DIRECT METHODS IN SUPERSPACE

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Abstract

With conventional direct methods and many other methods for single-crystal structure analysis, the sample is treated as an ideal crystal, which possesses exact three-dimensional periodicity. However an important category of crystals, incommensurate crystals, do not have three-dimensional periodicity. According to the representation of de Wolff [Acta Cryst. A30 (1974) 777-785] and Janner & Janssen [Acia Cryst. A36 (1980) 399-408; 408-415], incommensurate crystals are regarded as the three-dimensional hypersection of a higher-dimensional periodic structure. Based on this representation a multidimensional direct-method has been developed. With this method incommensurate crystals are first treated in multi-dimensional space to solve the phase problem and then by cutting the resultant multidimensional Fourier map with the three-dimensional physical space to obtain the structure. The phasing procedure is divided in two stages. In the first stage phases of main reflections are developed using a modified Sayre equation involving only main reflections. While in the second stage phases of the satellite reflections are derived based on another modified Sayre equation, which relates phases of satellites with those of main reflections. In contrast to other methods of solving incommensurate structures, no preliminary assumption on either the corresponding basic structure or the modulation form is needed through out the process. The method has been successfully applied to X-ray as well as electron diffraction data and has been incorporated with an image processing technique in high-resolution electron microscopy. Examples are given on the study of incommensurate modulation in the Bi-based high Tc superconductors.

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1. What is an incommensurate modulated structure?

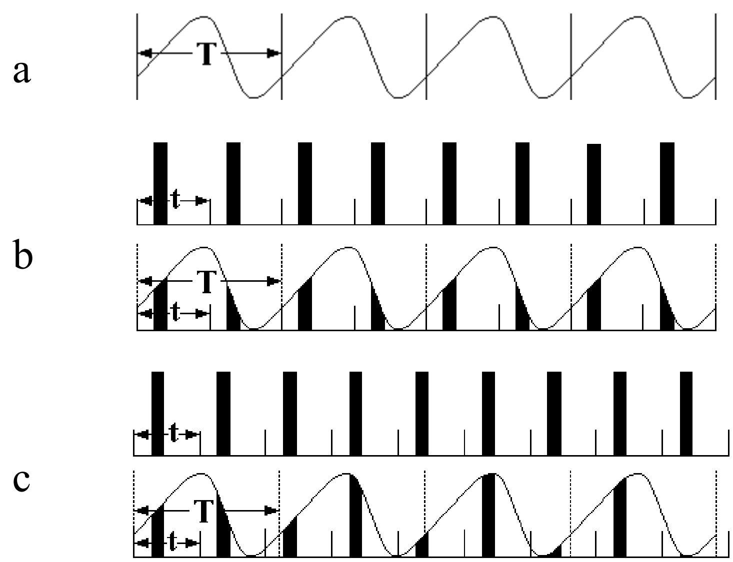

Figure 1. Occupational modulation of a one-dimensional Structure (a) modulation wave with a period equal to **T**; (*b*) upper row: one-dimensional regular structure with atoms shown as thick vertical lines and with a period equal to **t**; lower row: the resulting commensurate modulated structure; (*c*) upper row: one-dimensional regular structure; lower row: the resulting incommensurate modulated structure

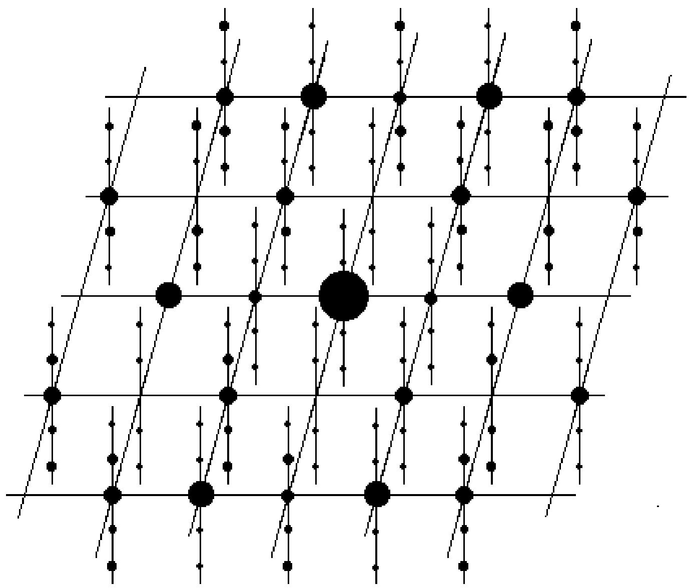

Figure 2. Schematic diffraction pattern of an incommensurate modulated structure. The vertical line segments indicate projected lattice lines parallel to the fourth dimension

