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VARIATION OF SUPERLATTICE STRUCTURE OF THE $Bi_2Sr_{2-x}CuO_{6-y}$ SUPERCONDUCTOR WITH COMPOSITION AND THERMAL HISTORY

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ABSTRACT

Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$, ($0.1 < x < 0.5$, $0 < y < 0.5$), were examined using x-ray diffraction techniques. Diffractometer scans of θ-2θ taken normal to the cleavage planes displayed the even (00ℓ) reflections from $\ell = 2$ to 26. Weak satellite peaks were observed on either side of each main (00ℓ) reflection, and their intensities relative to the main peak increased as 2θ was increased. With decreasing Sr content, the satellite peaks systematically moved away from the position of the main reflection. In contrast, the positions of the satellite peaks did not change with oxygen content which was varied by up to 0.5 oxygen atoms per formula unit. Since T_c in these crystals is sensitive to oxygen content while the superstructure modulation is not, it is unlikely that superconductivity and the structure modulation are directly related. As shown by a more detailed study of these peaks using a four-circle diffractometer and x-ray precession methods, the satellites that appear in θ-2θ scans are actually the mosaic tails of relatively intense superstructure peaks, positioned off from $\mathbf{c}^*$ in the $\mathbf{b}^*$ direction of reciprocal space. Depending on the Sr content of the crystals, generally incommensurate modulations were found with the superstructure periodicity ranging between $\sim 1/5\mathbf{b}^* + 0.29\mathbf{c}^*$ and $\sim 1/5\mathbf{b}^* + 0.65\mathbf{c}^*$. The modulation in $Bi_2Sr_{2-x}CuO_{6-y}$ has two components. The component along the $\mathbf{b}^*$ direction is similar to the superstructure observed in $Bi_2Sr_2CaCu_2O_7$ crystals and thus is probably due to the mismatch between the Bi_2O_2 layer and the CuO_2 layer. The additional component along $\mathbf{c}^*$ may be due to the ordering of Sr vacancies.

INTRODUCTION

A characteristic feature of the homologous family of superconducting phases $(BiO)_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$ ($n = 1, 2, 3$) is that their crystal structures are modulated. Their general structure is layered, built of alternating slabs of defect perovskite structure and distorted rock-salt structure. The subcell is orthorhombic with $a \approx b \approx 5.4$ Å and $c \approx 2(9 + 3.2\ n)$ where n is the number of adjacent CuO_2 layers; see [1] and references therein. Numerous diffraction investigations (electron, x-ray, neutron) have revealed several distinct superstructure modulations, determined to be both commensurate and incommensurate. We have been studying the formation conditions and superconducting properties of the $n = 1$ member, $Bi_2Sr_{2-x}CuO_{6-y}$ [2, 3], first discovered by Michel et al. [4]. Here we report single-crystal x-ray diffraction observations of the superstructure in $Bi_2Sr_{2-x}CuO_{6-y}$ and its relationship to Sr and O content. Given that this phase tolerates a range of Sr and O content, important questions are whether the structure modulations vary with composition and, moreover, whether the modulations are related to the superconducting properties.

EXPERIMENTAL

The single crystals of the n = 1 phase were grown from $Bi_2Sr_{2-x}Cu_{1.5}O_{6-y}$, x = 0, 0.15, 0.25, 0.5, 0.75 composition melts. High-purity Bi_2O_3, $SrCO_3$ and CuO were used in starting compositions which were ground together and placed in alumina, platinum, gold, or zirconia (yttrium-stabilized) crucibles. These compositions were completely molten at 950°C. Generally, runs were sintered at 800°C initially, to drive off CO_2, then soaked at 950 to 1000°C to form a completely homogenized melt, then cooled at various rates. Ambient atmospheres of air or flowing oxygen were used. In all runs, reaction occurred to varying extent with the alumina and zirconia crucibles. For long duration runs (several days) the crucible walls were attacked severely and Al- or Zr-bearing compounds formed at the margins. In platinum crucibles, run products would bond to the platinum making removal of the sample difficult. Large crystal size (2 × 2 × 0.1 cm) was promoted by excess CuO in the starting composition, otherwise only small plumose crystal aggregates were obtained. Generally, the run products consisted of fan-shaped and curved aggregates of broad (00ℓ) cleavage surfaces. The crystal plates would nucleate on the crucible walls, and larger crystal size was promoted by larger volumes of melt. Cooling times from 0.5 to 7 days produced crystals with no significant differences in size. The crystal size and their c-axis mosaic spread markedly decrease and increase, respectively, with decreasing nominal Sr content.

