Structural Disorder in $YSr_2Cu_2CoO_7$ and Substituted Variants

T. G. N. BABU, J. D. KILGOUR, P. R. SLATER, AND C. GREAVES

Superconductivity Research Group, School of Chemistry, University of Birmingham, Birmingham B15 2TT, England

The phase $YSr_2Cu_2CoO_7$ (orthorhombic, $Ima2$) is structurally related to $YSr_2Cu_2GaO_7$, but has a component of disorder associated with the oxygen sublattice. Substitutions of small amounts of Ba for Sr, or Cu for Co, have been studied, and shown by powder diffraction methods to increase the level of disorder. $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$ and $YSr_2Cu_{2.25}Co_{0.75}O_7$, for example, have been shown by neutron diffraction to have tetragonal symmetry ($P4/mmm$), which appears related to significant displacements of some of the oxygen ions. The nature of the disorder in the parent phase is discussed and compared with the structural observations on substituted derivatives. © 1993 Academic Press, Inc.

Introduction

The structure of $YSr_2Cu_2GaO_7$ (*1, 2*), Fig. 1, is closely related to that of $YBa_2Cu_3O_7$, and may be derived from it by substituting Sr for Ba, and replacing the chains of planar 4-coordinate Cu(1) sites by chains of corner-linked GaO_4 tetrahedra. The axes (a, b, c) of the orthorhombic $YSr_2Cu_2GaO_7$ unit cell ($Ima2$) are related to those of $YBa_2Cu_3O_7$ ($a' = 3.82$ Å, $b' = 3.88$ Å, $c' = 11.67$ Å) by $a = 2c'$, $b = \sqrt{2}b'$, $c = \sqrt{2}a'$. The GaO_4 chains are parallel to c (equivalent to $\langle 110 \rangle$ directions of the $YBa_2Cu_3O_7$-type subcell) and have a staggered configuration in adjacent layers, Fig. 1. It is interesting to note that the tetrahedral layers are very similar to those found in some oxygen-deficient perovskites with the brownmillerite structure, e.g., $Ca_2Fe_2O_5$ (*3*), Ca_2FeAlO_5 (*4*), $Sr_2Fe_2O_5$ (*5, 6*), Sr_2CoFeO_5 (*7*). In these materials, which contain alternate layers of tetrahedrally and octahedrally coordinated cations, each tetrahedral chain has cooperative oxygen displacements with one of two equiva-

lent senses, (+) or (−). If all chains have identical displacements, the symmetry is $Ima2$ (equivalent to the previously reported $Ibm2$ with a change of axes). Powder diffraction studies of $Sr_2Fe_2O_5$ (*5*) and Sr_2CoFeO_5 (*7*), however, implied incomplete order between the chains and an "averaged" structure with equal amounts of (+) and (−) chains and the symmetry $Imma$ (equivalent to $Icmm$). $YSr_2Cu_2GaO_7$ appears to be well ordered with unidirectional oxygen displacements according to the polar $Ima2$ space group (*1, 2*).

The slight preference of Co^{3+} for the tetrahedral site in Sr_2CoFeO_5 (*7, 8*), and the apparent preference of Co ions for the Cu(1) sites in $YSr_2Cu_{3-x}Co_xO_7$ (*9, 10*), encouraged us to examine the possibility of synthesizing $YSr_2Cu_2CoO_7$, an analogue of $YSr_2Cu_2GaO_7$. After the successful synthesis of this phase and subsequent structural analysis from neutron powder diffraction, the investigation was extended to include the effects of substituted variants. During these studies, structural data on $YSr_2Cu_2CoO_7$

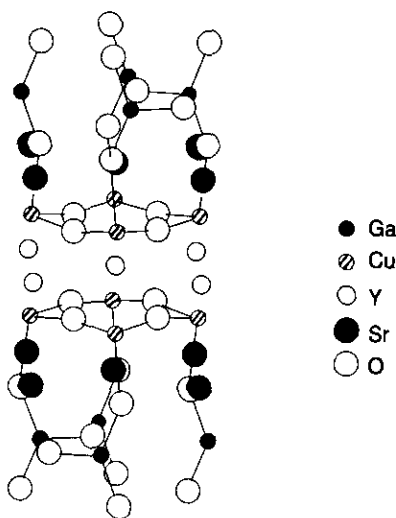FIG. 1. The structure of $YSr_2Cu_2GaO_7$ viewed approximately along [001], the direction of the chains of GaO_4 units.

