Ultra-Small-Angle X-ray Scattering Profile of Colloidal Silica Crystal of 4-fold Symmetry

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Abstract: Several orders of Bragg diffraction were observed by ultra-small-angle X-ray scattering (USAXS) for colloidal silica particles with the average radius being 560 Å and with narrow size distribution (standard deviation being 8%) in a salt-free aqueous dispersion in a capillary. Diffraction peaks were displayed at such small angles as $149 \times n''$ with n being an integer. The same profile was observed when the capillary was rotated around its axis by $(90 \times m)°$ (m: integer). Furthermore, a different profile was found at $(45 + 90 \times m)°$ with the first peak at $109''$. Thus the USAXS profiles indicate 4-fold symmetry of a colloidal crystal in the dispersion. It was concluded that a body-centered-cubic lattice was maintained with the [001] direction being vertically upward and parallel to the capillary axis and with the lattice constant a being 3000 Å. The closest interparticle distance obtained from the value of a was 2600 Å, while the average distance from the overall concentration was 2900 Å, indicating the non-space-filling nature of the crystal.

I. Introduction

In a previous paper,[1] we described an ultra-small-angle X-ray scattering (USAXS) apparatus using the Bonse–Hart principle[2] and its application to the structural study of colloidal silica dispersions. The USAXS apparatus enabled us to detect scattered X-rays at very low angles (down to an arc of 4″) with high resolution. We observed several orders of Bragg diffraction, the first peak being at 150″. The same diffraction profile was observed at each multiple angle of 60° when the vertically held capillary containing the dispersion was rotated around its axis. It was concluded that a body-centered-cubic (bcc) lattice was maintained with the (110) plane parallel to the capillary wall and with the [1̄11] direction of the crystal vertically upward, showing the 6-fold symmetry. In the present article, we report a most recently found 4-fold symmetry for the same colloidal silica dispersion, at the same concentration as before.

II. Experimental Section

To save space, we describe here only essential aspects of the experimental procedures. More detailed information is given in our previous paper.[1] The colloidal silica (KE-P10W) was kindly donated by Nippon Shokubai Co. Ltd., Osaka, in the form of aqueous dispersion. The particles had a z-average radius R of 560 Å with a standard deviation of 8%, as determined by fitting the USAXS profiles under high salt condition to the form factors for isolated spheres. The net charge density was 0.06 μC/cm^2, while the analytical charge density was 0.24 μC/cm^2, determined by conductivity measurements and conductometric titration, respectively. The X-ray apparatus consisted of a generator, Rotaflex RU-300 (60 kV–300 mA, target: Cu), and a Bonse–Hart camera. In the present experiments, Ge crystals were used in the Bonse–Hart camera. The incident and scattered X-rays were highly parallel in the horizontal plane, but not in the vertical plane. The scattering profile was obtained from a dispersion introduced in a glass capillary with ion-exchange resin particles. The capillary was kept vertical for 4 days after the dispersion was introduced.

III. Results and Discussion

The scattering intensity $I(2\bar{\theta})$ was measured with the second crystal rotated in the horizontal plane with respect to a vertical
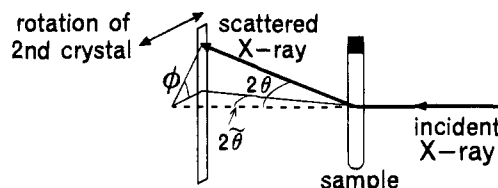

Figure 1. Diffraction from a crystal in the capillary out of the horizontal plane.

axis by $2\bar{\theta}$. As shown in Figure 1, the $2\bar{\theta} = 0$ is defined as the line where the incident X-ray beam out of the first Ge crystal (without a sample) is reflected from the second crystal. The $2\bar{\theta}$ is equal to $2\theta \cos \phi$, where 2θ is the true scattering angle and ϕ is the angle made by the horizontal plane with the plane defined by the paths of the incident and scattered X-rays.[3]

The scattering profiles were obtained at various rotation angles ω of the capillary with respect to the (vertical) capillary axis in order to change the orientation of a single crystal found in the capillary. The capillary was also rotated by $\bar{\theta}$ to make the angle between the incident beam and the lattice plane equal to the reflection angle.

