Method for restoration of X-ray absorption fine structure in sparse spectroscopic ptychography

Nozomu Ishiguro\textsuperscript{a,b,c,*} and Yukio Takahashi\textsuperscript{a,b,c,d}

\textsuperscript{a}International Center for Synchrotron Radiation Innovation Smart (SRIS), Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan, \textsuperscript{b}Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan, \textsuperscript{c}RIKEN SPring-8 Center, Koto 1-1-1, Sayo, Hyogo 678-5148, Japan, and \textsuperscript{d}Institute for Materials Research, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan.

*Correspondence e-mail: nozomu.ishiguro.c1@tohoku.ac.jp

The spectroscopic ptychography method, a technique combining X-ray ptychography imaging and X-ray absorption spectroscopy, is one of the most promising and powerful tools for studying the chemical states and morphological structures of bulk materials at high resolutions. However, this technique still requires long measurement periods because of insufficient coherent X-ray intensity. Although the improvements in hardware represent a critical solution, breakthroughs in software for experiments and analyses are also required. This paper proposes a novel method for restoring the spectrum structures from spectroscopic ptychography measurements with reduced energy points, by utilizing the Kramers–Kronig relationship. First, a numerical simulation is performed of the spectrum restoration for the extended X-ray absorption fine structure (EXAFS) oscillation from the thinned theoretical absorption and phase spectra. Then, this algorithm is extended by binning the noise removal to handle actual experimental spectral data. Spectrum restoration for the experimental EXAFS data obtained from spectroscopic ptychography measurements is also successfully demonstrated. The proposed restoration will help shorten the time required for spectroscopic ptychography single measurements and increase the throughput of the entire experiment under limited time resources.

1. Introduction

X-ray spectromicroscopy is a powerful tool for studying the chemical states and morphological structures of bulk materials at high resolutions (de Groot \textit{et al.}, 2010; Kaulich \textit{et al.}, 2011; Hitchcock, 2015; Spence \textit{et al.}, 2021). The contrasts of absorption, phase shift, fluorescence, photoelectrons and so on are recorded at each incident X-ray photon energy, and the energy stack of the obtained images provides spatially resolved X-ray spectra. The spectra around the absorption photon energy of the target elements (especially in the hard X-ray region) are known as the X-ray absorption fine structure (XAFS). The XAFS spectrum is divided into two sections: the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The XANES region is located around ~50 eV from the absorption edge and reflects the local electron structure around the absorbed atom (\textit{e.g.} valence or electron orbital symmetry). The EXAFS region, located at a higher-energy region than the XANES region, exhibits oscillation structures resulting from the scattering of photoelectrons with surrounding atoms from the absorption center. By analyzing this EXAFS oscillation
structure, we can acquire information regarding the local coordination structures (e.g. coordination numbers and interatomic distances).

Among the various X-ray imaging techniques, X-ray ptychography using coherent X-ray diffraction represents one of the most promising techniques for achieving higher spatial resolutions. X-ray ptychography is a scanning version of coherent X-ray diffraction imaging (Rodenburg et al., 2007; Thibault et al., 2008). The sample is scanned in-plane with a step size smaller than the incident beam size, and a coherent X-ray diffraction pattern is recorded at each sample position. The images of both the sample and the probe (illuminating X-rays) can be reconstructed from the recorded multiple-frame diffraction patterns. The retrieved sample image is obtained as a complex transmission function, whose amplitude and argument reflect the absorption and phase shift of the sample, respectively. In recent years, the developments and applications of a combination of X-ray ptychography with spectroscopy (known as spectroscopic ptychography imaging) have been enthusiastically reported (Shapiro et al., 2014, 2020; Hirose et al., 2018; Wu et al., 2018; Uematsu et al., 2021).

Although the power of spectroscopic ptychography measurements has been well demonstrated, it remains a challenging experiment, primarily because of the enormous measurement time required to produce multiple diffraction patterns for the in-plane sample scanning of the sample and the energy scan of the monochromated incident X-rays. In our previous studies at SPRing-8 (Hyogo, Japan), it took 6–8 h to obtain a data set of spectroscopic ptychography measurements for the XANES region (Hirose et al., 2018; Uematsu et al., 2021), and it took 3 days to obtain one for the EXAFS region (Hirose et al., 2020). One reason for this low throughput is the insufficient intensity of the coherent X-rays produced by the synchrotron radiation facilities. New-generation synchrotron radiation facilities with smaller beam emittances can provide brighter coherent X-rays, which will reduce the measurement time for spectroscopic ptychography experiments (Shimosaki et al., 2013; Henderson, 2015; Raimondi, 2016; Tanaka et al., 2016; Schroer et al., 2018). In addition to the hardware improvements, breakthroughs in software for both experiments and analyses are also required.

Compressed sensing is a technique for recovering a signal from a reducing quantity of measurement data (i.e. significantly below the Nyquist rate) (Candes et al., 2006; Donoho, 2006). The key to successful compressed sensing is to determine the sparsity of information and then reduce the number of measurements in that sparse information direction. A well known approach is to apply total variation regularization in the image reconstruction, to reduce the number of measurements (Sidky & Pan, 2008). This approach is well adapted for the reconstruction of three-dimensional X-ray computed tomography (CT) imaging; it assumes that the real-space image of the sample is smooth and has sparsity in its boundaries. The use of a redundant dictionary of the morphological structures, either predetermined before reconstruction or adaptively defined during the reconstruction processes, has also been reported for low-dose X-ray CT and coherent diffraction imaging (Xu et al., 2012; Cherukara et al., 2020). Another approach is to use sparse substances/phases when configuring the entire sample. Shiga et al. (2016) reported sparse modeling of electron energy loss spectroscopy and energy-dispersive X-ray spectroscopy imaging data using non-negative matrix factorization methods. Gao et al. (2021) have successfully visualized three-dimensional chemical state images of vanadium phosphorus oxide catalyst pellets from sparse ptychographic X-ray transmission spectro-tomography measurements with 1/10 smaller projection angles than those satisfying the Crowther sampling criteria at each energy. In their study, principal components analysis was used in the reconstruction process, to restrict the number of chemical (spectral) modes in the three-dimensional image. Chang et al. (2020) have demonstrated the reconstruction of sparse spectroscopic ptychography data using a dictionary of known or partially known reference spectral data. These approaches are all powerful methods to recover the sample information in specific sample conditions; however they are not completely universal with regards to the morphological or chemical properties of the sample.

In this study, we propose a novel technique for restoring the spectrum structure from reduced measurement energy points in spectroscopic ptychography, by utilizing the Kramers–Kronig relationship (KKR) between the absorption and phase contrasts. The KKR is a universal relationship between the response functions in physical systems (e.g. resonance phenomena); it is based on the law of causality. In X-ray optics, the KKR holds between the real and imaginary parts of the anomalous scattering terms in the atomic scattering factors $f'$ and $f''$. Typical X-ray spectroscopies and microscopies (e.g. XAFS, diffraction anomalous fine structure, X-ray reflection spectroscopy, X-ray absorption and phase contrast imaging) measure either of $f'$ or $f''$, and the obtained parameters are often transformed using the KKR (Pickering et al., 1993; Jacobsen et al., 2004; Watts, 2014; Abe et al., 2016). On the other hand, spectroscopic ptychography has some unique characteristics: the reconstructed sample object function includes both $f_0 + f'$ and $f''$ ($f_0$ is a constant term of the atomic structure factor), and both spectra can be directly and simultaneously obtained. In principle, the phase-retrieval calculation reconstruction proceeds independently from the KKR, and reconstruction improvement has been reported using the KKR as a constraint (Hirose et al., 2017). Here, two types of simultaneously obtained spectral information (i.e. $f'$ and $f''$, or absorption and phase) in the KKR are treated as the real and imaginary parts of the response frequency function $\chi(\omega)$. The response to the physical impulse excitation by X-ray photons represents a real function and is identified only after the impulse occurs. Thus, the response function $\tilde{\chi}(t)$, which is the inverse Fourier transform of $\chi(\omega)$, is $0$ at $t < 0$ and exhibits the real signals only at $t \geq 0$. This indicates that the absorption and phase spectra feature some sparsity in their spectral structures. Herein, we consider the restoration of spectral (spectro-microscopic) data based on the spectral sparsity behind causality. First, we performed a numerical simulation of the EXAFS oscillation spectrum restoration from the thinned...
2. Principle of spectrum restoration using the KKR

