Supercond. Sci. Technol. 5 (1992) 69–72. Printed in the UK

Structural features of the incommensurate modulation in the Pb-doped Bi-2223 high-T_c phase revealed by direct-method electron diffraction analysis

Y D Mo†, T Z Cheng‡, H F Fan†‡, J Q Li†§, B D Sha‡, C D Zheng†, F H Li† and Z X Zhao†§

† Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China
‡ Laboratory of Structure Analysis, University of Science and Technology of China, Hefei 230026, People's Republic of China
§ National Laboratory for Superconductivity, Chinese Academy of Sciences, PO Box 603, Beijing 100080, People's Republic of China

Received 10 September 1991

Abstract. Structural modulation waves in the Pb-doped Bi-2223 ($Bi_2Sr_2Ca_2Cu_3O_x$) phase are observed for the first time on the potential distribution function projected along the ***a*** axis. The newly developed multidimensional direct methods were used. Unlike the previous techniques, there is no need to assume any modulation model before the modulation waves can be seen directly from the resulting Fourier map. The symmetry of the title compound belongs to the four-dimensional space group P^{Bbmb}_{111} with three-dimensional unit cell parameters $a = 5.49$ Å, $b = 5.41$ Å, $c = 37.1$ Å, $\alpha = \beta = \gamma = 90°$ and the modulation wavevector $q = 0.117b^*$. Occupational and positional modulations are obvious for most atoms. Disordered oxygen atoms arranged perpendicular to the ***b*** axis bridging the Cu(2)–Ca–Cu(1)–Ca–Cu(2) layers were observed.

1. Introduction

The Pb-doped Bi-2223 phase is the highest-T_c phase in the Bi–Sr–Ca–Cu–O system. There have been very few reports on the structural investigation of this phase, since single crystals suitable for x-ray diffraction analysis are extremely difficult to prepare. Ikeda *et al* [1] obtained high-resolution electron micrographs of the Pb-doped Bi-2223 phase. Incommensurate modulation was observed but only very limited structural details have been recognized. The electron diffraction study by Li *et al* [2] gave the super-space group and the corresponding unit cell parameters but no further details on the modulation. Sequeira *et al* [3] reported an analysis using the neutron powder diffraction technique, from which only the average structure has been determined. There remains great interest on the incommensurate modulation of the Pb-doped Bi-2223 phase. The present work is based on the symmetry and unit cell parameters found by Li *et al* [2] and the average structure obtained by Sequeira *et al* [3]. Experimental data were measured from the electron diffraction pattern normal to the ***a*** axis. Diffraction analysis led to the potential distribution function projected along this axis. Since the length of this axis is rather short (5.49 Å), there could be hardly any overlap of symmetrically independent metal atoms on the projection.

2. Experiment

Specimens used for taking electron diffraction photographs were prepared by grinding and ion thinning. A Hitachi H-9000 electron microscope was used to carry out the electron diffraction experiment. Figure 1 shows the electron diffraction pattern normal to the ***a*** axis. One-dimensional modulation parallel to the ***b*** axis is clearly seen. All the main and satellite reflections can be indexed as $0klm$ using a four-dimensional reciprocal lattice, the lattice vector of which is expressed as $H = ha^* + kb^* + lc^* + mq$ where a^*, b^* and c^* are reciprocal vectors of ***a***, ***b*** and ***c***, which define the unit cell for the average structure in three-dimensional space. q ($= 0.117b^*$) is the modulation wavevector. The modulation wave is thus parallel to the ***b*** axis with a period of 46.2 Å which is 8.54 times longer than b.

