

## ***Ab initio* Molecular-Dynamics Study of Structural and Electronic Properties of Liquid MgSiO<sub>3</sub> under Pressure**

Ryo YOSHIMURA, Satoshi OHMURA and Fuyuki SHIMOJO

*Department of Physics, Kumamoto University, Kumamoto 860-8555*

(Received September 30, 2010)

The structural and electronic properties of liquid MgSiO<sub>3</sub> under pressure are investigated by *ab initio* molecular-dynamics simulations. At ambient pressure, most Si atoms have the same coordination even in the liquid state as in the crystalline phase, i.e., each Si atom is bonded to two bridging oxygens twofold-coordinated to Si, and two nonbridging oxygens onefold-coordinated to Si. It is found that the structural defects, such as fivefold- or threefold-coordinated Si atoms, are always formed with the rearrangement of Si-O covalent bonds in the atomic diffusion processes. The population analysis clarifies that maximum of the diffusivity in the pressure dependence is originated from the increasing of the number of defects under compression.

### **§1. Introduction**

The structural and dynamic properties of liquid silicates have been attracted the interest of many scientists because of the importance in the earth's mantle. In addition, the magnesium-rich silicate minerals are the primary constituents of the earth mantle,<sup>1)</sup> and are also present as major phases in chondrite meteorites and interplanetary dust.<sup>2),3)</sup>

In ambient conditions, crystalline magnesium silicate (MgSiO<sub>3</sub>) has a SiO<sub>4</sub> tetrahedral unit in which each silicon atom is coordinated to four oxygen atoms with single bonds.<sup>4)</sup> A high-pressure phase appears at a pressure of about 25 GPa under compression. There is a SiO<sub>6</sub> octahedral unit in this structure. Each Mg atom is coordinated to 12 oxygens with bond lengths ranging from 2.014 to 3.12 Å and O-Mg-O angles ranging from 52.19° to 70.89°.<sup>5)</sup> The ideal value of an O-Mg-O angle for a regular MgO<sub>12</sub> polyhedron is 60°. The small variations in the Si-O distances and the small deviation of the O-Si-O angles from 90° (88.5° – 91.5°) show that the SiO<sub>6</sub> octahedron is much more regular than the MgO<sub>12</sub> polyhedron.

Since it would be difficult to clarify the diffusion mechanism in liquid MgSiO<sub>3</sub> experimentally, theoretical studies would be needed. However, only a few theoretical studies of atomic diffusion have been reported so far,<sup>6)</sup> while their crystalline phases have been extensively investigated.<sup>7)</sup> Molecular dynamics (MD) simulations<sup>6)</sup> with empirical interatomic potentials have been used for the diffusion mechanism of oxygen ions in Me<sub>2</sub>O·SiO<sub>2</sub> (Me = Li, Na, K, Cs) melts at 2000 K. Although effects of alkali ions have been examined on the structure of transient complexes temporarily formed in alkali silicate systems, the effects of electronic properties are still unclear.

In this paper, we carry out *ab initio* MD simulations of liquid MgSiO<sub>3</sub> under pressure. We obtain the atomic forces quantum mechanically from the electronic-structure calculations. The purpose of our study is to clarify the microscopic mech-

Table I. Pressure  $P$ , temperature  $T$  and number density  $\rho$  used in this study.

$P$ (GPa)	$T$ (K)	$\rho$ ( $\text{\AA}^{-3}$ )
0.1	2500	0.068
9.5	2900	0.086
21.1	3300	0.099
48.9	4500	0.113
97.8	5500	0.132
149.1	6000	0.146
198.2	7000	0.156

anism of atomic diffusion in the liquid state from first principles. We are unaware of investigations of the diffusion mechanism in liquid silicates based on first-principles theories though some first principles studies of liquid  $\text{MgSiO}_3$  under pressure have already been reported.<sup>8),9)</sup> We discuss how Si-O bonds are exchanged, accompanying the diffusion of atoms in detail. Such findings are important not only for understanding the equilibrium properties of liquid  $\text{MgSiO}_3$  but also for properties of basic liquids in the earth's mantle.