2.1. Data handling of the KKR for spectroscopic ptychography data

The KKR between the real and imaginary parts of the anomalous terms in the atomic scattering factors $f'$ and $f''$ is shown as

$$
\begin{align*}
\left\{ \begin{array}{l}
\phi(x, y, E) = -\arg[T(x, y, E)], \\
\mu(x, y, E) = -2 \ln |T(x, y, E)|,
\end{array} \right.
\end{align*}
$$

where $x$ and $y$ are the two-dimensional coordinates of the sample image in the plane, and $E$ is the photon energy of the incident X-rays. The phase $\phi(x, y, E)$ and absorption $\mu(x, y, E)$ are expressed via $f'$ and $f''$ as

$$
\begin{align*}
\phi(x, y, E) &= \frac{\hbar c r_e}{E} \int_0^\infty \frac{\rho_i(x, y, z) Z_i(x, y, z)}{\omega^2 - \omega^2} \, d\omega' := K_{\phi}[f''(\omega)], \\
\mu(x, y, E) &= \frac{2 \hbar c r_e}{E} \int_0^\infty \frac{\rho_i(x, y, z) f''_i(x, y, z, E)}{\omega^2 - \omega^2} \, d\omega' := K_{\mu}[f'(\omega)],
\end{align*}
$$

where $h$ is the Planck constant, $c$ is the light speed in a vacuum, $r_e$ is the Thomson scattering constant (classical electron radius), $\rho_i(x, y, z)$ is the density of the $i$th element atoms and $Z_i$ is that element’s atomic number (Davis, 1994; Warren, 1990). Thus, the KKR [equation (1)] between $\phi(E)$ and $\mu(E)$ is expressed as

$$
\begin{align*}
\phi^{\text{out}}(E) &= \frac{1}{E} K_{\phi}[E \phi^{\text{in}}(E), a], \\
\mu^{\text{out}}(E) &= \frac{2}{E} K_{\mu}[E \phi^{\text{in}}(E), b, c].
\end{align*}
$$

Here, the KKR in equation (4) required an additional three parameters $a$, $b$, and $c$, owing to the constant terms of the atomic structure factor $f_0, i(= Z_i)$, as shown in the first term in the upper equation in (3). Also, they are used to describe the behavior of the optical constants at energies beyond the data range at both ends [details of the KKR calculation of the finite number of $\phi(E)$ and $\mu(E)$ array data in this paper are provided in Appendix A]. Parameters $a$, $b$, and $c$ are chosen using the least-squares method as

$$
a = \arg \min_{a \in \mathbb{R}} \left\| \phi^{\text{in}}(E) - \frac{1}{E} K_{\phi}[E \phi^{\text{in}}(E), a] \right\|^2, \\
\left\{ \begin{array}{l}
(b, c) = \arg \min_{b, c \in \mathbb{R}} \left\| \mu^{\text{in}}(E) - \frac{2}{E} K_{\mu}[E \phi^{\text{in}}(E), b, c] \right\|^2.
\end{array} \right.
$$

2.2. Proposed iterative algorithm of spectral restoration

The KKR is mathematically the same as the Hilbert transform. The mathematical definitions of the Hilbert transform for the response frequency functions $f(\omega), f_{\text{id}}(\omega)$, are described as

$$
\begin{align*}
\mathcal{F}[f(\omega)] &= \tilde{f}(t), \\
\mathcal{F}[f_{\text{id}}(\omega)] &= i \text{sgn}(t) \tilde{f}(t),
\end{align*}
$$

where $\mathcal{F}$ is the Fourier transform operator. Equation (1) holds when $\text{sgn}(t) \tilde{f}(t)$ is the causality function, where $\tilde{f}(t) = 0$ when $t < 0$. Equation (7) shows that the Hilbert transform shifts the $f(\omega)$ phase by $\pm \pi/2$. This fact indicates that $f'(\omega)$ and $f''(\omega)$ at a certain frequency $\omega$ (or energy $E$) contain information on the others at the frequencies around $\omega$. It is known from the sampling theorem that the perfect reconstruction of an original signal with a frequency of less than $\omega_{\text{sam}}/2$ (Nyquist frequency) is ensured by measurement with the sampling rate $\omega_{\text{sam}}$ (Shannon, 1949). However, if both $f'(\omega)$ and $f''(\omega)$ are recorded at the same time as the sampling rate $\omega_{\text{sam}}$, it is expected that reconstruction of the signal above the Nyquist frequency will be possible (Tseng & Lee, 2017). This point can be easily understood with the following example: suppose we have $f'(\omega)$ wiggled signal data, which happen to pass through zero at each sampling point. $f'(\omega)$ sampling points alone do not give us any information about this wiggle structure. However, since there is a $\pm \pi/2$ phase shift between $f'(\omega)$ and $f''(\omega)$, the wiggle structure is found in $f''(\omega)$ at the sampled point.

Next, we consider the KKR-based spectral restoration of $\phi(E)$ and $\mu(E)$ with reduced energy points. Although $\phi(E)$ and $\mu(E)$ in the KKR require a continuous data set from $E = 0$ to $E \rightarrow \infty$ theoretically, we can only obtain a data set with a finite number of energy points. The fewer the energy points in the data set of $\phi(E)$ and $\mu(E)$ we have, the less accurate the KKR is. At the very least, we require a sufficient number of energy points. Here, we consider the iterative spectral restoration process starting from the input observed data set of $\phi^{\text{obs}}(E)$ and $\mu^{\text{obs}}(E)$ at the sparse (thinned) energy points of $E = E^{\text{thinned}}_m (m = 0, \ldots, N)$, to the output data set $\phi^{\text{restored}}(E)$ and $\mu^{\text{restored}}(E)$, to increase the increasing energy points of $E = E^{\text{interpol}}_m (m = 0, \ldots, M; M > N)$ (where the superscript interp denotes interpolated). We define function $\epsilon(\phi(E), \mu(E))$ to express the extent to which $\mu(E)$ and $\phi(E)$ satisfy the KKR, as follows:
If the ideal phase and absorption spectra \([\phi^{(\text{ideal})}(E), \mu^{(\text{ideal})}(E)]\) completely satisfy the KKR, the equation
\[
\epsilon[\phi^{(\text{ideal})}(E), \mu^{(\text{ideal})}(E)] = 0
\]
is valid.

We have first considered the restoration of the sparse phase and absorption spectra as the result of the following problem, including a constraint from the input data set of \([\phi^{(\text{obs})}(E_{m}^{\text{thinned}}), \mu^{(\text{obs})}(E_{m}^{\text{thinned}}})\]:
\[
[\phi^{(\text{restored})}(E_{m}^{\text{interp}}), \mu^{(\text{restored})}(E_{m}^{\text{interp}})] = \arg \min_{\phi, \mu} \sum_{m=0}^{M} \left\| \epsilon[\phi(E_{m}^{\text{thinned}}), \mu(E_{m}^{\text{thinned}})] \right\|^2 + \lambda \sum_{m=0}^{M} \left( \phi(E_{m}^{\text{thinned}}) - \phi^{(\text{obs})}(E_{m}^{\text{thinned}}) \right) \left( \mu(E_{m}^{\text{thinned}}) - \mu^{(\text{obs})}(E_{m}^{\text{thinned}}) \right)
\]
Here, \(\lambda\) denotes the Lagrange multiplier and \(l\) represents the norm-dimension for the Lagrangian function term, selected as \(l = 2\) in this paper. However, this approach to solving equation (10) did not work well. The strong constraint was only presented at the observed (thinned) energy points \(E = E_{m}^{\text{thinned}}\) and caused undesired oscillations at other restored energy points. Some gentle constraints should also be applied to the energy points \(E = E_{m}^{\text{interp}}\) in the restored spectra. Thus, we propose a spectral restoration using an alternative constraint from the input data set, as shown in Fig. 1.

