Defocus image contrast in hexagonally-ordered mesoporous material

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A transmission electron microscope was used to characterize a powder form of hexagonally-ordered mesoporous silica material. The structural symmetry built into this amorphous material allowed one to obtain three characteristic images, i.e. a hexagonal honeycomb structure and wide/narrow parallel lines. These images were found to originate primarily from phase contrast, which changed sensitively with defocusing. To further understand the contrast behaviour of these images, an analytical form of the defocus contrast theory was developed and applied to the simulation of the characteristic wide/narrow parallel line images. The simulation was found to be in good qualitative agreement with experiments, where changes in focus conditions and specimen thickness were predicted to alter the contrast in the resulting parallel-line type images.

1. Introduction

A wide variety of ordered mesoporous silica materials have been synthesized and explored extensively in recent years for possible applications in drug delivery, catalysis, and sensors. A transmission electron microscope (TEM) has been a key analytical tool to characterize this class of materials. Most recently, we made a detailed TEM study of a mesoporous silica material containing a hexagonally-ordered pore structure and confirmed that the pore structure becomes clearly visible only by phase contrast, which can be introduced by defocusing. In an optical sense, therefore, this class of materials was found to be a phase object. An application of the defocus technique led to the discovery of three characteristic images, i.e. a hexagonal honeycomb structure and wide/narrow parallel lines, which are observable from three symmetry directions associated with this hexagonally-ordered material. These image features were used for determining the pore structure/dimensions of the hexagonally-ordered silica material. Although no theoretical assessment on the validity of the measurement was made, the measured pore dimensions were found to be in good agreement with data obtained by other beam techniques, such as a low-angle X-ray diffraction method.

The defocus technique has been applied previously for imaging other types of phase objects, such as voids, organic impurity molecules, impurity-segregated grain boundaries, or magnetic domains. Similar to the case of hexagonally-ordered mesoporous silica particles, these objects show up by phase contrast upon defocusing. The images of such defocused objects become visible as a result of the appearance of Fresnel fringes around them. It should be cautioned that Fresnel fringes do not appear at the exact boundaries of the phase objects. In fact the location of Fresnel fringes changes with the magnitude and sign of defocus. Thus care has to be taken if one wishes to use Fresnel fringes for measuring the size of phase objects. Prompted by such an uncertainty in the use of defocused images, Rühle analyzed defocus images theoretically by formulating a defocus contrast theory and computed the image contrast of radiation-induced voids/gas bubbles. Nakahara applied the Rühle’s formulation and simulated the defocused images of organic molecules and voids included in electrodeposited metals.

Clearly, a similar uncertainty also exists in the defocused images of hexagonally-ordered mesoporous materials. There are several publications that attempt to interpret the observed defocus images of ordered mesoporous materials correctly first by modelling the geometry of phase objects and then by simulating the images of the proposed model. Alfredsson and Anderson first obtained a model of cubically-ordered silica, MCM-48, using a concept of the gyroid minimum surface and then simulated its images. A similar modelling/simulation approach was taken recently for solving the structure of SBA-15 mesoporous materials. Zhou simulated rosary pattern images associated with a chain of metal-containing clusters observed in hexagonally-ordered mesoporous materials. Ohsuna et al. modeled the coiled pore structure of a mesoporous material, followed by computer simulation using the standard fast Fourier/inverse Fourier transforms that take the transfer function into account. Except for the work by Ohsuna et al., all the authors relied on a commercial software program called “Cerius2”, which is a molecular modeling and simulation software package.

Despite several sophisticated image simulations, no systematic studies on the contrast behaviour of simple line images most frequently observed in ordered mesoporous materials have been done previously. Motivated by the lack of such studies, we modelled the entire body of a hexagonally-ordered mesoporous material as a phase object and then applied this structural model to the defocus contrast theory. The present approach is different from previous simulation work in that the theoretical formulation is completely analytical as opposed to numerical. Using this theory, TEM
images of the wide/narrow parallel lines observed in this material were simulated as a function of the amount/sign of defocus and specimen thickness. It will be shown that computer simulations can be reliably used to predict contrast behavior of the defocus images.

