

Directed Self-Assembly of Block Copolymers into Twin BCC-Sphere: Phase Transition Process from Aligned Hex-Cylinder to BCC-Sphere Induced by a Temperature Jump between the Two Equilibrium Phases

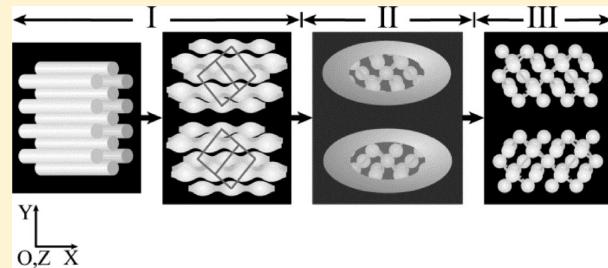
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ABSTRACT: We explored *in situ* a “directed” self-assembly of block copolymers into a twinned body-centered cubic sphere (bcc-sphere) with a special orientation via the **order–order phase transition** from a specially aligned hexagonal cylinder (hex-cyl) by using time-resolved synchrotron small-angle X-ray scattering and transmission electron microscopy. We elucidated that the hex-cyl with its cylinder axis and {11} lattice plane aligned respectively parallel to the OX axis and the OXZ plane was epitaxially transformed into the twin bcc-sphere with its twin axis ⟨111⟩ and twin plane {112} having respectively the “directed orientation” parallel to the OX axis and the OXZ plane. We found that the directed self-assembly involves a three-step nucleation growth (NG) process as follows. Step I corresponds to a pretransition process, where hex-cyl undergoes the cooperative and periodic undulation of the cylinders with their pinching or bulging points being spatially arranged with the “bcc symmetry” which is attained in bcc-sphere after completion of the transformation (designated as “undulated hex-cyl”). Moreover, the undulation fluctuations modes found to have the degeneracy in the form of the undulations with bcc-symmetry A and those with bcc-symmetry A' which have the twin relationship to each other. Step II involves NG of two types of bcc-sphere (designated as A- and A'-sphere which have a mirror symmetry with respect to the {112} plane parallel to the OXZ plane) formed with an equal statistical weight in the matrix of the undulated hex-cylinder; Grains of bcc-sphere grow at the expense of the matrix phase at a faster growth rate parallel to ⟨111⟩ axis than normal to it. Step III involves impingements of bcc-sphere A and A' with their twin planes {112} as their grain boundaries and with their twin axes ⟨111⟩ parallel to the OXZ plane and the OX axis, respectively. Thus, the volume-filling A- and A'-spheres accompanied by spatial rearrangements toward a more perfect bcc-sphere are inevitably directed to form twin bcc-sphere composed of bcc-sphere A and A'.



1. INTRODUCTION

Phase transition processes and mechanisms in block copolymers (bcps) have been extensively and intensively investigated from practical view points to control their patterns with nano-periodicity at will and from scientific view points that bcps are considered to be one of the best model systems to investigate precisely and deeply phase-transition mechanisms and processes of soft matters because of their **slow dynamics**.^{1–5} It is well-known that bcps exhibit the phase transitions called **order–order transition (OOT)** in the weak segregation regime by **changing temperature**.^{6,7} Among various OOT's, the OOT between cylindrical microdomains in hexagonal symmetry (hex-cylinder) and spherical microdomains in body-centered cubic symmetry (bcc-sphere) also has been investigated theoretically^{2,8–16} and experimentally.^{17–28}

Although many experimental studies have been reported so far, most of them used static methods, in which temperature-dependent steady structures were measured as a function of temperature (T); Transient structures evolved during the OOT process were observed as a function of time t after vitrifications of the structures at given t 's by **quenching the systems under investigation below their glass transition temperatures, T_g** . There has been little report which explored *in situ* and *at real time* the isothermal OOT processes induced by temperature jumps between the two equilibrium phases. Especially, there is no report on *in situ* and *real time* studies of the OOT process and mechanism from hex-cylinder to bcc-sphere, except for one

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report by Kim and his co-workers.²⁴ Therefore, in this study, we aim to elucidate *in situ* and *at real time* the processes and mechanisms of the thermally induced OOT from hex-cylinder to bcc-sphere.

The reason why the OOT process and kinetics from hex-cylinder to bcc-sphere, induced by temperature jumps (*T*-jump) between the two equilibrium phases, have been hardly explored *in situ* and *at real time* is presumably because the OOT occurs rapidly. The rapid OOT is expected because of the small energy barrier for the OOT between the two phases as predicted by Matsen.¹⁶ The rapid OOT has made it difficult to follow the OOT process *in situ* and *at real time* by conventional experimental methods. Therefore, in this study, we followed the isothermal OOT process with time-resolved synchrotron radiation small-angle X-ray scattering (SR-SAXS) detected by a fast response CCD (charge-coupled device)-based X-ray detector developed in the collaboration of the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan and SPring-8, Japan Synchrotron Radiation Research Institute, Hyogo, Japan.²⁹

Generally, bcp in ordered states have a polygrain structure rather than a single crystal, because the grain size does not extend over a macroscopic scale. Microdomain structures in each grain are coherent having the same orientation, but those in different grains have different orientation in principle. This orientation distribution of the microdomain structures attributed to the polygrain structures could make it difficult to investigate the OOT process, because a structural change occurring in a particular direction within each grain is orientationally averaged due to existence of many grains having different orientations on SAXS measurements and transmission electron microscopy (TEM) observations. In order to facilitate observing precisely and profoundly the OOT process, we employed highly aligned hex-cylinder with almost a single orientation as an initial state. For this purpose, hex-cylinder was aligned by imposing a large amplitude oscillatory shear (LAOS). The alignment could be a big advantage in TEM observations, because it helps obtaining the images showing characteristic lattice images, which avoids misidentifications of microdomain structures which might happen on inspecting the projected images of a small region of the sample. In this respect it is interesting to note the 2D SAXS patterns obtained for the specimens having a small number of larger grains composed of hex-cylinder and those composed of bcc-sphere.²⁶

We aim to explore transient microdomain structures evolved during the isothermal OOT process in real-space observations and analyses with TEM too on the specimen quenched at particular times during the OOT processes; The interesting times for quenching were pinpointed by *in situ* reciprocal-space observations and analyses with the time-resolved SR-SAXS experiments. Our combined real-space and reciprocal-space analyses, which are complementary and reinforcing each other, on the OOT process will focus on (i) exploring the initial stage of the process which is theoretically anticipated^{2,11–13} to involve cooperative, periodic undulations of hex-cylinder with their pinching and bulging points having the spatial arrangement of “bcc symmetry” with a “directed orientation or alignment” as will be clarified in due course. We shall hereafter define the structure as “undulated hex-cylinder”. Experimental studies of Koppi et al.,¹⁸ Sakurai et al.,¹⁹ Kim et al.,²³ and Kimishima et al.²⁶ postulated the undulated hex-cylinders as an intermediate structure existing in the OOT process from

hex-cylinder to bcc-sphere transition with the static method. Ryu and Lodge^{22,25} made important experimental contributions to this problem: They observed for the first time the undulated cylinder-like structure based on 2D SAXS patterns and TEM images taken by changing temperatures in the stable hex-cylinder phase. We consider it is important to capture *in situ* and *at real time* existence of the undulated hex-cylinder with the reciprocal-space analyses during the isothermal structural transformation process induced by the *T*-jump. (ii) We shall focus also on the epitaxial^{16–19,26,27} structural transformation mechanism involved by the isothermal OOT process. In the OOT process, the cylindrical microdomains are broken into a series of spherical microdomains so that the cylinder axes are transformed into the ⟨111⟩ direction of bcc-sphere. Matsen suggests the nucleation and growth process for the OOT from past experiments^{18,26,27} and his theoretical calculations.¹⁶ We will demonstrate and illuminate that: (iii) the nucleation and growth process develop two kinds of grains: one composed of bcc-sphere A and the other composed of bcc-sphere A' with the directed orientation to be detailed later in the matrix of the undulated hex-cylinder phase at the initial stage; The bcc-sphere A and A' grow at the expense of the matrix phase and fill a whole sample space at the final stage, the process of which leads to a directed self-assembly of twin bcc-sphere A and A'. We shall define later A- and A'-sphere and their directed orientation.

2. EXPERIMENTAL METHODS

2.1. Samples. We employed a polystyrene-block-polyisoprene-block-polystyrene triblock copolymer (SIS) (Vector4111, Dexco Polymers Co.) in this study. The weight-averaged molecular weight, M_w , is 1.4×10^5 , the polydispersity index, M_w/M_n , (M_n is the number-averaged molecular weight) is 1.11, and the weight fraction of polystyrene (PS) is 0.183.^{20,30–32} The sample was dissolved into toluene with a small amount of antioxidant (Irganox 1010, Ciba-Geigy Group) and cast into film specimens of ca. 1 mm in thickness from the 10 wt % toluene solution by evaporating the solvent slowly in a fume hood for 1 week.³³ This film specimen is referred to as an as-cast film which has the randomly oriented polygrain structure. The OOT temperature, T_{OOT} , of the film specimen were reevaluated to be 185 °C from the static SAXS experiments in the heating cycle from 178 to 200 °C. This T_{OOT} is slightly different from that reported previously,³² because the film specimens prepared newly for this study are different from those used previously. The lattice disordering/ordering transition (LDOT)^{34,35} temperature, T_{LDOT} , was evaluated to be 215 °C. T_{LDOT} has been conventionally defined as the order-disorder transition (ODT) temperature, T_{ODT} .

2.2. Special Alignment of Hex-Cylinder. In order to align hex-cylinder, LAOS was imposed on the as-cast films by means of the hydraulic sample-deformation device developed in our laboratory. The details about the sample-deformation device were given elsewhere.³⁶ The Cartesian coordinate OXYZ and the shear cell in this study are defined in Figure 1 together with the important temperatures relevant to this work. Three pieces of an as-cast film, which is 10 mm in length in the OX direction (the shear direction) and 5 mm in width in the OZ direction (the vorticity or neutral direction), were stacked together and then were pressed at 180 °C by sandwiching them between two brass plates, so that the total thickness was 2.5 mm along the OY direction (the shear gradient direction). The sinusoidal shear strain, γ , $\gamma = \gamma_0 \exp(i\omega t)$, with strain amplitude (γ_0) of 1.0 and angular frequency (ω) of 0.5113 rad/s was applied to the specimen at 180 °C for ca. 90 min under nitrogen atmosphere by moving the lower brass plate parallel to the other. The linear dynamic mechanical behavior of the specimen at 180 °C and $\omega = 0.5113$ rad/s is close to the terminal flow region.²⁰ The oscillatory shear strain was stopped at $\gamma = 0$ and at the end of the 450th cycle of strain. After cessation of LAOS, the specimen was rapidly frozen together with the shear cell with liquid

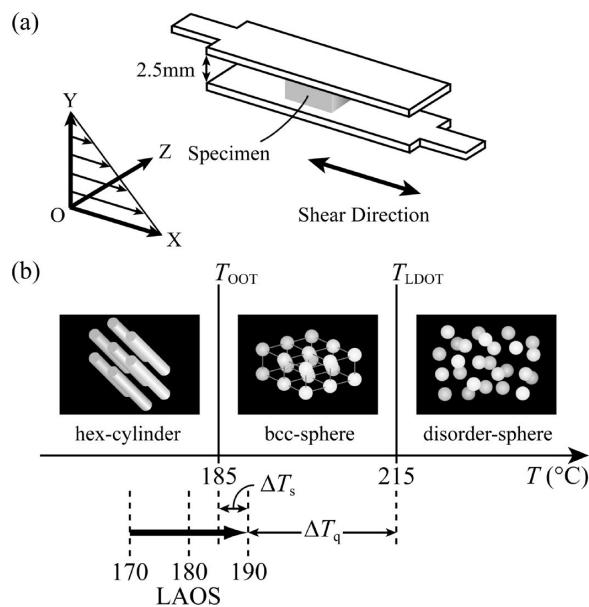


Figure 1. (a) Sample deformation device (shear cell) for aligning hex-cylinder and the definition of the Cartesian coordinate $OXYZ$, where the OX , OY , and OZ axes are parallel to the shear direction, shear gradient direction, and neutral or vorticity direction, respectively. (b) Schematic illustration of the microdomain structures and important temperatures in this study. ΔT_s and ΔT_q define the degree of superheating for hex-cylinder with respect to T_{OOT} and the degree of supercooling for bcc-sphere with respect to T_{LDOT} , respectively. T_{LDOT} is identical to the conventionally defined T_{ODT} .

nitrogen, taken out from the shear cell, and kept at room temperature. The specimens thus prepared are designated hereafter “as-aligned specimen”.

2.3. OOT from Hex-Cylinder to Bcc-Sphere. The isothermal OOT from the aligned hex-cylinder to bcc-sphere was induced as follows by the T -jump from $170\text{ }^\circ\text{C}$, where hex-cylinder exists at equilibrium, to $190\text{ }^\circ\text{C}$, where bcc-sphere exists at equilibrium, i.e. the degree of the superheating with respect to T_{OOT} , ΔT_s , being given by $\Delta T_s = 5\text{ K}$, but the quench depth with respect to T_{LDOT} , ΔT_q , being large, $\Delta T_q = 25\text{ K}$ (see Figure 1b). The as-aligned specimen in the sample holder as described in section 2.2 was put in a heater block³⁷ regulated at $170\text{ }^\circ\text{C}$ for 2 min. A preliminary SAXS experiment showed that the 2D SAXS pattern did not change at all after 2 min. Therefore, we considered that the as-aligned specimen prepared at $180\text{ }^\circ\text{C}$ reached the equilibrium state at $170\text{ }^\circ\text{C}$ in 2 min. After reaching the equilibrium state, the aligned specimen in the sample holder was rapidly transferred manually into the other heater block³⁷ regulated at $190\text{ }^\circ\text{C}$ set on the optical bench of the incident X-ray beam and then the time-resolved SAXS experiment was started. The starting time was set zero at the time when the specimen in the sample holder was put into the heater block regulated at $190\text{ }^\circ\text{C}$.