First, \(\phi^{(\text{obs})}(E_{m}^{\text{thinned}})\) and \(\mu^{(\text{obs})}(E_{m}^{\text{thinned}})\) were converted to \(\phi^{(\text{const})}(E_{m}^{\text{interp}})\) and \(\mu^{(\text{const})}(E_{m}^{\text{interp}})\), respectively, via linear interpolation \([1-1]\) in Fig. 1. In the \(j\)th iteration trial, \(\phi^{(\text{KK})}(E_{m}^{\text{interp}})\) and \(\mu^{(\text{KK})}(E_{m}^{\text{interp}})\) were calculated from \(\phi^{(\text{const})}(E_{m}^{\text{interp}})\) and \(\mu^{(\text{const})}(E_{m}^{\text{interp}})\) using the KKR \([1-2]\) in Fig. 1, as follows:

\[
\phi^{(\text{KK})}(E_{m}^{\text{interp}}) = \frac{1}{E} K_{1} \left[ E \frac{\mu^{(\text{const})}(E_{m}^{\text{interp}}), a}{2} \right]
\]
\[
\mu_{j}^{(\text{KK})}(E_{m}^{\text{interp}}) = \frac{2}{E} K_{2} \left[ \phi^{(\text{const})}(E_{m}^{\text{interp}}), b, c \right].
\]

Then, \(\phi^{(\text{KK})}(E_{m}^{\text{interp}})\) and \(\mu_{j}^{(\text{KK})}(E_{m}^{\text{interp}})\) were clamped linearly, such that \(\phi(E)\) and \(\mu(E)\) passed through the reference \(\phi^{(\text{obs})}(E)\) and \(\mu^{(\text{obs})}(E)\), respectively, at \(E = E_{n}^{\text{thinned}}\) \(n = 0, \ldots, N\) \([1-3]\) in Fig. 1. The clamped data were expressed as \(\phi_{j+1}^{(\text{const})}(E_{m}^{\text{interp}})\) and \(\mu_{j+1}^{(\text{const})}(E_{m}^{\text{interp}})\), respectively, as follows:
\[
\phi_{j+1}^{(\text{const})}(E_{m}^{\text{interp}}) = \phi_{j}^{(\text{KK})}(E_{m}^{\text{interp}}) + \phi^{(\text{obs})}(E_{m}^{\text{thinned}}) - \phi^{(\text{obs})}(E_{m}^{\text{thinned}})
\]
\[
\mu_{j+1}^{(\text{const})}(E_{m}^{\text{interp}}) = \mu_{j}^{(\text{KK})}(E_{m}^{\text{interp}}) + \mu^{(\text{obs})}(E_{m}^{\text{thinned}}) - \mu^{(\text{obs})}(E_{m}^{\text{thinned}})
\]

Here, \(\phi_{j+1}^{(\text{const})}(E_{m}^{\text{interp}})\) and \(\mu_{j+1}^{(\text{const})}(E_{m}^{\text{interp}})\) were used as the input for the next iteration trial. The final answers after the \(J\)th trial were output as \(\phi^{(\text{restored})}(E)\) and \(\mu^{(\text{restored})}(E)\), respectively.

3. Restoration of thinned absorption and phase spectra of a calculation model

3.1. Calculation model

The model X-ray absorption \(\mu(E)\) (XAFS) and phase \(\phi(E)\) spectral data (for demonstrating the restoration) were calculated from the crystal structure of MnO (ICSD-9864; Sasaki et al., 1980) using the FEFF9.6 code (Rehr et al., 2010). The X-ray absorption and phase spectra at the Mn K edge were calculated from 6344 to 8068 eV. This energy range includes the EXAFS oscillation at \(k = 200\) nm\(^{-1}\) in \(k\) space, and the energy point intervals of the original model \(\mu(E)\) and \(\phi(E)\) were set to \(\Delta k = 0.5\) nm\(^{-1}\), which is applicable in many EXAFS analyses (Ravel & Newville, 2005). Then, the original model \(\mu(E)\) and \(\phi(E)\) were thinned into \(\Delta k = 1, 2, 4, 8\) and 16 nm\(^{-1}\) intervals.

3.2. EXAFS analysis

EXAFS results were extracted and analyzed using ordinary methods in the XAFS analysis software (Ravel & Newville, 2005). The edge energy \(E_{0}\) of the manganese sample was set to \(E_{0} = 6543.6\) eV. Background substitution and edge normalization were performed via curve fitting in the pre-edge and post-edge region. Then, the EXAFS oscillation \(\chi(k)\) was extracted using the background spectrum calculated via spline smoothing. The \(k^{3}\)-weighted EXAFS oscillation \(k^{3}\chi(k)\) was Fourier-transformed into \(R\) space \([\tilde{G}(R) = \mathcal{F}[k^{3}\chi(k)]]\), where curve fitting was performed. The fitting parameters for each Mn–X (X = O, Mn) bond shell were coordination number.
(CN), interatomic distance \((R_{\text{Mn-X}})\), correction-of-edge energy \((\Delta E_0)\) and Debye–Waller factor \((\sigma^2)\). The phase shifts and backscattering amplitude for each shell were calculated with the FEFF9.6 code for a model MnO crystal structure. The quality of curve-fitting analysis is evaluated using the \(R\) factor, which is defined as follows:

\[
R_{\text{fit}}^2 = \frac{\sum_{\text{fit}} \| \tilde{X}(\text{fit})(R) - \tilde{X}(\text{data})(R) \|^2}{\sum_{\text{fit}} \| \tilde{X}(\text{data})(R) \|^2}.
\]

Similarly, the quality of spectral restoration in the fitting range in \(R\) space is evaluated using the \(R\) factor against reference (original) data, which is defined as follows:

\[
R_{\text{ref}}^2 = \frac{\sum_{\text{ref}} \| \tilde{X}(\text{ref})(R) - \tilde{X}(\text{data})(R) \|^2}{\sum_{\text{ref}} \| \tilde{X}(\text{data})(R) \|^2}.
\]

3.3. Numerical simulation

The thinned X-ray absorption and phase spectra data generated from the MnO crystal structure model were subsequently restored to the original sampling rate \((\Delta k = 0.5 \text{ nm}^{-1})\) by the proposed algorithm in Fig. 1. The number of iterations in each trial was set to 100. Fig. 2 shows the original, thinned and restored X-ray absorption and phase spectra. Fig. 3 shows the error profiles of the iterative restoration, for the restored and original X-ray absorption and phase spectra [Fig. 3(A)], and for before and after the KK transform [Fig. 3(B)]. The errors in the KK transforms of the original X-ray absorption and phase spectra [(a) in Figs. 3(A) and 3(B)] were \(1.5 \times 10^{-4}\) and \(9.5 \times 10^{-5}\), respectively, attributable to the insufficiency of the finite number of data points. On the other hand, the thinned spectra in the XANES energy region were well restored within the interval until \(\Delta k = 4 \text{ nm}^{-1}\) [(b)–(d) in Figs. 2(A)–2(D)], and their errors with respect to the originals were restricted to below \(1.5 \times 10^{-3}\) (absorption) and \(3.3 \times 10^{-4}\) (phase) [(b)–(d) in Fig. 3(A)].
However, their fine structures were blurred [(e) and (f) in Figs. 2(A)–2(D)] and the errors against the originals were increased to $8.2 \times 10^{-3}$ (absorption) and $5.0 \times 10^{-3}$ (phase) when the interval exceeds $\Delta k = 8$ nm$^{-1}$ [(e) and (f) in Fig. 3(A)].