## §2. Method of calculation

In our MD simulations, a system of 120 (24 Mg + 24 Si + 72 O) atoms in a cubic supercell is used under periodic boundary conditions. The equations of motion for atoms are solved via an explicit reversible integrator<sup>10)</sup> with a time step of  $\Delta t = 1.2$  fs. The atomic forces are obtained from the electronic states calculated by the projector-augmented-wave method<sup>11),12)</sup> within the framework of density-functional theory. The generalized gradient approximation<sup>13)</sup> is used for the exchange-correlation energy. The plane wave cutoff energies are 30 and 250 Ry for the electronic pseudo-wave-functions and the pseudo-charge-density, respectively. The energy functional is minimized using an iterative scheme.<sup>14),15)</sup> Projector functions are generated for the  $3s$ ,  $3p$  and  $3d$  states of Mg and Si, and the  $2s$  and  $2p$  states of O.

For each pressure (0 – 200 GPa), the temperature is set to be the melting point plus about 500 K. To determine the density of the liquid state under compression, constant-pressure MD simulation<sup>16)</sup> is performed for 2.4 ps at given pressure. The static and diffusion properties are investigated by MD simulations in the canonical ensemble.<sup>17),18)</sup>

## §3. Results and discussion

### 3.1. Structure factor

Figure 1 shows the pressure dependence of the structure factor of liquid  $\text{MgSiO}_3$ . The solid and dashed lines display the X-ray and neutron structure factors,  $S_X(k)$  and  $S_n(k)$ , respectively.  $S_X(k)$  is obtained from the partial structure factors  $S_{\alpha\beta}(k)$ , shown in Fig. 2, with the X-ray scattering factors, and  $S_n(k)$  is calculated from

$S_{\alpha\beta}(k)$  with the neutron-scattering lengths. At pressures below 10 GPa, clear peaks exist at about  $k = 2.0$  and  $4.4 \text{ \AA}^{-1}$  in the profiles of  $S_X(k)$  and  $S_n(k)$ . Note that the overall profile of  $S_X(k)$  at 0 GPa is consistent with the experimental  $S_X(k)$  of the vitreous state.<sup>19)</sup> While only  $S_n(k)$  has another peak at  $3.0 \text{ \AA}^{-1}$  at lower pressures, the corresponding peak grows in  $S_X(k)$  at higher pressures. With increasing pressure, the peak at about  $k = 2.0 \text{ \AA}^{-1}$  in both  $S_X(k)$  and  $S_n(k)$ . A remarkable feature exhibited in  $S_X(k)$  and  $S_n(k)$  is the small peak at about  $k = 1.2 \text{ \AA}^{-1}$  at 0 GPa, which means that the spatial correlation exists on an intermediate distance  $\sim 6 \text{ \AA}$ . This peak disappears under pressure.

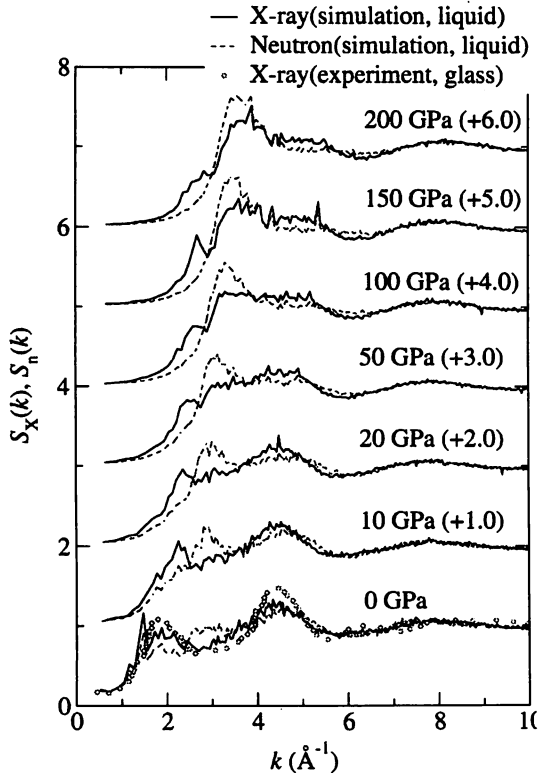


Fig. 1. Pressure dependence of the total structure factors. The solid and dashed lines indicate the X-ray and neutron structure factors,  $S_X(k)$  and  $S_n(k)$ , respectively. The open circles at 0 GPa are the experimental values for glass  $\text{MgSiO}_3$ . The curves are shifted vertically as indicated by the figures in parentheses.

