

***Ab initio* molecular-dynamics study of pressure-induced glass-to-crystal transitions in the sodium system**

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We study pressure-induced glass-to-crystal transitions in the sodium system. We apply an order- N *ab initio* molecular-dynamics (MD) method to study the transition. We use an isothermal-isobaric condition with an orbital-free density functional. The system contains 128 atoms in a supercell. We simulate the system at temperatures higher and lower than the glass-transition temperature $T_g = 120$ K. At 50 K the pressure enhances the onset of crystallization from the glass. The system crystallizes at pressures greater than 2.75 GPa during which the crystalline atoms appear after the complete annihilation of the icosahedral clusters. At 290 K the system crystallizes at 10^{-3} GPa, during which the atoms appear before the annihilation of the clusters. The application of 1 GPa at this temperature retards the crystallization which is consistent with experiments on metallic glasses. Crystallization occurs after the clusters annihilate completely which is the same feature as the transitions at 50 K. The existence of the clusters disturbs the crystallization at high pressures irrespective of temperature. The icosahedral clusters are unstable and transform to other clusters at high pressures, although the clusters are elastically stable and the hardest within ± 0.07 GPa at 0 K [Masaru I. Aoki and Kazuo Tsumuraya, *J. Chem. Phys.* **104**, 6719 (1996)]. The MD methods with the empirical pair potential is found to be insufficient to simulate the transition in this system.

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I. INTRODUCTION

Ab initio molecular-dynamics (AIMD) methods have begun to be used extensively for studies of condensed systems, since they can evaluate exact forces between atoms. The methods have been applied to the electronic structure analyses of bulks, clusters, and surfaces. The methods have also begun to be applied to studies of disordered systems such as amorphous silicon. There has been, however, no study of the application of the methods to studies of metal glasses. In the present study we apply the AIMD method to investigate the pressure-induced glass-to-crystal transition of a sodium glass.

Klement, Willens, and Duwez¹ were the first to create a metallic glass (Au-Si) through rapid quenching from the liquid. Since then the properties and the structures of the glasses have been studied from both experimental and theoretical points of view. Glass formation in metallic systems by rapid quenching has been, however, experimentally succeeded in only in two- or multiple-component alloy systems. The glassy state of the pure metal has been formed only by vapor quenching.² This is because glass formation in monatomic systems requires ultrafast quenching rates which are experimentally inaccessible.

MD simulations have successfully modeled glass formation even for the pure metals. The advantage of the simulation is that we can simulate conditions which are difficult or impossible to attain in laboratories. The method also give complete information about the positions and the velocities of all atoms in the systems, which makes microscopic and statistical analyses possible. MD simulations have been used extensively for studies of glass transitions,³⁻⁸ their local

structure analyses,⁴⁻⁸ and crystallization processes.^{3,6,9,10} There have existed various methods^{4,5} for the local structure analyses in the random states simulated by the MD simulations. Among them, the Voronoi polyhedron method has been one of the most powerful tools for analyses.¹¹ Finney¹² was first to applied this method to analyze the microscopic structures in the random system.

MD simulations of single-component glasses have shown that their pair-distribution functions (PDF's) give a split second peak in the glass state. Tsumuraya and Watanabe have clarified its origin by use of Voronoi polyhedra analysis.¹³ The local PDF's around the icosahedral clusters gave the sharpest second peak splitting, from which they concluded that the splitting was due to the second and third shells of the icosahedral packing of the atoms in the glass states. The icosahedral clusters have the highest packing fraction.¹³ The central atoms of the clusters are energetically most stable in the glass.¹³ The clusters are elastically the hardest, which has been clarified in a previous paper with the AIMD method.¹⁴ Kondo and Tsumuraya⁸ have investigated the temperature dependence of the number of the icosahedral clusters on quench rates of liquids by use of an empirical MD (EMD) method. They investigated the formation and annihilation processes in the supercooled liquid and clarified the number to increase with decreasing cooling rate. Yonezawa⁴ has studied the crystallization process from a supercooled Lennard-Jones (LJ) liquid by use of the EMD method, indicating that the glass formed with a lower quenching rate is more stable against crystallization than the glass formed with a higher rate. This was attributed to the formation of the multishell clusters with icosahedral symmetry in the relaxed glass. Yonezawa⁴ investigated the time developments of the numbers of the icosahedral clusters and the crystalline atoms dur-

ing the crystallization process. The clusters coexisted with the crystalline atoms at the first stage of the crystallization and then the number of the clusters decreased with time in the crystallization process.

