Structure of Liquid Boron

S. Krishnan,[1] S. Ansell,[2] J. J. Felten,[1] K. J. Volin,[2] and D. L. Price[2]
[1]Containerless Research, Inc., 906 University Place, Evanston, Illinois 60201
[2]Argonne National Laboratory, Argonne, Illinois 60439

(Received 14 April 1998)

The structure factor $S(Q)$ and the pair distribution function $g(r)$ has been measured for liquid boron in the temperature range 2600–2000 K, extending over both the normal and supercooled liquid states. The bond length and coordination number of the first coordination shell are similar to those reported for the crystalline and amorphous solid forms, but the second and third coordination shells are broader and shifted to higher distances. The insulator-metal transition that takes place in boron upon melting is associated with a relatively small change in both volume and short-range order. [S0031-9007(98)06684-8]

PACS numbers: 61.20.Ne, 61.10.Eq, 61.43.–j

Boron and boron-rich borides have numerous technological applications, particularly where a hard and light material is required. Boron-rich solids are characterized by a series of uncommon crystal structures associated with unusual bonding in the solid state [1]. They range from superconducting metals to wide-gap insulators, and can have very high or very low thermal conductivity. This large range of properties derives from the unusual character of covalent bonding in pure boron and modifications of the bonding when other elements are added to the boron network.

The crystalline phases of boron are among the most complex structures reported for a pure element [2]. Over 50 crystalline modifications of pure boron have been proposed. It is now accepted that most of these are stabilized by small amounts of impurities, and only the α- and β-rhombohedral, and possibly the tetragonal, forms are considered as pure boron [1]. Amorphous forms of boron have also been studied, and a recent neutron diffraction study has reported that the short-range structure resembles that of the β-rhombohedral (B_{105}) crystal [3]. This phase, obtained on crystallization from the melt, is considered to be the thermodynamically stable state at all temperatures below the melting point. The α-rhombohedral (B_{12}) phase transforms to the β phase above about 1200 °C [1].

The crystal structures of boron and boron-rich borides are dominated by the B_{12} regular icosahedral unit. In the α-rhombohedral form, the icosahedra are connected via a combination of two-center and three-center bonds, so that the average coordination of six of the boron atoms in each icosahedron is six and that of the other six atoms is seven, giving a mean coordination of 6.5 [1]. Approximately $\frac{1}{3}$ of the bonds are directed outward from the pseudofivefold axes and participate in the intericosahedral bonding, while the remainder participate in intraicosahedral bonding. In the β-rhombohedral structure, the icosahedra are surrounded by pentagonal pyramids, producing a 105-atom unit cell with an average coordination number of 6.6 [1,2]. When metallic elements are added to pure boron, they are incorporated within the intericosahedral network, the icosahedra themselves being rarely broken in boron-rich metallic compounds [1,2].

There are few experimental measurements on liquid boron, due to the fact that boron is extremely reactive with any container even in the high-temperature solid state; in the liquid it reacts with any known container. The literature indicates that boron undergoes an insulator-metal transition upon melting and expands by approximately 5% [4], in contrast to silicon or germanium that also undergo an insulator-metal transition on melting but *contract* by about 10%.

Vast *et al.* [5] recently performed *ab initio* molecular dynamics (MD) simulations of solid and liquid boron. They used a cell of 48 atoms and employed two different pseudopotentials to evaluate the structural properties and dynamics of the liquid. Their results for the liquid at 2600 K gave peaks in $g(r)$ at 1.71 and 3.18 Å with an average coordination of about 6. The structure exhibited a broad bond-angle distribution with peaks at 56° and 108° corresponding to the intraicosahedral angles: the corresponding peaks for the crystal occur at 60° and 108°. Bond angles corresponding to the intericosahedral bonds were noticeably absent. They concluded that the icosahedral and pentagonal pyramidal arrangements of boron atoms are destroyed upon melting and that liquid boron assumes an open-packed structure with sixfold coordination.

The electrical conductivity calculated from the MD simulation is very high—about $2.5 \cdot 10^4$ $(\Omega\ \mathrm{cm})^{-1}$ compared with $\sim 10^{-12}$ $(\Omega\ \mathrm{cm})^{-1}$ in the solid—consistent with an insulator-metal transition on melting. The electrical conductivity of liquid boron has not been measured. It has been estimated [6] to be above 10^3 $(\Omega\ \mathrm{cm})^{-1}$ from the fact that a 15-mm-diameter bar can be rf heated at 450 kHz.

