Single crystal of colloidal silica particles in a dilute aqueous dispersion as studied by a two-dimensional ultrasmall-angle x-ray scattering

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A two-dimensional ultrasmall-angle x-ray-scattering apparatus was constructed with a full width at the half maximum of the intensity profile of the incident x-ray beam being about 17 s of arc. This apparatus enabled us to obtain the scattering intensity as a function of the scattering vector. The scattering profile of a colloidal crystal of silica particles in an aqueous dispersion was studied and analyzed with the aid of a method by Busing and Levy. The diffraction planes corresponding to 22 scattering peaks observed were uniquely identified; The lattice system was determined to be body-centered-cubic with a lattice constant of 3800 Å and its [111] was parallel to the capillary axis. [S0163-1829(98)04906-6]

For investigation of the internal structure of materials in the range of microns and submicrons, ultrasmall-angle x-ray scattering (USAXS) is useful and has actually been applied, for example, to some colloidal and polymeric systems.[1–3] This technique has several advantages over other techniques, especially for turbid and/or liquid systems where conventional small-angle x-ray scattering, light scattering, and microscopy cannot be used.[1–3] However, the USAXS cannot easily be applied for oriented systems because of the smearing effect[4–6] in a Bonse-Hart camera[7] in which x rays are collimated only in one plane. Thus, a modified version, which we call the two-dimensional ultrasmall-angle x-ray scattering (2D USAXS) apparatus,[7,8] has been sought and constructed in our laboratory for the purpose of structural analyses of oriented materials.

An interesting phenomenon in colloidal systems is that electrically charged colloidal spheres with a monodisperse size distribution form an ordered structure under no-salt and low-salt conditions. Such ordered structures have been studied by the USAXS technique, though mostly for disoriented systems such as dispersions containing powderlike crystal distribution.[1–3] In the present work, the 2D USAXS apparatus was applied for the structural analyses of an oriented crystal of colloidal silica particles in an aqueous dispersion.

The 2D USAXS apparatus [Rigaku Co. (Tokyo, Japan)], is composed of a rotating anode x-ray generator (Rotaflex RU-H3R, 60 kV - 300 mA, target: Cu) and a 2D Bonse-Hart camera.[7,8] The optical system of the Bonse-Hart camera is shown in Fig. 1. In this camera, two sets of two channel-cut single crystals of Ge are used to collimate the x-ray beam in both the horizontal and vertical planes. The x rays which reflect on the (111) planes of the first and second crystals are monochromatic and highly parallel to each other. The wavelength λ of the x ray is 1.54 Å ($K\alpha$ line). The cross section of the x-ray beam is about 1×1 mm^2. By the Bragg reflection at the third and fourth crystals, the diffracted x rays at the proportional counter are also highly parallel to each other. As shown in Fig. 2, the full width at the half maximum (FWHM) of the intensity profile of the direct x-ray beam against the rotation angles ω_{C3} and ω_{C4} of the third and fourth crystals is about 17 s of arc, indicating that the apparatus can be applied to structural analysis in a range up to about 2 μm. From the profile which is almost symmetric with respect to the direction where the intensity is maximum ($\omega_{C3}=\omega_{C4}=0$), the high collimation as a point focusing geometry is confirmed. Then the smearing effect is regarded as negligible.

Here, we note that in the 1D USAXS apparatus where only one set of the crystals (which corresponded to the first and fourth crystals in Fig. 1) is used, the x rays are not parallel in the vertical plane and then the detected intensity is

