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Redox mechanism for the generation of holes in $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$: A neutron-diffraction study

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Our neutron-diffraction study of the single Tl-O layered $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ system ($x=0.0$, 0.4, 0.7, and 1.0) shows that the in-plane Cu-O(2) bond length decreases monotonically with increase of x. This is consistent with the introduction of holes in CuO_2 layers or the appearance of superconductivity in the sample with $x=0.4$ ($T_c=22$ K) and increase of T_c with x, $T_c=25$ and 30 K for samples with $x=0.7$ and 1.0, respectively. Further, the valence of copper, derived from Cu-O bond length, increases with increase of x despite the fact that the O content decreases as x increases. This clearly suggests that the internal redox mechanism due to the overlap of the empty Tl 6s band with the filled Cu $3d_{x^2-y^2}$ band is responsible for the generation of holes, and therefore superconductivity, in these materials.

I. INTRODUCTION

Various mechanisms have been proposed[1-3] for the generation of holes in p-type Tl-based cuprate superconductors. In the double-Tl-O-layered $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ ($n=1-3$) compounds (Tl-2), where the Tl 6s band is broader due to eight Tl:Tl near neighbors, holes are largely generated by the preexisting redox mechanism[4] involving the overlap of the Tl 6s band with the Cu $3d_{x^2-y^2}$ band [Fig. 1(a)] and thereby transferring 3d electrons to the Tl 6s empty band.

In the single-Tl-O-layered $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$ ($n=1-6$) compounds (Tl-1), holes are generated mainly due to the oxygen excess nonstoichiometry.[5] This is suggested by the chemical formula also. In these compounds, since there are only four Tl:Tl near neighbors, the bottom of the Tl 6s band lies above the Fermi level [Fig. 1(b)] and does not overlap with the Cu $3d_{x^2-y^2}$ band.[4] This is consistent with the fact that $TlBaLaCuO_5$, a derivative of the simplest Tl-1 ($n=1$) compound, is a semiconductor.[6] It was surprising, however, that this compound undergoes a semiconductor to (super)conductor transition upon substituting smaller Sr^{2+} ions for bigger Ba^{2+} ions, i.e., by applying chemical pressure.[7] In $TlBa_{1-x}Sr_xLaCuO_5$ systems, superconductivity appears for $x=0.4$ and T_c increases with increase of x and reaches a maximum ($T_c=32$ K) for $x=1.0$.[8] Substitution of the Sr^{2+} ion for the Ba^{2+} ion raises the filled Cu $3d_{x^2-y^2}$ band sufficiently, overlapping with the empty Tl 6s band, thereby generating holes.[9] This hypothesis has been supported by x-ray photoelectron studies[8] and infrared and Raman spectroscopic measurements[10] on $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ systems. The results