There have been many experimental studies on the pressure-induced glass-to-crystal transitions for metal^{15,16} and covalent^{17–21} bonded glasses. The pressure enhanced the crystallization of the amorphous semiconductors of arsenic¹⁷ or germanium¹⁸ at room temperature. The pressure retarded the crystallization of the metal glasses at higher temperatures than the glass transition temperatures T_g due to the increased viscosity with pressure.^{15,16}

In the present paper we have studied the pressure-induced glass-to-crystal transition in the sodium system at temperatures lower and higher than the glass transition temperature T_g .^{6–8,13} We focus our attention to the effect of pressure on the clusters in the glass and investigate whether or not they are stable under pressure. We use the isothermal-isobaric AIMD method with an orbital free density functional (OFDF). Pearson, Smargiassi, and Madden²² have developed an order- N method²³ to simulate large systems. Although there have been many experimental studies on the crystallization of glasses,^{3,4,24,25} the effect of pressure is unknown. We investigate the pressure effects by use of Voronoi polyhedron analysis.

The AIMD method has been developed by Car and Parrinello²⁶ (CP), and it has become one of the powerful tools to explore both the dynamical and the statistical properties of the condensed systems. In the AIMD method we solve the coupled equations for ions and electrons in the system for the trajectory to nearly trace the correct Born-Oppenheimer potential surface. As the method is based on Kohn-Sham (KS) theory, the kinetic energy of the electrons is evaluated by solving the KS equation, which requires a substantial computational time depending on the number of orbitals. If we evaluate the kinetic energy without solving the equation, then the total energy of the electronic system can be obtained in a short computational time. Pearson *et al.* used a Perrot functional²⁷ as the kinetic energy functional which depends only on the electron density. The functional is a corrected form of the Thomas–Fermi–von Weizsäcker energy functional. This method has also been applied to study the static and dynamic structure factors in sodium liquid²⁸ and the geometrical analysis of metal clusters²⁹ and silicon surfaces.³⁰ They calculated the lattice parameter, bulk modulus, vacancy formation energy, and phonon dispersion curve in the sodium crystalline system.^{22,31} These were in good agreement with the experimental values. The method allows us to treat large systems such as disordered systems, layered structures, large clusters, and so on. In the previous paper we have applied the method to study the local elasticity of the atoms in the sodium glass system.¹⁴

The computational details of the simulations are described in Sec. II. In Sec. III, we show the crystallization processes under pressures and results of the Voronoi polyhedron analysis. In Sec. IV, we discuss why pressure enhances the crystallization through the equations of states of the systems. Finally, conclusions are given in Sec. V.

II. COMPUTATIONAL DETAILS

A. Glass formation

We obtain the initial positions of the atoms in the glass by use of the EMD method with a pair potential for the sodium

system.³² The equation of motion is integrated by a modified Verlet algorithm with time mesh 5×10^{-3} ps. The system has 128 atoms in cubic supercell of which the volume is fixed to 30 261.869 a.u. The temperature was controlled by a modified momentum scaling method.³³ We heat the crystalline state to 381 K, which is higher than the melting temperature by 10 K, and hold at the temperature for 30 ps. The system is stepwise quenched by 40 K at every 100 steps down to 21 K. The quench rate corresponds to 8.00×10^{13} K s⁻¹.

B. Compression of glass

We simulate the pressure-induced crystallization process with the isothermal-isobaric AIMD method with the OFDF. We use the Verlet’s leapfrog algorithm to integrate the CP-type coupled equations for both the atomic and electronic systems with time mesh 50 a.u. ($= 1.2094 \times 10^{-3}$ ps). The steepest decent (SD) method is used to optimize the volume. We heat the glass to temperatures 50 and 290 K and hold at the temperatures with a Nosé-Hoover thermostat.³⁴ The glass transition temperature of the present system has been found to be 120 K for the same cooling rate by use of the empirical potential.^{6–8,13} The cutoff energy is set to 12.0 Ry and the number of fast-Fourier-transformed (FFT) meshes 32 768 [$= (2^5)^3$]. We use the Topp-Hopfield local pseudo-potential³⁵ for the atoms and the Ceperley-Alder exchange-correlation energy functional.³⁶ We obtain the initial charge density to be the superposition of the atomic charge densities. We hold the glass at 10^{-3} GPa (10 atm) for 7.26 ps in order to relax the atom positions and then compressed the glass states with hydrostatic pressures from 1 to 6 GPa for up to 29.0 ps at 50 K.

