Towards a limited XANES refinement in strongly correlated systems

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Three components of O1 atom displacements have been derived from the direct fit of the polarized ***Ellab*** Cu *K*-edge XANES spectrum of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ superconductor. The best fit is achieved for a 60 to 40% mixture of *2x2* undistorted antiferromagnetic and modified charge density wave (MCDW) domains. The local structure of the MSDW is characterized by correlated displacements of $\Delta O1_{\|}$=0.12±0.04, $\Delta O1_{\perp}$=0.25±0.08, and $\Delta O1_z$=0.12±0.1 Å. An agreement factor over the range of 8980-9040 eV is 2-3 times smaller than it may be obtained from single-electron MS calculations. This improvement comes from accounting for many-body excitations and the relationship between electronic and local structure in the CuO_2 planes.

Keywords: local structure, XANES refinement, domains.

1. Introduction

It is well known that XANES is directly sensitive not only to inter atomic distances, as the conventional EXAFS, but also to the absolute position of the atoms and, therefore, may be used for refinement of a local structure on an atomic length scales. This advantage of XANES is rarely used in practice, especially for the strongly correlated systems, such as HTSCs, CMRs, and mixed valence compounds where the presence of many-body electronic configurations and strong coupling between the local and electronic structures add complexity to the interpretation of XANES spectra.

A direct Cu *K*- edge XANES refinement of the local structure of the CuO_2 planes in the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ superconductor is presented. Preconditions for this refinement are the standard EXAFS analysis and some knowledge of the electronic structure. Recent EXAFS analysis of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ (Ignatov *et al*., 1999) imply that three different Cu-O1 distances may be extracted at least up to T < 100 K: R_U =1.96±0.01, R_{D1} =1.85±0.02, and R_{D2}=2.10±0.02 Å with the fraction of strongly distorted Cu-O1 bonds of 40±10%. Complex electronic structure of Cu-based superconductors could be satisfactory described in terms of multiple-band Hubbard model those parameters are available from the UPS, O $1s_{1/2}$ and Cu $3p_{3/2}$ XPS as well as the O *K*- and Cu L_3-edge XAS experiments (Eskes & Sawatzky). We will introduce these parameters in Sect. 3. It's worth mentioning that the EXAFS and the electronic structure parameters *are fixed* all through this work. Only three components of O1 displacements ($\Delta O1_{||}$, $\Delta O1_{\perp}$, $\Delta O1_z$) which are restricted to those allowed by the pair distribution function obtained from the Cu *K*-edge EXAFS will be refined.

2. General formulation

Calculated Cu *K*-edge XANES spectra were obtained as a convolution product of the single-electron transition from the Cu 1*s* core-level to the unoccupied electronics states, $I(\omega)$ and spectrum of many-body excitations in the electronic states of the CuO_2 planes in the presence of Cu 1*s* core-hole, $S(\varepsilon)$ (Mahan):

$$\sigma(\omega) = \int S(\varepsilon) I(\omega - \varepsilon) d\varepsilon \qquad (1)$$

$$S(\varepsilon) = \sum \left| \left\langle \Psi_f^i \middle| \Psi_0 \right\rangle \right|^2 \delta(\varepsilon - E_i + E_0) \qquad (2)$$

that is valid as soon as the interaction between *N*-hole final states and n*p* photoelectron can be neglected. Ψ_0 is the ground state with energy E_0 and Ψ_f is the *i*-th excited state with energy E_i referred to Hamiltonians in the initial H_0 and final states H_f respectively. H_0 has been taken as a two-dimensional Peierls-Emery Hamiltonian in the hole representation (see, for example, Yonemitsu *et al*., 1992). In the final states $H_f = H_0 + H_c$, H_c is subjected to the 1*s*-3*d* inter-hole Coulomb repulsion, Q.

The components of O1 atom displacements from their undistorted positions in the *T* '- structure were derived from a list-square minimization of an agreement factor:

$$R = \frac{1}{M} \sum_i^M \frac{| XANES^{\exp}(E_i) - XANES^{Cacl}(E_i) |}{XANES^{\exp}(E_i)} \qquad (3)$$

over the energy range of 8980-9040eV, containing M~220 points.

