ADVANCES IN PHYSICS: X, 2016
VOL. 1, NO. 1, 55–80
http://dx.doi.org/10.1080/23746149.2016.1142830

REVIEW ARTICLE

Visualizing charge densities and electrostatic potentials in materials by synchrotron X-ray powder diffraction

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1. Benefits of SXPD in visualizing materials properties

X-ray scattering by electrons provides a lot of information on electron distributions in materials (Figure 1). It is widely recognized that synchrotron X-ray powder diffraction (SXPD) can identify atomic configurations as a result of electron localization [1,2]. Meanwhile, the visualization of itinerant electrons as chemical bonding and electrostatic interaction, which results in visualizing materials properties, involves many practical difficulties even by synchrotron sources. The application of the maximum entropy method (MEM) [3]
to SXPD data have succeeded in visualizing charge densities $\rho(r)$ (Figure 1(c)) [4]. On the other hand, measuring of a series of data for charge density studies took several days and furthermore needed a substantial amount of powder specimen around hundreds of milligrams. In particular, that was the case of materials containing heavy elements since the scanning method (Figure 2) had to be employed to measure high-counting statistics data up to high diffraction angles without absorption correction. These contexts did not allow a wider application of SXPD to materials science. The progress of synchrotron sources has brought many benefits to powder diffraction experiments in terms of absorption correction and angular

*Figure 1.* (a) The interaction between electron charge and X-rays, which is an electromagnetic wave. Information obtained on the basis of the interaction: (b) atomic configuration $r$, (b) charge density $\rho(r)$, and (c) electrostatic potential $U(r)$.

*Figure 2.* Basic components of a typical SXPD beamline with a Soller slit. The photograph shows BL-3A of Photon Factory.
resolution as well as collection time and the amount of powder specimen. Taking advantage of high-energy X-rays over 20 keV delivered at third-generation synchrotron sources such as SPring-8, each Bragg reflection can be measured at the same time with transmission geometry (Figure 3). In the setup, diffraction data need no correction in intensity due to the decay of storage ring current as well as absorption even in the case of heavy materials. As for data collection time, brilliant X-rays have allowed to collect data with a maximum intensity of million counts within one hour. In addition, the amount of powder specimen can be reduced from hundreds of milligram to hundreds of microgram. A smaller amount of powder specimen enables charge density studies in a wide range of functional materials [5]. Consequently, electrostatic potentials $U(r)$ (Figure 1(d)) in addition to charge densities have been obtained from SXPD data, leading to a better understanding of materials properties in terms of electrostatic interaction. Furthermore, compared with single crystal diffraction, in which case data measured with different crystal angles need to be merged into one data-set, powder diffraction has proved to be favourable to in situ and/or operando measurements, particularly for irreversible physical and chemical phenomena [6].

In the present paper, we review SXPD instrumentation for charge density mapping and electrostatic potential imaging, revisiting orbital/charge ordering studies in manganites, in situ charge density studies in photo-induced transition materials, etc. Finally, we discuss the application of SXPD to aperiodic systems.
2. Instrumentation for high-energy SXPD

High-energy X-rays delivered from third-generation synchrotron sources such as European Synchrotron Radiation Facility (ESRF), Advanced Photon Source (APS), SPring-8 and others allow us to employ transmission geometry for SXPD. There are two ways of taking advantage of third-generation synchrotron X-rays for powder diffraction. One is to obtain high angular resolution by analyser crystals in front of point detectors [7,8]. The other is to obtain high counting statistics data by position-sensitive or area detectors [9]. ID31 [7] of ESRF is designed to collect data with higher angular resolution up to 0.001° in 2θ, aiming at solving crystal structure from a powder specimen. On the other hand, the powder diffraction beamline at SPring-8 has focused on charge density studies by the MEM. For the purpose, a Debye–Scherrer camera equipped with an imaging plate as the X-ray detector (Figure 3) has been developed at the powder diffraction beamline BL02B2 [10]. The camera radius is set at 286.48 mm, in which case one pixel (50 μm²) on the imaging plate corresponds to 0.01° in 2θ. Both the hardware and software are user-friendly designed so that not only crystallographers, but also materials scientists can obtain high counting statistics data of several samples in one day. The concept has inspired other beamlines at SPring-8, such as BL44B2 [11] and BL15XU [12] for materials scientists, and BL19B2 [13] for industrial users, to employ the Debye–Scherrer method. Furthermore, the powder diffraction beamline at Australian Synchrotron [14] and a vacuum-type Debye–Scherrer camera [15] have been facilitated by successful experiments at SPring-8 powder diffraction beamlines.

2.1. X-ray optics for SXPD

The width of powder diffraction profiles is partly determined by optical parameters. One of these parameters is energy resolution of incident X-rays. In the case of synchrotron sources, monochromatic beams are obtained through a monochromator from white X-rays. Si 111 double crystal monochromators have typically been employed for SXPD experiments, the energy resolution of which is of the order of $10^{-4}$ in $\Delta E/E$. To avoid the degradation in energy resolution due to beam divergence, a collimating mirror should be installed above a monochromator. These two optical components are followed by another mirror, which focus monochromatic beams on a specimen mounted on a diffractometer.

Harmonics contaminate diffraction data when monochromators are used. In the case of the use of Si 111 crystals, 222 and 333 planes diffract second and third harmonics, respectively. To reduce the diffraction intensity by these planes, the surface of mirrors is commonly coated with metals. At BL02B2 of SPring-8, the mirror made of Si above the Si 111 monochromator is partly coated with Pt and Ni, in which case the optimal surface for X-ray energy is selected among three materials Si, Pt and Ni (Figure 3(a)). At BL44B2 of SPring-8, the Si mirror below
the Si 111 monochromator is coated with Pt all over the surface, in which case the cut-off energy varies with the glancing angle of the mirror. With increasing the angle, the cut-off points shift to lower energies. Consequently, the available energy ranges up to 35 keV with a photon flux of the order of $10^{11}$ photons s$^{-1}$.

