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P. Lightfoot, S.-Y. Pei, J. D. Jorgensen
Materials Science Division
Argonne National Laboratory
Argonne, IL 60439

and

A. Manthiram and J. B. Goodenough
Center for Materials Science and Engineering
University of Texas at Austin
Austin, TX 78712

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EXCESS OXYGEN DEFECTS IN LAYERED CUPRATES

P. Lightfoot[1], Shiyou Pei[1], J. D. Jorgensen[2], X.-X.Tang[3], A. Manthiram[3] and J. B. Goodenough[3], (1)Science and Technology Center for Superconductivity and (2) Materials Science Division, Argonne National Laboratory, Argonne, IL 60439 and (3) Center for Materials Science and Engineering, University of Texas at Austin, Austin, TX 78712.

ABSTRACT

Neutron powder diffraction has been used to study the oxygen defect chemistry of two non-superconducting layered cuprates, $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$, having a T*-related structure, and $La_{1.85}Sr_{1.15}Cu_2O_{6.25}$, having a structure related to the that of the newly discovered double-layer superconductor $La_{2-x}Sr_xCaCu_2O_6$. The role played by oxygen defects in determining the superconducting properties of layered cuprates is discussed.

INTRODUCTION

Defects are known to play a critical role in the synthesis and superconducting properties of the high T_c oxide superconductors (1). The unique role played by excess oxygen doping has been elegantly demonstrated in the $La_2CuO_{4+\delta}$ system by Jorgensen et al. (2), who showed that superconductivity in this system in fact results from a subtle phase separation into an oxygen-rich superconducting phase and a stoichiometric non-superconducting phase, both having orthorhombic structures based on the K_2NiF_4, or T structure. Due to the relatively small defect concentration, it was not possible to locate the excess oxygen defect in the neutron powder diffraction study of $La_2CuO_{4+\delta}$. However, a later study of the isostructural La_2NiO_{4+y} (y ~ 0.18) unambiguously determined the excess oxygen to be located in an interstitial site in the La_2O_2 rock-salt like layers of the structure (3).

Two structures closely related to the T structure are the T' and T* structures, differing only in the positions of the oxygen atoms within the lattice,

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leading to square planar and square pyramidally coordinated copper, respectively. In view of the similarities between these structures, it may be expected that similar interstitial oxygen defects could also occur in these systems, and may indeed play a critical role in determining the electronic behaviour of these systems, both of which have been made superconductive (4,5). In this paper we describe the observation, by neutron powder diffraction, of such a defect in the T* phase $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$ (6). We also describe the identification of the excess oxygen location in the double-layer phase $La_{1.85}Sr_{1.15}Cu_2O_{6.25}$ (7), and discuss this in the light of the related, recently discovered (8) superconducting phase $La_{1.6}Sr_{0.4}CaCu_2O_6$.

EXPERIMENTAL

A powder sample of $La_{1.25}Dy_{0.75}CuO_4$ was obtained from stoichiometric quantities of La_2O_3, Dy_2O_3 and CuO, fired at 950°C for 12h and then at 1050°C for a further 20h. Fluorination was achieved by a low-temperature anion exchange reaction, by reacting $La_{1.25}Dy_{0.75}CuO_4$ with ZnF_2 in an evacuated sealed tube at 280°C for 48h.

$La_{1.85}Sr_{1.15}Cu_2O_{6.25}$ was obtained by firing intimately mixed La_2O_3, $SrCO_3$ and CuO in 1 atm O_2 according to the following scheme: 1000°C (20h), 1050°C (20h), 500°C (12h), 450°C (12h), 400°C (12h), 350°C (12h) and 300°C (12h). This procedure was found to maximise the oxygen content for a 1 atm O_2 anneal. Neutron powder diffraction data were collected on the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source. Data were analysed by the Rietveld method.

RESULTS AND DISCUSSION

$La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$. Our refinement (6) shows that this phase adopts an orthorhombically distorted structure based on that of the T* phases (9). Incorporation of the excess anion content occurs in an interstitial site in the La_2O_2 rocksalt layers of the