The single-electron Cu *K*-edge XANES spectrum, $I(\omega)$, was calculated in real space using the formalism of multiple scattering (MS) of a photoelectron in a 45-atom cluster. The spectrum was convoluted with the Lorentz function with the broadening factor, Γ, taken as the sum of the core-hole lifetime (~1.2eV), the resolution of the spectrometer (~0.5eV), and the photoelectron lifetime that was assumed to increase proportionally from zero at the E_f to the value of 1.75eV at E=9050 eV.

The excitation spectrum, $S(\omega)$, was introduced to correctly account for the perturbations in the electronic structure of the CuO_2 planes upon the sudden switching on of the Cu 1*s* core-hole. In the *Z*-approximation the $S(\omega)$ is given by the sum over all *f*-th final *N*-hole states projected on to the ground state *N*-hole wavefunction without the core-hole (Eq. 2). The Lanczos technique was employed for numerical diagonalization and spectral calculation of $S(\omega)$ in the 2D cluster of 12 atoms with periodic boundary conditions.

3. Results and discussion

Very different configurations can be obtained at a fixed strength of the electron-lattice coupling as the strength of the Cu on-site repulsion U_d is varied representation (Yonemitsu *et al*., 1992). When U_d is rather small, a charge-density wave (CDW) is the ground state. The CDW was accompanied by symmetrical breathing displacements of the O1 atoms with respect to the Cu sites. A bond-order wave (BOW) occurred with U_d growth. In these states, one of four O1 atoms is strongly displaced to increase the bond-charge density on the corresponding short Cu-O bonds forming an asymmetric covalent molecule. Additional increase in U_d results in a mixture of a spin-Peierls (SP) and antiferromagnetic (AF) states. In the SP states, every second strong Cu-O-Cu bond arising in the BOW is replaced by two localized Cu spins with suppressed O1 atom displacements. When U_d is large, the pure AF states, which are characterized by the absence of O1 displacements, occurrs.

To satisfy the EXAFS results all but the AF configurations were *modified* by introducing the $\Delta O1_{\perp}$ and $\Delta O1_z$ displacements. Some of the modified CDWs (MCDWs) displacements are shown in Fig. 1(a-c). Breathing distortions were combined with various types of correlated (over 4 unit cells) O1 distortions, such as rigid rotation (a), orthorhombic (b), and rhombic (c) in-plane distortions of the CuO_4 plaquettes. These plaquettes were also allowed to tilt about the (110) axis, giving rise to out-of-plane $\Delta O1_z$ displacements. Modified BOW (MBOW) and modified SP+AF(MSP+AF) domains are shown in Fig. 1(d,e).

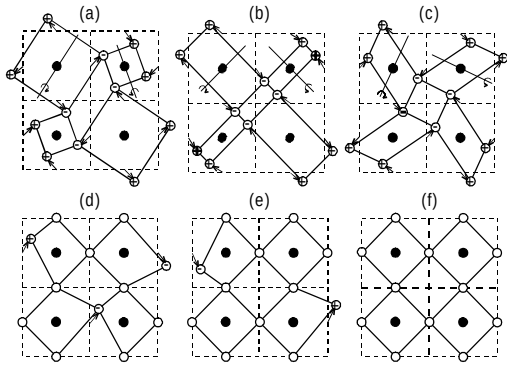

Figure 1
Sketch of some displacement configurations (domains) in the CuO_2 planes of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ used for XANES calculations. Open(closed) circles denote the positions of the O1(Cu) atoms. The in-plane displacements are marked by arrows. The out-of-plane displacements are illustrated by '+' and '-'. Modified charge density waves (MCDW) are represented by (a) rigid rotation, (b) orthorhombic, and (c) rhombic distortions of the CuO_4 plaquettes. Bars with arrows show the tilt axes and tilt directions for the corresponding plaquettes. (d) Modified bond-order wave (MBOW), (e) Modified spin-Peierls (MSP) + antiferromag-netic (AF), (f) AF domains.