Five photographs were taken with different exposure times for the same electron diffraction pattern. This is an analogue of the multifilm method in x-ray crystallography for the collection of diffraction intensities. A

0953-2048/92/020069 + 04 $04.50

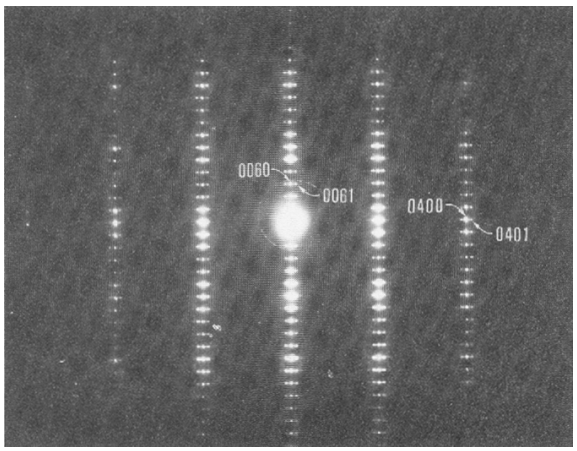

Figure 1. Electron diffraction pattern of the Pb-doped Bi-2223 phase taken with the beam direction parallel to the *a* axis.

Perkin-Elmer PDS microdensitometer data acquisition system with a 20 × 20 μm^2 aperture was used to digitize the photographs. The whole pattern was divided into 2251 × 2251 pixels. The integrated intensity of each reflection was obtained by summing up the density, $\ln(I_0/I)$, of the pixels within the diffraction spot and then subtracting the background. Diffraction intensities were finally calibrated with the exposure time. Structure factor amplitudes were obtained as the square root of diffraction intensities. The R factor for the discrepancy of symmetrically related reflections is 0.12 for the main and 0.13 for the satellite reflections. There are in total 112 independent $0klm$ reflections including 42 main and 70 first-order satellite reflections. A few second-order satellites were also observed; however, they are much weaker than the first-order ones and hence are neglected in the following analysis.

3. Structure analysis

The structure analysis was carried out in four-dimensional space. The four-dimensional real and reciprocal unit cells are defined respectively as

$$\boldsymbol{a}_1 = \boldsymbol{a}, \quad \boldsymbol{a}_2 = \boldsymbol{b} - 0.117\boldsymbol{d}, \quad \boldsymbol{a}_3 = \boldsymbol{c}, \quad \boldsymbol{a}_4 = \boldsymbol{d}$$

and

$$\boldsymbol{b}_1 = \boldsymbol{a}^*, \quad \boldsymbol{b}_2 = \boldsymbol{b}^*, \quad \boldsymbol{b}_3 = \boldsymbol{c}^*, \quad \boldsymbol{b}_4 = 0.117\boldsymbol{b}^* + \boldsymbol{d}$$

where $\boldsymbol{d}$ is the unit vector normal to the three-dimensional space, i.e. a unit vector simultaneously perpendicular to the vectors $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$, $\boldsymbol{a}^*$, $\boldsymbol{b}^*$ and $\boldsymbol{c}^*$. An atom in the four-dimensional space without modulation will have the shape of an infinite straight bar parallel to the fourth dimension $\boldsymbol{a}_4$. Occupational modulation will periodically change the width, while positional modulation will periodically change the direction of the bar. Our task is to find such a periodic change, the modulation wave, for each atom from the four-dimensional Fourier map. The incommensurate modulated structure can be obtained by cutting the four-dimensional Fourier map with a three-dimensional hyperplane normal to the direction $\boldsymbol{a}_4$. For details of the multi-dimensional representation of incommensurate modulated structures the reader is referred to the papers by de Wolff [4], de Wolff *et al* [5] and Yamamoto [6]. The phases of $0kl0$ main reflections were calculated from the known average structure, while the phases of $0klm$ satellite reflections were derived by the phase extension starting from the known phases of main reflections using the multidimensional direct method proposed by Hao *et al* [7]. A Fourier map was then calculated with the amplitudes of structure factors and phases from the average structure and from the direct-method phase extension. This gave a four-dimensional potential distribution function projected along the $\boldsymbol{a}$ axis, i.e.

