



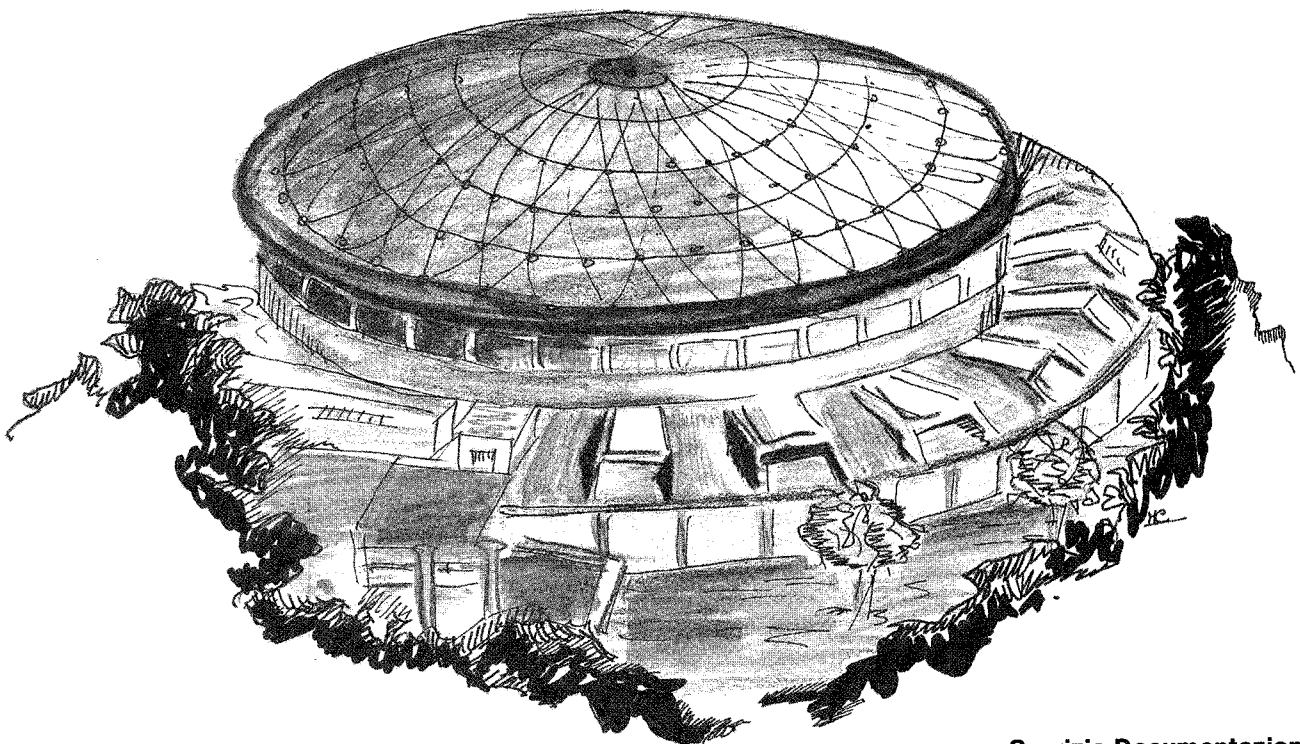
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**THEORETICAL CALCULATIONS OF X-RAY ABSORPTION NEAR EDGE
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ABSTRACT

We present a theoretical analysis of x-ray-absorption-near-edge structure (XANES) at Sr K-edge in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds based on the experimental results of Z. Tan et al. published in Phys. Rev Lett. **64**, 2715 (1990). Our analysis substantially confirms the conclusions of that paper though it suggests the possibility of some distortion around the photoabsorber and/or a different position of the trapped oxygen due to the doping mechanism.

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Since the discovery of high- T_c superconductors several studies [1] of the x-ray-absorption (XAS) spectra at the various edges of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds have been performed to interpret the local geometrical and electronic structure of these superconductors whose properties change according to the amount of Sr doping. For examples the superconductivity transition temperature shows a peak at $x=0.15$ and can be shown to correlate with the hole concentration due to the presence of Sr atoms [2].