● Ga
⊘ Cu
○ Y
● Sr
○ O

were reported by other workers (*11*). The close structural relationship with $YSr_2Cu_2GaO_7$ was confirmed, but the oxygen ions shared by neighboring Co ions in the tetrahedral chains were less well ordered than in $YSr_2Cu_2GaO_7$. In this paper we report a neutron diffraction investigation concerning the nature of order in $YSr_2Cu_2CoO_7$ and related cation substituted materials: $YSr_{2-x}Ba_xCu_2CoO_7$ and $YSr_2Cu_2Co_{1-x}Cu_xO_7$.

Experimental

The possible synthesis of materials of the type $RESr_2Cu_2CoO_7$ was examined using standard solid state ceramic methods and high purity reagents: RE_2O_3 (RE = Y, La, Nd, Sm, Eu, Dy), CuO, Co_3O_4, $SrCO_3$. Intimate, stoichiometric mixtures were fired three times at 1000°C for 20 hr in air, with intermediate grinding. Samples of $YSr_{1-x}Ba_xCu_2CoO_7$ and $YSr_2Cu_2Co_{1-x}Cu_xO_7$ were prepared similarly, using appropriate ratios of $SrCO_3$ and $BaCO_3$ for the former material. Samples were characterized using X-ray

powder diffraction (Philips PW 1050/70 using $CuK\alpha$ radiation) and oxygen contents were estimated using thermogravimetric analysis (heating to 930°C in a mixture of 10% hydrogen in nitrogen). The possibility of superconducting behavior was examined by ac susceptibility methods using dense sintered samples and low fields (5 mOe; 1 kHz) in a system calibrated against $YBa_2Cu_3O_7$.

Ambient temperature time-of-flight neutron diffraction data were collected from ca. 8-g samples of $YSr_2Cu_2CoO_7$ and $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$, using the diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. The structures were refined (for $0.7 < d$ 2.4 Å and $0.5 < d < 2.3$ Å, respectively) using the Rutherford Appleton program TF15LS, which is based on the Rietveld method and the Cambridge Crystallography Subroutine Library (*12*, *13*). Neutron scattering lengths used were 0.775 (Y), 0.702 (Sr), 0.7718 (Cu), 0.253 (Co), 0.525 (Ba), and 0.5805 (O), all $\times 10^{-12}$ cm.

Results and Discussion

Single phase samples of stoichiometry $RESr_2Cu_2CoO_7$ were obtained for all RE cations examined except La, for which a multiphase product was formed. All the single phase products were orthorhombic and appeared to be isostructural with $YSr_2Cu_2GaO_7$ (*1*, *2*). The partial replacement of either Co by Cu, e.g., $YSr_2Cu_{2.25}Co_{0.75}O_7$ (*9*), or Sr by Ba, e.g., $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$, was found to induce a transition to tetragonal symmetry, presumably due to disordering within the tetrahedral layers containing Co. Since $YSr_2Cu_{2.25}Co_{0.75}O_7$ had already been analyzed by neutron powder diffraction (*9*), the samples $YSr_2Cu_2CoO_7$ and $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$ were examined to allow comparison, and hence to provide insight into the nature of these order–disorder transitions. Thermogravimetric analysis implied that all samples described in this report had
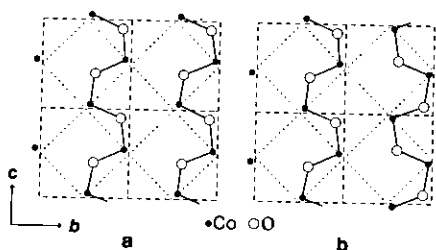
FIG. 2. Representations of layers of tetrahedral Co ions: (a) the atom displacements in all chains are identical, type (+); (b) the atom displacements in adjacent chains are antiparallel, type (+), (−).

