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# Pressure dependence of the structure of liquid group 14 elements

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## Abstract

X-ray diffraction has been measured for liquid group 14 elements at high pressures using synchrotron radiation. Static structure factors  $S(Q)$  and pair distribution functions  $g(r)$  show different pressure dependences for liquid silicon, liquid germanium and liquid tin. In liquid silicon, a significant change in the local structure occurs between 8 and 14 GPa. In liquid germanium, an anisotropic contraction of local structure occurs continuously with increasing pressure. In liquid tin, the structure contracts almost uniformly. These pressure dependences are discussed in relation to the pressure-induced phase transitions in crystalline phases and the changes in bonding between atoms.

## 1. Introduction

Pressure dependences of the structure of liquids have been studied for various liquid metals by means of x-ray diffraction measurements under pressure using synchrotron radiation [1–3]. The measurements have revealed that contractions of liquid alkali metals are almost uniform [3–5], whereas those of liquids in which atoms are covalently bonded such as liquid selenium [6, 7], liquid tellurium [8] and liquid iodine [9, 10] are anisotropic. In these covalent liquids, the nearest neighbour distance increases with increasing pressure in spite of volume contraction.

At normal pressure, the group 14 elements silicon, germanium and tin crystallize into the diamond structure, in which atoms are covalently bonded with the  $sp^3$  hybridized orbitals, and form three-dimensional networks. Tin also crystallizes into the beta-tin structure at higher temperature. With increasing pressure, silicon and germanium transform into dense-packed structures through successive pressure-induced phase transitions. At the same time, the coordination number, CN, increases on the transitions; the diamond structure (CN = 4) transforms

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to the beta-tin structure (CN = 4+2), and then to the simple hexagonal structure (CN = 6+2). Many other stable and metastable structures have also been reported [11–14]. On the other hand, the high pressure form of tin is a body-centred tetragonal structure. A semiconductor to metal transition occurs on the phase transition from the diamond to beta-tin structure.

The melting curves under pressure for crystalline silicon and germanium with the diamond structure have negative slope. From the Clausius–Clapeyron relation the volume of liquid is smaller than that of crystal, which indicates that the local structure of liquid differs from the diamond structure. Liquid silicon and liquid germanium are metallic even at normal pressure.

Numerous experimental [15–17] and theoretical [18–20] studies have suggested that the local structure of liquid silicon and germanium at normal pressure is somewhat similar to a beta-tin structure (the high pressure form) rather than the diamond structure (the stable form). The bond angle distribution is, however, extremely broad compared with that for the high pressure form of crystal [16, 18–20].

For liquid group 14 elements at normal pressure, the static structure factor of liquid,  $S(Q)$ , and the pair distribution function,  $g(r)$ , show a systematic change from light elements to heavy elements [15]:

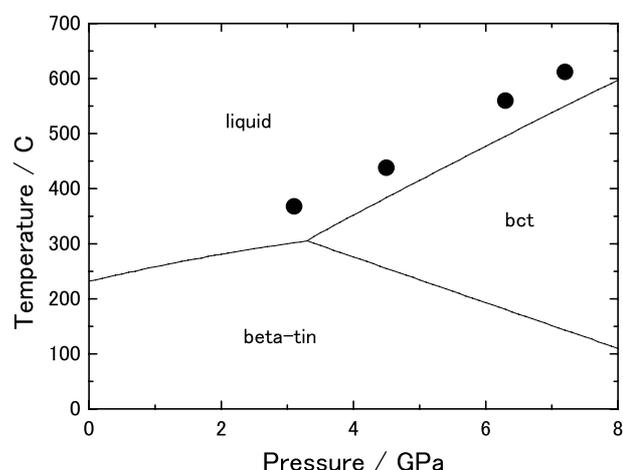
- (1) The height of the first peak of  $S(Q)$  is small for the light elements.
- (2) The static structure factor  $S(Q)$  has a distinct hump or shoulder on the immediate right-hand side of the first peak, and the height is large for the light elements.
- (3) The ratio of the second peak position of  $S(Q)$  to the first peak position,  $Q_2/Q_1$ , is large for the light elements.
- (4) The height of the first peak of  $g(r)$  is small for the light elements.
- (5) The CN is small for the light elements.
- (6) The dip between the first and the second peaks of  $g(r)$  is quite shallow for the light elements.

