

A MODEL FOR THE SUPERSTRUCTURE OF $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$

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A model is proposed for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$. It involves the addition of one in ten oxygen atoms in the BiO planes and a displacement of the surrounding atoms. This model is consistent with electron microscope, neutron and X-ray diffraction data. In particular it is consistent with the symmetry determined by convergent beam electron diffraction and with details of the high resolution electron microscope image contrast.

1. Introduction

The very marked long period superstructure in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ poses a problem for the complete determination of its structure. However, it is now agreed that the average or basic structure is as determined by X-ray diffraction [1,2] and by neutron powder diffraction [3,4]. See fig. 1. A review of the structural determination of the $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{2n+6}$ series is given in ref. [5]. An important step in the structural investigation of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ was the determination of the space group of the average structure as A_{maa} or $A_{2\text{aa}}$ and its four dimensional superspace group as either $N_{111}^{A_{\text{maa}}}$ or $N_{111}^{A_{2\text{aa}}}$ by Withers et al. [6] using convergent beam electron diffraction. High resolution electron microscopy (HREM) has also provided very useful information about local atomic displacements and density variations associated with the superstructure. See for example refs. [7-17].

The complete structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ has yet to be obtained from single crystal X-ray (or possibly neutron) data when sufficiently good crystals become available. As the first attempts using X-rays have shown [18] this is not straightforward, since scattering from the oxygen beam is too small to allow precise determination of their positions. Nevertheless an analysis of single crystal X-ray diffraction

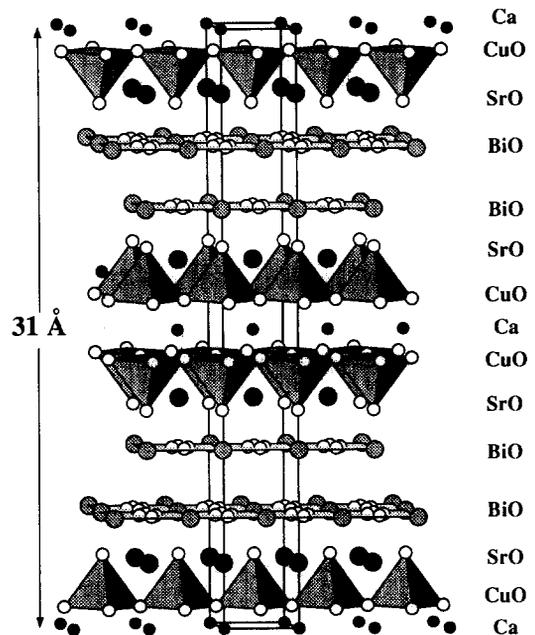


Fig. 1. The structure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ as determined by neutron powder diffraction. The oxygen in the BiO planes are seen to be displaced towards the line joining the Bi atoms.

patterns does provide some clues about the superstructure [19,20]. Also, examination of the directions of static displacements obtained from neutron

powder refinements of the average structure gives additional information about the oxygen atom displacements.

Several models for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ have been proposed, but none have successfully explained all the structural data. Proposed models include:

- (a) an ordering of Bi depleted zones [21],
- (b) additional oxygen in the BiO planes [22,23],
- (c) an ordering of Sr vacancies [24], or
- (d) an ordering of the orientation of Bi^{3+} lone pairs [23].

(a) The superstructure model involving an ordering of Bi depleted and Bi enriched zones was first proposed by Maeda et al. [21] and elaborated in more detail by Matsui et al. [14]. This model was inspired by their very beautiful high resolution electron microscope images in the [010] orientation, which show clearly the modulation of position and intensity in the BiO phases and the tilting of the perovskite columns. They suggest that there is either a periodic replacement of Bi by Sr and/or Ca atoms accompanied by lattice distortions, or that only distortions of the Bi site occur without atom replacement. In particular they simulate images for a model where three Bi atoms in ten are replaced by Sr. This model involving Bi replacement by Sr is not supported by single crystal X-ray diffraction patterns which indicate that the superstructure is largely displacive in nature [19], nor is it in accord with X-ray microanalysis results which indicate that these superconductors may be deficient in Sr and Ca [23,24]. As well, this model only has the correct symmetry in the [010] orientation.