C. Local average density analysis

In order to characterize the electron density distribution around individual atoms, we introduce the local average density $\overline{\rho}_q$ (Ref. 14) around atom q using

$$\overline{\rho}_q \equiv \frac{Z_q}{\Omega_q}, \quad (1)$$

where the electron charge Z_q in the sphere S_q with radius η_q and Ω_q is the volume of the sphere. We chose the radius η_q to be twice as large as the radius of the atomic sphere which has the same volume as the corresponding Voronoi polyhedron. Expanding the density $\rho(\vec{r})$ with the spherical harmonics, we obtain the charge Z_q integrating the density $\rho(\vec{r})$ within the sphere S_q instead of the atomic sphere. The density $\overline{\rho}_q$ can be a measure of the local atomic bonding between the atom q and the coordinated atoms. The atomic sphere is too small to appreciate the charges contributing to the atomic bonding. We normalize the density $\overline{\rho}_q$ so as to satisfy

$$\frac{1}{N_q} \sum_q \overline{\rho}_q \equiv \overline{\rho}, \quad (2)$$

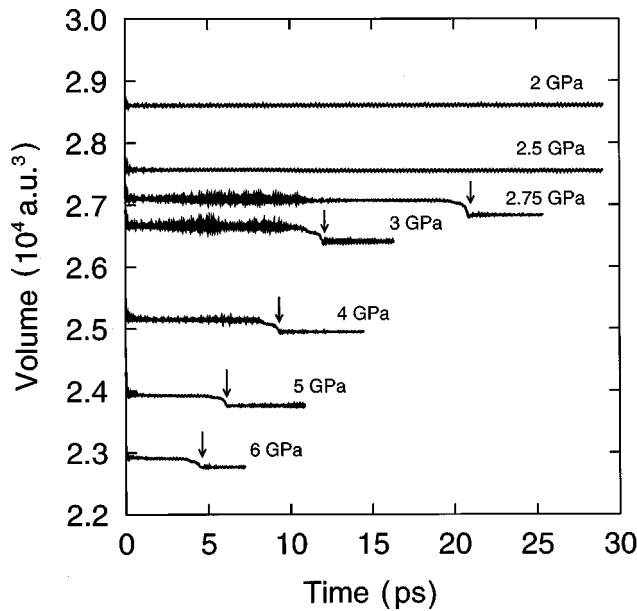


FIG. 1. Variation of the volume of the supercell under pressures as a function of time. The origin of the time is taken at the start of the application of pressures to the system. The arrows indicate the times corresponding to the drastic volume decrements.

where N_q is the number of atoms in the supercell and $\bar{\rho}$ is the average density of the whole system. The normalized density $\bar{\rho}_q$ can be a measure of the density variations at different volumes of the system.

III. RESULTS

A. Pressure-induced glass-to-crystal transition

Figure 1 shows the variation of the volumes at 50 K under pressures as a function of time. The average volume of the system at 10^{-3} GPa, which is just before the application of the pressures, has been 35 549.419 a.u. The volume has rapidly decreased when we apply the pressures to the system. The volumes have stabilized into their equilibrium values within 6×10^{-2} ps (= 50 steps), which is too short in time to be visible in Fig. 1. The drastic decrements of volumes appear at above 2.75 GPa, although no decrement appears at lower pressures than this critical pressure. The amounts of the decrements decrease with increasing pressure, and the ratios of the amounts to the volume are about 0.005. There exist volume fluctuations with time before the decrements. The times needed for the decrements decrease with increasing pressure, and the extent of the fluctuation decreases with increasing pressure. The origin of the fluctuations will be clarified later by use of the Voronoi polyhedron analysis.

Figure 2 shows the change of the PDF's when we have applied the pressures to the system. Figure 2(a) shows the PDF at 10^{-3} GPa which is just before the application of the pressure and that at 4 GPa which is immediately after that. The PDF at 10^{-3} GPa indicates the system to be a relaxed glass state from the second peak splitting into two peaks. The splitting is characteristic evidence of single-component glasses.⁴ We found that the local PDF around the center atoms of the icosahedral clusters had the sharpest second peak splitting of the PDF.⁴ We gave a model for it:¹³ The inner