In crystalline phases, with increasing pressure, the diamond, the beta-tin and the simple hexagonal structures contract uniformly without changing the axial ratio,  $c/a$  [13]. It is well known that the transition pressures of the lighter elements are higher than those of heavy elements [21]. However, this rule is broken in the transition from the beta-tin to the simple hexagonal phase: the transition pressure of silicon is lower than that of germanium. On the other hand, the contraction behaviour of liquid is quite different from that of crystal because the structure of liquid is free from periodicity and is in general allowed to have plural local structures.

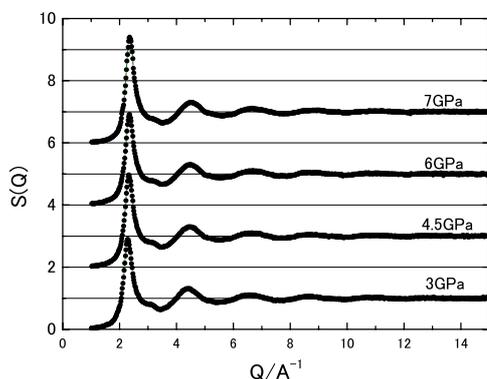
These features motivate us to study the pressure dependence structure of liquid group 14 elements under pressure, in which atoms are covalently bonded in three-dimensional networks and covalent bonds and metallic bonds coexist. X-ray diffraction analysis has been performed at high pressures and high temperatures using synchrotron radiation.

## 2. Experimental details

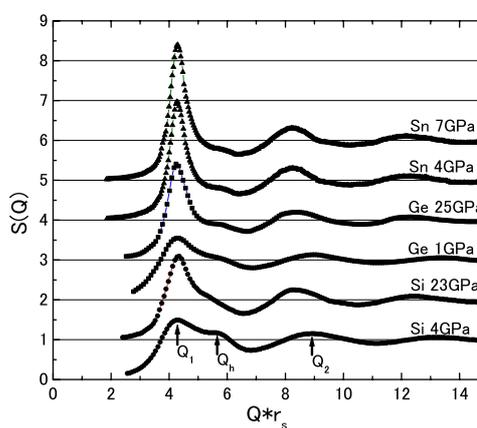
Pressure was generated by the cubic-anvil apparatus MAX80 installed on the AR-NE5C beamline and MAXIII on the BL14C2 beamline at the Photon Factory, KEK, and SPEED1500 installed on the BL04B1 beamline at SPring-8. By using synchrotron radiation with high brightness, high energy and small divergence, x-ray diffraction was measured with an energy-dispersive method. X-ray diffraction intensity was measured at various scattering angles. From the measured diffraction intensities, the static structure factors  $S(Q)$  of liquid metals were deduced after some corrections. Details of the procedures are given elsewhere [22, 8, 3]. The pair distribution functions  $g(r)$  were obtained by the Fourier transformation of  $S(Q)$ .



**Figure 1.** The phase diagram of tin. Dots show the positions where x-ray diffraction experiments were performed.



**Figure 2.**  $S(Q)$  results for liquid tin at high pressures.



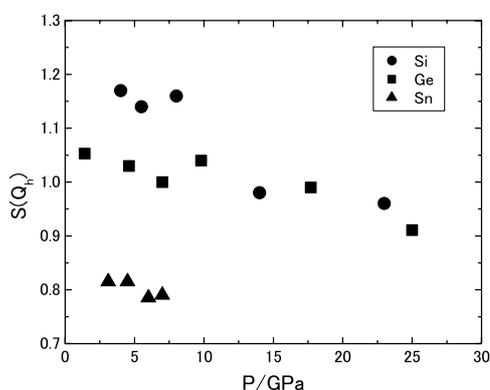
**Figure 3.** A comparison of  $S(Q)$  for liquid silicon, liquid germanium and liquid tin. In the figure, the horizontal axis is scaled by the product of  $Q$  and  $r_s$ . If the structure of liquid contracts uniformly, all the scaled  $S(Q)$  become the same.