oxygen contents of 7.0 ± 0.05. Although small variations in oxygen stoichiometry may exist from sample to sample, it is unlikely that these effects are relevant to the results of this study, and simple nominal compositions of the type $YSr_2Cu_2CoO_7$ are therefore used to describe all the samples investigated. None of the samples was found to be superconducting.

$YSr_2Cu_2CoO_7$

In general terms, the structure determined for $YSr_2Cu_2CoO_7$ is similar to that previously reported (11). The orthorhombic symmetry requires long-range order of the *direction* of the CoO_4 chains, but the *sense* of the atom displacements varies to give a defective structure containing partially occupied atom positions. The major atom displacements occur for the two "equatorial" O atoms, which lie in the plane of the Co atoms, and Fig. 2 shows schematic representations of such a plane containing (a) chains with identical, (+), displacements, and (b) chains with opposed, (+) and (−), displacements. The Co atoms, and particularly the "axial" O atoms above and below the planes, are subject to smaller shifts from their ideal positions. Structure refinement, Table I, indicated an equal distribution of (+) and (−) displacements, since each Co atom, and its coordination sphere, were split into two sites with an occupancy of 0.5 to

within one standard deviation. Although such a distribution of chains in an averaged structure corresponds to the higher symmetry *Imcm* space group, *Ima2* has been retained in Table I since it probably represents the local symmetry more exactly and allows direct comparison with related materials, e.g., $YSr_2Cu_2GaO_7$. In any given chain, we prefer to assume that *either* Co, O1, and O4 *or* Co', O1', and O4' are present, since models involving transitions from (+) to (−) displacements within a single chain such as that described by Huang et al. (11)) require substantial distortions of the Co stereochemistry at the boundaries. The temperature factors and magnitudes of the shifts for equivalent atoms in (+) and (−) chains were constrained to be equal, as were the temperature factors for O2 and O3 in the Cu layers. Since some of the positional parameters for Y, Sr, Cu, O2, and O3 were found to deviate insignificantly from their ideal values, these variables were fixed (no esd's in Table I) to aid the stability of the refinement. Neutron diffraction profiles for this refinement are shown in Fig. 3.

In contrast with the earlier structural report (11), which implied a 62%:38% ratio for the two chain types, a purely statistical distribution of the two chain types was indicated in the present study, and clear evidence (reduced *R*-factors) was found for split Co and O4 sites. It should be noted, however, that the 62%:38% ratio previously reported (11) differs by only three standard deviations from a simple 50%:50% mixture. It is therefore questionable whether this discrepancy is significant, and examination of samples prepared under a variety of conditions is required to obtain additional information. If we assume that the results imply structural features which are sample dependent, then a domain structure is likely, in which domain walls separate regions of (+) and (−) chain orientations. For small domain sizes a statistical distribution of chains would be expected,

TABLE I

STRUCTURAL PARAMETERS FOR $YSr_2Cu_2CoO_7$

Atom	Position	x	y	z	B_{iso} (Å²)	Unit cell occupancy
Y	4a	0.5	0	0	0.41(4)	4
Sr	8c	0.34863(8)	0.0042(8)	0.0000	0.53(3)	8
Cu	8c	0.42701(9)	0.0000	0.5000	0.48(3)	8
Co	4b	0.25	0.559(2)	0.048(2)	0.5(2)	2
Co'	4b	0.25	0.559(2)	−0.048(2)	0.5(2)	2
O1	4b	0.25	0.616(1)	0.393(1)	0.72(8)	2
O1'	4b	0.25	0.616(1)	−0.393(1)	0.72(8)	2
O2	8c	0.4340(2)	0.75	0.25	0.62(3)	8
O3	8c	0.4379(1)	0.25	0.75	0.62(3)	8
O4	8c	0.3250(1)	0.4692(7)	−0.023(1)	0.84(6)	4
O4'	8c	0.3250(1)	0.4692(7)	0.023(1)	0.84(6)	4

