling reported here have implications for classical nucleation theory. The results suggest that the change in the entropy across the liquid–solid interface is reduced as liquids are undercooled. Given Spaepen's entropic view [27] of the solid–liquid interfacial free energy, the interfacial free energy term will be reduced as a

function of temperature. Certainly the change in entropy from liquid to solid will be smaller for a liquid with the short-range structure of the nucleating solid than for a solid without this structure. The observed changes with supercooling would also reduce the volume free energy difference between the liquid and solid; however, the interfacial free energy term dominates and should significantly lower the work of formation of a critical nucleus. This will increase the nucleation rate at all temperatures and reduce the supercooling required for homogeneous nucleation.

Can these observations be extended to other liquids? Do the present results imply a universal behaviour for elemental liquids? The limited number of experimental observations and the lack of theoretical framework prevent a universal behaviour from being confirmed at this time. In molecular and network liquids, chemical ordering and phase selection also play a major role in the nucleation process and have to be taken into account. For a large number of one-component (monatomic) systems, the structure of the nucleating crystalline phases is fixed usually by the presence of an equilibrium solid phase that is stable over a wide temperature range. In some elements such as iron and the actinides, a number of allotropes occur near the melting point; structural studies in the supercooled state and phase selection studies for these elements have the potential to provide a stronger foundation for generalizing the ideas presented here. Should such a foundation be provided, it could be established that (i) the liquid coordination, nearest-neighbour distance and short-range structure in supercooled elemental liquids always approaches the corresponding properties of the crystalline phase which nucleates from the liquid, and (ii) when more than one phase can nucleate, the one which most closely matches the supercooled liquid structure is the crystalline phase that forms.

In conclusion, the generally accepted model of 12-fold coordination is seen to be an accurate description of the structure of monatomic liquids at temperatures near to and above the melting point. However, this model is not accurate in the supercooled liquid state. All of the present experimental results and prior results on other liquids show that the short-range structure of supercooled liquids approaches that of the crystalline phase that nucleates from the melt near the supercooling limit.

This work was supported by the US Department of Energy Small Business Innovative Research (SBIR phase I and phase II grants) and by the Division of Materials Science, Office of Basic Energy Sciences, under contract W-31-109-ENG-38. The authors thank Dr Paul Nordine, Dr William Hofmeister, Professor John Perepezko and Professor Ken Kelton for their valuable comments and critically reviewing the manuscript.

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