2. Multi-dimensional expression of incommensurate modulated structures

$$\mathbf{h} = h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3 + \dots + h_{3+n}\mathbf{b}_{3+n} \qquad (n = 1,2,\dots) \qquad (1)$$

where $\mathbf{b}_i$ is the i^{th} translation vector defining the reciprocal unit cell. The structure factor formula is written as

$$F(\mathbf{h}) = \sum_{j=1}^{N} f_{j(\text{mod})}(\mathbf{h}) \exp[i2\pi(h_1\bar{x}_{j1} + h_2\bar{x}_{j2} + h_3\bar{x}_{j3})] \qquad (2)$$

where

$$f_{j(\text{mod})}(\mathbf{h}) = f_j(h)\int_0^1 d\,\bar{x}_4 \cdots \int_0^1 d\,\bar{x}_{3+n} P_j(\bar{x}_4, \cdots, \bar{x}_{3+n}) \times \exp\{i2\pi[(h_1U_{j1} + h_2U_{j2} + h_3U_{j3}) + (h_4x_{j4} + \dots + h_{3+n}x_{j(3+n)})]\} \qquad (3)$$

The $f_j(h)$ on the right-hand side of (3) is the ordinary atomic scattering factor, P_j is the occupational modulation function and U_j describes the deviation of the j^{th} atom from its average position $(\bar{x}_{j1}, \bar{x}_{j2}, \bar{x}_{j3})$.

3. Modified Sayre equations in multi-dimensional space

It has been proved that the Sayre equation can easily be extended into multi-dimensional space. We have

$$F(\mathbf{h}) = \frac{\theta}{V}\sum_{\mathbf{h'}} F(\mathbf{h'})F(\mathbf{h}-\mathbf{h'}), \qquad (4)$$

here $\mathbf{h}$ is a multi-dimensional reciprocal vector defined as (1). The right-hand side of (4) can be split into three parts, i.e.

$$F(\mathbf{h}) = \frac{\theta}{V}\left\{\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{m}}(\mathbf{h}-\mathbf{h'}) + 2\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{s}}(\mathbf{h}-\mathbf{h'}) + \sum_{\mathbf{h'}} F_{\mathrm{s}}(\mathbf{h'})F_{\mathrm{s}}(\mathbf{h}-\mathbf{h'})\right\}. \qquad (5)$$

Where subscript m stands for main reflections while subscript s stands for satellites. Since the intensities of satellites are on average much weaker than those of main reflections, the last summation on the right-hand side of (5) is negligible in comparison with the second, while the last two summations on the right-hand side of (5) are negligible in comparison with the first. Letting $F(\mathbf{h})$ on the left-hand side of (5) represents only the structure factor of main reflections we have to first approximation

$$F_{\mathrm{m}}(\mathbf{h}) \approx \frac{\theta}{V}\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{m}}(\mathbf{h}-\mathbf{h'}). \qquad (6)$$

On the other hand, if $F(\mathbf{h})$ on the left-hand side of (5) corresponds only to satellites, it follows that

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{\theta}{V}\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{m}}(\mathbf{h}-\mathbf{h'}) + \frac{2\theta}{V}\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{s}}(\mathbf{h}-\mathbf{h'}). \qquad (7)$$

For ordinary incommensurate modulated structures the first summation on the right-hand side of (7) has vanished, because any three-dimensional reciprocal lattice vector corresponding to a main reflection will have zero components in the extra dimensions so that the sum of two such lattice vectors could never give rise to a lattice vector corresponding to a satellite. We then have

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{2\theta}{V}\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{s}}(\mathbf{h}-\mathbf{h'}). \qquad (8)$$

For composite structures on the other hand, since the average structure itself is a 4- or higher-dimensional periodic structure, the first summation on the right-hand side of (7) does not vanish. We have instead of (8) the following equation:

$$F_{\mathrm{s}}(\mathbf{h}) \approx \frac{\theta}{V}\sum_{\mathbf{h'}} F_{\mathrm{m}}(\mathbf{h'})F_{\mathrm{m}}(\mathbf{h}-\mathbf{h'}). \qquad (9)$$