Note. $a = 22.772(1)$ Å, $b = 5.4519(3)$, $c = 5.4095(3)$ Å; *Ima2*; $R_{wp} = 4.94\%$, $R_{exp} = 3.27\%$, $R_I = 5.78\%$.

whereas for large domains the simple *Ima2* symmetry of a single chain direction would be found. In this way, a distribution of domain sizes might be expected to give a chain distribution of between 50% : 50% and 100% : 0%, as observed. Alternatively, the assumption of an equal concentration of both chain types allows other possibilities, which involve disorder on a more microscopic level. From this viewpoint, the structural disorder proposed for similar layers of tetrahedral cations in perovskites (*3–7*) is relevant, and the large separation (11.4 Å) between adjacent Co layers along [100] suggests that an interlayer, rather than intralayer, type of disorder may be present in $YSr_2Cu_2CoO_7$. If so, each layer would consist solely of a given chain type, e.g., (+), with an equal probability of adjacent layers being of type (+) or (−). Of course, alternative possibilities, involving small regions of antiparallel order, are also compatible with the data. For example, chains within a single layer could exist in a (+), (−), (+), (−), . . . sequence over relatively short distances, or adjacent layers along [100] could prefer a similar antiparallel configuration. Electron diffraction and microscopy investigations

are currently being pursued to examine the microstructural details of this phase.

Some important bond distances and angles for $YSr_2Cu_2CoO_7$ are given in Table II. The shift of the Co atom along [001], which is clear in the present study but only inferred from the anisotropic thermal factor previously (*11*), explains the significant differences in Co–O distances and O–Co–O angles between the two studies. The Co displacements allow the Co to attain a more regular tetrahedral geometry, and the Co stereochemistry deduced from the present study is more similar to that reported for Ga in $YSr_2Cu_2GaO_7$ (*1, 2*). The layers of linked CoO_4 units provide an unusual example of tetrahedral Co(III) in an oxide environment, with a high spin d^6 electron configuration. The Co–O distances are very similar to the Co(Fe)–O distances for the tetrahedral layers in Sr_2CoFeO_5 (*7*).

$YSr_{1.8}Ba_{0.2}Cu_2CoO_7$ and $YSr_2Cu_{2.25}Co_{0.75}O_7$

The tetragonal structures of $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$ and $YSr_2Cu_{2.25}Co_{0.75}O_7$ (*9*) are closely related to that of $YBa_2Cu_3O_7$. For both materials, structure refinement clearly revealed two distinct O atom positions within
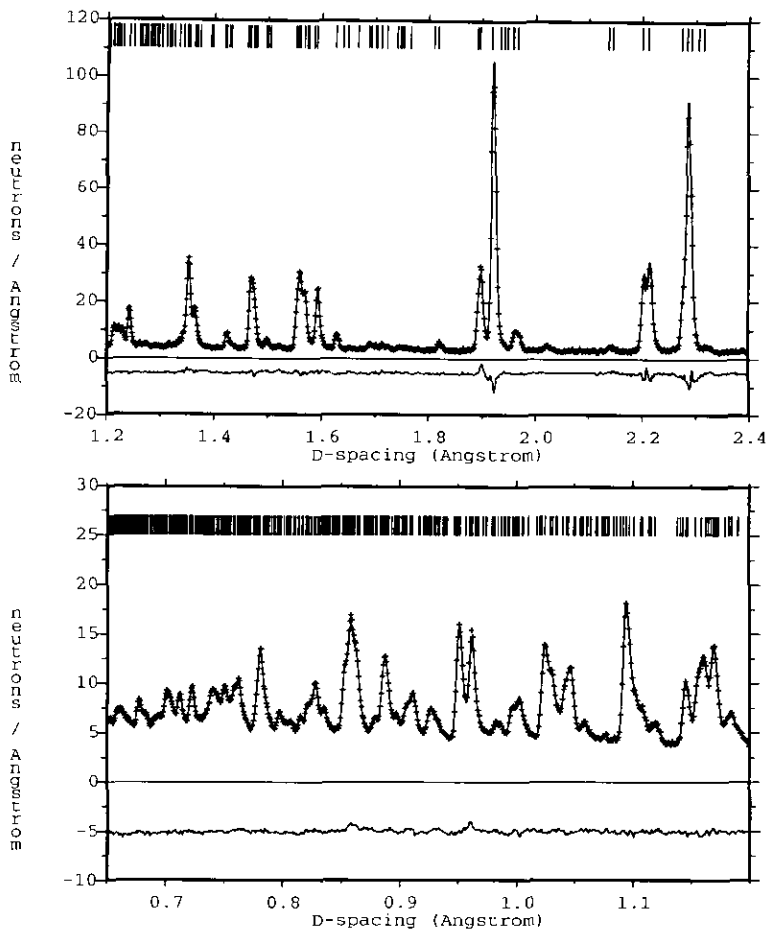
FIG. 3. Observed (crosses), calculated (solid line), and difference (offset by -5 neutrons/Å) neutron diffraction profiles for $YSr_2Cu_2CoO_7$. Reflection positions are marked at the top of the figure.