2.4. Time-Resolved SAXS Experiments. Time-resolved SAXS experiments at $190\text{ }^\circ\text{C}$ were conducted by using the synchrotron radiation at beamline 15A in the Photon Factory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, Tsukuba, Japan. The beamline has a demagnifying mirror-monochromator optics.³⁸ The wavelength, λ , of the incident X-ray beam is 0.150 nm and its spectral distribution is $\Delta\lambda/\lambda \cong 3 \times 10^{-3}$. The point-focused beam size at the sample position was $\sim 1.0\text{ mm}$ (vertical) \times $\sim 0.75\text{ mm}$ (horizontal). The SAXS intensity distribution was detected by a CCD-based X-ray detector. It consists of a beryllium-windowed X-ray image-intensifier (Be-XRII) (V5445P Hamamatsu Photonics K.K.) and a CCD. Two-dimensional (2D) SR-SAXS patterns were corrected for image distortions and nonuniformity of the detector sensitivity.³⁹

2.5. TEM Observations. TEM observations were conducted for the as-aligned specimen prepared at $180\text{ }^\circ\text{C}$ and transient structures evolved during the OOT process at $190\text{ }^\circ\text{C}$ as well. In order to observe the transient structures with TEM, the specimens were rapidly quenched into ice-water (at $0\text{ }^\circ\text{C}$) at given times after the onset of the OOT. The transient structures existed in situ at given t 's at $190\text{ }^\circ\text{C}$ could be frozen effectively in the quenched specimens because of the high T_g of the matrix PS phase (ca. $100\text{ }^\circ\text{C}$) in the bcp and the slow dynamics of the microdomains compared with the cooling rate used for the quench. The specimens for the TEM observations were prepared by microtoming into the ultrathin sections of thickness less than 50 nm [especially for Figures 11a-2, 11b-2, 13, and 14 (except for part d)] and $\sim 70\text{ nm}$ (for other TEMs) in thickness using a Reichert Ultracut S with the cryochamber FCS operated at $-100\text{ }^\circ\text{C}$ and a diamond knife (DiATOME, Switzerland). The thickness was judged from the interference color. The ultrathin sections were picked up on 100 mesh copper grids covered with a supporting film, which was prepared by casting 1% chloroform solution of poly(vinyl formal), and stained by the vapor of 2% osmium tetroxide [$\text{O}_3\text{O}_4(\text{aq})$] for 15 min at room temperature in order to stain selectively polyisoprene (PI) domains.^{40,41} The microdomain structures in the ultrathin sections were observed by a TEM (JEOL JEM-2000FXZ) operated at 120 kV .

3. RESULTS

3.1. Characterization of a Specific Orientation of Hex-Cylinder Aligned by the LAOS Deformation. We will first characterize a specific orientation of hex-cylinder aligned by the LAOS deformation. The specimens frozen rapidly below T_g after the cessation of LAOS were observed at room temperature from the OX , OY , and OZ directions with SR-SAXS and TEM. The Cartesian coordinates for the TEM images shown in Figures 2b-i ($i = 1$ to 3) and the hex-cyl models shown in Figure 2c-i are referred to those in the 2D SR-SAXS patterns shown in Figure 2a-i, respectively. The Miller indices of the diffraction spots from hex-cyl are identified as shown in Figure 2a-i.

The 2D SR-SAXS pattern shown in Figure 2a-1 taken with the incident beam along the OX direction exhibits hexagonal diffraction spots up to the fourth-order maximum at least, while the TEM image shown in Figure 2b-1 exhibits hex-cylinder with the orientation as schematically shown in Figure 2c-1. Thus, the cylinder axes are oriented parallel to the OX direction (the shear direction) and $\{11\}$ lattice plane of hex-cylinder is parallel to the OYZ plane (the shear plane). On the other hand, with the observation of the aligned hex-cylinder along the OY direction, the meridional diffraction spots can be clearly seen up to the third-order maximum in the 2D SR-SAXS pattern shown in Figure 2a-2; They are identified to be the multiple order diffractions from $\{10\}$ lattice plane as schematically shown in Figure 2c-2. The domain spacings $d_{\{10\}}$ in the TEM image shown in Figure 2b-2 is almost consistent with the Bragg spacings, $D_{\{10\}} = 2\pi/q_{m,\{10\}} = 28.6\text{ nm}$, derived from the 2D SR-SAXS pattern in Figure 2a-2. Here, $q_{m,\{hk\}}$ is magnitude of the scattering vector (q) at the first-order peak from $\{hk\}$ lattice plane of hex-cylinder, and q is defined by $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the wavelength of the incident X-ray and the scattering angle, respectively.

Upon observing hex-cyl with the incident beam along the OZ direction, the meridional diffraction spots can be clearly seen up to the second-order maximum as shown in Figure 2a-3, and they are identified to be the multiple order diffractions from $\{11\}$ lattice plane as schematically shown in Figure 2c-3. The domain spacing $d_{\{11\}}$ in the TEM image shown in Figure 2b-3 is almost consistent with the Bragg spacings, $D_{\{11\}} = 2\pi/q_{m,\{11\}} = 16.5\text{ nm}$, derived from the 2D SR-SAXS pattern in Figure 2a-3.

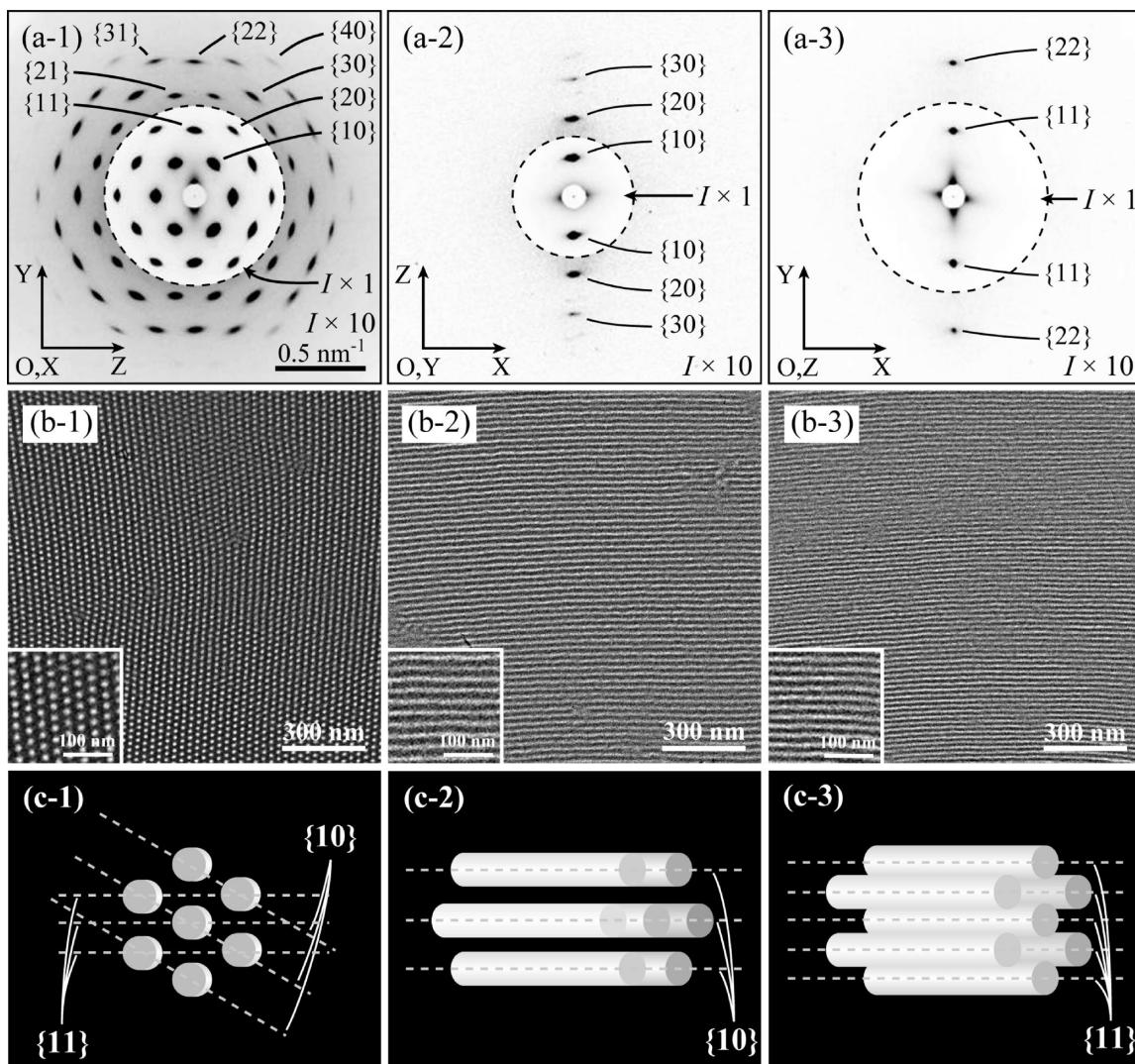


Figure 2. 2D SR-SAXS patterns for the specially aligned hex-cylinder with the incident X-ray beam along the OX axis (a-1), the OY axis (a-2), and the OZ axis (a-3). Their exposure times are (a-1) 6.048, (a-2) 1.208, and (a-3) 4.232 s, respectively. The intensity outside of the dashed circular line in parts(a-1) to (a-3) is multiplied by 10 times relatively to that inside the line. (b) Transmission electron micrographs observed with the electron beam along the OX axis (b-1), the OY axis (b-2), and the OZ axis (b-3). (c) Schematic illustrations of the aligned hex-cylinder viewed from the OX axis (c-1), the OY axis (c-2), and the OZ axis (c-3). The white broken lines represent the lattice planes {10} and {11}.

Thus, the intercylinder distance d_{cyl} is calculated to be 33.0 nm. Moreover the average radius of the cylinder R_{cyl} is separately determined to be 7.1 nm.⁴²

The aligned hex-cylinder has the specific orientation with respect to the Cartesian coordinate such that the cylinder axis, {10} lattice plane, and {11} lattice plane are parallel to the OX-axis, the OXY plane, and the OXZ plane, respectively. The shear-induced alignment of hex-cylinder had been a controversial subject: Either {11}⁴³ or {10} lattice plane^{44–48} was arranged parallel to the shear plane, i.e., the OXZ plane, with the cylinder axis commonly oriented parallel to the OX direction. Tepe et al.⁴⁹ reexamined the issue of cylinder orientation by varying the shearing conditions for PE-*b*-PEP diblock copolymer and elucidated the two distinct cylinder orientations: LAOS near T_{ODT} and well below T_{ODT} place {11} and {10} lattice planes parallel to the shear plane, respectively. From this point of view, our result seems to be consistent with the high temperature result of Tepe et al. We presented a possible interpretation of our results in reference and notes section.⁵⁰

In order to observe uniformity of the aligned hex-cylinder over a large area, a low magnification TEM image taken with the electron beam along the OX direction is shown in Figure 3a. It is confirmed that cylindrical microdomains are hexagonally packed with almost the same orientation over a quite wide area, as evidenced by the insets taken at various positions of the micrograph (a). The grain was too large to be taken it in a single micrograph, and its size perpendicular to the cylinder axes is much larger than $4 \times 4 \mu\text{m}^2$. Some defects can be discerned as shown in Figure 3, parts c and d; some cylindrical axes are slightly off-aligned from the OX direction as shown in Figure 3e–g. Moreover the {10} lattice plane is slightly curved along the shear gradient direction, as traced by the white line, l_1 , for example, while the alignment of the {10} lattice plane along the white line, l_2 , is almost perfect, for example.

Thus, hex-cylinder can be highly aligned after imposing LAOS under the condition described in section 2. The as-aligned specimens annealed at 170 °C for 2 min in order to attain an equilibrium state were employed as an initial state for

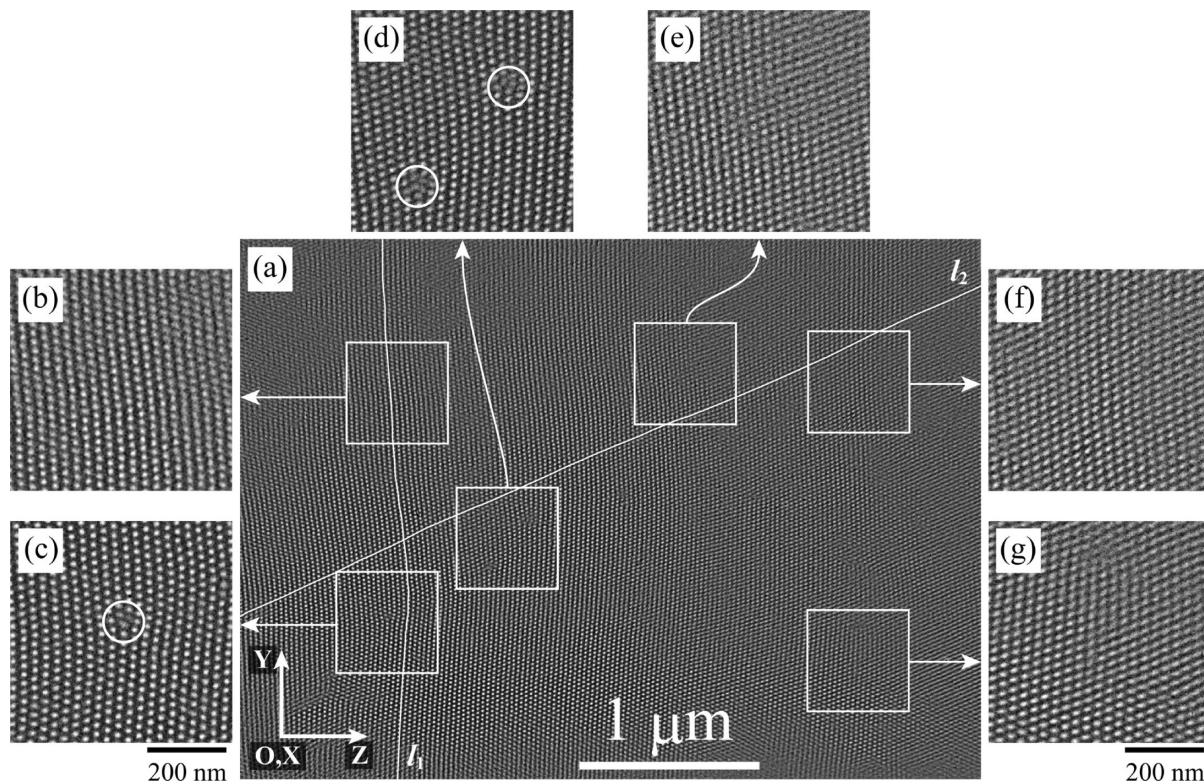


Figure 3. (a) Transmission electron micrographs for the aligned hex-cylinder observed with the electron beam along the OX direction. The white lines, l_1 and l_2 , indicate the traces of $\{10\}$ lattice plane of the cylindrical microdomains. Parts b–g show magnified micrographs for the areas encompassed by the white squares in part a. The white circles in parts c and d indicate the defects of the hex-cylinder.

the time-resolved SR-SAXS experiments for the isothermal OOT process at 190 °C.

