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Maximum entropy image deconvolution applied to structure determination for crystal $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$

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Abstract

Eight [100] images from a through-focus series of tetragonal crystal $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ were transformed separately into the structure images by means of maximum entropy image deconvolution. The constructed projected structure model based on the deconvoluted image is confirmed by image simulation. It is demonstrated that the image deconvolution is still successful even when some reflections fall in the vicinity of zero cross of contrast transfer function. The effectiveness and advantages of the technique are discussed.

Keywords: High-resolution electron microscopy; Maximum entropy image deconvolution; Nd–Ce–Cu–O; Crystal structure determination

1. Introduction

The discovery of $Nd_{2-x}Ce_xCuO_{4-\delta}$ as a member in the family of oxidic cuprate superconductors has led to intensive studies of its structural, magnetic, and electronic properties. This system is of great interest because the charge carriers in $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ are electrons as measured (Tokura et al., 1989; Tagaki et al., 1989; Hidaka and Suzuki, 1989) rather than holes as previously reported for other high-T_c cuprate superconductors. In addition, both the substitution of Ce^{4+} for Nd^{3+} in a narrow range ($0.13 < x < 0.17$) and a small degree of oxygen reduction are essential for the presence of superconductivity. In 2000, it was the first time to observe that the superconductivity could also exist beyond the region $0.13 < x < 0.17$ for $Nd_{2-x}Ce_xCuO_{4-\delta}$ single crystal (Klimczuk et al., 2000). The structure of compound $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ is isomorphic to that of the undoped parent crystal Nd_2CuO_4, the so-called T′ phase (Tokura et al., 1989), which is characterized by the absence of apical oxygen atoms between adjacent CuO_2 layers. Subsequently, the structure of $Nd_{2-x}Ce_xCuO_{4-\delta}$ was determined by high-resolution neutron powder diffraction technique (Kwei et al., 1989). It was confirmed that the crystal structure of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ remains tetragonal T′ phase with the *I*4/*mmm* symmetry.

In the present paper, the crystal structure of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ has been studied by high-resolution electron microscopy (HREM). It is well known that the image contrast changes with various parameters, especially the defocus value and sample thickness. Traditionally, in HREM the crystal structure determination is performed by using the trial-and-error method. With this method, one needs to find out the structure image that reflects the projected crystal structure from among a series of through-focus images, based on some known structure information. Then one or more structure models can be proposed and a series of theoretical images with different defocus value and different thickness are calculated for each model. Finally, the right structure model is determined by matching all the series of calculated images with the experimental ones. An alternative way of obtaining the structure image is to perform the posterior image processing, for instance, the image deconvolution (Li and Fan, 1979; Han et al., 1986) or exit wave reconstruction (Schiske, 1968; Uyeda and Ishizuka, 1974; Kirkland, 1984; Van Dyck and Op de Beek, 1990; Coene et al., 1996; Op de Beeck et al., 1996; Van Dyck et al., 1996; Allen et al., 2004; Hsieh et al., 2004). The present paper aims at demonstrating the effectiveness of image deconvolution technique rather than determining the structure itself.

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Under the weak-phase object approximation (WPOA) the image intensity is expressed as

$$\boldsymbol{I}(\boldsymbol{r}) = 1 + 2\sigma\varphi(\boldsymbol{r}) * \mathcal{F}^{-1}[W(H)] \quad (1)$$

where $\varphi(\boldsymbol{r})$ and $W(H)$ denote the projected potential distribution function (PPDF) and contrast transfer function (CTF), respectively, $\sigma = \pi/\lambda U$, λ denotes the wavelength and U the accelerating voltage of electrons, * and $\mathcal{F}^{-1}$ represent operators of convolution and inverse Fourier transform (FT), respectively. Obviously, $\varphi(\boldsymbol{r})$ and hence also the structure image can be obtained by performing the deconvolution to Eq. (1), once the CTF is known. The CTF depends on several parameters among which the defocus value is the key one to be determined.