TABLE II

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

Sr–O1 2.411(5)	Cu–O2 1.927(1) [×2]
–O2 2.744(2) [×2]	–O3 1.936(1) [×2]
–O3 2.785(2) [×2]	–O4 2.333(5)
–O4 2.969(5)	
–O4 2.594(5)	Co–O1 1.958(9)
–O4 2.882(5)	–O1 1.891(9)
–O4 2.642(5)	–O4 1.817(9) [×2]
O1–Co–O1 106.0(4)	
O1–Co–O4 98.9(4) [×2]	
O1–Co–O4 104.6(4) [×2]	
O4–Co–O4 140.0(4)	

the Co layers. In the refinements, Tables III and IV, the temperature factors for these two O atoms (O1 and O2) were constrained to be equal, and the occupancies varied to maintain a unit cell content of 7.0. Displacements of Co and the "axial" O4 atoms were allowed, in accordance with the general displacements observed in $YSr_2Cu_2CoO_7$. In $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$, the refinement indicated partial disorder of the Co and Cu between the tetrahedral and 5-coordinate positions (approximately 14% of Cu in the tetrahedral layers), similar to that reported in the Ca-substituted material $Y_{0.6}Ca_{0.4}Sr_2$-

TABLE III

STRUCTURAL PARAMETERS FOR YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$

Atom	Position	x	y	z	B_{iso} (Å^2)	Unit cell occupancy
Y	1d	0.5	0.5	0.5	0.25(2)	1
Sr	2h	0.5	0.5	0.1949(1)	0.82(2)	1.8
Ba	2h	0.5	0.5	0.1949(1)	0.82(2)	0.2
Co1	4l	0.059(3)	0	0	0.9(2)	0.86(2)
Cu1	4l	0.059(3)	0	0	0.9(2)	0.14(2)
Co2	2g	0	0	0.3548(1)	0.28(2)	0.14(2)
Cu2	2g	0	0	0.3548(1)	0.28(2)	1.86(2)
O1	4n	0.266(2)	0.5	0	0.86(9)	0.66(1)
O2	4n	0.103(4)	0.5	0	0.86(9)	0.34(1)
O3	4i	0.5	0	0.3722(1)	0.52(2)	4
O4	8s	0.048(1)	0	0.1536(2)	1.25(6)	2

Note. $a = 3.8424(1)$ Å, $c = 11.3959(4)$ Å; $P4/mmm$; $R_{wp} = 3.76\%$, $R_{exp} = 2.52\%$, $R_I = 6.77\%$.