### 3. Results and discussion

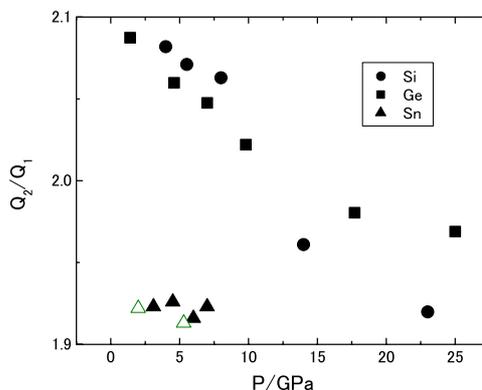
#### 3.1. $S(Q)$ under pressure

Figure 1 shows the pressure–temperature phase diagram of tin [23, 24]. The dots in the figure show the points where x-ray diffraction was measured. They are located at 50 K above the melting temperatures. The stable crystal structure is the beta-tin structure in the pressure region below the triple point and is the body-centred tetragonal structure in the higher pressure region as shown in the figure. Figure 2 shows  $S(Q)$  of liquid tin obtained at several pressures. With increasing pressure, the first, the second and the third peaks shift toward higher  $Q$  values. The shoulder persists up to 7.3 GPa without change of its height. Less change in the shape of  $S(Q)$  indicates that the structure of liquid tin contracts almost uniformly.

On the other hand, a different pressure dependence of  $S(Q)$  was observed for liquid germanium [25, 10]. With increasing pressure, the height of the first peak of  $S(Q)$  for liquid



**Figure 4.** Pressure dependences of  $S(Q_h)$  for liquid silicon, liquid germanium and liquid tin.



**Figure 5.** A comparison of the pressure dependences of  $Q_2/Q_1$  for liquid silicon, liquid germanium and liquid tin. Open triangles are the results for liquid tin taken from [27].

germanium increases, while the height of the shoulder peak which locates on the higher  $Q$  side of the first peak decreases but the shoulder peak still persists even at 25 GPa.

For liquid silicon,  $S(Q)$  has almost the same shape below 8 GPa, which indicates that the local structure of liquid contracts uniformly [26]. Between 8 and 14 GPa the local structure transforms to a denser structure.

To compare the pressure dependence of  $S(Q)$  among liquid group 14 elements, the  $S(Q)$  are shown in figure 3. In the figure, the horizontal axis is scaled by the product of  $Q$  and  $r_s$ , which is defined as the radius of the sphere whose volume is equal to the volume per atom. If the structure of liquid contracts uniformly, all the scaled  $S(Q)$  become the same. In liquid silicon, a drastic change in the shape of  $S(Q)$  is observed between 4 and 23 GPa: the heights of the first and the second peaks become larger and that of the shoulder becomes smaller. The positions of these peaks shift remarkably. In liquid germanium, similar changes occur between 1 and 25 GPa. We can see the tendency for the shape of  $S(Q)$  for light elements to approach that for heavy elements with increasing pressure.

To compare the change in the shape of  $S(Q)$ , we plotted several parameters which characterize  $S(Q)$ . First, we plotted the height of the hump or shoulder,  $S(Q_h)$ , in figure 4 against pressure. Here,  $Q_h$  is the position of the hump or shoulder and is assumed to be  $1.3Q_1$ , where  $Q_1$  is the position of the first peak, to avoid ambiguity in the determination of  $Q_h$ . This occurs because the first and the shoulder peaks are broad and these peaks overlap. As shown in the figure,  $S(Q_h)$  for liquid silicon is large over the whole pressure region compared with that for liquid tin. Below 8 GPa they are markedly large, and between 8 and 14 GPa a drastic drop of  $S(Q_h)$  occurs. For liquid germanium, it decreases continuously with increasing pressure, although at 25 GPa it is still larger than that of liquid tin. For liquid tin,  $S(Q_h)$  is small and less change was observed.

Next, we plotted the ratio of the position of the second peak to that of the first peak,  $Q_2/Q_1$ , in figure 5, against pressure. This quantity has been used to characterize the structure of liquids. For close-packed liquids,  $Q_2/Q_1$  typically takes the value of 1.86. As the anisotropy of the local structure increases,  $Q_2/Q_1$  increases. At normal pressure, it decreases in the order from a light element, silicon, to a heavy element, tin. The ratio for liquid silicon is remarkably larger than 1.86 below 8 GPa and it drops between 8 and 14 GPa. The value at 23 GPa is almost the same as that for liquid tin, although it is still larger than 1.86. On the other hand, with

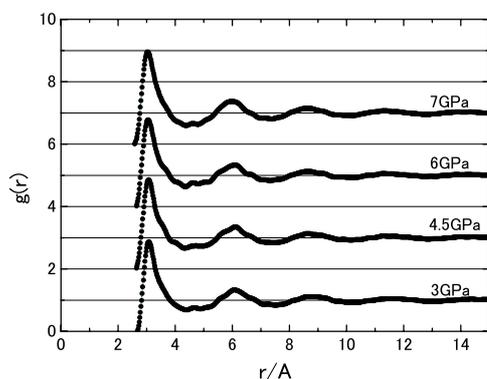


Figure 6.  $g(r)$  results for liquid tin at high pressures.