In the present work U_d was 9, 8, 7, and 6 eV for the AF, SP, BOW, and CDW domains, respectively. Other parameters (in eV) of the Hamiltonian employed for $S(\omega)$ calculations of all displacement configurations were: $\Delta = 0.5U_d - 1$, $t_{pd}^0 = 1, t_{pp}^0 = 0.7$, $U_p = 3, U_{pd} = 1, Q = 6$. Their physical means can be found in (Eskes & Sawatzky, 1991). The energy to displace each oxygen atom by $u_\parallel$ and $u_\perp$ was given by $E_d = \frac{1}{2}K_\parallel u_\parallel^2 + \frac{1}{2}K_\perp u_\perp^2 + \xi u_\perp^4$, where $K_\parallel = 7$ eV Å^{-2}, $K_\perp = 0.17$ eV Å^{-2}, $\xi = 0.7$ eV Å^{-4}. The electron-lattice coupling was introduced through functional relations of $t_{pd}(r) \propto r^{-4}$ and $t_{pp}(r) \propto r^{-3}$.

An example of the excitation spectrum of MCDW depicted in Fig. 1(b) is shown in the insert of Fig. 2. The number of the peaks in the $S(\omega)$ depends on the set of many-body states that, in our case, is as large as 792 (three-hole wavefunction in 12-site cluster). Only a few of the states contribute to $S(\omega)$, that is reminiscent of the cluster model (Chen *et al.*, 1987) utilizing U_d, Δ, and T_{dp}. However, this simple many-body model has two drawbacks compared to the extended one. Firstly, satellite positions are weakly Q-dependent since the holes pushed from the absorption site are redistributed over other atoms in the 12-site cluster. In the simple cluster model a large Coulomb repulsion may reverse the order of $3d^9$ and $3d^{10}L$ states in the final states. Secondly, $S(\omega)$ is clearly structure-dependent. This reliance is not reduced to structural dependences of the U_d, Δ, and T_{dp} that seems to be only option in the framework of the simple cluster model. New model includes all intrinsic loses allowed in N-hole system, but it misses the coupling between intrinsic and extrinsic loses because of the convolution product approximation, Eq. 1. It's worth mentioning that multiple-channel, MS theory properly accounting for intrinsic and extrinsic loses has been developed (Natoli *et al.*, 1990). However, it's a single-electron model, those excitation spectra were never evaluated numerically.

The best agreement between the calculated and the experimental XANES spectra shown in Fig. 4 was achieved for a model that is a mixture of the AF (Fig. 1(f)) and a the MCDW (Fig. 1b) domains taken in the ratio 60:40. The local structure of the MCDW domains can be characterized by the following correlated displacements: $\Delta O1_{||} = \pm 0.12$, $\Delta O1_\perp = \pm 0.25$, and $\Delta O1_z = \pm 0.12$ Å. It is interesting to notice that the MCDW and AF configurations cannot fit together directly. It is necessary to assume the presence of intermediate (I) domains, where the local structure relaxes from the MCDW to AF. We found that a modified spin-Peierls (MSP)+AF state (Fig. 1e) is quite appro-priate for description of the I-domains. It's most likely that the displaced O1 atoms within the I-domains are locally uncorrelated.

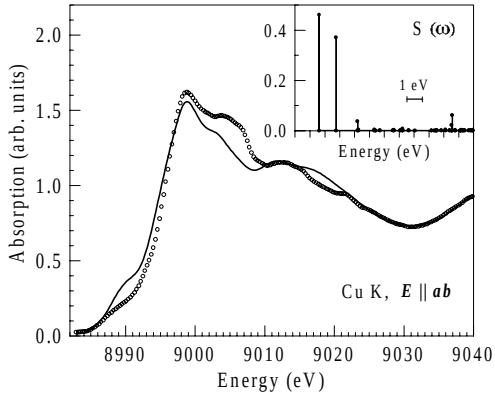

Figure 2
Comparison of experimental (dots) and calculated (solid line) XANES spectra. The solid line represent a best model consisting a 60 to 40% mixture of *2x2* undistorted antiferromagnetic and the MCDW domains. The agreement factor over the range of the figure is only 6.3 %. The excitation spectrum of the MCDW domains is shown in the insert. Notice that second peak is ~ 1 eV above the main peak. This sheds some light on typical energy shift and the spectral weight transfer that could be expected when realistic local structural distortions are taken into account.