$$\int_0^1 \varphi(x_1, x_2, x_3, x_4)\, \mathrm{d}x_1$$

where $\varphi(x_1, x_2, x_3, x_4)$ is the potential distribution function of the structure in four-dimensional space and is a four-dimensional periodic function. x_1, x_2, x_3 and x_4 are fractional coordinates in the direction of $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ and $\boldsymbol{a}_4$ respectively. Modulation waves were measured directly from $\int_0^1 \varphi(x_1, x_2, x_3, x_4)\, \mathrm{d}x_1$ for all atoms except two oxygen atoms, which overlap with Bi and Sr atoms respectively on the projection. Based on the modulation parameters of metal atoms and parameters of the average structure, Fourier recycling was carried out. All parameters except the temperature factor were adjudged after each cycle. The R factor decreased from 0.55 to 0.32 for the main reflections, and from 0.37 to 0.32 for the satellite reflections. Least-squares refinement led further to an R factor of 0.16 for the main and 0.17 for the satellite reflections. Details on the structure analysis will be published elsewhere.

4. Results and discussion

A section of the final Fourier $\int_0^1 \varphi(x_1, x_2, x_3, x_4)\, \mathrm{d}x_1$ at $x_2 = 0$ is shown in figure 2. It is seen that the potential at the sites of all metal atoms varies along the $\boldsymbol{a}_4$ direction. This indicates that occupational modulation exists for all metal atoms. Besides, the coordinate x_3 for the maximum potential of all metal atoms except Cu(1) also varies with x_4, indicating the existence of positional modulation for all but Cu(1) metal atoms. The maximum displacement perpendicular to the $\boldsymbol{a}_1$ axis is about 0.31 Å for Bi, 0.07 Å for Sr, 0.04 Å for Cu(2), 0.17 Å for Ca and 0.00 Å for Cu(1). By cutting $\int_0^1 \varphi(x_1, x_2, x_3, x_4)\, \mathrm{d}x_1$ normal to the $\boldsymbol{a}_4$ axis we obtained the Fourier projection $\varphi(y, z)$ of the incommensurate modulated structure in the three-dimensional real space, where y and z are fractional coordinates in the direction of $\boldsymbol{b}$ and $\boldsymbol{c}$ axes respectively. The result is shown in figure 3. Ten unit cells (a = 5.49 Å, b = 5.41 Å, c = 37.1

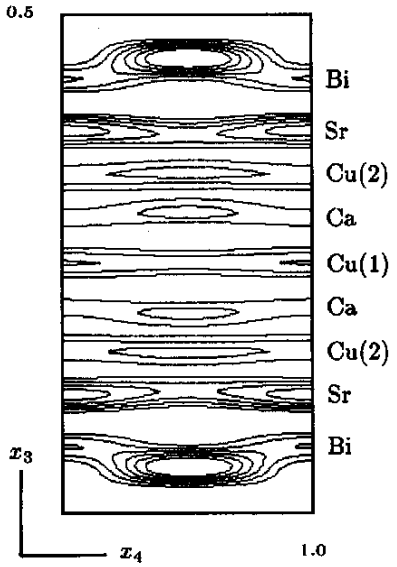

Figure 2. Contour map of the $\int_0^1 \varphi(x_1, 0, x_3, x_4)\, dx_1$, section of the projected four-dimensional Fourier map (potential distribution function) of the Pb-doped Bi-2223 phase.

Å) of the average structure are plotted along the ***b*** direction. Here we can see how the atoms are modulated from one unit cell to the other. Both occupational and positional modulations are evident for Bi atoms. The strong occupational modulation of Bi implies a large number of Bi vacancies disordered on the planes normal to the ***b*** axis. This explains the low average occupancy (0.66) for Bi atoms. The same feature is also found for Ca and Sr atoms. Another prominent feature that can be seen in figure 3 is that oxygen atoms of the Cu–O layers move towards the Ca layer, forming a disordered oxygen bridge across the layers of Cu(2)–Ca–Cu(1)–Ca–Cu(2). In addition, occupational and positional modulations along the ***b*** axis are also found for the disordered oxygen atoms.