Equation (6) indicates that the phases of main reflections can be derived by a conventional direct method neglecting the satellites. Equation (8) or (9) can be used to extend phases from the main reflections to the satellites respectively for ordinary incommensurate modulated structures or composite structures. This provides a way to determine the modulation functions objectively. The procedure will be in the following stages:

i) derive the phases of main reflections using Equation (6);
ii) derive the phases of satellite reflections using Equation (8) or (9);
iii) calculate a multidimensional Fourier map using the observed structure factor magnitudes and the phases from i) and ii);
iv) cut the resulting Fourier map with a 3-dimensional 'hyperplane' to obtain an 'image' of the incommensurate modulated structure in the 3-dimensional physical space;
v) parameters of the modulation functions are measured directly on the multidimensional Fourier map resulting from iii).

4. Incommensurate modulation in high Tc superconductors studied by multidimensional direct methods

Bi-2223

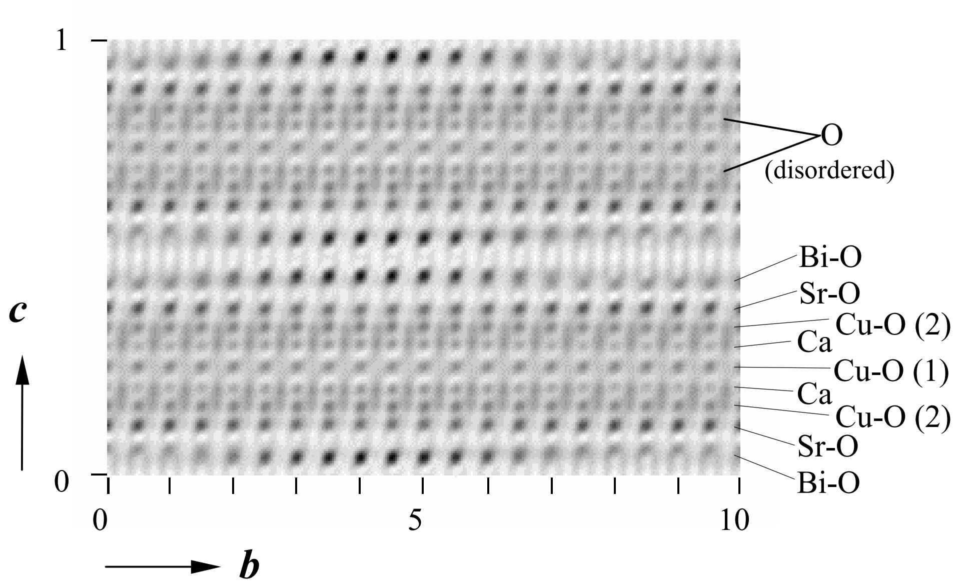

Figure 3. Potential distribution projected along the ***a*** axis, obtained by direct-method phasing of the *0klm* electron diffraction pattern (10 average unit cells are ploted along the ***b*** axis, while one unit cell is plotted along the ***c*** axis.):

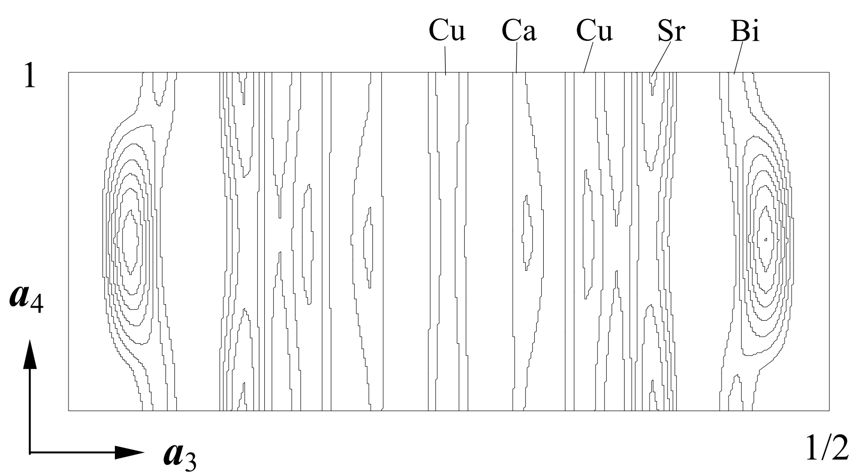

Figure 4. Hypersection of the direct-method phased 4D-Fourier map at $x_2 = 0$ projected along the ***a*** axis