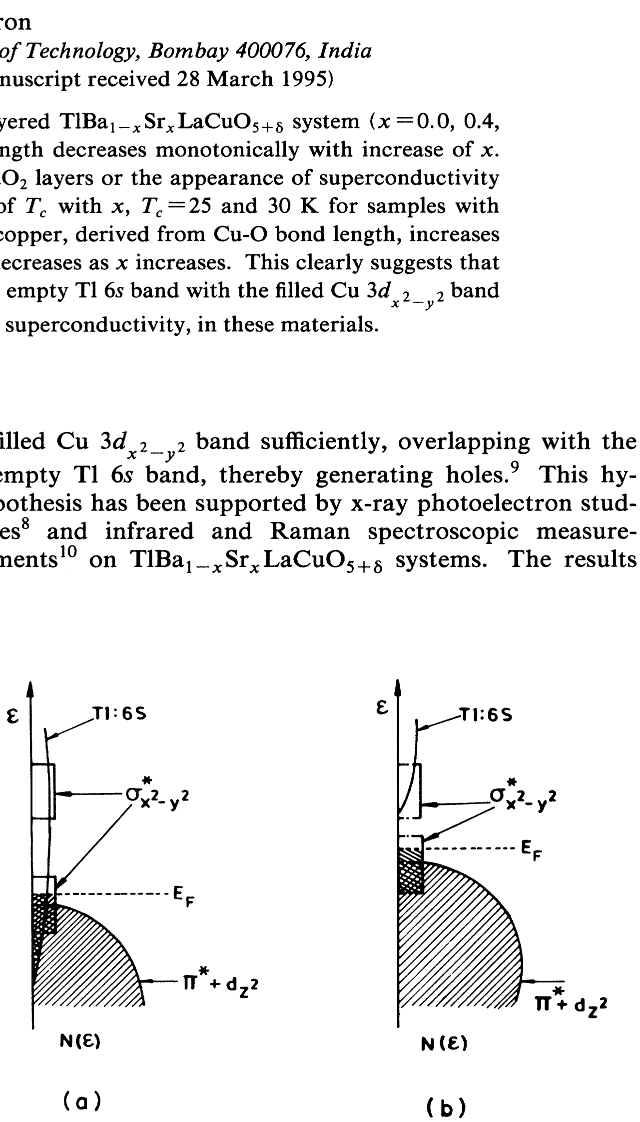

FIG. 1. Density of states $N(\epsilon)$ as a function of energy ϵ for (a) $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ and (b) $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, except for $TlBa_2CuO_5$ ($n=1$) (adapted from Ref. 4).

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of these studies were consistent with the redox mechanism responsible for the generation of holes in this system.

Recently, it has been proposed[11] that the superconductivity in $Tl_{1-y}LaBa_{1-z}Sr_zCuO_{5-x}$ systems depends on the Tl and oxygen content, ruling out the existence of the redox mechanism for the generation of holes. In order to establish the existence of the redox mechanism, it is essential to know accurately the cation and anion content. This is because the hole concentration depends strongly upon these two extrinsic factors also in addition to the redox mechanism which is an intrinsic mechanism for generation of holes. It is for this reason that we carried out a detailed neutron study in $TlBa_{1-x}Sr_zLaCuO_{5+\delta}$ ($x=0.0$, 0.4, 0.7, and 1.0) to determine precisely the occupancies of the Tl, LaBa(Sr), Cu, and O sublattices. These measurements leave no doubt about the existence of the redox mechanism in this material.

II. EXPERIMENT

The method of preparation of the $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ system has already been described elsewhere.[8] The phase purity of the samples was checked by the powder x-ray diffraction method. Superconductivity was studied by measuring the electrical resistance of the samples.

Powder neutron diffraction patterns (neutron wavelength, $\lambda=1.216$ Å) were recorded at room temperature at the Dhruva reactor. The instrument collimations were 0.7°-0.5°-0.5° from the in pile to the detector end. The patterns were analyzed by the Rietveld refinement method using a modified version of the program DBW3.2.[12] All positional, thermal (B), and occupancy (N) parameters were varied in addition to the cell constants, half-width, background parameters, zero angle, and scale factor. Occupancy and thermal parameters were varied in separate cycles. A Gaussian peak shape function was assumed.