3.2. Time-Resolved SR-SAXS. We will present results obtained by the *real-time* and *in situ* investigations on the time evolution of 2D SR-SAXS patterns viewed from the OX, OY, and OZ directions, which is induced by the *T*-jump from 170 to 190 °C.

3.2.1. Analysis of 2D Diffraction Patterns. Parts a–e of Figure 4 present the time evolution of the 2D SR-SAXS patterns viewed from the OZ direction. Figure 4a taken at 20.3 s after the *T*-jump shows the two meridional diffraction spots from $\{11\}$ lattice plane of hex-cylinder as illustrated in Figure 4a'. The four first-order diffraction spots along the two diagonal directions start to appear faintly at around 65.3 s as shown in Figure 4b and becomes remarkable at 115.3 s as shown in Figure 4c. They get stronger with time. The four second-order diffraction spots also start to appear faintly in the other two diagonal directions (see the pattern in part c) and get stronger with time (see the patterns in parts d and e). On the other hand, the two meridional diffraction spots get weaker with time (see the patterns in parts a to d) and can be faintly seen in Figure 4e taken at 915.3 s.

The 2D SR-SAXS pattern hardly changed at time longer than around 915.3 s after the *T*-jump. It means that hex-cylinder is almost completely transformed to bcc-sphere and the whole sample space is occupied by bcc-sphere. Therefore, the four first-order diffraction spots, the four second-order diffraction spots, and the two meridional diffraction spots, which correspond to the third-order diffraction, in the 2D SR-SAXS pattern shown in Figure 4e can be attributed to those from $\{110\}$, $\{200\}$, and $\{112\}$ lattice planes of the two bcc-spheres A and A' as illustrated in Figure 4, parts e'1, e'2, and e'3.

respectively. Both A and A' have common orientations with respect to their $\langle 111 \rangle$ axis and $\{112\}$ planes being parallel to the OX axis (the cylinder axis) and the OXZ plane ($\{11\}$ lattice plane of hex-cylinder), respectively: A and A' are in mirror symmetry with respect to the OYZ plane and the OXZ plane. Thus, it is found that the bcc-spheres A and A' form twin bcc-sphere A and A' with $\{112\}$ lattice plane as the twin plane parallel to $\{11\}$ lattice plane of hex-cylinder and the OXZ plane (the shear plane). Thus, $\{11\}$ lattice plane of hex-cylinder and the cylinder axis are transformed epitaxially into $\{112\}$ lattice plane and $\langle 111 \rangle$ axis of bcc-sphere, respectively.

The time evolution of the 2D SR-SAXS patterns viewed from the OX direction are shown in Figure 5. The hexagonal diffraction pattern did not change in the course of the OOT process, though the intensity of the diffraction spots become weaker with time, which is especially obvious for the higher-order diffraction spots. This indicates that the cylinder axes parallel to the OX direction, as illustrated in Figure 5a', is epitaxially transformed to $\langle 111 \rangle$ direction of the bcc-spheres A and A', and the first- and second-order diffraction spots are those from $\{110\}$, and $\{112\}$ lattice plane of bcc-sphere, as illustrated in Figure 5c'.

Finally, the time evolution of the 2D SR-SAXS patterns viewed from the OY direction is shown in Figure 6. The meridional diffraction spots did not change in the OOT process. The meridional first-order diffraction in Figure 6, parts a and c, can be attributed to diffraction from $\{10\}$ lattice plane of hex-cylinder and $\{110\}$ lattice plane of the bcc-spheres A and A'. Therefore, $\{10\}$ lattice plane of hex-cylinder as illustrated in Figure 6a' is transformed into $\{110\}$ lattice plane of the bcc-spheres A and A' as illustrated in Figure 6c'. $\{112\}$ lattice plane of the bcc-sphere A and A' exists parallel to the OXZ plane as also illustrated with dashed lines in Figure 6c'.

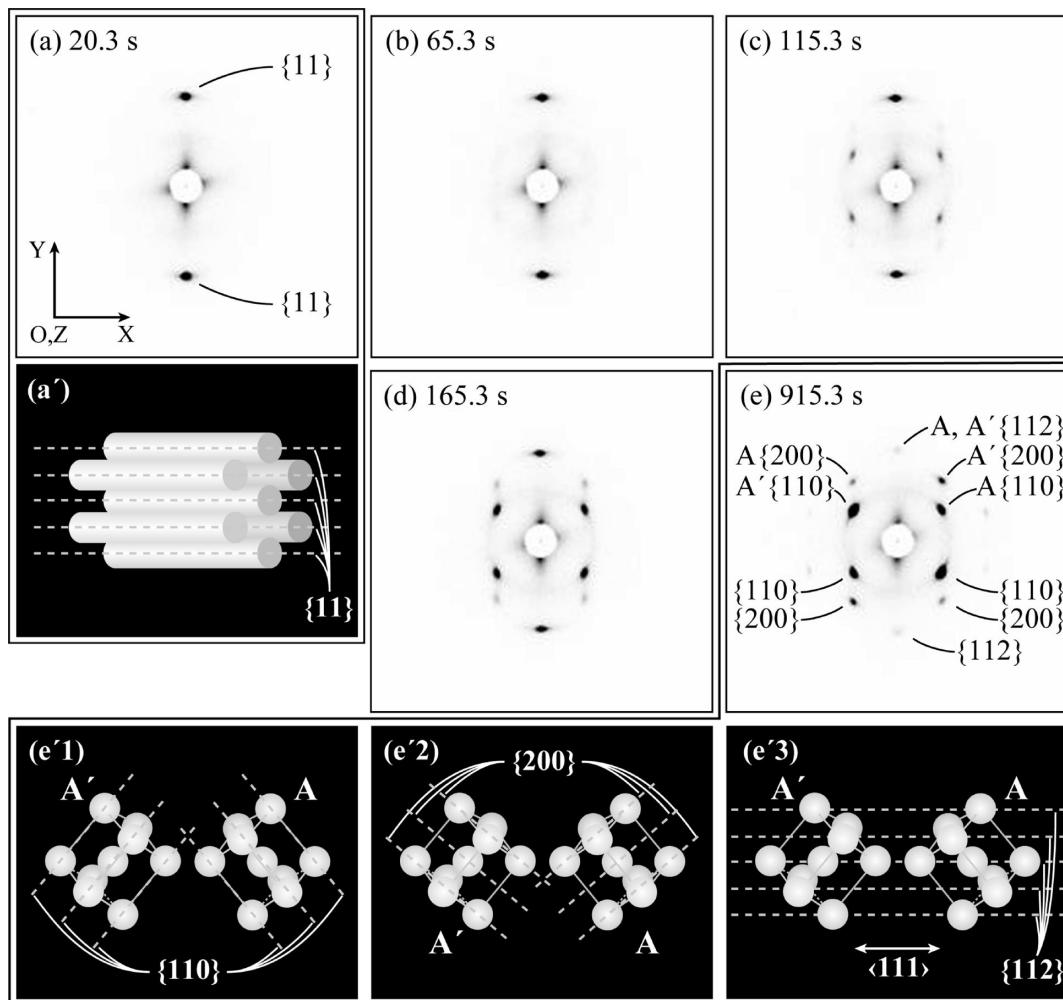


Figure 4. Time evolution of the 2D SR-SAXS pattern with the incident X-ray beam along the OZ axis, taken *in situ* at (a) 20.3, (b) 65.3, (c) 115.3, (d) 165.3, and (e) 915.3 s after the *T*-jump to 190 °C. The exposure time for each 2D pattern is 0.288 s. Part a' schematically illustrate the specially aligned hex-cyl with the cylinder axis and {11} plane parallel to the OX axis and the OXZ plane, respectively, while parts e'1, e'2, and e'3 schematically illustrate the unit cells of specially aligned bcc-sphere A and A' as characterized by the 2D SR-SAXS pattern shown in part e. The broken lines show the lattice plane of bcc-sphere, {110}, {200} and {112}. A and A' are in mirror symmetry with respect to the OXZ and OYZ plane, and their {112} plane and {111} axis are commonly oriented parallel to the OXZ plane and the OX direction, respectively.

Thus, the 2D SR-SAXS patterns taken from the three orthogonal directions are consistently interpreted to reflect the directed structural transformation from the specially aligned hex-cylinder to twin bcc-sphere A and A' via the epitaxial transformation mechanism as described above.

3.2.2. Quantitative Analyses of Diffraction Peak Profiles.

The symmetry change of the ordered phase induced by the OOT can be most clearly discerned with the SAXS pattern taken with the incident beam parallel to the OZ direction as shown in Figure 4. Therefore, in Figure 7, we focus on quantitative analyses of the time evolutions of the four first-order diffraction profiles, corresponding to {110} diffraction from bcc-sphere, and the two meridional diffraction profiles, corresponding to {11} diffraction from hex-cylinder plus {112} diffraction from bcc-sphere, the Bragg angle at the peak intensity for {11} diffraction being almost identical to that for {112} diffraction. These diffraction intensity distributions are presented as a function of the azimuthal angle μ and the magnitude of the scattering vector q_r in the polar coordinate defined in the top left corner in part b.

Figure 7a defines the Cartesian coordinate OXYZ and the time-resolved diffraction profiles to be presented in parts b–d. Figure 7b plots μ -dependence of the first-order diffraction maxima corresponding to {110} lattice plane of bcc-symmetry A and A', $I_{\{110\}}(\mu; t)$, as a function of time t . We deliberately use the term “bcc symmetry” in place of “bcc-sphere” here in order to emphasize that the structural entity reflecting {110} diffraction in the beginning of the OOT process is not sphere but rather the undulated hex-cylinder (the precursory bcc-sphere) with bcc-symmetry. It is interesting to note that the precursory structure appears to be already set in step I at $t < t_{cl}$, as will be further clarified later in conjunction with Figure 9. The term bcc-symmetry is defined hereafter to generally include bcc-sphere at the end of the OOT process, unless otherwise stated. In this plot, the intensity, $I_{\{110\}}(\mu; t)$, are integrated around $q_r = q_{m,\{110\}} = 0.22 \text{ nm}^{-1}$ in the range between $q_r = 0.190$ and 0.259 nm^{-1} , which includes $q_{m,\{110\}}(t)$ independent of t throughout the OOT process. Figure 7c plots the time evolutions of the intensity distribution of the first-order diffraction maximum corresponding to {110} diffraction from bcc-symmetry A' with respect to q_r , $I_{\{110\}}(q_r; t)$, sector-averaged over the range of μ .

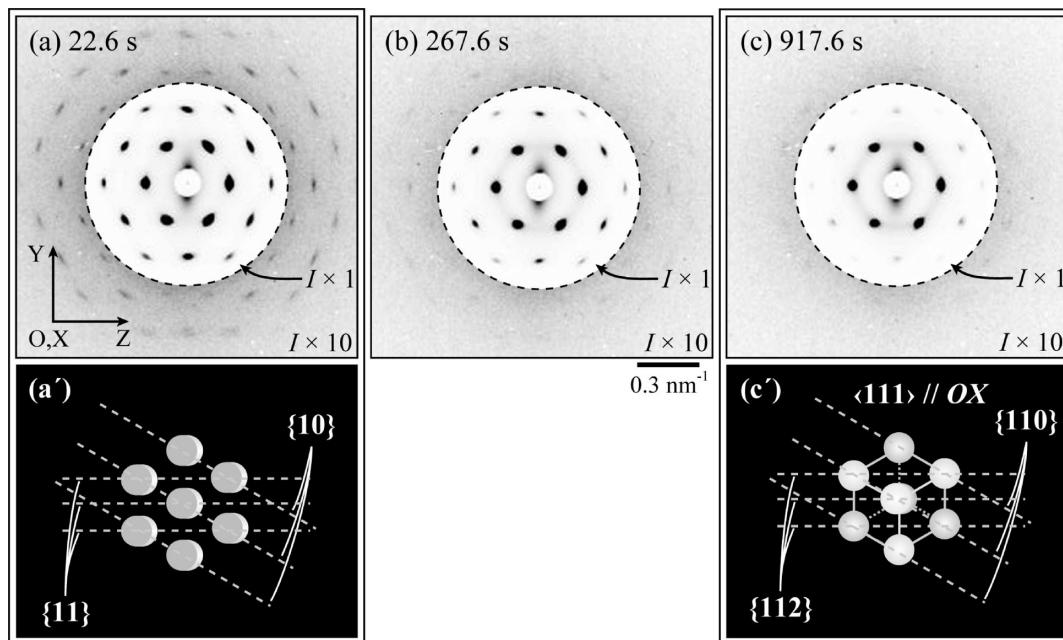


Figure 5. Time evolution of the 2D SR-SAXS pattern with the incident X-ray beam along the OX axis, taken *in situ* at (a) 22.6, (b) 267.6, and (c) 917.6 s after the T -jump to 190°C . The exposure time for each 2D pattern is 3.632 s. Parts a' and c' schematically illustrate the microdomain structures visualized from the 2D SR-SAXS patterns a and c, respectively. The intensity outside of the dashed circular line in parts (a) to (c) is multiplied by 10 times relatively to that inside the line.