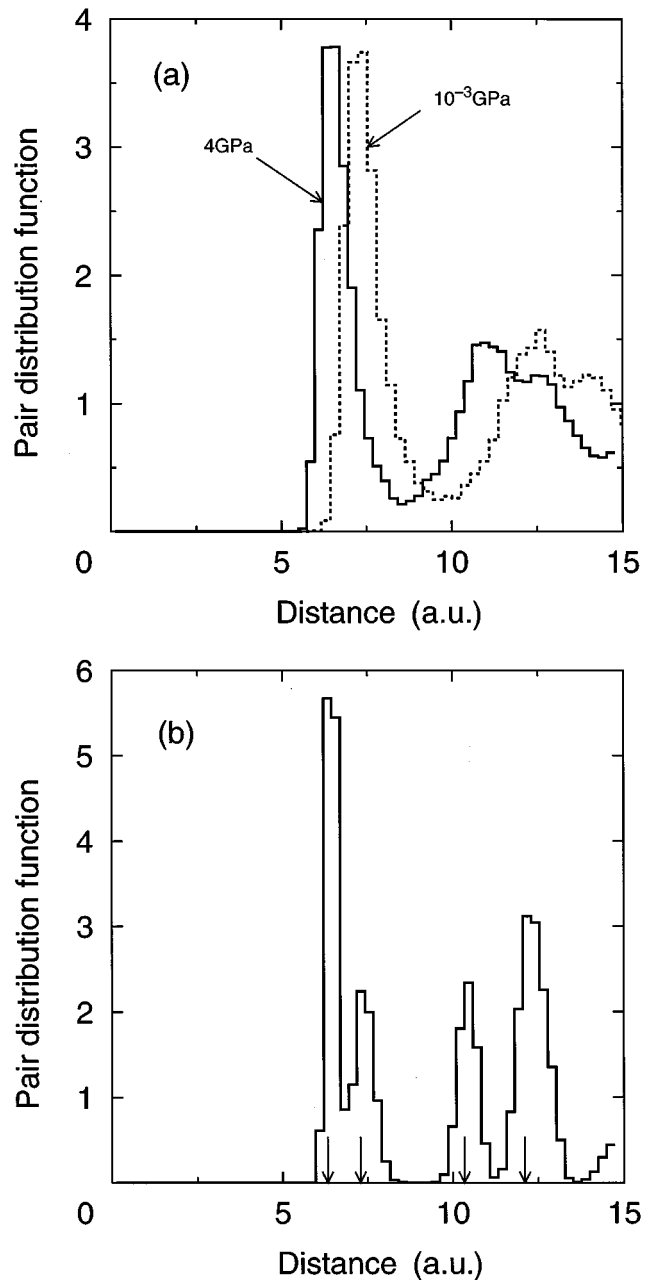


FIG. 2. Change of the PDF of the sodium system from 10^{-3} to 4 GPa. (a) The PDF in the glassy state under 10^{-3} GPa and the PDF before the crystallization under 4 GPa, (b) the PDF after crystallization under 4 GPa. The arrows correspond to the atom positions for the perfect bcc crystal under 4 GPa.

subpeak of the second peak is formed by the second shell of the cluster, which consists of 20 atoms, and the outer subpeak is formed by the third shell of the cluster, which consists of 12 atoms. Figure 2(a) shows that the peak positions of the PDF shift into shorter distances with the increase of pressure from 10^{-3} to 4 GPa. Figure 2(b) is the PDF obtained from the atom positions just after the volume decrement appeared in Fig. 1. The positions of PDF peaks coincide with those of the perfect bcc crystal at the same pressure which indicates the transition from the glass state into the crystalline structure. The volume decrements are attributed

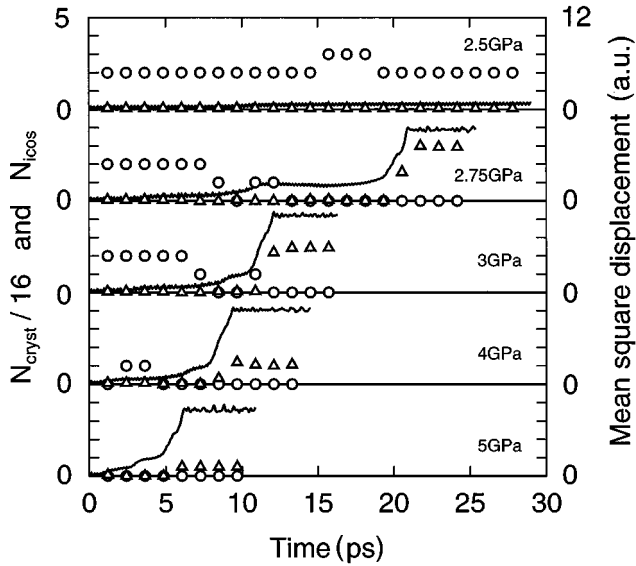


FIG. 3. Variations of the MSD, the number N_{icos} of icosahedral clusters, and the number N_{cryst} of crystalline atoms as a function of time at 50 K. The open circles correspond to the number N_{icos} of icosahedral clusters and the triangles the number N_{cryst} of crystalline atoms.

