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STRUCTURAL ASPECTS OF THE PHASE SEPARATION IN $\text{La}_2\text{CuO}_{4.032}$

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The average structure of superconducting $\text{La}_2\text{CuO}_{4.032}$ has been determined by single-crystal neutron diffraction data. The excess oxygen is located between two adjacent LaO layers. Its presence distorts the apical-oxygen sublattice in such a way that a short O-O bond is formed (1.64Å). By scanning several hkl reflections, we have confirmed that a phase separation occurs below room temperature. The peaks of one phase are in agreement with the space group Cmca and the unit cell proposed by Jorgensen et al. and Cox et al.. However, a monoclinic unit cell is needed to index the second phase reflections.

1. INTRODUCTION

It is well established today that La_2CuO_4 becomes superconducting with T_c 's between 28K and 40K either by cation doping on the La-sites or by raising the oxygen content to more than 4.

2. NEUTRON DIFFRACTION

We determined the structure of a superconducting ($T_c \approx 40\text{K}$) $\text{La}_2\text{CuO}_{4.032}$ single crystal from neutron diffraction data taken at room temperature and 15K¹. (Figure 1). Cmca space group was used in the refinement. We found that the La/Cu ratio is exactly 2 and that an excess oxygen O4 is present at $x=1/4$, $y=0.243(3)$, $z=1/4$ with an occupation factor $p(\text{O}4)=0.016(2)$. We found also that the site O3 at $x=0.031(5)$, $y=0.182(2)$, $z=0.100(5)$ was occupied with an occupation factor $p(\text{O}3)=0.024(2) \times 2$. Since this position is just 0.75Å from that of O1, it can only be occupied when O1 is empty. We found indeed that $p(\text{O}1)+p(\text{O}3)=1$. $P(\text{O}3)$ is also equal to 3 $p(\text{O}4)$. Consequently, it seems that each O4 is

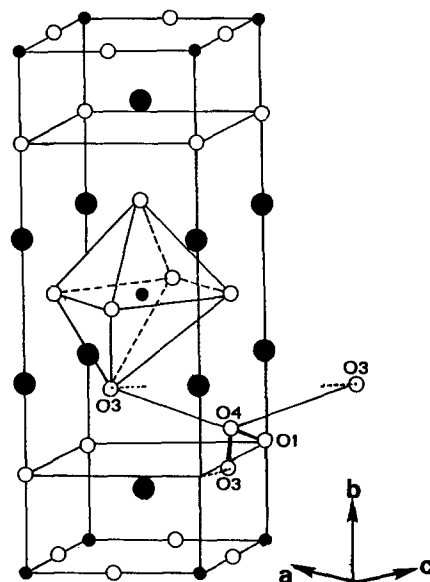


FIGURE 1

The structure of $\text{La}_2\text{CuO}_{4.032}$. Only half cell is shown.

responsible for the displacement of three O1 to O3. If O4 is surrounded by three O3 and one O1, one distance O3—O4 is $\approx 1.64\text{\AA}$ which is indicative of a strong covalent bond and of the formation of an $(\text{O}_2)^{2-}$ peroxyde grouping.

3. PHASE SEPARATION

Jorgensen et al.² have shown from powder neutron diffraction studies that a phase separation occurs near 320K. They indexed the neutron powder pattern of the two phases using Cmca space group for one (non superconducting, phase 1), and Fmmm space group for the other one (superconducting, phase 2). Their results were corroborated by Cox et al.³ who used x-ray synchrotron powder diffraction data taken at Brookhaven NSLS.

In order to verify whether or not our $\text{La}_2\text{CuO}_{4.032}$ crystal presented also the phase separation we have scanned several hkl reflections as a function of temperature (300K-120K) using x-ray ($\lambda\text{CuK}\alpha$) and neutron ($\lambda=1.265\text{\AA}$) diffraction. We confirmed Jorgensen and Cox results about the phase separation, which means that the structure determined from neutron data¹ is only an average structure. However, our results are not compatible with the Fmmm space group. We have tried to refine the structure of $\text{La}_2\text{CuO}_{4.032}$ using Fmmm space group and the neutron single crystal data. The results are not as satisfactory as those obtained with Cmca. An improvement is obtained when the oxygen atoms are allowed to vary over the general xyz position, one of them corresponding to Cmca. We also noticed that the reflections forbidden by F centering were not systematically calculated stronger than observed when Cmca space group was used, which would be the case if these reflections belonged to one phase only. Furthermore, 0kl reflections with k even and l odd, which are forbidden by F centering, exhibit also phase separation (Figure 2). This was more clearly observed on neutron data as these reflections are

mainly due to the oxygen atoms. The peaks were fitted with Gaussian functions. Those corresponding to the nonsuperconducting phase (Cmca) can be perfectly indexed with Cox et al. and Jorgensen et al. cell parameters. On the contrary, a monoclinic unit cell (a unique axis) is needed to index the second-phase reflections. This phase transition implies that an additional twinning occurs.

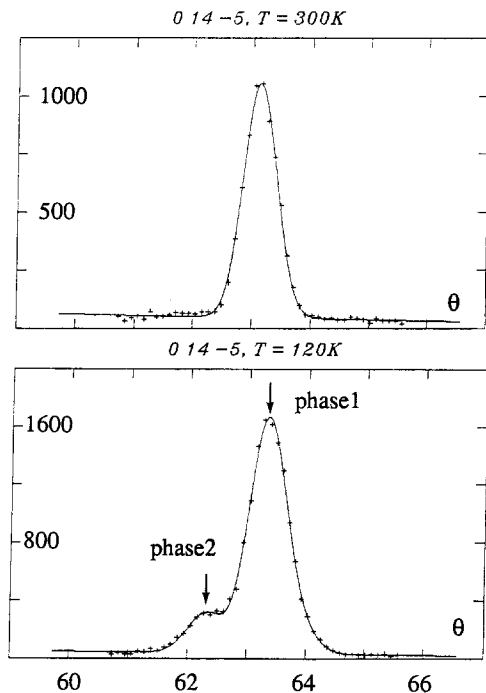


FIGURE 2

ω - 2θ scan of 0 14 5 reflection at 300K and 120K (neutron diffraction).

Crosses represent experimental points. The arrows indicate the peaks' positions as determined from fitting with Gaussian functions.

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