Viscosity of liquid boron

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Viscosity of liquid boron was measured over the temperature range from 2325 to 2556 K using an electrostatic levitation method combined with an oscillation drop technique. The results obtained revealed that the viscosity increases slowly with decreasing temperature from 2.2 mPa s at 2550 K to 2.6 mPa s at 2370 K, and substantially increases with further decrease in temperature below the melting temperature (T_m=2360 K), becoming as large as 6.4 mPa s at 2325 K. The increase in the viscosity suggests that clusters with extension may appear in supercooled liquid of boron.

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Boron (B) and B-rich compounds combine useful properties such as hardness, low density, and chemical inertness.[1] B-rich solids are characterized by a series of uncommon crystal structures associated with unusual bonding in the solid state. They range from superconducting metals to wide-gap insulators. The large range of properties originates from the peculiarity of the covalent bonding in pure B and modifications of the bonding when other elements are added to the B network.

The crystal structures of B and B-rich compounds are dominated by B_{12} units each of which consists of 12 B atoms and possesses the icosahedral structure. The atoms in the B_{12} icosahedral unit of B-based compounds are firmly connected by covalent bonds with each other and appear to be remarkably stable.[2] Moreover, the B_{12} icosahedral units also seem to survive in the amorphous B.[3] Thus, the question has been raised whether the icosahedral units may survive into liquid B.

Until very recently, there have been few experimental measurements on liquid B since it reacts with the walls of containers. The advent of levitation techniques made possible to handle a sample without contamination and to carry out the measurements on the physical properties of liquid B in the temperature region down to the supercooled state. The density and surface tension have been measured with a gas levitation technique.[4] Different density measurements have been performed with a vacuum electrostatic levitator, revealing that B contracts by nearly 3% upon melting.[5] The electrical conductivity of liquid B was measured using a contactless method coupled with gas levitation. It has been shown that the semiconducting property remains even in the liquid state.[6] X-ray diffraction and inelastic x-ray scattering measurements on liquid B were carried out coupled with gas levitation technique in order to address the question whether B_{12} icosahedral units may survive into the liquid state.[7,8] No evidence has been obtained on the survival of the icosahedral units into liquid. *Ab initio* molecular-dynamics simulations of liquid B also suggested that icosahedral arrangements are destroyed upon melting.[8,9] Both of these experimental and simulation studies seem to strongly deny the existence of B_{12}

icosahedral units in liquid B. Instead, as Price *et al.*[8] pointed out in their paper, there still remains possibility that small clusters such as pentagonal units could exist in liquid B. In the more deeply supercooled state of liquid B, if realized, it is expected that small clusters may be connected together and grow larger.

It is well known that the viscosity of liquid changes quite sensitively when the structural orderings such as the forming of large clusters or chain molecules occur in the liquid. In the elemental liquid metals, the temperature variation in viscosity is modest and usually obeys Arrhenius' relation over a wide temperature range including the supercooled states;[10] for instance, the viscosity of molybdenum (T_m=2896 K) increases from 5 mPa s at 3000 K to 7 mPa s at 2650 K following the Arrhenius relation.[11] On the contrary, the viscosity of the liquids forming quasicrystals or related crystals such as AlPdMn and TiZrNi in which a medium range order is considered to exist, substantially increases from 5 mPa s to 20 mPa s with decreasing temperature near the melting temperature and the temperature dependence of the viscosity clearly deviates from the Arrhenius' relation.[12,13] On the basis of these experimental findings, it is worthwhile to examine the possibility of the cluster formation in liquid B through the measurements of viscosity over a temperature range as wide and as low as possible. In the present paper, we report the temperature dependence of the viscosity of liquid B in a large temperature range that includes the supercooled states.

In this work, the electrostatic levitation method combined with the oscillation drop technique was used.[14] Samples were prepared by smashing crystalline lumps of B (99.9% purity, Furuuchi Chemical Corp., Japan) into small pieces. These pieces were melted into spheroids with 2 mm in diameter using an arc furnace under Ar atmosphere. The spheroid samples, charged by thermoelectronic effect, were then levitated one at the time in a high-vacuum environment (approximately 10^{-5} Pa) using electrostatic forces via a feedback loop. Two horizontal electrodes, separated by 10 mm, assured the vertical position control of the sample. The top electrode had a diameter smaller than that of the bottom elec-

trode. This generated a conical electrical field distribution that provided a horizontal field component and thus a natural restoring force toward the center. This, together with four spherical electrodes distributed radially at the height of a levitated sample, offered sufficient sample stability to perform measurements of physical properties. The sample was heated and melted using the focused radiation of three 50 W laser beams with wavelength of 10.6 μm generated by CO_2 laser. This configuration minimized sample oscillations and enhanced temperature uniformity. The radiance temperature was measured by pyrometry with wavelengths of 0.90 and 0.96 μm at a 120 Hz acquisition rate and was calibrated to the precise temperatures of sample by observing the melting plateau of B.