### 2.2. Imaging plate calibration for charge density studies

The following points as to fading effect, spatial resolution and sensitivity must be taken into account when accurate structure analysis such as charge density analysis is conducted using the imaging plate detector [16]. It has widely been recognized that X-ray images recorded on the imaging plate decay with time, which is referred to the fading effect of the imaging plate. It is important to mention here that it takes as long as several minutes to scan an imaging plate by a He–Ne laser. To keep the intensity decay below 1% during scanning, data should be read out at least twenty minutes after X-ray exposure. Note that the waiting time depends on the type of imaging plate, that is the fluorescence material and its thickness. Another approach with a decay curve fitting to the fading effect has been examined by Straaso et al. [15], in which case there is no need to wait for a long time but need to record time for the data correction. The spatial resolution of the imaging plate is determined by the scanning speed of the read-out system and the error of ±0.1% or so seems to be unavoidable. In the case of powder diffraction data, the error is not acceptable since the accumulation of the deviation reaches around ten pixels at high angles, leading to incorrect lattice parameters in data analysis. Tuning of the scanning speed using the standard sample has been able to make the deviation less than ±0.01%. A typical scanner can read out X-ray image in the dynamic range from $10^4$ to $10^5$. In general, millions of X-ray counts are necessary for charge density studies, however, most of commercial scanners are out of the range. To be able to collect high counting statistics data by SXPD, the applied voltage of the photomultiplier has been reduced into about a tenth compared to the initial state. Recognize that it was impossible to obtain charge densities by MEM analysis of SXPD data until the above-mentioned points have been considered.

### 2.3. Data correction

Given high-energy X-rays up to around 35 keV with the Debye–Scherrer geometry, diffraction data need no correction for diffracted intensity, in which case systematic errors can be minimized to obtain accurate charge densities. The storage ring current decays with time without the so-called top-up operation. If the scanning method has to be employed with lower X-ray energies or is applied to obtain high angular resolution data with analyser crystals, raw data must be corrected according to the decay in incident X-rays. In the case of the use of flat area detectors, each pixel on detectors has each glancing angle of incident X-rays,
and the sample-detector distance varies with diffraction angle. X-ray absorption effect by a sample becomes insignificant provided that the proper X-ray energy is selected for the diameter of the capillary and the sample composition. In the case of a material containing heavy element, such as PbTiO$_3$, the difference in absorption coefficient between 0° and 90° in 2$\theta$ is approximately 1.7% by using 30 keV X-rays and the capillary size with a diameter of 0.1 mm. This setup has allowed charge density analysis without any data correction, leading to evidence for Pb-O covalency in the ferroelectric PbTiO$_3$ [17].

2.4. Devices for temperature-variable experiments

Physical and chemical properties in materials often undergo significant changes with increasing and/or decreasing temperature, which are accompanied by structural phase transitions. There are cases to which this does not apply. To give an example, electronic transition from a non-superconductive to superconductive phase is caused by slight changes in bond distances and angles, accompanied with significant variations in chemical bonding [18]. The employment of the Debye–Scherrer geometry for SXPD facilitates a wide rage temperature experiment. This is because the geometry allows simultaneous measurements of Bragg reflections from a small amount of powder specimens, which means that each Bragg peak can be measured at the same temperature at once. Figure 4 shows high- and low-temperature blowers installed at the Debye–Scherrer camera at BL02B2 and BL44B2 of SPring-8. For high-temperature experiments from room temperature to 1100 K, heated nitrogen gas blows a glass capillary containing a powder specimen at a distance of about 5 mm. The low-temperature blower is available.
in the temperature range from 90 to 450 K by refrigerated nitrogen gas. Both setups allow automatic temperature-variable experiments with the horizontally scanning imaging plate [2] or on-line detectors. To achieve higher temperatures for powder specimens, the laser heating, which has been developed in the field of high-temperature and high-pressure experiments, is superior to conventional X-ray furnaces, especially for \textit{in situ} SXPD measurements. When using high-power laser, temperature calibration at the sample position should be done by non-contact sensors, e.g. high-resolution infrared thermography. Below liquid nitrogen temperature, the Debye–Scherrer camera is equipped with two types of low-temperature device (Figure 5). One is an open flow helium jet (Helijet by Agilent) and the other is a closed-cycle cryostat by ULVAC CRYOGENICS INC.; the former down to 15 K, the latter down to 4 K. The Helijet allows easy access to powder specimens but the capillary is likely to be covered with some frost, resulting in contamination in diffraction data. In contrast, the cryostat takes much time to align with a diffractometer but the temperature is lower and more stable than that of the Helijet without contamination. Furthermore, an electric field can be applied to a thin film by the cryostat. It is our expectation that low-temperature SXPD experiments under gas pressure are conducted by the cryostat, leading to

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{figure5.png}
\caption{(a–b) A helium gas jet system ($T < 100$ K) linked with the nitrogen gas flow system ($T > 90$ K) at BL44B2 of SPring-8. (c) A 4 K cryostat coupled to the Debye–Scherrer camera at BL44B2 by a goniometer and (d) a sample holder for applying electric field.}
\end{figure}
synchronization with gas adsorption isotherm. We can choose appropriate devices for different targets.

3. Preparation of powder specimens for charge density studies

A powder specimen with homogeneous grains is required especially for accurate structure analysis such as charge density analysis, providing homogeneous Debye–Scherrer rings. Standard powder specimens such as Si and CeO$_2$ are supplied with the average diameter of several microns, which means that there is no need to pay attention to preparation of powder specimens for oneself. Most of synthesized materials have a wide distribution of grain size. The common method by a sieve with fine meshes often fails to screen small grains due to the formation of coarse particles of small grains. In order to avoid the cohesion of small grains into coarse particles, a precipitation method (Figure 6) taking advantage of the grain sedimentation rate has been employed to obtain homogeneous Debye–Scherrer rings. The process for preparing homogeneous grains is as follows:

1. Grinding grains larger than several microns with an agate mortar.
2. Mixing the powder specimen with an organic solvent, e.g. ethanol, and giving the solution ultrasonic vibrations. (In the case of organic materials, special care should be taken in using organic solvents not to dissolve.)
3. Leaving the solution as it is until larger grains go down.
4. Putting the top clear layer with small grains in another container.
5. Leaving the solution as it is until large grains go down.
6. Putting the top clear layer with smaller grains into another container.