Recently, Z. Tan et al. [3] have studied experimentally the x-ray-absorption-near-edge structure (XANES) at Sr K-edge and La L₃-edge to clarify the physical effects of this type of doping. These systematic studies indicate the presence of an interstitial defect oxygen near Sr atom that is intrinsic to Sr-doped La₂CuO₄. This is indicated as a mechanism of hole doping similar to the case of oxygen-rich La₂CuO_{4+y}. These conclusions are based on the presence of a clear feature in the experimental XAS spectrum at about 20 eV from the rising edge in the Sr K XANES of La_{2-x}Sr_xCuO₄ compounds which must arise from the removal of the nearest apical oxygen when La is substituted by Sr under normal preparation conditions. This oxygen has normally a bond length of about 2.35Å. This experimental feature is generally present for an eightfold coordinated absorber with two set of four equivalent near neighbors. For sake of clarity we summarize their experimental results in Fig.1 where the La L₃ XANES spectrum of La₂CuO₄ (curve a) is compared with the Sr K XANES spectra of SrF₂ (curve b) and La_{2-x}Sr_xCuO₄ (curve c) compounds. The arrows indicate the peak under investigation (referred to in the following as feature A) that is absent in the ninefold-coordinated absorber (curve a).

For the high-T_c superconductors, the theoretical studies of XANES have been concentrated mostly on the Cu K-edge [1], but the edges of the rare-earth elements have not been well studied. We want both to fill this gap by presenting a set of one-electron multiple-scattering calculations of XANES spectra related to the Sr K-edge in La_{2-x}Sr_xCuO₄ and SrF₂ compounds and to the La L₃-edge in La₂CuO₄ material, and to substantiate theoretically the conclusion of Z. Tan et al. by showing model calculations with and without the apical oxygen.

All our calculations are based on the one-electron multiple-scattering theory [4], and the potentials are built from neutral atoms by superimposing the charge density obtained using the Clementi-Roetti tables for Cu, O and Sr atoms and the Herman-Skilmann wave-functions for La atom. The exchange part of the potential is obtained by the X- α method. The muffin-tin radii (MT) are chosen according to the Norman criteria [5] starting from the photoabsorber. We have allowed a 10% of overlapping between the various MT radii to simulate the atomic bond [6]. More details will be given in a forthcoming paper. The z axis in all our calculations is along the c axis of the compounds.

In Fig. 2 we report the theoretical calculation of the Sr K XANES in La_{2-x}Sr_xCuO₄ compound using a cluster without the apical oxygen. The Sr atom is eightfold coordinated and the atomic cluster used in the calculation is formed by 23 atoms and it has a C_{4v} symmetry. In Fig. 2 is also shown the decomposition of the total cross section in term of z and xy components. All the features in the experimental data are well reproduced both in relative amplitude and energy position although the Debye-Waller corrections as well the lifetime of photoelectron are not taken in account. Feature A is indicated with an arrow. This peak in the total cross section is weaker than the corresponding one in experimental spectrum but is clearly evident in the z component. In Fig. 3 is reported the same calculations with the apical oxygen i.e. we suppose that this atom is not removed when La is substituted by Sr and there is no local distortion of the tetragonal unit cell. The two main structures at about 0.5 Ry and 3.0 Ry are

practically unchanged while the feature A has disappeared in the total cross section. There is some reminiscence in the z polarization but now the structure is weaker and smoother than the corresponding one in the previous calculation. To clarify this aspect we report in Fig.4 the comparison between the two z-polarized calculations after a convolution to account core-hole lifetime. The solid line refers to the case without apical oxygen. In this last case the feature A is clear and well separated from the main peak at the edge. To conclude this theoretical analysis of the Sr K-edge we present in Fig. 5 the same calculation of Fig. 3 except that the apical oxygen is now at site $(1/2,0,1/4)$ in the tetragonal unit cell as suggested in ref. [3]. The Sr is still coordinated with nine oxygen neighbors, but the defect oxygen does not appear to suppress feature A, on the contrary this feature is now clear and well resolved in the theoretical total cross section although weaker than the experimental one. Moreover we observe now the presence of a further small structure at about 3.0 Ry from the first peak (beside the second big peak at higher energy) corresponding to a similar feature in the experimental spectrum at about 40-45 eV from the main peak. This last calculation is in better agreement with the experimental spectrum indicating that the missing apical oxygen remains in the structure. The only problem regards the intensity of the feature A that in all our calculations is weaker than the experimental one. This discrepancy can arise both/either from some inaccuracy of the potential used in the theoretical calculations and/or the fact that the Sr-induced defect oxygen is in a different location than the one used in our calculations. An other possibility is that there are some distortions of the local environment of Sr atom when it substitutes an La atom in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound that are not taken in account in our calculations. To conclude this analysis of Sr K-edge we want to mention that in the case of removal of oxygen atom other than the apical one the calculated XANES does not give any feature A.

