Strontium-Induced Oxygen Defect Structure and Hole Doping in $La_{2-x}Sr_xCuO_4$

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We have discovered that the apical oxygen with a 2.35-Å La-O bond length is removed when La is substituted by Sr in polycrystalline $La_{2-x}Sr_xCuO_4$ under normal preparation conditions. This apical oxygen can be partially filled by oxygen annealing. It is reasoned that a defect oxygen is trapped at an interstitial site near the Sr atom. We present evidence that this defect oxygen is intrinsic to Sr doping, independent of processing conditions. We propose that this defect oxygen serves as a mechanism for hole doping similar to that in the superconducting oxygen-rich La_2CuO_{4+y}.

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Sr and Ba doping of La_2CuO_4 produce a rich variety of physical properties including magnetism, superconductivity, a metal-insulator transition, and structural transformations as described by the complex phase diagram.[1-3] Charge-carrier holes are introduced by Sr and Ba doping. The superconducting transition temperature T_c of $La_{2-x}Sr_xCuO_4$ correlates with the hole concentration and shows a peak at $x \cong 0.15$.[2,4] The T_c of $La_{2-x}Ba_xCuO_4$, however, displays a local minimum at $x = 0.12$.[5,6] Although both Sr and Ba doping lower the tetragonal-to-orthorhombic structural transformation temperature, a low-temperature tetragonal phase is observed in $La_{2-x}Ba_xCuO_4$,[3,6] but apparently not in $La_{2-x}Sr_xCuO_4$.[7,8] The origin of the different effect of Sr and Ba doping on physical properties is presently unknown. In superconducting oxygen-rich La_2CuO_{4+y},[9-11] holes are doped by excess oxygen. The excess oxygen has been determined to locate at an interstitial site, $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ in the orthorhombic La_2CuO_4 unit cell.[12,13] Surprisingly, phase separation occurs[11] in La_2CuO_{4+y} and the superconducting T_c remains constant in the range of 34–38 K.[9-11] This value is close to the T_c of $La_{2-x}Sr_xCuO_4$ with optimum Sr doping ($x \cong 0.15$). The process of hole doping by excess oxygen in La_2CuO_4 and hole doping by Sr in $La_{2-x}Sr_xCuO_4$ may be related. In this paper, we report the first observation of a dopant-induced oxygen-vacancy defect structure in $La_{2-x}Sr_xCuO_4$ based upon systematic x-ray-absorption near-edge structure (XANES) studies. We propose that there exists an interstitial defect oxygen trapped near the Sr and discuss evidence that this Sr-induced defect oxygen is intrinsic to Sr-doped La_2CuO_4. In particular, we suggest that the defect oxygen serves as a mechanism for hole doping similar to that in oxygen-rich La_2CuO_{4+y}.

Polycrystalline samples of $La_{2-x}Sr_xCuO_4$ were prepared by normal solid-state reaction methods from mixtures of high-purity (99.999%) La_2O_3, CuO, and $SrCO_3$. After firing the mixtures at 950 °C in air, pellets were pressed and sintered in air at 1000 °C. Most of them were additionally sintered at 1100 °C for 24 h. Some were further annealed in 1-bar oxygen (500 °C for 140 h) or in vacuum (10^{-5} Torr, 700 °C). Our samples are single phase, and the $x = 0.07$, 0.10, 0.15, and 0.20 samples are superconducting with sharp magnetic transitions and large Meissner fractions (up to 75% for $x = 0.15$ samples).[14] X-ray-absorption measurements were carried out at beam lines X-23A2 and X-11A using Si(220) and Si(111) monochromators, respectively, at the National Synchrotron Light Source (NSLS).

