Incommensurate modulations in Bi-2212 high-T_c superconductor revealed by single-crystal X-ray analysis using direct methods

FU Zhengqing (付正清)* ***, LI Yang (李 阳)*, CHENG Tingzhu (程庭柱)**, ZHANG Yuheng (张裕恒)**, GU Binglin (顾秉林)*** and FAN Haifu (范海福)*

Received January 22, 1994

Abstract The incommensurate modulated structure of the $Bi_2Sr_2Ca_1Cu_2O_y$ high-T_c superocnductor has been studied by direct methods with X-ray diffraction data from a single crystal. The super-space group is N_{111}^{Bbmb} with three-dimensional unit cell parameters $a=0.54222$ nm, $b=0.5437$ nm, $c=3.0537$ nm, $\alpha=\beta=\gamma=90^\circ$ and the modulation wave vector $q=(0, 0.22, 1)$. 543 main reflections, 867 first-order and 469 second-order satellite reflections have been observed. Phases of main reflections are derived by a conventional direct-method program SAPI91. The phases of satellite reflections are derived by the program DIMS running with default control based on the known phases of main reflections. The atomic parameters of the basic structure and of the modulation so obtained consist with the results from other authors. For the first time the structure details of the incommensurate modulation in the Bi-2212 phase are observed directly without relying on any assumed model of modulation.

Keywords: structure analysis, incommensurate modulation, Bi2212 high-T_c superconductors, direct method.

The one-dimensional incommensurate modulation in the three Bi-based high-T_c superconducting phases (Bi2223, Bi2212 and Bi2201 corresponding to $n=3$, 2, and 1, respectively in the formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$) has been extensively studied in recent years[1—7]. So far, structural characteristics of Bi2212 have been studied by various methods[1—5]. However, there still exist some discrepancies among the results from different authors, i.e. (i) occupational/substitutional modulations and thermal modulations: theoretically, these two kinds of modulation have different appearances in Fourier maps, but it is difficult to accurately separate one from the other in practice; (ii) the modulation of the O atoms in Bi-O layers: it is pertinent as it provides the mechanism for the incorporation of extra O atoms in Bi-O layers and thereby contributes to the hole concentration in Cu-O planes which are considered essential in superconductivity. At present, there exist two different models of modulation proposed for the O atoms in the Bi-O layer: In the study by Yamamoto *et al.* using simultaneously X-ray and time-of-flight neutron-diffraction data[2], 4.76 extra O atoms were found per period of the modulation

* Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China.
** Laboratory of Structure Analysis, University of Science and Technology of China, Hefei 230026, China.
*** Department of Physics, Tsinghua University, Beijing 100084, China.

wave, which corresponds to one extra O atom per formula unit. In the studies by Petricek *et al.* based on X-ray single-crystal data[3] and by Gao *et al.* using the X-ray single-crystal and neutron powder data[5], however, a saw-tooth modulation model of O atoms in Bi-O layers was proposed, which leads the extra O atoms amount to 0.14 atoms per formula unit, or 0.67 O atoms per period of the modulation wave. This value is much lower than that obtained by Yamamoto[2].

All the refinement methods mentioned above need a starting model for both the modulation and basic structure. As is known, a better initial model could make the refinement easier and also guarantee the correctness of the results. Yet, it is often difficult to set up appropriate initial models of modulation by guess, especially when the modulation is complicated or abnormal. To solve this problem, the Sayre equation was extended into multi-dimensional space by Hao, Liu and Fan[8]. Based upon the modified Sayre equations, the computer program DIMS has been developed by Fu and Fan[9], which provides a good starting point for the subsequent refinement. The program has been proved to be very efficient with over 12 incommensurate modulated structures. The structure analysis of incommensurate-modulated structures is then put on an objective basis free from any preliminary assumption on the modulation. In this work, DIMS was used to study the one-dimensional incommensurately modulated structure of the Bi2212 superconducting phase. The result consists well with that of Coppens and his colleagues[3, 5]. The present study provides a direct observation on the incommensurate modulation of the Bi-2212 superconducting phase without relying on any assumed modulation model.