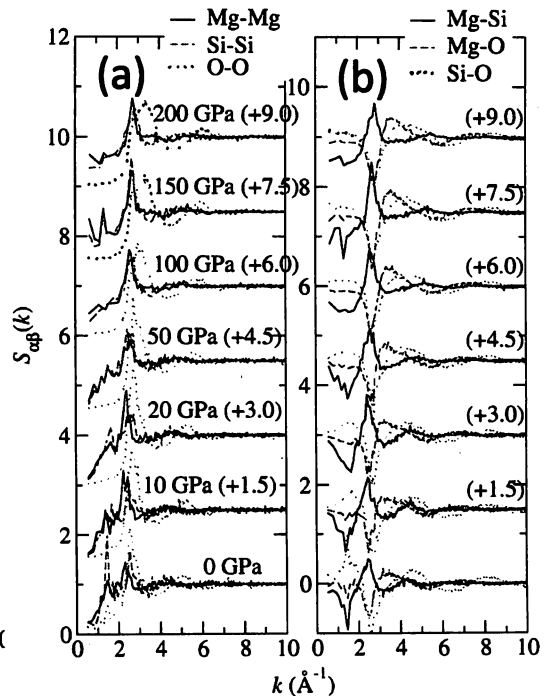


Fig. 2. Pressure dependence of the partial structure factors  $S_{\alpha\beta}(k)$ . (a)  $S_{\text{MgMg}}$  (solid),  $S_{\text{SiSi}}$  (dashed) and  $S_{\text{OO}}$  (dotted). (b)  $S_{\text{MgSi}}$  (solid),  $S_{\text{MgO}}$  (dashed) and  $S_{\text{SiO}}$  (dotted).

Figure 2 shows the Ashcroft-Langreth partial structure factors  $S_{\alpha\beta}(k)$ . The pressure dependence of the profiles of  $S_X(k)$  and  $S_n(k)$  is well understood from  $S_{\alpha\beta}(k)$ . At 0 GPa,  $S_{\text{SiSi}}(k)$  has peaks at about  $k = 1.2 \text{ \AA}^{-1}$ , which gives the corresponding peak in  $S_X(k)$  and  $S_n(k)$ . At lower pressures,  $S_{\text{MgMg}}(k)$ ,  $S_{\text{SiSi}}(k)$  and  $S_{\text{OO}}(k)$  have the peak at about  $k = 2.3 \text{ \AA}^{-1}$ . Because of the cancellation due to the existence

of a negative dip in  $S_{\text{MgO}}(k)$  and  $S_{\text{SiO}}(k)$ , no clear peak appears in  $S_{\text{X}}(k)$  around  $k = 2.3 \text{ \AA}^{-1}$ . With increasing pressure, all peaks shift to larger  $k$  in  $S_{\text{MgMg}}(k)$ ,  $S_{\text{SiSi}}(k)$  and  $S_{\text{OO}}(k)$ , whereas the negative dip changes only a little in  $S_{\text{MgO}}(k)$  and  $S_{\text{SiO}}(k)$ . Therefore, the peaks of  $S_{\text{X}}(k)$  and  $S_{\text{n}}(k)$  grow at the corresponding  $k$  when the pressure increases. At higher pressure, the main peak of  $S_{\text{MgMg}}(k)$  is as high as that of  $S_{\text{SiSi}}(k)$ .

### 3.2. Diffusivity

The diffusion coefficients  $D_{\alpha}$  for  $\alpha = \text{Mg}$ , Si, and O atoms are defined as

$$D_{\alpha} = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle |r_i(t) - r_i(0)|^2 \rangle \quad (3.1)$$

where  $r_i(t)$  is the position of the  $i$ -th atom at time  $t$ . Figure 3 shows  $D_{\alpha}$  as a function of pressure. Whereas  $D_{\text{Si}}$ ,  $D_{\text{O}}$  and  $D_{\text{Mg}}$  have maxima at 50 GPa,  $D_{\text{Mg}}$  has a minimum at 20 GPa. While  $D_{\text{Mg}}$  has larger values than  $D_{\text{O}}$  under pressures up to about 10 GPa,  $D_{\text{O}}$  becomes comparable with  $D_{\text{Mg}}$  at about 20 GPa.

