Influence of strong electron correlations on the form of the x-ray Cu K absorption spectra of $La_{2-x}Sr_xCuO_4$

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The influence of strong electron correlations on the x-ray Cu K absorption spectra has been investigated using the extended $p-d$ model and the sudden approximation. The structure of the vacant above-threshold single-electron Cu p states has been modeled by the SCF X_α scattered wave method. It has been shown that the Cu K spectrum is determined by a convolution of the spectra of single-electron absorption by vacant orbitals below and above the ionization threshold and of many-electron transitions within the system of valence electrons. This makes it possible to attribute the main peak of the Cu K spectrum of La_2CuO_4 to the Cu $d^{10}L$ configuration and the single high-energy satellite to the Cu d^9 configuration. The $LaSrCuO_4$ spectrum has been calculated with allowance for both singlet and triplet two-hole states of the CuO_4 cell. Comparison with experimental data reveals that the main two-hole state is a triplet, which also forms the absorption spectrum consisting of the main maximum corresponding to the Cu $d^{10}LL$ configuration and two satellites corresponding to the Cu d^9L and Cu d^8 configurations. All the theoretical spectra obtained agree well with the experimental data. © *1995 American Institute of Physics.*

1. INTRODUCTION

Rich information about the electronic structure of copper oxides can be obtained by x-ray and x-ray electron spectroscopy.[1] It is well known that strong electron correlations form the main features of the electronic structure of the compounds La_2CuO_4 and $YBa_2Cu_3O_6$, but the role they play in the mechanism of formation of the x-ray spectra has been studied much less well. In the literature there are just a few studies devoted to model calculations of x-ray electron spectra (Cu $2p$),[2,3] x-ray emission spectra (Cu K_α),[4] and x-ray absorption spectra (Cu $L_{2,3}$).[5] At the same time, there are direct experimental indications that strong electron correlations are involved in the mechanism of formation of the x-ray Cu K absorption spectrum of La_2CuO_4 (Ref. 6).

The mechanism of formation of these spectra has been considered in detail in earlier studies based on different forms of the single-electron nonempirical multiple scattering method.[7–10] These investigations have given an adequate description of all the features except the C peak lying 7 eV above the main peak. Increasing the size of a cluster to 50–60 atoms enabled the authors of Refs. 8–10 to obtain this peak only in xy polarization, whereas such a structure is also observed experimentally in z polarization.[6] As will be shown below, the C peak can be naturally obtained in a multi-electron approach.

The role of multi-electron effects in doped systems is much more important. This causes the Cu K spectrum of impurity electron states of $LaSrCuO_4$ to differ greatly from the spectrum of the undoped compound La_2CuO_4, these differences being expressed in a change in both the number and the relative intensities of the main peaks.[11] Since doping results in the appearance of contributions of the Cu d^8, Cu d^9L, and Cu $d^{10}LL$ configurations, in each of which there are two holes per formula unit, the effects of their strong Coulomb interaction are what determine the greater complexity of the spectra.

The mechanism by which the x-ray Cu K absorption spectra form is associated with excitation of the ground $1s$ level of copper by an x-ray photon with energy equal to or greater than the ionization potential of the $1s$ level and the transition of the $1s$ electron to the p orbital in the positive range of energies, with subsequent escape from the system. Since the wave function of this photoelectron depends only on the shape of the potential formed by the nearest neighbors of the absorbing atom and belongs to the parent system, it is possible to calculate the matrix elements of these x-ray transitions in the single-electron approximation. On the other hand, because of the strong Coulomb interaction of the core $1s$ hole with vacant bound states in the d^8, d^9L, and $d^{10}LL$ configurations, the K absorption spectra depend on the effects of the strong interelectron correlations, and this makes it necessary to take them into account adequately.

The aim of this paper is to calculate the Cu K absorption spectrum in the $La_{2-x}Sr_xCuO_4$ system with allowance for the effects of the strong electron correlations. To take into account these effects, we use exact diagonalization of the Hamiltonian of the multiband $p-d$ model for a CuO_4 cluster in the framework of the sudden perturbation model (sudden approximation). This gives us the energies and statistical weights of the various multi-electron configurations of the final states. The matrix elements of the $1s \rightarrow p(\varepsilon)$ x-ray transitions were calculated for the CuO_6^{10-} cluster by the nonempirical self-consistent field (SCF) X_α scattered-wave method, which allows the absorption spectra to be calculated in the single-electron approximation in the most consistent manner. The resulting spectra were synthesized using the profiles of the lines obtained by the scattered-wave method and also the

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statistical weights and energies of the configurations as determined by means of the multiband $p-d$ model.