1 The method

According to de Wolff[10] and Janner and Janssen[11], for an incommensurate modulated structure with one-dimensional modulation, reflections can be indexed as (h k l m) or equivalently (h_1 h_2 h_3 h_4) in a four-dimensional space, where a reciprocal lattice vector is expressed as

$$\hat{\boldsymbol{H}}=h_1\boldsymbol{a}_1^*+h_2\boldsymbol{a}_2^*+h_3\boldsymbol{a}_3^*+h_4\boldsymbol{a}_4^*, \tag{1}$$

with

$$\boldsymbol{a}_1^*=\boldsymbol{a}^*,\ \ \boldsymbol{a}_2^*=\boldsymbol{b}^*,\ \ \boldsymbol{a}_3^*=\boldsymbol{c}^*,\ \ \boldsymbol{a}_4^*=\boldsymbol{q}+\boldsymbol{d}. \tag{2}$$

Here $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$ are reciprocal lattice vectors of the three-dimensional basic structure, $\boldsymbol{q}$ is the modulation wave vector and $\boldsymbol{d}$ is a unit vector in the fourth dimension perpendicular to $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$. Vectors $\boldsymbol{a}_1^*$, $\boldsymbol{a}_2^*$, $\boldsymbol{a}_3^*$ and $\boldsymbol{a}_4^*$ define a reciprocal lattice in four-dimensional space. The incommensurate modulated structure can be described by a four-dimensional periodic structure with the corresponding lattice defined as $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ and $\boldsymbol{a}_4$. A position vector in the four-dimensional space is written as

$$\boldsymbol{X}=x_1\boldsymbol{a}_1+x_2\boldsymbol{a}_2+x_3\boldsymbol{a}_3+x_4\boldsymbol{a}_4, \tag{3}$$

while that in the three-dimensional space is denoted by

$$\boldsymbol{r}=x\boldsymbol{a}+y\boldsymbol{b}+z\boldsymbol{c}, \tag{4}$$

where $\boldsymbol{a}$, $\boldsymbol{b}$ and $\boldsymbol{c}$ are the reciprocal vectors of $\boldsymbol{a}^*$, $\boldsymbol{b}^*$, and $\boldsymbol{c}^*$, respectively. The modulation wave can be expressed in terms of a Fourier series. The vth component of the deviation $\boldsymbol{u}$ is given by

$$u_v=\sum_n \{U_v(n)\cos[2\pi n\boldsymbol{q}\cdot(\bar{\boldsymbol{r}}_v+\boldsymbol{L})]+V_v(n)\sin[2\pi n\boldsymbol{q}\cdot(\bar{\boldsymbol{r}}_v+\boldsymbol{L})]\}, \tag{5}$$

where v stands for x, y or z, $\bar{\boldsymbol{r}}$ for the atomic position in the basic structure, and $\boldsymbol{L}$ is a lattice vector. With this description, the Sayre equation[12] can be extended into the four-dimensional space[8]:

$$\boldsymbol{F}(\hat{\boldsymbol{H}})=(\theta/V)\sum_{\hat{H}'}\boldsymbol{F}(\hat{H}')\boldsymbol{F}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}'), \tag{6}$$

where θ is an atomic form factor and V is the unit cell volume of the three-dimensional basic structure. The right-hand side of (6) can be split into three parts, i.e.

$$\boldsymbol{F}(\hat{\boldsymbol{H}})=(\theta/V)\left[\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}')+2\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}')+\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}')\right], \tag{7}$$

where subscript m denotes the main reflections while subscript s denotes satellite reflections. As the satellite reflections are in average much weaker than the main reflections, to the first approximation of the main reflections, we have

$$\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}})=2(\theta/V)\sum_{H'}\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}'). \tag{8}$$

This implies that the phases of main reflections can be calculated by conventional direct method. On the other hand, let $\boldsymbol{F}(\hat{\boldsymbol{H}})$ on the left-hand side of (7) correspond to a satellite reflection. Then the first summation on the right-hand side of (7) will vanish. We thus have

$$\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}})=(\theta/V)\left[2\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}')+\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}')\right]. \tag{9}$$

Since terms in the second summation on the right-hand side of (9) will be in average much smaller than those of the first summation, (9) can be further simplified to give

$$\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}})=2(\theta/V)\sum_{\hat{H}'}\boldsymbol{F}_{\mathrm{m}}(\hat{\boldsymbol{H}}')\boldsymbol{F}_{\mathrm{s}}(\hat{\boldsymbol{H}}-\hat{\boldsymbol{H}}'). \tag{10}$$

Accordingly, phases of satellite reflections can be derived using eqs. (9) and (10) provided that the phases of main reflections are known[9] in advance. Therefore, we can calculate a Fourier map that reveals directly the details of the modulated structure before a model is

constructed.

