The structure of liquid Sb under pressure

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Abstract. Synchrotron x-ray diffraction measurements of liquid Sb under pressure have revealed that the structure in the low pressure range is not simple-cubic-like nor slightly Peierls-type distorted one, although the coordination number and the pair correlation function show some similarities to that of simple-cubic-like liquid. Structural changes were observed at around 3GPa and 6.5-9GPa. The changes of the peak positions and the coordination number are reported.

1. Introduction

The pressure dependence of the structure of liquids are currently attracting a lot of attention; liquid Phosphorus is a well-known example which shows a first-order liquid-liquid phase transition[1]. In this paper we study the structure of a heavier group-V element, liquid antimony (Sb), under pressure. For the crystalline phase, Sb is known to form A7 structure, which can be obtained by a Peierls-type distortion of a Simple Cubic (SC) structure[2]. In this A7 structure, the 6 nearest neighbors in the original SC structure splits into 3 nearest neighbors and 3 next nearest neighbors. On melting, it is known to transform to a denser structure in which the coordination number is 6[3]. On the other hand, a lighter element Arsenic (As) is known to preserve the A7-like structure on melting, and it is suggested that this is a Peierls distortion in liquid phase[4]. In liquid Sb, the Peierls distortion is thus suggested to disappear[5]. Theoretical works supported this suggestion, although there is a small discrepancy in that the structure is not-distorted at all[6] or slightly Peierls-type distorted[7]. However, the observed pair correlation function with a double-peak-like hump and a largely asymmetric first peak[3] does not have a good similarity to that of the SC-like liquid, which should be the not-distorted structure for A7-like liquid. In addition, it is known that SC structure is not stable in the crystalline phase for Sb. Furthermore, it is difficult to guess the bonding character by an one-dimensional x-ray diffraction measurement. The measurements under pressure have an advantage in that we can extract the bonding character such as covalency by the pressure dependence.

In the p-T phase diagram, Sb is known to have a melting curve with slightly negative slope and almost flat curvature up to 5GPa[8]. On the other hand, a lighter element As is known to have a melting curve with large positive slope with a large negative curvature[8]. Since the crystalline phase of both these elements is known to be A7 structure, the difference of these melting curves should be due to the difference in the structure of the liquid phase. We investigate the pressure dependence of the structure of the liquid phase to clarify this point.
There is one another interesting point to focus on. Recently the crystalline structure of Sb has been found to show a complex pressure sequence including incommensurate structures[9]. We measure the pressure range including the range of the triple point of A7, incommensurate Sb-II and liquid phase, and see the pressure sequence in the liquid phase.

2. Experimental
High-pressure high-temperature synchrotron x-ray diffraction measurements have been performed by use of the MAX80 system, installed at PF-AR, KEK, Japan. Measurements were performed at temperatures about 50K above the melting point of each pressure. The details of the measurement and analysis method is described in Ref.[10]. The momentum (Q) range was covered up to 18.3Å⁻¹.

3. Results
Figure 1 shows the pressure dependence of the structure factor S(Q) for liquid Sb. The height of the first peak increases and that of the hump next to it decreases with pressure increase. At the pressure 3-4GPa, the hump at 3.2Å⁻¹ shows a relatively large decrease in its height, whereas the hump position shift toward larger Q continuously with pressure increase. The second peak around 5 Å⁻¹ changes its shape from a double-peak like character to a single peak with pressure increase; the shoulder at right side of the second peak largely decreases its intensity at around 3GPa.

Figure 2 shows g(r) at each pressure. The first peak, hump, and the second peak positions are shown in Fig. 3 (a), (b), (c), respectively. The first peak position, R₁, in (a) shows an elongation or preservation of the nearest neighbor distance in spite of the pressure increase in the pressure range roughly up to 5GPa. This fact shows that the bonding character is still strongly covalent in this pressure range. At 9GPa, the first peak shows a remarkable broadening in the low r side. This shows a change of the bonding character at 6.5-9GPa. In (b), the hump position, Rₕ, shifts toward lower r with a large slope. We found that this contraction of the hump position is almost proportional to the molar volume. We note that the hump positions at high pressure range are not shown because the hump merges in to the first peak in the pressure range. In (c), the second peak position, R₂, shows a kink in the slope as a function of pressure at 3GPa.