Below, on the basis of the results obtained using these two models, we shall show that the main peak of the Cu K spectrum of the undoped compound corresponds to the Cu $d^{10}L$ configuration, while the single high-energy satellite corresponds to the Cu d^9 configuration. The spectrum of completely doped $LaSrCuO_4$ has been calculated both for the singlet and triplet two-hole states. Comparison with the experimental data shows that the ground state of two holes in the $LaSrCuO_4$ cell is a triplet, which also forms the absorption spectrum consisting of the main maximum corresponding to the Cu $d^{10}LL$ configuration and two satellites corresponding to the Cu d^9L and Cu d^8 configurations.

2. MULTI-ELECTRON DESCRIPTION OF THE X-RAY ABSORPTION SPECTRUM

Form of representation of the spectrum

We consider the form of the absorption spectrum in the approximation of a sudden perturbation due to the formation of an internal $1s$ hole. This is better known in single-electron calculations as the Larson model.[12,13] In copper-oxide high-temperature superconductors, multi-electron states need to be taken into account because of the strong Coulomb interaction of the $1s$ hole with the $3d$ electrons of copper. In the multi-electron approach, the Hamiltonian of the multiband $p-d$ model, which describes the valence state of the copper and oxygen, can be expressed in the hole representation[14–16]

$$
\begin{aligned}
&\mathcal{H}=\mathcal{H}_d+\mathcal{H}_p+\mathcal{H}_{pp}+\mathcal{H}_{pd},\\
&\mathcal{H}_d=\sum_r \mathcal{H}_d(r),\quad \mathcal{H}_d(r)=\sum_{\lambda,\sigma}\Big[(\varepsilon_{d\lambda}-\mu)d^+_{r\lambda\sigma}d_{r\lambda\sigma}\\
&\quad+\frac{1}{2}U_d n^{\sigma}_{r\lambda}n^{-\sigma}_{r\lambda}\Big]+\sum_{\sigma\sigma'}(V_d n^{\sigma}_{r1}n^{\sigma'}_{r2}\\
&\quad-J_d d^+_{r1\sigma}d_{r1\sigma'}d^+_{r2\sigma'}d_{r2\sigma}),\\
&\mathcal{H}_p=\sum_i \mathcal{H}_p(i),\quad \mathcal{H}_p(i)=\sum_{\alpha,\sigma}\Big[(\varepsilon_{p\alpha}-\mu)p^+_{i\alpha\sigma}p_{i\alpha\sigma}\\
&\quad+\frac{1}{2}U_p n^{\sigma}_{i\alpha}n^{-\sigma}_{i\alpha}\Big]+\sum_{\sigma\sigma'}(V_p n^{\sigma}_{i1}n^{\sigma'}_{i2}\\
&\quad-J_p p^+_{i1\sigma}p_{i1\sigma'}p^+_{i2\sigma'}p_{i2\sigma}),\qquad (1)\\
&\mathcal{H}_{pd}=\sum_{i,r}\mathcal{H}_{pd}(i,r),\\
&\mathcal{H}_{pd}(i)=\sum_{\alpha,\lambda,\sigma}(T_{\lambda\alpha}p^+_{i\alpha\sigma}d_{r\lambda\sigma}+\text{H.c.}+V_{\lambda\alpha}n^{\sigma}_{r\lambda}n^{\sigma'}_{i\alpha}\\
&\quad-J_{\lambda\alpha}d^+_{r\lambda\sigma}d_{r\lambda\sigma'}p^+_{i\alpha\sigma'}p_{i\alpha\sigma},\\
&\mathcal{H}_{pp}=\sum_{(i,j)}\sum_{\alpha\beta\sigma}(t_{\alpha\beta}p^+_{i\alpha\sigma}p_{j\beta\sigma}+\text{H.c.}),
\end{aligned}
$$