Chemical analyses of selected crystals were obtained using an International Scientific Instruments SEM equipped with a Princeton Gamma-Tech energy dispersive analysis of x-rays (EDAX) system. Cleavage surfaces were analyzed using an operating voltage of 15 keV and a 500 s counting time. Ceramic samples of $Bi_2Sr_2CuO_{6-y}$ were used as standards. Due to the reaction between the crucible and the melt, Sr contents were determined to be lower in general than the nominal compositions. In contrast, the Bi and Cu contents were determined to be 2.00 ± 0.05 and 1.00 ± 0.05, respectively.

As grown from the melt, the $Bi_2Sr_{2-x}CuO_{6-y}$ crystals were deficient in oxygen and typically no superconducting transition was observed by four-probe resistivity or ac magnetic susceptibility measurements made to T = 4.2 K. The low-temperature resistivity exhibited a semiconducting behavior. Thermogravimetric analysis traces of coarse aggregates of crystals in flowing oxygen show total weight gains of 0.85%, with the initial uptake beginning at about 450°C. The oxygen appears to be taken up by the $Bi_2Sr_{2-x}CuO_{6-y}$ crystals, and not a grain-boundary phase, as a collection of separate, single-crystals produced a similar weight gain (0.68 wt %). A 0.85 wt % gain in oxygen corresponds to ~0.4 oxygen atoms per formula unit. After $Bi_2Sr_{2-x}CuO_{6-y}$ crystals have been oxygenated, by heating them to 800–830°C for several hours in flowing oxygen, metallic resistivity and superconductivity above T = 4.2 K are restored. For crystals grown in alumina crucibles, oxygenated crystals show superconducting transition temperatures of 5 K (midpoint) at best, whereas those grown in zirconia crucibles show 8 K (midpoint). Minor Al contamination appears to markedly lower the transition temperature [3].

X-ray diffraction patterns (CuKα radiation) of powdered crystal aggregates confirm single-phase $Bi_2Sr_{2-x}CuO_{6-y}$ as the run product with no detectable impurities, although minor CuO is expected to be present along grain boundaries. Single crystals were examined also by x-ray diffraction using θ–2θ scans made with a SCINTAG diffractometer (equipped with a solid state Ge detector). These patterns display the even (00ℓ) reflections (implying a 2_1 screw along $[00\ell]$ for an orthorhombic crystal) from $\ell = 2$ to 26 as expected for $Bi_2Sr_{2-x}CuO_{6-y}$. For $\ell > 2$, weak satellite peaks are observed on either side of each main (00ℓ) reflection, and their intensities relative to the main peak increase as 2θ increases. With decreasing Sr content these satellites move systematically further away from the position of the main reflection (Fig. 1) [2]. These satellites that appear in θ-2θ scans