5. Conclusion

Knowing only average structures is not enough for an understanding of superconductivity. The techniques used in this study are capable of revealing something more than an average structure and leading, hopefully, to something new in our understanding. It is seen that multidimensional direct methods are powerful for the determination of incommensurate modulated structures without relying on any hypothetical modulation model. The use of electron diffraction instead of x-ray or neutron diffraction is proved to be successful for the crystal structure analysis of imperfect crystalline samples with small grain size and for locating oxygen atoms in the presence of heavy metal atoms.

The present study concluded that, in the Pb-doped Bi-2223 high-T_c phase, occupational and positional modulations exist simultaneously for all metal atoms, except Cu(1), and for some oxygen atoms. It also concluded that the Cu(2)–Ca–Cu(1)–Ca–Cu(2) layers are bridged by disordered oxygen atoms arranged on lines perpendicular to the ***b*** axis. The homogeneity of superconductivity should be strongly affected by the above features and by the fact that the modulation wavelength is much longer than the superconducting coherence length.

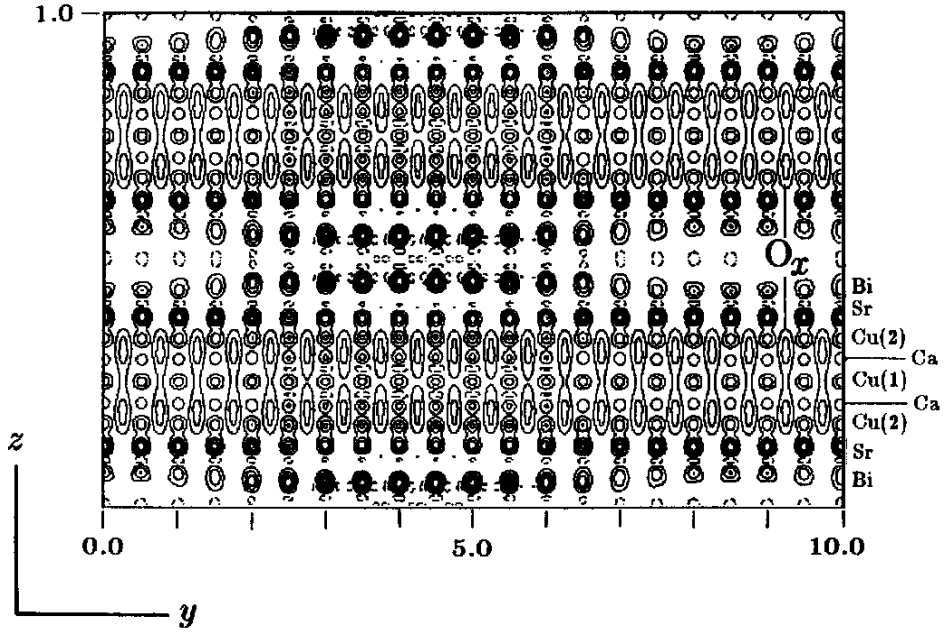

Figure 3. Contour map of the $\varphi(y, z)$, three-dimensional potential distribution function of the Pb-doped Bi-2223 phase projected along the ***a*** axis. Ten unit cells are plotted along the ***b*** axis, showing the period of modulation to be approximately 8.5 times the length of ***b***.

Acknowledgment

This work was supported in part by the National Natural Science Foundation of China.

References

[1] Ikeda S, Aota K, Hatano T and Ogawa K 1988 *Japan. J. Appl. Phys.* **27** L2040
[2] Li J Q, Yang D Y, Li F H, Zhou P, Zheng D N, Ni Y M, Jia S L and Zhao Z X 1989 *Prog. High-T_c Supercond.* **22** 441
[3] Sequeira A, Yakhmi J V, Iyer R M, Rajagopal H and Sastry P V P S S 1990 *Physica C* **167** 291
[4] de Wolff P M 1974 *Acta Crystallogr.* A **30** 777
[5] de Wolff P M, Janssen T and Janner A 1981 *Acta Crystallogr.* A **37** 625
[6] Yamamoto A 1982 *Acta Crystallogr.* A **38** 87
[7] Hao Q, Liu Y W and Fan H F 1987 *Acta Crystallogr.* A **43** 820