where $\varepsilon_{p\alpha}$ and $\varepsilon_{d\lambda}$ are the single-particle energies of the p and d hole orbitals α and λ, respectively; U_p,U_d are the Hubbard correlations; V_p and V_d are the matrix elements of the interatomic Coulomb repulsion on the same and on different orbitals of oxygen and copper; J_p,J_d are the Hund exchange integrals on the oxygen and copper atoms; $T_{\lambda\alpha}$ and $t_{\lambda\alpha}$ are the matrix elements of $p-d$ and $p-p$ hops between nearest neighbors; $V_{\lambda\alpha}$ and $J_{\lambda\alpha}$ are the matrix elements of the Coulomb and exchange interactions between copper–oxygen nearest neighbors; $n^{\sigma}_{r\lambda},n^{\sigma}_{i\alpha}$ are the operators of the hole numbers on copper and oxygen; and μ is the chemical potential calculated self-consistently and lying within the band gap for the undoped system. Obviously, the quality of the results obtained in this model will depend on the basis chosen, and therefore it is necessary to take into account as a minimum the $d_{x^2-y^2}$ and d_{z^2} copper orbitals and the p_x and p_y orbitals for all the oxygen atoms. At the same time, we have considered only the σ orbitals of the cluster that are formed by p states of oxygen, since the π orbitals formed by the interaction of the p states of oxygen and the $d_{x^2-y^2}$ and d_{z^2} states of copper are forbidden on grounds of symmetry, while the matrix elements of the π states generated solely by the p orbitals of oxygen are negligibly small. The energy of the $d_{x^2-y^2}$ orbital was taken equal to ε_d, whereas the energy of the d_{z^2} orbital was taken equal to Δ_d. The energy of the $p_{x,y}$ orbitals was taken equal to ε_p.

We regard the parameters of the Hamiltonian (1) as empirical; they were determined by comparing the electronic structure of the La_2CuO_4 ground state with optical and magnetic data (Ref. 17):

$$
\begin{aligned}
&U_p=U_d=\infty,\quad V_p=3\ \text{eV},\quad V_d=4.5\ \text{eV},\\
&J_p=J_d=0.5\ \text{eV},\quad T_{\lambda\alpha}=1.5\ \text{eV},t_{\lambda\alpha}=0.2\ \text{eV},\\
&V_{\lambda\alpha}=0.6\ \text{eV},\quad J_{\lambda\alpha}=0.2\ \text{eV},\quad \varepsilon_d=0,\\
&\Delta_d=1.5\ \text{eV},\quad \varepsilon_p=2\ \text{eV}.
\end{aligned}
$$

To reduce the number of parameters and without loss of generality, the largest Coulomb matrix elements within one orbital are assumed to be infinitely large.

The state of two holes in the CuO_4 cell may be a singlet (Zhang–Rice singlet[18]) or a triplet. Moreover, as is shown in Ref. 19, a crossover between the singlet and the triplet can occur for relatively small changes of the parameters. In our case the two-hole ground state is a triplet for $\delta=\varepsilon_p-\varepsilon_d=2$ eV and a singlet for $\delta=1.5$ eV.

For the CuO_4 cluster with two holes, the complete two-particle basis in the limit $U_d=U_p=\infty$ contains $2^2C_6^2=60$ states. Since the spin is a quantum number, the matrix of the Hamiltonian in this basis breaks up into four blocks, one corresponding to the singlet state (15×15) and three for the triplet states (6×6, 8×8, and 1×1). By exact diagonalization of these matrices, we obtain a set of two-particle molecular states and their energies with explicit allowance for the strong electron correlations. We note that the eigenstates in the two-hole cluster are always mixtures of the configurations d^8, d^9L, and $d^{10}LL$; moreover, in our model in the limit $U_d=\infty$ the configuration d^8 can be realized only if one of the d vacancies is localized on the d_{z^2} orbital and the other on $d_{x^2-y^2}$. The multiband $p-d$ model, including the method of exact diagonalization of the cluster in the configuration Cu d^9, is described in more detail in Ref. 17.

The Coulomb interaction of the holes in the $3d$ and $1s$ orbitals in the final state is described by adding to (1) the term

$$\mathscr{H}_{s,d}=V_{s,d}\sum d^{+}_{r\lambda\sigma}d_{r\lambda\sigma}n_{s\sigma'}, \tag{2}$$

where $n_{s\sigma}$ is the operator of the number of holes in the $1s$ orbital.