It is known[15,16] that Sr substitutes for La in $La_{2-x}Sr_xCuO_4$. We have directly confirmed this substitution in our samples by comparing the Fourier transform of the La L_3- and Sr K-edge EXAFS (extended x-ray-absorption fine-structure) spectra.[17] This confirmation is crucial for the purpose of identifying oxygen defects around the Sr atom. Figure 1(a) presents the La L_3 XANES for La_2CuO_4 and Sr K-edge XANES for air-quenched $x = 0.04$, 0.07, 0.10, and 0.20 $La_{2-x}Sr_xCuO_4$ samples. The difference between the main peak (white line) in the La L_3 and Sr K spectra originates from the d-like final states probed at the L_3 edge and the p-like final states probed at the K edge. We wish to concentrate on the peak at about 20 eV (feature A) that is present in the Sr spectra but is absent in the La spectra. Feature A is *strictly* absent in the La XANES of Sr-doped La_2CuO_4 (see also Ref. 18). This difference between the La L_3 and Sr K spectra is not due to atomic-like final states, since feature A is also present in the La L_3 XANES in the tetragonal T' phase[19] of $Gd_{1.90}La_{0.10}CuO_4$ as shown below. Feature A is observed to be independent of the Sr concentration, ruling out an impurity phase as its origin. The Sr and La atoms are at equivalent sites. Distortions around the Sr atom are likely to occur among the oxygen near neighbors and any distortion among the relatively distant cations should be a secondary effect. Therefore, feature A in the Sr spectra must arise from an oxygen near-neighbor configuration that differs from that of La and not from a cation effect.

We suggest that feature A in the Sr spectra can only arise due to the removal of the apical oxygen at 2.35 Å from the Sr atom [*apical oxygen* refers to O(4) in Fig. 3 hereafter]. This conclusion is based on the combined experimental results described in detail below and summa-

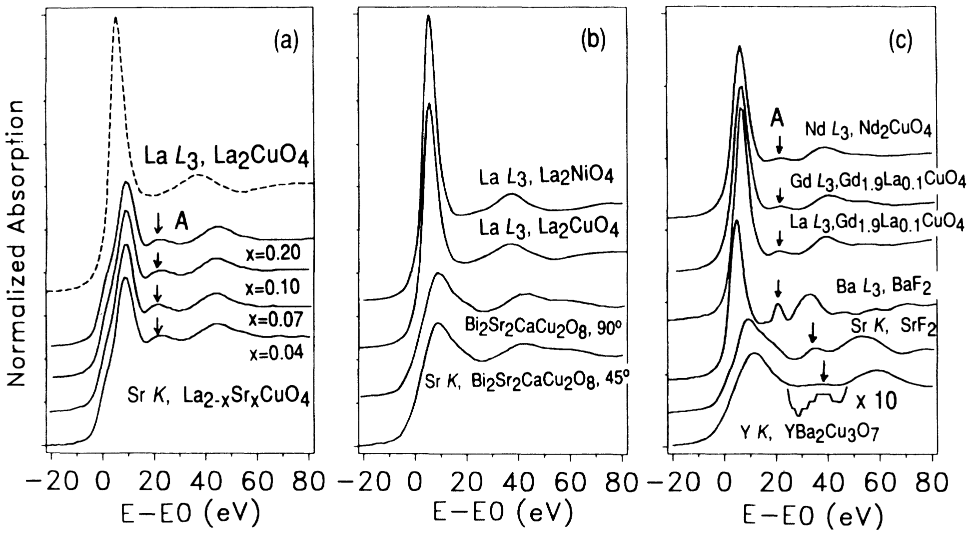

FIG. 1. (a) XANES spectra of air-quenched samples; feature A is present in Sr spectra but not in La spectra. (b) XANES for ninefold-coordinated absorbers similar to La in La_2CuO_4; feature A is absent. The Sr XANES on the $Bi_2Sr_2CaCu_2O_8$ single crystal is measured in fluorescence mode with the x-ray polarization vector at 45° and 90°, respectively, from the tetragonal c axis of the crystal. (c) XANES for eightfold-coordinated absorber, showing the presence of feature A.