Finally in Fig. 6 we present two theoretical calculations related to the La L_3 -edge in La_2CuO_4 (upper curve) and to the Sr K-edge in SrF_2 . Good agreement with the experimental data is obtained in both calculations and the feature A is observed only in the Sr K-edge in SrF_2 compounds where the photoabsorber is coordinated with eight fluorine atoms. Notice that the intensity of this peak is bigger than the corresponding one in the previous calculations and now it is rather in agreement with the experimental data confirming the goodness of the used potential. Moreover these last calculations clearly indicate that feature A is associated with an eightfold coordination in the first shell.

In conclusion our theoretical analysis of the Sr K-edge in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compounds clearly indicates that the Sr doping induces a removal of the apical oxygen in the first shell around the Sr atom and that this oxygen remains in the structure in agreement with the experimental findings of Z. Tan et al. Moreover there is the possibility that the defect oxygen is in different position than the $(1/2,0,1/4)$ and/or that some distortion of the first shell around Sr atom arises from the doping process. These two last possibilities are under investigation and the theoretical results will be published in a further paper.

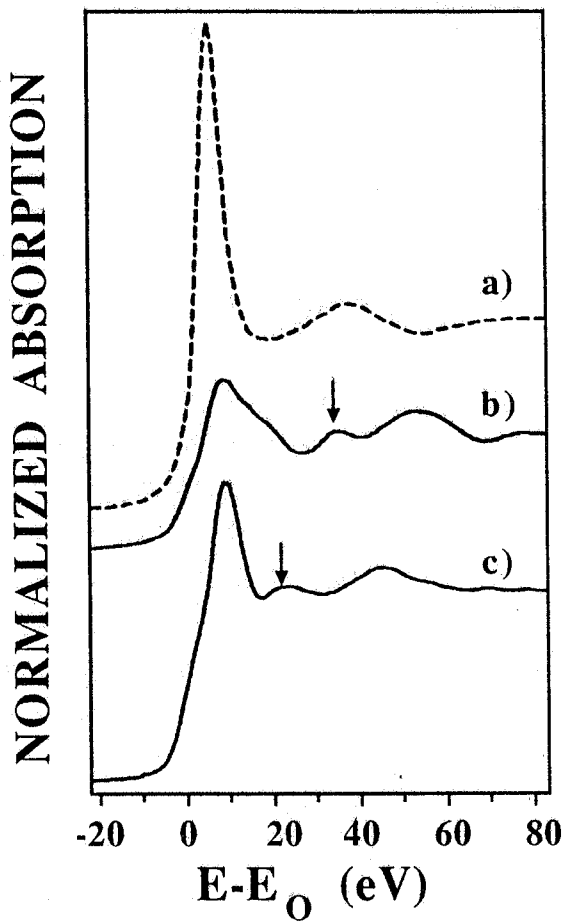
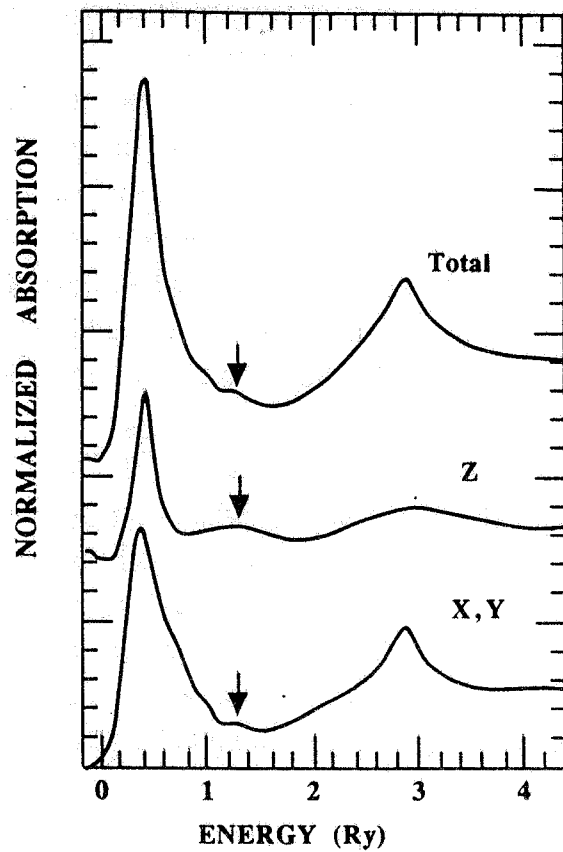