(b) A detailed model involving excess oxygen in the BiO layers was proposed by Zandbergen et al. [23]. They justified their model by electron microscope image simulations and with chemical evidence from substitution experiments. They showed for example that Sr^{2+} can be partially replaced by La^{3+} and concluded that this must be accompanied by excess O^{2-} in the lattice for charge compensation. The substitution of 50% Sr^{2+} by La^{3+} led to a decrease in the modulation periodicity from 4.7 to 3.4 times the basic unit cell. The major problem with the model proposed by Zandbergen et al. is that it only has the correct symmetry in the [010] projection and not in the [100] and [001] projections.

(c) It was suggested by Cheetham et al. [24] that an ordering of Sr atom vacancies could be the cause of the superstructure. This model was based on X-ray microanalysis results which indicated a Sr deficiency in all samples tested. For the same reasons as given for the Bi substitution model in (a) above this model is not supported by the single crystal X-ray diffraction data, nor is it in agreement with the image contrast seen in high resolution electron microscope images.

(d) The possible ordering of the orientation of Bi^{3+} lone pair electrons was discussed by Zandbergen et al. [23]. It is clear however that while such an ordering may exist, it is very unlikely that it is the sole cause of the large displacive modulation seen in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$.

In this note the structural information on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$ from HREM, X-ray and neutron diffraction are reviewed briefly and a model consistent with these data is proposed. This model has the formula $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$.

2. Electron microscopy

A résumé of the electron microscope and diffraction data can be seen in figs. 2 and 3. In the electron diffraction patterns, only the first and second order satellites are shown (fig. 2). The most important point to notice is the existence of the 011 type spot in the [100] orientation. It is the existence of these spots which differentiate the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ structure from its undistorted basic lattice or the "isomorphous" $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$. It is also important to note that this 110 spot must be considered as arising from the basic structure, since superstructure satellites are generated from it. (Figure 2, the [001] orientation.) Schematic representations of the corresponding high resolution electron microscope images are shown in fig. 3. The [110] projection image is not shown as it has the symmetry of the undistorted structure. It is clear from the [010] projection image that any model must involve waves of displacement with a variable distance between the Bi atoms in the BiO layers and tilting of the perovskite columns about the *b* axis. The presence of tilting of the perovskite columns about the *a* axis cannot be ascertained from these images because opposing tilts would be pro-

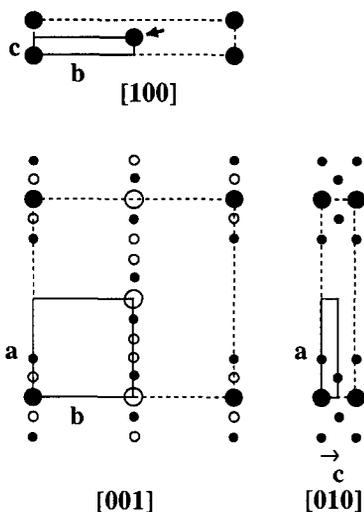


Fig. 2. Schematic electron diffraction pattern of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. ● and ○ represent diffraction spots of the basic lattice in and above the plane of the page respectively, while ● and ○ represent superlattice satellites in and above the plane of the page respectively.

jected on to the same plane. The [001] image is dominated by the $\sqrt{2}a_p \times \sqrt{2}a_p$ square net but a modulation in the intensity along the a axis of approximately $5a/2$ is evident (not shown on the diagram). For thicker crystals and/or higher defocus, lines of higher intensity displaced by $b/2$ between each band are visible; this means that the periodicity of the modulation is $5a$, not $5a/2$, and that there is a lateral component of displacement in the superstructure. Most important, in the [100] projection images there is a contrast feature of periodicity b in the BiO planes. This feature is displaced by $b/2$ in successive layers. None of the images of this type are sufficiently well characterized to predict the origin of this feature. It is this feature that gives rise to the 011 spot in the corresponding electron diffraction pattern (fig. 2) as discussed previously.

