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## High Temperature Superconductors: Electronic Structure Changes due to Replacement of La with Ba and Sr in the Cu-O-Based Systems

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The replacement of some La in  $\text{La}_2\text{CuO}_4$  with divalent atoms has been found to lead to high temperature superconductivity with  $T_C=30-40$  K. These superconductors have a bct layer perovskite structure with large anisotropies in their electronic band structure. Using first principles local density methods applied to both layer perovskite and the related cubic perovskite structures, we find that alloying on the La site leads to large changes in the chemical bonding of both structures, except near the Fermi level where a rigid band picture is reasonable. Large changes in the spectral density near the "dopant" atom occurs on both the nearby O and Cu atoms, and is not simply described by a Cu(2+)-Cu(3+) valence change. These results are consistent with recent x-ray absorption studies by Tranquada et al.

### 1. INTRODUCTION

The discovery of high temperature superconductivity in rare-earth copper oxides by Bednorz and Müller [1] and the subsequent extension of the critical temperature ( $T_C$ ) to the 90-100 K range by a large number of laboratories has raised intriguing questions regarding the origin of the coupling mechanism in these materials. The important questions are more fundamental even than the origin of the pairing interaction, however, since these copper oxides are **qualitatively different** from previous high  $T_C$  superconductors. These copper oxides are **ceramics** which in spite of being metallic possess a large degree of ionic character. As a result, the electronic structure and response, the effects of alloying and the character of the electron-phonon interaction may be qualitatively different from conventional superconductors.

### 2. DESCRIPTION OF THE CALCULATIONS

We have used the Linearized Augmented Plane Wave (LAPW) method [2] to investigate the electronic structure of  $\text{La}_2\text{CuO}_4$  and  $\text{LaBaCuO}_4$ . Since the layer perovskite structure is a relatively low symmetry bct structure and displays an unusual mixture of ionic and metallic characteristics, it is preferable to use the fully general form for the density and potential which we have implemented in our LAPW. For the cubic perovskites  $\text{MCuO}_3$ ,  $M=\text{La}, \text{Ba}$ , we have used the Augmented Plane Wave method in the muffin-tin approximation. In both sets of calculations the Hedin-Lundqvist form of local density exchange-correlation potential was used. A more complete description of the methods has been presented elsewhere [3].

### 3. DISCUSSION

A synopsis of the phenomenology of the La-Cu-O system is this. The pure La compound, which probably contains a few percent O vacancies, appears from the rise in resistivity at low temperature to be semiconducting. Investigation of its crystal structure revealed a unit cell-doubling distortion to an orthorhombic structure [4]. When Sr or Ba is substituted for La, however, the orthorhombic distortion is inhibited (or very nearly so), the material shows metallic resistance behavior, and it becomes superconducting at 30-40 K [1,5,6]. A central question then

is the role of the alkaline earth alloying. Does this replacement simply "dope" the semiconducting orthorhombic phase, thereby causing it to become metallic, and therefore superconducting? Does addition of Ba or Sr move the system away from an electronic instability, and therefore restore a crystal structure which is superconducting? This point of view has been taken by Mattheiss [7] and by Weber [8], who find a strong coupling between the in-plane Cu-O breathing mode and electronic states near the Fermi level. Finally, there is even the possibility that the divalent cation is essential to the pairing of electrons, such as might result from a Cu(2+) to Cu(3+) valence change or fluctuation.

It is such questions as these which have led us to study the influence of Ba on the electronic structure of  $\text{La}_2\text{CuO}_4$ . The question of the valence change is clear in our calculations: the electron which is lost when one La atom per unit cell is replaced with a Ba atom comes more or less equally from the Cu and the four O(x,y) atoms, that is, it simply comes from the O-Cu band crossing the Fermi level. Thus we find no support for the widely discussed Cu(2+)-Cu(3+) valence change, and this is in agreement with the x-ray absorption studies of Tranquada et al. [9].