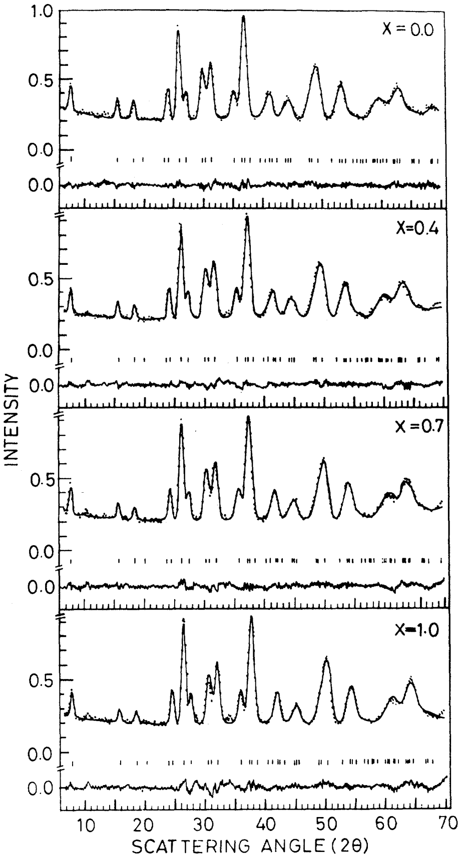

FIG. 2. Neutron diffraction pattern of $TlBa_{1-x}Sr_xLaCuO_5$ ($x=0.0$, 0.4, 0.7, and 1.0) system. The solid lines through the sets of (observed) points are the calculated profiles from Rietveld refinement based on the space group $P4/mmm$. The sets of small vertical lines below the data indicate the positions for the allowed reflections. The lower curve in each panel represents the difference between observed and calculated profiles.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns showed that all the samples are single phase. Electrical resistance measurements showed that the sample with $x=0$ is a semiconductor whereas samples with $x=0.4$, 0.7, and 1.0 are superconducting with $T_c=22$ K, 25 K, and 30 K, respectively.

Neutron diffraction patterns were refined on the basis of the standard 1:2:0:1 tetragonal structure (space group $P4/mmm$) and the fits are shown in Fig. 2. Occupancy of the Cu site was anchored at 100% as a reference, and the occupancy of the nine coordinated cationic site was refined by constraining the Ba:Sr:La ratio at the respective nominal composition for each sample. The occupancy of the O(2) sites in CuO_2 layers was observed to be 100% for all samples and so was kept fixed at 1.0. The O(3) ions in Tl-O layers exhibited anomalously large B values and a marginal excess occupancy at the O(3) site particularly for the Sr-free ($x=0$) sample. This was taken as an indication of oxygen disorder associated with the

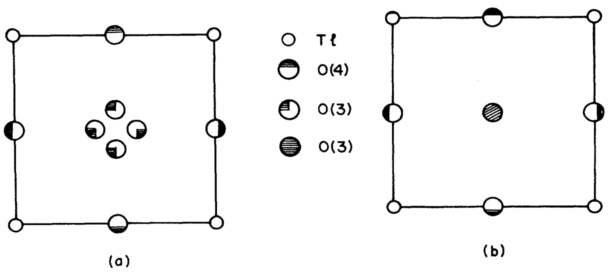

FIG. 3. Schematic representation of the distribution of O(3) in samples with (a) $x=0.0$ and (b) $x=0.4$, 0.7, and 1.0. In samples with $x=0.4$, 0.7, and 1.0, oxygen ion O(3) occupies a site $1c$ (1/2,1/2,0) in the unit cell (b). In samples with $x=1.0$, the oxygen ion O(3) is distributed randomly and equally among four sites $4n$ $(x,1/2,0)$ placed symmetrically about the site (1/2,1/2,0) (a).

O(3) site. Moreover, in earlier reports[13–15] on some of the Tl-based compounds, both Tl and O ions in the Tl-O layer have been shown to be displaced from their ideal position, leading to a short-range ordering because of the small size of the Tl^{3+} ion. Hence, a further set of refinements was carried out by allowing O(3) oxygen ions to occupy $4n$ sites, [see Fig. 3(a)] in the unit cell. This procedure led to significantly improved fits and B value for the $x=0$ sample with the B value decreasing from 13.6 to 8.0 initially, i.e., when O(3) oxygen was disordered, fixing all the other parameters. Subsequently, when the refinement in this "disorder" model was continued by floating the other variable parameters (for the $x=0$ sample), the B value of O(3) oxygen reduced to 7.5, obviously reflecting some inherent correlations between the parameters. This disorder model, however, did not lead to any significant improvements either in agreement factors or in the B values for the remaining three samples. Hence, the O(3) oxygens were retained on the unsplit sites for these samples. In fact, the B values of the

TABLE I. Positional and thermal (B) parameters for four samples of $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ obtained by neutron Rietveld refinement based on the space group $P4/mmm$. The scattering amplitudes used for Tl, Ba, La, Sr, Cu, and O are 0.89, 0.52, 0.83, 0.702, 0.770, and 0.58 fm, respectively. Figures in parentheses represent the e.s.d's referred to the last digit. (100N) represents the percentage site occupancy.