Figure 2 gives the logarithm of the USAXS intensity plotted against $2\bar{\theta}$. As seen from Figure 2a, sharp peaks were observed at diffraction angles of $(149 \times n)''$ with n being an integer. These peaks correspond to Bragg reflections from a colloid crystal, where the diffraction angle is written by $\sin\theta = n\lambda/2d$

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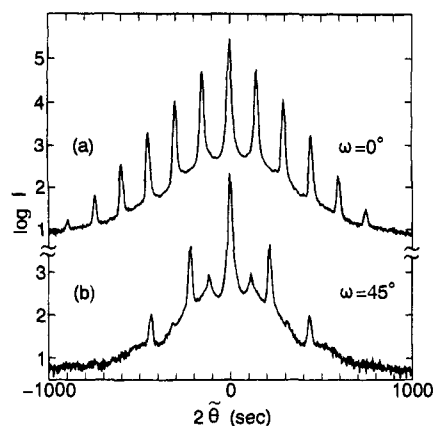
(2) Bonse, U.; Hart, M. *Z. Phys.* **1966,** *189,* 151.

(3) To facilitate understanding, let us consider diffraction from a crystal out of the horizontal plane shown in Figure 1. In our camera system, the rotation of the second crystal corresponds to moving a long and thin slit along the horizontal direction. The width of the slit in Figure 1 corresponds to the full width at half maximum of the rocking curve, namely 11.1 s for our Ge crystal. Then diffraction at an angle 2θ, which is the angle made by the incident beam in the horizontal plane with the scattered X-ray, can be detected when the second crystal is rotated by $2\bar{\theta}$, the angle between a vertical plane including the path of the incident X-ray into the sample and that containing the path of the scattered X-ray out of the sample. Considering the optical system, which has a smearing effect in the vertical direction, we have $2\theta = 2\bar{\theta}/\cos \phi$. It should be noted that the angle ϕ is equal to the angle between the lattice planes that give rise to the diffraction and the vertical plane that includes the path of the incident X-ray.

(4) The lattice plane is not strictly parallel to the incident X-ray but makes an angle $\bar{\theta}$ (negligibly small compared to the change in ω) with the incident X-ray.

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Figure 4. Side views from the direction almost parallel to the incident X-ray beams when the angle ω is (a) $(90 \times m)°$ or (b) $(45 + 90 \times m)°$. The lattice planes that give rise to diffraction are denoted by solid, dashed, and dotted lines with the corresponding Miller indices and the ϕ values.

Figure 2. The logarithm of the USAXS intensity $I(2\tilde{\theta})$ in counts per second plotted against the rotation angle $2\tilde{\theta}$ of the second Ge crystal. Sample: 3.76 vol % water dispersions of silica particles (radius: 560 Å, standard deviation: 8%). Measurements were taken 4 days after the dispersion was introduced into the capillary. Curve a: rotation angle of the capillary $\omega = 0°$. Curve b: $\omega = 45°$. Temperature: 25 $\pm$ 1 °C.
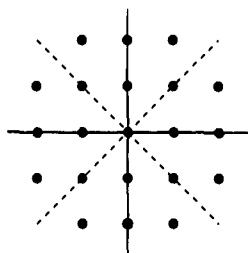

Figure 3. A top view (a projection on the horizontal plane) of the body-centered-cubic (bcc) lattice maintained in the capillary, with the [001] direction of the lattice being vertically upward and parallel to the capillary axis. The solid and dashed lines indicate the directions of the incident X-rays when the rotation angle ω is $(90 \times m)°$ and $(45 + 90 \times m)°$, respectively.

with d being the distance between the lattice planes. The observation of strong and sharp peaks with n up to 6 shows that a very large single crystal had grown in the capillary. Indeed we noticed a rather large crystal with a size comparable to the scattering volume (about $1 \times 2 \times 15$ mm) by visual observation of iridescence from the dispersion inside the capillary. The same several orders of diffraction were observed at each multiple angle of $90 \pm 1°$ when the capillary was manually rotated around its axis, in other words, at ω of $(90 \times m) \pm 1°$ with m being an integer.

Furthermore, the dispersion in this capillary displayed similarly sharp peaks at diffraction angles of $(109 \times n)''$ when the capillary was rotated by $(45 + 90 \times m) \pm 1°$ as shown in Figure 2b. No clear peaks could be observed at $\omega \neq 45 \times m \pm 1°$, although peaks with very low intensities [less than one-tenth that of the peaks shown in Figure 2b] were observed, which may be due to some small crystal grains in the capillary.