In this Letter, we present an experimental measurement of the atomic structure of liquid boron. Because of the high reactivity of boron with any container, we employed a levitation technique combined with synchrotron x-ray diffraction [7–9]. Approximately 3–4-mm-diameter, arc-melted specimens of 99.9995% pure boron were employed; these specimens could be prepared in the form of flat disks, supporting the previous observation of a low surface tension for the liquid [4]. X-ray diffraction of the starting material showed it to be the β-B_{105} rhombohedral phase. The specimens were cleaned before being introduced into the levitation system. Chemical analysis of the starting material provided by the supplier listed the major impurity to be carbon (<100 ppm). The x-ray diffraction measurements were made at the beam line X-25 at the National Synchrotron Light Source at a chamber pressure of 400 mbar, with a levitation gas flow rate of about 350 cm^3 per minute at STP of pure argon. The oxygen and nitrogen content in the levitation gas was less than 0.1 ppm. The residual oxygen was actually beneficial to the experiments because at high temperature it was possible to remove the residual carbon (in the boron specimens) by gasification of the carbon as CO, favored by 100:1 in comparison to gasification of boron as BO [10]. The specimens measured after the levitation experiments all had the β-rhombohedral phase, confirming the retention of high purity during the measurements.

A 270-W CO_2 laser was employed as the heat source to achieve liquid temperatures in the range 2000–2700 K. The melting point of boron has been previously measured to be 2360 ± 10 K [11]. One of the key factors in achieving stable liquid specimens was to defocus the laser beam at the specimen, which prevented the solid specimens from being thermally shocked and the liquid droplets from becoming unstable due to localized heating. Diffraction measurements were made at 2600, 2400, and 2090 K: these temperatures are uncertain by 25 K, due primarily to slow fluctuations during the experimental runs. The temperatures were measured using two different pyrometers with operating wavelengths of 0.65 and 2.0 μm and emissivity corrections were applied based on the observed radiance temperature at the known melting point: a radiance temperature of 2096 ± 5 K was measured by the 0.65 μm pyrometer giving a metallic-like emissivity of 0.31 ± 0.02. The somewhat large uncertainty is due to the corresponding uncertainty in the melting temperature [11]. The uncertainty in temperature arising from the temperature gradient is relatively small: while temperature gradients over the entire height of the sample were estimated to be in the range of 20–30 K, both the pyrometry and diffraction measurements sampled only the upper surface of the specimen. By reducing the laser power, it was possible to access the supercooled liquid state and maintain it for the durations needed for the diffraction measurements.

Diffraction data were obtained at x-ray energies of 8800, 12 000, and 14 980 eV. Scattered x rays were detected using a solid-state detector with 300 eV resolution over a 2θ angular range of 10°–110°, giving diffraction data over a scattering vector (Q) range of 1.2–13 Å^{-1}. The x-ray background and attenuation of the incident x rays by the ambient gas at the operating pressure in the experiment chamber were independently measured without a specimen. The data analysis, following procedures described previously [7–9], was modified to include the sample height in the beam as a parameter in fitting the data. Form factors were obtained from Baro *et al.* [12]; the temperature dependence of the form factors was obtained from Ref. [13]. Further details of the x-ray analysis procedure will be described in a forthcoming publication [14]. The analysis procedure used the density as a fitting variable, and the optimized result produced a volume expansion on melting of 5%, in good agreement with the value of 4.5% reported in Ref. [4].

The structure factor $S(Q)$ measured at temperatures of 2600, 2400 (normal liquid), and 2090 K (supercooled liquid), with an x-ray energy of 14 980 eV, is shown in Fig. 1. At all three temperatures, $S(Q)$ is characterized by a weak first peak at approximately 2.5 Å^{-1} followed by the main peak located at 4.4 Å^{-1}. Figure 2 shows the pair distribution function $g(r)$ at the same three temperatures. This was obtained with an inverse Fourier transform method employing a maximum entropy criterion [15] with $g(r)$ constrained to tend to one at large r. The peak positions and the coordination number of the first coordination shell are given in the upper part of Table I. The positions of the peaks in $g(r)$ are not significantly affected by the large temperature change, but there is a sharpening of the second and third peaks on supercooling. The coordination number of boron atoms within the first coordination shell rises slightly from 5.8 ± 1.0 to 6.2 ± 1.0 on supercooling (the relative error being considerably less than the absolute errors quoted).