2. Experimental

A powder of hexagonally-ordered mesoporous silica (HOMS) material was synthesised using the recipe described by Kleitz and co-workers. In a typical synthesis scheme, 6 g of Pluronic P123 surfactant was dissolved in a solution containing 217 cc distilled water and 10 cc HCl (35%), followed by the addition of butanol under stirring conditions at 35 °C. After 1 h, 12.9 g tetraethoxysilane (TEOS) was added to the solution and the mixture was left stirring at 35 °C for 24 h. The mixture was then heated in an autoclave under static conditions for 24 h at 100 °C. The surfactant was finally removed by a Soxhlet extraction method that uses ethanol as a solvent.

Low-angle X-ray powder diffraction patterns were recorded on a Philips X’Pert MPD PRO X-ray diffractometer (PW 3050/60) using Cu Kα radiation (λ = 0.154 nm) run at 40 kV and 35 mA. The instrument has an automatic divergent slit resulting in an irradiated length of 10 mm. The step size used was 0.01671 at 15 seconds per step in the low-angle range of 0.3°.

The porosity data of the HOMS were obtained using a Micromeritics ASAP 2010 system, which measured adsorption/desorption isotherms of nitrogen gas at 77 K. Using this analyzer, the pore volumes were calculated from the quantities of gas required to fill the pores. Prior to the measurements, the samples were out-gassed by heating under vacuum at 393 K for 12 h. The pore size data were then analyzed using the thermodynamics-based Barrett–Joyner–Halenda method and a non-local density functional theory on the desorption branch of the N2 isotherm.

Scanning electron microscopy (SEM) was done using a Hitachi S-5500 electron microscope. A TEM specimen was prepared by first mixing the HOMS powder in ethanol and then by placing the liquid drop onto a Formbar-backed carbon-coated copper grid. The majority of the TEM analysis was carried out using a JEOL JEM-2011 electron microscope (non-FEG TEM) operated at an accelerating voltage of 200 kV. The viewing directions for TEM observation. The three characteristic images, described as (a) a honey-comb structure, (b) wide parallel lines, and (c) narrow parallel lines, can be obtained through the three directions, which are high-symmetry orientations in this material. Here we refer the wide and narrow parallel lines as W- and N-type lines, respectively. The viewing directions for taking the images of the W- and N-type lines will be called Projections I and II, respectively.

It was confirmed that these images mainly originate from phase contrast. Fig. 3(a)–(c) demonstrate three images of the W-type lines taken at the over-focus, in-focus, and under-focus conditions, respectively. The image taken at zero focus (Δf ≈ 0) is very weak and is seen mostly by amplitude contrast. The defocused images (Δf ≠ 0), on the other hand, exhibit strong contrast, which is phase contrast induced by defocusing. For a mesoporous material, therefore, strongly-visible images are generated primarily by phase contrast superimposed with invisibly-weak amplitude contrast. The phase contrast image was found to vary sensitively with the sign/amount of defocus, Δf.

It is easily understood from Fig. 2 that the images of the W- and N-type lines do not show up in every particle,

3. Characterization of hexagonally-ordered mesoporous material

3.1 SEM

Fig. 1(a) shows an SEM image of a HOMS particle that contains a honeycomb-like hexagonally-ordered pore structure. A rectangular box marked in Fig. 1(a) is further magnified in Fig. 1(b), where the ordered honeycomb face containing a six-fold symmetry is clearly seen. The side view indicates that these ordered pores extend through the particle and form parallel channels (cf. Fig. 1(c)). Based on this result, a typical geometry of the mesoporous silica particle is drawn in Fig. 1(d).

3.2 TEM

Previous TEM results on a HOMS material are summarized briefly below. A TEM examination of the particles has revealed that each particle consists of amorphous silicon oxide, in which a channel of hexagonally-ordered pores is formed. In Fig. 2, we show the relationship between the geometry of the HOMS particle and the observed three characteristic TEM images. The arrows indicate the directions of TEM observation. The three characteristic images, described as (a) a honey-comb structure, (b) wide parallel lines, and (c) narrow parallel lines, can be obtained through the three directions, which are high-symmetry orientations in this material. Here we refer the wide and narrow parallel lines as W- and N-type lines, respectively. The viewing directions for taking the images of the W- and N-type lines will be called Projections I and II, respectively.
adopted a claim\textsuperscript{15} that the effect of spherical and chromatic aberrations can be ignored for the structural feature size of larger than 0.8 nm and for the magnitude of defocus larger than 0.4 \textmu m. Since most of our experimental conditions agree with this claim, we can take only the defocusing effect into account, thus ignoring spherical and chromatic aberrations. The general outgoing wave equation, $\psi_0(x, y, \Delta f)$, can be written in terms of Fourier optics;