Figure 6. Schematic diagram for preparation of homogeneous powder specimens.
(7) Drying the solution containing the precipitate by a heater, e.g. a hot-plate to obtain intermediate grains. (Especially for organic materials, special care should be taken in using the heater to avoid thermal decomposition.)

Even if the precipitation method seems to be successfully applied to the powder specimen, the specimen needs to be confirmed by SXPD measurements in a short exposure time in terms of the profile width of Bragg peaks and the granularity of Debye–Scherrer rings, leading to the estimation of measurement time for charge density studies. In case of peak broadening, which makes it difficult to separate overlapping peaks, the larger grains should be collected by reducing the waiting time in the third process. On the other hand, too sharp Bragg peaks often give rise to inhomogeneity on Debye–Scherrer rings, in which case the smaller grains should be collected by increasing the waiting time in the fifth process.

4. Charge density studies

High counting statics SXPD data can provide three-dimensional charge densities in materials. Charge density studies of silicon and diamond [19] by the MEM [3,20] are good examples to illustrate how SXPD data works for visualization of materials properties. Taking advantage of high-energy X-rays at SPring-8, the accuracy of experimental structure factors of silicon and diamond obtained by SXPD is comparable to that by the Pendellösung method [21]. In addition, the number of obtained structure factors in Si reaches 104, which is three times as many as that by the Pendellösung method. Consequently, accurate charge densities comparable with theoretical ones [22,23] have been successfully obtained. The cases of silicon and diamond indicate that the MEM charge density analysis of SXPD data is a promising tool to visualize materials properties, e.g. chemical bond and electrostatic properties [5,17,18,24–32].

Figure 7. In-plane and out-of-plane resistivities $\rho_{ab}$ and $\rho_c$ of NdSr$_2$Mn$_2$O$_7$ as a function of temperature.
4.1. Visualization of orbital ordering in manganites

The MEM analysis of SXPD data is applicable to a wide range of materials from inorganic to organic. The most typical application is a strongly correlated system, manganese oxides [33]. A layered manganese oxide NdSr$_2$Mn$_2$O$_7$ is known to exhibit anisotropic electrical resistivity at low temperatures as shown in Figure 7. Below 200 K, the in-plane resistivity $\rho_{ab}$ is of the order of $10^0$ Ω cm, whereas the out-of-plane resistivity $\rho_c$ is of the order of $10^2$ Ω cm. The anisotropy, however, cannot be described by the atomic-scale change obtained by the Rietveld analysis (Figure 8). The space group at 300 K is identical to that at 19 K. In addition, the bond lengths of Mn-O1 (out-of-plane) and Mn-O3 (in-plane) undergo virtually no change with decreasing temperature, maintaining a distance of 1.93 Å. As to the Mn-O2 (out-of-plane) length, a 2% reduction (0.04 Å) is observed at 19 K, although the variation is insufficient to understand the large anisotropic resistivity. In order to reveal the structural change on an electron-density scale, the charge-density analysis by MEM has been applied to SXPD data of NdSr$_2$Mn$_2$O$_7$ at 300 and 19 K. Figures 9(b) and (c) represent charge density contour maps at 300 and 19 K, respectively. It is found that the itinerant electrons of Mn are equally distributed among O1, O2, and O3 at 300 K. In contrast, the out-of-plane bonding is likely to disappear on the 0.6 e Å$^{-3}$ density level at 19 K. On the other hand, the in-plane electrons remain between Mn and O3, forming the two-dimensional bonding nature. The structural change on the electron-density scale can best be explained as follows (Figure 10). Mn$^{3+}$ has four 3$d$ electrons. Three of four electrons occupy $t_{2g}$ orbital: $d(xy)$, $d(yz)$ and $d(zx)$. One of four electrons occupies either $e_g$ orbital: $d(x^2 − y^2)$ or $d(3z^2 − r^2)$, which is referred to as ‘a degree of freedom in electron orbital’. The $d(x^2 − y^2)$ and $d(3z^2 − r^2)$ orbitals range over in-plane and out-of-plane oxygens, respectively. Based on charge densities at 300 K, in which case the materials shows the isotropic resistivity, it is predictable that the occupancy in the $d(x^2 − y^2)$ orbital are close to that in the $d(3z^2 − r^2)$ orbital. The anisotropic bonding nature found at 19 K indicates that the $e_g$ electron occupies the $d(x^2 − y^2)$ orbital rather than the $d(3z^2 − r^2)$ orbital. The argument can lead us to the conclusion that the $d(x^2 − y^2)$ orbital ordering at 19 K involves the large anisotropy in electrical resistivity. Here let us evaluate the difference between the orbital ordering and disordering phases in observed structure factors obtained based on MEM charge densities. Figure 11 shows a lower-angle part of observed structure factors $|F_{obs}|$ at 300 and 19 K with error bars. It has been found that there are no systematic differences in structure factors between 300 and 19 K. It is important to mention here that better statistics measurements for each Bragg reflection can minimize the magnitude of error, leading to visualization of orbital ordering as anisotropy of charge densities between Mn and O. After the application to NdSr$_2$Mn$_2$O$_7$, which has the A-type antiferromagnetic structure, the SXPD-MEM approach has been applied to different magnetic structured materials Nd$_{0.35}$Sr$_{0.65}$MnO$_3$ (C-type) [34] and Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (CE-type) [35]. Consequently,
Figure 8. Results of Rietveld analyses of NdSr$_2$Mn$_2$O$_7$ SXPD data. (a-b) and (c-d) show results at 300 K and 19 K, respectively.