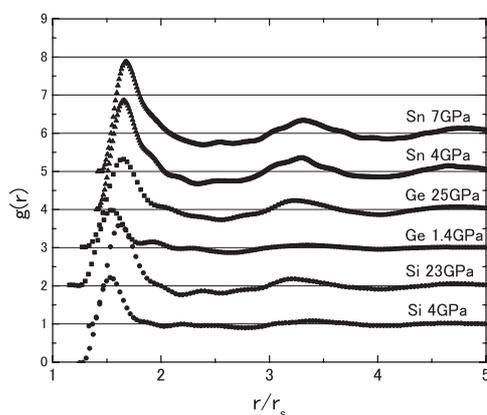


Figure 7. A comparison of  $g(r)$  for liquid silicon, liquid germanium and liquid tin. In the figure,  $r$  is scaled by  $r_s$ . If the structure of liquid contracts uniformly, all the scaled  $g(r)$  become the same.

increasing pressure that of liquid germanium decreases continuously. The value at 25 GPa is still larger than 1.86. For liquid tin, less change was observed with increasing pressure. The results for liquid tin in [27] are also shown in the figure for comparison. They are in good agreement with the present results.

### 3.2. $g(r)$ under pressure

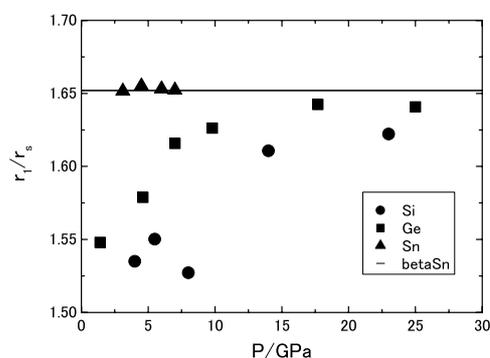
In figure 6,  $g(r)$  for liquid tin at several pressures is shown. With increasing pressure, the first, the second and the third peaks shift toward a lower  $r$  value. Less change in the shape of  $g(r)$  is observed, which indicates that the structure contracts almost uniformly.

Different pressure dependences among liquid group 14 elements are also observed in  $g(r)$ . In figure 7, the  $g(r)$  for liquid silicon, liquid germanium and liquid tin are shown where the interatomic distance,  $r$ , is scaled by  $r_s$ . If the structure of liquid contracts uniformly, all the scaled  $g(r)$  do not change with pressure. With increasing pressure, the shape of scaled  $g(r)$  for liquid silicon and liquid germanium changes:

- (1) The position of the first peak shifts toward a larger  $r$  value in spite of the volume contraction and its height becomes larger.
- (2) The dip between the first and the second peaks becomes deeper.

These changes indicate that the local structure contracts anisotropically. The shape of  $g(r)$  for liquid germanium at 25 GPa is almost the same as that for liquid tin at 4 and 7 GPa. In the case of liquid tin, the shape of  $g(r)$  does not change with increasing pressure.

To compare in more detail, we plotted the position of the first peak of  $g(r)$ ,  $r_1$ , in figure 8, where  $r_1$  is scaled by  $r_s$ . The values for liquid silicon below 8 GPa are much smaller than that for the beta-tin structure with the same volume (dashed line). With increasing pressure, the value for liquid silicon jumps to higher values although it is still smaller than that for the beta-tin structure even at 23 GPa. On the other hand,  $r_1$  for liquid germanium increases continuously with increasing pressure. It approaches the value for the beta-tin structure. For liquid tin, the values are almost the same as that for the beta-tin structure.



**Figure 8.** Pressure dependences of  $r_l/r_s$  for liquid silicon, liquid germanium and liquid tin. The value for the beta-tin structure is also shown as a solid line for comparison.