to the crystallization of the system from the glass state to the bcc crystalline phase. Other simulations at pressures above 2.75 GPa have shown the same PDF changes as this.

B. Voronoi polyhedron analysis

We analyze the microscopic structures in the systems by use of the Voronoi polyhedra. In the analysis, a local configuration around an atom is described by a signature $(n_3, n_4, n_5, \dots, n_\alpha, \dots)$, where n_α is the number of α -edged faces of the polyhedron. The existence of icosahedral clusters with $(0,0,12,0)$ signature has been confirmed to be one of the characteristic features in single-component glasses.^{4,37} We analyze the variation of the numbers of the clusters with time. The effects of the thermal vibrations on the atomic positions has been eliminated by averaging the atomic positions with time.

The number of the clusters has been 9 at the last stage of 10^{-3} GPa. No multishell cluster with an icosahedral symmetry has existed in the system. The numbers have decreased to 7 at 1 GPa and to 5 at 2 GPa. The numbers have been constant over 29 ps at pressures below 2 GPa. There have been two types of the clusters among them: the clusters formed by the applied pressures and the clusters surviving even under the pressures. The fractions of the numbers of the newly formed clusters to the total numbers of the clusters have been 0.14 at 1 GPa, 0.40 at 2 GPa, and 1.0 at pressures between 2.5 and 4 GPa. The fractions increase with increasing pressure in this range. The numbers, however, have been zero for pressures above 5 GPa.

Figure 3 shows the mean-square displacement (MSD) of the atoms as a function of time and the time development of the numbers of both the clusters and crystalline atoms. The crystalline atoms have $(0,6,0,8)$ signature since the system crystallizes into bcc structure. In the case of the simulation at

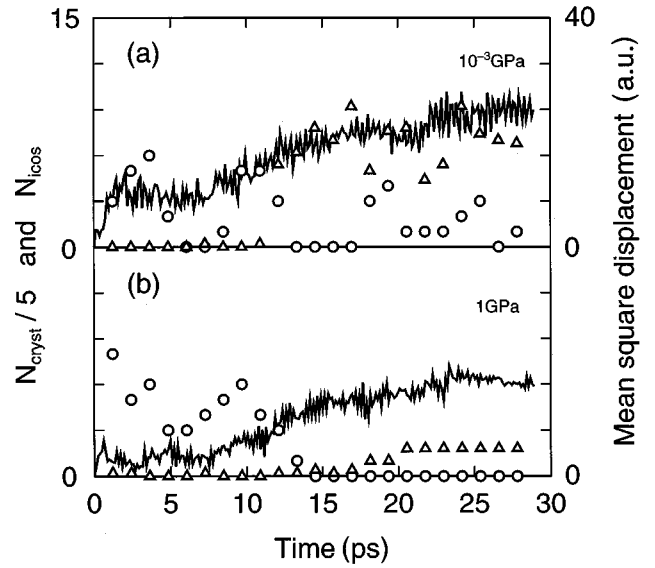


FIG. 4. Variations of the MSD, the number N_{icos} of icosahedral clusters, and the number N_{cryst} of crystalline atoms as a function of time at 290 K. The open circles correspond to the number N_{icos} of icosahedral clusters and the triangles the number N_{cryst} of crystalline atoms. (a) 10^{-3} GPa, (b) 1 GPa.

2.5 GPa, the MSD increases with time over the range of the simulation. The slope of the increment of the MSD is small, and there have existed several numbers of the clusters over the whole range of the simulation. No crystallization occurs within the range of the simulation time. This is also the case for the glasses at pressures less than 2.5 GPa.