3.1 Amplitude and phase correction.

Recalling that EXAFS is just the second term in the MS expansion of the XANES, the amplitudes and phase shifts (A&Ps) for each displaced configuration calculated, for instance, by FEFF code (Ankudinov *et al.*, 1998), can be corrected for the excitation spectrum, $S(\omega)$ as prescribed by Eq. 1. This correction provides a proper reply to the question raised by Egami and Billinge concerning the EXAFS data interpretation for HTSCs and other strongly correlated systems showing valence fluctuations. The point is whether or not the conventional EXAFS would give a reliable measure of the local distortions if the experimental spectrum is affected both by local distortions and by valence fluctuations. *Ab-initio* correction proposed works out the problem (Ignatov, 2001). Coming back to the practical aspects of A&Ps correction, as revealed from Fig. 2 and Eq. 2, the correction reduces to the appearance of several sine waves with their own scaling factors S^2_{0i} and energy shifts $\Delta E_i = E_i - E_0$.

3.2 Better R-value using conventional MS calculations?

A common practice of the XANES analysis is not to perform a direct fitting and not to report the R- factor, but to argue a "best visual similarities" between the spectra or "the presence of the main peaks" in the calculated XANES. Typical R-value is as large as 20-30%. In this work the R- factor is *only* 6.3%. To headline this results let me address a question of whether it is possible to obtain a lower R-value using conventional MS calculations. Lets assume that: (i) the local structure is a well known and given by trivial AF structure shown in Fig. 1(f); (ii) one can calculate the $I(\omega)$ function with a negligible error; and (iii) actual $S(\omega)$ is given by Eq. 2. The "experimental" spectrum (solid line) obtained from Eq. 1 is compared with the single-electron spectrum (dashed line) in Fig. 3. Notice that the R- value over the range of this figure is almost 14%

and it can't be improved any more in the framework of single-electron MS calculations because of (ii). Therefore, the new approach provides 2-3 times smaller agreement factor (6.3 vs. 14%) than one may expect to obtain using the conventional calculations.

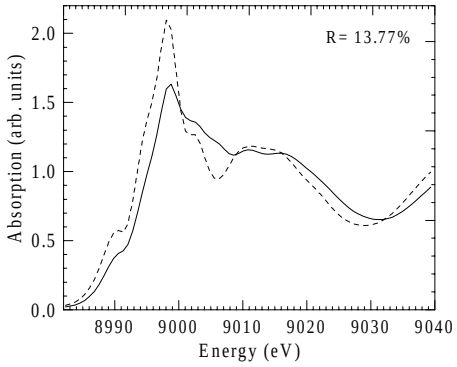

Figure 3
Effect of the $S(\omega)$ inclusion. The R- factor cannot be low than ~10-20% (14% in this plot) if $S(\omega)$ is not taken into account. Dashed line- single-electron MS spectrum (the $I(\omega)$ function) for AF configuration. Solid line - the "experimental" spectrum obtained from Eq. (2).