Sample	$x=0.0$	$x=0.4$	$x=0.7$	$x=1.0$
a (Å)	3.845(1)	3.805(1)	3.787(1)	3.760(1)
c (Å)	8.993(4)	8.915(3)	8.853(3)	8.804(4)
Tl (1a) (0,0,0)				
B	1.7(2)	1.9(2)	1.8(2)	1.7(2)
Nx	0.98(1)	0.99(1)	0.99(1)	1.02(1)
La (2h) (1/2,1/2,z)				
z	0.2981(6)	0.2925(5)	0.2913(5)	0.2897(7)
B	1.2(1)	0.5(1)	0.8(1)	1.0(1)
N	0.493(5)	0.499(5)	0.495(5)	0.501(6)
Ba (2h) (1/2,1/2,z)				
z	0.2981(6)	0.2925(5)	0.2913(5)	
B	1.2(1)	0.5(1)	0.8(1)	
N	0.493(5)	0.300(3)	0.149(1)	
Sr (2h) (1/2,1/2,z)				
z		0.2925(5)	0.2913(5)	0.2897(7)
B		0.5(1)	0.8(1)	1.0(1)
N		0.200(2)	0.347(3)	0.501(6)
Cu (1b) (0,0,1/2)				
B	0.5	0.5	0.5	0.5
N	1.0	1.0	1.0	1.0
O(1) (2g) (0,0, z)				
z	0.2252(7)	0.2281(6)	0.2288(6)	0.2298(7)
B	2.7(2)	1.2(2)	1.0(2)	0.3(1)
N	1.00(1)	1.00(1)	1.00(1)	1.00(1)
O(2) (2e) (1/2,0,1/2)				
B	1.5(1)	0.7(1)	0.6(1)	0.3(1)
N	1.0	1.0	1.0	1.0
O(3) (4n) (x,1/2,0)				
x	0.409(5)			
B	4.9(4)			
N	0.25			
O(3) (1c) (1/2,1/2,0)				
B		5.0(3)	4.6(3)	3.1(3)
N		0.98(1)	1.00(2)	0.97(2)
O(4) (2f) (1/2,0,0)				
B	1.0	1.0	1.0	1.0
N	0.087(8)	0.087(7)	0.060(7)	0.056(9)
O content	5.17	5.16	5.11	5.09
R_P	2.80	3.13	3.25	4.02
R_{WP}	3.73	4.01	4.11	5.26
R_e	1.81	1.74	1.83	2.28
R_B	0.68	0.94	1.19	1.08

unsplit O(3) oxygens in the samples were somewhat lower than that obtained for the O(3) oxygen in the $x=0$ sample even after splitting it. Further, the fits of the neutron diffraction patterns resulting from the model discussed above were not as good as generally obtained by us for many other high-T_c oxides.[16] Hence, based on a suggestion of Maeda *et al.*,[17] that the loose packing of Tl-O monolayers also gives rise to induction of interstitial oxygen, a further set of refinements was carried out by introducing partial oxygen occupancy at the $2f$ sites. This model (final model) led to much improved fits with all the samples showing significant oxygen occupancy at this interstitial site. The low R values of this model listed in Table I along with refined parameters and very good profile fits (Fig. 2) obtained strongly support this model. Table I summarizes our results of neutron Rietveld refinements.