The viscosity and surface tension of liquid B were determined by the oscillation drop technique.[15] In this technique, a $P_2 \cos(\theta)$-mode drop oscillation was induced to the liquid sample by superimposing a small sinusoidal electric field on the levitation field.[16,17] The transient signal that followed the termination of the excitation field was detected and analyzed. This was done several times at a given temperature and repeated for numerous temperatures. Using the characteristic oscillation frequency ω_c of the signal after correcting for nonuniform surface charge distribution,[18] the surface tension σ can be found from the following equation:[16]

$$\omega_c^2 = (8\sigma/r_0 3\rho)Y, \tag{1}$$

where r_0 is the radius of the sample, ρ is the density, and Y is a correction factor depending on the drop charge, the permittivity of vacuum, and the applied electric field. Similarly, using the decay time τ obtained from the same signal, the viscosity η was found by

$$\eta = \rho r_0^2/(5\tau). \tag{2}$$

In Eqs. (1) and (2), real-time values of the radius and density data,[19] determined with an UV imaging technique,[20] were used to prevent any distortion due to the evaporation of liquid sample on the physical properties being measured.

Figure 1 illustrates the temperature variation in the viscosity of liquid B. The viscosity is almost constant above the melting temperature. In the supercooled state, the viscosity substantially increases with decreasing temperature from 3 mPa s at 2360 K to 7 mPa s at 2315 K. As shown in the inset of Fig. 1, the viscosity data with temperature cannot be fitted by the Arrhenius' function. The substantial increase in the viscosity of liquid B suggests that structural orderings possibly occur in the supercooled state. Although there were no data in the literature available to compare with the present results, it is possible to compare our viscosity data on different liquid metals previously obtained by using the present same technique with others. These viscosity data are in agreement with those obtained by well accepted different methods.[21] The results of the present viscosity measurements for liquid B are equally considered to be reliable.

Figure 2 shows the temperature dependence of the surface tension of liquid B which was determined at the same time as that of the viscosity. The surface tension of liquid B, as ob-
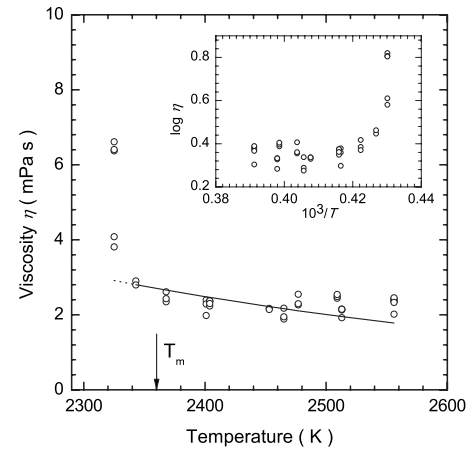

FIG. 1. Viscosity of liquid B as a function of temperature. Solid line shows the Arrhenius line. The inset shows the Arrhenius plot. The uncertainty of the viscosity measurements was estimated to be around 10%.

served in many other liquid metals, exhibited a linear behavior as a function of temperature and can be fitted by the relationship,

$$\sigma(T) = 1.06 \times 10^3 - 6.7 \times 10^{-2}(T - T_m) \ (\text{mN m}^{-1}). \tag{3}$$

The present data of surface tension agree well with those obtained by Millot *et al.*[4] using the aerodynamic levitation technique. The discrepancies between these data are almost 2% in the whole temperature range of both measurements which are within 5% in uncertainty in the present measurement.