$$
\psi_0(x, y, \Delta f) = C \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \psi(x', y') \exp \left[ \pm 2\pi i |\Delta f| \frac{r^2}{K} \right] \exp[2\pi i(\xi_1(x' - x) + \xi_2(y' - y))] \mathrm{d}x' \mathrm{d}y' \mathrm{d}\xi_1 \mathrm{d}\xi_2
$$

(1)

where $\psi(x', y')$ is the incoming wave function, $|\Delta f|$ the magnitude of defocus, $K$ the wavevector, and $C$ the constant. A minus-plus sign, $\mp$, in eqn (1) corresponds to the under- and over-focus cases, respectively. Integration of eqn (1) over $x'$, $\xi_1$, and $\xi_2$ yields the one-dimensional integral form\textsuperscript{26} applicable to calculating the W- and N-type line images of the structure;

$$
\psi_s(x, \Delta f) = (1 \mp i) \sqrt{\frac{K}{2|\Delta f|}} \exp(\pm 2\pi i|\Delta f|/K) \int_{-\infty}^{\infty} \psi(x) \exp \left[ \pm \frac{iK}{|\Delta f|} (x - x')^2 \right] \mathrm{d}x'
$$

(2)

The one-dimensional incoming wave function, $\psi(x')$, can be expressed as $\psi(x') = A\exp[\pm i\phi(x')]$. Since an amplitude contrast is ignored in the present calculation, a variation in amplitude can be set constant, i.e. $A = 1$, which leads to

$$
\psi(x') = \exp[\pm i\phi(x')]
$$

(3)

Substitution of eqn (3) into eqn (2) gives the final form of the outgoing wave function, $\psi_s(x, \Delta f)$, i.e.

$$
\psi_s(x, \Delta f) = (1 \mp i) \sqrt{\frac{K}{2|\Delta f|}} \exp(\pm 2\pi i|\Delta f|/K) \int_{-\infty}^{\infty} \exp[\pm i\phi(x')] \exp \left[ \pm \frac{iK}{|\Delta f|} (x' - x)^2 \right] \mathrm{d}x'
$$

(4)

The phase change, $\phi$, occurs within a specimen (regarded as a phase object), which has the mean inner potential (MIP), $V_0$, and the thickness, $t$. The phase change is then expressed as

$$
\phi = \frac{\pi tV_0}{\lambda E},
$$

(5)

where $E$ is the accelerating voltage and $\lambda$ the wavelength of an electron beam. Finally, in the evaluation of eqn (5) it is necessary to construct a structural model for this material, which will be described in the following section.

4.2 Model of phase object

In this section, we describe a structural model of the hexagonally-ordered mesoporous silica material that can be applied to eqn (5). In this model, we have to determine both the MIP, $V_0$, and
of the silica material and its thickness variation, \( t \), along the electron-beam direction. The entire body of the material consists of amorphous silicon oxide, the MIP value of which can be found in the literature; for a thermal oxide, \( V_0 = 10.51 \pm 0.35 \) V (undensified), whereas for a deposited oxide, \( V_0 = 11.19 \pm 0.35 \) V (undensified) and \( 10.58 \pm 0.69 \) V (densified).

Assuming that the pores are hexagonally-ordered hexagons, we propose a structural model for the material along the two directions, Projections I and II, which give rise to line images described as the W- and N-types. Fig. 4(a) and (b) show the two cross-sections for the Projections I and II, in which various dimensions are inserted using two basic parameters, \( d \) (pore diameter) and \( w \) (wall thickness). It should be noted that our model is in two-dimensions, ignoring a geometrical variation along the pore axis. A change in pore thickness along the Projections I and II over one thickness period is plotted against the lateral dimension, \( x \), in a hexagonally-ordered mesoporous particle (see Fig. 5). Here it should be remembered that the pore thickness varies periodically along the thickness (electron-beam) direction. Thus one period of thickness can be shown to be \((d + w)\) for the Projection I and \( \sqrt{3}(d + w) \) for Projection II. In Fig. 5, the vertical axis denotes the thickness of a pore region along the electron-beam direction over one thickness period. Accordingly, the thickness, \( t \), becomes a function of \( x \), i.e. \( t = t(x) \) and thus eqn (5) is rewritten as

\[
\phi(x) = \frac{\pi t(x) V_0}{\lambda E} = \beta t(x)
\]

where \( \beta = \frac{2\pi}{\lambda} \).