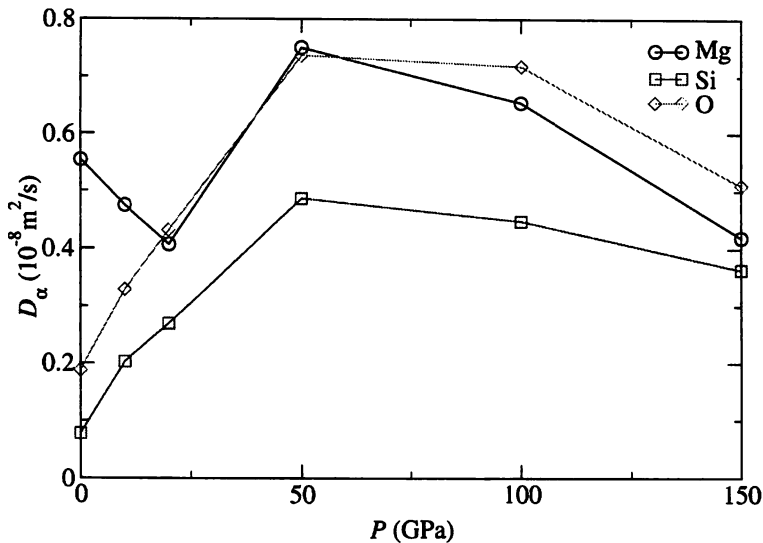


Fig. 3. Pressure dependence of the diffusion coefficients  $D_{\alpha}$  for  $\alpha = \text{Mg}$  (circles), Si (squares) and O (diamonds) atoms.

### 3.3. Mechanism of atomic diffusion

It is found, from the distribution of coordination numbers, that Si atoms are mainly coordinated to four O atoms; two O atoms bridge two adjacent Si atoms, and the other two O atoms are coordinated to only one Si atom, as in the crystalline phase even though atoms diffuse in the liquid state. However, it is unclear how Si-O bonds are exchanged with the diffusion of atoms in the liquid state while retaining the covalent bonds. To clarify the mechanism of atomic diffusion, we investigate the time evolution of the bonding nature by utilizing population analysis. The bond-overlap population  $O_{ij}(t)$ , which gives a semiquantitative estimate of the strength of

the covalentlike bonding between the  $i$ -th and  $j$ -th atoms, is calculated as a function of time.

The diffusion events are shown in Figs. 4 and 5, where covalent bonds are exchanged around the intermediate defect structure with the fivefold- and sixfold-coordinated Si, respectively. As shown in the top panel of Fig. 4,  $O_{Si-O1}(t)$  begins to increase at about 67.15 ps, which means that a covalent bond is formed between Si and O1. We can see this new Si-O bond in the snapshot at 67.25 ps. Due to the formation of the bond, Si is overcoordinated to five O atoms. Since the overcoordination is energetically unstable, one of covalent bonds around the fivefold-coordinated Si atom is broken. It is seen that  $O_{Si-O2}(t)$  becomes almost zero for  $t > 67.70$  ps, and the covalent bond between Si and O2 disappears in the snapshot at 67.75 ps.