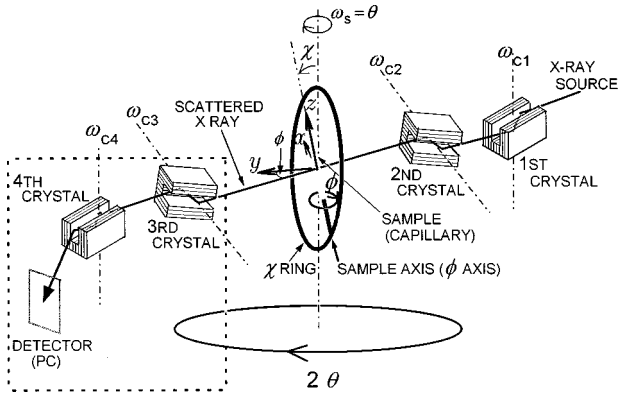

FIG. 1. Optical system of the two-dimensional ultrasmall-angle x-ray-scattering apparatus. The Ge single crystals were cut parallel to the (111) planes. The mechanism of the sample rotation is as follows. The vertical ring (χ ring) can be rotated by ω_s about the vertical axis. $\omega_s=0$ when the axis of the χ ring is parallel to the x-ray beam. In order to change the direction of the scattering vector, we rotate the sample by χ in the plane made by the χ ring and by ϕ about the sample axis shown in the figure. $\chi=0$ when the sample axis is vertical, and $\phi=0$ when the x axis of the coordinate system associated with the sample is in the plane of the χ ring. The y axis is normal to the plane of the χ ring when $\phi=0$, and the z axis constitutes a right-handed rectangular coordinate system with the x and y axes. For changing the magnitude of the scattering vector, fixing $\omega_{C3}=\omega_{C4}=0$, we rotate the third and fourth crystals together with the detector, which are surrounded by the dashed line in the figure, by 2θ about the vertical axis at the sample, keeping the rotation angle ω_s of the sample being equal to θ (bisecting position).

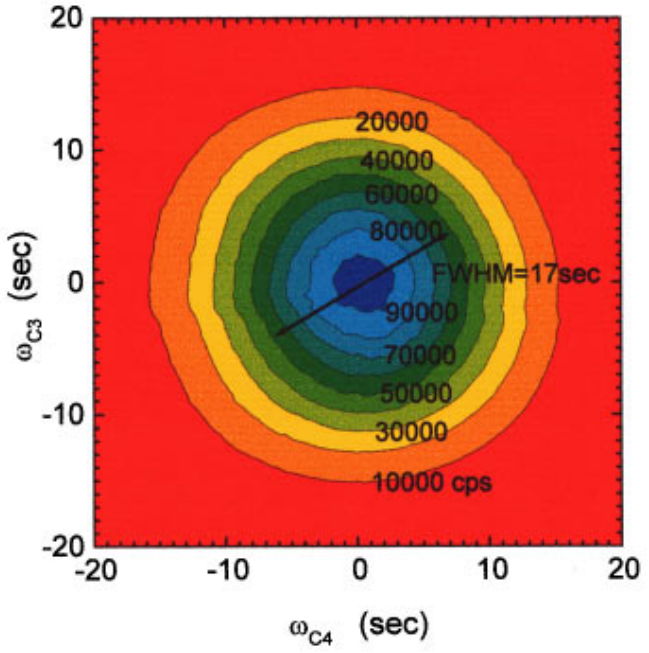

FIG. 2. (Color). Contour plot of the intensity of the direct x-ray beam against the rotation angles (ω_{C3} and ω_{C4}) of the third and fourth crystals.

smeared. Owing to this smearing effect, it is difficult to analyze 1D USAXS data from oriented systems to obtain the scattering intensity as a function of the scattering vector. In contrast, the desmearing of data from the disoriented sample is easy.[4] Indeed we determined the crystal structure of colloidal silica particles in dispersions by 1D USAXS in the previous studies,[5,6] but we then needed to assume the lattice structure and the orientation of the crystal grain. This is not the case for the 2D USAXS, however, as will be shown below.

In order to apply the 2D USAXS to oriented systems such as colloidal single crystals, we need to measure the intensity $I(\mathbf{q})$ as a function of the scattering vector $\mathbf{q}$. Since our 2D USAXS apparatus is equipped with the mechanism of rotating the sample, as shown in Fig. 1 as in three-circle diffractometers[9] used in the wide-angle x-ray-diffraction measurement, we can directly measure the scattered intensity $I(\mathbf{q})$ at each scattering vector $\mathbf{q}$ with the components (q_x, q_y, q_z) written by

$$\mathbf{q} = (q \cos\chi \cos\phi, q \cos\chi \sin\phi, q \sin\chi), \qquad (1)$$

where q is the magnitude of the scattering vector [$q = (4\pi/\lambda)\sin\theta$ with 2θ being the scattering angle].

