

CHARGE TRANSFER AND BOND LENGTHS

CONF-890335--269

IN  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{6+y}$

DE90 002241

By

P. F. Miceli, J. M. Tarascon, L. H. Greene and P. Barboux  
Bellcore  
Red Bank, NJ 07701

James D. Jorgensen  
Materials Science Division  
Argonne National Laboratory  
Argonne, IL 60439

and

J. J. Rhyne and D. A. Neumann  
National Institute of Standards and Technology  
Gaithersburg, MD 20899

May 1989

The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. W-31-109-ENG-38. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes.

**DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted to the Proceedings of the Materials Research Society Meeting, San Diego, CA, April 24-28, 1989.

\*This work is supported by U.S. Department of Energy, Basic Energy Sciences - Materials Sciences, under contract #W-31-109-ENG-38.

MASTER  
dk

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## CHARGE TRANSFER AND BOND LENGTHS IN $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{6+y}$

P. F. MICELI\*, J. M. TARASCON\*, L. H. GREENE\*, P. BARBOUX\*,  
J. D. JORGENSEN\*\*, J. J. RHYNE\*\*\* and D. A. NEUMANN\*\*\*

\*Bellcore, Red Bank NJ 07701

\*\*Argonne National Laboratory, Argonne IL 60439

\*\*\*National Institute of Standards and Technology,  
Gaithersburg MD 20899

### ABSTRACT

We discuss the effects of doping on the Cu chain sites in  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{6+y}$ . The relationship between bond lengths obtained from neutron scattering and charge transfer is evaluated in terms of bond valence. In particular, it is concluded that removing an oxygen from the chains transfers one electron to the planes.

### INTRODUCTION

A feature common to the copper-oxide high temperature superconducting compounds is that they are antiferromagnetic insulators or metallic superconductors, depending on the doping as, for example, in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ("214").  $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$  ("123") differs from "214", however, as it contains two crystallographically distinct Cu sites. The Cu2 sites ("planes") are similar to those in "214" whereas the Cu1 site ("chain") exhibits two-fold coordination at  $y=0$  and four-fold coordination at the superconducting composition,  $y=1$ . In this paper, we demonstrate that the effect of doping (i.e. changes in both  $x$  and  $y$ ) in the Cu1 layer is to transfer charge from the chains to the planes, which then suppresses  $T_c$ . In this respect, "123" is unique among the Cu-oxide superconductors.

Besides changing the oxygen content,  $y$ , doping can also be achieved by substituting transition metals for Cu which then leads to the suppression of  $T_c$  [1-3]. Such substitutions fall into two classes, divalent (eg. Ni and Zn) and trivalent (eg. Co, Fe and Al). Structural studies [3-11] show that the trivalent substitutions primarily occupy the Cu1 site whereas the divalent substitutions have been reported to occupy the Cu2 site or both sites and there is still some disagreement on the exact proportions. In analogy with substitutions for Cu in "214" [12,13], it is found that  $T_c$  decreases rapidly with divalent substitution concentration in "123" since the defects are introduced directly into the  $\text{CuO}_2$  planes. In contrast, a much weaker suppression of  $T_c$  with trivalent substitution into the Cu1 site is observed.