The power of the iterative restoration is more clearly demonstrated in the EXAFS region. The EXAFS oscillations thinned above $\Delta k = 4$ nm$^{-1}$ intervals exhibited apparently deteriorated structures [(d)–(f) in Figs. 2(E) and 2(F)]. However, EXAFS results thinned to $\Delta k = 4$ and 8 nm$^{-1}$ intervals were successfully restored; here, the radial distributions of Mn–O and Mn–Mn were recovered to the original level [(d) and (e) in Figs. 2(E) and 2(F)]. Therefore, the limitation of the iterative restoration is considered to be found between thinnings of $\Delta k = 8$ and 16 nm$^{-1}$ intervals [(e) and (f) in Figs. 2(E) and 2(F)].

Next, curve-fitting analysis was performed upon the original, thinned and restored EXAFS oscillations, to consider the quantitative limits of the iteration restoration (Table 1).

The model MnO features a rock-salt-type structure, including Mn–O with CN$_{\text{Mn–O}} = 6$ and interatomic distance $R_{\text{Mn–O}} = 0.2225$ nm, and Mn–Mn with CN$_{\text{Mn–Mn}} = 12$ and interatomic distance $R_{\text{Mn–Mn}} = 0.3115$ nm as the first and second coordination spheres, respectively. The results of the curve-fitting analysis are consistent with the values for the model MnO crystal structure, at least as long as the data points are thinned to $\Delta k = 2$ nm$^{-1}$ intervals [(a), (b-i) and (c-i) of Table 1].

Table 1

<table>
<thead>
<tr>
<th>Shell</th>
<th>CN$_{\text{Mn–X}}$</th>
<th>$R_{\text{Mn–X}}$ (nm)</th>
<th>$\Delta E_f$ (eV)</th>
<th>$\sigma^2$ (10$^{-6}$ nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>Original ($\Delta k = 0.5$ nm$^{-1}$), $R_{\text{Mn–X}}^{\text{ref}} = 0.14%$</td>
<td>Mn–O 5.9 ± 0.1 0.223 ± 0.001 1.5 ± 0.1 12.1 ± 0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mn–Mn 13.3 ± 0.1 0.314 ± 0.001 −0.5 ± 0.1 12.1 ± 0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

However, their fine structures were blurred [(e) and (f) in Figs. 2(A)–2(D)] and the errors against the originals were increased to $8.2 \times 10^{-3}$ (absorption) and $5.0 \times 10^{-3}$ (phase) when the interval exceeds $\Delta k = 8$ nm$^{-1}$ [(e) and (f) in Fig. 3(A)].

The power of the iterative restoration is more clearly demonstrated in the EXAFS region. The EXAFS oscillations thinned above $\Delta k = 4$ nm$^{-1}$ intervals exhibited apparently deteriorated structures [(d)–(f) in Figs. 2(E) and 2(F)]. However, EXAFS results thinned to $\Delta k = 4$ and 8 nm$^{-1}$ intervals were successfully restored; here, the radial distributions of Mn–O and Mn–Mn were recovered to the original level [(d) and (e) in Figs. 2(E) and 2(F)]. Therefore, the limitation of the iterative restoration is considered to be found between thinnings of $\Delta k = 8$ and 16 nm$^{-1}$ intervals [(e) and (f) in Figs. 2(E) and 2(F)].

Next, curve-fitting analysis was performed upon the original, thinned and restored EXAFS oscillations, to consider the quantitative limits of the iteration restoration (Table 1).

The model MnO features a rock-salt-type structure, including Mn–O with CN$_{\text{Mn–O}} = 6$ and interatomic distance $R_{\text{Mn–O}} = 0.2225$ nm, and Mn–Mn with CN$_{\text{Mn–Mn}} = 12$ and interatomic distance $R_{\text{Mn–Mn}} = 0.3115$ nm as the first and second coordination spheres, respectively. The results of the curve-fitting analysis are consistent with the values for the model MnO crystal structure, at least as long as the data points are thinned to $\Delta k = 2$ nm$^{-1}$ intervals [(a), (b-i) and (c-i) of Table 1]. The CNs of Mn–O and Mn–Mn bonds for the EXAFS data thinned to $\Delta k = 4$ nm$^{-1}$ intervals were underestimated compared with the model structure [(d-i) of Table 1]. Curve fitting of the EXAFS data thinned to the $\Delta k = 8$ nm$^{-1}$ interval failed completely [(e-i) of Table 1]. However, the estimated results of CNs of the Mn–O and Mn–Mn bonds were quantitatively recovered by the restoration of the thinned EXAFS with $\Delta k = 4$ and 8 nm$^{-1}$ intervals [(d-ii) and (e-ii) of Table 1].

The spectral data quality for quantitative EXAFS analysis, whether thinned or restored, can be discussed...
roughly in terms of $R$ factors against original data $[R_f^{\text{(ref)}}]$. $R_f$ values for the successful EXAFS curve-fitting analysis are below 5%, while those for data that failed in restoration exceed 40%.

According to the sampling theorem, signals can be completely restored if their frequencies $\omega_{\text{sig}}$ are less than half the data-sampling frequency $\omega_{\text{sam}}$ ($\omega_{\text{sig}} < \omega_{\text{sam}}/2$). Thus, the EXAFS oscillation data with $\Delta k = 0.5, 1, 2, 4$ and 8 nm$^{-1}$ can potentially estimate radial distributions less than $R = \pi/2(2\Delta k) = 3.14, 1.57, 0.785, 0.393$ and 0.196 nm, respectively, according to the sampling theorem. In the case of the Mn—Mn bond with a 0.3115 nm distance was ranged around $R = 0.33$ nm in the Fourier transform ($R$ space) at $k = 30$–180 nm$^{-1}$. Thus, the EXAFS data thinned to the $\Delta k = 4$ nm$^{-1}$ interval were at the borderline at which quantitative analysis of Mn—Mn became possible, and the data thinned to $\Delta k = 8$ nm$^{-1}$ were completely out of range, as in (d) and (e) in Figs. 2(E) and 2(F) and Table 1. However, as described above, the EXAFS data thinned to $\Delta k = 4$ and 8 nm$^{-1}$ intervals were recovered via iterative restoration using the KKR, although this failed for the data thinned to $\Delta k = 16$ nm$^{-1}$. These results indicate that the proposed iterative restoration algorithm can extend the limits of the sampling theorem to twice its size ($\omega_{\text{sig}} < \omega_{\text{sam}}$).

4. Restoration of experimental thinned absorption and phase spectra
4.1. Experimental model

The experimental model of the X-ray absorption and phase spectra was obtained from the reconstructed absorption and phase image stack of spectroscopic ptychography measurements for MnO particles (Kojundo Chemical Laboratory Co. Ltd, 99.9%, size 5–10 μm), which was reused from a previous study (Hirose et al., 2020). The particles were scanned over 14 × 14 points with 250 nm separation and 4.0 s exposure. The number of energy points was 173, and the interval $\Delta k$ in the $k$ space was approximately 1 nm$^{-1}$. Absorption and phase images were reconstructed using an extended ptychographical iterative engine (ePIE) algorithm (Maiden & Rodenburg, 2009) with a probe of two mixed states (Thibault & Menzel, 2013; Burdet et al., 2016). Pixel sizes in real space were set to 12 nm at all X-ray energies, and iterations were continued up to 1000 cycles with illumination position correction (Dwivedi et al., 2018) at every 200 cycles after 500 iteration cycles. The shift of the sample position with respect to the X-ray energy was also corrected by phase-only correction. Figs. 4(A) and 4(B) show the reconstructed absorption and phase images of the MnO particles. The size of the region of interest (ROI) was set to 1200 × 1200 nm (100 × 100 pixels), and the model X-ray absorption $\mu(E)$ and phase $\phi(E)$ spectra [Figs. 4(C) and 4(D)] were extracted from the ROI in the corresponding reconstructed images. Then, the experimental model $\mu(E)$ and $\phi(E)$ were thinned into $\Delta k \simeq 2, 3, 4, 5, 6$ and 8 nm$^{-1}$ intervals to simulate sparse spectroscopic ptychography measurements. For the analysis reference, the Mn K-edge EXAFS spectrum ($\Delta k \simeq 0.5$ nm$^{-1}$) of the same MnO reagent was measured by transmission mode on the SPring-8 BL37XU beamline.