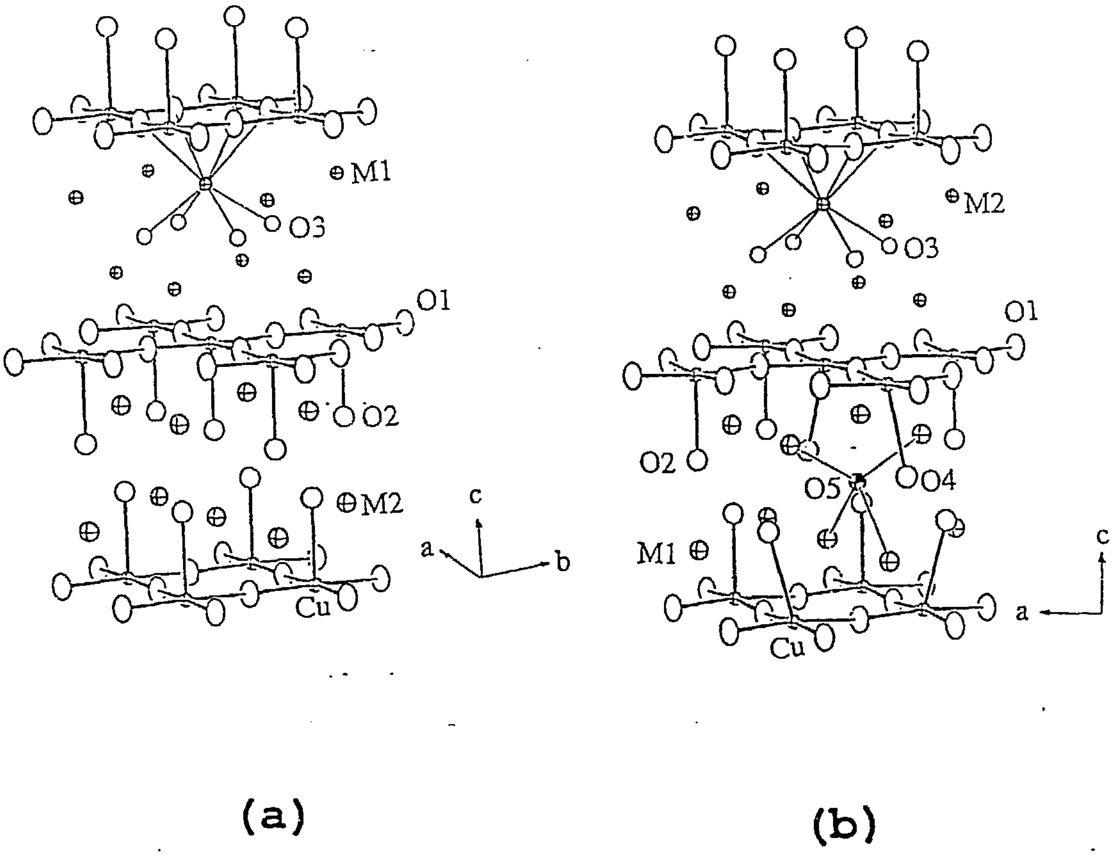

Figure 1. (a) Idealized tetragonal T* structure, showing alternating T' (top half) and T (bottom half) layers. (b) The distorted T* structure of $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$, showing incorporation of the interstitial defect, O(5). Favorable coordination of O(5) to four M(1) and four displaced anion, O(4), sites occurs. Note that only half of the true unit cell (which is rotated by 45° around the c-axis, relative to (a)) is shown, for ease of comparison of the two structures.

structure, and not in the vacant "apical" position in the T' -type half of the structure. This type of interstitial defect is directly analogous to that previously observed in $La_2NiO_{4.18}$ (3) and that thought to be the doping mechanism responsible for superconductivity in $La_2CuO_{4+\delta}$ (2).Accommodation of the defect requires displacement of the four neighboring apical oxygens on to new sites, in order to provide favorable anion-anion contacts. A comparison of the undistorted (tetragonal) $La_{1.25}Dy_{0.75}CuO_4$ and the distorted $La_{1.25}Dy_{0.75}CuO_{3.75}F_{0.5}$, showing incorporation of the anion defect, is presented in Figure 1. Interestingly, high oxygen partial pressures are often found necessary to make the T* phases superconducting (10,11). Hence, although the present phase does not superconduct, it is not unreasonable that a similar type of defect may again turn out to be the doping mechanism responsible for superconducting behavior in the T* phases.

$La_{1.85}Sr_{1.15}Cu_2O_{6.25}$.The structure adopted by this phase (7) is an oxygen-deficient variant of the well-known $Sr_3Ti_2O_7$ structure (n=2 member of the Ruddlesden-Popper series $AO.nABO_3$). A view of the structure is shown in Figure 2. Previous refinements of the structures of cuprates of this type, $La_2SrCu_2O_6$ (12) and $La_{1.9}Ca_{1.1}Cu_2O_6$ (13), have suggested a zero, or very small occupancy of the O(3) site between neighboring CuO_5 pyramidal layers. For the present case, where a significantly higher oxygen content has been obtained, we have shown unambiguously that the inter-layer site can accommodate a high concentration of excess oxygen. Indeed, our work suggests transfer of a small, but significant amount of the in-plane oxygen (O1) to the inter-layer site. It is interesting to compare this phase with the recently discovered (8) superconducting system $La_{2-x}Sr_xCaCu_2O_6$ (maximum T_c = 60K at x = 0.4). Izumi et al. (13) showed that in $La_{1.9}Ca_{1.1}Cu_2O_6$, Ca has a strong preference for the smaller, M(1) site between the CuO_2 layers. Thus it would be expected that in $La_{2-x}Sr_xCaCu_2O_6$ the Ca would also adopt the M(1) site, thus leading to a relatively short (~3.3Å) Cu-Cu distance, and inhibiting the occupancy of the O(3) site. This system, therefore,