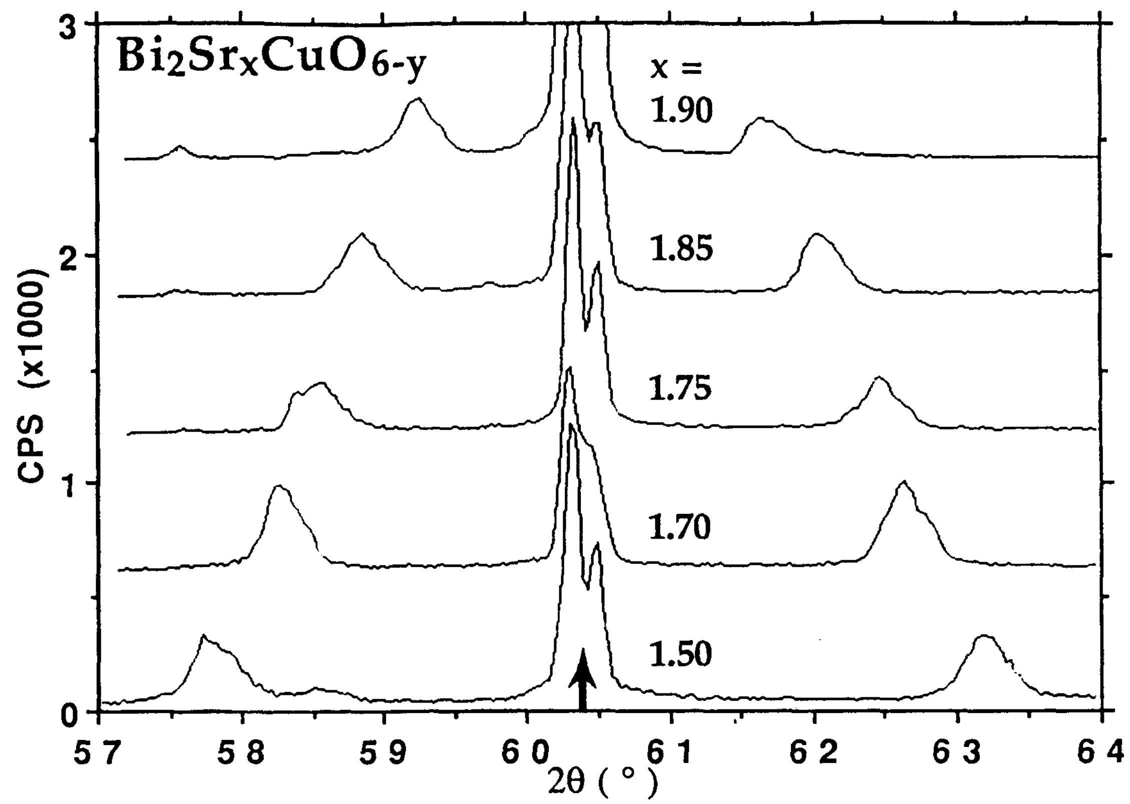

Fig. 1. For $Bi_2Sr_{2-x}CuO_{6-y}$ single crystals, (00ℓ) diffraction patterns (θ–2θ scans, CuKα radiation) display satellite peaks around the main reflections, shown here for (0 0 16), which shift away from the main peak with decreasing Sr content. The satellites are actually mosaic tails of strong superstructure reflections located out ~1/5 along **b***. To emphasize the changing periodicity of the superstructure the overlapped and offset patterns are aligned with the (0 0 16) CuKα doublet positioned at the arrow which is correct for the 1.5 Sr crystal. The Sr contents (±0.05) labelled on each curve were determined for each crystal using EDAX and a set of ceramic standards. The Bi and Cu contents were determined to be 2.00 ± 0.05 and 1.00 ± 0.05, respectively.

are actually the mosaic tails of relatively intense superstructure peaks, positioned off from **c*** in the **b*** directions of reciprocal space. That these superstructure reflections can be observed at all in θ-2θ scans of (00ℓ) cleavage surfaces is because of the relatively large **c**-axis mosaic spread (0.5 to 5°) of the crystals. Two geometrical consequences of the fact that the satellite peaks do not actually lie along the (00ℓ) axis are 1) they are somewhat asymmetrically spaced in 2θ on either side of the main reflection, and 2) the intensity of satellites increases around main reflections with larger ℓ.

The three-dimensional positions of the satellite peaks were studied in greater detail using a Huber four-circle diffractometer and by precession methods. The four-circle diffractometer was equipped with a LiF monochromator crystal to direct $CuK\alpha_1$ radiation onto the sample and a Ge analyzer crystal after the sample to select the elastically scattered x-rays. Detailed intensity maps of the satellite positions around selected main reflections were made for several samples with different Sr contents. Both first- and second-order satellites were found and the results confirmed that the average positions of satellites measured using the SCINTAG two-axis diffractometer provided a good estimate of the **c*** component of the superstructure modulation. The measurements also verified that, in addition to the component along **c***, the satellites are also displaced from the main reflections by a generally incommensurate distance of ~1/5**b***. In fact, the satellites typically appeared in a pseudo-fourfold arrangement around the main reflection, i.e., modulations along ±**a*** and ±**b***. We believe this arrangement results from the symmetry equivalence of the +**b** and -**b** directions, the presence of twin domains contained within the orthorhombic ($a - b \approx 0.01$ Å) crystals, and 90° twist boundaries perpendicular to the **c** axis. Our observation that the satellite intensities varied greatly among the different positions around the main reflections supports this contention. The intensity profiles of the satellites were in general broader (and often asymmetric with a tail towards the main reflection) in the 2θ direction than the main reflections, indicating the presence of some disorder in the superstructure modulation.

