EXCESS OXYGEN DEFECTS IN LAYERED CUPRATES

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

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.

September 1990

Submitted to International Conference on Chemistry of Electronic Ceramic Materials,
Sojourner Inn, Teton Village, Wyoming, 8/17-22/90

Work was performed under the auspices of the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences, under Contract W-31-109-ENG-38 (J.D.J.) and the National Science Foundation, Office of Science and Technology Centers under Contract #STC-88-09854 (P.L., S.-Y.P.).
EXCESS OXYGEN DEFECTS IN LAYERED CUPRATES

P. Lightfoot¹, Shiyou Pei¹, J. D. Jorgensen², X.-X. Tang³, A. Manthiram³ and J. B. Goodenough³, (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, La₅.2₂Dy₀.₇₅Cu₀₃.₇₅F₀.₅, having a T*-related structure, and La₁.₈₅Sr₁.₁₅Cu₂O₆.₂₅, having a structure related to that of the newly discovered double-layer superconductor La₂₋ₓSrₓCaCu₂O₆. 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 Tc oxide superconductors (1). The unique role played by excess oxygen doping has been elegantly demonstrated in the La₂CuO₄⁺δ 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 K₂NiF₄, 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 La₂CuO₄⁺δ. However, a later study of the isostructural La₂NiO₄+y (y ~ 0.18) unambiguously determined the excess oxygen to be located in an interstitial site in the La₂O₂ 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,
leading to square planar and square pyramidal coordination of 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 superconducting (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$_2$O$_{6.25}$ (7), and discuss this in the light of the related, recently discovered (8) superconducting phase La$_{1.6}$Sr$_{0.4}$CaCu$_2$O$_6$.

EXPERIMENTAL

A powder sample of La$_{1.25}$Dy$_{0.75}$CuO$_4$ was obtained from stoichiometric quantities of La$_2$O$_3$, Dy$_2$O$_3$ 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$_2$O$_{6.25}$ was obtained by firing intimately mixed La$_2$O$_3$, 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$_2$O$_2$ 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$_2$NiO$_4$$_{18}$ (3) and that thought to
be the doping mechanism responsible for
superconductivity in La$_2$CuO$_4$$_{8}$ (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$_2$O$_6.25$. The structure adopted by this phase
(7) is an oxygen-deficient variant of the well-known
Sr$_3$Ti$_2$O$_7$ structure (n=2 member of the Ruddlesden-Popper
series AO$_n$ABO$_3$). A view of the structure is shown in
Figure 2. Previous refinements of the structures of
cuprates of this type, La$_2$SrCu$_2$O$_6$ (12) and La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_6$
(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 (01) to the inter-layer site. It is
interesting to compare this phase with the recently
discovered (8) superconducting system La$_{2-x}$Sr$_x$CaCu$_2$O$_6$
(maximum T$_c$ = 60K at x = 0.4). Izumi et al. (13) showed
that in La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_6$, 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$_x$CaCu$_2$O$_6$ 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$_2$O$_{6.25}$. Note that the O(3) site, which is completely vacant in the case of La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_6$, is partially occupied in the present case.
easily maintains the pseudo-two-dimensional nature believed to be required for superconductivity. In \( \text{La}_{1.85}\text{Sr}_{1.15}\text{Cu}_{2}\text{O}_{6.25} \), the Cu-Cu distance is correspondingly greater (3.756\AA{}), 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 \( \text{La}_{1.85}\text{Sr}_{1.15}\text{Cu}_{2}\text{O}_{6.25} \) 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 \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) 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.

ACKNOWLEDGEMENTS

This work was supported by the NSF-Office of Science and Technology Centers under contract #STC-8809854 (PL, SP), U.S. Department of Energy, BES, under contract #W-31-109-ENG-38 (JDJ) and the R.A. Welch Foundation, Houston, TX (XXT, AM, JBG).

REFERENCES

16. B. Dabrowski et al. (this meeting).