Figure 9. (a) Structure model with a (2 0 0) plane of NdSr$_2$Mn$_2$O$_7$ and MEM charge densities on the (2 0 0) plane at (b) 300 K and (c) at 19 K. Contour lines are drawn from 0 to 4.0 e Å$^{-3}$ at intervals of 0.2 e Å$^{-3}$. 
MEM charge densities at 300 K (Figure 12(a)) and 30 K (Figure 12(b)) in Nd$_{0.35}$Sr$_{0.65}$MnO$_3$ have identified the $d(3z^2-r^2)$ orbital ordering, which is consistent with that predicted from the spin ordering. Results of the half-doped manganite Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ are described in Section 5.2. These findings have facilitated charge density studies under extreme conditions at high pressure and low temperature in La$_{1.04}$Sr$_{1.96}$Mn$_2$O$_7$ (Figure 12(c)) [36].

4.2. In situ charge density studies

High-energy SXPD has the advantage of measuring each Bragg reflection at the same time by employing the Debye–Scherrer method. The utilization of the simultaneity allows in situ charge density studies under external stimuli such as photo
excitation [37], gas adsorption [38,39], and hydrostatic pressure [36,40,41]. To investigate photo-excited states on a charge density resolution, the in situ photo excitation setting has been developed at BL02B2 [37,42] and BL44B2 [43] of SPring-8. As shown in Figure 13, the setup consists of a shutter, neutral-density filters, two mirrors, and a focusing lens. The Debye–Scherrer cameras are equipped with an optical microscope under a capillary sample to view the focus of laser as well as align the capillary. The temperature of samples is variable in a wide range between 90 and 1100 K by two nitrogen gas flow devices. The most important point for charge density studies under photo excitation is to irradiate each grain in a quartz glass capillary with the visible laser, leading to a growth in an excited phase. The penetration depth of visible laser into the sample is estimated to be several microns at the most, which varies with optical properties of the sample. To overcome the difficulties, a capillary in the form of hollow cylinder with the thickness of 100 μm has been devised. In the case of dark samples, furthermore, quartz glass powders are mixed with sample powders in such a way that the laser light penetrates the capillary sample. The setup for in situ charge density studies have been applied to a spin crossover complex, Fe(phen)$_2$(NCS)$_2$, which is known to exhibit a kind of photo-induced phase transition, the light induced excited spin state trapping (LIESST) below around 60 K [44]. The LIESST metastable phase at 30 K lasts for 9 h after the laser irradiation. The present study focuses on a non-metastable state observed at 100 K. In contrast to the LIESST state, optical measurements have identified that the lifetime of the non-metastable state is less than several seconds. When the laser with a power of 202 mW and a wavelength of 532 nm irradiates the powder sample of Fe(phen)$_2$(NCS)$_2$ at 92 K, a new phase is likely to replace the original one, indicating nearly homogeneous excitation by

Figure 11. Observed structure factors with error bars for a lower-angle part of Bragg reflections at 300 K and 19 K of NdSr$_2$Mn$_2$O$_7$. 
the laser. It is found that the new phase disappears after irradiation, indicating that the photo excitation induces a dynamical crystal phase. Figure 14 shows charge densities and electrostatic potentials obtained by the method described in Section 5.1. Based on these findings, we conclude that photo excitation reduces bonding nature between Fe and N without charge transfer. Such electrostatic properties suggest the existence of a high-spin phase with suppressed thermal vibration [37].

4.3. Characteristics of the MEM charge density studies

The MEM provides total charge densities in a unit cell based on structure factors, which are extracted by the Rietveld refinement prior to the MEM analysis [5]. It is
Figure 13. *In situ* photo-excitation setup installed in the Debye–Scherrer camera at BL02B2.

Figure 14. (a) Molecular model of Fe(phen)$_2$(NCS)$_2$ and its charge densities (b) before and (c) during photo excitation. Contour lines are drawn from 0 to 4.0 e Å$^{-3}$ at intervals of 0.2 e Å$^{-3}$. Electrostatic potentials on the 0.45 e Å$^{-3}$ surface (d) before and (e) during photo excitation.
known that the MEM charge densities are not free from a bias due to a spherical
atom model used in the Rietveld refinement. Especially in the case of complex
materials, a significant peak overlapping in diffraction data makes it difficult to
reduce the bias. In addition, the magnitude of the errors in structure factors affects
the resultant MEM charge densities. This is because a convergence criterion for
the MEM analysis is that the structure factors based on the MEM charge densities
are consistent with the observed structure factors within their standard deviations
[3]. Bindzus and Iversen [45] have investigated these effects on the MEM charge
densities in detail with the commonly used Rietveld refinement programs. From
the viewpoint of SXPD experiments, we emphasize that it is important to measure
higher angular resolution and high counting statistics data with lower background.
For the more detailed analysis of charge densities, a combination of the MEM
analysis with the multipole modelling [46] is preferable, in which wider Q range
data are needed to optimize a large number of fitting parameters.

5. Electrostatic potential imaging

Experimental electrostatic potentials could provide complementary information
to experimental charge densities for a better understanding of materials properties.
In most cases, nevertheless, electrostatic potentials have been obtained theoretically based on the point charge model. Several approaches [47,48] have been proposed to directly derive electrostatic potentials from observed structure factors. Bragg reflections obtained by experiments, however, is always limited in number. It is well known that the Fourier transform using the finite number of structure factors suffer from the nonphysical Gibbs’s oscillation, leading to some artefacts in resultant charge densities [3] and electrostatic potentials. Su and Coppens [49] and Spackman [50] have attempted to calculate electrostatic potentials based on the multipole expansion, which allows a deconvolution to static structure factors comparable with theoretical calculations. On the other hand, Tanaka et al. [51] have proposed an alternative approach to experimental electrostatic potentials based on charge densities obtained by the MEM, which provides dynamic structure factors. This section describes the new approach and its applications to a metal-insulator transition material and others.