Detailed maps of satellite positions were made using the four-circle diffractometer for a single crystal sample ($Bi_2Sr_{1.85}CuO_{6-y}$) in both the as-grown (semiconducting to T = 4.2 K) and oxygenated (metallic with superconducting T_c = 8 K) states. For this crystal, the superstructure satellites were located at ~0.19**b***+ 0.39**c*** and they did not shift appreciably as the oxygen content (and resistivity) were changed.

Single crystals of $Bi_2Sr_{2-x}CuO_{6-y}$ with nominal values for x of 0, 0.15, 0.25, 0.50, 0.75 also were examined by x-ray precession methods, using long exposure (hk0) and (h0ℓ) photographs recorded with Ni-filtered CuKα radiation. In these photographs the arrangement of satellite peaks described above was observed around a large number of reflections (h or k = 0, 2; ℓ = 0 to 14) in a single photograph.

DISCUSSION

Previous investigations of the superstructure of $Bi_2Sr_2CuO_6$ have reported several types of structural modulation. One observed modulation is incommensurate with superstructure satellites only along the [0k0] direction [5]. Another is commensurate with superstructure satellites at 1/5**b*** + 2/5**c*** with respect to the subcell [6], and an overall monoclinic supercell. Other reported superstructures include modulations of ~1/5**b*** plus components along **c*** which may be either incommensurate [7] or commensurate at 1/3**c*** [1] or 1/2**c*** [8].

As suggested in preliminary work [2] and shown in Fig. 1, we find that the modulation vector depends principally on the Sr content. Measurements made with the four-circle diffractometer and from precession photographs show more precisely that the superstructure peaks are positioned at ~1/5b* ± α**c*** where α increases with decreasing Sr content (we assumed the ± sign is a result of symmetry equivalence). Fig. 2 is a schematic composite of (0kℓ) precession photographs depicting the changing position of the superstructure satellite in the neighborhood of the (0 0 16) reflection. Although the satellite positions shift along **c*** as a function of Sr content, they appear to be invariant with changes in oxygen content. The satellites are also observed in the (h0l) reciprocal lattice plane; however, this is probably due to twinning or 90° twist boundaries normal to **c**.

In certain aspects, the satellite positions we observe are similar to those reported for the more widely studied n = 2 and 3 phases [8, 9, 10]. For the n = 2 phase, reports of satellites along [0k0] near 1/5**b*** predominate, and the superstructure has been variously attributed to some distortion of the Bi_2O_2 layer with concurrent puckering of the neighboring CuO_2 layer. This distortion may result from ordered vacancies, substitutional disorder, or ordering of the direction of the Bi^{+3} $6s^2$ lone electron pair. We view the modulation in the n = 1 phase as a superposition of two components. The incommensurate ~1/5**b*** component probably has similar origins as in the n = 2 phase, and thus may be due to the