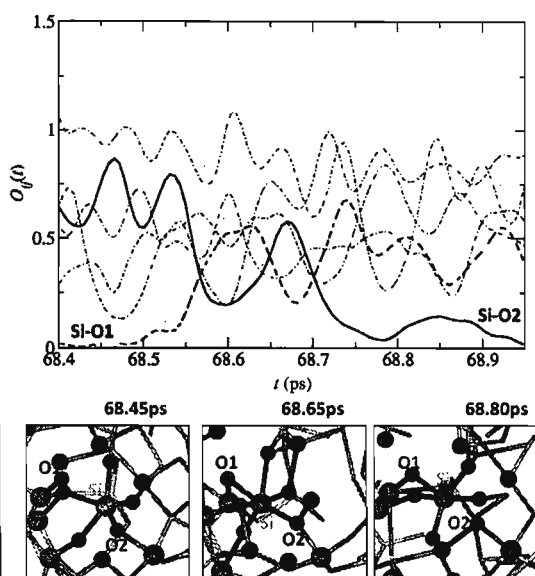
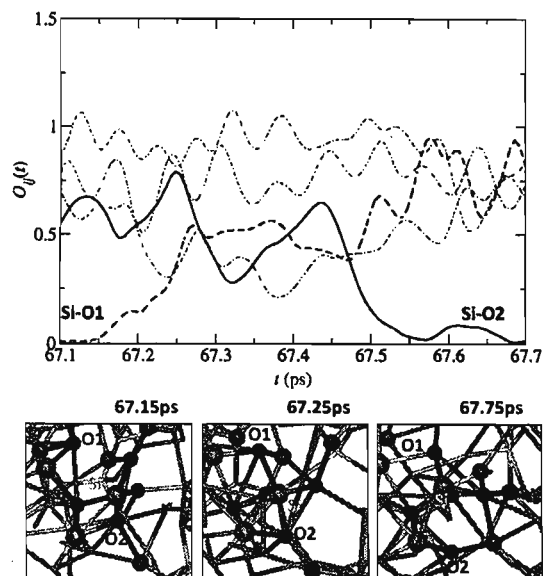


Fig. 4. (Top panel) The time evolution of bond-overlap populations  $O_{ij}(t)$  for  $i = Si$  and  $j \in O$  in the process of atomic diffusion with transient fivefold-coordinated Si. The thick solid and thick dashed lines indicate  $O_{Si-O2}(t)$  and  $O_{Si-O1}(t)$ , respectively. (Bottom panel) Atomic configurations at  $t = 67.15$ ,  $67.25$  and  $67.75$  ps.

Fig. 5. (Top panel) Same as Fig. 4 but for sixfold-coordinated Si. (Bottom panel) Atomic configurations at  $t = 68.45$ ,  $68.65$ , and  $68.80$  ps.

Above 10 GPa, a number of Si atoms have fivefold coordination as shown in the snapshot at 68.45 ps in the bottom panel of Fig. 5.  $O_{Si-O1}(t)$  begins to increase at about 68.50 ps, because O1 approaches 'Si' to form a new covalent bond. We can see this new Si-O1 bond in the snapshot at 68.65 ps. Then the octahedron, i.e., sixfold-coordinated Si, is formed. The sixfold coordination is maintained for about 0.2 ps. At 68.80 ps, the Si-O2 bond is broken as  $O_{Si-O2}(t)$  becomes almost zero for  $t > 68.80$  ps.

Figure 6 shows a diffusion event, in which covalent bonds are exchanged around a transient defect structure with threefold-coordinated Si atom. As seen in the top

panel, initially  $O_{\text{Si-O1}}(t)$  and  $O_{\text{Si-O2}}(t)$  are almost zero and finite, respectively, for  $t < 66.55$  ps. Note that O1 is overcoordinated to three Si atoms (see the snapshot at 66.55 ps).  $O_{\text{Si-O1}}(t)$  and  $O_{\text{Si-O2}}(t)$  cross each other at about 66.63 ps, and finally  $O_{\text{Si-O2}}(t)$  becomes almost zero, while  $O_{\text{Si-O1}}(t)$  is finite for  $t > 66.70$  ps. This means that a covalent bond between Si and O1 is broken, and the Si-O2 bond is formed, as seen from the time evolution of  $O_{\text{Si-O1}}(t)$  and  $O_{\text{Si-O2}}(t)$ . Note also that the twofold coordination of O1 is recovered after this event. Especially the Si-O bonds except the Si-O1 and Si-O2 bonds are retained while switching the covalent bonds. Around 66.63 ps, the Si atom has threefold coordination with  $sp^2$ -like bonding. In this way, the Si-O bonds are exchanged with the formation of undercoordinated Si atoms in liquid  $\text{MgSiO}_3$ . It is, however, necessary to generate adjacent overcoordinated O atoms, such as threefold-overcoordinated O1 in the initial stage of the event.