Substitution of eqn (6) into eqn (4) will yield the final form of \( \psi_d(x, \Delta f) \). As seen in Appendix A, eqn (A4) and (A8) provide the final forms of \( \psi_d(x, \Delta f) \) for the Projections I and II and allow us to compute a systematic image change as a function of the amount/sign of defocus, \( \Delta f \), and the thickness, \( t(x) \). It can be shown that eqn (A4) and (A8) are fully analytical and are expressed as a function of Fresnel cosine and sine integrals.

5. Results and discussion

In the present intensity calculation of the W- and N-type lines, we chose the MIP value of silicon dioxide to be \( V_0 = 11.0 \) V, which is the average of the published values. The two geometrical parameters, \( d \) (pore diameter) and \( w \) (wall thickness), used for constructing the two cross-sections in Fig. 4 were experimentally determined from low angle X-ray diffraction and nitrogen adsorption analyses. Substituting these values into eqn (6), we computed various intensity profiles and simulated images for the W- and N-type lines. These images were first exported in the Postscript format and some of the images were then converted to the bitmap, which was further smoothed using a Gaussian blurring method that allows one to remove pixel-related noise.

5.1 Projection I

First we illustrate the effect of focusing on the W-type line images of the 100 nm thick particle in Fig. 6. It is seen that there is a contrast reversal upon a change in the sign of defocus from the underfocus \((\Delta f = -2 \text{ or } -3 \mu \text{m})\) to the overfocus \((\Delta f = +2 \text{ or } 3 \mu \text{m})\) conditions. In Fig. 7, we tabulate computed intensity profiles for the W-type lines for various values of defocus and thickness in underfocus conditions. The corresponding simulated images are shown in Fig. 8. The horizontal and vertical axis of each intensity profile in Fig. 7 is the same as that given in the graphs of Fig. 6. All the images
exhibit strong contrast and contain periodically-spaced 10 dark lines, which are the same as the number of lateral periodicity, $n$, input into eqn (A1) to (A4). With increasing amount of defocus and thickness, the intensity of the dark lines gets stronger and their width becomes wider, while the width of the bright lines becomes narrower. Although the width of the dark and bright lines changes with defocus and thickness, the combined width of the dark and bright lines remains constant. The combined width is the periodicity of the images and is the same for all the cases, as will be described below.

To further illustrate the image characteristics of the W-type, we show one typical image that was simulated for $\Delta f = -3 \text{ mm}$ and $t = 100 \text{ nm}$ in Fig. 9, where several parameters are
inserted. Here an average distance between the dark lines is designated as $P_D$, whereas that between the bright lines is marked with $P_B$. The widths of the dark and bright lines are indicated with symbols, $S_D$ and $S_B$, respectively. From the symmetry property of the periodic images, the following relationship can exist among these parameters:

$$P_D = P_B = S_D + S_B,$$

which corresponds to the width of one lateral periodicity. From Fig. 4, the width of the lateral periodicity for the Projection I is $(\sqrt{3}/2)(d + w)$, which leads to the following relationship;

$$P_D = P_B = S_D + S_B = (\sqrt{3}/2)(d + w) \quad (8)$$

It is important to note that the relationship (cf. eqn (8)) is independent of $\Delta f$ and thickness. In other words, the value of $P_D$, $P_B$, or $S_D + S_B$ can be used to evaluate the magnitude of $(\sqrt{3}/2)(d + w)$, regardless of $\Delta f$ and thickness. For the purpose of self-consistency, our simulation work was verified by measuring the value of $P_D$ in Fig. 9 and then by comparing it with the value of $(\sqrt{3}/2)(d + w)$.