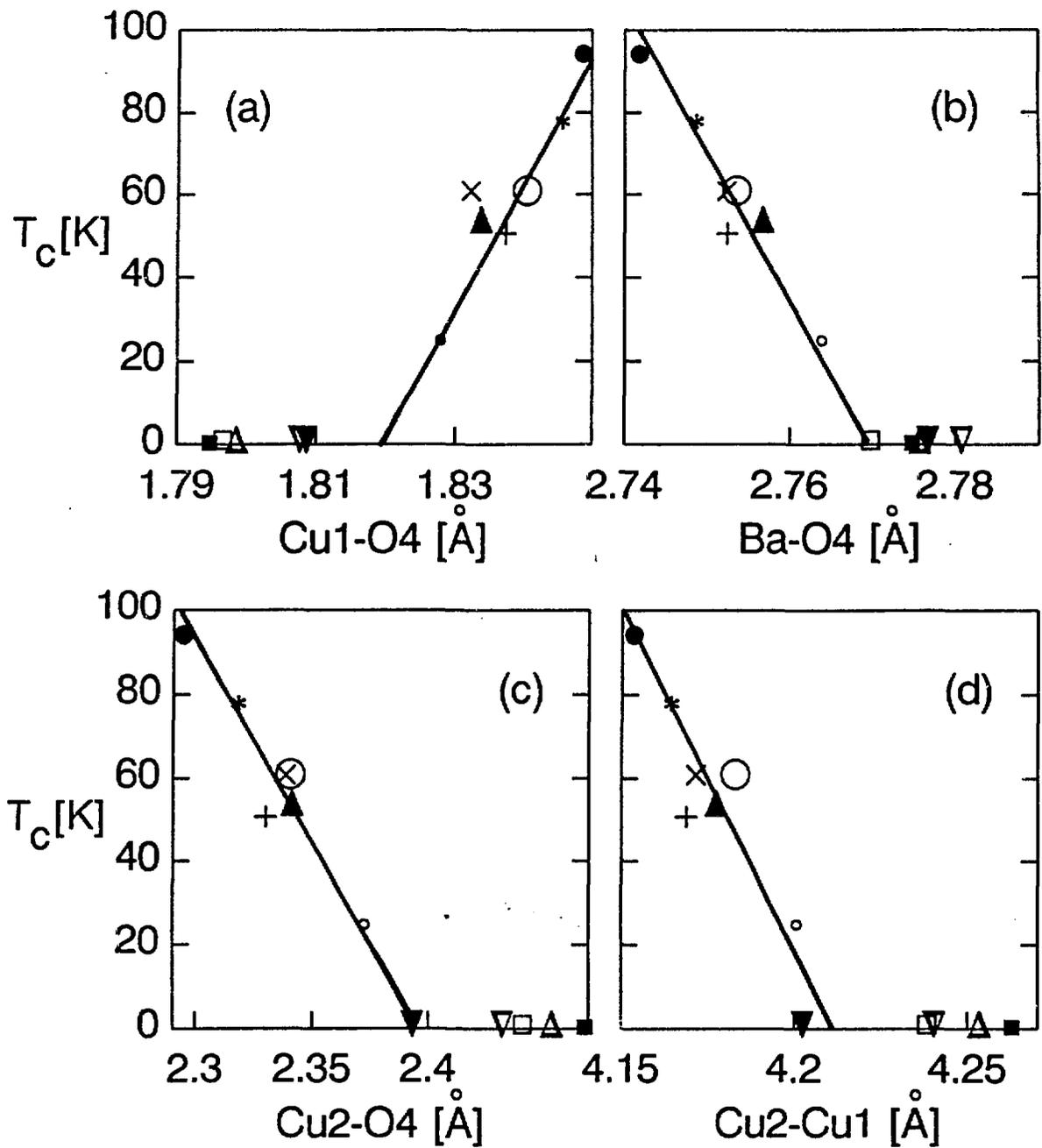


Fig. 1:  $T_c$  vs. Bond Lengths.