2 Experimental

Single crystals with the nominal composition of $Bi_{1.8}Sm_{0.2}Sr_2Ca_2Cu_3O_y$ were grown and examined by SEM scanning electron microscope to confirm the existence of Sm. A single crystal with dimensions 0.38, 0.15 and 0.01 mm in the ***a***, ***b*** and ***c*** directions was selected for X-ray diffraction data collection on an ENRAF NONIUS CAD4 diffractometer using MoKα radiation. 543 main reflections, 867 first-order and 469 second-order satellites were collected and were used for the structure determination.

3 Structural determination

As shown in sec. 2, the 543 main reflections can be considered as the diffraction data of a conventional three-dimensional crystal associated with the basic structure, which has the space group *Bbmb*. A rough model of the basic structure was first derived by the three-dimensional direct-method program SAPI91[13], followed by several cycles of Fourier recycling. Thus, a set of phases of the 543 main reflections was obtained. Then, the phases of all the 867 first-order and 469 second-order satellite reflections were derived by DIMS with the default control using the phases of main reflections as input. The four-dimensional Fourier map was calculated with the amplitudes of structure factors and phases derived above. To give a visual impression on the characteristics of the modulated structure, the x_3-x_4 section of the Fourier map is shown in fig. 1, while the three-dimensional electron density distribution map projected along the ***a*** asix is given in