5.1. An approach to electrostatic potentials and electric fields based on MEM charge densities

Electrostatic potentials \( U(r) \) in a solid state are a summation of two components: nucleus charge \( U_{\text{nuc}}(r) \) and electron charge \( U_{\text{ele}}(r) \).

\[
U(r) = U_{\text{nuc}}(r) + U_{\text{ele}}(r)
\]

(1)

\( U_{\text{ele}}(r) \) is described by a summation in the reciprocal lattice \( G \) as

\[
U_{\text{ele}}(r) = -4\pi \sum_G \frac{\tilde{\rho}(G)\exp(iGr)}{|G|^2}
\]

(2)

where \( \tilde{\rho}(G) \) is the Fourier component of electronic charge densities \( \rho(r) \). Structural factors \( F(G) \) is expressed with the volume \( \Omega \) in the real space as

\[
F(G) = \Omega \tilde{\rho}(G)
\]

(3)

Equation (2), therefore, is rewritten by

\[
U_{\text{ele}}(r) = -4\pi \sum_G \frac{F(G)\exp(iGr)}{\Omega|G|^2}
\]

(4)

As \( F(G) \) in Equation (4), we employ not the limited number of observed structure factors but the sufficient number of structure factors extrapolated by MEM \( F_{\text{MEM}}(G) \) [4] as follows, which facilitates convergence of Equation (4).

\[
F(G) \approx F_{\text{MEM}}(G)
\]

(5)

On the other hand, the \( U_{\text{ele}}(r) \) is estimated by the conventional Ewald’s method [52]. Accordingly, the \( U(r) \) is represented by
where $R_t$, $Z_t$, and $l$ are the position vector of the $t$-th basis atom relative to the lattice point, the atomic number of the $t$-th basis atom and the lattice point vector, respectively. The function erfc($\eta$) is the complementary error function. $\eta$ is a variable, which should be determined so that both summations in real and reciprocal lattices converge rapidly. It is confirmed that the resultant potentials are not due to the value of $\eta$, given that the summation is done with the sufficient number of lattice points in real and reciprocal spaces. This approach provides experimental-based electrostatic potentials without any assumption, as opposed to conventional methods, such as the multipole expansion [49]. Electric fields are given by taking the gradient of Equation (6):

$$U(r) = 4\pi \sum_G \frac{\sum_t Z_t \exp\left(-|G|^2/\eta^2 - iG R_t\right) - F_{MEM}(G)}{\Omega |G|^2} \times \exp(iG r)$$

$$+ \sum_l \sum_t \frac{Z_t}{|r - l - R_t|} \text{erfc}\left(\eta |r - l - R_t|\right)$$

(6)

This approach has been applied to ferroelectric PbTiO$_3$ to compare the theoretical results. Figures 15(a) and (b) show the $z$ component of electric fields on the isosurface of charge densities at 300 K and that obtained by ab initio calculations [53], respectively. Electric fields obtained from electrostatic potentials indicate the existence of the dipolar polarization in Pb ions, which is qualitatively in agreement with that by the theoretical prediction. A quantitative analysis by comparison between experimental and theoretical results leads to a better understanding of ferroelectric properties in PbTiO$_3$.

5.2. Visualization of charge ordering in a half-doped manganite

In the strongly correlated electron system such as manganese oxides, three degrees of freedom in electron, orbital, charge and spin play an important role in electronic properties. For example, the MEM analysis of XPD data has revealed orbital ordering in NdSr$_2$Mn$_2$O$_7$ [33]. On the other hand, an insight into charge ordering is difficult to derive from charge densities due to hybridized orbital between Mn and O. Electrostatic interactions between atoms are more sensitive to a small charge disproportionation. A low-temperature insulating Na$_{0.5}$Sr$_{0.5}$MnO$_3$ has been investigated by the electrostatic potential imaging method based on
MEM charge densities. Figures 16(a) and (b) show charge densities at 300 and 18 K of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$, respectively. Strong anisotropy between Mn1 and O4(5) in charge densities at 18 K can be ascribed to orbital ordering of Mn $e_g$ electrons.

**Figure 16.** Charge densities (a) at 300 K and (b) at 18 K of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. (c) represents an orbital ordering model based on the charge densities at 18 K. Contour lines on the (0 1 0) plane are drawn from 0 to 4.0 e Å$^{-3}$ at intervals of 0.2 e Å$^{-3}$.

**Figure 17.** Electrostatic potentials (a) at 300 K and (b) at 18 K of Nd$_{0.5}$Sr$_{0.5}$MnO$_3$. (c) represents a charge ordering model based on the electrostatic potentials at 18 K. Contour lines on the (0 1 0) plane are drawn from −1.0 to 2.0 e Å$^{-1}$ at intervals of 0.3 e Å$^{-1}$.
In contrast, isotropic charge distributions between Mn and O2 are observed at 300 K, indicative of orbital disordering. The orbital disorder–order transition is highly suggestive of charge ordering related to its metal-insulator transition because Mn\(^{3+}\) and Mn\(^{4+}\) have one \(e_g\) electron and no \(e_g\) electron, respectively. To corroborate the existence of charge ordering, the electrostatic potential imaging has been carried out based on the MEM charge densities. Contour maps of electrostatic potentials are shown in Figure 17. A sharp contrast in potential distributions is found between Mn1 and Mn2 at 18 K, proving that the charge disproportionation of Mn\(^{3+}\) and Mn\(^{4+}\) occurs at the low-temperature insulating phase. As opposed to 18 K, all manganese ions appear to be charged equally at 300 K. Thus, electrostatic potentials provide fundamental understandings on the charge-ordered insulating system [35].

### 5.3. Applications of electrostatic potential imaging to a diversity of materials

A typical transition metal cyanide RbMn [Fe(CN)\(_6\)] shows a cubic to tetragonal transition at around 220 K, accompanied by a spin transition [54]. We have performed charge density analysis by MEM and SXPD to understand the origin of the magnetic transition. On careful comparison with theoretical charge densities based on a local density approximation, anisotropic charge distributions around

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**Figure 18.** (a) Structure model with a (1 0 0) plane of RbMn[Fe(CN)\(_6\)], its experimental charge densities at 92 K, and (c) its theoretical charge densities. Contour lines are drawn from 0 to 4.0 e Å\(^{-3}\) at intervals of 0.2 e Å\(^{-3}\).
Mn$^{3+}$ at 92 K is interpreted in terms of the strong $p - d$ hybridization (Figure 18) [26]. Furthermore, electrostatic potential analysis has identified that potentials around Mn drastically change with decreasing temperature, whereas potentials around Fe undergo virtually no change (Figure 19). These findings indicate that the transferred electrons from Mn to Fe spreads over the hexacyanoferrate ([Fe(CN)$_6$]) via the strong Fe$_{t_{2g}}$ – CN$\pi^*$ hybridization at the low-temperature tetragonal phase [55]. The similar phenomenon has been observed in a transition metal cyanide containing water, K$_{0.34}$Co [Fe(CN)$_6$]$_{0.75}$ 3.6H$_2$O by charge density [30] and electrostatic potential analyses [56].