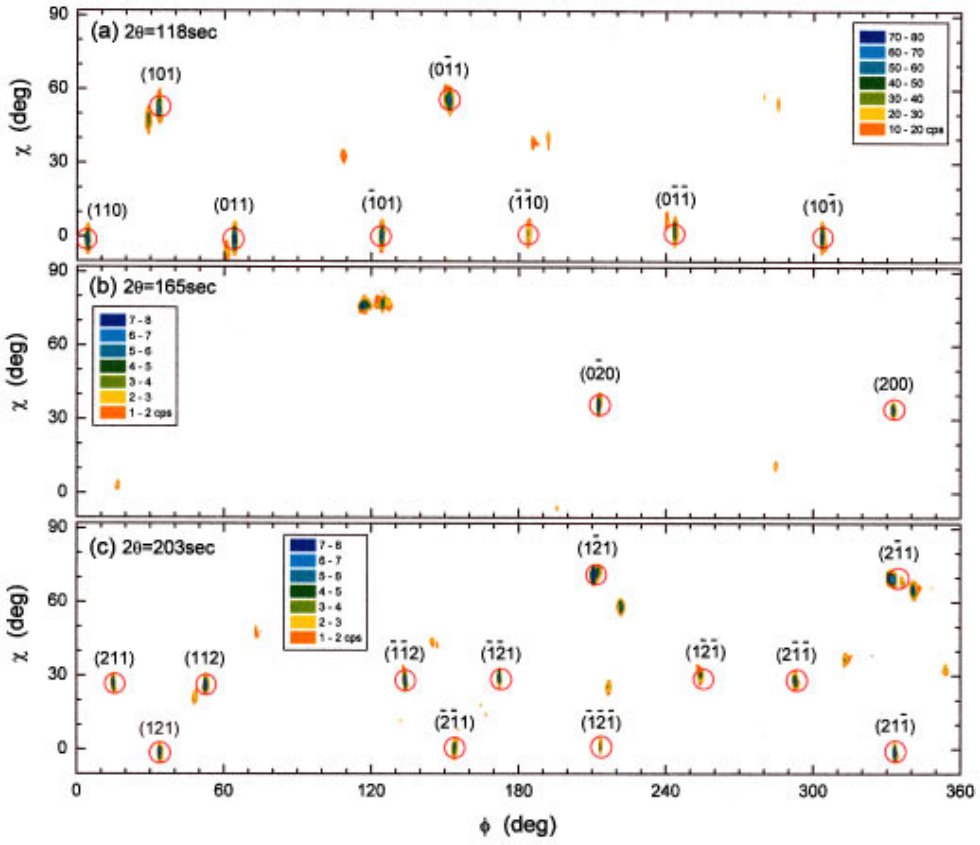

FIG. 3. (Color). Contour plots of the 2D USAXS intensities against χ and ϕ for colloidal silica dispersion in water. The concentration of silica was about 2.5 vol %. (a), $2\theta = 118$ s; (b), $2\theta = 165$ s; (c), $2\theta = 203$ s. The red circles indicate the calculated position of the diffraction peak considering body-centered-cubic lattice with lattice constant being 3800 Å and with [111]‖capillary. The diffraction peaks were assigned to the corresponding diffraction planes indicated by Miller indices.

The sample used in this work is a colloidal silica dispersion. The original dispersion KE-P10W in water was donated by Nippon Shokubai Co., Ltd. (Osaka, Japan), and it is dialyzed against Milli-Q water for 16 days. Using 1D USAXS, the average radius of the silica particles is 560 Å, and the standard deviation of the particle size is 8%.[10] The dispersion is put into a quartz capillary (inner diameter: ~2 mm) with ion-exchange resin particles [AG501-X8(D), Bio-Rad Lab., Richmond, CA] for further deionization. The concentration of the silica is about 2.5 vol %.

Figure 3 shows contour plots of the 2D USAXS intensities from the colloidal silica dispersion against the rotation angles χ and ϕ of the sample. The magnitudes of the scattering vectors are 2.33×10^{-3}, 3.26×10^{-3}, and 4.02×10^{-3} Å^{-1}, for Figs. 3(a), 3(b), and 3(c), which are obtained at scattering angles of 118, 165, and 203 s of arc, respectively. Then the measurements are done by changing the direction of the scattering vector with its fixed magnitude. From the diffraction peaks observed, it is clear that an ordered structure is formed in the capillary. The intensity is dependent on ϕ and χ, indicating that the structure is oriented. The measurements are performed for every 20 s of the 2θ, which is comparable to the FWHM of the direct beam, in order not to miss any diffraction peaks. Then, it is found that no other diffraction peaks than shown in Fig. 3 are observed at other scattering angles less than 203 s. We note here that the accumulation time for each data point is only 0.2–1.0 s, indicating that sufficiently high intensity to identify the diffraction peak is obtained even when the rotating anode generator is used as an x-ray source. It took more than one day to get each profile of Fig. 3, because the number of data points is very large; 3835×52 points.[11]

