INSTITUTE OF PHYSICS PUBLISHING SUPERCONDUCTOR SCIENCE AND TECHNOLOGY

Supercond. Sci. Technol. **18** (2005) 813–817 doi:10.1088/0953-2048/18/6/004

New superconducting phase of $Sr_2CuO_{2+\delta}Cl_{2-y}$ with 0201-type structure synthesized under high pressure

H Yang, Q Q Liu, R C Yu[1], F Y Li and C Q Jin

Laboratory for Extreme Condition Physics, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, PO Box 603, Beijing 100080, People's Republic of China

E-mail: rcyu@aphy.iphy.ac.cn

Received 7 March 2005
Published 25 April 2005
Online at stacks.iop.org/SUST/18/813

Abstract

K_2NiF_4-type $Sr_2CuO_{2+\delta}Cl_{2-y}$ superconductor was synthesized with partial substitution of oxygen for apical chlorine using a high-pressure technique. This phase has been studied by transmission electron diffraction, convergent beam electron diffraction, x-ray powder diffraction, energy dispersive analysis of x-ray, electron energy loss spectroscopy and high-resolution electron microscopy. The crystal structure with a space group of $I4/mmm$ has been determined, and the lattice parameters are obtained as $a = b = 0.394$ nm and $c = 1.564$ nm. Edge dislocations with Burgers vector $b = \frac{1}{2}c$ are observed in the phase.

1. Introduction

The undoped parent compound $Sr_2CuO_2Cl_2$ with the apical sites outside the CuO_2 planes fully occupied by chlorine is an antiferromagnetic Mott insulator with a Néel temperature of 256 K [1]. There are three types of oxyhalide cuprates with the K_2NiF_2 structure, i.e., $Sr_2CuO_2Cl_2$, $Sr_2CuO_2F_2$ and $Ca_2CuO_2Cl_2$. In the latter two compounds the superconductivity could be induced when doped with proper holes [2–6], so it is possible that $Sr_2CuO_2Cl_2$ can be converted into a superconductor when doped with sufficient carriers. Tohyama and Maekawa [7] theoretically predicted that the maximum T_c of $Sr_2CuO_2Cl_2$ would be 26 K if proper hole doping could be achieved. Novikov *et al* [8] proposed that the optimal hole concentration would be 0.35–0.38 holes per unit cell. However, Hiroi *et al* [5] attempted to dope $Sr_2CuO_2Cl_2$ with sodium and potassium, but there was no indication of substitution or hole carrier doping.

In 1995, Jin *et al* [9, 10] reported a high-pressure synthesized Sr–Ca–Cu–O–Cl superconductor with the 0212-type ($La_2SrCu_2O_6$-type) structure, which has superconductivity at 80 K induced by partial substitution of oxygen for apical chlorine. Later, the 0223-type Sr–Ca–Cu–O–Cl superconducting phase with a T_c of 35 K and higher members of the same homologous series have also been synthesized by partial substitution of oxygen for apical chlorine [11]. These works have proved that hole doping of a copper oxyhalide by partial substitution of oxygen for apical chlorine is considered to be another effective way to induce superconductivity in it. In 1998, Tatsuki *et al* [12] reported that they successfully doped holes to $Sr_2CuO_2Cl_2$ by partial substitution of oxygen for apical chlorine using a high-pressure technique, but superconductivity was absent in their samples even when the nominal hole content reached 0.55 per unit cell. They speculated that the amount of mobile holes in the CuO_2 sheets of $Sr_2CuO_{2+\delta}Cl_{2-y}$ was not enough to cause superconductivity. In the present study, we succeeded in synthesizing K_2NiF_4-type $Sr_2CuO_{2+\delta}Cl_{2-y}$ superconductor (transition temperature $T_c = 30$ K for $y = 0.8$) with partial substitution of oxygen for the apical chlorine by using a different high-pressure technique. The details of the synthetic procedures and its superconductivity are given in [13]. The successful synthesis of K_2NiF_4-type $Sr_2CuO_{2+\delta}Cl_{2-y}$ superconductor provides an opportunity to further understand the role of the apical oxygen atoms in high-T_c cuprate superconductors.