Bi-2212

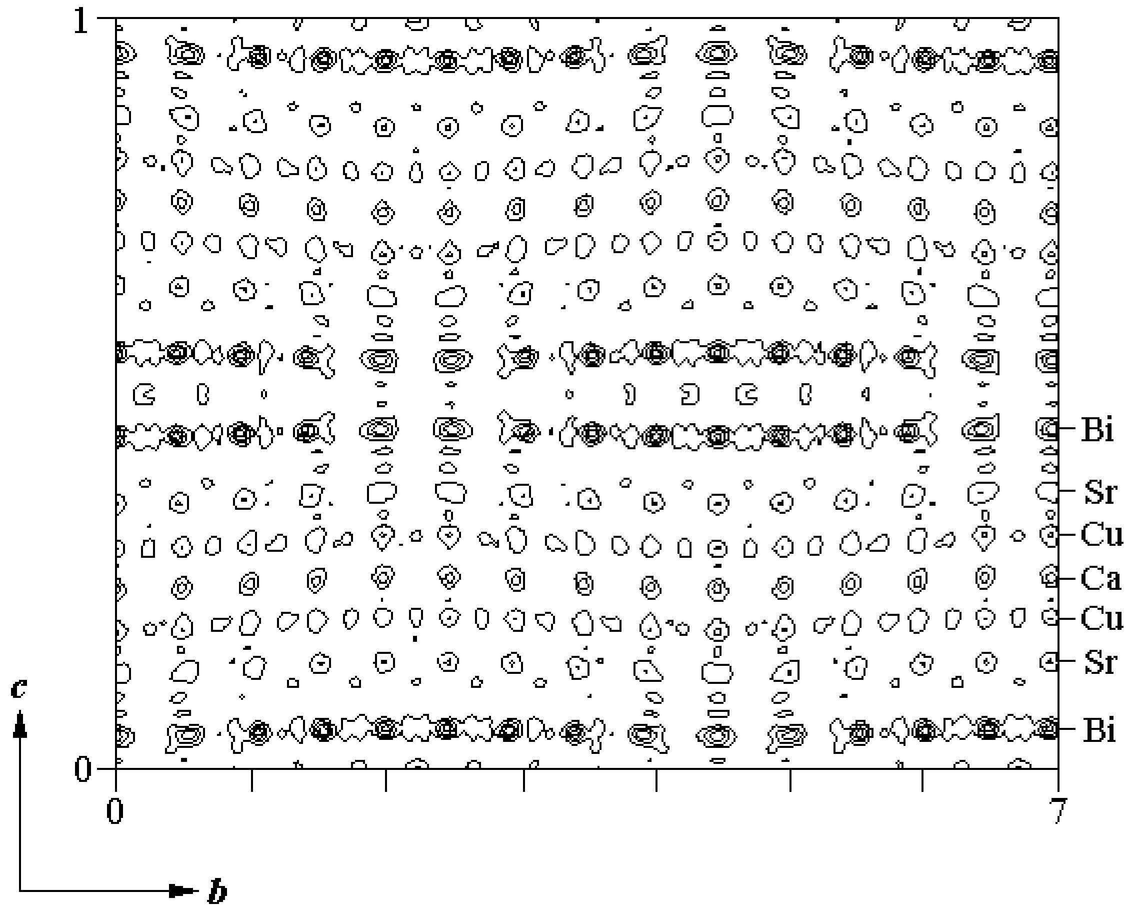

Figure 5. Electron density distribution projected along the ***a*** axis, obtained by direct-method phasing of the *0klm* X-ray diffraction data (7 average unit cells are plotted along the ***b*** axis, while one unit cell is plotted along the ***c*** axis.):