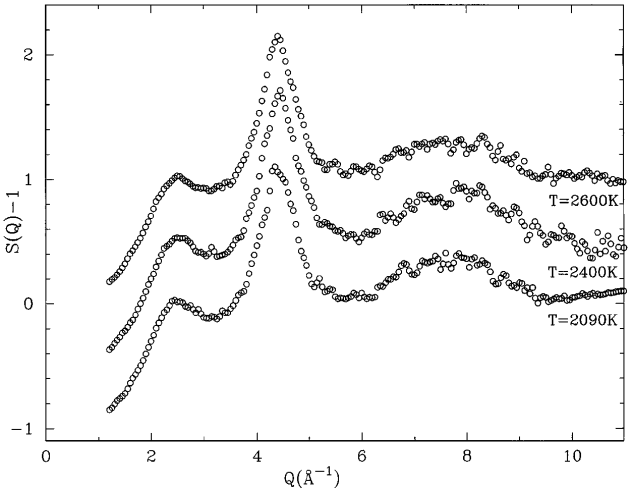

FIG. 1. The x-ray structure factor for liquid boron at three temperatures of 2600, 2400, and 2090 K. The upper curves are displaced by 0.5 and 1 unit for clarity.

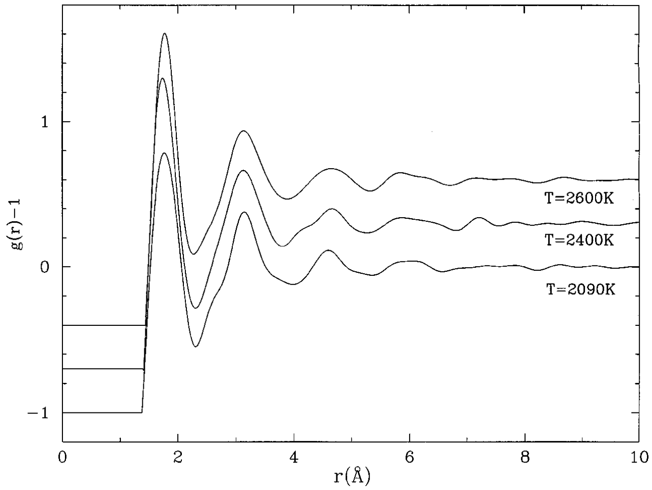

FIG. 2. The pair distribution function for liquid boron at three temperatures of 2600, 2400, and 2090 K. The upper curves are displaced by 0.3 and 0.6 units for clarity.

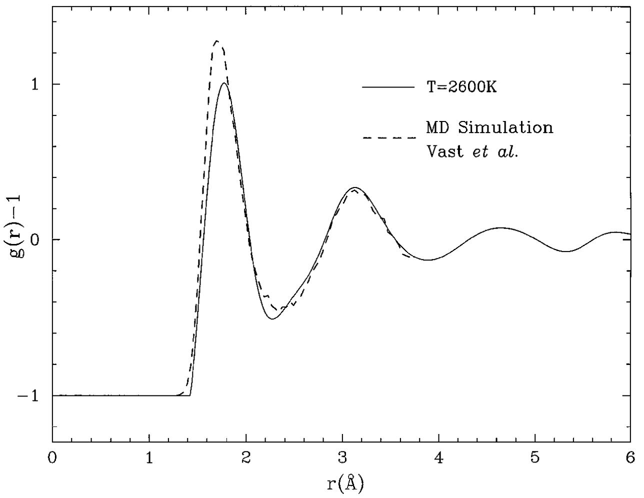

FIG. 3. Comparison of the pair distribution function for liquid boron at 2600 K obtained in the present Letter with the MD results obtained by Vast *et al.* [5].

The present results for $g(r)$ are compared with those obtained by Vast *et al.* [5] with *ab initio* MD in Fig. 3 and the bottom of Table I. The agreement is seen to be reasonable for the first two peaks, although the first peak is slightly stronger and shifted to the left in the MD. The MD results are limited by the size of the simulation—48 atoms—so there are no data beyond 3.5 Å; for the same reason, the $S(Q)$'s cannot be realistically compared.