Cu$_2$CoO$_7$ (*11*). Although refinement of the YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$ structure has been previously reported by us (*9*), it has been reexamined to allow displacements of the tetrahedrally coordinated Co/Cu atoms to be consistent with the YSr$_2$Cu$_2$CoO$_7$ structure reported here. It should be noted that the *R*-factors for this refinement, Table IV, are identical to those obtained for the earlier model. The neutron diffraction profiles for YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ are shown in Fig. 4.

It is interesting to consider in more detail the nature of the orthorhombic–tetragonal transition induced in YSr$_2$Cu$_2$CoO$_7$ by the partial substitution of either Ba for Sr or Cu for Co. It appears highly relevant that the tetragonal phases YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ and YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$ (and those previously studied, e.g., YSr$_2$Cu$_{2.3}$Al$_{0.7}$O$_7$, YSr$_2$Cu$_2$FeO$_{7+x}$ (*9*)) all have some Cu in the tetrahedral layer in addition to the main substituent ion. It is therefore necessary to discuss why the presence of Cu should cause the disordering, and the structural implications of O1

TABLE IV

STRUCTURAL PARAMETERS FOR YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$

Atom	Position	x	y	z	B_{iso} (Å^2)	Unit cell occupancy
Y	1d	0.5	0.5	0.5	0.32(3)	1
Sr	2h	0.5	0.5	0.1965(2)	0.70(3)	2
Co1	4l	0.061(3)	0	0	1.0(2)	0.75
Cu1	4l	0.061(3)	0	0	1.0(2)	0.25
Cu2	2g	0	0	0.3543(2)	0.37(2)	2
O1	4n	0.271(5)	0.5	0	1.2(1)	0.76(4)
O2	4n	0.16(1)	0.5	0	1.2(1)	0.24(4)
O3	4i	0.5	0	0.3720(1)	0.55(2)	4
O4	8s	0.044(2)	0	0.1524(2)	0.94(7)	2

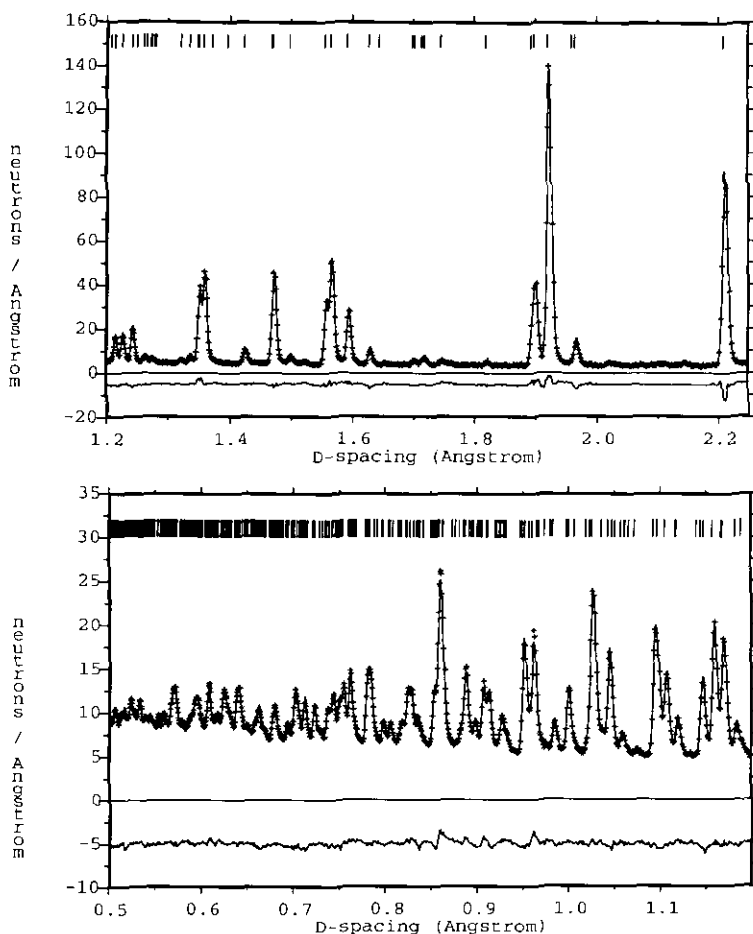*Note.* $a = 3.8282(2)$ Å, $c = 11.4126(5)$ Å; $P4/mmm$; $R_{wp} = 3.12\%$, $R_{exp} = 1.84\%$, $R_I = 5.21\%$.