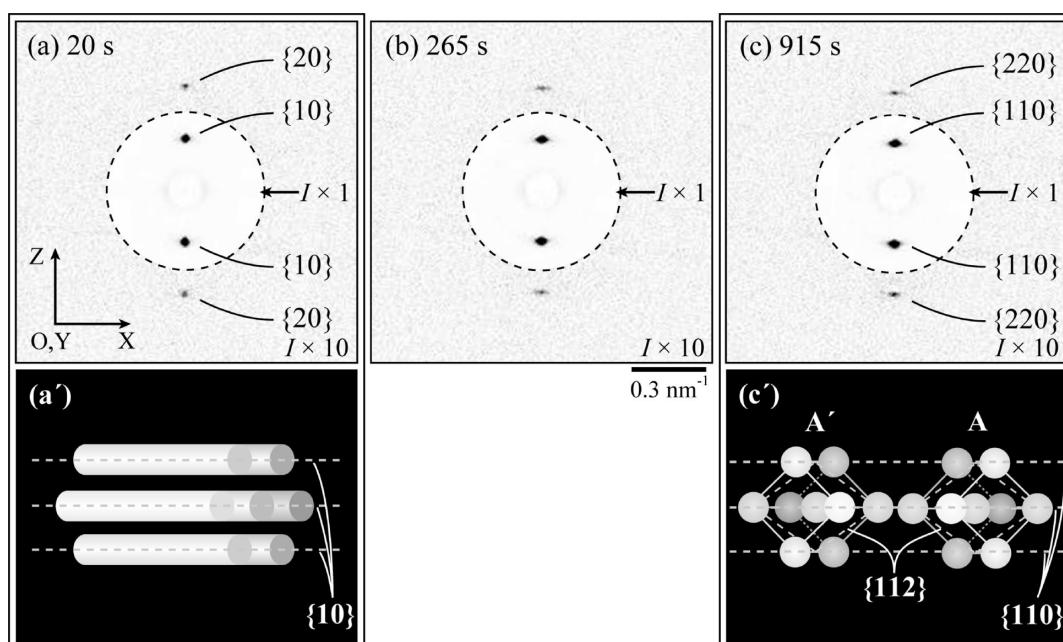


Figure 6. Time evolution of the 2D SR-SAXS pattern with the incident X-ray beam along the OY axis, taken *in situ* at (a) 20, (b) 265, and (c) 915 s after the T -jump to 190°C . The exposure time is 14.688 ms. The intensity outside of the dashed circular line in parts (a) to (c) is multiplied by 10 times relatively to that inside the line. (a') and (c') schematically illustrate hex-cylinder and the unit cell of bcc-sphere A and A' together with {10} lattice plane for hex-cylinder and {110} and {112} lattice planes for bcc-sphere A and A', as characterized by the 2D SR-SAXS patterns (a and c), respectively.

between $\mu = 40$ and 70° as defined in the inset to part c, while Figure 7d plots $I_{\{11\}/\{112\}}(q_r; t)$ for the first-order diffraction maximum corresponding to hex-cylinder plus {112} diffraction corresponding to bcc-symmetry, sector-averaged over the range of μ between $\mu = 170$ and 190° as defined in the inset to part d.

Parts b and c in Figure 7 revealed that both the first-order diffraction peak intensity at $\mu = 54, 126, 234$, and 306° and at $q_r = 0.22 \text{ nm}^{-1}$ and that at $\mu = 54^\circ$ and at $q_r = 0.22 \text{ nm}^{-1}$ started

to increase at $t > 40$ s without changing the peak position with respect to μ and q_r , respectively, as the precursory structure of bcc-symmetry (the undulated hex-cyl) starts to appear. It became larger, as the precursory structure and/or bcc-sphere further grows and eventually reached a steady value at $t \geq 600$ s. On the other hand, Figure 7d shows the scattering profile $I_{\{11\}/\{112\}}(q_r; t)$ around {11} diffraction due to hex-cylinder, the undulated hex-cylinder, and {112} diffraction due to bcc-sphere.

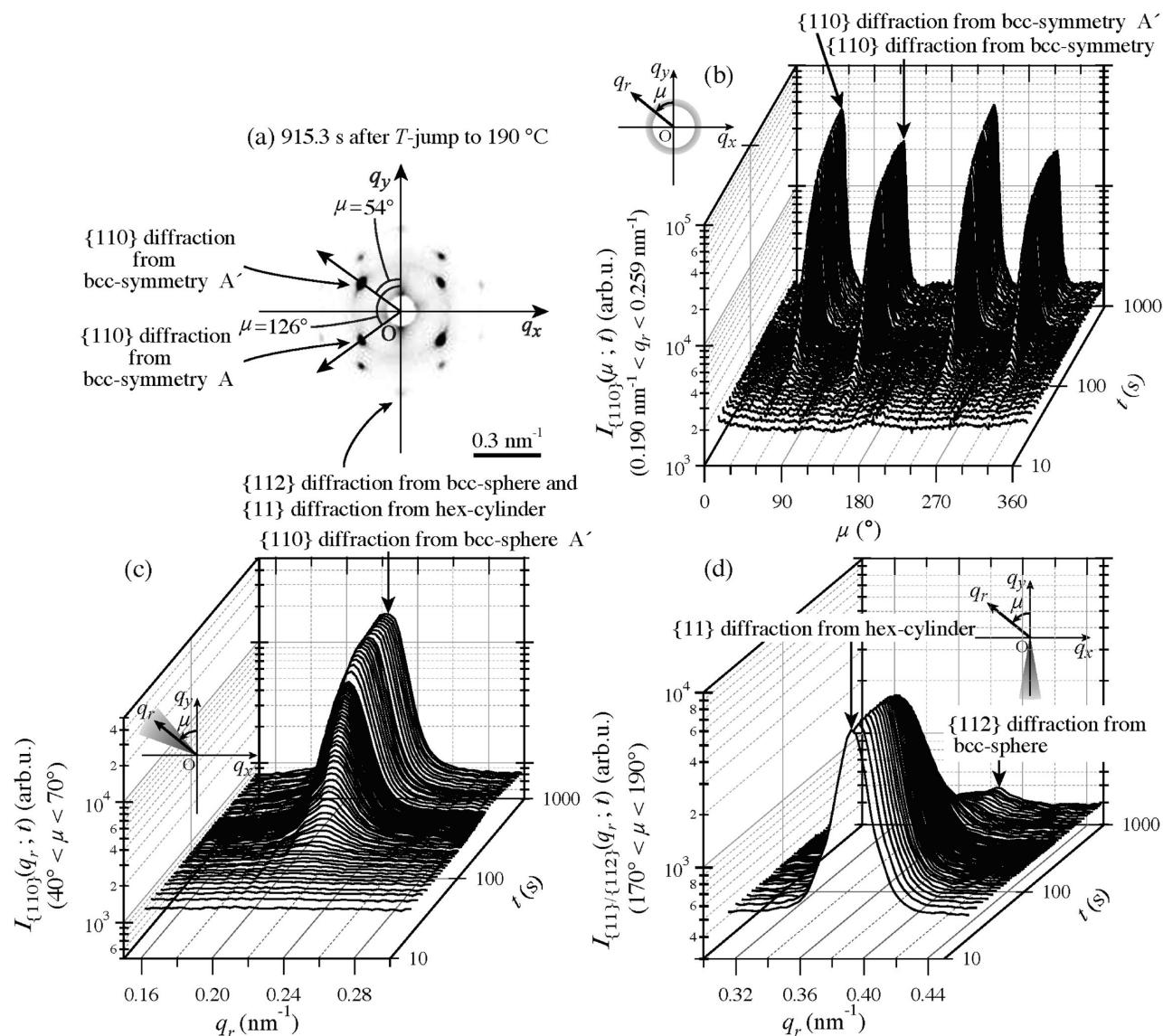


Figure 7. (a) Definition of the Cartesian coordinate OXYZ for the 2D SR-SAXS patterns taken at 915.3 s after the T-jump to 190 °C with the incident X-ray beam along the OZ axis. (b) Time evolution of azimuthal angle, μ , dependence of the first-order diffraction maxima from {110} diffraction of bcc-symmetry A and A'. The azimuthal angle μ is defined in part b: μ increases counterclockwise from zero along the q_y direction. The intensities are integrated in the range of q_r between $q_r = 0.190$ and 0.259 nm^{-1} , where q_r is the scattering vector in polar coordinates. (c) Time evolutions of the intensity distribution for {110} diffraction of bcc-sphere A', with respect to q_r sector-averaged in the range of μ between $\mu = 40$ and 70° , and (d) that for {11} diffraction of hex-cylinder plus {112} diffraction of bcc-symmetry sector-averaged in the range of μ between $\mu = 170$ and 190° .

To describe more specifically and clearly, {11} diffraction of hex-cylinder contributes to the scattering peak intensity only in the beginning of the OOT: The relative contribution of {11} diffraction of hex-cylinder, {112} diffraction from the precursory structure, and {112} diffraction of bcc-sphere to the scattering peak intensity changes with time in the course of the OOT, and eventually only {112} diffraction of bcc-sphere contributes to the scattering peak intensity in the end of the OOT.

4. DISCUSSION

4.1. Quantitative Reciprocal-Space Analysis of the OOT Process. In order to follow the OOT process more precisely and deeply, we plotted the time evolutions of the characteristic scattering parameters presented in Figure 7, as shown in Figure 8. Figure 8 shows (a) the peak intensity $I_{m,\{110\}}(t)$ of $I_{\{110\}}(q_r; t)$ at $q_r = q_{m,\{110\}}(t)$ shown in Figure 7,

parts b and c, (b) the azimuthal angle $\mu_{m,\{110\}}(t)$ at the peak intensity $I_{m,\{110\}}(t)$ for {110} diffractions, (c) the peak intensity $I_{m,\{110\}}(t)$ and $\sigma_{q,\{110\}}^2(t)$ for {110} diffraction, where σ_q is the half-width at half-maximum of the diffraction peak at $q_r = q_{m,\{110\}}(t)$, and (d) the peak intensity $I_{m,\{11\}/\{112\}}(t)$ of $I_{\{11\}/\{112\}}(q_r; t)$ at $q_r = q_{m,\{11\}/\{112\}}(t)$ and the corresponding values $\sigma_{q,\{11\}/\{112\}}^2(t)$ for {11}/{112} diffraction.

The overall trend observed in the time evolutions of the characteristic scattering parameters shown in Figure 8 suggests that the OOT process is classified into three steps, I, II, and III, separated by the two critical times, t_{c1} and t_{c2} , as shown in the top of part a at which some of the parameters characteristically change. Parts a and b of Figure 8 present the time evolutions of the peak intensity and the azimuthal angle at the diffraction peaks for {110} diffraction. The peak intensity I_m starts to increase gradually right after the T-jump in step I as seen in the

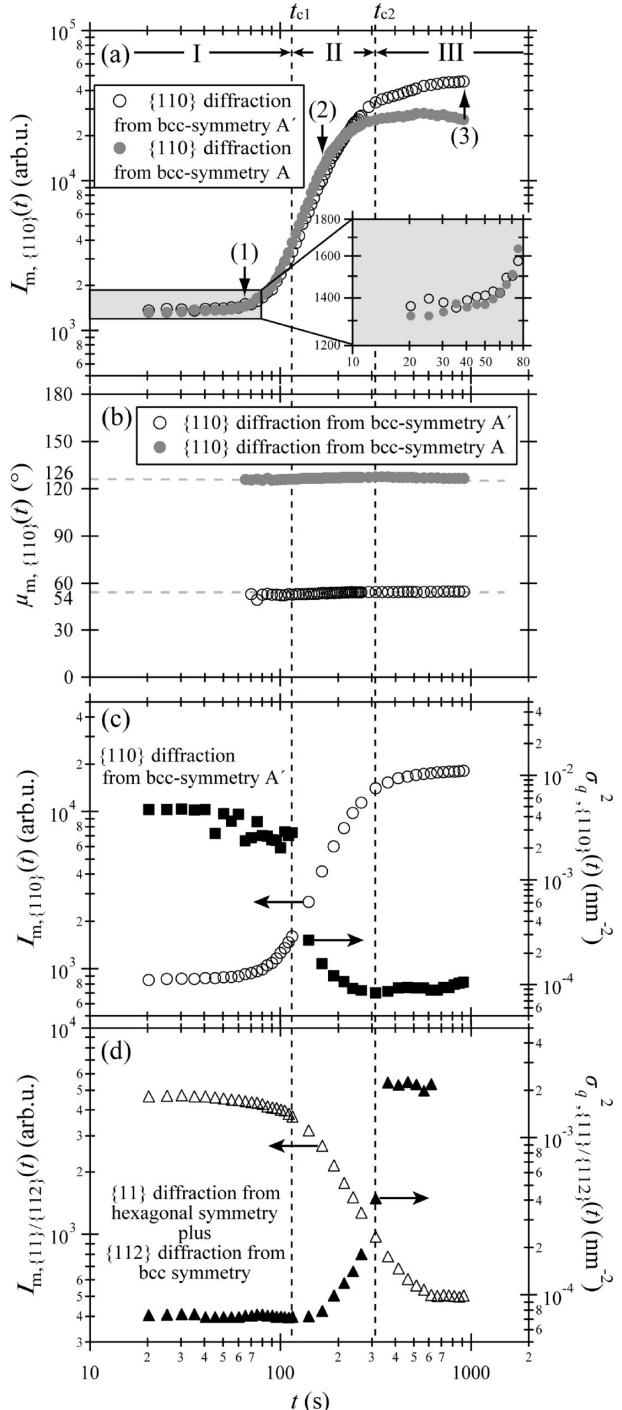


Figure 8. (a) Time evolutions of the peak intensity in the $\{110\}$ diffraction from bcc-symmetry A and A' shown in Figure 7b. The inset magnifies the intensity scale of the part encompassed by the rectangle. The specimens are frozen below the T_g for the TEM observations at the time specified by the arrows marked with (1)–(3). (b) Time evolutions of the azimuthal angle at the diffraction peaks, $\mu_{m,\{110\}}(t)$, from the $\{110\}$ lattice plane of bcc-sphere A and A' in Figure 7b. (c) Time evolutions of the peak intensity from the $\{110\}$ lattice plane and the square of the half-width at half-maximum, $\sigma_{q,\{110\}}^2(t)$, for the $\{110\}$ diffraction of bcc-symmetry A' in Figure 7c. (d) Time evolutions of the peak intensity and $\sigma_{q,\{110\}/\{112\}}^2(t)$ for $\{111\}$ diffraction from hex-cyl plus $\{112\}$ diffraction from the bcc-symmetry in Figure 7d. The time evolutions of the characteristic scattering parameters classify the kinetic pathway for the structural transformation driven by the OOT into the three steps, I, II, and III, separated by the characteristic times, t_{c1} and t_{c2} , as specified on the top of part a.