FIG. 1 - The experimental curves measured by Z.Q.Tan et al. Curve a refers to the La L₃-edge of La₂CuO₄ compound, curve b to the Sr K-edge of SrF₂ compound and curve c to the Sr K-edge of La_{2-x}Sr_xCuO₄ compound.

FIG. 2 - Theoretical XANES spectrum at the Sr K-edge in La_{2-x}Sr_xCuO₄ compound without the near-neighbor apical oxygen. The arrow indicates the feature A in all polarization components.



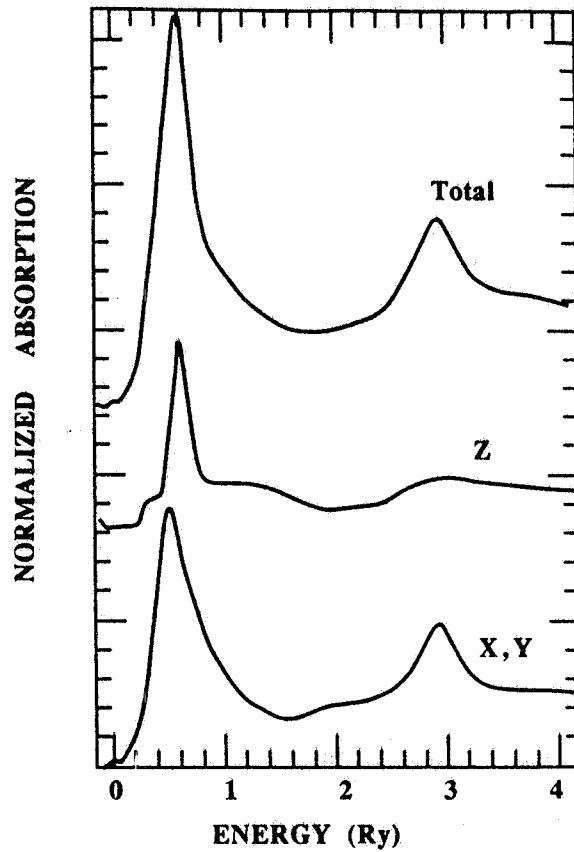


FIG. 3 - The same calculation of the preceding figure assuming a ninefold coordination of the Sr atom.

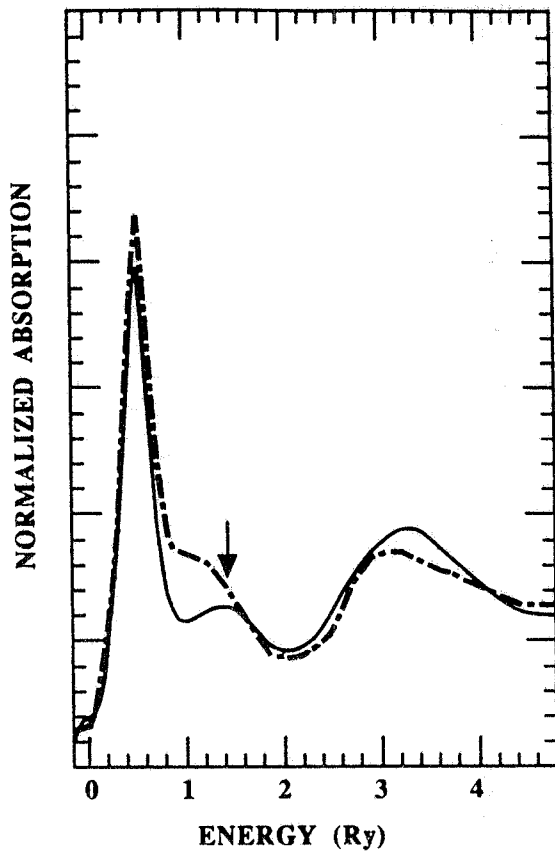


FIG. 4 - Comparison between the two z-polarized components of the preceding calculations after a convolution with a Lorentzian broadening function. The dot-dashed line refers to the case with apical oxygen. Arrow indicates feature A.