The present results for $g(r)$ in the supercooled liquid at 2090 K are compared in Fig. 4 and Table I with those for the α- and β-rhombohedral and tetragonal crystalline forms and for amorphous boron obtained by Delaplane *et al.* [3]. For purposes of comparison, thermal broadening corresponding to room temperature has been applied to the $g(r)$ functions of the crystalline forms. The three crystalline and amorphous forms are quite similar in the region of the first peak but differ in the locations and intensities of the subsequent peaks. In Ref. [3] the similarity between the β-rhombohedral and amorphous forms is cited as evidence for the survival of icosahedral units in the amorphous solid. The "first sharp diffraction peak" observed in the $S(Q)$ of the amorphous solid at low Q could be ascribed to the presence of icosahedral units, since the random packing of units of diameter d is known to produce such a peak at $Q \sim 2\pi/d$ [16]. However, a recent *initio* MD simulation of amorphous boron [17] did not produce such units, and it is known that network structures with an appropriate length scale can also produce such peaks [18].

The survival of B_{12} icosahedral units in the amorphous solid, proposed in Ref. [3], raises the question whether they may also survive into the liquid. The good agreement of the present results with the *ab initio* MD simulation [5], which certainly do not contain such units, or even the pentagonal based pyramids that constitute the icosahedra in the solid, might be taken as evidence to the contrary. However, the restricted size of the MD cell would in any case make it difficult for such units to be incorporated, even if there was a tendency for them to be formed in a larger simulation. Furthermore, the icosahedral units appear to be remarkably stable in boron and boron-rich compounds [1,2].

TABLE I. Peak positions in pair distribution function and nearest-neighbor coordination number for liquid and solid phases of boron.

Temp. (K)		r_1 (Å)	r_2 (Å)	r_3 (Å)	C_n	Ref.
Normal liquid	2600 ± 25	1.76 ± 0.03	3.15 ± 0.08	4.7 ± 0.1	5.8 ± 1.0	This Letter
Normal liquid	2400 ± 25	1.78 ± 0.03	3.16 ± 0.08	4.7 ± 0.1	5.8 ± 1.0	This Letter
Superc. liquid	2090 ± 25	1.78 ± 0.03	3.15 ± 0.08	4.6 ± 0.1	6.2 ± 1.0	This Letter
Amorphous	RT	1.80[a]	2.93[a]	4.38	6.3[a]	[3]
α-rhombh.	RT	1.802	2.99, 3.58[b]	4.31	6.5	[1]
β-rhombh.	RT	1.803	3.03	4.56	6.6	[1]
Tetragonal	RT	1.802	2.92	4.47	6.5	[1]
Liquid (MD)	2600	1.71	3.18	···	6.0	[5]

[a] Values obtained from the $g(r)$ plot differ slightly from those quoted in Ref. [3].
[b] Double peak.

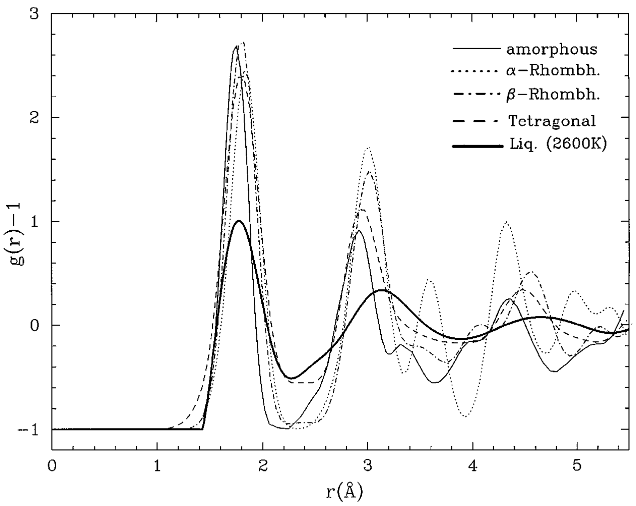

FIG. 4. Comparison of the pair distribution function for liquid boron at 2600 K with those for the amorphous, α- and β-rhombohedral, and tetragonal solid forms.