3. X-ray diffraction

X-ray diffraction patterns of single crystals are [3,19,20] similar to those seen in electron diffraction patterns, but the intensities differ. Since X-ray diffraction is not affected by multiple diffraction, these diffraction patterns give additional informa-

tion about the nature of the superstructure. The general increase in intensity of satellites with distance from the origin indicates that the superstructure is largely displacive. Also the very low intensity of satellites of low order equatorial $0k0$ spots implies that the net lateral displacement (i.e. displacements perpendicular to the modulation direction) must be very small, except possibly for the oxygen atoms which are weak scatterers for X-rays. Thus the lateral displacements observed in [001] electron microscope images may be simply the enhancement of a very small displacement, or a displacement of oxygen atoms. Such enhancement can be produced by multiple diffraction of electrons.

4. Neutron powder diffraction

The neutron powder refinement of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ structure [3,4] gives the average structure shown in fig. 1. The oxygen atoms are seen to be displaced towards the line joining the Bi atoms, that is the oxygen atoms are displaced in a [110] direction. Thus the oxygen atoms in the BiO planes have a component of displacement perpendicular to the [100] direction of the modulation. The thermal parameters on the Bi atoms are also high, indicating considerable displacements of these atoms.

5. A model for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

Of the four different types of superstructure model listed above only the model with additional oxygen in the BiO planes was found to fit all this structural data. The contrast seen in the [010] projection limits the choice to models involving modification of the BiO planes. The contrast in the BiO layer is not consistent with rows of missing Bi atoms as suggested by Kapitulnik [25]. Nor is there any evidence in the X-ray diffraction pattern for broad Bi deficient bands as suggested by Maeda et al. [21]. The ordering of the Bi^{3+} lone pairs is not sufficient alone to cause the large displacements of the Bi atoms seen in the images. Different projections of the proposed model are shown in figs. 4 and 5. The insertion of additional oxygen in the BiO layers is accompanied by an expansion of the surrounding lattice prefer-

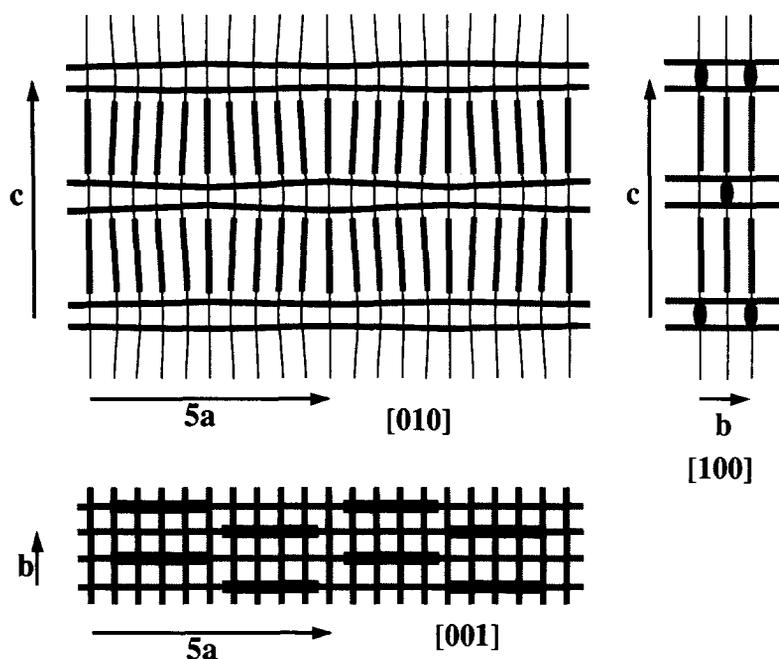


Fig. 3. Schematic representations of HREM images of [010], [100] and [001] projections of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. The [110] image is not shown since it has the symmetry of the basic lattice. In the [001] projection image the superstructure modulation with an approximately $5a/2$ periodicity is not shown, although it is the strongest contrast feature in this projection.

entially in the [100] direction. It is supported that the oxygen atoms move towards the line joining the Bi–Bi bond as required by the neutron results. The tilting of the perovskite columns is then dictated by the displacements in the BiO plane. The close proximity of interstitial O^{2-} to the Bi^{3+} cations leads to speculation as to whether at least some of the Bi is present as Bi^{5+} . The scanning tunneling microscope images of the cleaved (001) surface of Kapitulnik [25], can be interpreted as one in ten rows of Bi^{5+} (black because they give no signal) in a bright Bi^{3+} lattice. It thus remains a possibility that the BiO layers play the role of electron reservoirs.