inset to Figure 8a and eventually reaches an almost steady value in step III at $t > t_{c2}$. The slightly different peak-intensity levels between bcc-sphere A and A' in step III may reflect the ratio of their populations. It looks that bcc-sphere A' is a little more abundant than bcc-sphere A. However the different intensity might occur even in the case of the populations of bcc-sphere A and A' being equal, if the A sphere is slightly tilted with respect to the incident beam so that some grains of bcc-sphere A are tilted into off-diffraction positions, possibly due to thermal stress involved in the OOT process. The value of $\mu_{m,\{110\}}(t)$ for bcc symmetry A' (open circles) and that for A (filled circles) did not change at all in the course of the OOT. They were kept at 54 and 126° , respectively, which are almost identical to the theoretical values of bcc-sphere with $\{112\}$ plane and $\langle 111 \rangle$ axis parallel to the OXZ plane and OX axis, respectively. This indicates that the bcc symmetry is kept in the microdomain structures during the OOT process, as the theories predict.^{9,11,12}

Figure 8c plots the time evolutions of the peak intensity and $\sigma_{q,\{110\}}^2(t)$ where the time evolution of the peak intensity shown already in part (a) was deliberately presented here as a reference. The values $\sigma_{q,\{110\}}^2(t)$ are very large and slightly decreased in step I. It sharply decreased in the beginning of step II at $t > t_{c1}$ and reached a steady value in step III. Figure 8d shows the time evolutions of the peak intensity and $\sigma_{q,\{11\}/\{112\}}^2(t)$, presented in Figure 7d. The peak intensity and $\sigma_{q,\{11\}/\{112\}}^2(t)$ kept almost a constant value in step I. The peak intensity started to only slightly decrease at $t > 40$ s in step I. It decreased sharply at $t \geq t_{c1}$ in step II and then gradually reached the steady intensity level at $t \geq t_{c2}$ in step III. On the other hand, σ_q^2 started to gradually increase in the beginning of step II at $t \geq t_{c1}$, then very sharply increased near the end of step II, and reached the constant value in step III at $t > t_{c2}$.

The cylindrical microdomains themselves to undulate, break, and transform into spherical microdomains during the OOT process. The time, t_{c1} , is the critical time for the onset of the transition, and step I is the pretransitional or incubation period. The change in the peak intensity in parts a or c and d as well as the change in σ_q^2 in part c in step I must elucidate that hex-cylinders cooperatively undulate with the bcc-symmetry as pointed out earlier and with the amplitude of the undulation increasing with time. The small and almost constant values of $\sigma_{q,\{11\}/\{112\}}^2(t)$ in step I, as shown in part d, interestingly imply that the lattice spacing of $\{111\}$ plane for hex-cylinder and that of $\{112\}$ plane of the precursory structure are well registered and subjected to very small distortions. However, the lattice spacing $\{110\}$ newly developed in step I is not well registered yet as evidenced by the large values $\sigma_{q,\{110\}}^2(t)$ in part c. $\sigma_{q,\{110\}}^2(t)$ slowly decreased with t and then very rapidly decreased in the beginning of step II where the lattice spacing $\{110\}$ is well registered and the bcc-symmetry is well established.

In step II, main structural changes occur for the OOT process, including cooperative breakup of the cylinders at the pinching points and relaxation of the broken-up cylinders into spheres with increasing perfection of the bcc symmetry, as evidenced particularly clearly in part c with respect to the increasing peak intensity and decreasing $\sigma_{q,\{110\}}^2(t)$ with t . The increase of $\sigma_{q,\{11\}/\{112\}}^2(t)$ in step II as shown in part d is a consequence of $\sigma_{q,\{11\}}^2(t)$ in hex-cylinder having the 2D symmetry being smaller than that in bcc-sphere having the 3D symmetry. Finally bcc-sphere is expected to attain an increasing perfection with time in step III as shown by the gradual increase of the peak intensity to the steady value as evidenced by part c.

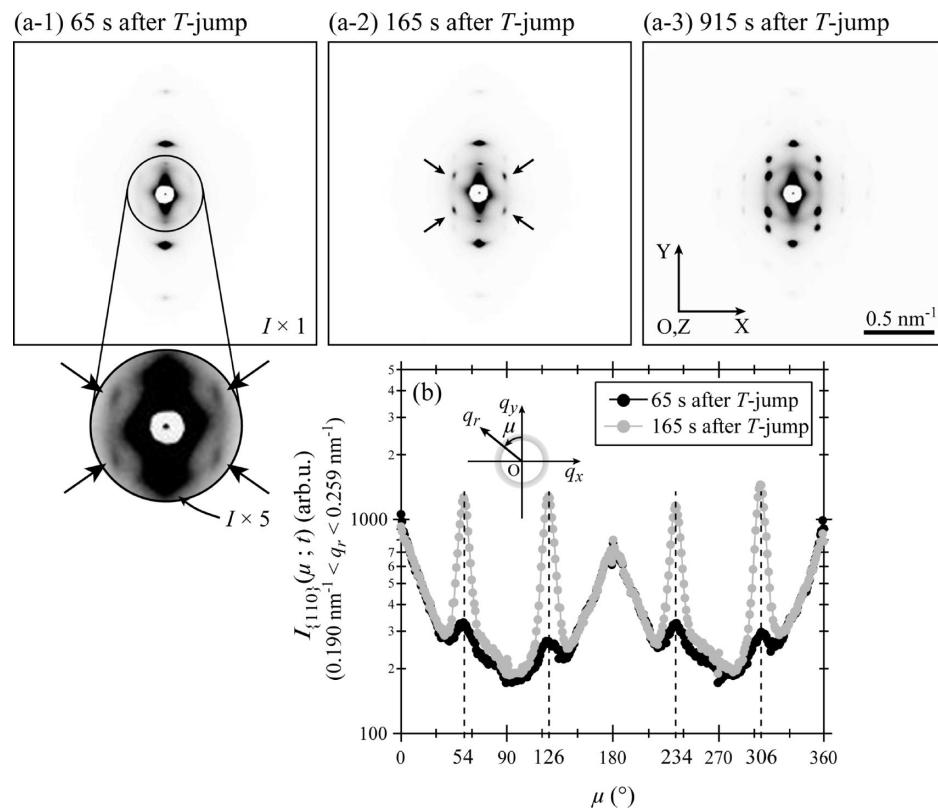


Figure 9. 2D SR-SAXS patterns with the incident X-ray beam along the OZ axis, measured for the specimens frozen at (a-1) 65 s [point (1) in Figure 8a], (a-2) 165 s [point (2) in Figure 8a], and (a-3) 915 s [point (3) in Figure 8a] after the T -jump to 190°C . The exposure times to take the patterns shown in parts a-1 to a-3 is 8.464 s. The arrows in (a-1) and (a-2) highlight the first-order diffraction maxima in the diagonal directions at $\mu = 54, 126, 234$, and 306° . (b) Azimuthal angle, μ , dependence of the first-order diffraction maxima in parts a-1 and a-2. The definition of μ is shown in the inset to part b and is the same as in Figure 7. The intensities of the diffraction maxima were integrated in the range of q between $q_r = 0.190$ and 0.259 nm^{-1} .

In order to clarify the structural changes predicted from the time-resolved SAXS intensities in each step, the specimens were frozen at the time specified by the arrows marked with (1)–(3) in Figure 8a for the TEM observations.

4.2. Ex-Situ Real-Space Analysis of the OOT Process with TEM Method. **4.2.1. Conservation of Structures Developed at 190°C after Vitrification of the Specimens.** The TEM method inevitably requires to vitrify the samples subjected to the OOT for given period of times at 190°C by rapidly quenching them below the T_g . It is crucial for us to rigorously check whether or not the structures existed in situ before the quenching are identical to those after the quenching. For this purpose, we compared the SAXS patterns from specimens taken in situ at given times at 190°C with those for the corresponding specimens taken at room temperature after quenching them below the T_g . In this work, we took the 2D SR-SAXS patterns for the specimens frozen at the times specified by the arrows marked with (1)–(3) in Figure 8a at room temperature and compared them with those taken in situ at 190°C shown in Figure 4b, d, and e, respectively.

Figure 9 shows the 2D SR-SAXS patterns, taken with the incident beam parallel to the OZ direction as shown by the attached coordinate shown in part a-3, from the specimens frozen below the T_g at (a-1) 65, (a-2) 165, and (a-3) 915 s after the T -jump to 190°C , and (b) μ -dependence for the first-order diffraction maxima of the patterns shown in Figure 9, a-1 and a-2. These 2D SR-SAXS patterns can be found to be qualitatively identical to the corresponding patterns taken in situ before quenching, as shown in Figure 4, parts b, d, and e. More

quantitative comparisons of the patterns before and after the quenching will be presented later in Figure 10. The pattern obtained at 65 s after the T -jump typically reflects the pretransitional structure in step I [at point (1) in Figure 8a]. The four diffraction maxima in the diagonal directions are recognized only faintly at $\mu_{m,\{110\}} = 54, 126, 234, 306^\circ$ as indicated by the arrows shown in Figure 9a-1 and also by the μ -dependence of the peak intensity shown in Figure 9b (black symbols).

It is anticipated that this signature indicates a pretransitional state in the OOT: The positions of $\mu_{m,\{110\}}$ as shown by the arrows in Figure 9a-1 elucidate that the bcc symmetry has already emerged in the undulated hex-cylinders. The pattern at 165 s after the T -jump reflects the transient structure in transition period from hex-cylinder to bcc-sphere in step II [point (2) in Figures 8a]. The four diffraction maxima in the diagonal directions can now be more clearly seen at the same azimuthal angles as the pattern shown in part a-1, as indicated by the arrows in Figure 9a-2 and in the profile shown in Figure 9b (filled gray circles). The pattern at 915 s after the T -jump reflects the structure in the final stage in step III [point (3) in Figure 8a]. The diffraction spots up to the third-order maximum shown in Figure 9a-3 indicate that the sample space is completely occupied by well-ordered bcc-sphere A and A'. The first-order diffraction peaks in Figure 9a-3 were so intense that the peak intensity was saturated, so that its μ -dependence was omitted deliberately in Figure 9b. However the positions of the diffraction maxima are utterly unchanged, having the same $\mu_{m,\{110\}}$ and $q_{m,\{110\}}$.

Figure 10 quantitatively compares $I_{\{110\}}(q_r; t)$ around the first-order peak for the specimens before (open circles) and after the

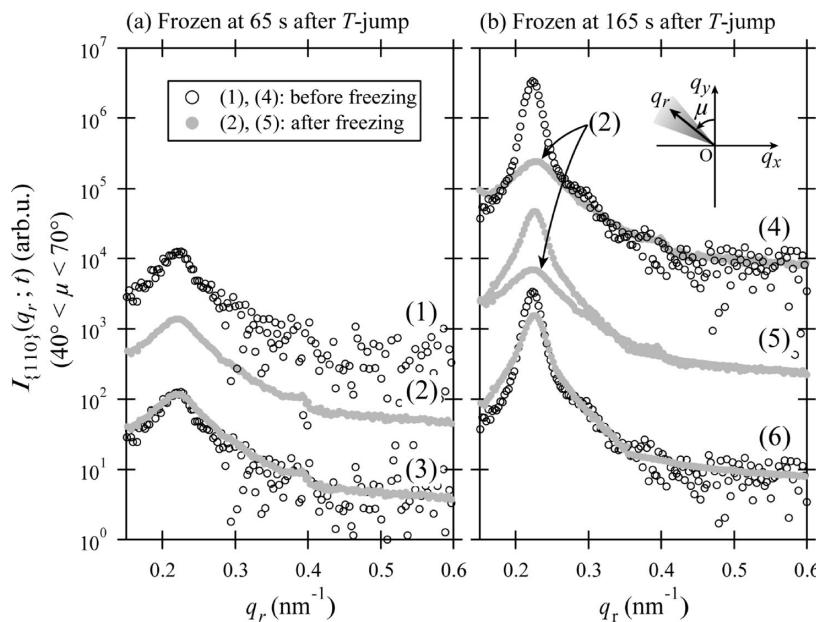


Figure 10. Comparisons of the scattering profiles $I_{\{110\}}(q_r, t)$ defined in Figure 7 before and after the freezing below the T_g at 65 (a) and 165 s (b). Profiles (1) and (4) for the specimens before freezing are vertically shifted relative to those (2) and (5) for the specimens after freezing, respectively. Profiles (3) and (6) are obtained by superposing profiles (1) and (2) and profiles (4) and (5) at the peak intensity, respectively. Profile (2) underneath profiles (4) and (5) is matched to profiles (4) and (5) at the high- q and low- q -tails of profiles (4) and (5) by a vertical shift of profile (2).