It is interesting to compare the value of viscosity of liquid B in the temperature range where Arrhenius' relation holds with those of other liquid metals. The value is larger by several factors than those of liquid alkali metals such as Li, Na, and K,[22] and is nearly the same as those of liquid Ga (Ref. 23) which belong to 13 elements group in the periodic
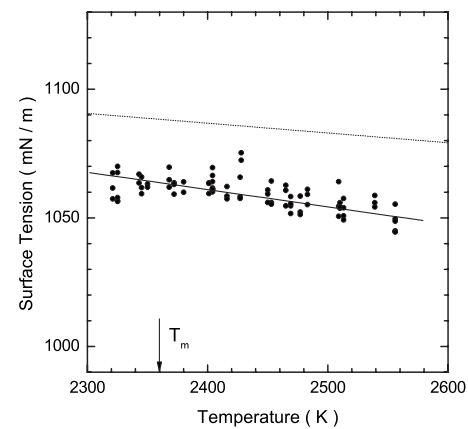

FIG. 2. Surface tension of liquid B as a function of temperature. Solid line shows the fitting by the Eq. (3). Dashed line shows the surface-tension data by Millot *et al.* (Ref. 4). The uncertainty of the surface-tension measurements was estimated to be better than 5% from the response of the oscillation detector and from the density measurements.

table as B does. Also, it would be interesting to look at the longitudinal viscosity η_l of liquid B which was obtained by the high-resolution inelastic x-ray scattering measurements[8] since η_l relates to the shear viscosity η_s through the bulk viscosity η_b, following the equation obtained by the generalized theory of hydrodynamics,[24] $\eta_l = 4/3 \eta_s + \eta_b$, in which our present viscosity data can be used for η_s. The value of η_l for liquid B at 2370 K was estimated to be about 15 mPa s and was extracted to the long-wavelength limit.[8] The value is again almost the same as that of liquid Ga (Ref. 23) and much larger than those of liquid Li, Na, and K for which the values of η_l are between 2 and 3 mPa s.[25] The difference between η_l and η_s in liquid B is quite large and as the result η_b is about 12 mPa s. It is noted that the value is rather large compared with those of liquid alkali metals, the values of which are about $1-2$ mPa s. Also, the ratio η_b/η_s of liquid B is more than twice as large as those for liquid alkali metals. Thus, one of the most prominent features from view of the viscosity may be that liquid B has a large value of η_b. As is well known, the η_b means a viscosity response against a volume change accompanying the compression or expansion and closely relates to the bulk modulus. Therefore, the large η_b indicates a strong stiffness of liquid B, possibly arising from the directional bonding of pentagonal clusters. The existence of such clusters was suggested by Price et al.[8] It is noteworthy that liquid Ga is known to be a nonsimple liquid metal and to have an anomalous structural feature in the structure factor.[26] The large η_b of liquid Ga, as well as liquid B, may come from their peculiar nature in the local atomic arrangements and their bindings, different from those of simple liquid metals.

The substantial increase in the viscosity shows the uniqueness of supercooled liquid B since the temperature dependence of almost all the elemental liquids follows the Arhenius' equation except for liquid sulfur and selenium for which viscosities dramatically increase with decreasing temperature forming long polymeric chains.[27,28] The increase in the viscosity of liquid B in the supercooled states suggests that there appear some extending clusters or structural units with a long lifetime in the supercooled states. Price et al.[8] have proposed that small clusters with pentagonal structure could appear in the liquid B above the melting temperature (2400 K) and also in supercooled state at 2340 K. It is noticed, however, that the temperature dependence of viscosity of liquid B still follows the Arhenius' equation in the temperature range where the x-ray diffraction measurements were made. Therefore, the substantial increase in the viscosity in the supercooled liquid B observed in the lower temperature range might be caused by the other origin except for the pentagonal unit. In the supercooled states below 2325 K, the growth of clusters could be favored resulting in the substantial increase in viscosity: the pentagonal units could be connected each other and grow largely, and the lifetime of such large cluster could be long enough to increase the macroscopic viscosity as observed in the present experiments. It is quite interesting to study in what manner the growth of clusters occurs with much deeper supercooling. It is important to investigate the atomic structure and dynamics of the supercooled states below 2325 K. We plan to investigate the dynamics of the supercooled states by the high-resolution inelastic x-ray scattering and the medium and long-range structural orders by the small-angle x-ray scattering measurements.

In conclusion, the surface tension and viscosity of B were measured over the temperature range from 2325 to 2556 K using an electrostatic levitation method combined with the oscillation drop technique. The viscosity increases substantially with decreasing temperature in the supercooled state. The increase suggests the existence and the growth of clusters in the supercooled liquid B. *In situ* investigations on the atomic structure and dynamics in the supercooled states of liquid B using synchrotron-radiation facility are planned.

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