The model we propose thus consists of a periodic insertion along the a axis of pairs of oxygen atoms in the Bi_2O_2 layers. One oxygen atom pair is inserted after every five unit cells along the a axis. These interstitial oxygen atoms are located on the line joining the Bi–Bi atoms in the BiO plane. The displacements of all the other atoms can be considered as the relaxation of the structure due to the insertion of oxygen atoms.

If one supposes that the interstitial oxygen can be

inserted at an integral (fig. 4a) or half integral (fig. 4e) multiple of the basic unit cell a , then the symmetry of the [100] projection depends on the periodicity of the superstructure. The symmetry of the [100] projection is as shown in fig. 2 for an integral periodicity and is unchanged from the basic lattice for a half integral periodicity. In a study of La doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [23] a periodicity of $3.4a$ was observed, together with the symmetry expected for this model for a half integral superstructure period.

The variations observed in the average period of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ superstructure, depending on preparation conditions, can be explained by a variation in the distance between oxygen interstitials. As discussed in Hewat et al. [7–9] an ordered sequence of blocks of different lengths can give rise to a non-integral average periodicity. The most commonly observed case for undoped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is a sequence of $5+5+5+4$ giving an average repeat of $4.75a$.

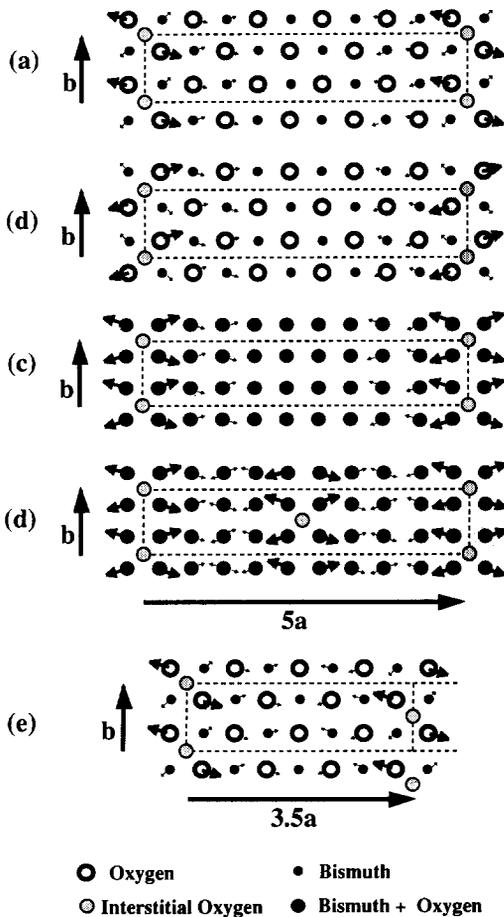


Fig. 4. Schematic representations of the proposed model for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$: The [001] projection. (a) One BiO plane. (b) The next BiO plane. (c) A projection of two BiO planes. (d) A projection of the complete unit cell. Only the BiO planes are represented. (e) One BiO plane for a superstructure with a one half integral ($3.5a$) "repeat". The true repeat is of course $7a$.

6. Discussion

A model for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$ is proposed which is consistent with all available structural data. It involves one in ten additional oxygen atoms in the BiO planes giving a formula of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$. This model predicts a direct correlation between the number of oxygen interstitials and the superstructure period. It must of course be verified by a complete structural determination by a single crystal X-ray and/or neutron diffraction, for

which it should provide a useful starting model.

Matsui et al. [14] simulated the [010] projection image for partial replacement of Bi by Sr and Zandbergen et al. [23] simulated the same projected image for their oxygen interstitial model. Both simulations give satisfactory fits for this projection particularly as the heavy atom positions were taken directly from the images. This is a demonstration of the fact that high resolution electron microscopy cannot be used to establish a variable heavy metal occupancy particularly where variable interatomic distances are involved, nor can it be used to directly locate oxygen atom interstitials in a heavy metal atom lattice as is the case here. It is also important to appreciate that in the [100] projection, i.e. looking down the direction of the superlattice modulation, the projected atomic columns include atoms with slightly different displacements perpendicular to the projection. In this case there are five different atomic displacements per column. With so many adjustable parameters it is not realistic to suppose that a good fit between real and simulated images will give a unique solution for the model.