In this paper, we mainly report structural characteristics of the $Sr_2CuO_{2+\delta}Cl_{2-y}$ superconductor studied by means of electron diffraction (ED), convergent beam electron diffraction (CBED), x-ray powder diffraction (XRD), energy dispersive analysis of x-ray (EDX), parallel electron energy loss spectroscopy (EELS) and high-resolution transmission electron microscopy (HRTEM).

[1] Author to whom any correspondence should be addressed.

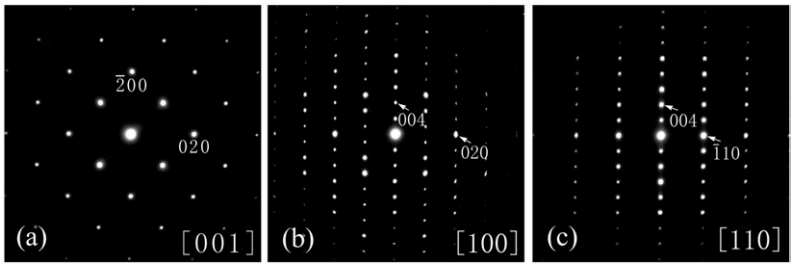

Figure 1. ED patterns of $Sr_2CuO_{2+\delta}Cl_{2-y}$. (a) [001]; (b) [100]; (c) [110].

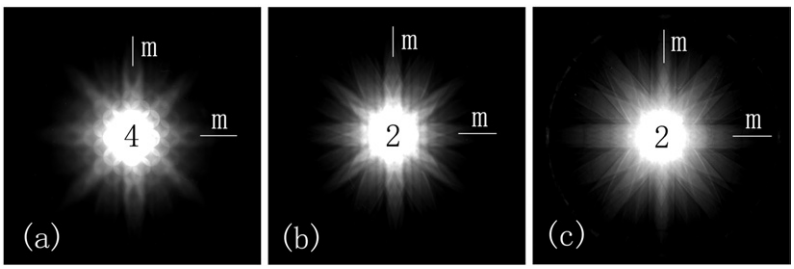

Figure 2. CBED patterns of $Sr_2CuO_{2+\delta}Cl_{2-y}$. (a) [001], fourfold symmetry and two mirror planes are clearly seen; (b) [100] and (c) [110], twofold symmetry and two mirror planes are clearly seen.

2. Experiments

The compound was synthesized at 1050 °C for 1 h under 6 GPa using Sr_2CuO_3 and $Sr_2CuO_2Cl_2$ which were prepared as precursors by a conventional solid state reaction method. The details of the sample preparation are given in [13]. Thin samples for ED, CBED, EDX, EELS and HRTEM studies were prepared by mechanical thinning followed by argon ion milling. A liquid nitrogen cold stage was used during ion milling to reduce the damage by ion beams. ED and CBED experiments were carried out on Philip CM 12 with large angle tilt at 100 keV, and EDX, EELS and HRTEM measurements were performed on a Tecnai F20 electron microscope operated at 200 keV with a field emission gun.

3. Results and discussion

The ED and HRTEM investigations on a large number of grains of the sample suggest that the sample is almost single phase, and the structural characteristics of the phase were characterized by means of ED, CBED, XRD and HRTEM.