$\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_7$	▲
$\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{6.4}$	△
$\text{YBa}_2\text{Cu}_{2.2}\text{Co}_{0.8}\text{O}_{7.3}$	▽
$\text{YBa}_2\text{Cu}_{2.2}\text{Co}_{0.8}\text{O}_{6.9}$	∇
$\text{YBa}_2\text{Cu}_{2.7}\text{Co}_{0.3}\text{O}_{6.9}$	○
$\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$	●
$\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$	○
$\text{YBa}_2\text{Cu}_3\text{O}_{6.4}$	□
$\text{YBa}_2\text{Cu}_3\text{O}_{6.1}$	■
$\text{YBa}_2\text{Cu}_{2.9}\text{Al}_{0.1}\text{O}_7$	*
$\text{YBa}_2\text{Cu}_{2.8}\text{Al}_{0.2}\text{O}_7$	×
$\text{YBa}_2\text{Cu}_{2.7}\text{Al}_{0.3}\text{O}_7$	+

## CHARGE TRANSFER

It has been previously reported [4] that for doping within the Cu1 layer,  $T_c$  systematically decreases with the Cu1-O4 bond length (the O4 site is the bridging oxygen between Cu1 and Cu2). This is also the shortest bond length in the system so that it is very sensitive to electronic changes of the Cu1. Figures 1 (a)-(d) show that this relationship is part of a more general structural response which is schematically illustrated in fig.2. Of particular importance is that as  $T_c$  decreases, not only does the Cu1-O4 shorten, but the Ba ion also moves towards the Cu2 layer. Because Ba is a well defined divalent ion, such behavior suggests that a larger fraction of the Ba electrons will be shared with the Cu2 layer rather than with the Cu1 layer, thereby filling the holes which are necessary for superconductivity in this compound. It should be noted that the relationships shown in fig.1 hold for both oxygen content changes as well as for transition metal substitution, which is quite remarkable.

We now semi-quantitatively address the relevance of the various bonds to charge transfer using the established empirical relationship [17] between bond valence and bond length. There are two basic types of Cu-O bonds. Short bond lengths (1.8 to 1.9 Å) have a bond valence of  $\sim 0.5 e^-$ . Thus, two-fold coordinated Cu is monovalent and four-fold is divalent with three-fold coordination being highly unfavorable. This is the likely driving force for the oxygen superlattices in the chain layers observed [18] for intermediate oxygen contents. The apex positions for higher oxygen coordination (5 and 6-fold) are always found to be at longer distances (2.3 to 2.4 Å) corresponding to  $\sim 0.15 e^-$  bond valence, which is significantly smaller than for the short bonds. Thus, we are justified to think in terms of "CuO<sub>2</sub> planes" since the apex positions in higher than 4-fold coordination configurations lead only to small effects.

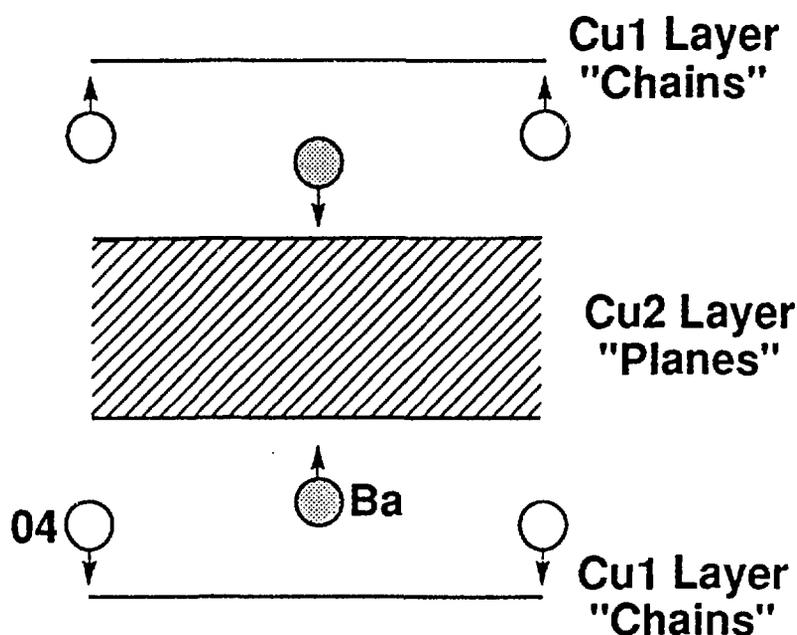


Fig. 2: Schematic representation of charge transfer and bond length changes in the "123" compound. The Cu2 layer contains two CuO<sub>2</sub> planes and Y. As the Cu1 layer is doped by trivalent ions for Cu or by removing oxygen, charge is transferred via the Ba ion. The bond lengths respond as shown.