The multi-electron wave function of the system before the formation of the hole in the core $1s$ orbital of copper can be written in the form

$$\Psi_{in}=\varphi^{2}_{1s}\Psi^{(pd)}_{in,0}, \tag{3}$$

where φ_{1s} is the wave function of the $1s$ electron and $\Psi^{(pd)}_{in,0}$ is the wave function of the ground state of the system of valence electrons of the copper and oxygen with energy $E^{(pd)}_{in,0}$ described by the Hamiltonian (1) under the condition $n_d+n_p=n_h=$const, where n_d and n_p are the concentrations of the holes in the d states of copper and p states of oxygen, and n_h is the number of holes in the cell and is equal to 1 or 2 depending on the degree of doping.

The wave function of the system in the final state can be written in the form

$$\Psi^{(m)}_{f}=\varphi_{1s}\varphi_{p}\Psi^{(pd)}_{f,m}, \tag{4}$$

where φ_p is the wave function of the photoelectron in the p state with energy ε_p, and $\Psi^{(pd)}_{f,m}$ is the wave function of the term with number m of the system of p and d electrons in the final state with energy $E^{(pd)}_{f,m}$. Here the index m ranges over all possible states of the Hamiltonian $\mathscr{H}+\mathscr{H}_{s,d}$ calculated subject to the condition $n_s=1$.

The energies of the initial and final states are

$$E_{in}=2\varepsilon_{1s}+E^{(pd)}_{in,0}, \quad E_{f,m}=\varepsilon_{1s}+\varepsilon_{p}+E^{(pd)}_{f,m}, \tag{5}$$

and the energy absorbed by the x ray is

$$\hbar\omega=\varepsilon_{p}-\varepsilon_{1s}+\Delta E_{m}, \quad \Delta E_{m}=E^{(pd)}_{f,m}-E^{(pd)}_{in,0}. \tag{6}$$

The electronic structure of copper oxides can be well described in the hole representation, in which we shall also find wave functions and energy eigenvalues in the sectors of the Hilbert space with fixed number of holes $n_h=1$ and 2 by exact diagonalization of the Hamiltonians (1) and (1)+(2).

In the hole representation, the energy ΔE_m in (6) simply changes sign: $\Delta E^{(h)}_{m}=-\Delta E_{m}$. The probability of absorption of an x ray is

$$W_{m}=|\langle\Psi_{in}|e\mathbf{r}|\Psi^{(m)}_{f}\rangle|^{2}$$
$$=|\langle\varphi_{1s}|e\mathbf{r}|\varphi_{p}\rangle|^{2}|\langle\Psi^{(pd)}_{in,0}|\Psi^{(pd)}_{f,m}\rangle|^{2}. \tag{7}$$

If there is no strong Coulomb interaction of the inner $1s$ hole with the valence vacancies, $V_{sd}=0$, the states $\Psi^{(pd)}_{in,0}$ and $\Psi^{(pd)}_{f,m}$ are orthogonal and the final factor in (7) is

$$\langle\Psi^{(pd)}_{in,0}|\Psi^{(pd)}_{f,m}\rangle=\delta_{m,0}.$$

In this case, the transition probability is determined solely by the matrix element $\langle\varphi_{1s}|e\mathbf{r}|\varphi_{p}\rangle$, which can be calculated in the single-electron method.

However, because of the Coulomb interaction (2) the states of the valence p and d electrons (holes) before and after photoionization are nonorthogonal. Therefore, not only the ground term but also various excited terms of the final state contribute to the absorption spectrum.

We denote by $I_{XAS}(\omega)$ and $I^{(0)}_{XAS}(\omega)$ the intensities of the x-ray absorption by the $1s$ state calculated, respectively, with allowance for the multi-electron effects and only in the single-electron approach. We also introduce $I_m(\Delta E)$, the spectrum of electron $p-d$ transitions in the valence band, which is determined by the final factor in (7). The spectrum I_m consists of a set of δ functions, the intensity of the main peak is proportional to $|\langle\Psi^{(pd)}_{in,0}|\Psi^{(pd)}_{f,0}\rangle|^{2}$, and the satellites, which are separated from the main peak by energy $E^{(pd)}_{f,m}-E^{(pd)}_{f,0}$, have intensity determined by $|\langle\Psi^{(pd)}_{in,0}|\Psi^{(pd)}_{f,m}\rangle|^{2}$, with $m\neq 0$.