FIG. 4. Observed (crosses), calculated (solid line), and difference (offset by -5 neutrons/Å) neutron diffraction profiles for $YSr_{1.8}Ba_{0.2}Cu_2CoO_7$. Reflection positions are marked at the top of the figure.

and O2, Fig. 5a, in the tetragonal structure. In addition, the influence of Ba substitutions on the Co/Cu distribution in $YSr_{1.8}Ba_{0.2}Cu_2$ CoO_7 needs rationalization.

An averaged tetragonal unit cell is consistent with a domain structure in which small domains of perfectly ordered unidirectional tetrahedral chains are separated by boundaries across which the direction of the chains is altered. Such a model of small regions of perfectly ordered $YSr_2Cu_2CoO_7$ would, however, give a single oxygen position in the tetrahedral layer of the tetragonal averaged cell (see Fig. 5b), corresponding to O1 in Tables III and IV. In fact, such a disordered model of the ideal $YSr_2Cu_2CoO_7$ structure would give O1 coordinates of $(0.276, \frac{1}{2}, 0)$, which agree well with Tables III and IV. It therefore seems likely that O2 atoms are coordinated to Cu atoms substituted at the Co sites. It must be recognized that each O1 and O2 will be linked to two cations, so unless there is considerable clustering of the Co and Cu atoms, the assumption that there exist only Cu–O2 and Co–O1 bonds is, at most, a convenient approxima-
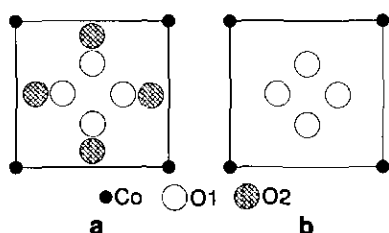
●Co   ○O1   ◉O2

    a   b

FIG. 5. (a) The arrangement of O1 and O2 atoms in the Co layers for the disordered tetragonal stuctures of YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ and YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$. (b) The expected oxygen arrangement for an averaged structure containing domains of YSr$_2$Cu$_2$CoO$_7$, with a statistical distribution of chain directions between the domains.

tion. Nevertheless, the assumption of a planar geometry for Cu with Cu at (0, 0, 0), similar to the Cu1 sites in YBa$_2$Cu$_3$O$_7$, allows us to confirm that the Cu–O2 distances are reasonable for Cu^{3+}. Estimates of Co–O and Cu–O distances in YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ and YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$ are given in Table V, and bond valence sum calculations (14), using the parameter $r_0 = 1.73$ for Cu^{3+} (15), suggest bond valence sums of 2.97 and 2.88 for Cu in YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ and YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$, respectively. Given the fact that the O1 and O2 sites are linked to two Co/Cu ions, the precise relationship between the Cu and O2 unit cell contents will depend on microstructural details. For YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$, the Cu and O2 occupancies are similar, but in

YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ an excess of O2 is indicated. A possible explanation for this may be found in the role played by Ba in causing the Co/Cu disorder, which is discussed below.