A series of ED patterns was obtained from the sample, and three main zones [001], [100] and [110] are shown in figures 1(a)–(c), respectively. It is clearly seen that the diffraction spots in figure 1(a) construct centered square arrays, indicating a tetragonal lattice, and the diffraction spots in figure 1(b) suggest a systematic absence in the $00l$ and $0k0$ reflections when l and k are odd. Some spots are indexed in the patterns. The observed extinction rules in the diffraction patterns obtained in the experiments are:

$$hkl : h + k + l = 2n$$

$$hk0 : h + k = 2n$$

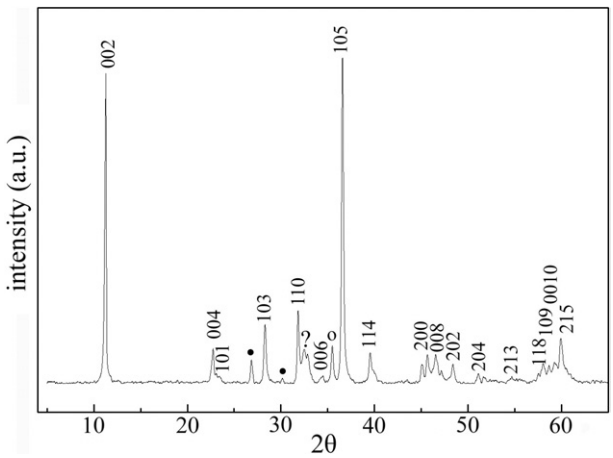

Figure 3. X-ray powder diffraction pattern for the sample $Sr_2CuO_{2+\delta}Cl_{2-y}$. The major phase can be indexed into the Cl-0201 structure with space group $I4/mmm$. The impurity phases were identified to be CuO (○), $SrCl_2{\cdot}Sr(OH)_2{\cdot}H_2O$ (●), and unknown phase (?).

$$0kl : k + l = 2n$$

$$00l : l = 2n$$

$$0k0 : k = 2n.$$

Figures 2(a)–(c) show the CBED patterns along the [001], [100] and [110] zone axes, respectively. It is clear that two perpendicular mirror planes exist in each of the patterns. Fourfold symmetry is clearly seen in figure 2(a) and twofold symmetry obviously exists in both patterns of figures 2(b) and (c). The CBED patterns denote that the crystal structure belongs to the point group $4/m2/m2/m$. According to the

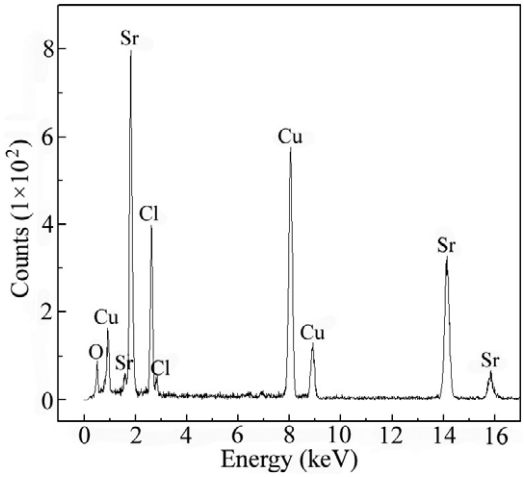

Figure 4. A typical TEM-EDX chart for a well grown grain in the phase $Sr_2CuO_{2+\delta}Cl_{2-y}$.

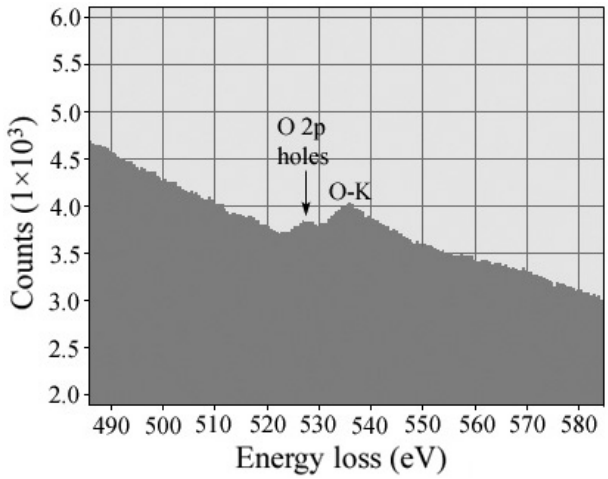

Figure 5. O 1s absorption edge of $Sr_2CuO_{2+\delta}Cl_{2-y}$. One observes a pre-peak at 528.5 ± 1 eV, which corresponds to transitions from the O 1s core state into doped unoccupied O 2p states near E_F.

analyses of the ED patterns and the CBED patterns, the space group $I4/mmm$ is the definite choice. Using the space group $I4/mmm$, most of the peaks in the x-ray powder diffraction pattern can be indexed (see figure 3). Based on the proposed space group and the XRD, the structural parameters of the phase were refined by using the software Fullprof, and the results were reported in [13]. The refined cell constants $a = b = 3.9435(2)$ Å and $c = 15.6426(1)$ Å are in good agreement with those derived from the ED patterns.