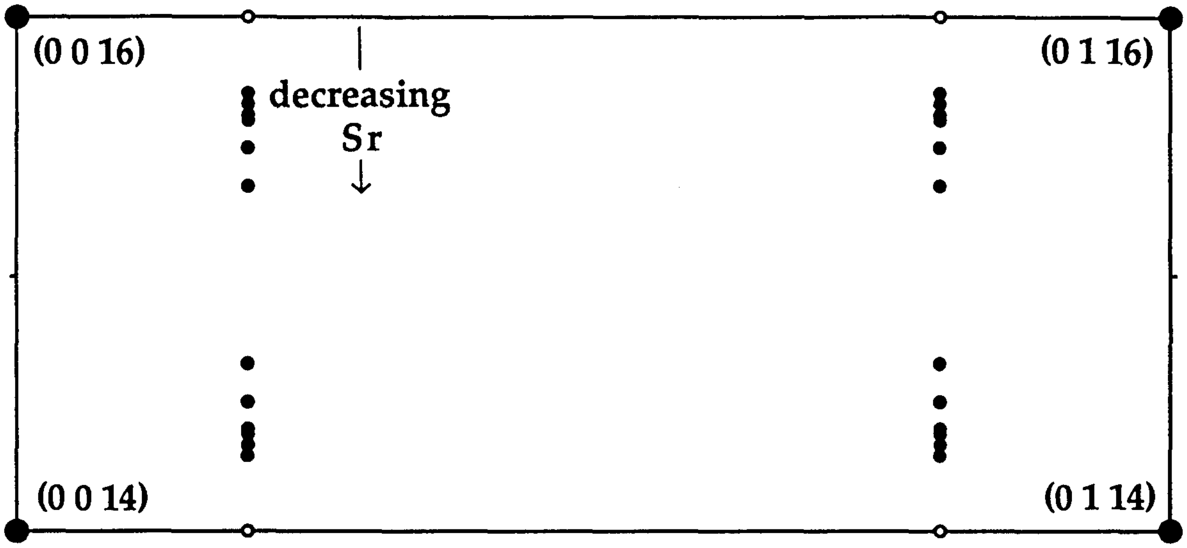

Fig. 2. Schematic composite of (0kℓ) precession photographs of $Bi_2Sr_{2-x}CuO_{6-y}$ crystals that shows the changing position of superstructure satellites in the neighborhood of the (0 0 16) reflection as a function of Sr content. Solid circles (small = superstructure, large = subcell) are observed reflection positions and open circles are predicted reflection positions. Both symmetry equivalent variants of the satellite positions are shown.

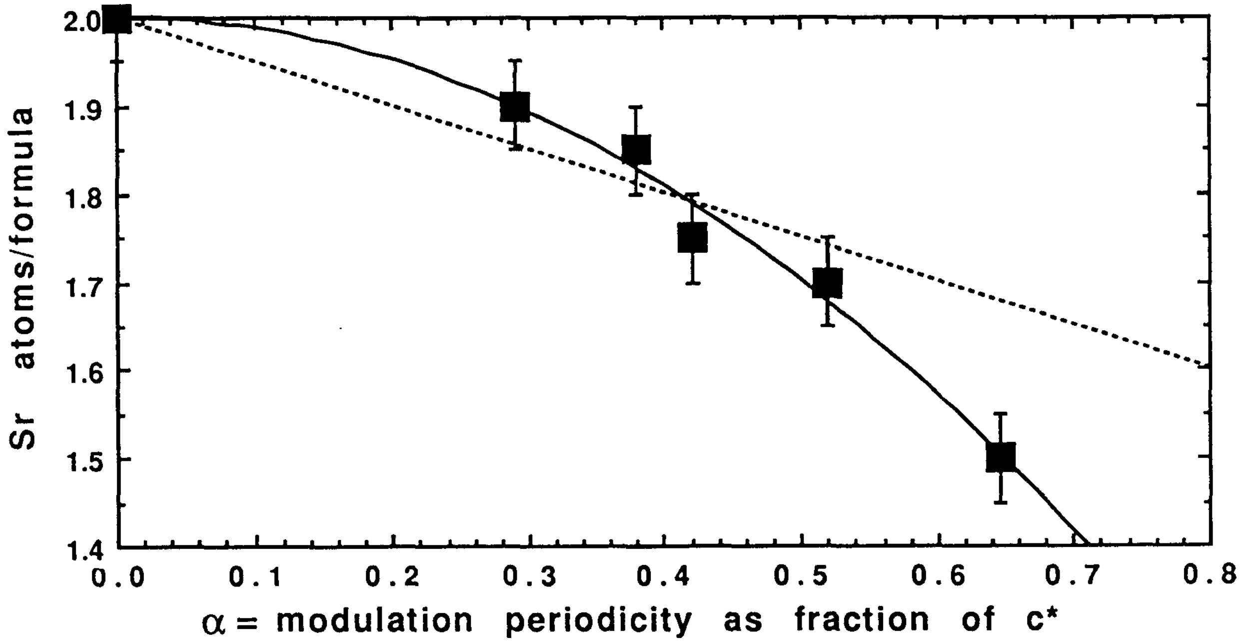

Fig. 3. Relationship between Sr content and the superstructure modulation along [00ℓ]. The data points are measured from Fig. 1, and fit with a second order polynomial (r^2 = 0.98). The point at 2.0 Sr per formula unit was the assumed Sr content for the ceramic standard, and according to the model proposed should have no superstructure modulation along [00ℓ]. The dashed curve is a theoretical model for the simple case of ordering Sr vacancies in a one-dimensional lattice with a subcell of 24.6 Å.