Although the Cu<sub>2</sub>-O<sub>4</sub> bond length undergoes a large change with T<sub>c</sub> (see fig.1c), the above discussion leads to the conclusion that only a fraction of 0.15 e<sup>-</sup> would contribute to charge transfer (~0.04 e<sup>-</sup> per CuO<sub>2</sub> plane) -- which is too small to be the dominant effect. Alternatively, the Ba ion provides the strongest coupling between the chain and plane layers. When oxygen is removed, Ba goes from 10-fold to 8-fold coordination, giving ~0.4 e<sup>-</sup> charge transfer per CuO<sub>2</sub> plane (or twice that per unit cell), assuming that the Ba-O<sub>4</sub> bond valence does not change. This assumption is actually quite reasonable since the Cu<sub>1</sub>-O<sub>4</sub> bond valence is expected to be the same for both the 2-fold and 4-fold geometries. Thus, the "bond valence" between the Ba and the oxygens in the Cu<sub>2</sub> layer increases, thereby filling the holes (or equivalently lowering the formal valence of the Cu<sub>2</sub>). As seen in fig.1, trivalent substitutions behave similarly to oxygen deficiency, which is a consequence of the higher valence of the substitution.

It is worth noting that the bond lengths determined from neutron diffraction yield an averaged value. For example, sites which are missing an oxygen would have different local bond lengths. However, the measured average bond lengths reflect the average bond valences so that it is still meaningful to discuss continuously changing bond lengths as in fig.1.

These results are summarized in fig.2 where two Cu layers or units can be distinguished. As the system is doped on the Cu<sub>1</sub> layer, charge transfer is mediated by the Ba ions. The systematic behavior found in fig.1 is a consequence of doping on the Cu<sub>1</sub> layer only -- for example, we would not expect precisely the same bond length changes when doping on the Cu<sub>2</sub> sites with divalent substitutions or when substituting for Ba. For example, trivalent substitutions (eg. Nd, La) for divalent Ba will bring extra oxygen into the chains as well as transfer charge to the planes without the need for a significant displacement of the bond lengths [19].

Our analysis of charge transfer according to bond valence arguments gives ~0.9 e<sup>-</sup> per unit cell. This is consistent with and is complementary to x-ray absorption measurements [20] on YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6+y</sub> which show that Cu is formed in an amount slightly less than 1-y as oxygen is removed. Thus, it is reasonable to conclude that the removal of one oxygen, O<sup>2-</sup>, converts a Cu<sub>1</sub> from Cu<sup>2+</sup> to Cu<sup>1+</sup> and transfers an electron to the planes. This is also consistent with the observations [20,21] of T<sub>c</sub> decreasing proportional to y.

## MAGNETISM

With the addition of the magnetic ion, Co, T<sub>c</sub> is suppressed and the compound becomes an antiferromagnetic insulator for x>0.4. The fact that it becomes insulating indicates that Co does more than just induce magnetic ordering. Furthermore, a similar suppression of T<sub>c</sub> (as well as bond length changes) occurs when Al is substituted. These observations provide strong evidence that the loss of superconductivity upon trivalent substitution in "123" arises from charge transfer rather than from magnetic pair breaking.

In analogy with the pure Cu compound ( $x=0$ ), Co substitutions at low concentration also exhibit antiferromagnetic ordering or superconductivity, depending on the oxygen content and has recently been studied by neutron scattering [22-24]. As shown in fig.3, there are two antiferromagnetic states: AF1 corresponding to magnetic ordering on the planes sites, and AF2 corresponding to the subsequent magnetic ordering of the chain sites.