The model we propose is consistent with the observed symmetry of all three principal projections and with the general location of image contrast features. This is an improvement on all previously proposed models, none of which have the correct symmetry in all three principal projections.

On completion of this note we received a preprint of an article by Torardi et al. [26] which describes single crystal X-ray structural refinements of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ and related Y doped crystals. They have refined the average structure and find a partial occupation of oxygen atoms in the BiO planes on the sites as we propose here. However they go on to propose a model for the superstructure with lines of interstitial oxygen atom pairs along the a axis, i.e. along the direction of the superstructure. While this model does not agree with the HREM observations, which indicate variable Bi-Bi displacements along the a axis, the location of interstitial oxygen pairs in the BiO planes does support our own model.

Note added in proof. After completion of this work we received a preprint by Le Page et al. [27] in which they describe the single crystal X-ray refinement of the complete structure of $\text{Bi}_{10}\text{Sr}_{15}\text{Fe}_2\text{O}_{46}$, which has a commensurate superstructure and is apparently

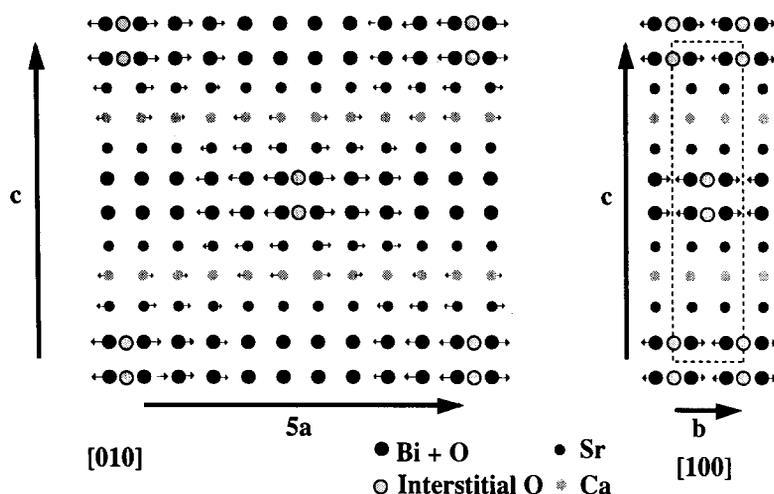


Fig. 5. Schematic representations of the proposed model for the superstructure of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.2}$: The [010] and [100] projections. The Cu and O atoms are not shown. Only the interstitial O atoms in the BiO plane are shown.

isomorphous with $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. They find oxygen atom interstitials as we propose with a relaxation of the lattice around them, however the displacements of some of the oxygen atoms are not identical to our model.