rized here. First, *feature A is totally absent for ninefold-coordinated Sr and La with a near-neighbor configuration as in the case of La in* La_2CuO_4 *[Fig. 1(b)]*; thus, the existence of feature A in the Sr spectra of $La_{2-x}Sr_xCuO_4$ indicates that the oxygen coordination configuration around Sr differs from that around La. Feature A is generally present for an eightfold-coordinated absorber with *two sets of four equivalent near neighbors*, in particular, for Sr in SrF_2 and La in $Gd_{1.90}La_{0.10}CuO_4$ [Fig. 1(c)]. Although fourfold [e.g., Ge in $GeCl_4$ (Refs. 20 and 21)] and twelvefold coordinations [e.g., Sr in $SrTiO_3$ (Ref. 22)] can also give rise to a feature similar to feature A, these two configurations for Sr in $La_{2-x}Sr_xCuO_4$ are incompatible with diffraction results[15,16] and can also be ruled out by oxygen-content considerations. Second, *feature A is suppressed in oxygen-annealed* $La_{2-x}Sr_xCuO_4$ *samples and can be subsequently recovered by vacuum annealing.* This shows that feature A is associated with removal of oxygen. Removal of the nearest apical oxygen (2.35 Å) will leave the Sr coordinated with two sets of four oxygen atoms. Removel of oxygen atoms other than the one at 2.35 Å from the Sr atom is not likely to give rise to feature A. We conclude from the combination of these results that in the air-quenched $La_{2-x}Sr_xCuO_4$ (which shows feature A) the apical oxygen at 2.35 Å is removed. Note that the Sr is still coordinated with nine oxygen neighbors taking into account the defect oxygen proposed below. But the defect oxygen does not appear to suppress feature A probably because of its relative position with respect to the eight oxygen atoms on the regular lattice.

Figure 1(b) presents XANES spectra for ninefold-coordinated absorbers with oxygen near-neighbor configurations similar to that of La in La_2CuO_4. These are La in La_2NiO_4 and Sr in a $Bi_2Sr_2CaCu_2O_8$ (Ref. 16) single crystal with two different x-ray polarization directions. Feature A is completely absent in these spectra. Figure 1(c) shows XANES spectra for the eightfold-coordinated absorber with two sets of four equivalent oxygen or fluorine near neighbors. These are La, Nd, and Gd atoms in T' compounds, Sr and Ba in fluorides, and Y in $YBa_2Cu_3O_7$.[16] Clearly, feature A is present in all these spectra. Its existence is independent of the type of absorber, ruling out the different EXAFS phase shifts of the absorber as its origin. Feature A shows up in both L_3- and K-edge XANES, again excluding atomiclike final-state effects.

Physically, feature A originates from multiple scattering of the photoelectron by the nearest anion neighbors, in our case the oxygen or fluorine atoms. This is indicated by the fact that feature A is of relatively high frequency in k (photoelectron wave-vector) space, which implies a long scattering path in real space. Assignments of the long scattering path with cation neighbors are ruled out by the absence of feature A in the La XANES, La having the same cation neighbors as Sr. Bouldin *et al.*[21] have shown that in the Ge K-edge XANES of gas-phase $GeCl_4$ (Refs. 20 and 21) a feature similar to feature A arises solely from multiple scattering by the Cl nearest neighbors. The absence of feature A in the La XANES of La_2CuO_4 is due to the presence of the apical oxygen at 2.35 Å, which destroys the multiple-scattering contributions.