By comparing the density of states  $N(E)$  of  $\text{La}_2\text{CuO}_4$  and  $\text{LaBaCuO}_4$  near the number of electrons for  $x=0.0-0.2$ , we can ascertain whether a rigid band model is reasonable for describing the bands near  $E_F$  in  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ . The rigid band picture has been invoked without explicit justification by several workers, based on its success (for small alloy concentrations) in many metallic systems. In the present materials, which have a high degree of ionic character and for which the alloying involves replacing the  $\text{La}^{3+}$  ion with a  $\text{Ba}^{2+}$  ion, the rigid band picture must be suspect. Our results show, however, that near  $E_F$  this picture should give a reasonable description of  $N(E)$ , and therefore apply about equally well to both Ba and Sr additions. Well below  $E_F$ , on the other hand, the spectral density on both the Cu and O(z) atoms near the Ba atom is rearranged substantially. These shifts may produce changes in the polarizability of the material which will affect the electronic response, which could in turn be important in either phononic or electronic pairing mechanisms.

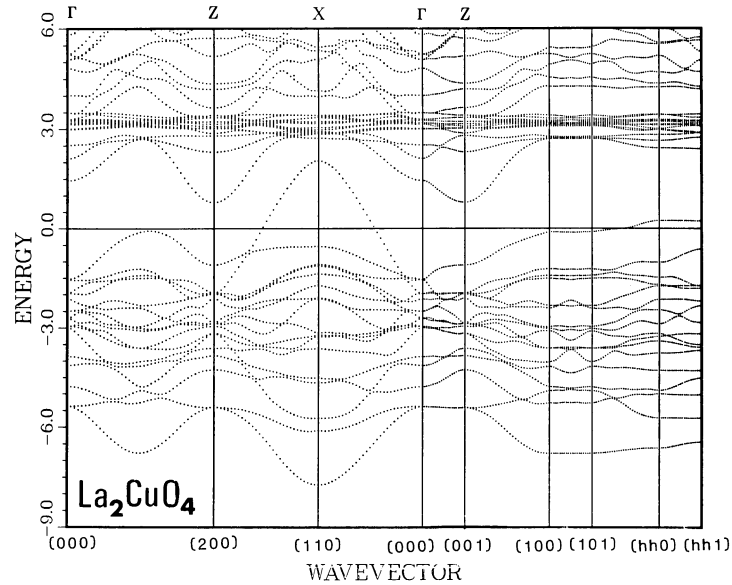


Figure 1. Band structure of  $\text{La}_2\text{CuO}_4$  along several directions, given in units of  $(\pi/a, \pi/a, 2\pi/c)$ ,  $h=1/2$ . High symmetry points are labelled at the top.

Using the rigid band picture, then, we can give the band theory prediction of the effects of varying the Ba (or Sr) concentration  $x$ . A van Hove singularity occurs in the density of states (published previously [3]) at  $x=0.14$ , which is also very near the concentration at which the measured  $T_C$  is found to be a maximum. The band structure along several directions is shown in Fig. 1, where the position of the van Hove singularity along the  $(k_x, 0, 0)$  direction is reflected in the band which comes within 0.1 eV of  $E_F$ . We find  $N(E_F, x=0.14)=29$  states/Ry-cell, compared to  $N(E_F, x=0.0)=16$  states/Ry-cell, which leads to an increase in the McMillan-Hopfield parameter (one component of the electron-phonon interaction strength) by 20% for the Cu atom and nearly 50% for the in-plane O atom. The studies of the electron-phonon coupling strength and resulting values of  $T_C$  are presented elsewhere in these proceedings.

#### 4. ACKNOWLEDGMENTS

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#### REFERENCES

- [1] J. G. Bednorz and K. A. Müller: *Z. Phys.* **B64**, (1986)189.
- [2] S.-H. Wei and H. Krakauer: *Phys. Rev. Lett.* **55**, (1985)1200, and references therein.
- [3] W. E. Pickett, H. Krakauer, D. A. Papaconstantopoulos and L. L. Boyer: *Phys. Rev.* **B35**, (1987)xxxx.
- [4] J. D. Jorgensen et al.: *Phys. Rev. Lett.* **58**, (1987)1024.
- [1] J. G. Bednorz and K. A. Müller: *Z. Phys.* **B64**, (1986)189.
- [5] R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Rietman: *Phys. Rev. Lett.* **58**, (1987)408.
- [6] C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang: *Phys. Rev. Lett.* **58**, (1987)405.
- [7] L. F. Mattheiss: *Phys. Rev. Lett.* **58**, (1987)1028.
- [8] W. Weber: *Phys. Rev. Lett.* **58**, (1987)1371.
- [9] J. M. Tranquada, S. M. Heald, A. Moodenbaugh and M. Suenaga: *Phys. Rev.* **B35**, (1987)xxxx.