Figure 4
Experimental model X-ray absorption and phase spectra for MnO particles obtained from Mn K-edge spectroscopic ptychography. Reconstructed (A) absorption and (B) phase image of MnO particles at 6600 eV. Red squares in (A) and (B) are the ROI for extracting X-ray absorption and phase spectra. Extracted (C) XAFS and (D) phase spectra.

Figure 5
Flowchart for restoration and noise removal of experimental thinned absorption and phase spectra.

Ishiguro and Takahashi • Method for restoration of X-ray absorption fine structure
4.2. Extension of the spectrum restoration algorithm using KKR for experimental data

As Figs. 4(C) and 4(D) show, the X-ray absorption and phase spectra from the experimental data included some noise (compared with the calculation model spectra). Here, we treated the 'noises' of X-ray absorption $\mu(E)$ and phase $\phi(E)$ as components that did not satisfy the KKR. The KK transform of spectral data with non-negligible noise will amplify their errors, resulting in failure of spectral restoration. We considered extending the proposed algorithm in Fig. 1 such that the spectral restoration and noise removal were performed simultaneously. Fig. 5 shows the extended algorithm of spectral restoration for experimental data. In this process, the spectral restoration block in Fig. 1 was nested within the iteration loop for noise removal. The process began with thinned (sparse) experimental X-ray absorption $E_{thinned}$ and iteration cycles $t$. (1) Error profiles of $E_{thinned}$ were processed via spectrum restoration (shown in Fig. 1); then, $E_{thinned}^{(ideal)}$, $E_{thinned}^{(denoise)}$, and $E_{thinned}^{(kk)}$ were obtained.

When the noises of $\phi$ and $\mu$ were defined as $\delta\phi(E)$ and $\delta\mu(E)$, respectively, the relationships between the observed and ideal $\phi$ and $\mu$ values could be represented as

$$\begin{align*}
\phi^{(obs)}(E) &= \phi^{(ideal)}(E) + \delta\phi(E), \\
\mu^{(obs)}(E) &= \mu^{(ideal)}(E) + \delta\mu(E).
\end{align*}$$

Thus, the noises of $\mu^{(kk)}_{thinned}$ and $\phi^{(kk)}_{thinned}$, $\delta\mu_{thinned}$ and $\delta\phi_{thinned}$, could be estimated iteratively using the Newtonian method of substituting equation (15) into equation (8) [(2–2) in Fig. 5] (details provided in Appendix B). Then, $\phi^{(denoise)}_{thinned}$ and $\mu^{(denoise)}_{thinned}$ were updated to $\phi^{(idealt)}_{thinned}$ and $\mu^{(idealt)}_{thinned}$ using reversibly interpolated $\delta\mu_{thinned}$ and $\delta\phi_{thinned}$ and updating factors $\alpha_\phi$ and $\alpha_\mu$. [(2–3) and (2–4) in Fig. 5], as follows:

Figure 6: Evaluation of parameters $\delta E$, $\alpha_\phi$, and $\alpha_\mu$, and iteration cycles of spectrum restoration noise removal for experimental thinned (sparse) X-ray absorption and phase spectra obtained from spectroscopic ptychography measurement: (A) evaluation of energy width $\delta E$; (B) evaluation of updating factor values $\alpha_\phi$ and $\alpha_\mu$; (C) evaluation of updating factor ratio between $\alpha_\phi$ and $\alpha_\mu$. (1) Error profiles of $\phi(E)$ and $\mu(E)$ obtained via KK transform, and restored spectra of (2) absorption and (3) phase under different parameter conditions. (D) Restored spectra of (1) absorption and (2) phase with different iteration cycles at $\delta E = 0.01$, $\alpha_\phi = 0.4$ and $\alpha_\mu = 0.1$. 

4.3. Demonstration of spectrum restoration noise removal for experimental X-ray absorption and phase spectra

First, we evaluated the restoration and noise removal of the proposed algorithm, as shown in Fig. 5. Here, δE, αφ and αµt are the parameters of the process; they must be evaluated in advance. The original experimental spectra of φ(E) and μt(E), which feature a k interval (Δk) of approximately 1 nm⁻¹, were used to evaluate the restoration and noise-removal process. The experimental original data were restored such that Δk ≥ 0.5 nm⁻¹. The iteration cycle of restoration was fixed at J = 50, and the noise removal was repeated K = 500 cycles at most. Fig. 6 shows the error profiles and restored spectra of φ(E) and μt(E) under different parameter conditions. The values of parameters δE, αφ and αµt were selected so that the errors of φ(E) and μt(E) for before and after the KK transform [Figs. 6(A1), 6(C1) and 6(D1)] were smaller and converged quickly, and the spectrum structures were not broken down. The ΔE appearing in the Jacobian of the ε[φ(E), μt(E)] applied in the Newtonian method for noise estimation [(2-2) in Fig. 5] was changed to 0.5, 0.1 and 0.01, with αφ and αµt being fixed at 0.1 [Fig. 6(A)]. Although the converged error value is not entirely different, a smaller ΔE shows a smaller temporal worsening of the φ(E) and μt(E) errors. Thus, ΔE = 0.01 was chosen. Next, αφ and αµt were varied by tenths to 1, 0.1 and 0.01 [Fig. 6(B)]. Larger αφ and αµt (= 1) exhibited failed spectral restoration, whereas smaller αφ and αµt (= 0.1) exhibited slow convergence. Thus, the order of αφ and αµt was focused on the 0.1 order. Finally, the ratio of αφ and αµt was changed [Fig. 6(C)] where αφ = 0.4 and αµt = 0.1 seemed to result in a moderate degree of error convergence and spectral restoration. In addition to the values of δE, αφ and αµt, the number of iteration cycles for noise removal K affects the quality of the spectral restoration. Although the increase of iteration cycle K resulted in smaller φ(E) and μt(E) errors under the KK transform, the fine structure of the spectra was gradually lost by excess noise removal, as shown in Fig. 6(D). Because the errors of restored φ(E) and μt(E) output by the calculation model converged at 10⁻⁴ order (Fig. 3), the J = 50 iteration cycle of spectral restoration and noise removal was considered to be sufficient [Fig. 6(C)].

The spectral restoration and noise removal of experimentally thinned (sparse) X-ray absorption and phase spectra were then demonstrated with the iteration cycle of restoration and noise removal at J = 20 and K = 50 cycles, respectively. The energy width δE and update factors of μt(E) and φ(E) were fixed at δE = 0.01, αφ = 0.4 and αµt = 0.1, respectively. Fig. 7 shows the original, thinned and restored X-ray absorption and phase spectra, and Fig. 8 presents the error profiles of the iterative restoration for before and after the KK transform. Table 2 shows the results of the curve-fitting analysis for the original, thinned and restored EXAFS oscillations, to quantitatively evaluate the limits of the spectral restoration and noise removal. The restoration of the X-ray absorption spectra, especially in the XANES region, seemed to perform well with data thinned to Δk ≅ 6 nm⁻¹ [(a)-(f) in Figs. 7(A) and 7(C)]; meanwhile the restored absorption spectra from Δk ≅ 8 nm⁻¹ interval data lost some of their fine structure [(g) in Figs. 7(A) and 7(C)]. On the other hand, the restoration

$$\begin{align*}
\phi_{k+1}^{(\text{denoise})}(E_{n}^{(\text{thinned})}) &= \phi_{k}^{(\text{denoise})}(E_{n}^{(\text{thinned})}) \\
+ \alpha_{\phi} \delta \phi_{k}(E_{n}^{(\text{thinned})}), \\
\mu_{k+1}^{(\text{denoise})}(E_{n}^{(\text{thinned})}) &= \mu_{k}^{(\text{denoise})}(E_{n}^{(\text{thinned})}) \\
+ \alpha_{\mu} \delta \mu_{k}(E_{n}^{(\text{thinned})}).
\end{align*}$$

(16)