### 3.3. Discussion

For liquid silicon, the structure contracts almost uniformly below 8 GPa. The beta-tin structure can be regarded as a distorted-diamond structure with a tetragonal axial ratio of  $c/a = 0.5$ . Therefore, the distorted-diamond structure with an intermediate  $c/a$  ratio between 0.5 and 1.4 may be a candidate structure for the liquid. However, the change in  $c/a$  ratio is extremely large and the transition from the diamond structure to the beta-tin structure is irreversible in the crystalline phases. Several metastable forms of crystalline silicon have been found [21] and the high pressure phase easily transforms to an amorphous state [28]. In the liquid phase, structures are free from periodicity and have a broad distribution in the nearest neighbour distance and the bond angles. At high temperatures, plural local structures are allowed to increase the entropy and to minimize the free energy.

Recently, Balashchenko [29] modelled the structure of liquid silicon under pressure by the computer simulation using the Schommers algorithm. His simulated structure gave an excellent agreement with the diffraction data under pressure. The calculated effective pair potential shows that the first minimum becomes deeper above 14 GPa. This suggests that a change in bonding occurs, especially in the metallicity in the bonding. He also analysed the structure of liquid silicon using Voronoi polyhedra, and concluded that the number of Voronoi polyhedra changes sharply between 8 and 14 GPa.

Koga *et al* [30] analysed the structure of liquid germanium by using tight-binding molecular dynamics simulations. They found that the bonding in liquid germanium is to be interpreted as a mixture of covalent and metallic bonding, and that as pressure increases, the ratio of the covalent bonds decreases, although they still exist at pressures as high as 24 GPa. From the bond angle distribution, they also found that the covalent contribution to the local structure of liquid germanium changes from a 'distorted' beta-tin structure in the low pressure region to a 'pure' beta-tin structure in the high pressure region.

The contraction behaviour of liquid group 14 elements shows marked contrast with those of other liquids. The liquid alkali metals contract uniformly with pressure, by reducing the effective radius of the hard sphere due to the screening effects of conduction electrons. The liquid chalcogens in which atoms are covalently bonded in a two-dimensional network or one-dimensional chains contract anisotropically: the intermolecular distances decrease with increasing pressure, which weakens the intra-chain interaction, resulting in an increase of the bond length in spite of the volume contraction. Liquid halogen consisting of diatomic molecules, in which two atoms are covalently bonded, also contracts anisotropically: the

intermolecular distance decreases remarkably, while the bond length of the diatomic molecule increases with increasing pressure.

In crystalline phases of group 14 elements, the diamond, the beta-tin and simple hexagonal structures contract uniformly without changing the  $c/a$  ratio with increasing pressure. Because of the low coordination number, all these structures are regarded as three-dimensional network structures bonded with covalent bonds. In crystalline silicon, the beta-tin structure is stable between 12 and 16 GPa. The width of the pressure region is extremely small compared to that for crystalline germanium (11–75 GPa). The transition pressure from beta-tin phase to the simple hexagonal phase for silicon is much lower than that of crystalline germanium. This difference was considered to originate from the presence of d electrons above the Fermi energy in germanium [31]. On the other hand, the high pressure form of crystalline tin is a body-centred tetragonal structure rather than a simple hexagonal structure. This may arise from the strong metallic character of the bonding. These differences in stability of the beta-tin structure may give different pressure dependences of the structures of liquids.

#### 4. Conclusion

Systematic studies of the structure of liquid group 14 elements under high pressure reveal that the pressure dependences are different for liquid silicon, liquid germanium and liquid tin. Liquid silicon contracts with increasing pressure without significant changes in the local structure up to 8 GPa, and then transforms to a denser structure between 8 and 14 GPa. An anisotropic contraction of the local structure occurs continuously in liquid germanium up to 25 GPa. Liquid tin contracts almost uniformly although it still has anisotropic local structure. These pressure dependences are different from those of liquid alkali metals, which have only spherical metallic bonds. The coexistence of a three-dimensional network of covalent bonds and metallic bonds in liquid group 14 elements may give complicated pressure dependences of the structures of liquids. The differences in the stability of the beta-tin structure under pressure among liquid silicon, liquid germanium and liquid tin may give different pressure dependences of the structures of the liquids.

#### Acknowledgments

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