Table II shows a very short Sr–O1 distance, 2.411 Å, between Sr and the oxygen within the layers of tetrahedral Co ions. The reason for this short bond becomes apparent when considering the tetragonal structures, shown schematically in Fig. 5a. The distance corresponds to the bond from Sr at $(\frac{1}{2}, \frac{1}{2}, z)$, above and below the center of the basal layer of Fig. 5a, to the O1 site. The movement of O1 from the ideal $(0, \frac{1}{2}, 0)$ position in the YBa$_2$Cu$_3$O$_7$ structure causes a substantial decrease in this Sr–O distance. Given typical Ba–O distances of 2.7–3.0 Å (e.g., Ba–O distances of 2.74–2.99 Å in YBa$_2$Cu$_3$O$_7$ (16)), the substitution of Ba for Sr in YSr$_2$Cu$_2$CoO$_7$ necessarily requires a structural rearrangement with respect to the O1 position. The simple displacement of O1 to O2, Fig. 5a, would provide an increase to the more acceptable value of 2.695 Å. The consequential reduction in Co–O distances to values which are suitable for Cu, could provide the mechanism for the Co/Cu disorder which occurs following Ba substitution. The fact that the occupancy of O2 in YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ is higher than in YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$, even though the concentration of Cu in the tetrahedral layers is less, may therefore relate to additional oxygen displacements due to the large size of Ba. Unfortunately, the nature of the data currently available renders it impossible to reach definitive conclusions concerning the precise structural characteristics of these disordered phases.

The bond valence sum calculations suggest a formal oxidation state of +3 for the Cu located in the Co layers, and additional support is provided by the fact that the oxygen content appears unaffected by such substitution. Although it is normal for Cu^{3+} ions to have essentially planar stereochemistry,

TABLE V

Co–O and Cu–O Bond Distances (Å) for YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$ and YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$

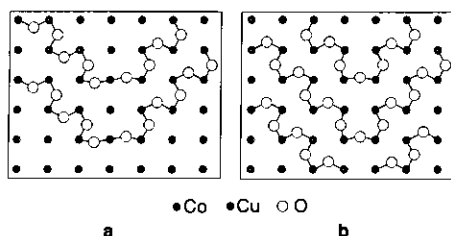| YSr$_{1.8}$Ba$_{0.2}$Cu$_2$CoO$_7$	YSr$_2$Cu$_{2.25}$Co$_{0.75}$O$_7$
Co–O1 2.080(5)	Co–O1 2.076(5)
–O1 1.979(5)	–O1 1.975(5)
–O4 1.798(5) [×2]	–O4 1.786(5) [×2]
Cu–O2 1.961(6) [×2]	Cu–O2 2.01(2) [×2]
–O4 1.750(6) [×2]	–O4 1.74(2) [×2]

•Co •Cu o O

a   b

FIG. 6. Schematic representations of how the presence of Cu in the Co layers may provide tetragonal symmetry. Domains of $YSr_2Cu_2CoO_7$ structure may terminate at either planar Cu, (a), or tetrahedral Cu, (b).The domain boundaries are associated with a change in the direction of the chains of tetrahedral cations as indicated. For clarity, the metal–oxygen bonds in a restricted number of chains are shown.

tetrahedral Cu^{3+} ions are known, e.g., in $Sr_5Pb_3CuO_{12}$ (17), and should be considered. The presence of Cu ions with either stereochemistry can, in fact, provide a plausible explanation for the tetragonal structure observed for materials containing mixed Co/Cu layers. Figure 6 shows how planar or tetrahedral CuO_4 units, with a different bond distance from CoO_4 units, could terminate chains of CoO_4 tetrahedra in a given direction, and result in a change in direction through 90°. In this way, the Cu ions could form boundaries between microdomains with the $YSr_2Cu_2CoO_7$ structure. Such a material, containing mutually perpendicular chains, would have an overall tetragonal symmetry consistent with that determined, provided the domain size was sufficiently small. For planar CuO_4 units, however, it is difficult to conceive of simple structures without the presence of cations with different coordination. For example, in Fig. 6a, the Co ion midway between the two Cu ions is 2-coordinate. In this respect, a flattened tetrahedral arrangement for the Cu, similar to that in $Sr_5Pb_3CuO_{12}$ (17), appears preferable as shown in Fig. 6b. An electron microscopy examination of these materials is currently taking place in order to compare their microstructural characteristics with those of $YSr_2Cu_2CoO_7$.

Acknowledgments

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