The cross over from AF1 to superconductivity is related to the doping in the planes and is characteristic of these Cu-oxide compounds. AF2 is a new magnetic state due the substitution of a magnetic ion on the chain site. However, it is surprising to find that the transition temperature for AF2 also decreases with increasing oxygen content just as the upper transition, AF1. This is opposite to what is expected from a simple ionic model, since increasing the oxygen content would tend to raise the chain site valence as well as strengthen the superexchange among the chain sites -- both would favor increasing transition temperature for increasing oxygen content. Therefore, the detailed behavior of AF2 seems to be intimately related to the charge transfer which occurs as oxygen is removed and the results of fig.3 provide a simple, but rigorous test for theoretical models of the electronic properties of this compound.

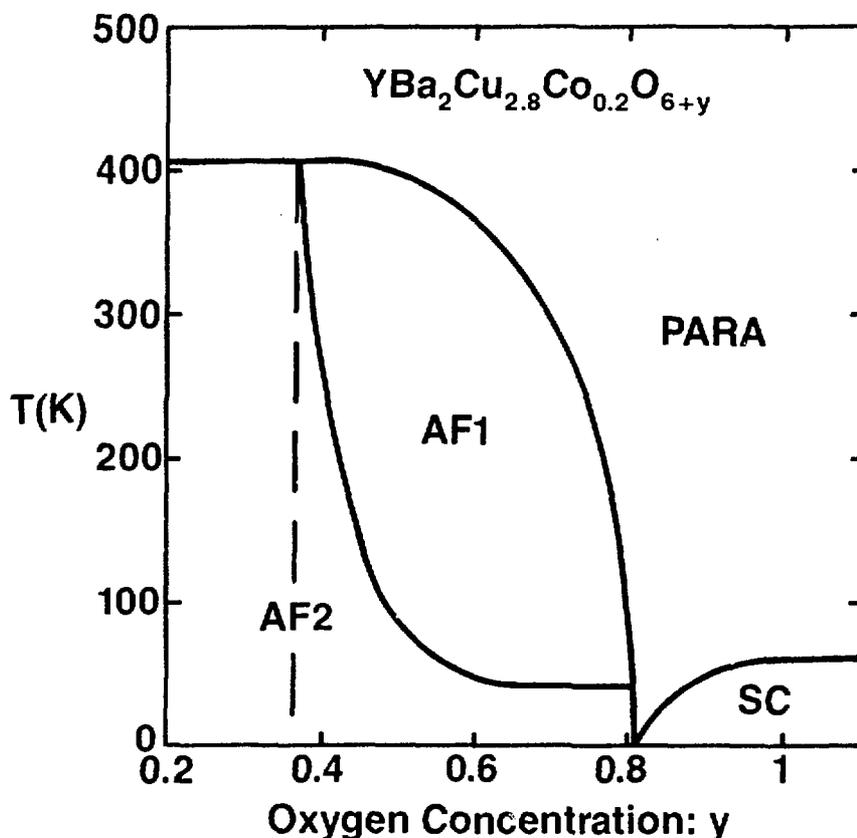


Fig. 3: Diagram showing the antiferromagnetic (AF) and superconducting (SC) behavior for  $\text{YBa}_2\text{Cu}_{2.8}\text{Co}_{0.2}\text{O}_{6+y}$  as a function of oxygen content. AF1 corresponds to AF ordering of the planes whereas AF2 corresponds to the subsequent ordering of the chains and is a new magnetic state induced by the Co substitution. Note that the transition temperatures for both AF1 and AF2 decrease with increasing oxygen content.

## ACKNOWLEDGEMENT

One of us (J. D. J.) gratefully acknowledges support from the U. S. Department of Energy, Basic Energy Science, Material Sciences under contract number W-31-109-ENG-38.