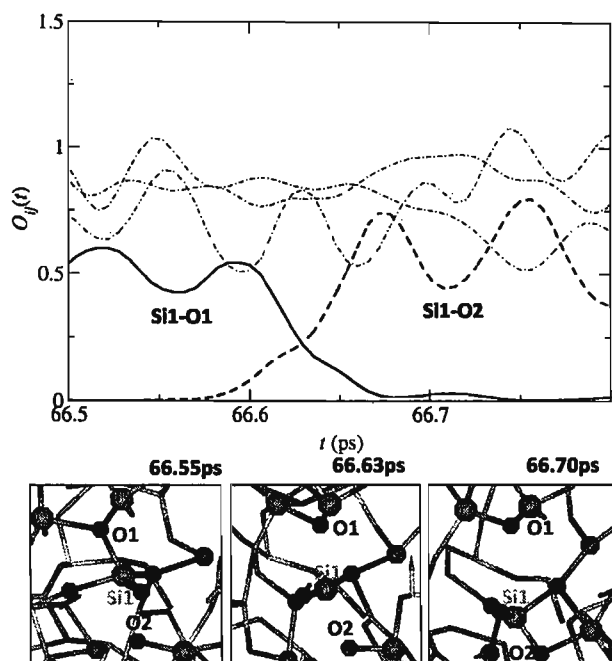


Fig. 6. (Top panel) Same as Fig. 4 but for threefold-coordinated Si. (Bottom panel) Atomic configurations at  $t = 66.55$ , 66.63, and 66.70 ps.

#### §4. Summary

The microscopic mechanism of atomic diffusion in liquid  $\text{MgSiO}_3$  has been investigated by *ab initio* molecular-dynamics simulations. It has been confirmed that, even in the liquid state, silicon atoms are predominantly fourfold-coordinated to hetero atoms with single covalent bonds at ambient conditions, as in the crystalline and vitreous states. We have found that there appears a structural defect whenever atomic diffusion occurs accompanied with the covalent-bond exchanges. The formation mechanism of such defect structure has been discussed in detail using the time

evolution of the bond-overlap populations between atoms. The number of structural defects increases gradually with compression. Therefore, atomic diffusion events related to overcoordinated Si occur easily. As a result,  $D_{Si}$  and  $D_O$  increase up to 50 GPa.

### Acknowledgments

The authors thank Research Institute for Information Technology, Kyushu University for the use of facilities. The computation was also carried out using the computer facilities at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

### References

- 1) G. R. Helfrich and B. J. Wood, *Nature* **412** (2001), 501.
- 2) F. J. Molster et al., *Nature* **401** (1999), 563.
- 3) J. Dorschner and T. Henning, *Astrophys. Rev.* **6** (1995), 271.
- 4) Y. Ohashi, *Phys. Chem. Miner.* **10** (1984), 217.
- 5) H. Horiuchi, E. Ito and D. Weidner, *Am. Mineral.* **72** (1987), 357.
- 6) J. Diefenbacher and P. F. McMillan, *J. Phys. Chem.* **105** (2001), 7973.
- 7) G. V. Bereznoi and G. G. Boiko, *Glass Phys. Chem.* **31** (2005), 145.
- 8) T. S. Duffy, *Rep. Prog. Phys.* **68** (2005), 1811.
- 9) L. Stixrude and B. Karki, *Science* **310** (2005), 297.
- 10) J. T. K. Wan et al., *J. Geophys. Res.* **112** (2007), B03208.
- 11) M. Tuckerman, B. J. Berne and G. J. Martyna, *J. Chem. Phys.* **97** (1992), 1990.
- 12) P. E. Blöchl, *Phys. Rev. B* **50** (1994), 17953.
- 13) G. Kresse and D. Joubert, *Phys. Rev. B* **59** (1999), 1758.
- 14) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* **77** (1996) 3865.
- 15) G. Kresse and J. Hafner, *Phys. Rev. B* **49** (1994), 14251.
- 16) F. Shimojo, R. K. Kalia, A. Nakano and P. Vashishta, *Comp. Phys. Comm.* **140** (2001), 303.
- 17) S. Nosé, *Mol. Phys.* **52** (1984), 255.
- 18) W. G. Hoover, *Phys. Rev. A* **31** (1985), 1695.
- 19) C. W. Martin, J. B. Chris, A. T. Jean and S. Sujatha, *Chem. Geol.* **213** (2004), 281.