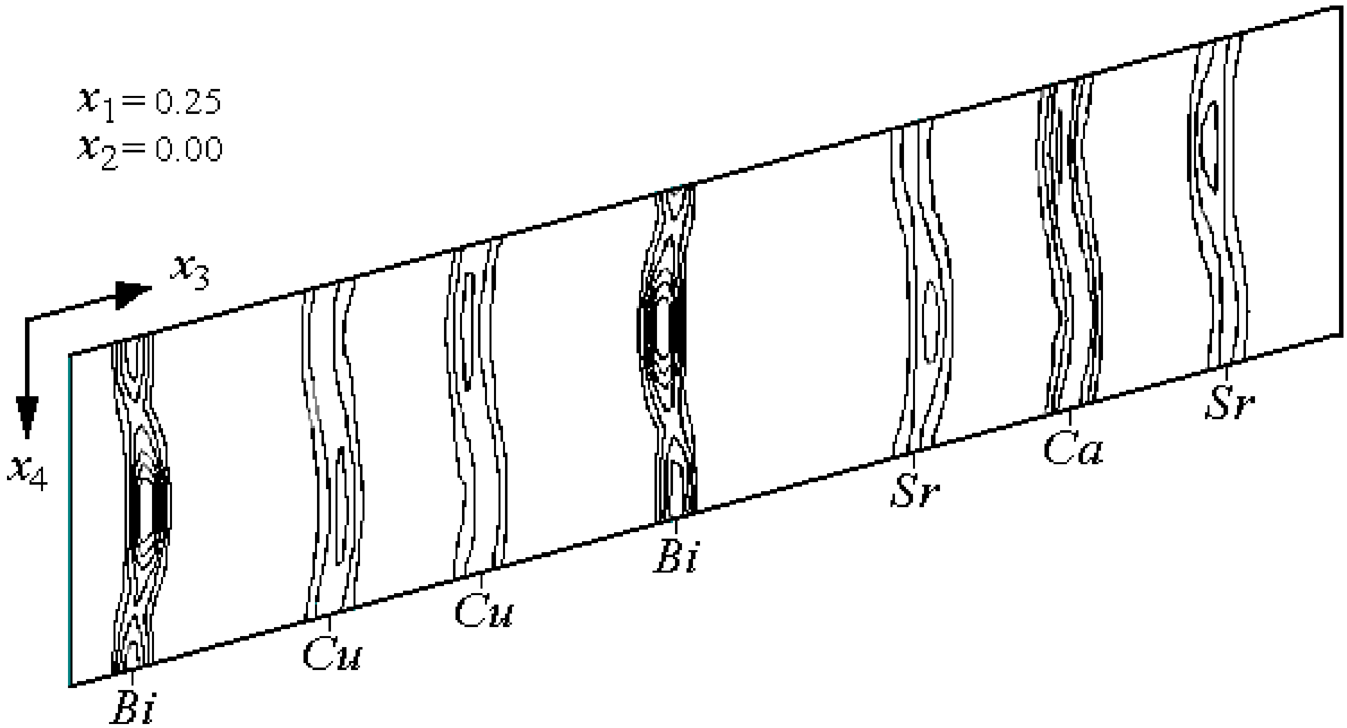

Figure 6. Hypersection of the direct-method phased 4D-Fourier map showing the modulated metal atoms:

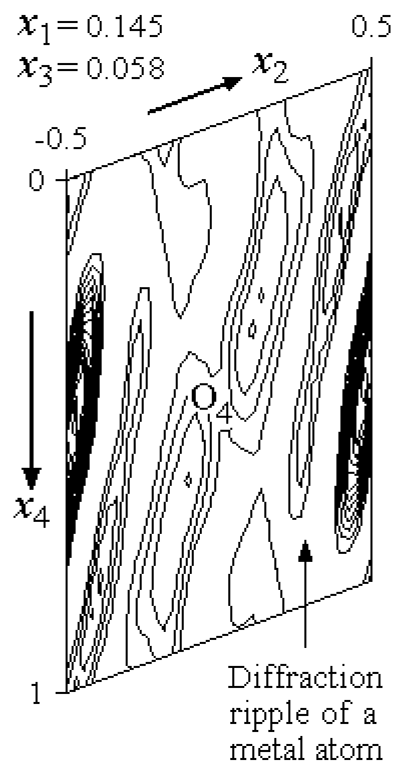

Figure 7. Hypersection of the direct-method phased 4D-Fourier map showing the sawtooth modulation of the oxygen atom O4