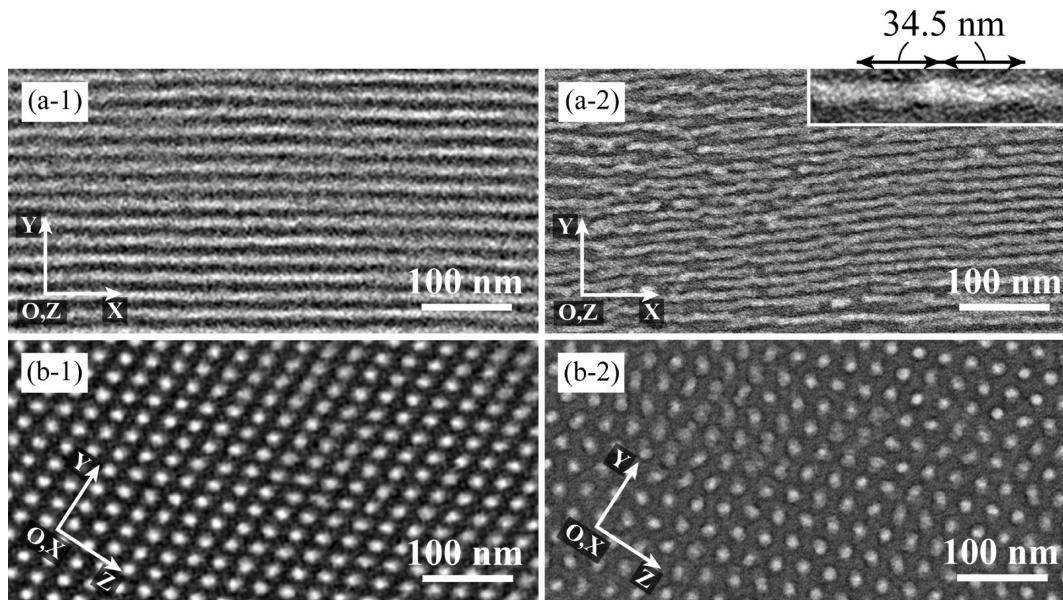


Figure 11. Transmission electron micrographs (a-1 and b-1) taken with the electron beam along the OZ axis and the OX axis for the aligned hex-cylinder at 170 °C before the T-jump, respectively, and those (a-2 and b-2) taken under the same condition as in parts a-1 and a-2, for the specimen frozen at 65 s [point (1) in Figure 8a] after the T-jump to 190 °C, respectively. A special care was taken to obtain the ultrathin section thinner than ~50 nm, as judged from the interference color.

vitrification (filled gray circles). The two profiles (1) and (2) in part a and those (4) and (5) in part b are separately presented with a vertical shift to avoid an overlap in order to facilitate detailed inspections of each profile. On the other hand, they are vertically shifted to overlap at the peak intensity in profile (3) in part a and profile (6) in part b in order to analyze the identity of these two profiles. The profiles were obtained in situ at 65 s and 165 s, after the onset of the OOT for profiles (1) and (4), respectively, and then the specimen was frozen below the T_g to take profiles (2) and (5), respectively. The SAXS profiles (1)

and (4) were taken with an exposure time of 0.288 s, while those (2) and (5) were taken with an exposure time of 8.464 s.

The identity of profiles (1) and (2) in part a revealed that the structure developed in situ in step I is successfully vitrified for the TEM observation. However, profiles (4) and (5) in part b indicate some difference as clearly seen in some disparity of the overlapped profiles (6). The detailed analyses of profiles (4) and (5) reveal that they are composed of a sharp peak and a broad peak; the sharp peak is superposed on the top of the broad peak; The broad peak (2) in part a can be nicely fitted with the low and high q tail of profiles (4) and (5) as demonstrated by

the superposed profiles (4) and (2) and profiles (5) and (2) in part b. This elucidates that the profiles very well reflect contributions from both nucleated grains of the bcc-sphere A' and the undulated hex-cylinders in the matrix phase of the grains. The disparity of profiles (4) and (5) as seen in the overlapped profiles (6) in part b reflect simply the difference of the two contributions between the specimens used before and after quenches, since we carelessly used different specimens for the *in situ* observations and for the observations after the vitrification. Nevertheless, the analyses of the profiles prove a success of the vitrification for the TEM observations. Needless to say we can avoid the disparity of the profiles before and after the vitrification as seen in profiles (6), if we used the same specimens.

Having verified the conservation of the *in situ* existing structures at 190 °C in the specimens after the quenching, we now discuss the frozen transient structures evolved during the OOT with the TEM.

4.2.2. Step I (Pretransition Period). Parts a-2 and b-2 in Figure 11 show the TEM images for the specimen frozen at 65 s after the *T*-jump [point (1) in Figure 8a] observed with the electron beam along the OZ and OX direction, respectively. The corresponding image for the aligned hex-cylinder at 170 °C before the *T*-jump is shown in Figure 11, parts a-1 and b-1, respectively, as a reference. It is observed in Figure 11a-2 that hex-cylinder undulated periodically, while the hex-cylinder in part a-1 is straight. The undulation spacing [$D_{un} = (3/2)^{1/2}(2\pi/q_{m,\{110\}})$] estimated from the magnitude of the scattering vector, $q_{m,\{110\}}$, at the first-order diffraction maximum, $D_{un} = 34.5$ nm, is roughly consistent with that observed in the inset of Figure 10a-2.

Parts b-1 and b-2 of Figure 11 show the TEM images taken normal to the cylinder axis. The image shown in part b-1 for the straight hex-cylinder reveals that the cross sections of the cylinders have a uniformly bright contrast with a sharp contrast variation across the interface with the dark matrix phase; they have rather a uniform diameter too. On the other hand, the image shown in part b-2 for the undulated hex-cylinders reveals that the cross sections have nonuniform brightness with a gradual contrast variation across the interface; they have a rather nonuniform diameter. Since the straight and undulated cylinders have highly aligned along the OX axis, there are no orientation fluctuations of the cylinder axes over the thickness of the ultrathin section less than ~50 nm. Thus, the differences of the two cross-sectional images (b-1 and b-2) as described above is not due to the orientation fluctuations. They must reflect whether or not the undulation exists. The nonuniformity in the brightness and diameter in the cross-sectional image of the cylinder in part b-2 relative to those in part b-1 is a consequence of varying location of the center of bulging point of the undulated cylinder along the thickness direction in the ultrathin section of thickness less than 50 nm.

The 2D SR-SAXS pattern in Figure 9a-1 and the μ -dependence of the first-order diffraction maxima observed in the pretransitional period suggest that the undulated cylinders having the twin bcc symmetry A and A' must exist in the system. We tried to confirm this evidence by means of the real space observations with TEM for the specimen successfully frozen at 65 s in step I after the *T*-jump. Figure 12 might offer a hint for us to find the trend described above. The figure was obtained on the same specimen and under the same condition as in Figure 11 but with a slightly larger magnification. It shows more or less uniformly undulated hex-cylinder where parts b and c encompassed by white rectangles in part a might infer the undulated hex-cyl with bcc-symmetry A' and that with bcc-symmetry A as indicated in the enlarged

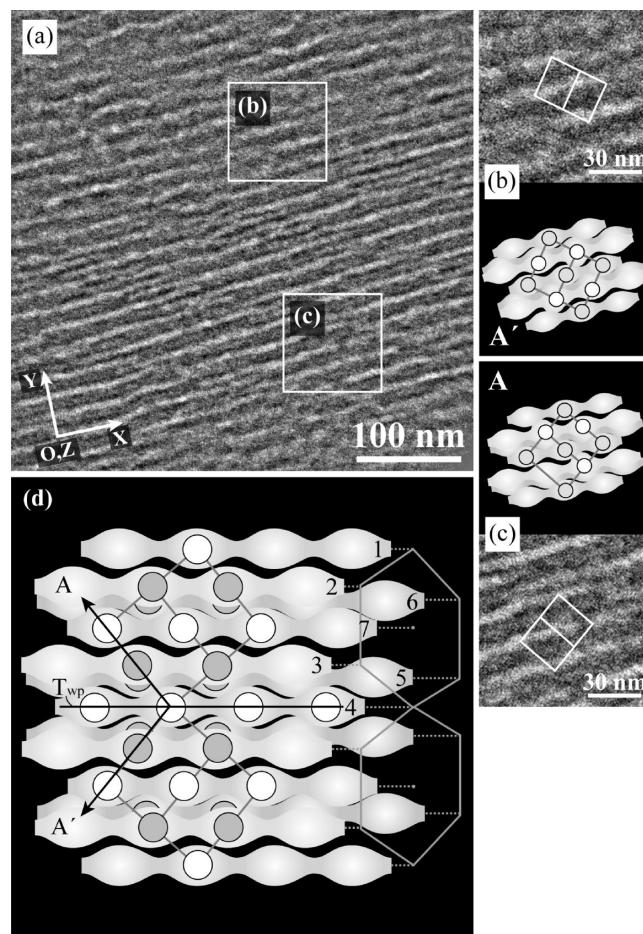


Figure 12. (a) Transmission electron micrographs taken with the electron beam along the OZ axis for the specimen frozen at 65 s [point (1) in Figure 8a] after the *T*-jump to 190 °C. (b) Enlarged image of a part of image a encompassed by the white square labeled b together with a sketch illustrating the unit cell of the bcc-symmetry A' and the model for A'. (c) Enlarged image of a part of image a encompassed by the white square labeled c together with a sketch illustrating the unit cell of the bcc-symmetry A and the model for A. (d) Schematic illustration for twin bcc-symmetry A and A' with the twin plane indicated by the line T_{wp} parallel to the OXZ plane. The position of the bulging points shifts along the arrow A and A' with increasing the displacement of the axis of the undulated cylinder with respect to the twin plane.

images b and c together with their schematic models, respectively. The undulated hex-cyl with bcc-symmetry A and that with A' are different only with respect to the spatial arrangement of the pinching points and bulging points as schematically shown in part d: The centers of the bulging points shift along the arrow A for the one with bcc-symmetry A but along the arrow A' for the one with bcc-symmetry A' with respect to a common twin plane indicated by the line T_{wp} . The undulation fluctuation modes observed in our 2D SR-SAXS and TEM correspond to the most unstable modes predicted by Laradji et al.^{11,12} [especially Figures 7 and 9 of ref 12]. Beyond this theoretical prediction, the experimental results further suggest existence of the degeneracy of the fluctuation modes in the form of the undulated cylinders having twin bcc-symmetry A and A' which are eventually directed to develop into the twin bcc-sphere composed of bcc-sphere A and A' at the end of the OOT. We must admit that the real images shown in parts a–c are still very ambiguous to unequivocally support the model

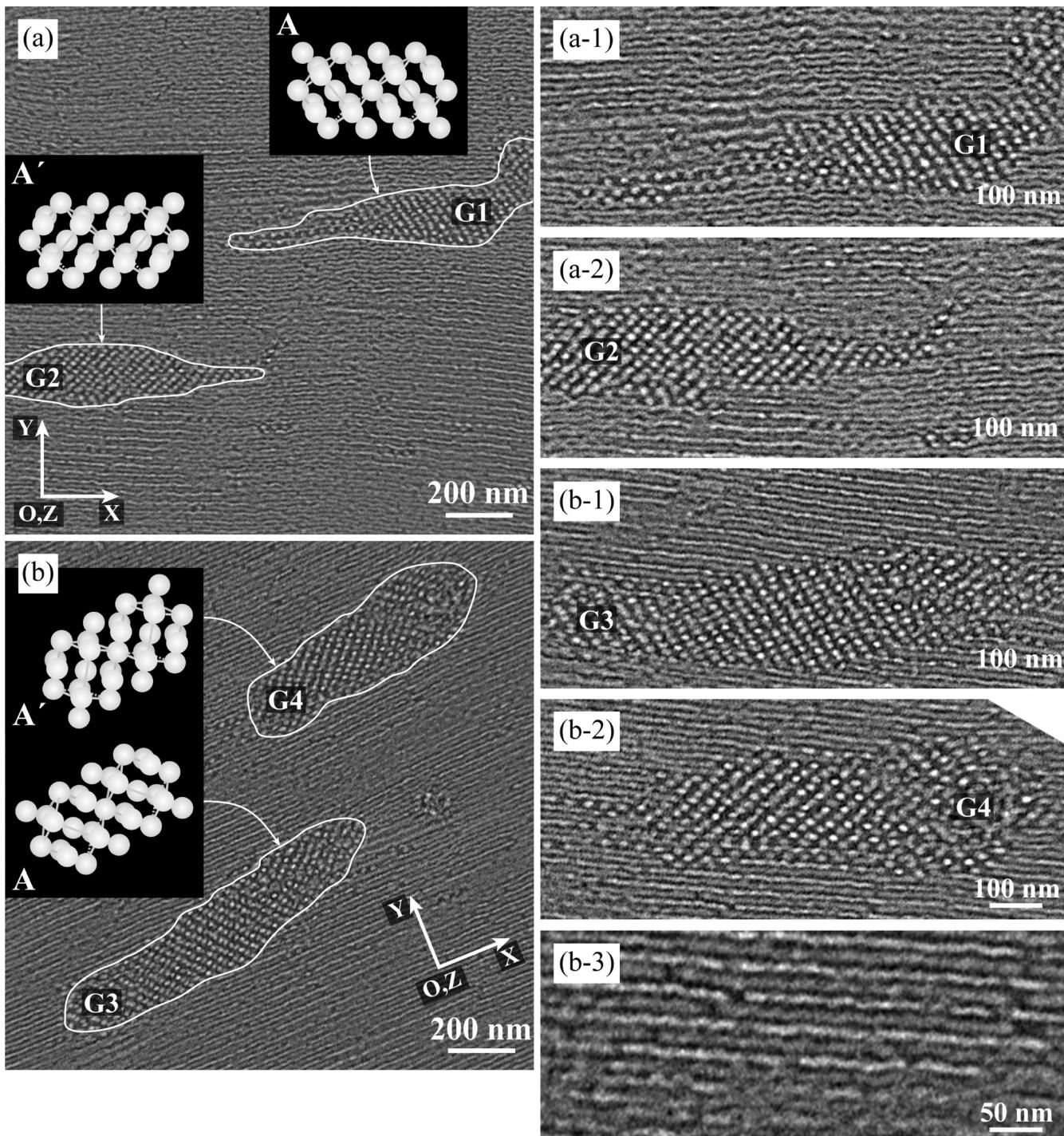


Figure 13. (a and b) Two typical transmission electron micrographs taken at different areas of the specimens frozen at 165 s [point (2) in Figure 8a] after the T -jump to 190 °C, observed with the electron beam along the OZ direction. The white solid lines encompass grains of bcc-sphere G1 and G2 in part a and G3 and G4 in part b in the matrix of the undulated cylinders. Parts a-1, a-2, b-1, and b-2 are the enlarged images for the grains G1 to G4, respectively. The grains G1 and G3 are composed of bcc-sphere A as shown in the insets of parts a and b, while grains G2 and G4 are composed of bcc-sphere A' as shown in the insets of parts a and b. (b-3) Micrograph which enlarges the matrix phase shown in part b.

shown in part d. The investigation along this line deserves future work.