It is our expectation that the quantitative analysis of electrostatic potentials and electric fields leads to a deeper understanding of the relation between electrostatic and electronic properties. Low thermal conductivity in thermoelectric materials such as clathrates has been better understood in terms of rattler modes by Christensen et al. [57]. Fujiwara et al. [58] have successfully parameterized the relation between electrostatic properties and thermal conductivity in type-I clathrates $X_8$Ga$_{16}$Ge$_{30}$ ($X$ = Sr, Ba) in terms of electrostatic interactions between the host molecules and guest atoms. In the paper, the rattling factor has been defined as $f_R = V_{EP}/V_{cov}$, where $V_{EP}$ denotes a volume of the area surrounded by the local-minimum surface of electrostatic potentials, and $V_{cov}$ refers to a volume $(4\pi r_{cov}^3/3)$ of cage using atomic coordination using the covalent radius $r_{cov}$. It is
believed that thermal conductivity could be predicted on the basis of the rattling factors, leading to the development of novel thermoelectric materials. The quantitative analysis in clathrates has allowed an approach to materials properties from a different aspect. Indeed, a quantitative analysis of charge densities using electrostatic potentials has been performed on superconducting F-doped LaFeAsO \[59\] and ferroelectric Bi$_2$SiO$_3$ \[60\] to understand materials properties. Recently, Kosone et al. \[61\] have visualized electrostatic properties in a Hofmann-type porous coordination polymer, \{Fe(pz)\}[Pd(CN)$_4$] \(pz = pyrazine\), by \textit{in situ} SXPD measurements under H$_2$ adsorption coupled with Raman spectroscopy. Consequently, they have succeeded in discovering the fast ortho-para conversion process of H$_2$ in the coordination nano space. In addition, the electric field imaging is considered to be a powerful tool for visualization of diffusion paths of ionic conduction species. The electric field analysis is under way to understand the superionic conduction mechanism by contrast with molecular dynamics simulations.

5.4. \textbf{Complementary use of neutron diffraction}

For the MEM-based electrostatic potential imaging, the nucleus charge has been approximated by the point charge, taking no account of the distribution of nucleus charge. The anisotropic distribution of nucleus charge is employed only when anisotropic thermal factors are introduced in the Rietveld analysis. However, X-rays are scattered by not nucleus but electron. To obtain electrostatic potentials taking into account the distribution of nucleus charge, it is highly recommended that SXPD and neutron diffraction studies be conducted in a closely coordinated manner for a deeper understanding of electrostatic interactions in materials.

6. \textbf{Towards nano-scale materials properties by SXPD}

As described in the present review paper, third-generation synchrotron sources has much improved diffraction data quality and dramatically reduced the measurement time without data correction, leading to electrostatic potential imaging as well as charge density mapping in a variety of crystalline materials. In our method, however, the range of application has been restricted to crystals, assuming long-range order structure. There are an increasing number of complex materials such as nano materials and disordered materials \[62\]. The crystallographically challenged materials have intrinsic short- and/or medium-range order structure. X-ray total scattering has been recognized as one of the powerful techniques for visualizing such nanostructure \[63\]. In APS, the rapid acquisition pair distribution function (PDF) data collection have been intensively conducted using high-energy X-rays up to 100 keV and a flat-type detector in a short camera distance, which enable data collection with high $Q$ in a single shot \[64\]. To obtain sufficient real-space resolution in PDF, it is preferable that the maximum $Q$ ranging between 20
and 40 Å⁻¹ should be measured with good statistics. In this setup, however, accurate structure analysis such as charge density mapping and electrostatic potential imaging is unfeasible due to significant overlapping of Bragg reflections by a combination of high-energy X-rays and near-field flat detectors. It is our expectation that the use of intermediate energies between 30 and 60 keV allows to collect data for both average and local structure analyses in a single shot. Indeed, PETRA III has constructed a powder diffraction beamline for both PDF and MEM studies with 60 keV [65,66]. This versatile method could give us a deeper insight into material properties despite periodicity of materials. At BL44B2 of SPring-8, we have assembled a curved detector system, which consists of twelve MYTHEN modules (DECTRIS Ltd.), to conduct MEM-based potential and PDF studies with intermediate X-ray energies. So far, Swiss Light Source [67] and others [68,69] have successfully developed the MYTHEN detector system, which, however, needs twice measurements to fill a gap between modules. Our system can cover the 2θ range from 0 to 120° continuously with a completely gapless configuration. The details of the system are described in another paper [70]. By using this system, electrostatic properties taking into account nano-scale structure will be visualized under external stimuli such as temperature, gas pressure, photo excitation, electric field and so on.

Acknowledgements

The synchrotron radiation experiments were performed at BL02B2 and BL44B2 of SPring-8 with the approval of Japan Synchrotron Radiation Research Institute and RIKEN, respectively. Fruitful discussion with Prof. Yutaka Moritomo of University of Tsukuba is greatly appreciated. Special thanks goes to Prof. Eiji Nishibori of University of Tsukuba and Prof. Emeritus Makoto Sakata of Nagoya University for their valuable suggestions. The authors are deeply indebted to Prof. Masaki Takata of RIKEN SPring-8 Center and Tohoku University for his steadfast support and encouragement.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by JSPS KAKENHI [grant numbers 15740191, 17740205, and 25871142] (to K.K.) and by CREST, Japan Science and Technology Agency (to K.K.).