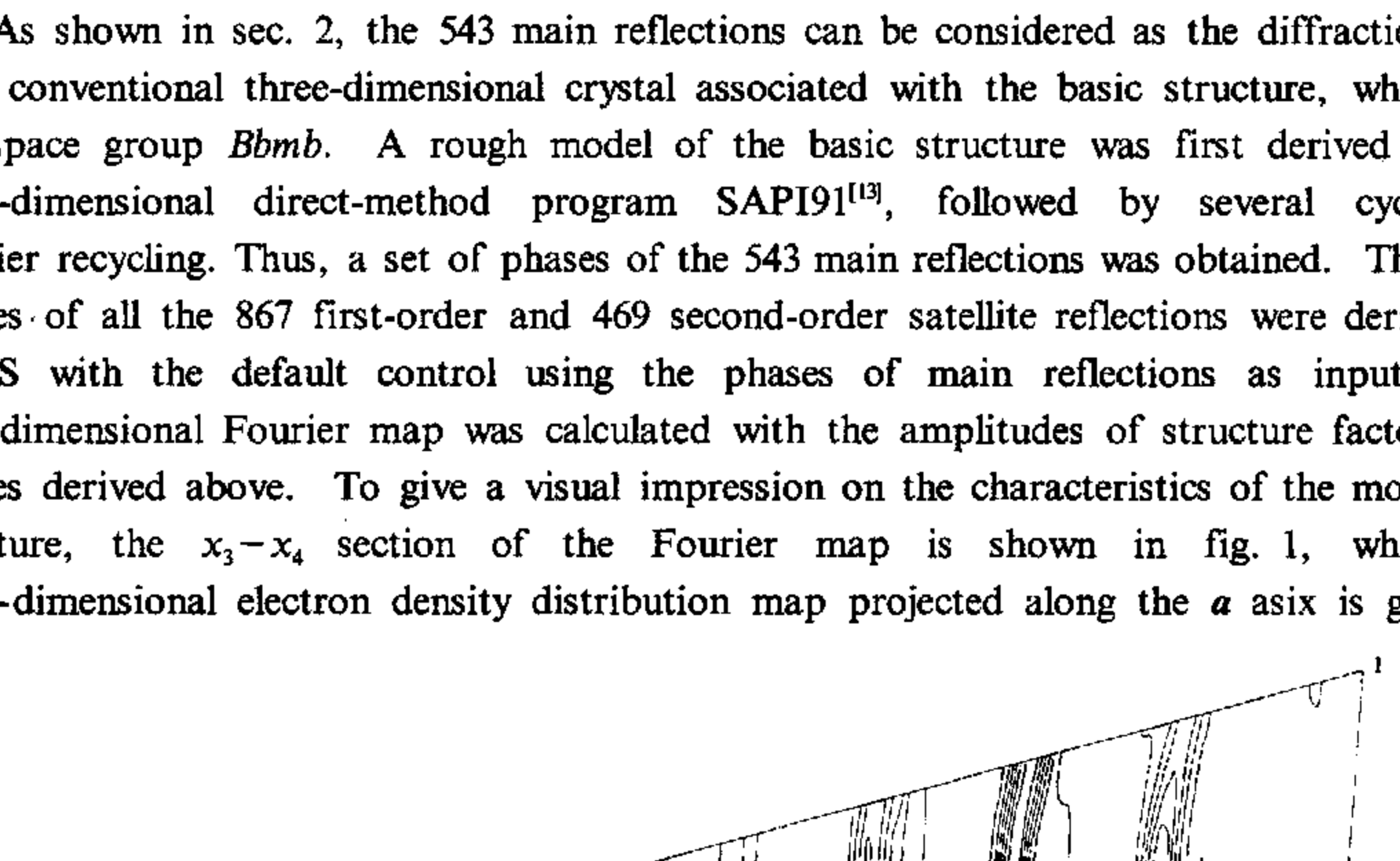

Fig. 1. A section ($x_1=0.25$, $x_2=0$) on the four-dimensional Fourier map containing: Bi, Sr, Ca, Cu.