The results show two interesting features: the ω dependence and the magnitude of $2\tilde{\theta}$ at the peak positions. All the experimental data can be explained by assuming a bcc structure with the [001] direction of the single crystal being vertically upward and parallel to the capillary axis and with a lattice constant a of 3000 Å. Figure 3 shows a top view of the lattice points of the crystal from the [001] direction which is vertically upward. As readily seen by the solid lines indicating the direction of the incident X-ray in Figure 3, the vertical axis has a 4-fold symmetry. Thus, exactly the same diffraction patterns (Figure 2a) may be expected for $\omega = (90 \times m)°$. A similar
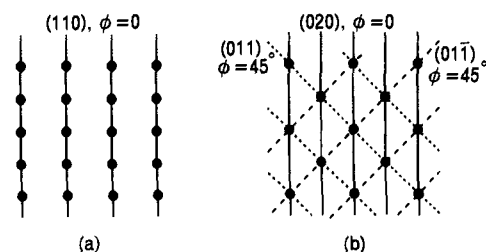
situation arose at $\omega = (45 + 90 \times m)°$ as indicated by the dashed lines in Figure 3.

In Figure 4, side views from the direction almost parallel[4] to the incident X-ray are shown for $\omega = (90 \times m)°$ and $(45 + 90 \times m)°$, parts a and b, respectively. The lattice planes that give rise to diffraction are denoted by solid lines with the corresponding Miller indices and the ϕ values. Using the relation $2\tilde{\theta} = 2\theta \cos\phi$, the Bragg law, and $d_{hkl} = a/(h^2 + k^2 + l^2)^{1/2}$ for the bcc lattice, we can calculate the $2\tilde{\theta}$ value. It was concluded from Figure 4a that the profiles at $\omega = (90 \times m)°$ (Figure 2a) correspond to diffraction from the (110) planes with $\phi = 0$, the calculated value of $2\tilde{\theta}$ being $(150 \times n)''$ [observed: $(149 \times n)''$]. It was inferred from Figure 4b that the profiles in Figure 2b correspond to the (020) reflections with $\phi = 0$, the calculated $2\tilde{\theta}$ being $(212 \times n)''$ [observed: $(218 \times n)''$], and also to the (011) and (01$\bar{1}$) reflections with $\phi = 45°$, the calculated $2\tilde{\theta}$ being $(106 \times n)''$ [observed: $(109 \times n)''$]. Thus all the observed values of $2\tilde{\theta}$ could be consistently explained by the bcc lattice system with a single value for a (3000 Å).

The present results have been confirmed by an independent study by the Kossel line analysis by Sogami and Yoshiyama.[5] In the previous work,[1] it was clearly demonstrated that, for the same silica dispersion and at the same concentration but in a different capillary, the [1$\bar{1}$1] direction of the bcc structure was parallel to the capillary axis so that a 6-fold symmetry manifested itself. This time we found a 4-fold symmetry, indicating that the [001] direction is parallel to the capillary axis. We note that, for these two orientations, two or three of the {110} planes of bcc lattices are parallel to the vertical (not horizontal) surface of the capillary. This result is consistent with the previous observation of colloid crystals obtained by microscopic study[6] and by the Kossel line analysis.[5,7,8] This orientation is acceptable since it is the "most closely packed". As a cause of this packing, the influence of gravitation may be ruled out because it has been observed for a vertically held surface. As one of the most important factors, we suggest a very long-range attractive interaction between the glass surface and the like-charged particles, which causes a higher concentration of particles near the surface than in the bulk. This positive adsorption was noticed recently by us,[9] by Thomas et al. in a neutron reflection study of cationic micelle solutions,[10] and by Ito et al. in a confocal laser-scanning microscopy study of ionic

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latex particles.[11] It can be easily understood that the increased concentration facilitates crystallization near the surface.

Accepting the fact that the {110} planes are favored near the surface, there remains the question as to why a large single crystal grew with different symmetries in different capillaries. Our interpretation is as follows: A large number of nascent crystals with the [1$\bar{1}$1] or [001] direction parallel to the capillary axis would be present near the wall. It is not possible that these crystals simultaneously grow to a single crystal with a definite orientation. Here the Ostwald ripening mechanism steps in, in other words, a larger crystal grows to the single crystal at the expense of smaller ones, whichever of the two orientations it may have. Although there would be a large number of small nascent crystals in the interior of the dispersion, they appear not to be important in the process of the orientation determination, since they show rotational diffusion so that a specific orientation cannot be preferred.

It is also noteworthy that we have never observed any other orientations for large crystals of the colloidal silica particles under investigation.

It is mentioned that the lattice constant (3000 Å), the closest interparticle spacing (2600 Å), and the average spacing (2900 Å) obtained in the present work were the same as those in the previous paper.[1] Thus, the non-space-filling nature[12-19] of the single crystal and contraction during crystallization[20-22] were confirmed.

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