An examination of Table I shows that the cations occupy the regular sites and are stoichiometric. On the other hand the occupancies of oxygen in the nonsuperconducting sample are different from the superconducting samples. The sites ($2g$) and ($2e$) account for four oxygens ($2O_1$ and $2O_2$, respectively) both in nonsuperconducting ($x=0.0$) and superconducting samples ($x=0.4$, 0.7, and 1.0). The fifth oxygen occupies the site ($1c$) in the superconducting samples [Fig. 3(b)] whereas in the nonsuperconducting sample ($x=0.0$) it occupies the fourfold ($4n$) sites [Fig. 3(a)]. It is instructive to note that in all the samples, there is a partial occupancy of oxygen at $2f$ sites. Eventually, the total occupancy of O ions is greater than 5 ($\delta>0$) and decreases with increase of x.

Interatomic distances are given in Table II. The Tl-O(3) distance in the sample with $x=0.0$ is larger than the sum of ionic radii (2.29 Å) for Tl^{3+} and O^{2-}, supporting that the Tl-O(3) plane is disordered because of the loose packing. Increasing the Sr content (x) causes a monotonic decrease in unit cell volume (Fig. 4) as expected from the ionic-radii considerations. This leads to a systematic decrease in the in-plane Cu-O(2) bond length (see Table II) which is dependent on the charge density in the CuO_2 layers. It can be seen (Table II) that the in-plane Cu-O(2) bond length for all values of x is one-half of the a parameter. This reflects that the in-plane O(2)-Cu-O(2) bond angle is 180° even though the bulky Ba ions are replaced by smaller Sr ions. Further, the large decrease of the a parameter or in-plane Cu-O(2) bond length suggests that the holes are generated in the antibonding band of CuO_2 layers and the hole concentration increases with increase of x, which is consistent with the increase of T_c.

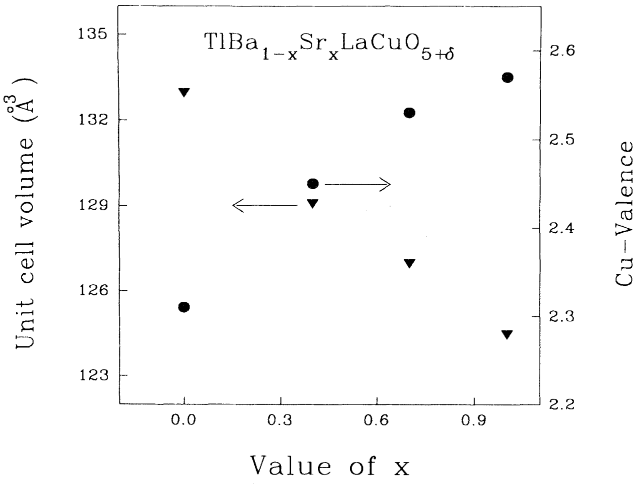

FIG. 4. Variation of unit cell volume with x. Decrease of cell volume is in agreement with the substitution of smaller Sr^{2+} ions for bigger Ba^{2+} ions. Variation of the valence of copper with x is also shown in this figure. The increase of copper valence with x is consistent with the increase of T_c.

TABLE II. Interatomic distances (Å) in the four samples of $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$.

Sample	$x=0.0$	$x=0.4$	$x=0.7$	$x=1.0$
Tl-O(1)×2	2.025(7)	2.034(5)	2.026(5)	2.023(6)
-O(3)×2	2.48(1)	2.691(1)	2.678(1)	2.658(1)
-O(3)×2	2.97(2)	2.691(1)	2.678(1)	2.658(1)
Tl-O(4)×4	1.922(1)	1.903(1)	1.893(1)	1.880(1)
Ba/La-O(1)×4	2.797(2)	2.751(2)	2.734(1)	2.710(2)
-O(2)×4	2.643(4)	2.654(3)	2.646(3)	2.638(4)
-O(3)×1	2.705(6)	2.608(5)	2.579(4)	2.551(6)
Cu-O(1)×2	2.471(7)	2.424(6)	2.401(5)	2.379(6)
-O(2)×4	1.922(1)	1.903(1)	1.893(1)	1.880(1)