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References

- [1] J.M. Tarascon, Y. Le Page, P. Barboux, B.G. Bagley, L.H. Greene, W.R. McKinnon, G.W. Hull, M. Giroud and D.M. Hwang, *Phys. Rev. B* 37 (1988) 9382.
- [2] S.A. Sunshine, T. Siegrist, L.F. Schneemeyer, D.W. Murphy, R.J. Cava, B. Batlogg, R.B. Van Dover, R.M. Fleming, S.H. Glarum, S. Nakahara, R. Farrow, J.J. Krajewski, S.M. Zahurak, J.V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp and W.F. Peck, *Phys. Rev. B* 38 (1988) 893.
- [3] P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, A.W. Hewat, E.A. Hewat, J.L. Hodeau, M. Marezio, J.L. Tholence and D. Tranqui, *Proc. Interlaken, Physica C* 153-155 (1988) 623.
- [4] P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, A.W. Hewat, E.A. Hewat, J.L. Hodeau, M. Marezio, J.L. Tholence and D. Tranqui, *Physica C* 156 (1988) 189.
- [5] P. Bordet, J.J. Capponi, C. Chaillout, J. Chenavas, A.W. Hewat, E.A. Hewat, J.L. Hodeau and M. Marezio, to be published in: *Studies of High Temperature Superconductors*, ed. A.V. Narlikar (Nova Science, New York).
- [6] R.L. Withers, J.S. Anderson, B.G. Hyde, J.G. Thompson, L.R. Wallenberg, J.D. Fitzgerald and A.M. Stewart, *J. Phys. C* 21 (1988) L417.
- [7] E.A. Hewat, P. Bordet, J.J. Capponi, C. Chaillout, J.L. Hodeau and M. Marezio, *Proc. Interlaken, Physica C* 153-155 (1988) 619.
- [8] E.A. Hewat, M. Dupuy, P. Bordet, J.J. Capponi, C. Chaillout, J.L. Hodeau and M. Marezio, *Nature* 333 (1988) 53.
- [9] E.A. Hewat *Proc. Colloq. SFME, Lille, J. de Micros. Spect. Electr.* 13 (1988) 88.
- [10] M. Hervieu, C. Michel, B. Domenges, Y. Laligant, A. Lebaill, G. Ferey and B. Raveau, *Modern Phys. Lett. B* 2 (1988) 491.
- [11] H.W. Zandbergen, Y.K. Huang, M.J.V. Menken, J.N. Li, K. Kadowaki, A.A. Menovsky, G. Van Tendeloo and S. Amelinckx, *Nature* 332 (1988) 620.
- [12] H.W. Zandbergen and P. Groen, *Solid State Commun.* 66 (1988) 397.
- [13] P.L. Gai and P. Day, *Physica C* 152 (1988) 335.
- [14] Y. Matsui, H. Maeda, Y. Tanaka and S. Horiuchi, *Jap. J. Appl. Phys. Part 2*, 27 (1988) L372.
- [15] S. Ikeda, H. Ichinose, T. Kimura, T. Matsumoto, H. Maeda, Y. Ishida and K. Ogawa, *Jap. J. Appl. Phys. Part 2*, 27 (1988) L999.
- [16] K. Hiraga, M. Hirabayashi, M. Kikuchi and Y. Syono, *Jap. J. Appl. Phys., Part 2*, 27 (1988) L573.
- [17] D. Shindo, K. Hiraga, M. Hirabayashi, M. Kikuchi and Y. Syono, *Jap. J. Appl. Phys. Part 2*, 27 (1988) L1018.
- [18] Y. Gao, P. Lee, Coppens, M.A. Subramanian and A.W. Sleight, *Science* 241 (1988) 954.

- [19] P.A. Albouy, R. Moret, M. Potel, P. Gougeon, J. Padiou, J.C. Levet and H. Noel, to appear in *J. de Physique- Brèves Comm.*
- [20] K. Kawaguchi, S. Sasaki, H. Mukaida and M. Nakao, *Jap. J. Appl. Phys. Part 2*, 27 (1988) L1015.
- [21] H. Maeda, Y. Tanaka, M. Fukutomi, T. Asano, K. Togano, H. Kumakura, M. Uehara, S. Ikeda, K. Ogawa, S. Horiuchi and Y. Matsui, *Proc. Interlaken, Physica C 153* (1988) 602.
- [22] R.J. Cava, B. Batlogg, S.A. Sunshine, T. Siegrist, R.M. Fleming, K. Rabe, L.F. Schneemeyer, D.W. Murphy, R.B. Van Dover, P.K. Gallagher, S.H. Glarum, S. Nakahara, R.C. Farrow, J.J. Krajewski, S.M. Zahurak, J.V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp, W.F. Peck and E.A. Rietman, *Proc. Interlaken, Physica C 153-155* (1988) 560.
- [23] W.W. Zandbergen, W.A. Groen, F.C. Mijlhoff, G. van Tendeloo, S. Amelinckx *Physica C 156* (1988) 325.
- [24] A.K. Cheetham, A.M. Chippindale and S.J. Hibble, *Nature* 333(1988) 21.
- [25] A. Kapitulnik, presented at the 1988 E-MRS Fall Meeting, to be published in *Science*.
- [26] C.C. Torardi, J.B. Parise, M.A. Subramanian, J. Gopalakrishnan and A.W. Sleight, preprint.
- [27] Y. LePage, W.R. McKinnon, J.-M. Tarascon, P. Barboux, preprint.