3.3 Other displacement configurations (domains)?

1) In order to provide the 60:40 ratio for undistorted to distorted CuO_2 bonds as obtained by the EXAFS one must choose the MCDW or MBOW domains as a strongly distorted component. Direct XANES calculations show that the spectra became worse for the MBOW domains. Therefore, one should search among the MCDW domains.
2) It was found that the only MCDW domains that are appropriate are those characterized by a correlated displacement of O1 atoms. Configurations with uncorrelated displacements give very smooth XANES spectra.
3) The number of configurations characterized by correlated displacements of O1 atoms within the 2x2 elementary unit cell is finite. Those that have central symmetry with respect to the Cu site are given in Fig. 1 of the manuscript. More sophisticated displacement models could not be excluded. The XANES is a local sensitive technique that probes the electronic and local structure within ~5 Å with respect to absorbing atom that justifies to bring of the 2x2 model. In this sense the refinement presented in this paper is a *limited* local structure refinement.
4) The number of independent parameters in the fit, N_{ind}, is resolution-limited: $N_{ind} \propto M^{*}\Delta E/\Delta\Gamma$, where ΔE is a typical energy between the data point and $\Delta\Gamma$ is a spectrometer resolution. The estimated number of degrees of freedom, $\nu = N_{ind} - P$ ~70 that is much larger than number of varied parameters, P=3 (for three components of O1 atom displacements).
5) Assuming a 95% (2δ) confidence interval the statistical errors have been estimated as $d\mathrm{O1}_{\|}$=±0.06, $d\mathrm{O1}_{\perp}$=±0.08, and $d\mathrm{O1}_{z}$ =±0.1 Å for the $\Delta\mathrm{O1}_{\|}$, $\Delta\mathrm{O1}_{\perp}$, and $\Delta\mathrm{O1}_{z}$, respectively. Using a brut force method I made sure, that the point $\Delta\mathrm{O1}_{\|}$=0.12, $\Delta\mathrm{O1}_{\perp}$=0.25, and $\Delta\mathrm{O1}_{z}$=0.12 Å is the only minimum in the range of the statistical errors. It's clear, that neither the AF nor the MCDW configurations shown in Fig. 1(a,c) do not belong to the indicated interval. For 2δ confidence intervals in EXAFS and XANES, the "improved" estimation for uncertainties is given by $\pm min.\{|\, d\mathrm{O1}_{i}^{(\mathrm{EXAFS})} \,|, |\, d\mathrm{O1}_{i}^{(\mathrm{XANES})}|\}$, where i runs through the {‖,⊥,z}. The simplest estimate for the EXAFS insertions can be expressed as: $d\mathrm{O1}_{\|}^{(\mathrm{EXAFS})} \leq 2dR$, $d\mathrm{O1}_{\perp}^{(\mathrm{EXAFS})} = d\mathrm{O1}_{z}^{(\mathrm{EXAFS})} \sim (R_{D1}+dR)sin(\theta_{max})$, where θ_{max} is from the insert of Fig. 2, (Ignatov *et al*., 1999), but R_{D1} and R_{D2} are replaced by $R_{D1}+dR$ and $R_{D2}+dR$, respectively. For dR=0.02 Å one finds: $d\mathrm{O1}_{\|}^{(\mathrm{EXAFS})}$=±0.04, $d\mathrm{O1}_{\perp}^{(\mathrm{EXAFS})} = d\mathrm{O1}_{z}^{(\mathrm{EXAFS})}$=±0.35 Å. XANES refinement fails to improve the EXAFS estimation for $d\mathrm{O1}_{\|}$, but it provides dramatic improve-ment for $d\mathrm{O1}_{\perp}$ and $d\mathrm{O1}_{z}$. A final result of the combined EXAFS and XANES refinements may be formulated as follows: the MCDW domains have the local symmetry indicated in Fig. 1(b) and characterized by correlated displacements of $\Delta\mathrm{O1}_{\|}$=0.12±0.04, $\Delta\mathrm{O1}_{\perp}$=0.25±0.08, and $\Delta\mathrm{O1}_{z}$=0.12±0.1 Å

4. Conclusion

The local structure of the CuO_2 planes of the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ superconductor can be explained if three type of domains are superimposed: (i) the undistorted AF [Fig. 1(f)], (ii) the locally orthorhombic, heavily distorted MCDW [Fig. 1(b)]; and (iii) the intermediate, say, MSP+AF [Fig. 1(d)]. For the mixture of the AF and the MCDW, the agreement factor over the range of 8980-9040eV is ~6.3% that is the best value yet achieved in the field to the best of my knowledge. The still low intensity of the calculated shake-up peak could have two origins: (i) $S(\omega)$ is evaluated in the Z-approximation and (ii) $I(\omega)$ is calculated using non self-consistent-field potential. The final state rules need to be systematically tested (Ignatov, 2001). The second limitation can be worked out, for example, by the recent edition of the FEFF code (Ankudinov *et al*., 1998).

In summary, a new genuine many-body approach for the $S(\omega)$ calculations is presented. In combination with the old idea of multiple-channel absorption (Mahan, 1974) it's expected to improve K-edge XANES calculations. Though a number of approximations are made, calculations of the $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ superconductor show that: (1) The agreement factor is reduced 2-3 times if the $S(\omega)$ is included, so that one can go from the qualitative "visual" towards quantitative R-factor analysis of XANES spectra; (2) The $S(\omega)$ introduces additional broadening, thereby reducing insertion in the energy-dependent broadening. It also rescales the energy. (3) The ab-inito correction for theoretical amplitudes and phase shifts is proposed. (4) The new approach contains very rich physics involving the relationship between the electronic and local structures that is introduced implicitly through the Hamiltonian (Ignatov, 2001). In particular, the MCDW configuration depicted in Fig. 1(b) not only gives the best fit of the XANES data but also minimizes the ground state energy for the Cu_4O_8 cluster in the many-body calculations.

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