At 2.75 GPa, the MSD increases with time, increases rapidly during the annihilation process of the clusters, and becomes constant after the annihilation. The time ranges of the disappearance of the clusters in Fig. 3 correspond to those of the volume fluctuations in Fig. 1. The crystalline atoms begin to appear long after the annihilation of the clusters during which the MSD increases rapidly, showing the crystallization of the system. It takes 8 ps from the complete annihilation at 13 ps to the complete crystallization at 21 ps, during which the electronic total energy of the system has decreased by 8.9×10^{-3} Ry per 128 atoms. There have been no icosahedral clusters or crystalline atoms during the constant MSD region. The simulations at other pressures indicate that the pressure enhances the crystallization process and the time ranges with the constant MSD's decrease with increasing pressure.

The numbers of the crystalline atoms after the crystallization have been 47 at 2.75 GPa, 39 at 3 GPa, 17 at 4 GPa, 8 at 5 GPa, and 5 at 6 GPa. The numbers decrease with increasing pressure. Although the number is maximum at 2.75 GPa, the fraction of the number to the total number of atoms is only 0.367 because of the insufficient relaxation.

We have simulated the pressure-induced glass-to-crystal transition at a higher temperature than the glass transition temperature 120 K, although so far we have simulated at a lower temperature than the temperature. First, we have simulated the transition at 290 K at 10^{-3} GPa. Figure 4(a) shows the time developments of the numbers of the clusters and the crystalline atoms and the MSD of the atoms. The number of

crystalline atoms begins to increase at 11 ps and the system crystallizes. The number of the clusters decreases with time, with fluctuation. The annihilation process of the clusters has overlapped with the formation process of the crystalline atoms, although their existence has not overlapped during the simulations at 50 K, which has been shown in Fig. 3. The coexistence is due to the higher temperature and the lower pressure of the simulation than the conditions in Fig. 3. The average volume of the system has been 37 794.833 a.u. There is sufficient volume in space for the crystalline atoms to coexist with the clusters at 10^{-3} GPa. The same effect of the pressure on the crystallization was also observed in the LJ system at around atmospheric pressures.⁴

Secondly, we have simulated the transition at a higher pressure at 1 GPa. Figure 4(b) shows the time developments of the MSD and the numbers of clusters and crystalline atoms. We compare the results of this figure with those in Fig. 4(a). This pressure retards the onset of crystallization by 6 ps compared with that at 10^{-3} GPa. This is attributed to the increased viscosity at the increased pressure. This pressure effect is in agreement with the experiments of the metal glasses.^{15,16}

IV. DISCUSSION

In the previous paper we clarified the volume stability of the Voronoi polyhedra at 0 K for the abundant signatures in the sodium glass. The stability was evaluated by the volume changes of the polyhedra with pressures, in the range of which the signatures of each atom were conserved: The magnitudes of the pressures were confined within an elastic region of ± 0.07 GPa at 0 K. The volume stability increased with decreasing volume of Voronoi polyhedron. The local average density $\bar{\rho}_q$ around the atoms increased with decreasing volume of Voronoi polyhedron. Thus the volume stability was proportional to the local average density $\bar{\rho}_q$. This was explained by the free-electron theory in which the bulk modulus B is represented by $B \approx \bar{\rho}^{-5/3}$.³⁸ The clusters were the highest local average density $\bar{\rho}_q$. The clusters had the highest volume stability among the signatures. In the present study the clusters, however, have annihilated under pressures higher than 2.75 GPa at 50 K and under 1 GPa at 290 K. This and the previous studies indicate that the clusters are unstable under the high-pressure region, although they are stable under elastic compression.

The present simulation has shown that the clusters coexist with crystalline atoms at low pressures of 10^{-3} GPa. This is because the crystalline nuclei seem to propagate into the glassy region, since there exists sufficient space in the system at low pressure. At higher pressures, however, crystalline atoms with (0,6,0,8) signatures have appeared after the complete annihilation of the clusters. This is because there exists a strong repulsive correlation between the clusters and crystalline atoms in the compressed system, since the cluster has no translational symmetry and there exists insufficient space in the system.

Now let us clarify why the pressure has enhanced the crystallization in the simulation. In order to evaluate the energy difference between the crystal and glass systems, we have obtained the equations of states of their systems. Using the optimized atom positions for the glass in the supercell at 50 K under 10^{-3} GPa, we have further optimized the atomic