mismatch between the Bi_2O_2 layer and the CuO_2 layer. Changes in the $\mathbf{b}^*$ modulation as a function of Sr content appear to be small, and are difficult to determine due to the mosaic nature of the crystals. The second component of the modulation lies along the $\mathbf{c}^*$ direction and clearly varies with the Sr content. Fig. 3 shows the experimentally determined relationship between the modulation periodicity along $\mathbf{c}^*$ and Sr content as determined by EDAX. Ordering of Sr vacancies along $[00\ell]$ provides a plausible explanation of this relationship, since the supercell size decreases approximately as the Sr content decreases (Fig. 3). Accordingly, all the reported modulations in the $n = 1$ phase can be understood as crystals of different Sr content. Our experience has been that alumina and zirconia crucibles react to varying degrees with melt compositions used to grow the $n = 1$ phase, so that Sr is removed. That Sueno et al. [9] observe a similar **c**-axis modulation in the $n = 2$ and 3 crystals suggests that Sr deficiency probably occurs in these phases also. Indeed, this suggestion already has been made [10, 11]. The possibility exists that the superstructure locks into discrete commensurate modulations for what appears to be a continuous range of Sr content (2.0 to 1.5 Sr/formula unit); however, this cannot be determined without additional and more accurate data.

CONCLUSIONS

1. The positions of the superstructure satellites in $Bi_2Sr_{2-x}CuO_{6-y}$ do not change with oxygen content, which varies by up to 0.5 oxygen atoms per formula unit. Since the as-grown oxygen-deficient crystals were semiconducting and could be made superconducting by oxygen annealing, it is unlikely that superconductivity and the structure modulation are related.

2. The positions of the superstructure satellites in $Bi_2Sr_{2-x}CuO_{6-y}$ do change with decreasing Sr content, and modulations may result with the superstructure periodicity of $\sim 1/5\mathbf{b}^* + \alpha\mathbf{c}^*$ where $\alpha = 0.29$ to 0.65. This provides a working model that encompasses the previously reported superstructure modulations.

3. The modulation in $Bi_2Sr_{2-x}CuO_{6-y}$ has two components. The $\sim 1/5\mathbf{b}^*$ periodicity probably is due to the mismatch between the Bi_2O_2 layer and the CuO_2 layer as in the $n = 2$ phase. The additional component along $\mathbf{c}^*$ may be due to ordering of Sr vacancies.

4. The satellite peaks around the (00ℓ) reflections recorded in θ-2θ scans of $Bi_2Sr_{2-x}CuO_{6-y}$ single crystals provide a sensitive, yet quick and simple, measure of the Sr content.

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REFERENCES

1. C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, E. M. McCarron, J. C. Calabrese, K. J. Morrissey, T. R. Askew, R. B. Flippen, U. Chowdhry, and A. W. Sleight, in High Temperature Superconductivity, edited by R. M. Metzger (Gordon and Breach Science Pub., New York, 1989), p. 217.
2. B. C. Chakoumakos, P. S. Ebey, B. C. Sales, and Edward Sonder, Journal of Materials Research, in press.
3. E. Sonder, B. C. Chakoumakos, B. C. Sales, Physical Review B, submitted.
4. C. Michel, M. Hervieu, M. M. Borel, A. Grandin, F. Deslandes, J. Provost, and B. Raveau, Z. Physik B 68, 421 (1987).
5. J. M. Tarascon, W. R. McKinnon, P. Barboux, D. M. Hwang, B. G. Bagley, L. H. Greene, G. W. Hull, Y. LePage, N. Stoffel, and M. Giroud, Phys. Rev. B 38, 8885 (1988).
6. M. Onoda and M. Sato, Solid State Commun. 67, 799 (1988).
7. G. Van Tendeloo, H. W. Zandbergen, and S. Amelinckx, Solid State Commun. 66, 927 (1988).
8. J. L. Tallon, R. G. Buckley, P. W. Gilberd, M. R. Presland, I. W. M. Brown, M. E. Bowden, L. A. Christian, and R. Goguel, Nature 333, 6169 (1988).
9. S. Sueno, R. Yoshizaki, I. Nakai, K. Ohishi, and A. Ono, Jap. J. Appl. Phys. 27, L1463 (1988).
10. C. H. Chen, D. J. Werder, S. H. Liou, H. S. Chen, and M. Hong, Phys. Rev. B 37, 9834 (1988).
11. H. Nagano, R. Liang, Y. Matsunaga, M. Sugiyama, M. Itoh, and T. Nakamura Jap. J. Appl. Phys. 28, L364 (1989).
12. P. Lee, Y. Gao, H. S. Sheu, V. Petricek, R. Restori, P. Coppens, A. Darovskikh, J. C. Phillips, A. W. Sleight, and M. A. Subramanian, Science 244, 62 (1989).