4.2.3. Step II (Transition Period). Figure 13 shows typical TEMs for the specimen frozen at 165 s in step II after the T -jump [point (2) in Figure 8a], observed with the electron beam along OZ direction. Figure 13a demonstrates that the grains composed of bcc-sphere, designated as G1 and G2, are explicitly observed in the matrix of undulated cylinder,

magnified images of which are shown in parts a-1 and a-2. More precisely, the grains G1 and G2 are composed of bcc-sphere A and A', respectively, as defined in Figure 4e'i. Figure 13b shows another representative area showing the grains G3 and G4 composed of bcc-sphere nucleated and grown from the matrix of the undulated hex-cyl. Parts b-1–b-3 present the magnified images of the grains G3 and G4 and the matrix phase, respectively, which clearly reveals bcc-sphere A, bcc-sphere A',

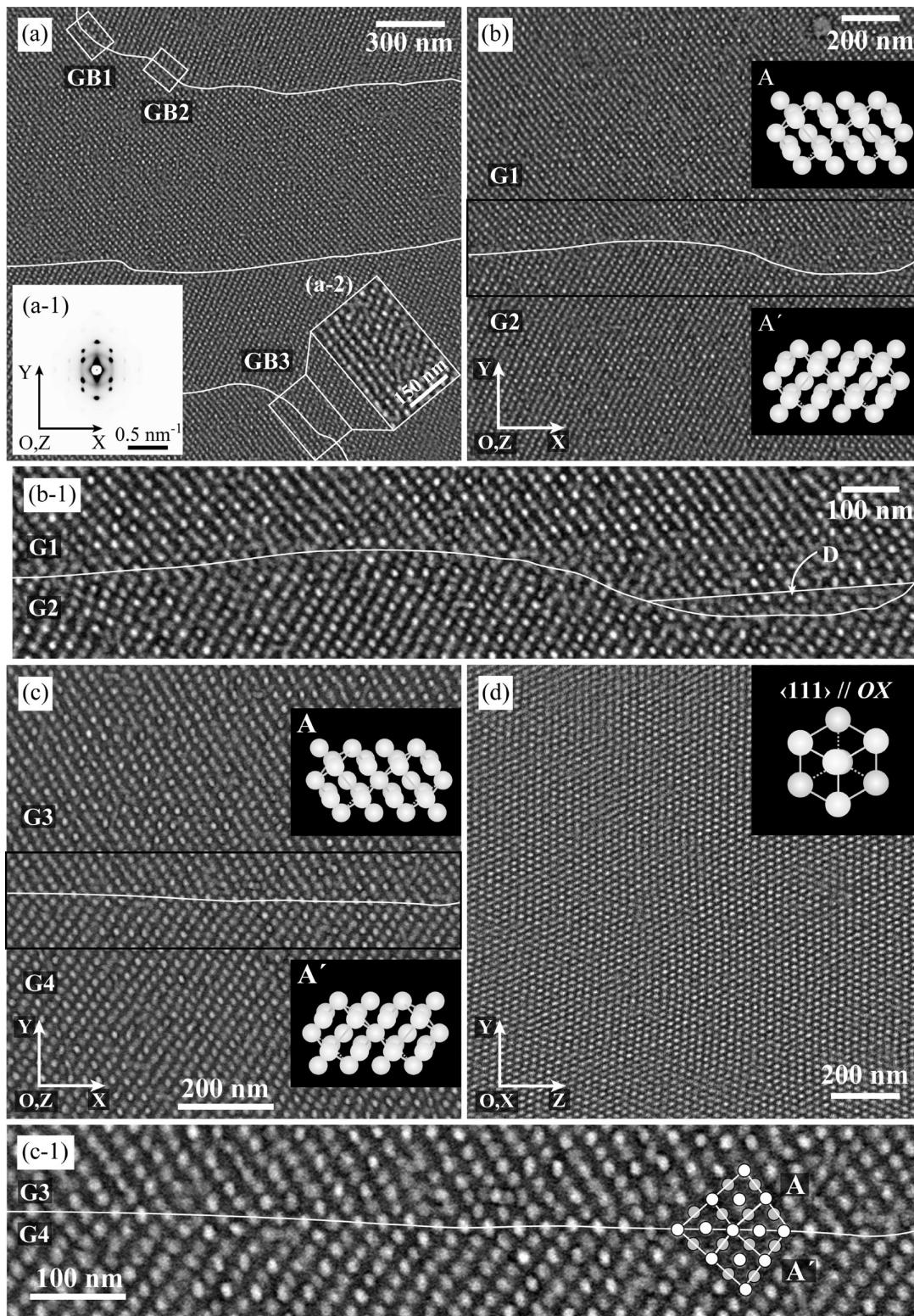


Figure 14. Transmission electron micrographs for the specimen frozen at 915 s [point (3) in Figure 8a] after the T -jump to 190 °C, observed with the electron beam along the OZ direction. Key: (a) image taken with the lowest magnification; (b and c) image taken with the intermediate magnification in different areas in the specimens together with the schematic illustrations showing bcc-sphere A and A' in each grain. The white solid line traces a twin plane as the grain-boundary plane between bcc-sphere A and A' except for the ordinary grain-boundary planes defined by GB1 to GB3 in part a, the fine morphology of which is shown typically in the inset (a-2) obtained for GB3 with a higher magnification. (b-1 and c-1) Micrographs with the highest magnification which enlarge the region encompassed by the black rectangle in parts b and c, respectively, together with a sketch of the twin plane forming the grain boundary. Part b-1 shows the region encompassed by the white line labeled D where the lattice mismatches and distortions are found at and above the twin plane, respectively. Part c-1 sketches the twin plane and the lattices of bcc-sphere A and A' at the twin plane with white lines. (d) Micrograph observed with the electron beam along the OX direction. The inset shows schematic illustration of the bcc-sphere.

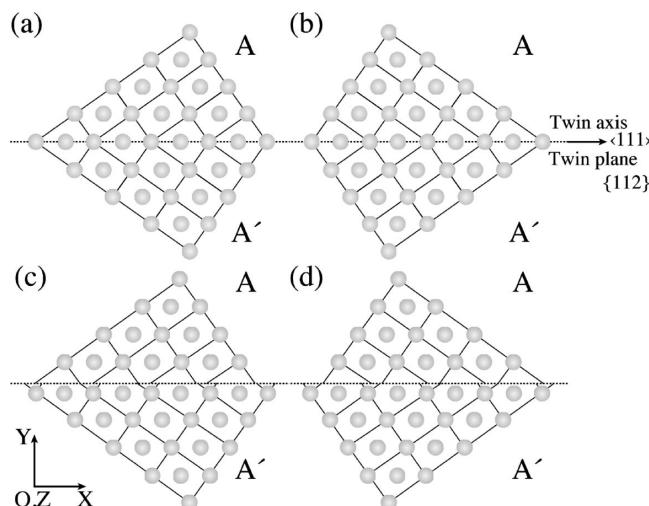


Figure 15. (a and b) Schematic illustration of twin bcc-sphere A and A' with the lattice matching at the twin plane. (c and d) Twin bcc-sphere A and A' with the lattice mismatching. The twin plane {112} and twin axis <111> are parallel to the OXZ plane ({111} plane of hex-cylinder) and the OX axis (the cylinder axis), respectively.

and the undulated hex-cylinders, respectively. These results elucidate that the grains composed of bcc sphere A and A' are nucleated with an equal statistical weight from the matrix phase composed of the undulated hex-cyl and grow preferentially toward <111> direction of the bcc lattice, which corresponds to the cylinder axis and the OX axis, at the expense of the matrix phase. Interestingly, this indicates that the growth of the grains parallel to <111> direction of bcc lattice is faster than that perpendicular to it.

4.2.4. Step III (Final Period). Figure 14a typically shows a low magnification TEM image for the specimen frozen at 915 s in step III after the T-jump [point (3) in Figure 8a], observed with the electron beam along the OZ direction. The image shows the volume-filled bcc-sphere A and A', as revealed by the 2D SR-SAXS patterns shown in the inset a-1, composed of four grains with their boundaries sketched by white lines. Parts b and c show images of another areas of the specimen, taken with a higher magnification than part a, which are composed of two grains with their boundaries sketched by white lines. The grain G1 composed of bcc-sphere A and the grain G2 composed of bcc-sphere A', as shown in part b and illustrated in the insets, and the grain G3 composed of bcc-sphere A and G4 composed of bcc-sphere A', as shown in part c and illustrated in the insets, face each other at the grain boundary extended along the OX axis and form a twin plane parallel to the OXZ plane. The magnified micrographs of the regions encompassed by the black rectangle in parts b and c are shown in parts b-1 and c-1, respectively. The enlarged micrographs clearly elucidate (i) almost perfect matching of the lattices of bcc-sphere A and A' on the grain boundary plane and (ii) the grain boundary plane being equal to the twin plane, as sketched in right-hand side of part c-1 with white lines for the twin plane and the lattices of bcc-sphere A and A'.

Thus, it is revealed that the volume-filling bcc-sphere A and A' in step III are directed to form twin bcc-sphere A and A' with specific orientation as characterized by the twin plane parallel to the OXZ plane, {111} lattice plane of hex-cylinder, and {112} lattice plane of bcc-sphere, and by the twin axis parallel to <111> axis of bcc-sphere and the cylinder axis. We should note that there are lattice mismatches on the twin plane or lattice distortions in the region near the twin plane as illustrated by the region marked D encompassed by the white

line on right-hand side and on the top of the twin plane shown in part b-1. The grain boundaries encompassed by the white rectangles labeled by GB1 to GB3, for example, in part a are inclined to the OXZ plane and the OX direction. As shown in the enlarged image of the GB3 in the inset a-2, these grain boundaries do not form the twin plane but form ordinary grain boundaries. Figure 14d shows the micrograph observed perpendicular to the OX direction. The micrograph evidently shows that bcc-sphere has a hexagonal symmetry with <111> direction of bcc-sphere parallel to the OX axis and with a long-range order. There is no difference between bcc-sphere A and bcc-sphere A' in the image viewed from this direction.

Figure 15 shows schematically A/A'-twin with a perfect lattice matching on the twin plane (parts a and b) as representatively shown in Figure 14c-1 and an imperfect lattice matching (parts c and d) as representatively shown in region D in part b-1. A sufficiently long time annealing at a high temperature in the bcc-sphere phase would heal the lattice mismatching. Thus, we succeeded in observing the transient structure developed at a particular time in each step during the OOT process induced by the T-jump into the stable bcc-sphere phase.

4.2.5. Comparisons with Other Experimental Results. Now, we compare our work concerning the undulated hex-cylinder developed transiently in step I above the T_{OOT} during the isothermal OOT process with the works reported by Ryu et al.^{22,25} on the undulated hex-cylinder developed in the stable hex-cylinder phase below the $T_{OOT} = 193$ °C. The two systems are different: Our undulated hex-cylinder was developed above the T_{OOT} and hence in the nonequilibrium (or unstable) condition for hex-cylinder, while their undulated hex-cylinder was developed below T_{OOT} and hence in the equilibrium (stable) condition for hex-cylinder. Nevertheless the two undulated hex-cylinders have universality on (1) the bcc-symmetry, and naturally on (2) the degeneracy of the bcc-symmetry, i.e., our case being bcc-symmetry A and A' vs their case being bcc-symmetry B and B' to be discussed later.

Although their report infers the nucleation growth of the undulated cylinders in the matrix of nonundulated (or straight) hex-cylinder at 183 °C, i.e., 10 °C below the T_{OOT} , we could not ever observe the coexistence of the undulated cylinders and the straight hex-cylinder in step I: Whenever we discerned

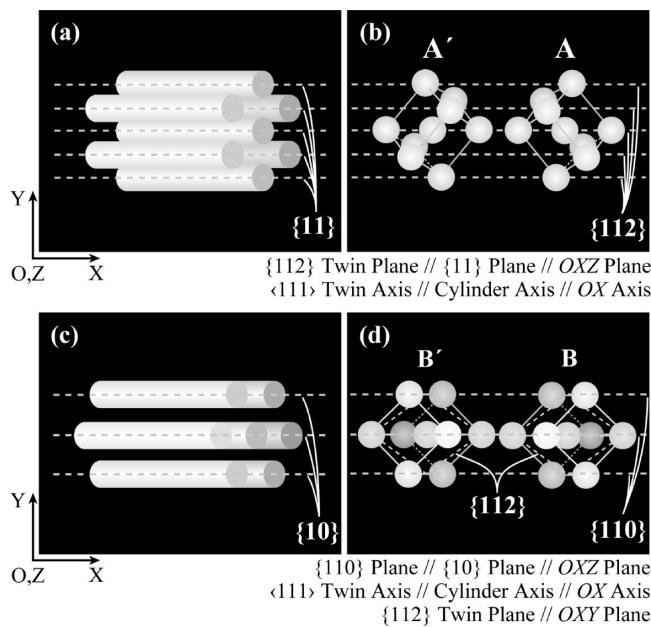


Figure 16. Directed self-assembly of the aligned hex-cyl (a) into twin bcc-sphere A and A' (b), and directed self-assembly of the aligned hex-cylinder (c) into twin bcc-sphere B and B' (d).

the undulated cylinders, they spread everywhere in the whole sample space. Our results basically elucidate that: the hex-cylinder is cooperatively undulated throughout the whole sample space with the amplitude of the undulation increasing with time. In this step, the energy barrier for the nucleation of the undulated hex-cylinder in the matrix of the straight hex-cylinder does not appear to be significant. It seems as if the curvature instability of hex-cylinder at $\Delta T_s = T - T_{OOT} = 5$ K drives spinodally the periodic and cooperative undulation of hex-cylinders. Then in step II grains of bcc-sphere are nucleated in the matrix of the undulated hex-cylinder when the thermally excited amplitude of the undulation in the cylinder diameter exceeds a critical value. Thus, in step II, we can clearly discern the coexistence of bcc-sphere and the undulated hex-cylinder, and here in this step II, the energy barrier for the nucleation appears to play a significant role.