There are different methods to determine the defocus value, either in the process of image deconvolution (Uyeda and Ishizuka, 1974; Unwin and Henderson, 1975; Hovmöller et al., 1984; Kirkland, 1984; Han et al., 1986; Tang and Li, 1988; Hu and Li, 1991), or independent of it. Here the one in the process of image deconvolution based on the principle of maximum entropy (Hu and Li, 1991) has been employed. The work of crystal structure determination by image deconvolution in combination with image simulation was firstly published in 1997 (Jiang et al., 1997), where the image deconvolution is based on the direct method. The present work is analogous to it, but the method of image deconvolution is based on the principle of maximum entropy. Besides, the crystal structure determination was treated as an ab initio process to show the power of maximum entropy image deconvolution technique, though the structure of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ had been reported before.

2. Experimental

The single crystal sample of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ was prepared by the traveling-solvent-floating-zone (TSFZ) method in an atmosphere of Ar_2/O_2 mixed gas flow. Powders of raw materials Nd_2O_3 99.99% (calcified at 950 °C), CeO_2 99.99% and CuO 99.99% were mixed thoroughly in alcohol, then calcified at 950 °C in air for 12 h. The mixture was ground and pressed into a rod and sintered at 1040 °C for 12 h in air. The crystals were crushed into fine fractures in an agate mortar and dispersed in alcohol. The suspending powders were transferred onto a copper grid covered with holey carbon film. The electron diffraction and HREM observations were carried out with JEM-2010 high-resolution electron microscope operated at accelerating voltage 200 kV. The point resolution of microscope is slightly better than 0.2 nm. The electron diffraction camera length was calibrated with diffraction rings of thin golden foil evaporated onto the holey carbon film. The images were digitized with an Agfa scanner.

3. Diffraction patterns and images

Electron diffraction study indicates that the crystal structure of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ belongs to the tetragonal system. Fig. 1(a) and (b) show the [001] and [100] electron diffraction patterns (EDPs), respectively. The determined lattice parameters are $a = 0.394$ nm, $c = 1.209$ nm. They are in agreement with those given by X-ray diffraction (Jia et al., 2003).

The systematic extinction condition seen in [001] and [100] EDPs (Fig. 1) indicates a body-centered tetragonal lattice. Hence, the possible plane groups for [100] projected structure are *cm* and *c*2*mm*.

A through-focus series of [100] images were taken with the focus step about 5 nm. Eight of them without seriously drift and/or distortion, were selected for image deconvolution processing. The one taken near the Scherzer focus (Scherzer, 1949) condition is shown in Fig. 2 together with the inset corresponding diffractogram obtained by Fourier transforming a relatively thin image area.

4. Symmetry averaging

A slight symmetry distortion in images is inevitable owing to the crystal tilt and beam tilt even the microscope

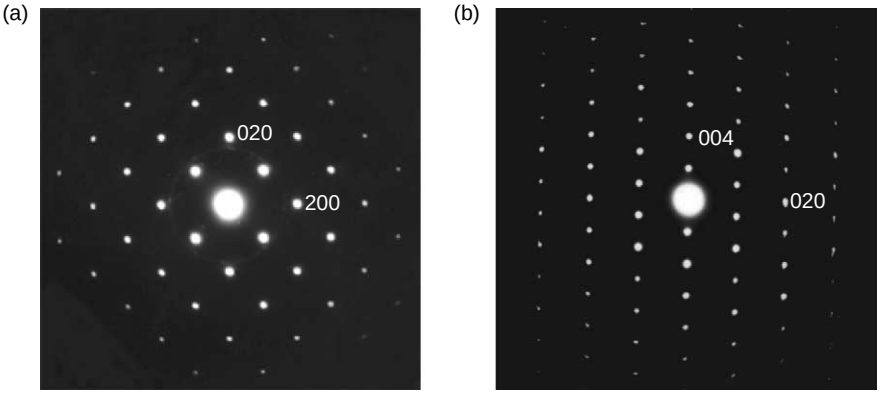

Fig. 1. (a) [001] and (b) [100] EDPs of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$.