Based on the present simulation result, we can use the W-type line images to estimate the value of the lateral periodicity, $(\sqrt{3}/2)(d + w)$, by measuring either $P_D$ or $P_B$. The property of constancy given in eqn (8) is important in
obtaining some quantitative values of this material. It can be easily shown that even if a specimen is tilted away from the exact Projection I up to the maximum angle of $3.5^\circ$,14 practically no effect is expected on the magnitude of $P_D$, $P_B$, or $S_D + S_B$. Thus as long as the W-type images are visible even under the off-symmetry condition, the relationship given in eqn (8) can be used reliably. Finally, some fine lines present within the dark or bright lines in the simulation cannot be easily seen experimentally. This is discussed in more detail in Section 5.5.

5.2 Projection II

Theoretical intensity profiles for the N-type lines are tabulated in Fig. 10 for various values of defocus, $\Delta f$, and thickness, $t$. The corresponding simulated images are shown in Fig. 11. Similar to the case of the W-type lines, the image contrast is seen to become stronger with increasing defocus and thickness. In addition to the intensity change, the relative width of these dark/bright lines is seen to be a function of defocus and thickness. Contrary to the W-type lines, however, all the N-type line images are generally very weak. Although the number of the lateral periodicity, $n$, was chosen to be 17, not all the images exhibit the same number of dark or bright lines. In fact the periodicity could be doubled, depending on the magnitude of defocus and thickness. The cause of line doubling with defocusing is due to proximity in the projected features, which induce strong lateral beam interference. As long as the images contain the same number of periodicity, the following relationship similar to that given in eqn (8) can be obtained;

$$P_D = P_B = S_D + S_B = (1/2)(d + w)$$

It is possible to obtain quantitative data from the N-type lines using eqn (9), but care should be taken as to whether the number of the periodicity is consistent with the original structure. However, the probability of finding the N-type line images in the particle was found to be very small.14 This is due to the fact that (1) the N-type lines exhibit lower contrast than the W-type lines and (2) the available range of orientation angles for observing the N-type lines is smaller than that of the W-type lines.14

5.3 Thickness effect

Computer-simulated images of the W- and N-type lines at $\Delta f = -3 \mu m$ are plotted against film thickness in Fig. 12(a) and (b). These images, which can be regarded as a wedge region of the particle, offer useful information as to how the image changes with thickness at a constant amount of defocus. The behavior of the W-type image with thickness appears to be straightforward without a significant image change, whereas the image of the N-type lines exhibits a complex change in the thicker region (100–150 nm). This trend was already seen in Fig. 10 and 11.

5.4 Through-focus series

Another form of useful image display is a through-focus intensity map (TFIM) plotted at a constant thickness. Fig. 13(a) and (b) are two TFIMs simulated for the Projections I and II of a 100 nm thick specimen, respectively. This type of map contains a series of images given in Fig. 8 and 11, thus providing a quick overall view of an image change with defocus at a constant specimen thickness. It should be noted that the pattern of the TFIMs in Fig. 13 will change with a different thickness value. A similar map was previously presented by Nakahara17 and Dunin-Borkowski.18

It should be pointed out that the overfocus part of the TFIM provides a physically meaningful picture. The reason is...
as follows. In the TEM, planes below the specimen correspond to the overfocus plane and the magnitude of overfocus increases with increasing distance from the bottom of a specimen. The overfocus part of the map, therefore, is equivalent to the current density (intensity) distribution of electrons moving downward after undergoing a phase change inside a specimen. If we combine the geometry of a specimen with the TFIM’s overfocus part, we understand how an electron moves below the specimen. The cross section of a network of hexagonal pores in a 100 nm thick mesoporous silica for the Projection I is illustrated in Fig. 14(a) and the overfocus part of the corresponding TFIM is shown in Fig. 14(b). Here near the exit surface, bright lines emanate from the wall region. It can be envisioned that the phase of an electron wave in the high-density region is retarded, making electrons from the surrounding region move into this wall region. Consequently, a bright electron beam appears below the wall region.