With allowance for the notation introduced above, it follows from (7) that

$$I_{XAS}(\hbar\omega)=\sum_{m} I^{0}_{XAS}(\hbar\omega-\Delta E^{(h)}_{m})I_{m}(\Delta E^{(h)}_{m}). \tag{8}$$

Thus, the complete absorption spectrum is the convolution of two spectra: the discrete spectrum I_m of transitions within the system of p and d electrons (holes) and the continuous spectrum $I^{(0)}$ of $1s\rightarrow p(\varepsilon)$ transitions. To calculate the latter, we can use any nonempirical method. However, to calculate the multi-electron component of the spectrum, we use exact diagonalization of the multi-electron Hamiltonian with explicit allowance for the effects of the strong electron correlations.

Single-electron calculation of the Cu *K* absorption spectra

At the present time, the most consistent method used to calculate the x-ray absorption spectra of nd metals above the ionization threshold in the single-electron approach is the SCF (self-consistent field) X_α scattered wave method.[20] In the present work, we calculated the electronic structure of the CuO_6^{10-} cluster by means of the X_α-OMEGA package (Ref. 21), and to calculate the electron wave functions and intensities of the $Cu1s\rightarrow Cup(\varepsilon)$ x-ray transitions in the dipole approximation in the continuous region of energies we used the X_α-CONTINUOUS code (Ref. 22).

A characteristic feature of the scattered wave method is, in addition to the use of the usual Slater approximation for the exchange-correlation term $V_{ex}=-6\alpha[(3/8\pi)\rho(r)]^{1/3}$ [α is the Slater constant of the exchange interaction chosen for each species of atom in accordance with Ref. 23, and $\rho(r)$ is the total electron density at the point r], the use of the so-called muffin-tin (MT) approximation for the form of the potential created by the nuclear and electron charges. In this approximation, the complete space of a molecule or cluster is divided into regions of three types: 1) atomic spheres, at the center of which there are the nuclei of atoms with radii chosen in accordance with Norman's procedure (Ref. 24); 2) the intersphere region; 3) an outer sphere, the center and radius of which are chosen by requiring minimization of the intersphere region and touching of the atomic spheres. Within regions 1 and 3, the potential is averaged spherically, while in region 2 it is taken to be constant. In our view, this approximation is rather crude, but with the scattered-wave

technique it does enable one to use a very large basis (up to $l=12$) and calculate the electron wave functions and, therefore, the intensities of the x-ray transitions both below and above the ionization threshold.

The parameters of the CuO_6^{10-} cluster were chosen in accordance with the internuclear separations given in Ref. 25. In this paper, we do not give calculations of the CuO_6^{9-} cluster, which in the single-electron approximation corresponds formally to the state of Cu+3, since it was shown in Ref. 26 that the form of the Cu K spectra of these two clusters is practically the same and reflects in the first place the details of the potential determined by the atoms of the immediate environment. The effective absence of differences between the Cu K spectra of these two clusters is explained by the fact that, first, in $La_{2-x}Sr_xCuO_4$ compounds there are no vacant bound states of Cu p type and, hence, in the spectra there are no below-threshold lines sensitive to the occupation numbers, second, the atomic structure of these two clusters remains the same or is changed little, and, third, the density of p states near the ionization threshold, where the line profile is most sensitive to changes in the electronic structure, is low, and therefore both the energy position and the relative intensities of the main peaks are unchanged.

Synthesis of resulting spectra

The form of the final spectra, taking into account not only the density of the above-threshold single-electron states of p type and the degree of doping of the compound $La_{2-x}Sr_xCuO_4$ but also the effects of the strong correlations in the doped and undoped cells, were synthesized by adding the profiles of the single-electron spectra in accordance with Eq. (8). Thus, the spectrum of the undoped La_2CuO_4 was formed from the single-electron spectrum of the Cu $d^{10}L$ configuration with weight 0.765 and energy 2.7 eV and the single-electron spectrum of the configuration Cu d^9 with weight 0.235 and energy 10.6 eV. The spectrum of $LaSrCuO_4$ with singlet two-hole ground state was also formed from the spectra of two configurations: Cu $d^{10}LL$ with weight 0.849 and energy 2.3 eV and Cu d^9LL with weight 0.144 and energy 12.1 eV. The spectrum of $LaSrCuO_4$ with triplet ground state of two holes is formed from the spectra of three configurations: Cu $d^{10}LL$ with weight 0.630 and energy 3.425 eV, Cu d^9L of x^2-y^2 nature with weight 0.151 and energy 11.7 eV, and Cu d^9L of z^2 nature + Cu d^8 with weight 0.219 and energy 16.5 eV. The spectrum of the doped compound $La_{1.8}Sr_{0.2}CuO_4$ was constructed from the spectrum of La_2CuO_4 with weight 0.8 and the spectrum (singlet or triplet) of $LaSrCuO_4$.