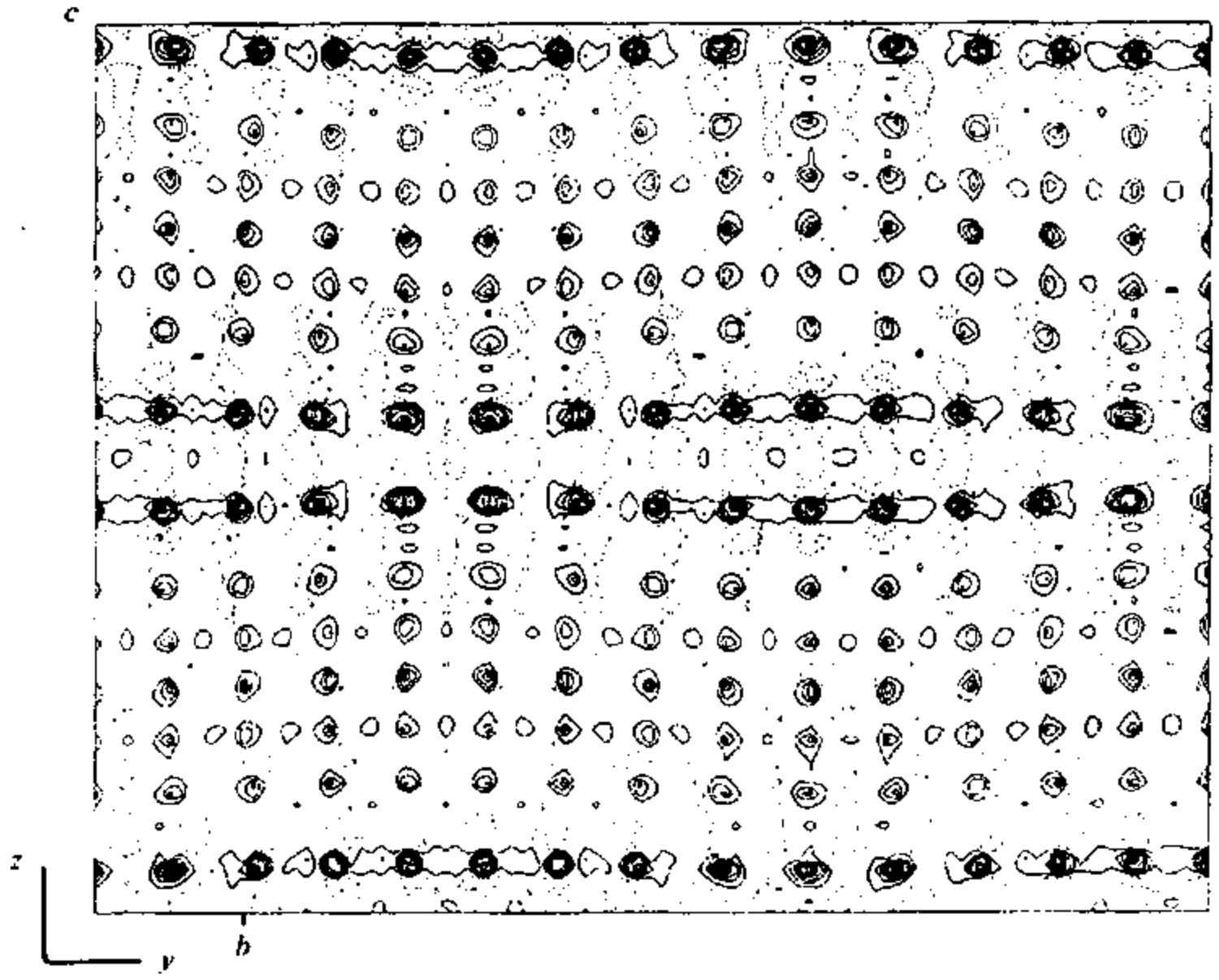

Fig. 2. The incommensurate modulated structure in three-dimensional space projected along the *a* axis. Dotted lines represent negative values.