The composition analysis for the phase was performed on tens of well grown grains using TEM-EDX (figure 4 shows a typical TEM-EDX chart for a grain) and the analysed average Sr, Cu and Cl atomic ratio is 2:1:1.38, which is very close to that obtained from the XRD refinement [13]. The results obtained from TEM-EDX and the refinement of XRD data suggest that there is insufficient Cl fully occupying the apical site. As the sample was synthesized under a high oxidizing pressure, it is reasonable to assume that a few oxygens are in turn incorporated in the apex. On the other hand, the increase of the c axis length ($a = 0.394$ nm, $c = 1.564$ nm for $Sr_2CuO_{2+\delta}Cl_{2-y}$, while $a = 0.397$ nm, $c = 1.561$ nm for $Sr_2CuO_2Cl_2$ [1]) is considered to be the enhancement of Coulomb repulsion between the adjacent chlorine (monovalent) layers resulting from the introduction of oxygen (divalent). In order to confirm the partial substitution of oxygen for apical chlorine, parallel-EELS studies were also carried out on these well grown grains. The EELS spectra show that a pre-peak (about 528.5 eV) exists in the O K ionization edge (see figure 5). The pre-peak which is attributed to transitions from O 1s core state into doped unoccupied O 2p states near E_F reveals the presence of holes at the CuO_2 plane caused by partial substitution of oxygen for apical chlorine.

In order to further clearly reveal structural characteristics of the phase, we also studied it by HRTEM. Figures 6(a) and (b) show HRTEM images taken along the [100] and [110] zone axes, respectively. The layered structure is clearly seen in both images. In figure 6(a), it is clear that neighbouring blocks with a single CuO_2 layer are separated by a rock-salt bi-layer block formed by Sr and (Cl, O) atom planes, and shifted half a unit cell along the a (or b) direction. The corresponding ED patterns, which indicate the details about the layered structure, are inserted on the top right-hand corner of the HRTEM images. (Cl, O) atoms are clearly seen to deviate severely from Sr atom planes and consequently to form new rock-salt sheets. According to the data of the XRD Rietveld analysis, the (Cl, O) rock-salt sheet deviates from the Sr rock-salt sheet by about 1.23 Å. The distance between two rock-salt Sr bi-layers is about 4.5 Å. This distance is larger than 4.452 Å [1] for the parent compound $Sr_2CuO_2Cl_2$ and also larger than

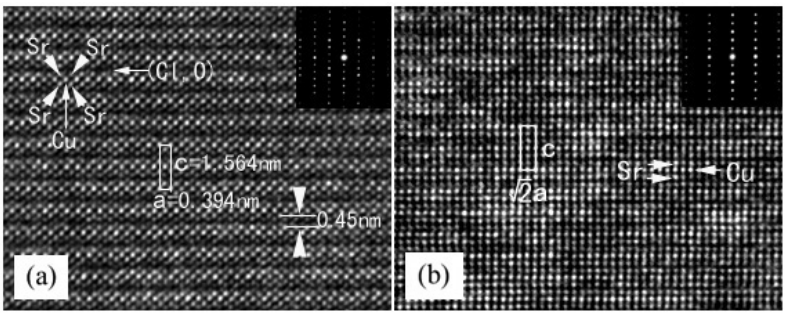

Figure 6. HRTEM images of $Sr_2CuO_{2+\delta}Cl_{2-y}$. (a) along [100]; (b) along [110]. In both images, one unit cell is outlined using white lines, and Sr, Cu and (Cl, O) elements are marked by small white arrows. The distance between two rock-salt Sr bi-layers is shown in (a).