4.3. Directed Self-Assembly of Specially Aligned Hex-Cylinders into Twin Bcc-Spheres A and A'. The specially aligned hex-cylinder with the cylinder axis and {11} plane parallel to the OX axis and the OXZ plane, respectively, as modeled in Figure 16a, can epitaxially create only two kinds of specially oriented bcc-sphere, bcc-sphere A and A', as modeled in Figure 16b, through the OOT from hex-cylinder to bcc-sphere. Since the OOT involves nucleation and growth of the grains composed of A and A' spheres with equal statistical weight in the matrix of the undulated cylinders. When they grow into the volume-filling state at the expense of the undulated cylinders, they are directed to form the twin bcc sphere composed of bcc-sphere A and A' as schematically shown in Figure 15. The number density of the twin planes developed depend on number of nuclei of bcc-sphere formed or more profoundly number of twin planes developed in the undulated hex-cylinder phase, which in turn must depend on the superheating ΔT_s from T_{OOT} defined in Figure 1. Another type of twin bcc-sphere designated as twin bcc-sphere B and B' is directed to be formed through the OOT with hex-cylinder having a special orientation specified by the cylinder axis and {10} lattice plane parallel to the OX axis and the OXZ plane, respectively, as schematically illustrated in Figures 16, parts c and d. The B/B' twin has twin plane and twin axis parallel to {112} lattice plane and <111> axis which are parallel to the OXY plane and the OX-axis, respectively. We think this is the case reported by Ryu et al.^{22,25}

4.4. ΔT_s -Dependence of the OOT Process: Nucleation Growth vs Spinodal Decomposition. So far we restricted to present the OOT process only at a given superheating $\Delta T_s = 5$ °C above the $T_{OOT} = 185$ °C which is induced by the T -jump from the equilibrium hex-cyl at $T = 170$ °C to the equilibrium bcc-sphere at $T = 190$ °C. We found that the OOT at $\Delta T_s = 5$ °C involves first the spinodal growth of the undulation fluctuations from hex-cyl and then the NG of bcc-sphere from the undulation fluctuations. The theory predicts with increasing ΔT_s , the OOT mechanism changes from the NG mechanism to the spinodal decomposition (SD) mechanism. Having been motivated by this theoretical prediction, we now present our preliminary experimental results, in which only 2D SR-DSAXS results are available, on the ΔT_s -dependence of the OOT mechanism in Appendix.

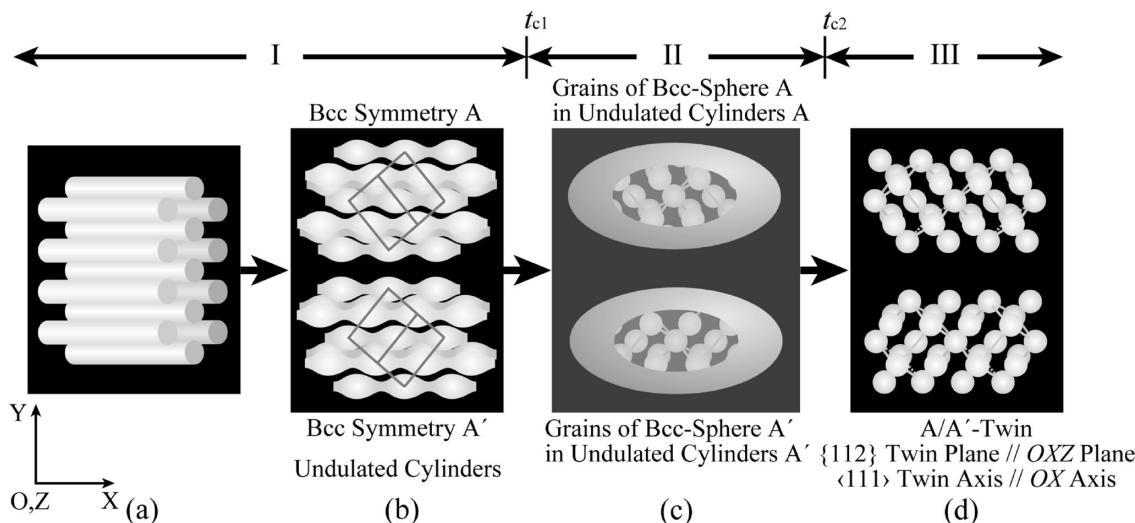


Figure 17. Schematic illustration of the kinetic pathway of the structural transformation via the OOT from the specially aligned hex-cylinder to twin bcc-sphere A/A'.

5. CONCLUSIONS

In this study, we investigated *in situ* and *at real time* the thermally induced OOT process from hex-cylinder to bcc-sphere for the SIS triblock copolymer by means of the time-resolved SR-SAXS measurements as well as by means of the TEM observations of the specimens frozen at particular times during the OOT process. The particularly interesting times at which the TEM observations should be conducted were pinpointed by the time-resolved SR-SAXS measurements. The SAXS measurements also assisted to confirm that there are almost no significant structural changes before and after the freezing the specimens at these times.

Hex-cylinder was first aligned by imposing LAOS, so that the cylinder axes are oriented parallel to the OX direction (the shear direction) and $\{11\}$ plane of hex-cylinder is parallel to the OXZ plane (the shear plane). We elucidated a whole kinetic pathway of the epitaxial structural transformation process from hex-cylinder to bcc-sphere such that $\{11\}$ plane of hex-cylinder and the cylinder axis are transformed into $\{112\}$ plane and $\langle 111 \rangle$ axis of bcc-sphere, respectively.

Figure 17 summarizes conclusions obtained in this work. We defined the two critical times, t_{c1} and t_{c2} , in Figure 8 on the basis of the characteristic changes of the scattering parameters with time. The critical times classify the whole kinetic pathway into three steps where steps I, II, and III are the pretransitional period, the transition period, and the final period, respectively. After the T -jump to 190°C , 5°C above the T_{OOT} , the highly aligned hex-cylinder as detailed above and specified in part a becomes thermally unstable and starts to be cooperatively undulated with their pinching points and bulging points being closely arranged in space with the “bcc symmetry” as schematically shown in part b. The two states of bcc-symmetry are degenerated: They are bcc-symmetry A and A' as also shown in part b which are supposed to each other by the rotation around the cylinder axis, i.e., the twin axis. The so-called undulated hex-cylinder starts to be formed throughout the whole sample space in the pretransitional step (step I defined in Figure 8), as shown in the micrograph of Figures 11a-2 and 12a. The undulations tend to have essentially the “bcc symmetry” as indicated by the 2D SR-SAXS pattern in Figure 9, parts a-1 and b, which is eventually attained by the bcc-sphere A and A' after the completion of the OOT. The amplitude of the undulation of the cylinder diameter grows with time as indicated by the increase of the peak intensity in step I as shown in Figure 8a or Figure 8c without essentially changing the peak position with respect to $\mu_{m,\{110\}}$ and $q_{m,\{110\}}$, which reveals itself that the bcc symmetry and the wavelength of the undulations also are essentially kept unchanged during the course of the OOT. It is important to note that we do not observe coexistence of grains composed of the undulated hex-cylinders and the matrix composed straight hex-cylinder. This may elucidate that the cooperative undulation occurs essentially according to the spinodal mechanism, driven by instability of the interface curvature of the cylinders at the given $\Delta T_s = 5\text{ K}$ (see Figure 1) and the spatial packing effects of the undulated cylinders.

When the thermally activated amplitude of the undulation reach a critical value (at $t \cong t_{c1}$ in Figure 8), the undulated cylinders start to be transformed into bcc-sphere, keeping the same bcc symmetry as indicated by the unaltered positions of $\mu_{m,\{110\}}$ in Figure 8b and Figure 9b. The OOT proceeds via the nucleation and growth process in step II (the transition period $t_{c1} < t < t_{c2}$), where the grains composed of bcc-sphere A and A' are nucleated in the matrix of the undulated hex-cylinder A and

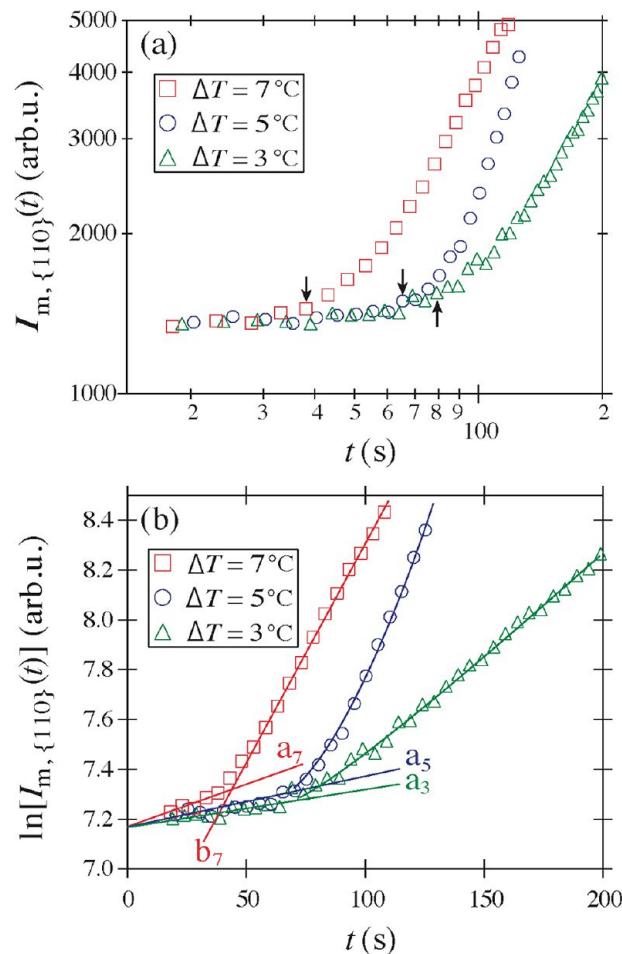


Figure 18. Time evolutions of $I_{m,\{110\}}(t)$ as a function of representative ΔT_s values in the double logarithmic plot (a) and in the plot of natural logarithm vs linear time (b).

A', respectively, as schematically shown in Figure 17c and in the micrographs of Figure 13, parts a and b. They preferentially grow parallel to the $\langle 111 \rangle$ direction of a bcc lattice, which corresponds to the cylindrical axes too, at a faster rate than the rate perpendicular to it, giving rise to the anisotropic grain shape, as really shown in Figure 13 and shown schematically in Figure 17c, at the expense of the undulated cylinders in the matrix. At the end, bcc-sphere A and A' are impinged each other, and the sample space is fully occupied by them, as shown in Figure 14 at $t > t_{c2}$ to result in the directed self-assembly into twin bcc-sphere A and A'. The twin plane exists at the grain boundaries essentially parallel to the OXZ plane as schematically shown in Figure 17d and as shown by the micrographs shown in Figure 14.

APPENDIX: ΔT_s -DEPENDENCE OF THE OOT PROCESS

Figure 18 presents time evolutions of $I_{m,\{110\}}(t)$, which is defined in section 4.1, as a function of representative ΔT_s values in the double logarithmic plot (part a) and in the plot of natural logarithm vs linear time (part b). Part a elucidates that the pretransitional (or incubation) period naturally becomes shorter with increasing ΔT_s as indicated by the arrows. Part b elucidates that the peak intensity change at the pretransitional period is exponential at all ΔT_s and hence $\ln I_{m,\{110\}}$ increases linearly with t as shown by the straight lines a_3 , a_5 and a_7 . Hence

the undulation fluctuation modes grow spinodally at all the ΔT_s values. However the time evolutions of $\ln I_{m,\{110\}}(t)$ at $\Delta T_s = 3$ and 5 in the transition process from the undulation fluctuation modes to bcc-sphere is given by sigmoidal curves as shown by the solid lines added for visual guides that show only the first half of the sigmoidal curves before the inflection points. Thus, the time-evolutions of $I_{m,\{110\}}$ themselves are not given by the exponential functions. However the time evolution of the corresponding part of the $\ln I_{m,\{110\}}$ at $\Delta T_s = 7^\circ\text{C}$ is given by a straight line as shown by b_7 . Thus, $I_{m,\{110\}}$ itself increases exponentially with t at $\Delta T_s = 7^\circ\text{C}$. The preliminary results suggest that the transition from the undulating fluctuations modes to bcc-sphere occurs spinodally at the large superheating of $\Delta T_s = 7^\circ\text{C}$, while the transition occurs according to the NG mechanism at $\Delta T_s = 3$ and 5°C ; at $\Delta T_s = 7^\circ\text{C}$, the SD rate in the pretransition period is different from that in the transition period. It is crucial to verify the growth processes of bcc-sphere via SD and NG in step II by means of real-space observations with TEM. This deserves future works.

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(50) On the basis of the “affine deformation” hypothesis, the conformational entropy loss of the coronar PI chains emanating from the interface of the PS cylinders due to shear deformation must be the same for the two specific orientations of the lattice planes, i.e., {11} lattice plane and {10} lattice plane parallel to the shear plane. Thus, the bulk elastic free energy cost for the shear deformation is expected to be identical between the two specific lattice orientation for hex-cyl. However, the elastic entropy loss of the coronar PI chains at the surface between the shear cell and the block copolymer films is larger for the {11} lattice plane orientation than for the {10} lattice plane orientation, because the PI chains in the former orientation are more stretched than those in the latter orientation. Thus, the interfacial elastic energy cost for the shear deformation is expected to favor the {10} lattice plane orientation relative to the {11} lattice plane orientation at low temperatures. However at high temperatures, if attractive interactions between the cell surface and PI chains become weak, slippages between the cell surface and the PI chains occur statistically more frequently in the {11} lattice orientation than in the {10} lattice orientation. Thus, the slippages, which relax the stress, are expected to favor the {11} lattice orientation relatively to the {10} lattice orientation at high temperatures.