![Figure 1: S(Q) of liquid Sb at high pressures](image1)

![Figure 2: g(r) of liquid Sb at high pressures](image2)
4. Discussion
At the lowest pressure, the ratio of the second peak position to the first peak position, \( R_2/R_1 \), is 1.36, which is near the value for the SC-like structure, \( \sqrt{2} = 1.41 \). The coordination number at the lowest pressure was estimated to be around 5, which is acceptable as a SC-like liquid with vacancies. These facts show the structure in the low pressure range are somewhat SC-like for liquid Sb. However, the contraction behavior largely differ between the first peak position and the hump position. The preservation or elongation of the bond length clearly shows that there is still strong covalency in the system. The fact that the hump position largely contracts with pressure shows that the bond angle is changing largely with pressure. These contraction behaviors thus show that SC-like liquid structure is not stable at any pressure range, even though the structure may be somewhat SC-like. This will be the preferable contraction behavior in liquid state without periodicity, i.e., changing the bond angle is a more preferable response to the pressure than shortening the bond length. We note that SC structure is neither stable at any pressure range in the crystalline-pressure sequence for Sb. Even in the case of liquid As where the SC structure is stable in wide pressure range in crystal, we found that the SC-like liquid can not be observed in any pressure range[11].

We may thus suggest that the pressure sequence in the liquid phase do not have a stable SC-like structure, even though there may be a relationship to the SC-like structure. The points about this suggestion are the shape of \( g(r) \) and \( S(Q) \) with remarkable hump next to the first peaks, as well as their pressure dependences. For example, the first peak of \( g(r) \) does not sharpen but broadens up to 3GPa. When SC-like liquid is achieved, the first peak should sharpen, because the peak positions for 3 nearest neighbors and 3 next nearest neighbors are expected to merge to form a one peak. Although the shape of the peak due to the 3 nearest neighbors are expected to broaden with pressure because of the change of the bonding character, the fact that there does not appear a sharp minimum between the first peak and the hump positions shows that the structure is not SC-like. The broadening thus denies the suggestion that liquid Sb is nearly SC-like structure with a small Peierls-type distortion remaining in it. Also, we may say that the structure of liquid Sb is not SC-like at any pressure, although there are some similarity to it in low pressure range. The main difference is the asymmetric character of the first peak and an absence of the sharp minimum between the first peak and the hump positions.

The ratio \( R_2/R_1 \) at the lowest pressure is 1.36, which is smaller than 1.41, and decreases with pressure increase. This point also denies the expectation that the structure of liquid Sb at ambient pressure is weakly Peierls-distorted one.

![Figure 3](image-url)
At around 3GPa, an interesting changes were observed in S(Q) and g(r), as stated in the previous section. Since the triple point of the phase diagram for the two crystalline phases and the liquid phase locates at 5GPa, this change in the liquid phase was observed in rather lower pressure range than that for crystalline phase. We note that our result is consistent with the result in Ref.[12] by Umnov et al., although they observed other transitions not only the one at 3GPa.

Turning now to the coordination number(CN), it is estimated to be 4.7 at 0.7GPa. This estimation is by the definition of the integration up to the maximum position in the radial distribution function (RDF) and multiply 2. This value is correctly predicted by an ab initio molecular dynamics simulation[7]. Another definition, the integration up to the first minimum position of RDF, results in 5.3. This difference between two definitions reflect the asymmetric shape of the first peak. The coordination number increases with pressure, and becomes 7 at the highest pressure. CN thus changes from 5 to 7 by pressure increase up to 9GPa. This is in good contrast to the liquid As which shows CN nearly 3 at low pressure range[4,11]. Thus the difference of the melting curve is mainly due to the A7-like loosely packed structure in liquid As at low pressures. The A7-like liquid is less denser, and this results in the large slope of the melting curve, and it is thus compressible, which causes a large negative curvature in the curve. On the other hand, liquid Sb shows already a dense structure at low pressure range.

5. Conclusion
We measured the structure of liquid Sb under pressure up to 9GPa. The structure in the low pressure range was found to have some similarity to the simple-cubic-like liquid, but it was found to be different from it. The ratio of the second peak to the first peak of g(r), R_2/R_1, was found to be smaller than root 2 at the lowest pressure, 0.7GPa, and found to decrease with pressure. The width of the first peak of g(r) does not sharpen but broadens with pressure up to 3 GPa, and the shape of the first peak shows asymmetric character. The first minimum between the first peak and the hump positions of g(r) does not appear as a sharp minimum in any pressures. These facts show that the structure of liquid Sb does not take simple-cubic-like structure nor slightly Peierls-type distorted structure.

At around 3 and 6.5-9GPa, we observed structural changes. At 3-4GPa, we observed a change in the contraction behaviour and a change in the height of the hump of S(Q). This change is located in the lower pressure range than the triple point in the phase diagram. At 6.5-9GPa, the change was mainly observed in the low-r side of the first coordination shell, which indicates a change of the bonding character.

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