5.5 Comparison with experiments

Exact matching of experimental images to simulated ones was found to be very difficult due to a number of experimental variations, particularly in the void geometry. First of all, we assumed that the shape of pores is an ideal hexagon. A careful TEM examination of the honeycomb cell structure in Fig. 2(a) has indicated that these pores are not exactly hexagonally-shaped but are rounded without corners/facets. Namely, the pore shape is almost circular or elliptical rather than being hexagonal. As long as images are taken at a large defocus distance, however, they should not be affected significantly by the detail of the pore shape. In other words, the shape of the wavefront becomes similar at a large defocus distance regardless of the void shape. Another variation associated with the voids can be examined along the pore tunnel direction. Fig. 15 shows 6 examples of typical W-type line images taken from the HOMS material. All the images exhibit similar dark/bright periodic lines, qualitatively consistent with simulations shown in Fig. 8. A close inspection of these experimental images, however, reveals that the dark/bright lines are not always straight but are locally bent. Furthermore, the line images are seen to contain roughness along the pore line. These variations in the pore geometry further contribute to a difficulty in image matching with simulations.

In addition to the strong dark/bright lines seen in the W-type line images, our simulations also revealed the weak dark line (WDL) between the strong white line images in the underfocus condition and the weak bright line (WBL) between the strong bright lines in the overfocus case (see Fig. 6). These
two types of weak lines, however, have not been seen in our experimental images taken by the conventional non-FEG TEM. Since our image simulations assume a perfectly coherent beam, they were thought to be closer to those of experimental images taken by a FEG-type TEM, which offers a more coherent beam. Consequently, we decided to examine the effect of beam coherence on the W-type line images of the HOMS particle using both FEG and non-FEG TEMs. As was already demonstrated, both the WDL and WBL images contained in the simulation of Fig. 6 were not visible on any experimental micrographs recorded by the non-FEG TEM (Fig. 16a and b). On the other hand, if the images were taken using the FEG TEM, the WBL showed up in the overfocused micrographs, as seen in Fig. 16(d), but the WDL did not appear in the underfocused image. In fact this result is consistent with the simulations, which indicate that the WDL image is weaker than the WBL (see Fig. 6). Nevertheless, beam coherency is one of the important factors that contribute to the appearance of the weak lines such as WBL, which is predicted by simulations.

Finally, we compare experimental and simulated images for varying defocus conditions (Fig. 17) and from the two Projections I and II (Fig. 18). Fig. 17 shows the effect of the sign of defocus ((a) $\Delta f \approx +2.0 \, \mu m$ and (b) $\Delta f \approx -2.0 \, \mu m$) on the W-type line images obtained by the conventional non-FEG TEM. The corresponding simulations are shown in Fig. 17(c) and (d). In Fig. 18, experimental W- and N-type line images ((a) and (b)) taken along the two symmetry directions of the HOMS material are compared with the

![Fig. 12](image1.png)  
**Fig. 12** Computer-simulated images of (a) the W lines (Projection I) and (b) the N lines (Projection II) plotted as a function of film thickness.

![Fig. 13](image2.png)  
**Fig. 13** Simulated images of (a) W-type parallel lines and (b) N-type parallel lines displayed as a function of the amount and sign of defocus, $\Delta f$ (see text).
Fig. 14 An intensity distribution showing how the intensity of a plane wave changes after passing through a 100 nm thick mesoporous silica particle containing hexagonally-ordered pores. (a) The cross section of a network of hexagonal pores projected along the Projection I and (b) a computed electron distribution map that illustrates how electrons travel down after passing through the sample shown in (a).

Fig. 15 Selected TEM images of W-type lines observed in a hexagonally-ordered mesoporous silica material. All the images were recorded on the JEOL 2010 TEM in underfocus ($\Delta f < 0$, $|\Delta f| \approx 2.0 \mu m$) conditions.

Fig. 16 Comparison of W-type line images recorded on a non-FEG TEM (JEOL 2010) with Cs $\sim 1$ mm ((a) and (b)) and a FEG TEM (JEOL 2100F) with Cs $\sim 0.5$ mm ((c) and (d)). Note that a faint white line is present inside the black parallel lines taken in the overfocus image by the FEG TEM (cf. Fig. 16(d)), whereas it is absent by the non-FEG TEM (Fig. 16(b)).

Fig. 17 Comparison of experimental images ((a) and (c)) of the W-type lines of a hexagonally-ordered mesoporous silica material with the corresponding simulations ((b) and (d)). (a) $\Delta f \approx +2.0 \mu m$ and (b) $\Delta f \approx -2.0 \mu m$.

Fig. 18 Comparison of experimental images ((a) and (b)) taken along the two symmetry directions of a hexagonally-ordered mesoporous silica material with the corresponding simulations ((c) and (d)). The arrows indicate viewing directions (Projections I and II).