We emphasize that the weights and energies given here for the various multi-electron configurations were obtained using previously fixed values of the parameters of the Hamiltonian (1) (Ref. 17).

3. DISCUSSION OF THE RESULTS

Figure 1 shows the experimental[11] and theoretical single-electron Cu K spectra of La_2CuO_6. It can be seen that the synthesized spectrum with allowance for the multi-electron effects corresponds well to the experimental spectrum both

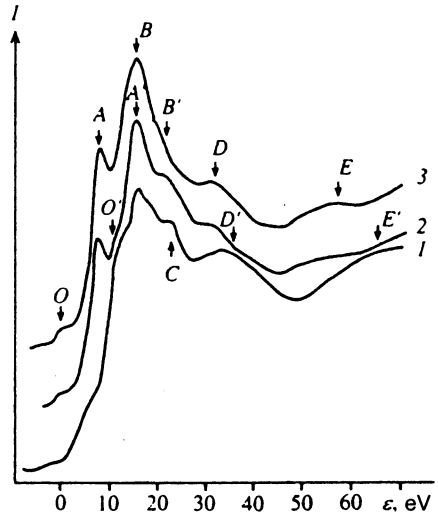

FIG. 1. Experimental[11] (*1*) and theoretical (*2*) Cu K spectra with allowance for multi-electron effects and the theoretical single-electron absorption spectrum (*3*) of La_2CuO_4. The peaks O, A, B, D, and E correspond to the main line (configuration $d^{10}L$) and O', A', B', D', and E' to a shake-up satellite with energy 7.8 eV relative to the main line (configuration d^9).

as regards the energy positions of the peaks and their relative intensities. It is true that the long-wavelength part of the spectrum in the region of peak A is an exception. It has already been noted in the literature that certain differences of the theoretical peak A, both as regards the relative intensity and the energy position in the CuO_6^{10-} cluster, are due solely to the small size of the cluster.[8-10]

As the multielectron calculation showed, the main line in the Cu K spectrum corresponds to the configuration $d^{10}L$ (weight 0.91^2, peaks O,A,B,D,E) and the single strong short-wavelength shake-up satellite (peak C in the experimental spectrum) with energy 7.8 eV relative to the main line reflects the configuration d^9 (weight 0.91^2, peaks O',A',B',D',E'). Thus, the experimental peak must be compared with the theoretical peak B' and is due not only to scattering of photoelectrons by atoms of the environment in La_2CuO_4, as follows from the literature,[8-10] but also reflects the contribution of the configuration Cu d^9 in the investigated compound.

The form of the experimental Cu K spectrum of the impurity states of $LaSrCuO_4$ ("trivalent copper") is much more complicated[11] (Fig. 2). Comparison of the experimental[11] (curve *1*) and theoretical Cu K spectra of $LaSrCuO_4$ with singlet (curve *3*) and triplet (curve *2*) ground states indicates that the triplet is the two-hole ground state of $LaSrCuO_4$ in the doped system $La_{2-x}Sr_xCuO_4$. Its main line (peaks O, A, B, D, and E) corresponds to the configuration $d^{10}LL$ with weight 0.91^2 and small admixtures of the states d^9L (x^2-y^2, weight of the configuration 0.39^2) and d^9L (z^2, weight of the configuration 0.12^2). The first satellite (peaks O', A', B', D', and E') corresponds mainly to the state d^9L (x^2-y^2, weight of the configuration 0.90^2) with a small admixture of the configuration $d^{10}L$ (weight 0.39^2). The second satellite (peaks O'', A'', B'', D'', and E'') reflects the density of the states d^9L (z^2, weight of the configuration 0.81^2) and d^8L (weight of the configuration 0.57^2) with a small admixture of