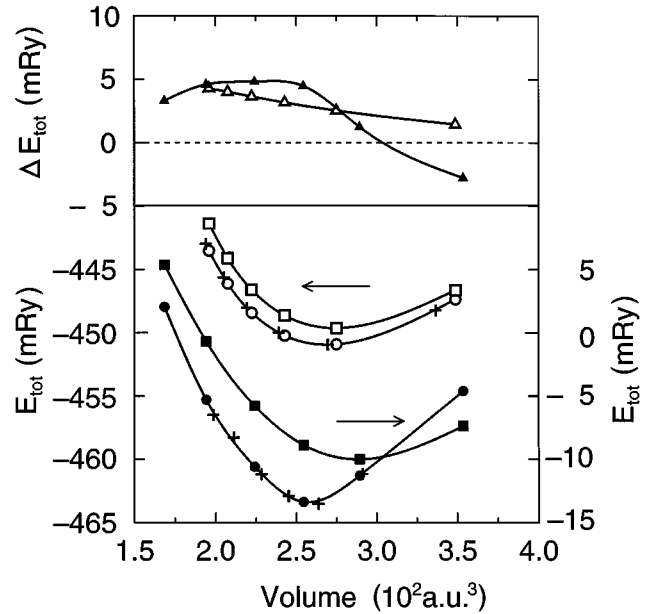


FIG. 5. Equation of states for the glass and the bcc crystal. The open squares are the energies of the glass system and the plus marks of the bcc crystal obtained by the AIMD method. The explanation for the open circles is given in the text. The solid symbols are the respective energies obtained by the EMD method. The open triangles are the differences of the energies between the two phases for the AIMD method and the solid triangles for the EMD method.

positions, the volume of the system, and the electron density in the glass system at 0 Pa by use of the SD method. Next, we optimized the volumes and electron densities at $-1, 1, 2, 3,$ and 4 GPa fixing the scaled coordinates of the atoms. The fraction of the convergence of the total energies has been 10^{-15} . In Fig. 5 we show the total energies per atom at 0 K of the glass system as a function of volume per atom. We also show in the figure the total energies for the bcc crystal system as plus marks which have been obtained by the same procedures as for the glass. The corresponding volumes decrease as shown in the figure, the decrements of which correspond to the volume decrements shown in Fig. 1. In order to evaluate the energy differences ΔE_{tot} between the systems, we have recalculated the energies of the crystal system using the corresponding volumes of the glass system. The energy difference corresponds to the driving energy for the crystallization from the glass to the crystal systems. The energy is also shown in Fig. 5. The energy increases with decreasing volume, i.e., with increasing pressure. This is a reason for the enhancement of the crystallization with pressure.

The equation of states and the driving energies obtained by the EMD method are also shown in Fig. 5. The energy is negative in a large volume region, has a maximum at volume 224.2 a.u., at 2 GPa, and begins to decrease with decreasing volume. The time for the crystallization in the EMD method has been the shortest at 2 GPa, at 50 K corresponding to the maximum driving energy of it. The existence of the negative driving energy and the maximum indicates that the EMD method is inadequate to simulate the pressure-induced glass-to-crystal transition in the present system. Thus empirical potentials are insufficient to simulate the transition under

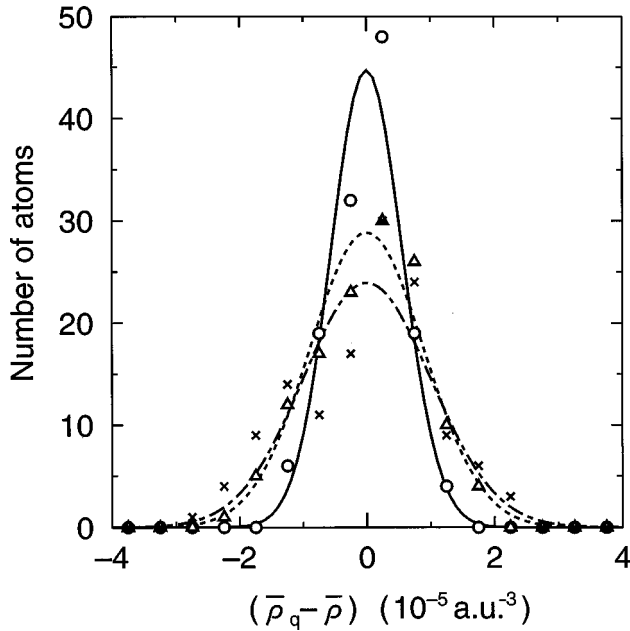


FIG. 6. Distribution of $\bar{\rho}_q - \bar{\rho}$. The open circles indicate the distribution for 10^{-3} GPa, which is fitted to a Gaussian function with a solid line for visual guidance. The open triangles indicate the distribution for 2 GPa and the crosses for 4 GPa together with their Gaussian fitting curves.

high pressures. This is because the potentials neglect the pressure effect on Friedel oscillations which play an important role in metallic bonding since the pressure changes the electron densities of the compressed systems.