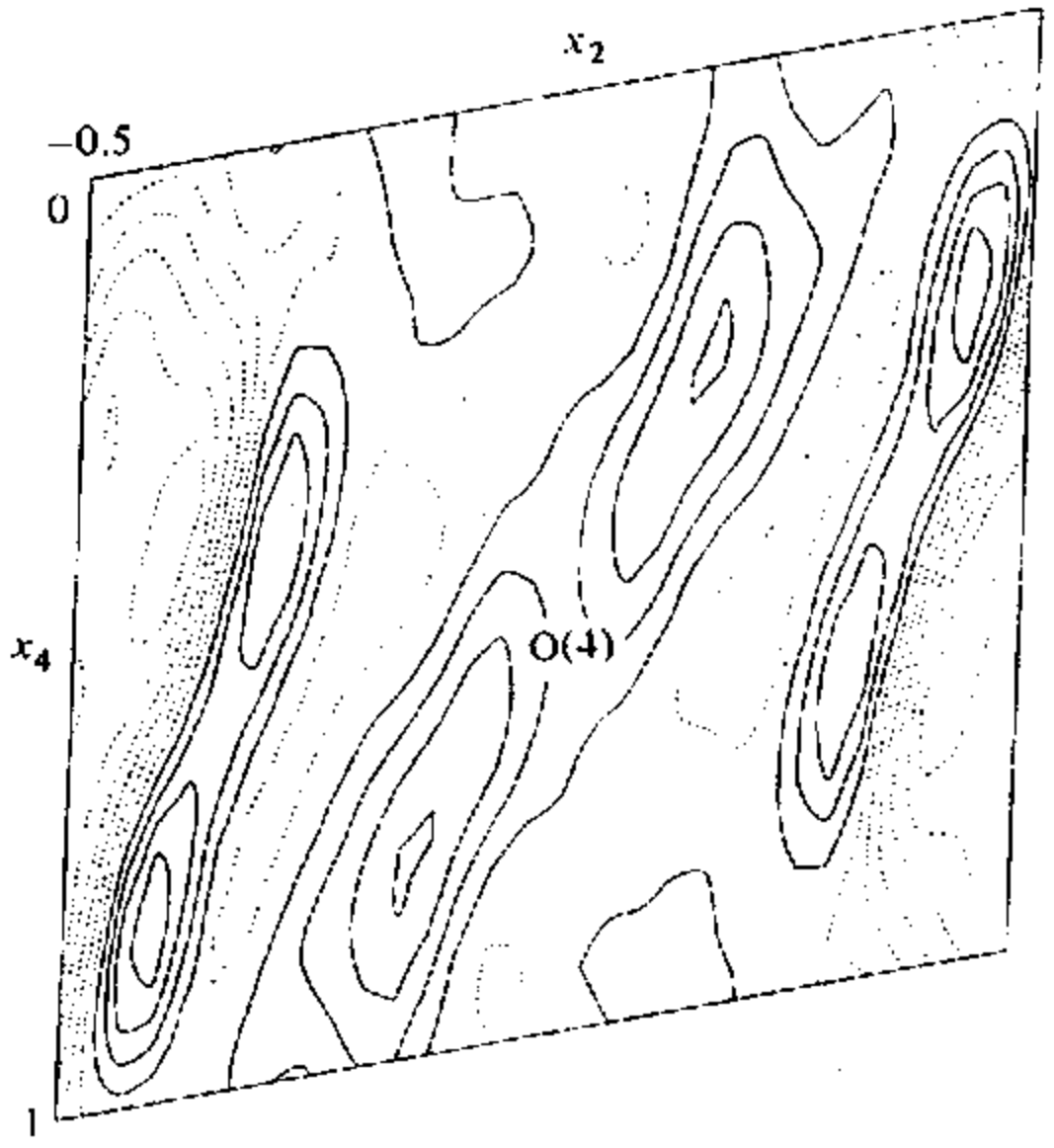

Fig. 3. A section ($x_1=0.145$, $x_3=0.0584$) on the four-dimensional Fourier map containing oxygen atoms in Bi -O layer ($x_1=0.145$, $x_3=0.0584$). Dotted lines represent negative values.

fig. 2. The atomic positions were searched in the four-dimensional space. The positional parameters thus obtained are listed in table 1. The modulation waves were then measured directly form the four-dimensional Fourier map for all the metal atoms and the oxygen atoms, which are also shown in table 1. The results in table 1 consist well with those from the structure refinement with the same superspace group[1, 2] except for the modulation of oxygen atoms in Bi-O layers. The measurement indicates that the displacement of the oxygen atoms in BiO layers cannot be properly described by a superposition of harmonic functions (5) using only a few harmonic components. In fact, the fourdimensional Fourier maps indicate that the modulation wave of these oxygen atoms is sawtoothlike (see fig. 3) which should be described by a sawbooth-shaped function. This result consists with that obtained by Coppens and his colleagues[3, 5]. By assigning the occupational and thermal

Table 1 Positional parameters of the basic structure and the amplitude of the displacive waves

Atom			cos(2πt)	cos(4πt)	sin(2πt)	sin(4πt)
Bi	x	7713	8	0		
	y	0			703	93
	z	510	−51	−1		
Sr	x	2519	−9	14		
	y	0			440	104
	z	1383	−85	−6		
Ca	x	2500	1	0		
	y	0				
	z	2500	−97	0		
Cu	x	7494	0	1		
	y	0			82	−1
	z	1953	−92	−6		
O1	x	0			12	−18
	y	2496			113	−4
	z	1960	−84	−1		
O2	x	5000			36	2
	y	2500			102	21
	z	1967	−82	0		
O3	x	2787	63	−35		
	y	5000			1008	530
	z	1184	−75	2		
O4	x	1450	*	*		
	y	0			*	*
	z	584	*	*		

The third column represents the parameters for the basic structure. The fourth to seventh columns are the amplitudes of the harmonic components of the displacive modulation waves. All the values have been multiplied by a factor 10^4. An asterisk * indicates that the modulation wave cannot be properly described by a super-position of harmonic functions (5) using only a few terms. A blank indicates that the component is not allowed by the symmetry.

parameters, 1.0 and 0.01 nm^2 to all the atoms, the overall *R*-factor is 27.5%, which is a fairly good value for a structure model before least-squares refinement.

4 Discussion

Although there have already been numerous reports on the determination of incommensurate modulated structure of the Bi-2212 superconducting phase, the present study directly revealed the details of the modulation for the first time on a Fourier map without relying on any given model. The structural details including the modulation of oxygen atoms were clearly recognized on the original direct-method phased *E*-map and were stable during the subsequent Fourier recycling and least-squares refinement.