Feature A is largely suppressed in $La_{2-x}Sr_xCuO_4$ by oxygen annealing and is fully recovered by vacuum annealing the oxygen-annealed samples. Examples are given in Fig. 2 for the oxygen-annealed $x=0.07$ and 0.10

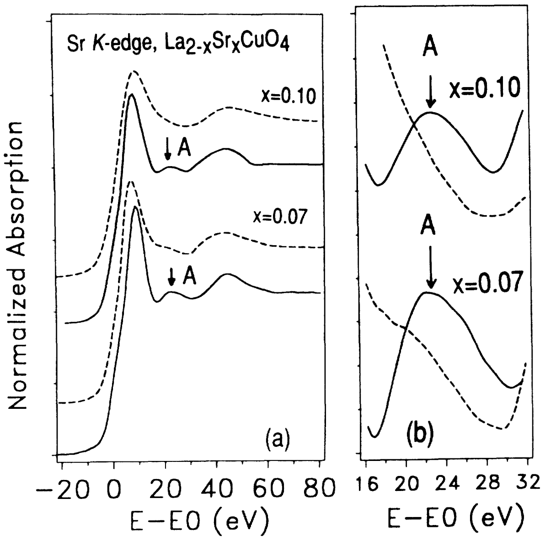

FIG. 2. (a) Sr *K*-edge XANES spectra for oxygen-annealed (500 °C, 140 h), and subsequently vacuum-annealed (700 °C, 48 h), $La_{2-x}Sr_xCuO_4$. (b) The region of feature *A*. The spectrum for the oxygen-annealed $x=0.07$ sample is more typical than the $x=0.10$ sample in that feature *A* is not completely suppressed.

samples (dashed line) and the same oxygen-annealed samples after vacuum annealing. Clearly, feature *A* is suppressed by the oxygen anneal, indicating that the empty O(4) site has become partially filled after the oxygen anneal. Vacuum annealing fully recovers feature *A* indicating that the apical O(4) atom is readily removed. A comparison of Sr EXAFS data between the oxygen-annealed and vacuum-annealed samples shows qualitative agreement with this interpretation of XANES data, i.e., oxygen annealing partially fills O(4) sites and vacuum anneal removes filled O(4). However, reliable quantitative EXAFS analysis is limited since three distinct but overlapping Sr-O distances are present. The white line and the EXAFS oscillations are broadened in the oxygen-annealed samples due to the presence of O(4). However, the suppression of feature *A* cannot be attributed to a broadening effect.

Removal of the O(4) apical oxygen is consistent with a number of other experimental results on $La_{2-x}Sr_xCuO_4$. In a recent interpretation of Cu nuclear-quadrupole-resonance data for $x=0.15$, 0.20, and 0.30 samples, two differentiated Cu sites were suggested.[23] The removal of an apical oxygen near Sr makes the local environment of one Cu differ from the other Cu atoms. Shear defects were recently observed in Sr-doped La_2CuO_4 in which edge-sharing copper-oxygen octahedra were identified.[24] Two edge-sharing octahedra correspond to one less apical oxygen as compared to the regular corner-sharing octahedra, in qualitative agreement with the removal of the apical oxygen concluded from our results. The apparent contradiction between the removal of the apical O(4) and the full occupancy obtained in the neutron-diffraction studies[15,16] is not surprising, considering the interstitial defect oxygen proposed below. The large thermal factor with the largest component perpendicular to the *c* axis obtained by the refinement of diffraction data[16] may result from the oxygen-defect structure.

The apical oxygen in *air-quenched* samples is missing, and based on a large number of reported results[2,4,25] as well as our results, these samples are not oxygen deficient. This requires oxygen at a defect site(s) and leads us to propose a Sr-induced defect oxygen. The oxygen content of our samples determined by a direct oxygen analysis[26] is all slightly greater than 4.0; thus these samples are not oxygen deficient. Sharp superconducting transitions and large Meissner fractions are supportive of this. Therefore, the missing apical oxygen must remain in the structure, but at a defect site. The oxygen content of 4.0 requires that the amount of Sr-induced oxygen defect is about equal to the Sr concentration. Such a precise control of the amount of defect oxygen by Sr suggests that the defect oxygen is trapped in the vicinity of the Sr atom. Hence the picture emerges that the Sr creates and traps the defect oxygen. Excess oxygen atoms in La_2NiO_{4+y} and La_2CuO_{4+y} are approximately located at $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in the orthorhombic unit cell.[12,13] Even though the details of the oxygen-defect structure in $La_{2-x}Sr_xCuO_4$ remain to be determined, it is safe to assume that the defect is similarly located in the La_2O_2 layer and is near the Sr atom. A simplified picture for this oxygen-defect structure is shown in Fig. 3. In analogy to La_2NiO_{4+y},[13] we have labeled the defect oxygen as O(3) and assumed its location at a $(\frac{1}{2},0,\frac{1}{4})$ position in the tetragonal *T* structure. From results on oxygen-annealed samples and a then vacuum-annealed sample (see below), there is evidence that the defect oxygen O(3) is intrinsic for Sr doping, independent of processing