## REFERENCES

1. G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du and C. L. Chien, *Phys. Rev. B* **35**, 8782 (1987).
2. Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. A. Oki, K. Hoshino, A. A. Miniami and T. Fujita, *Nature* **328**, 512 (1987).
3. J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz and S. Sunshine, *Phys. Rev. B* **37**, 7458 (1988).
4. P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, F. J. Rotella and J. D. Jorgensen, *Phys. Rev. B* **37**, 5932 (1988).
5. T. Siegrist, L. F. Schneemeyer, J. V. Waszczak, N. P. Singh, R. L. Opila, B. Batlogg, L. W. Rupp and D. W. Murphy, *Phys. Rev. B* **36**, 8365 (1987).
6. Y. K. Tao, J. S. Swinnea, A. Manthiram, J. S. Kim, J. B. Goodenough and H. Steinfink, *J. Mater. Res.* **3**, 248 (1988).
7. P. Bordet, J. L. Hodeau, P. Strobel, M. Marezio and A. Santoro, *Solid State Comm.* **66**, 435 (1988).
8. G. Roth, G. Heger, B. Renker, J. Pannetier, V. Caignaert, M. Hervieu and B. Raveau, *Physica C* **153-155**, 972 (1988).
9. R. S. Howland, T. H. Geballe, S. S. Laderman, A. Fischer-Colbrie, M. S. Scott, J. M. Tarascon and P. Barboux, submitted to *Phys. Rev. B* 1989.
10. G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, F. H. Streitz, C. L. Chien, J. J. Rhyne and J. A. Gotaas, *Nature* **332**, 238 (1988).
11. T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono and M. Hirabayashi, *Jpn. J. Appl. Phys.* **27**, L354 (1988).
12. J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner and E. J. McNiff, *Phys. Rev. B* **36**, 8393 (1987).
13. G. Xiao, A. Bakhshai, M. Z. Cieplak, Z. Tesanovic and C. L. Chien, *Phys. Rev. B* **39**, 315 (1989).

14. D. C. Johnston, A. J. Jacobsen, J. M. Newsam, J. T. Lewandowski, D. P. Goshorn, D. Xie and W. B. Yelon, in *Chemistry of High Temperature Superconductors*, ed. by D. L. Nelson, M. S. Wittingham and T. F. George (American Chemical Society, Washington, DC, 1987), p. 136.
15. T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono and M. Hirabayashi, *Jpn. J. Appl. Phys.* **26**, L1727 (1987).
16. P. F. Miceli, unpublished.
17. I. D. Brown and K. K. Wu, *Acta Crystallogr. B* **32**, 1957 (1976).
18. C. Chaillout, M. A. Alario-Franco, J. J. Capponi, J. Chenavas, P. Strobel and M. Marezio, *Solid State Comm.* **65**, 283 (1988).
19. J. D. Jorgensen, unpublished.
20. J. M. Tranquada, S. M. Heald, A. R. Moodenbaugh and Y. Xu, *Phys. Rev. B* **38**, 8893 (1988).
21. Y. J. Uemura et. al., *Phys. Rev. B* **38**, 909 (1988).
22. P. F. Miceli, J. M. Tarascon, L. H. Greene, P. Barboux, M. Giroud, D. A. Neumann, J. J. Rhyne, L. F. Schneemeyer and J. V. Waszczak, *Phys. Rev. B* **38**, 9209 (1988).
23. P. F. Miceli, J. M. Tarascon, P. Barboux, L. H. Greene, B. G. Bagley, G. W. Hull, M. Giroud, J. J. Rhyne and D. A. Neumann, *Phys. Rev. B* **39**, (1989), in press.
24. P. F. Miceli, J. M. Tarascon, B. G. Bagley, L. H. Greene, P. Barboux, G. W. Hull, M. Giroud, J. J. Rhyne and D. A. Neumann, *Proc. X Winter Meeting on Low Temperature Physics* (World Scientific Publishing, 1989) in press.