Table 2

<table>
<thead>
<tr>
<th>Shell</th>
<th>CN_{Mn−X}</th>
<th>R_{Mn−X} (nm)</th>
<th>ΔE_0 (eV)</th>
<th>σ² (10⁻⁵ nm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a-i)</td>
<td>Experimental original (Δk ≅ 1 nm⁻¹), R_{0}^{Mn−O} = 0.82%, R_{0}^{Mn−Mn} = 4.35%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn−O</td>
<td>5.3 ± 6.6</td>
<td>0.224 ± 0.012</td>
<td>4 ± 10</td>
<td>12 ± 20</td>
</tr>
<tr>
<td>Mn−Mn</td>
<td>9.0 ± 5.5</td>
<td>0.311 ± 0.004</td>
<td>−3 ± 5</td>
<td>6 ± 5</td>
</tr>
<tr>
<td>(a-ii)</td>
<td>Thinned from (a-i), R_{0}^{Mn−O} = 0.60%, R_{0}^{Mn−Mn} = 6.26%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn−O</td>
<td>6.3 ± 1.1</td>
<td>0.226 ± 0.002</td>
<td>5 ± 1</td>
<td>13 ± 3</td>
</tr>
<tr>
<td>Mn−Mn</td>
<td>10.6 ± 0.9</td>
<td>0.309 ± 0.001</td>
<td>−5.5 ± 0.7</td>
<td>7.2 ± 0.8</td>
</tr>
</tbody>
</table>

$$\begin{align*}
R_{\text{fit}}(\kappa) &= \sum_{k} \left( \frac{\text{Ref}^{\text{thinned}}(\kappa) - \text{Ref}^{\text{thinned}}(\kappa)}{\text{Ref}^{\text{thinned}}(\kappa)} \right)^{2} \cdot \% \\
R_{\text{ref}}(\kappa) &= \frac{\text{Ref}^{\text{thinned}}(\kappa)}{\text{Ref}^{\text{ori}}(\kappa)} \cdot \% \\
\sigma^{2} &= \sum_{k} \left( \frac{\text{Ref}^{\text{thinned}}(\kappa) - \text{Ref}^{\text{thinned}}(\kappa)}{\text{Ref}^{\text{thinned}}(\kappa)} \right)^{2} \cdot \% \\
\text{Chi}^{2} &= \left( \frac{\text{Ref}^{\text{thinned}}(\kappa) - \text{Ref}^{\text{thinned}}(\kappa)}{\text{Ref}^{\text{thinned}}(\kappa)} \right)^{2} \cdot \%
\end{align*}$$

![research papers](image-url)
of the phase spectra shows a larger phase correction from the original data compared with restoration of the absorption spectra [(a)–(f) in Figs. 7(B) and 7(D)]. Curve-fitting analysis for the EXAFS oscillation of the original experimental data shows the result of $CN_{Mn-O} = 5.3 \pm 0.6$ and $RMn-O = 0.224 \pm 0.012$ nm at the Mn–O bond and $CN_{Mn-Mn} = 9.0 \pm 5.5$ and $RMn-Mn = 0.311 \pm 0.004$ nm at the Mn–Mn bond [(a–i) of Table 2]. These results are consistent with (but have slightly smaller $CN_{Mn-Mn}$ than) reference MnO EXAFS oscillation data by transmission mode measurement, where $CN_{Mn-O} = 7.6 \pm 1.3$ and $RMn-O = 0.222 \pm 0.002$ nm at the Mn–O bond and $CN_{Mn-Mn} = 12.7 \pm 1.3$ and $RMn-Mn = 0.312 \pm 0.001$ nm at the Mn–Mn bond [(h) of Table 2]. Compared with $k^3\chi(k)$ and its Fourier transform of reference MnO data [(h) of Figs. 7(E) and 7(F)], the EXAFS oscillations extracted from the thinned data gradually lost their oscillation structure attributed to the radius distribution around $R = 0.4–0.5$ nm as $\Delta k$ exceeds $3$ nm$^{-1}$ [dashed black line in (c)–(g) of Figs. 7(E) and 7(F)]. The radius distribution peaks belonging to Mn–O and Mn–Mn bonds in the Fourier transform gradually become smaller when $\Delta k$ exceeds $5$ nm$^{-1}$ [dashed black line in (e)–(g) in Figs. 7(E) and 7(F)]. The results of curve-fitting analyses also showed either a decrease in the $CN_{Mn-Mn}$ value or complete failure of the analysis [(c–i)–(g–i) of Table 2]. By processing the proposed spectral restoration, the EXAFS oscillation structure was recovered especially at larger $R$ ranges around $R = 0.4–0.5$ nm, with the data thinned to $\Delta k \approx 2–4$ nm$^{-1}$ [red solid line of (b)–(d) in Figs. 7(E) and 7(F)]. However, the benefits of restoration were not so apparent at the fitting $R$ range ($R = 0.14–0.34$ nm). Still, the error of curve-fitting analysis $R_{\text{fit}}$ was reduced by spectral restoration by maintaining the CNs and interatomic distances of the Mn–O and Mn–Mn bonds close to those of the reference EXAFS data [(a–ii)–(d–ii) of Table 2]. The restoration of the EXAFS oscillation thinned to $\Delta k \approx 5–6$ nm$^{-1}$ intervals exhibited some recovery with respect to the radius

![Figure 7](image-url)

**Figure 7**
Restoration and noise removal of X-ray absorption and phase spectra for MnO particles from spectroscopic ptychography measurements: (A) Mn K-edge absorption spectra; (B) phase spectra; (C), (D) expansion of (A) and (B), respectively, at the XANES energy region; (E) $k^3$-weighted EXAFS oscillations; (F) Fourier transform of $k^3$-weighted EXAFS ($k = 30–100$ nm$^{-1}$). (a) Experiment original data ($\Delta k \approx 1$ nm$^{-1}$), data thinned to (b) $\Delta k \approx 2$ nm$^{-1}$, (c) $\Delta k \approx 3$ nm$^{-1}$, (d) $\Delta k \approx 4$ nm$^{-1}$, (e) $\Delta k \approx 5$ nm$^{-1}$, (f) $\Delta k \approx 6$ nm$^{-1}$, (g) $\Delta k \approx 8$ nm$^{-1}$ intervals, and (h) reference data by transmission XAFS measurement ($\Delta k \approx 0.5$ nm$^{-1}$). Dashed black line, original/thinned data; solid red line, restored and noise-removed data; solid black line, reference data.
distribution peak belonging to the Mn—Mn bond. However, the Mn—O bond peak structure did not restore well [solid red line of (e)–(f) in Figs. 7(E) and 7(F)]. Curve-fitting results were not consistent with the reference values [(e-ii) and (f-ii) of Table 2]. Finally, the restoration apparently failed for the thinned EXAFS oscillation with a $\Delta k \simeq 8$ nm$^{-1}$ interval [solid red line of (g) in Figs. 7(E) and 7(F), and (g-ii) of Table 2]. $R$ factors against reference EXAFS data $R_{f}^{(\text{ref})}$ tend to be below 15% with the successfully analyzed data, while those for failed EXAFS data tend to exceed 50%.

The thinnig (sparse) limit for restoring the experimental X-ray absorption and phase spectra from spectroscopic ptychography measurements, to the extent that they can be used for quantitative EXAFS analysis of the first Mn—O bond shell and second Mn—Mn bond shell, was considered as $k$ intervals with approximately $\Delta k \leq 4$ nm$^{-1}$. This limit is approximately half the limit for the theoretical model absorption/phase spectra without any noise components ($\Delta k \leq 8$ nm$^{-1}$). The limit reduction is attributable to the opening degree of freedom for noise removal. Note that the restored and noise-removed experimental EXAFS oscillations lost their structure in the small-R region when the EXAFS oscillation data were thinned at large $\Delta k$ intervals. In particular, deterioration in the values of $CN_{\text{Mn—O}}$ and $R_{\text{Mn—O}}$ was observed from these data. This is a reverse trend in restoring the calculated spectra model, in which the radius distribution peak belonging to the Mn—Mn bond. However, the Mn—O bond peak structure did not restore well [solid red line of (e)–(f) in Figs. 7(E) and 7(F)]. Curve-fitting results were not consistent with the reference values [(e-ii) and (f-ii) of Table 2]. $R$ factors against reference EXAFS data $R_{f}^{(\text{ref})}$ tend to be below 15% with the successfully analyzed data, while those for failed EXAFS data tend to exceed 50%.