The increase of the driving energy for crystallization with pressure is closely related to the change of the electron density distribution in the system. Here we discuss the change of the local average densities and the atomic forces under pressures at 0 K in order to remove the thermal vibration. Figure 6 shows the distributions of the deviation $\bar{\rho}_q - \bar{\rho}$ in the glass systems at 0, 2, and 4 GPa. The local average density $\bar{\rho}_q$ has been given in Eq. (1). The general average density $\bar{\rho}$ has increased from 3.636×10^{-3} a.u. at 0 GPa to 4.495×10^{-3} a.u. at 2 GPa and to 5.100×10^{-3} a.u. at 4 GPa. The distributions have been fitted to Gaussian functions. A perfect crystalline system gives a δ function for the distribution function. Figure 6 shows that the width of the distributions becomes broad with increasing pressure. This is due to the charge transfers among atoms under pressures, which increase the forces among the atoms. The forces enhance the crystallization.

In order to confirm this, we show the distribution of the magnitude of the forces under 0, 2, and 4 GPa in Fig. 7. The magnitude of the forces is within 10^{-4} a.u. at 0 Pa. The distributions of the forces become broad with increasing pressures. This is the same feature as the densities in Fig. 6.

V. CONCLUSIONS

We have studied the pressure-induced glass-to-crystal transition of the sodium glass with the AIMD method. We have used the isothermal-isobaric MD method with the OFDF. The system contains 128 atoms in the supercell. We

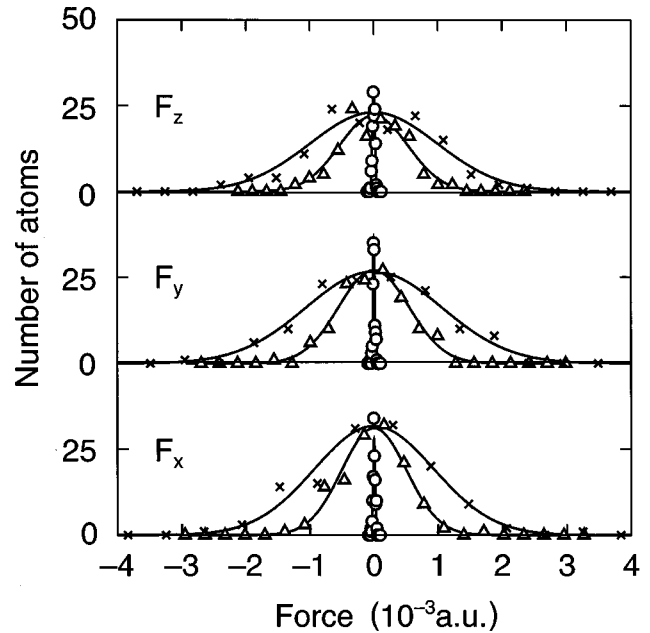


FIG. 7. Distribution of the three components (F_x , F_y , and F_z) of the atomic forces. The open circles represent the distribution for 10^{-3} GPa, the triangles for 2 GPa, and the crosses for 4 GPa. They are fitted to Gaussian functions for visual guidance.

have simulated the transition at temperatures higher and lower than the glass transition temperature $T_g = 120$ K of the system.

At a temperature 50 K lower than T_g , the pressure has enhanced the crystallization at pressures greater than 2.75 GPa, during which the icosahedral clusters annihilate and then crystalline atoms appear: The crystalline atoms have appeared after the complete disappearance of the clusters. At a temperature 290 K higher than T_g , the system has crystallized at a low pressure of 10^{-3} GPa, during which the time region of the existence of the clusters has overlapped with that of the appearance of the crystalline atoms. The application of the pressure with 1 GPa at this temperature has retarded the crystallization of the system which is in agreement with experiments on metal glasses.^{15,16} The crystalline atoms have appeared after the complete annihilation of the clusters, which is consistent with the simulation under the pressures at 50 K. The existence of the clusters has disturbed the formation of the crystalline atoms at high pressures irrespective of temperature. The present simulation has predicted the clusters to be unstable at high pressures, although our earlier work¹⁴ clarified the clusters to be elastically the most hardest and stable at within ± 0.07 GPa at 0 K. However, much remains to be studied for a comprehensive understanding of why the clusters are unstable at high pressures above 1 GPa.

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