References

[1] J.B. Hastings, W. Thomlinson and D.E. Cox, J. Appl. Cryst. 17 (1984) p.85–95.
[2] P. Norby, J. Appl. Cryst. A30 (1997) p.21–30.
[3] M. Sakata and M. Sato, Acta Cryst. A46 (1990) p.263–270.
[4] M. Takata, E. Nishibori, M. Sakata, and Z. Kristallogr. 216 (2001) p.71–86.
[5] M. Takata, Acta Cryst. A64 (2008) p.232–245.
[6] A.K. Cheetham and A.L. Goodwin, Nat. Mater. 13 (2014) p.760–762.
[7] A.N. Fitch, J. Res. Natl. Inst. Stand. Technol. 109 (2004) p.133–142.
[8] S.P. Thompson, J.E. Parker, J. Potter, T.P. Hill, A. Birt, T.M. Cobb, F. Yuan and C.C. Tang, Rev. Sci. Instrum. 80 (2009) p.075107.
[9] P. Sarin, R.P. Haggerty, W. Yoon, M. Knapp, A. Berghaeuser, P. Zschack, E. Karapetrova, N. Yang and W.M. Kriven, J. Synchrotron. Rad. 16 (2009) p.273–282.
[10] E. Nishibori, M. Takata, K. Kato, M. Sakata, Y. Kubota, S. Aoyagi, Y. Kuroiwa, M. Yamakata and N. Ikeda, Nucl. Instrum. Methods Phys. Res. A. 467–468 (2001) p.1045–1048.
[11] K. Kato, R. Hirose, M. Takemoto, S. Ha, J. Kim, M. Higuchi, R. Matsuda, S. Kitagawa and M. Takata, AIP Conf. Proc. 1234 (2010) p.875–878.
[12] M. Tanaka, Y. Katsuya and A. Yamamoto, Rev. Sci. Instrum. 79 (2008) p.075106.
[13] K. Osaka, T. Matsumoto, K. Miura, M. Sato, I. Hirosawa and Y. Watanabe, AIP Conf. Proc. 1234 (2010) p.9–12.
[14] K.S. Wallwork, B.J. Kennedy and D. Wang, AIP Conf. Proc. 879 (2007) p.879–882.
[15] T. Straasø, J. Becker, B.B. Iversen and J. Als-Nielsen, J. Synchrotron. Rad. 20 (2013) p.98–104.
[16] Y. Amemiya, J. Synchrotron Rad. 2 (1995) p.13–21.
[17] Y. Kuroiwa, S. Aoyagi, A. Sawada, J. Harada, E. Nishibori, M. Takata and M. Sakata, Phys. Rev. Lett. 87 (2001) p.217601.
[18] E. Nishibori, M. Takata, M. Sakata, H. Tanaka, T. Muranaka and J. Akimitsu, J. Phys. Soc. Jpn. 70 (2001) p.2252–2254.
[19] E. Nishibori, E. Sunaoshi, A. Yoshida, S. Aoyagi, K. Kato, M. Takata and M. Sakata, Acta Cryst. A63 (2007) p.43–52.
[20] H. Tanaka, M. Takata, E. Nishibori, K. Kato, T. Iishi and M. Sakata, J. Appl. Cryst. 35 (2002) p.282–286.
[21] T. Saka and N. Kato, Acta Cryst. A42 (1986) p.469–478.
[22] A. Fukumoto, Phys. Rev. B. 42 (1990) p.7462–7469.
[23] Z.W. Lu, A. Zunger and M. Deutsch, Phys. Rev. B. 47 (1993) p.9385–9410.
[24] T. Noritake, M. Aoki, S. Towata, Y. Seno, Y. Hirose, E. Nishibori, M. Takata and M. Sakata, Appl. Phys. Lett. 81 (2002) p.2008–2010.
[25] Y. Shimakawa, H. Imai, H. Kimura, S. Kimura, Y. Kubo, E. Nishibori, M. Takata, M. Sakata, K. Kato and Z. Hiroi, Phys. Rev. B. 66 (2002) p.144110.
[26] K. Kato, Y. Moritomo, M. Takata, M. Sakata, M. Umekawa, N. Hamada, S. Ohkoshi, H. Tokoro and K. Hashimoto, Phys. Rev. Lett. 91 (2003) p.255502.
[27] S. Aoyagi, K. Kato, A. Ota, H. Yamochi, G. Saito, H. Suematsu, M. Sakata and M. Takata, Angew. Chem. Int. Ed. 43 (2004) p.3670–3673.
[28] A. Ohno, S. Sasaki, E. Nishibori, S. Aoyagi, M. Sakata and B.B. Iversen, Phys. Rev. B. 76 (2007) p.064119.
[29] S.J. Kim, C. Moriyoshi, S. Kimura, Y. Kuroiwa, K. Kato, M. Takata, Y. Noguchi and M. Miyayama, Appl. Phys. Lett. 91 (2007) p.062913.
[30] J.E. Kim, K. Kato, M. Takata, T. Shibata and Y. Moritomo, Phys. Rev. B. 79 (2009) p.132105.
[31] S. Kastbjerg, N. Bindzus, M. Sondergaard, S. Johnsen, N. Lock, M. Christensen, M. Takata, M.A. Spackman and B.B. Iversen, Adv. Funct. Mater. 23 (2013) p.5477–5483.
[32] E. Nishibori, H. Hyodo, K. Kimura and M. Takata, Solid State Sci. 17 (2015) p.27–31.
[33] M. Takata, E. Nishibori, K. Kato, M. Sakata and Y. Moritomo, J. Phys. Soc. Jpn. 68 (1999) p.2190–2193.
[34] K. Kato, M. Takata, E. Nishibori, M. Sakata, N. Hamada and Y. Moritomo, J. Phys. Soc. Jpn. 74 (2005) p.2137–2140.
[35] K. Kato, Y. Moritomo, M. Takata, H. Tanaka and N. Hamada, Phys. Rev. B. 77 (2008) p.081101(R).
[36] K. Kato, Y. Ohishi, M. Takata, E. Nishibori, M. Sakata and Y. Moritomo, Phys. Rev. B. 71 (2005) p.012404.