In addition, we note that we cannot improve the quality (signal-to-noise ratio) of the spectral data themselves and restore buried information using the proposed restoration algorithm. Although the experimental data reused from previous work were corrected in the energy range 6.5–7.4 keV (which corresponds to $k = 150$ nm$^{-1}$), quantitative curve-fitting analysis of the EXAFS oscillation is available only to $k = 100$ nm$^{-1}$, whether the spectra were restored or not. The quality of the spectral data is determined only by the measurement system (dynamic range of the detector, thermal stability etc.) and the measurement condition (exposure time etc.). All this proposed algorithm can achieve is a reduction of the measuring energy points.

5. Demonstration of the restoration of spatially resolved spectra reconstructed from sparse spectroscopic ptychography

Finally, we have attempted to restore the spatially resolved X-ray absorption/phase spectra from the energy stack of a reconstructed object function of sparse spectroscopic ptychography. To demonstrate sparse spectroscopic ptychography measurements, the energy stack of the coherent

![Figure 8](image1.png)

**Figure 8**
Error profiles of iterative restoration for thinned X-ray absorption $\mu^{(\text{restore})}(E)$ and phase $\phi^{(\text{restore})}(E)$ spectra of MnO particles from spectroscopic ptychography measurements. Solid line, errors of $\mu^{(\text{restore})}(E)$; dashed line, errors of $\phi^{(\text{restore})}(E)$ by KK transform. (a) Experiment original data ($\Delta k \approx 1$ nm$^{-1}$), (b) $\Delta k \approx 2$ nm$^{-1}$, (c) $\Delta k \approx 3$ nm$^{-1}$, (d) $\Delta k \approx 4$ nm$^{-1}$, (e) $\Delta k \approx 5$ nm$^{-1}$, (f) $\Delta k \approx 6$ nm$^{-1}$ and (g) $\Delta k \approx 8$ nm$^{-1}$.

![Figure 9](image2.png)

**Figure 9**
Restoration and noise removal of spatially resolved Mn $K$-edge X-ray (A) absorption and (B) phase spectra at three arbitrary points of MnO particles from sparse spectroscopic ptychography measurements: (1) restored images at 6600 eV; (2) restored spatially resolved spectra; (3) their expansion at the XANES energy region. (C) Spatially resolved $k^{4}$-weighted EXAFS oscillations and (D) their Fourier transforms ($k = 30$–100 nm$^{-1}$). The resolution of the spectra was 48 x 48 nm. Dashed black line, sparse experimental data; solid line, restored and noise-removed data.
diffraction pattern data for the MnO particles was thinned to the $k$ interval approximately $\Delta k = 4 \text{ nm}^{-1}$, where some benefits of spectral restoration for EXAFS analysis are found. The thinned energy stack of the object function was reconstructed under the same conditions as described in Section 4.2. Then, the thinned absorption and phase spectra at each pixel of the reconstructed sample image (pixel size 12 nm; 400 $\times$ 400 pixels) were restored using GPU parallel processing of the proposed algorithm in MATLAB. Spatially resolved EXAFS oscillations of the MnO particle sample were obtained from the $4 \times 4$ binned (48 $\times$ 48 nm) restored absorption spectra. Fig. 9 presents the results of the restoration of spatially resolved spectra from the sparse spectroscopic ptychography measurements. The X-ray absorption and phase spectra at each pixel (12 nm pixel size) were successfully restored, though the correction of the phase spectra tended to exceed that of the absorption spectra [Figs. 9(A2) and 9(B2)]. Additionally, negligible deterioration was found in the real-space image of both absorbance and phase images in Figs. 9(A1) and 9(B1), compared with the corresponding images in Figs. 4(A) and 4(B). Furthermore, the extracted EXAFS oscillations and their Fourier transforms at three arbitrary points in the MnO particles did not conflict with those shown in Figs. 7(E) and 7(F). Each spatially resolved EXAFS (with 48 $\times$ 48 nm pixel size) was then processed into parallel-curve fitting using GPUs. Fig. 10 shows the resulting curve-fitting images of the EXAFS. Although certain influences of image artifacts remained (especially in Mn—O bonds), the real-space distributions of $\text{CN}_{\text{Mn—O}}$, $R_{\text{Mn—O}}$, $\text{CN}_{\text{Mn—Mn}}$ and $R_{\text{Mn—Mn}}$ were consistent with a theoretical MnO structure ($\text{CN}_{\text{Mn—O}} = 6$, $R_{\text{Mn—O}} = 0.2223 \text{ nm}$, $\text{CN}_{\text{Mn—Mn}} = 12$ and $R_{\text{Mn—Mn}} = 0.3115 \text{ nm}$).

6. Conclusion

In this study, we have demonstrated the restoration of sparse absorption and phase spectra, obtained from the phase recovery reconstruction of spectroscopic ptychography measurements. The only requirement for the proposed algorithm was that the spectra of both $f'$ and $f''$ (which are mutually related by the KKR) were recorded simultaneously at the $\omega$ (or $E$) sampling points. There were no other requirements in real- or inverse-space conditions, and the phase-retrieval reconstruction of ptychographic coherent imaging was entirely independent. The KKR holds in every three-dimensional object in real space, and absorption/phase shifts are integrated into the X-ray axis direction as an independent pixel in a two-dimensional projection image. Although we only demonstrate an example of a homogeneous material in this paper, we think the method is still applicable for the spectroscopic ptychography images of heterogeneous materials. Additionally, if there is a measurement system in which $f'$ and $f''$ spectra are recorded simultaneously, although this is also quite challenging to a correct sufficient frequency (energy) point, the proposed restoration algorithm will also help. This algorithm does not improve the quality of the spectra, but is helpful for the recovery of information from sparse spectroscopic data. However, we can improve the data quality via efficient time management of the entire measurement. For example, the quality of EXAFS can be improved by increasing the available exposure time of ptychographic imaging at the high-$k$-range energy point, by reducing the recording time for unnecessary energy points that can be restored. The spectroscopic ptychography method has considerable potential for correcting not only the morphological information of the sample but also the chemical state information (e.g. elemental composition, valence, local symmetry, coordination number and interatomic distance of chemical bonds) in real space with high spatial resolution. By maximizing the structural information of sample material targets according to the limited measurement time provided for users, the application of spectroscopic ptychography methods can be expanded further to three-dimensional measurements combined with computed tomography, or
**APPENDIX A**

**KK transformation of fragmented \( \mu \) and \( \phi \) array data**

Although the KK transform was theoretically applied to continuous \( \mu(E) \) and \( \phi(E) \) in the energy range from 0 to \( \infty \), we can only obtain fragmented and limited energy ranges of \( \mu(E_n) \) and \( \phi(E_n) (n = 0, \ldots, N) \) experimentally. To apply the KK transform of the experimental data correctly, interpolation and extrapolation of \( \mu(E) \) and \( \phi(E) \) in this study were processed as follows, with reference to Watts' study (Watts, 2014). First, the energy ranges of the Cauchy principal integration in KK transforms were blocked into \( 0 \leq E < E_0 \), \( E_n \leq E < E_{n+1} \) \( (n = 0, \ldots, N - 1) \) and \( E \geq E_N \) ranges, as follows:

\[
K_1 \left[ \frac{1}{2} \mu(E), a \right] = \left[ \frac{1}{\pi} \int_{0}^{E_0} \frac{E^2 \mu^{(\text{lowE})}(E')}{E^2 - E'^2} \, dE' \right] = \frac{1}{\pi} \int_{E_n}^{E_{n+1}} \frac{E^2 \mu^{(\text{lowE})}(E')}{E^2 - E'^2} \, dE' + \frac{1}{\pi} \int_{E_{n+1}}^{E} \frac{E^2 \mu^{(\text{lowE})}(E')}{E^2 - E'^2} \, dE' + \frac{1}{\pi} \int_{E}^{E_0} \frac{E^2 \mu^{(\text{lowE})}(E')}{E^2 - E'^2} \, dE' + \frac{a}{E} \quad (17)
\]