We now comment upon the nonsuperconducting-superconducting nature of these samples on the basis of correlation between T_c and the bond valence sum (BVS) of copper.[18] For the nonsuperconducting sample with $x=0$, the empirical value of bond valence ($=+2.31$) of copper calculated from the relation[19] $V=\Sigma_i \exp[(r_0-r_i)/B_0]$ [where $r_0(\mathrm{Cu})=1.679$ and $B_0=0.37$] is lower than that expected for a superconducting material based on the data of de Leeuw *et al.*[18] Similarly, the bond valence for copper in other samples with $x=0.4$, 0.7, and 1.0 is calculated to be $+2.45$, $+2.53$, and $+2.57$, respectively. These values, being empirical, are to be taken only to represent the trend of the variation of the charge on the copper as a function of x. The fact that the sample with $x=0$ is semiconducting suggests that the hole concentration or the valence of copper is less than the critical one or the holes are localized due to disorder. We believe that the cause for the sample being nonsuperconducting is that the hole concentration in the $x=0.0$ sample is less than the critical one which is in agreement with the study of correlation between T_c and bond valence sum of copper. As mentioned above, this correlation requires that for a compound having low T_c (~ 35 K) with Ba/Sr ions in nine coordination and copper in six coordination, the bond valence of copper is high ($\sim +2.5$).[18] As x increases, *bond valence of copper increases* as shown in Fig. 4, and superconductivity sets in.

It is instructive to note that the copper valence and T_c increase with x despite the fact that the oxygen content decreases. Thus, if oxygen concentration alone was responsible for the generation of holes, the hole concentration or T_c should have decreased as x increased contrary to what we observe. This clearly points out the presence of another mechanism, the internal redox mechanism, of the generation of holes involving an internal charge transfer from Cu $3d_{x^2-y^2}$ to the empty Tl 6s bands, through an increased overlap brought about by chemical pressure. Charge transfer between Tl ions and CuO_2 layers is consistent with the large shifts of the only one observed out-of-plane Raman-active phonon in $TlBa_{1-x}Sr_xLaCuO_5$.[10] Since Tl and Cu ions are connected through apical oxygen O(1) and bonding between the Tl and O(1) is antibonding, the charge transfer from CuO_2 layers to Tl ions should result in an increase in the Tl-O(1) bond length. In contrast, we observe a small decrease which is consistent with the increase of the Raman-active phonon frequency. This decrease in Tl-O(1) is due to decreasing O(4) occupancy in Tl-O layers and also because of the importance of the difference in ionic sizes ($r_{Ba^{2+}}=1.47$ Å and $r_{Sr^{2+}}=1.31$ Å for nine-coordination) involved.

The charge on Tl ions can be calculated (i) by applying charge neutrality criteria assuming formal valence states of +3 for La, +2 for Ba/Sr, and using the empirical values of the BVS of copper (ii) by applying directly the BVS method using a r_0 value for the Tl^{3+} ion as deduced from the approximate formula given by Brown and Altermatt.[19] By applying the first method, the calculated values of charge on Tl ions are observed to decrease by about 0.5 as x increases from 0 to 1.0, whereas the second method shows a somewhat lower reduction (~ 0.13) in the charge of Tl ions. This is consistent with the redox mechanism for carrier generation in this system. We emphasize again that these calculations are meant to get an idea about the trend. The tolerance factor consideration[20] also supports the redox mechanism for the generation of holes in this system. The absence of noticeable disorder of O(3) oxygen (occupying 1/2, 1/2, 0 sites) in the sample with $x=0.4$, 0.7, and 1.0 also supports that the size of the Tl ion increases or the valence state of thallium is reduced with increase of x. However, we cannot totally rule out the presence of a small amount of residual disorder which is reflected in the somewhat large B values obtained for them. These values indicate that Tl atoms are present in a mixed valence state, rather than a random mixture of Tl^{3+} and Tl^{1+} ions, as has been shown experimentally by the x-ray photoemission spectroscopy (XPS) method.[8]