In the present Letter, diffraction data taken at the lowest x-ray energy, extending the Q range down to values low enough to observe a strong Bragg peak in the crystalline solid at 0.8 Å^{-1}, did not indicate any first sharp diffraction peak which, as remarked above, could be expected if significant numbers of icosahedra were present. In addition, the significant shifts and broadening of the second and third peaks in the $g(r)$ function of the liquid relative to the corresponding peaks in the solid forms suggest that the intermediate-range structure is rather different. In the α-rhombohedral form, the peak at 2.99 Å is associated with the icosahedra and that at 3.58 Å with intericosahedral bonding. Thus, the relatively broad peak in the liquid centered at 3.15 Å may indicate that rather small numbers of icosahedra are present.

In this paper we have presented the first atomic structure measurements on normal and supercooled liquid boron. The short-range structure is surprisingly similar to that of the crystalline and amorphous solids, with little change in bond length but a broadening of the first coordination shell, preserving the coordination number around a value of 6. Supercooling produces a slight sharpening of the second and third coordination shells. Agreement with *ab initio* MD results for the normal liquid is reasonably good, given the restricted cell size of the reported simulation. No conclusive statement can be made at present regarding the intermediate-range order, including the existence of pentagonal pyramids or icosahedra in the liquid. The results show, however, that boron is unique among covalently bonded solids in undergoing an insulator-metal transition on melting with a modest volume expansion and little change in short-range structure.

This work was supported by U.S. Department of Energy (DOE) 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 No. W-31-109-ENG-38. The authors thank Dr. L. Berman of the X-25 beam line for his help. The National Synchrotron Light Source at Brookhaven National Laboratory is supported by the Divisions of Materials Sciences and Chemical Sciences of DOE. The authors also thank Dr. M.-L. Saboungi, Dr. P. Nordine, and Professor J. Enderby for their comments, Dr. N. Vast for providing the numerical MD results, and Dr. R. Sheldon for his help with the crystal data.

[1] R. Naslain, *Boron and Refractory Borides,* edited by V. I. Matkovich, (Springer-Verlag, New York, 1977).

[2] K. C. Buschbeck, *Boron Compounds, Elemental Boron, and Boron Carbides,* Gmelin Handbook of Inorganic Chemistry Vol. 13 (Springer, Berlin, 1981).

[3] R. G. Delaplane, T. Lundstrom, U. Dahlborg, and W. S. Howells, in *Boron-Rich Solids,* edited by D. Emin, T. L. Aselage, A. C. Switendick, B. Morosin, and C. L. Beckel, AIP Conf. Proc. No. 231 (AIP, New York, 1991), p. 241.

[4] F. N. Tawadze, I. A. Bairamashvili, G. V. Tsagareishvili, and D. V. Hantadze, Stud. Cercet. Metal. **10**, 49 (1965).

[5] N. Vash, S. Bernard, and G. Zerah, Phys. Rev. B **52**, 4123 (1995).

[6] J. K. R. Weber (private communication).

[7] S. Krishnan, J. J. Felten, J. E. Rix, J. K. R. Weber, P. C. Nordine, S. Ansell, M. A. Beno, and D. L. Price, Rev. Sci. Instrum. **68**, 3512 (1997).

[8] S. Ansell, S. Krishnan, J. K. R. Weber, J. J. Felten, P. C. Nordine, M. A. Beno, M.-L. Saboungi, and D. L. Price, Phys. Rev. Lett. **78**, 464 (1997).

[9] S. Ansell, S. Krishnan, J. J. Felten, and D. L. Price, J. Phys. Condens. Matter **10**, L73 (1998).

[10] P. C. Nordine (private communication).

[11] S. Krishnan, P. C. Nordine, J. K. R. Weber, and R. A. Schiffman, High Temp. Sci. **31**, 45 (1991).

[12] J. Baro, M. Roteta, J. M. Fernandez-Varea, and F. Salvat, Radiat. Phys. Chem. **44**, 531 (1994).

[13] J. Chihara, J. Phys. F **17**, 295 (1987).

[14] S. Ansell and D. L. Price (to be published).

[15] A. K. Soper, Inst. Phys. Conf. Proc. R. Soc. **97**, 711 (1989).

[16] S. C. Moss and D. L. Price, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritzsche, and S. R. Ovshinsky (Plenum, New York, 1985), pp. 77–95; D. L. Price, S. C. Moss, R. Reijers, M.-L. Saboungi, and S. Susman, J. Phys. C **21**, L1069 (1988).

[17] G. Galli and F. Gygi, Bull. Am. Phys. Soc. **43**, 318 (1998).

[18] G. Galli and M. Parrinello, J. Chem. Phys. **95**, 7504 (1991).