The detail in the experimental images slightly differs from simulations, the overall image topography is in good qualitative agreement.
6. Conclusions

Using the defocus contrast theory that treats the whole body of the mesoporous particle as a phase object, we simulated the images of the observed wide/narrow lines as a function of the sign/amount of defocus and specimen thickness. This is the first time that this methodology has been applied analytically to simulations of TEM images of mesoporous materials and allows the effect of the amount/sign of defocus to be predicted. The spacing of the periodic dark/bright lines seen in the wide line images was found to remain consistent for changes in defocus and can therefore be used to obtain quantitative values associated with this material. Prediction of the images from the narrow type lines, on the other hand, indicates that the contrast is much weaker than that from the wide type lines. A prediction of the effect of particle thickness on the resulting TEM images indicates that thicker samples give better contrast for the wide type lines, but give a more complex pattern for the narrow type lines, suggesting that an analysis of the wide type lines is more reliable for taking quantitative measurements.

Appendix A

1 Projection I

The outside region of the mesoporous material is considered to be the void region of thickness of the material considered. For one period of thickness, the effective film thickness is \( d + w \), making \( \phi(x) = -\beta(d + w) \).

\[
\psi_A(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \int_{-\infty}^{\infty} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 
\]

(A1)

\[
\psi_B(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \sum_{n=0}^{\infty} \left[ \int_{\frac{k}{2}(d + w) + \frac{k}{2}d}^{\frac{k}{2}(d + w) + \frac{k}{2}d} e^{i\phi_n(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{k}{2}(d + w) + \frac{k}{2}d}^{\frac{k}{2}(d + w) + \frac{k}{2}d} e^{i\phi_{n+1}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{k}{2}(d + w) + \frac{k}{2}d}^{\frac{k}{2}(d + w) + \frac{k}{2}d} e^{i\phi_{n+2}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{k}{2}(d + w) + \frac{k}{2}d}^{\frac{k}{2}(d + w) + \frac{k}{2}d} e^{i\phi_{n+3}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' \right] 
\]

(A2)

\[
\psi_C(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \int_{-\infty}^{\infty} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 
\]

(A3)

The formula of \( \phi_2(x), \phi_1(x), \phi_3(x), \phi_4(x) \), and \( \phi_5(x) \) can be determined from Fig. 10.

\[
\psi_D(x) = \psi_A(x) + \psi_B(x) + \psi_C(x) 
\]

(A4)

2 Projection II

The outside region of the mesoporous material is considered to be the void region of thickness of the material considered. For one period of thickness, the effective film is \( \sqrt{3}(d + w) \), making \( \phi(x) = -\sqrt{3}\beta(d + w) \).

\[
\psi_A(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \int_{-\infty}^{\infty} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 
\]

(A5)

\[
\psi_B(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \sum_{n=0}^{\infty} \left[ \int_{\frac{3k}{2}(d + w) + \frac{k}{2}d}^{\frac{3k}{2}(d + w) + \frac{3k}{2}d} e^{i\phi_n(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{3k}{2}(d + w) + \frac{k}{2}d}^{\frac{3k}{2}(d + w) + \frac{3k}{2}d} e^{i\phi_{n+1}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{3k}{2}(d + w) + \frac{k}{2}d}^{\frac{3k}{2}(d + w) + \frac{3k}{2}d} e^{i\phi_{n+2}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 

+ \int_{\frac{3k}{2}(d + w) + \frac{k}{2}d}^{\frac{3k}{2}(d + w) + \frac{3k}{2}d} e^{i\phi_{n+3}(x')} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' \right] 
\]

(A6)

\[
\psi_C(x) = \frac{(1 - i)}{2} \sqrt{\frac{K}{\pi \Delta f}} \exp(i \Delta f/K) \int_{-\infty}^{\infty} \exp\left(\frac{ik}{\Delta f}(x - x')^2\right) dx' 
\]

(A7)

The formula of \( \phi_2(x), \phi_1(x), \phi_3(x), \phi_4(x) \), and \( \phi_5(x) \) can be determined from \( \iota(x) \) listed in Fig. 10.

\[
\psi_D(x) = \psi_A(x) + \psi_B(x) + \psi_C(x) 
\]

(A8)

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References