One of the most interesting features on the modulation of high T_c super-conducting oxides is the modulation of oxygen atoms. Different results have been reported in previous studies. Our result gives direct evidence of the so-called sawtoothlike modulation of oxy-

gen atoms in Bi-O layers (see fig. 3). This is consistent with that obtained by Coppens and his colleagues[3,5] from a least-squares refinement procedure starting with a given model.

In the *ab initio* determination of structure modulation by a least-squares refinement procedure, it is often difficult to distinguish occupational modulation from temperature-factor modulation. However, this would not be a problem if we could calculate Fourier map before constructing the modulation model. Both occupational modulatio and temperature-factor modulation cause variation in height of atoms. However in the former case the higher atoms occupy a broader area on the Fourier map while, in the latter case the higher atoms occupy a narrower area. As is seen in fig. 2, the metal atoms especially bismuth atoms have temperature-factor modulation rather than occupational modulation. This result is again consistent with that of Coppens and his colleagues[3, 5].

References

1 Gao, Y., Lee, P., Coppens, P. *et al.*, The incommensurate modulation of the 2212 Bi-Sr-Ca-Cu-O superconductor, Cu-O superconductor, *Science*, 1988, 241: 954.

2 Yamamoto, A., Onoda, M., Takayama-Muromachi, E. *et al.*, Rietveld analysis of the modulated structure in the superconducting oxide $Bi_2(Sr, Ca)_3Cu_2O_{8+x}$, *Phys. Rev.*, 1990, B42: 4228.

3 Petricek, V., Gao, Y., Lee, P. *et al.*, X-ray analysis of the incommensurate modulation in the 2:2:1:2 Bi-Sr-Ca-Cu-O superconductor including the oxygen atoms, *Phys. Rev.*, 1990, B42: 387.

4 Kan, X. B., Moss, S. C., Four-dimensional crystallographic analysis of the incommensurate modulation in a $Bi_2Sr_2CaCu_2O_8$ single crystal, *Acta Cryst.*, 1992, B48: 122.

5 Gao, Y., Coppens, P., Cox, D. E., *et al.*, Combined X-ray single-crystal and neutron powder refinement of modulated structures and application to the incommensurately modulated structure of $Bi_2Sr_2CaCu_2O_{8+y}$, *Acta Cryst.*, 1993, A49: 141.

6 Gao, Y., Coppens, P., Ye, J. *et al.*, The incommensurate modulation in the $Bi_2Sr_{2-x}Ca_xCuO_6$ superconductor, and its relation to the modulation in $Bi_2Sr_{2-x}Ca_xCu_2O_8$, *Physica*, 1990, C160: 431.

7 Mo, Y. D., Cheng, T. Z., Fan, H. F. *et al.*, Structure features of the incommensurate modulation in the Pb-doped Bi-2223 high-T_c phase revealed by direct-method electron diffraction analysis, *Supercond. Sci. Technol.*, 1992, 5: 69.

8 Hao, Q., Liu, Y. W., Fan, H. F., Direct methods in superspace. I. Preliminary theory and test on the determination of incommensurate modulated structures, *Acta Cryst.*, 1987, A43: 820.

9 Fu, Z. Q., Fan, H. F., DIMS-a direct method program for incommensurate modulated structures, *J. Appl. Cryst.*, 1994, 27: 124.

10 Wolff, P. M. De, The pseudo-symmetry of modulated crystal structures, *Acta Cryst.*, 1974, A33: 777.

11 Janner, A., Janssen, T., Symmetry of periodically distorted crystals, *Phys. Rev.*, 1977, B15, 643.

12 Sayre, D., The squaring method: A new method for phase determination, *Acta Cryst.*, 1952, 5: 60.

13 Fan, H. F., Yao, J. X., Zheng, C. D., *SAPI*-91: *A Computer Program for Automatic Solution of Crystal Structures From X-ray Diffraction Data*, 1991, Institute of Physics, Chinese Academy of Sciences, Beijing.