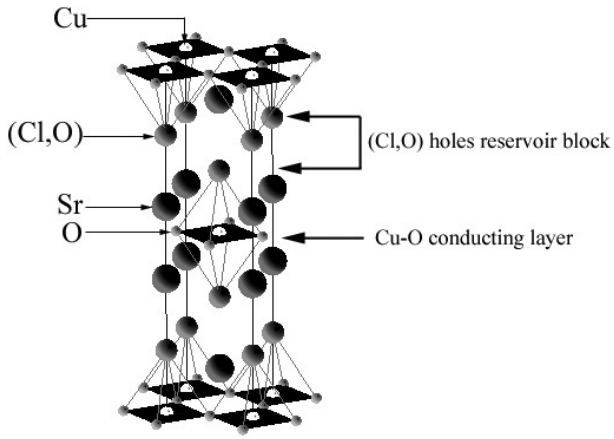

Figure 7. Proposed structure model of $Sr_2CuO_{2+\delta}Cl_{2-y}$. The (Cl, O) hole reservoir block and the CuO_2 conducting layer are shown using thick arrows.

the distances for other superconductors such as $Sr_2CuO_2F_{2+\delta}$ (3.178 Å) [3] and $Sr_{2.3}Ca_{0.7}Cu_{2.2}O_{4.6}Cl_{1.3}$ (4.4 Å) [9]. The increase of the distance between two rock-salt Sr bi-layers can be explained by the expansion of the Sr–Cl rock-salt block due to enhanced Coulomb repulsion between the adjacent chlorine (monovalent) layers resulting from the introduction of oxygen (divalent). In both images, one unit cell is outlined by a white solid line and the lattice constants obtained from the images agree with those obtained from XRD Rietveld analysis and ED patterns. The elements Sr, Cu and (Cl, O) are also indicated by white arrows in the images.

Based on the analysis of the HRTEM images and the data obtained from the Rietveld refinement of the x-ray data, a reasonable structure model is proposed in figure 7. Due to the partial substitution of oxygen (divalent) for apical chlorine (monovalent), the reservoir block with holes is built. The holes are transferred to the CuO_2 conducting layer by the connection between the apical oxygen in the hole reservoir block and the Cu in the CuO_2 conducting layer. The role of apical oxygen in high-T_c superconductors has been suggested in several experiments and theories [14–18].

The electron diffraction patterns and HRTEM images were simulated from the proposed model using the simulation program Cerius 2.0 installed at Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences. The simulated ED patterns (right column) and the experimental ones (left column) are shown in figure 8 for comparison. The simulated HRTEM images along the [001] and [100] zone axes are embedded in the left-hand corner of the bottom of the experimental ones and presented in figures 9(a) and (b), respectively. It is clear that the simulated ED patterns and HRTEM images are in good agreement with the experimental ones, which indicates that the proposed crystal structure is reasonable.

Edge dislocations existing in some areas of the phase were also observed, and the corresponding HRTEM image is shown in figure 10. Three edge dislocations in the image are marked by A, B and C. The dislocation line along [100] (or [010]) is produced by inserting one (001) layer block with half a unit cell along the c direction, and the Burgers vector b is $\frac{1}{2}c$. In fact, linear defects (dislocations) were observed in other high-T_c copper oxide superconductors by HRTEM [19–22]. In general,