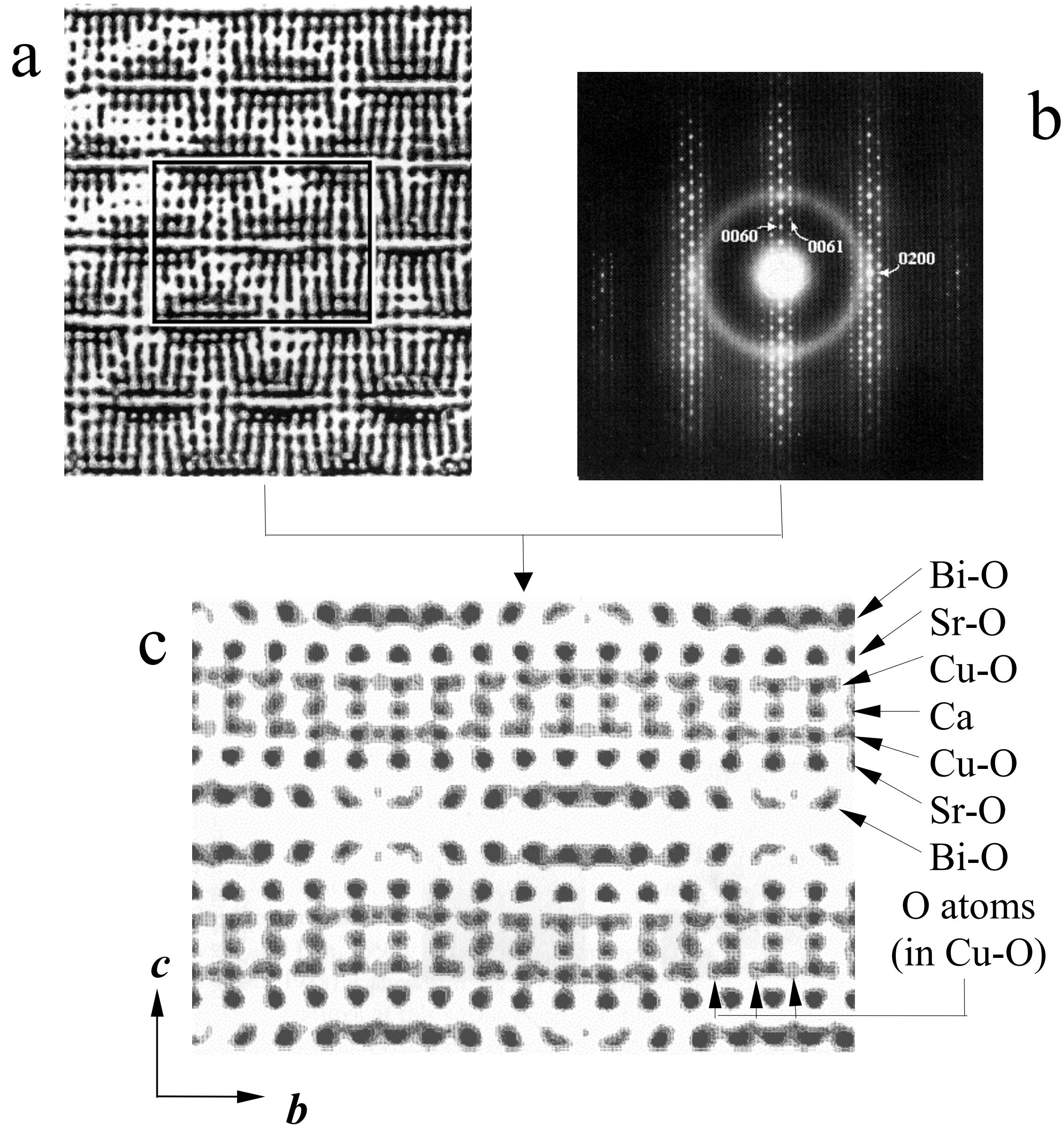

Figure 8. Image processing for the Bi-2212 superconductor. (a) experimental EM taken with the incident electron beam parallel to the ***a*** axis; (b) the corresponding ED pattern; (c) the 3-dimensional potential distribution projected along the ***a*** axis on an area of $8\boldsymbol{b}\times1\boldsymbol{c}$. The structure-factor magnitudes used for calculating (c) were from the ED, while the phases were from the direct-method phase extension based on the deconvolution of (a). The experimental EM is provided by Dr. S. Horiuchi.