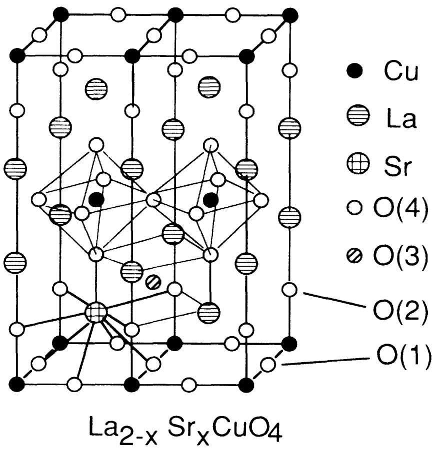

FIG. 3. A simplified model proposed for the Sr-induced oxygen-defect structure of $La_{2-x}Sr_xCuO_4$. The defect oxygen O(3) is approximately at $(\frac{1}{2},0,\frac{1}{4})$ in the tetragonal unit cell. Possible distortions of other apical oxygen positions due to the presence of O(3) are neglected for simplicity. The apical oxygen O(4) (nearest to Sr) is at most partially occupied.

conditions. We propose that holes are doped into the CuO_2 plane through the Sr-induced defect oxygen O(3) in a way similar to that proposed[11,13] for the superconducting oxygen-rich La_2CuO_{4+y}.

We now discuss further experiments on oxygen-annealed and vacuum-annealed samples. An oxygen-annealed (500 °C) $x=0.07$ sample has the apical O(4) sites partly filled. Vacuum annealing (500 °C, 48 h) of this oxygen-annealed sample removes all the O(4) atoms as indicated by feature A in the Sr XANES data. However, this vacuum-annealed sample exhibited[14] a sharp superconducting transition at T_c of 17 K and a 37% Meissner fraction in a field of 2.5 G. This suggests that the vacuum-annealed sample has O(3) occupied. The defect O(3) must also exist in the oxygen-annealed sample because it is very unlikely that the defect oxygen O(3) in the air-quenched sample moves to the O(4) site during oxygen annealing and moves from O(4) back to O(3) during vacuum annealing at the same temperature. Thus, the defect oxygen O(3) is intrinsically associated with Sr doping rather than created by certain processing conditions. The oxygen-annealed samples have fully occupied O(3) and partially occupied O(4) and thus its oxygen content is greater than 4.00. The apical O(4) atom also dopes holes into the sample, consistent with our observation[14] of noticeably higher T_c values for the oxygen-annealed samples. Partly based on our experimental results, we propose a scheme for the oxygen behavior under thermal processing in the $x \leq 0.15$ samples. Annealing in vacuum or inert gases first removes any filled apical O(4) easily, and then may remove (not as easily) some of the defect O(3) depending on the annealing conditions. Superconductivity can be destroyed completely only if a large amount of the O(3) atoms are removed and the hole concentration is reduced below a certain value. Annealing in oxygen first fills any empty O(3) sites, then fills the O(4) sites partially.

An oxygen deficiency has been generally observed[2,4] in $La_{2-x}Sr_xCuO_4$ samples prepared in air as the value of x exceeds about 0.15. This may be due to the fact that the concentration of the Sr-induced O(3) is limited to about 0.15 per unit cell for samples prepared in this manner. The oxygen deficiency arises from a loss of the defect oxygen O(3) [the apical O(4) site is empty already]. In the high-Sr-concentration ($x > 0.15$) region, the empty apical O(4) site is filled upon oxygen annealing,[17] but the partly empty O(3) site may not be filled. The hole doping and local structure are likely to be different from the low-Sr-concentration region.