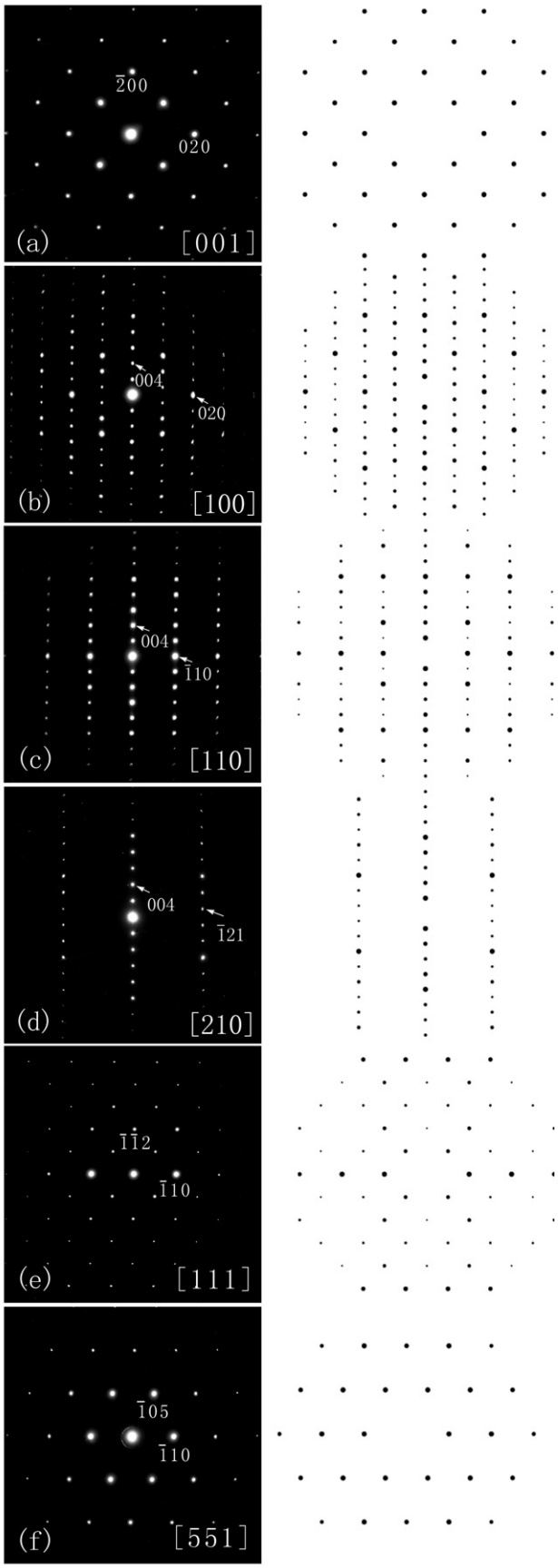

Figure 8. Electron diffraction patterns of $Sr_2CuO_{2+\delta}Cl_{2-y}$. Left column: experimental patterns; right column: simulated patterns.

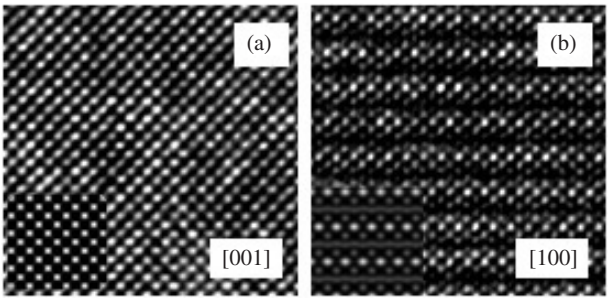

Figure 9. Simulated HRTEM images. The simulated HRTEM images along [001] and [100] are embedded in the bottom left-hand corner of the experimental ones, respectively. (a) along [001]; (b) along [100].

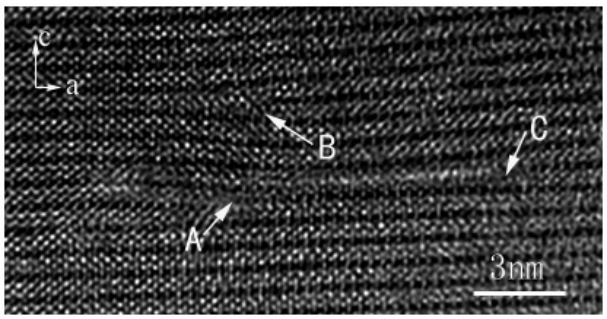

Figure 10. HRTEM image of a region of edge dislocations. Three edge dislocations are marked by A, B and C using white arrows.

structure defects, such as the edge dislocations described in the paper, can increase the critical current intensity by flux pinning.