\[
K_2[\phi(E), b, c] = \frac{2E}{\pi} \int_{0}^{E_0} \frac{E' \phi^{(\text{lowE})}(E')}{E'^2 - E^2} \, dE' + \frac{2E}{\pi} \int_{E_n}^{E_{n+1}} \frac{E' \phi^{(\text{lowE})}(E')}{E'^2 - E^2} \, dE' + \frac{2E}{\pi} \int_{E}^{E_0} \frac{E' \phi^{(\text{lowE})}(E')}{E'^2 - E^2} \, dE' + \frac{b}{E} + c \text{ Corr}(E), \quad (18)
\]

where \( \phi^{(\text{lowE})}(E) \), \( \mu^{(\text{lowE})}(E) \), \( \phi_n(E) \), \( \mu_n(E) \), \( \phi^{(\text{highE})}(E) \) and \( \mu^{(\text{highE})}(E) \) are interpolated and extrapolated \( \phi(E) \) and \( \mu(E) \) functions at the corresponding energy ranges. In the energy range of \( E_n \leq E < E_{n+1} \) \( (n = 0, \ldots, N - 1) \), \( \mu(E) \) is interpolated as follows:

\[
\mu_n(E) = \frac{\mu(E_{n+1}) - \mu(E_n)}{E_{n+1} - E_n} E - E_n + \mu(E_n)
\]

\[
(E_n \leq E < E_{n+1}). \quad (19)
\]

At the higher energy range of \( E \leq E_N \), \( \mu(E) \) is extrapolated to be proportional to \( E^{-3} \), according to the first term of Victoreen's equation (Lytle et al., 1975). \( \mu^{(\text{highE})}(E) \) can be expressed as follows:

\[
\mu^{(\text{highE})}(E) = \frac{\mu(E_N)}{E^3}. \quad (E \geq E_N). \quad (20)
\]

In the lower energy range of \( 0 \leq E < E_0 \), \( \mu(E) \) is extrapolated to the value at \( E = E_0 \) as follows:

\[
\mu^{(\text{lowE})}(E) = \frac{\mu(E_0)}{E_0^3}. \quad (0 \leq E < E_0). \quad (21)
\]

In the energy range of \( E_n \leq E < E_{n+1} \) \( (n = 0, \ldots, N - 1) \), \( \phi(E) \) is interpolated as follows:

\[
\phi_n(E) = \left[ \frac{\phi(E_{n+1}) - \phi(E_n)}{E_{n+1} - E_n} \right] E - E_n + \phi(E_n)
\]

\[
(E_n \leq E < E_{n+1}). \quad (22)
\]

In the higher energy range of \( E \leq E_N \), \( \phi(E) \) is extrapolated (proportional to \( E^{-1} \)) as follows:

\[
\phi^{(\text{highE})}(E) = \frac{\phi(E_N)}{E}. \quad (E \geq E_N). \quad (23)
\]

In the lower energy range of \( 0 \leq E < E_0 \), \( \phi(E) \) is extrapolated as follows:

\[
\phi^{(\text{lowE})}(E) = \frac{\phi(E_0)}{E_0} - \frac{E}{E_0} \frac{\phi(E_N)}{E}. \quad (0 \leq E < E_0). \quad (24)
\]

In addition to the interpolation and extrapolation of \( \mu(E) \) and \( \phi(E) \), a correction due to the atomic scattering factor \( f_0 \) is needed. Therefore the term proportional to \( E^{-1} \) is added to the free parameters \( a \) and \( b \) in equations (17) and (18). In equation (18), extrapolations of \( \phi(E) \) at both lower and higher energy ranges are often insufficient. Hence, to compensate for the influence of \( f_0 \), the term proportional to \( \text{Corr}(E) \) is added to equation (18) with free parameter \( c \), where \( \text{Corr}(E) \) is expressed as

\[
\text{Corr}(E) = \frac{2}{\pi} \int_{0}^{E_0} \frac{1}{E^2 - E'^2} \left( 1 - \frac{E'}{E_0} \right) \, dE' + \frac{2}{\pi} \int_{E}^{\infty} \frac{1}{E^2 - E'^2} \left( 1 - \frac{E'}{E} \right) \, dE'. \quad (25)
\]

**APPENDIX B**

**Iterative restoration and noise removal of absorption and phase spectra using Newton methods**

Iterative noise removal of absorption \( \mu(E) \) and phase \( \phi(E) \) spectra was performed by zeroizing the function

---

*(Image of text as PDF)*
\[ \mathbf{J}(\phi(E), \mu(E)) = \begin{bmatrix} \frac{\partial}{\partial \phi(E)} & \frac{\partial}{\partial \mu(E)} \end{bmatrix} \mathbf{e}(\phi(E), \mu(E)) \]

\[ \approx \begin{bmatrix} \frac{1}{E} & 1 \\ 0 & \frac{1}{E^2} - \frac{E^2}{\pi E^2 - E^2} \delta E \end{bmatrix} \quad (E' \neq E). \]

If \( \mu^{(\text{ideal})}(E) \) and \( \phi^{(\text{ideal})}(E) \) ideally satisfy the KKR, the equation

\[ \mathbf{e}(\phi^{(\text{ideal})}(E), \mu^{(\text{ideal})}(E)) = 0 \quad (27) \]

is valid. The experimental data \( \mu^{(\text{obs})}(E) \) and \( \phi^{(\text{obs})}(E) \) are described using \( \mu^{(\text{ideal})}(E) \) and \( \phi^{(\text{ideal})}(E) \) and noise terms \( \delta \mu(E) \) and \( \delta \phi(E) \) as follows:

\[ \begin{align*}
\phi^{(\text{obs})}(E) &= \phi^{(\text{ideal})}(E) + \delta \phi(E), \\
\mu^{(\text{obs})}(E) &= \mu^{(\text{ideal})}(E) + \delta \mu(E).
\end{align*} \quad (28) \]

Substituting equation (28), and approximating under the condition that \( \delta \mu(E) \) and \( \delta \phi(E) \) are sufficiently smaller than \( \mu^{(\text{obs})}(E) \) and \( \phi^{(\text{obs})}(E) \), equation (27) can be expressed as follows:

\[ \mathbf{e}(\phi^{(\text{obs})}(E), \mu^{(\text{obs})}(E)) - \mathbf{J}(\phi^{(\text{obs})}(E), \mu^{(\text{obs})}(E)) \left[ \begin{array}{c} \delta \phi(E) \\ \delta \mu(E) \end{array} \right] \approx 0. \quad (29) \]

By solving equation (29), \( \delta \mu(E) \) and \( \delta \phi(E) \) were estimated as follows:

\[ \left[ \begin{array}{c} \delta \phi(E) \\ \delta \mu(E) \end{array} \right] \approx \mathbf{J}^{-1}(\phi^{(\text{obs})}(E), \mu^{(\text{obs})}(E)) \mathbf{e}(\phi^{(\text{obs})}(E), \mu^{(\text{obs})}(E)). \quad (30) \]

Acknowledgements

We thank Dr Makoto Hirose for collecting experimental data for spectroscopic photocopying. We also thank Professor Dam Hieu Chi (Japan Advanced Institute of Science and Technology, JAST, Japan) for analytical discussions. Reference XAFS measurements in transmission mode were performed at SPring-8 BL37XU (proposal No. 2022A1430).

Funding information

This work was supported by the Japan Society for the Promotion of Science (JSPS) KAKENHI (grant Nos. JP18H05253, JP19H05814, JP20K15375 and JP20K20523) and Iketani Science and Technology Foundation (ISTF) (grant No. 0331102-A). It was also supported in part by the ‘Dynamic Alliance for Open Innovation Bridging Human, Environment and Materials’ project from the Ministry of Education, Culture, Sports, Science and Technology of Japan (MEXT).