IV. CONCLUSIONS

Our neutron structural studies on $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ systems shows that the substitution of the smaller Sr^{2+} ion for the bigger Ba^{2+} ion in $TlBa_{1-x}Sr_xLaCuO_{5+\delta}$ results in a decrease of lattice parameters. Further, the in-plane Cu-O bond length decreases monotonically with Sr substitution, consistent with the increase of T_c or hole concentration. The O(3) oxygen in the Tl-O layer is disordered markedly only in the nonsuperconducting sample ($x=0.0$) and occupies the fourfold (4n) sites whereas in the superconducting samples this disorder is not so significant. Our studies reveal the presence of oxygen in the interstitial (2f) positions. The total oxygen content decreases with increase of x. Despite the decrease of oxygen content, T_c increases with x, which clearly suggests that the redox mechanism in these materials is responsible for the generation of holes.

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[1] J. B. Parise, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, A. W. Sleight, and E. Prince, Physica C **159**, 239 (1989).

[2] A. W. Sleight, M. A. Subramanian, and C. C. Torardi, Mater. Res. Bull. **14**, 45 (1989).

[3] R. J. Cava, Science **247**, 656 (1990).

[4] D. Jung, M. H. Whangbo, N. Herron, and C. C. Torrardi, Physica C **160**, 381 (1989).

[5] C. Martin, A. Maignan, J. Provost, C. Michel, M. Hervieu, R. Tournier, and B. Raveau, Physica C **168**, 8 (1990).

[6] A. Manthiram, M. Paranthaman, and J. B. Goodenough, J. Solid State Chem. **88**, 155 (1990).

[7] M. A. Subramanian, Mater. Res. Bull. **25**, 191 (1990).

[8] A. Sundaresan, C. S. Gopinath, A. S. Tamhane, A. K. Rajarajan, M. Sharon, S. Subramanian, R. Pinto, L. C. Gupta, and R. Vijayaraghavan, Phys. Rev. B **46**, 6622 (1992).

[9] M. H. Whangbo and M. A. Subramanian, J. Solid State Chem. **91**, 403 (1991).

[10] T. Mertelj, A. Sundaresan, L. C. Gupta, M. Sharon, and D. Mihailovic, Solid State Commun. **88**, 271 (1993).

[11] K. S. Najundaswamy, A. Manthiram, and J. B. Goodenough, J. Solid State Chem. **111**, 83 (1994).

[12] D. B. Wiles and R. A. Young, J. Appl. Cryst. **14**, 149 (1981).

[13] A. W. Hewat, E. A. Hewat, J. Brynestad, H. A. Mook, and E. D. Specht, Physica C **152**, 438 (1988).

[14] D. E. Cox, C. C. Torardi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Phys. Rev. B **38**, 6624 (1988).

[15] W. Dmowski, B. H. Toby, T. Egmi, M. A. Subramanian, J. Gopalakrishnan, and A. W. Sleight, Phys. Rev. Lett. **61**, 2608 (1988).

[16] A. Sequeira, Physica B **174**, 311 (1991).

[17] T. Maeda, K. Sakuyama, R. Izumi, H. Yamauchi, H. Asano, and S. Tanaka, Physica C **175**, 393 (1991).

[18] D. M. de Leeuw, W. A. Groen, L. F. Feiner, and E. E. Havinga, Physica C **166**, 133 (1990).

[19] I. D. Brown and D. Altermatt, Acta Crystallogr. B **41**, 244 (1985).

[20] A. Sundaresan, A. S. Tamhane, L. C. Gupta, M. Sharon, R. Pinto, and R. Vijayaraghavan, Phys. Rev. B **49**, 13 127 (1994).