4. Conclusion

$Sr_2CuO_{2+\delta}Cl_{2-y}$ superconductor with a space group $I4/mmm$ has, for the first time, been synthesized with partial substitution of oxygen for apical chlorine by using high-pressure technique. ED, CBED, XRD, EDX, EELS and HRTEM studies have been performed in order to characterize the phase. It is obvious that holes were introduced into our sample by partial substitution of oxygen for apical chlorine. The crystal structure built of the carrier reservoir block and CuO_2 conducting layer supplies a good example for the study of the role of apical oxygen in superconductivity. Some regions containing dislocations have been observed in our sample.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant Nos 50321101, 50332020 and 5041009) and the State Key Development Program for Basic Research of China (Grant No 2002CB613301).

References

[1] Miller L L, Wang X L, Wang S X, Stassis C, Johnston D C, Faber J and Loong C K 1990 *Phys. Rev.* B **41** 1921
[2] Al-Mamouri M, Edvards P P, Greaves C and Slaski M 1994 *Nature* **369** 382
[3] Fujihara S, Masuda Y, Jin J S, Kimura T and Tanabe K 1997 *Physica* C **290** 63
[4] Hiriri Z, Kobayashi N and Takano M 1994 *Nature* **371** 139
[5] Hiroi Z, Kobayashi N and Takano M 1996 *Pyhsica* C **266** 191
[6] Tatsuki T, Adachi S, Itoh M, Tamura T, Wu X J, Jin C Q, Koshizuka N and Tanabe K 1995 *Physica* C **255** 61
[7] Tohyama T and Maekawa S 1996 *J. Phys. Soc. Japan* **65** 667
[8] Novikov D L, Freeman A J and Jorgensen J D 1995 *Phys. Rev.* B **51** 6675
[9] Jin C Q, Wu X J, Laffez P, Tatsuki T, Tamura T, Adachi S, Yamauchi H, Koshizuka N and Tanaka S 1995 *Nature* **375** 301
[10] Jin C Q, Wu X J, Laffez P, Tatsuki T, Tamura T, Adachi S, Yamauchi H, Koshizuka N and Tanaka S 1995 *Adv. Supercond., VIII Proc. Int. Symp. on Supercond.* (Tokyo: Springer) p 351
[11] Tatsuki T, Adachi S, Tamura T and Tanabe K 1998 *Physica* C **306** 67
[12] Tatsuki T, Adachi S, Tamura T and Tanabe K 1998 *Physica* C **303** 41
[13] Liu Q Q, Qin X M, Yu Y, Li F Y, Dong C and Jin C Q 2005 *Physica* C **420** 23
[14] Murayama C, Môri N, Yomo S, Takagi H, Uchida S and Tokura Y 1989 *Nature* **339** 293
[15] Müller K A 1990 *Z. Phys.* B **80** 193
[16] Matsukawa H and Fukuyama H 1990 *J. Phys. Soc. Japan* **59** 1723
[17] Tohyama T and Maekawa S 1990 *J. Phys. Soc. Japan* **59** 1760
Tohyama T and Maekawa S 1990 *Physica* B **165/166** 1019
[18] Ohta Y, Tohyama T and Maekawa S 1991 *Phys. Rev.* B **43** 2968
[19] Gao Y, Merkle K L, Bai G, Chang H L M and Lam D J 1991 *Physica* C **174** 1
[20] Pan V M, Kasatkin A L, Svetchnikov V L and Zandbergen H W 1993 *Cryogenics* **33** 21
[21] Svetchnikov V, Pan V and Traeholt C 1997 *IEEE Trans. Appl. Supercond.* **7** 1396
[22] Jooss Ch, Guth K, Schofield M A, Beleggia M and Zhu Y 2004 *Physica* C **408** 443