From the observed values of 2θ, ϕ, and χ at the diffraction peaks, we can calculate the scattering vector using Eq. (1). In the analysis of the diffraction data to determine the crystal structure, we follow the procedure by Busing and Levy.[9] We use a 3×3 matrix, which is called matrix **UB**,[9] to connect the scattering vector q_x, q_y, and q_z at the diffraction peak with the Miller indices h, k, and l of the diffraction planes of an expected colloidal single crystal, as follows:

$$\begin{pmatrix} q_x \\ q_y \\ q_z \end{pmatrix} = \mathbf{UB} \times \begin{pmatrix} h \\ k \\ l \end{pmatrix}. \tag{2}$$

Consequently, we determine the matrix **UB** as

$$\mathbf{UB} = \begin{pmatrix} 1.21 & 1.11 & -0.07 \\ -0.59 & 0.73 & 1.35 \\ 0.93 & -0.98 & 0.93 \end{pmatrix} \times 10^{-3}\ \text{Å}^{-1}. \tag{3}$$

It is found that a colloidal single crystal is formed in the dispersion, and that the lattice structure is body-centered-cubic (bcc) with a lattice constant of 3800 Å. Furthermore it is found that the direction of the [111] is parallel to the capillary axis. The crystal planes corresponding to the observed diffraction peaks are shown by Miller indices.

Conversely, by assuming a bcc single crystal with the lattice constant and the direction found above, we estimate the peak position using Eqs. (1)–(3) and the results are indicated by red circles. The good agreement between observed and calculated positions in Fig. 3 is noteworthy. The information derived here concerning the lattice system and orientation are consistent with the previously obtained one[5,6] and reconfirms the incorrectness of classical theories of colloidal interaction, though we would like to refer the readers to these earlier publications for detailed discussion.

It should be noted that only the position of the diffraction peak is discussed in the present analysis; the peak intensity and the width are not considered. Though detailed consideration will be given to these quantities in forthcoming papers, we would like to briefly discuss the peak width in order to explain the ellipsoidal shape of the peak observed (Fig. 3). First we estimate the expected peak width on the χ and ϕ scale considering the FWHM of the incident beam. In this case the width (FWHM) $\Delta\chi$ and $\Delta\phi$ would be $4\sin^{-1}(17\ \text{s}/8\theta)$ and $4\sin^{-1}[\sin(17\ \text{s}/4)/\cos\chi]$, respectively, for $\chi\neq90°$. At $2\theta=118$ s, $\Delta\chi$ is about 8°, whereas the $\Delta\phi$'s are 17 and 30 s at $\chi=0$ and 55°, respectively. Thus the diffraction peak is ellipsoidal.[12]

In summary, a 2D USAXS apparatus was constructed and applied for structure analysis of an oriented system, namely a crystal of colloidal silica particles in a dilute dispersion. The diffraction profile was conveniently obtained as a function of the scattering vector and analyzed by the method proposed by Busing and Levy.[9] The diffraction planes corresponding to the observed 22 peaks could be identified, from which the lattice system was concluded to be bcc with a lattice constant of 3800 Å and its [111] was parallel to the capillary axis. Further detailed study at various concentrations and temperature is in progress.

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[11] Because the peak width on the ϕ axis is smaller than 1° as seen from Fig. 3, the 3835 measurements had to be done at every

0.1°. On the other hand, that in the χ axis was about 10° so that the 52 measurements were carried out at every 2°.

[12] The observed width $\Delta\chi$ in Fig. 3(a) is almost the same as the value calculated in the text. Since the peak width is also related to the finite size of crystals and/or their imperfection, the above agreement might suggest that these two factors are not detectable in the present cases. On the other hand, the width $\Delta\phi$ observed is to be broadened by the nonideality in parallel alignment of the diffraction planes and is in fact much larger than calculated. Thus the FWHM factor is not important.