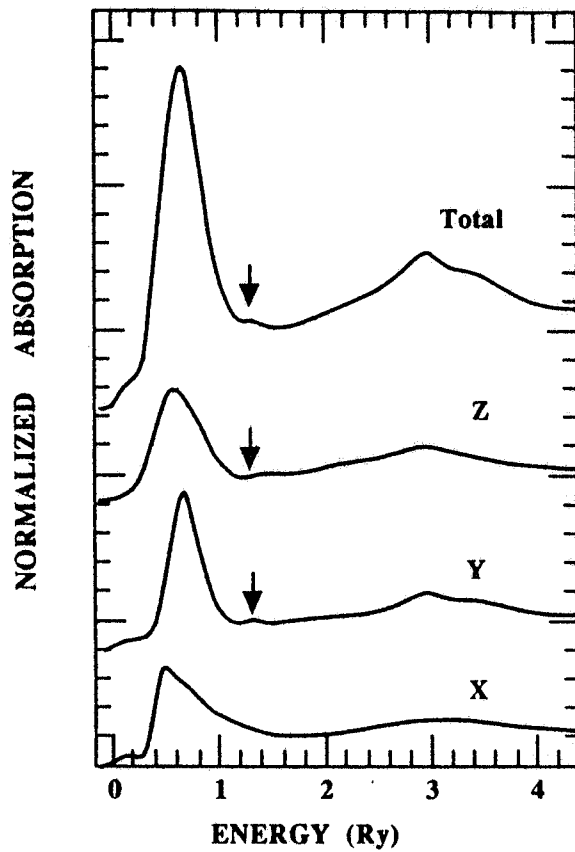


FIG. 5 - Theoretical XANES spectrum at Sr K-edge of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compound with a induced defect oxygen at $(1/2, 0, 1/4)$ site in the tetragonal unit cell.

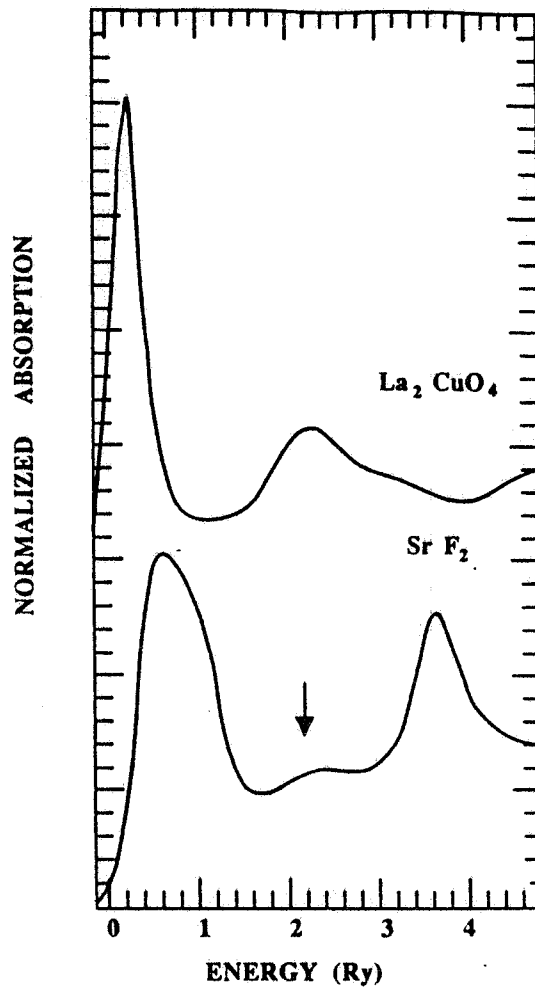


FIG. 6 - Theoretical XANES spectra at La L_3 -edge of La_2CuO_4 (upper curve) and at Sr K-edge of SrF_2 compounds. The arrow in the lower curve corresponds to feature A.

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