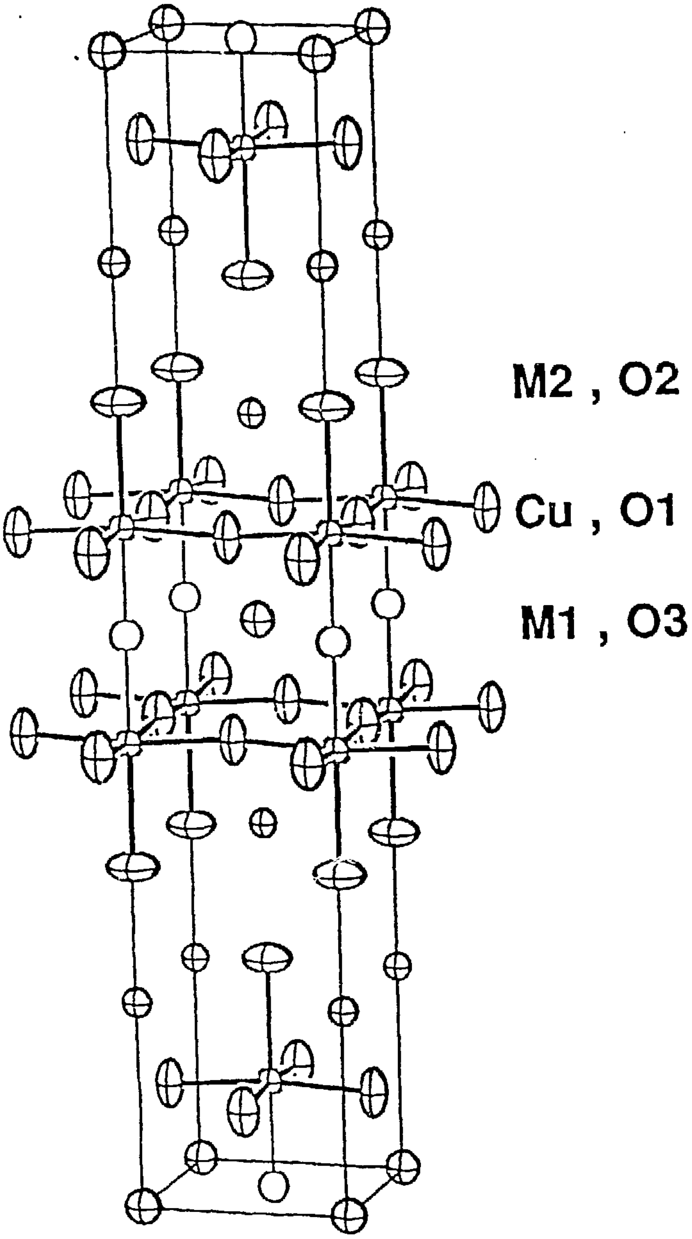

Figure 2. Structure of $La_{1.85}Sr_{1.15}Cu_2O_{6.25}$. Note that the O(3) site, which is completely vacant in the case of $La_{1.9}Ca_{1.1}Cu_2O_6$, is partially occupied in the present case.

easily maintains the pseudo-two-dimensional nature believed to be required for superconductivity. In $La_{1.85}Sr_{1.15}Cu_2O_{6.25}$, the Cu-Cu distance is correspondingly greater (3.756Å), facilitating the occupancy of the inter-layer O(3) site, and thus leading to the partial breakdown of the 2D nature of the structure. Further careful structural work will show whether such ideas may help to explain the absence of superconductivity in $La_{1.85}Sr_{1.15}Cu_2O_{6.25}$ and related phases (14).

CONCLUSIONS

We have presented two examples of the way in which oxygen defects play a critical role in the structural chemistry of the layered cuprates, and suggest that such defects may have a profound effect on the electronic properties of these systems. Clearly, before any definitive statements relating defect chemistry to superconductivity may be made, more structural data will be required. We have so far only examined the simplest systems. Neutron powder diffraction will play a central role in the elucidation of the defect structures of more complex systems. However, it is also clear, for example in the $Nd_{2-x}Ce_xCuO_4$ system (15, 16), that the differences between superconducting and non-superconducting samples is very subtle, and defect chemistry on a local scale may provide the key to the understanding of these systems in the future.

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