In summary, we have directly observed a Sr-induced oxygen-vacancy defect structure in $La_{2-x}Sr_xCuO_4$. The Sr doping introduces a local structural distortion such that the apical O(4) site becomes unoccupied in air-quenched samples and vacuum-annealed samples but the oxygen content is maintained close to 4.00. The O(4) site can be partially filled in oxygen-annealed samples and T_c increases slightly with partially filled O(4). We have suggested that an interstitial defect oxygen O(3) is trapped near the Sr atom independent of the processing condition. It is proposed that the O(3) serves as a mechanism that dopes holes into the CuO_2 plane. This defect structure model and hole doping through the defect oxygen provide a unifying approach of relating the superconductivity in the oxygen-rich La_2CuO_{4+y} and Sr-doped La_2CuO_4. Our results suggest a new approach for studying the physical properties related to divalent cation doping in the La_2CuO_4 system.

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[1] For example, R. J. Birgeneau and G. Shirane, in *Physical Properties of High Temperature Superconductors I*, edited by D. M. Ginsberg (World Scientific, Singapore, 1989); A. Weidinger *et al.*, Phys. Rev. Lett. **62**, 102 (1989).

[2] J. B. Torrance *et al.*, Phys. Rev. Lett. **61**, 1127 (1988).

[3] J. Axe *et al.*, Phys. Rev. Lett. **62**, 2751 (1989).

[4] M. W. Shafer, T. Penny, and B. L. Olson, Phys. Rev. B **36** 4047 (1987).

[5] A. R. Moodenbaugh *et al.*, Phys. Rev. B **38**, 4596 (1988).

[6] T. Suzuki, M. Tagawa, and T. Fujita, Physica (Amsterdam) **162–164C**, 983 (1989).

[7] R. M. Fleming *et al.*, Phys. Rev. B **35**, 7191 (1987).

[8] J. B. Torrance *et al.*, Phys. Rev. B **40**, 8872 (1989).

[9] J. M. Tarascon *et al.*, in *Novel Superconductivity*, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 705.

[10] J. E. Schirber *et al.*, Physica (Amsterdam) **152C**, 121 (1988).

[11] J. Jorgensen *et al.*, Phys. Rev. B **38**, 11 337 (1988).

[12] C. Chaillout *et al.*, Physica (Amsterdam) **158C**, 183 (1989).

[13] J. D. Jorgensen *et al.*, Phys. Rev. B **40**, 2187 (1989).

[14] M. E. Filipkowski *et al.* (to be published).

[15] R. J. Cava *et al.*, Phys. Rev. B **35**, 6716 (1987).

[16] For a recent review, see K. Yavon and M. Francois, Z. Phys. B **76**, 413 (1989).

[17] Z. Tan *et al.* (unpublished).

[18] J. M. Tranquada *et al.*, Phys. Rev. B **35**, 7187 (1987).

[19] V. B. Grande *et al.*, Z. Anorg. Allg. Chem. **428**, 120 (1977).

[20] B. M. Kincaid and P. Eisenberger, Phys. Rev. Lett. **34**, 1361 (1975).

[21] C. E. Bouldin *et al.*, Phys. Rev. B **38**, 10816 (1988).

[22] H. Kageyama *et al.*, J. Phys. (Paris), Colloq. **47**, C8-757 (1986).

[23] K. Yoshimura *et al.*, J. Phys. Soc. Jpn. **58**, 3057 (1989).

[24] P. L. Gai and E. M. McCarron, III, Science (to be published).

[25] K. Kreedhar and P. Ganguly, Phys. Rev. B **41**, 371 (1990).

[26] B. L. Chamberland (unpublished).