[37] K. Kato, M. Takata, Y. Moritomo, A. Nakamoto and N. Kojima, Appl. Phys. Lett. 90 (2007) p.201902.
[38] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa, K. Kato, M. Sakata and T.C. Kobayashi, Angew. Chem. Int. Ed. 44 (2005) p.920–923.
[39] Y. Kubota, M. Takata, R. Matsuda, R. Kitaura, S. Kitagawa and T.C. Kobayashi, Angew. Chem. Int. Ed. 45 (2006) p.4932–4936.
[40] M. Sakata, T. Itsubo, E. Nishibori, Y. Moritomo, N. Kojima, Y. Ohishi and M. Takata, J. Phys. Chem. Solids 65 (2004) p.1973–1976.
[41] S. Aoyagi, S. Toda, E. Nishibori, Y. Kuroiwa, Y. Ohishi, M. Takata and M. Sakata, Phys. Rev. B. 78 (2008) p.224102.
[42] Y. Moritomo, K. Kato, A. Kuriki, A. Nakamoto, N. Kojima, M. Takata and M. Sakata, J. Phys. Soc. Jpn. 71 (2002) p.2609–2612.
[43] J. Kim, K. Kato, Y. Moritomo and M. Takata, AIP Conf. Proc. 1234 (2010) p.256–259.
[44] M. Marchivie, P. Guionneau, J.A.K. Howard, G. Chastanet, J.-F. Létard, A.E. Goeta and D. Chasseau, J. Am. Chem. Soc. 124 (2002) p.194–195.
[45] N. Bindzus and B.B. Iversen, Acta Cryst. A68 (2012) p.750–762.
[46] H. Svendsen, J. Overgaard, R. Busselez, B. Arnaud, P. Rabiller, A. Kurita, E. Nishibori, M. Sakata, M. Takata and B.B. Iversen, Acta Cryst. A66 (2010) p.458–469.
[47] E.F. Bertaut, J. Phys. Chem. Solids 39 (1978) p.97–102.
[48] R.F. Stewart, Chem. Phys. Lett. 65 (1979) p.335–342.
[49] Z. Su and P. Coppens, Acta Cryst. A48 (1992) p.188–197.
[50] M.A. Spackman, Chem. Rev. 92 (1992) p.1769–1797.
[51] H. Tanaka, Y. Kuroiwa and M. Takata, Phys. Rev. B. 74 (2006) p.172105.
[52] P.P. Ewald, Ann. Phys. Leipzig. 369 (1921) p.253–287.
[53] R.E. Cohen, Nature 358 (1992) p.136–138.
[54] S. Ohkoshi, H. Tokoro, M. Utsunomiya, M. Mizuno, M. Abe and K. Hashimoto, J. Phys. Chem. B. 106 (2002) p.2423–2425.
[55] K. Kato, Y. Moritomo, H. Tanaka, H. Tokoro, S. Ohkoshi and M. Takata, J. Phys. Soc. Jpn. 76 (2007) p.123602.
[56] J. Kim, H. Tanaka, K. Kato, M. Takata and Y. Moritomo, Appl. Phys. Express 4 (2011) p.025801.
[57] M. Christensen, A.B. Abrahamsen, N.B. Christensen, F. Juranyi, N.H. Andersen, K. Lefmann, J. Andreasson, C.R.H. Bahl and B.B. Iversen, Nat. Mater. 7 (2008) p.811–815.
[58] A. Fujiwara, K. Sugimoto, C.-H. Shih, H. Tanaka, J. Tang, Y. Tanabe, J. Xu, S. Heguri, K. Tanigaki and M. Takata, Phys. Rev. B. 85 (2012) p.144305.
[59] J. Kim, A. Fujiwara, T. Sawada, Y. Kim, K. Sugimoto, K. Kato, H. Tanaka, M. Ishikado, S. Shamoto and M. Takata, IUCrJ 1 (2014) p.155–159.
[60] Y. Kim, J. Kim, A. Fujiwara, H. Taniguchi, S. Kim, H. Tanaka, K. Sugimoto, K. Kato, M. Itoh, H. Hosono and M. Takata, IUCrJ 1 (2014) p.160–164.
[61] T. Kosone, A. Hori, E. Nishibori, Y. Kubota, A. Mishima, M. Ohba, H. Tanaka, K. Kato, J. Kim, J.A. Real, S. Kitagawa and M. Takata, R. Soc. Open Sci. 2 (2015) p.150006.
[62] S.J.L. Billinge, Physics 3 (2010) p.25.
[63] S.J.L. Billinge and M.G. Kanatzidis, Chem. Commun. (2004) p.749–760.
[64] P.J. Chupas, X. Qiu, J.C. Hanson, P.L. Lee, C.P. Grey and S.J.L. Billinge, J. Appl. Cryst. 36 (2003) p.1342–1347.
[65] A.-C. Dippel, N. Bindzus, D. Saha, J.T. Delitz, H.-P. Liermann, N. Wahlberg, J. Becker, E.D. Bojesen and B.B. Iversen, Z. Anorg. Allg. Chem. 640 (2014) p.3094–3099.
[66] A.-C. Dippel, H.-P. Liermann, J.T. Delitz, P. Walter, H. Schulte-Schrepping, O.H. Seeck and H. Franz, J. Synchrotron. Rad. 22 (2015), pp. 675–687.
[67] A. Bergamaschi, A. Cervellino, R. Dinapoli, F. Gozzo, B. Henrich, I. Johnson, P. Kraft, A. Mozzanica, B. Schmitt and X. Shi, J. Synchrotron. Rad. 17 (2010) p.653–668.
[68] S.P. Thompson, J.E. Parker, J. Marchal, J. Potter, A. Birt, F. Yuan, R.D. Fearn, A.R. Lennie, S.R. Street and C.C. Tang, J. Synchrotron. Rad. 18 (2011) p.637–648.
[69] R.G. Haverkamp and K.S. Wallwork, J. Synchrotron. Rad. 16 (2009) p.849–856.
[70] K. Kato et al., in preparation.