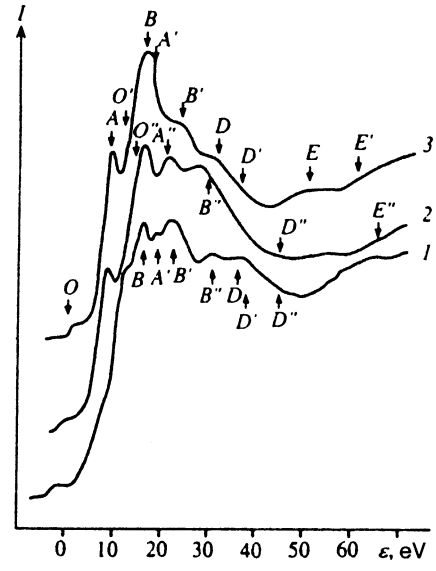

FIG. 2. Experimental[11] (*1*) and theoretical Cu K spectra with triplet (*2*) and singlet (*3*) ground states. The peaks O, A, B, D, and E correspond to the main peak (state d^{10}), the peaks O', A', B', D', and E' correspond to the first satellite [state d^9L (x^2-y^2)], and the peaks O'', A'', B'', D'', and E'' correspond to the second satellite [states $d^9L(z^2)$ and d^8].

the configuration d^9L $(x^2-y^2$, weight $0.12^2)$. Under the experimental spectrum, the corresponding indices identify the configurations to which we have attributed the observed peaks. A certain difference in the relative intensities and energy positions of the theoretical peaks A' and B' can, in our view, be explained primarily by an overestimation of the relative intensity of the peak A in the single-electron calculation. Naturally, this will bring with it a certain distortion of the shape of the final spectrum.

The model spectrum of the doped compound $La_{1.8}Sr_{0.2}CuO_4$ (Fig. 3), synthesized using the spectrum of the triplet state, hardly differs from the spectrum of the parent compound La_2CuO_4.

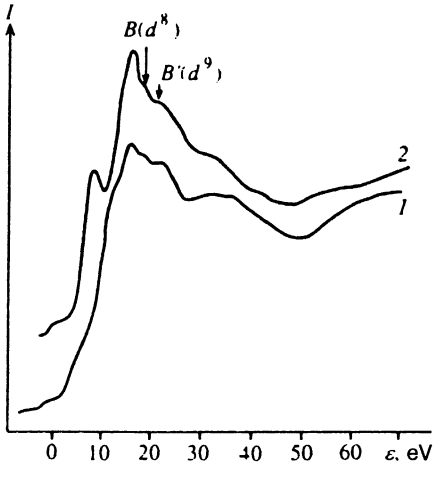

FIG. 3. Experimental[11] spectrum of $La_{1.85}Sr_{0.15}CuO_4$ (*1*) and theoretical spectrum of the compound $La_{1.8}Sr_{0.2}CuO_4$ (*2*) synthesized using the triplet ground state of the impurity electron states. The peak $B'(d^9)$ belongs to the configuration d^9 of the original system, and the peak $B(d^8)$ to the configuration $d^{10}LL$ of impurity states with two electron vacancies per formula unit.

Admittedly, there is some difference for the peak $B(d^8)$, which corresponds to the configuration $d^{10}LL$ of the impurity states of the fully doped compound $LaSrCuO_4$ and is separated from the principal maximum $B(d^9)$ belonging to the configuration $d^{10}L$ of the original material by 2 eV.

In conclusion, we note that we have described the effects of doping under the assumption that all this does is change the concentration of the holes while the form of the Hamiltonian and the values of its parameters are unchanged. Strictly speaking, this is not the case. There are impurity effects such as fluctuations of the parameters of the crystal field near the Sr ion. The change in the charge state of the ions affects their position in the lattice, and this leads to an observable deformation of the octahedra and to a structural transition from the ortho- to the tetragonal phase with increasing Sr concentration. A detailed comparison with the experiment, which has a high resolution, requires allowance to be made for these factors. However, in our approach we take into account only the main change of the electronic structure on doping, namely, the appearance of intragap states due to the change in the occupations of the two-hole terms. These states are well known for all doped insulating copper oxides and, from the point of view of experiment, their appearance is the main change of the spectra with the concentration at low concentrations. As x is increased, it is these states that form the metallic band that is apparently responsible for the superconductivity.

4. CONCLUSIONS

Thus, on the basis of our theoretical calculations we can draw the following conclusions.

1. The absorption spectrum in the multi-electron approach is determined by convolution of the spectra of single-electron absorption by vacant orbitals below and above the ionization threshold and by the spectra of multi-electron transitions within the system of valence electrons.

2. In the x-ray Cu K absorption spectrum of the compound La_2CuO_4, the main maximum reflects the density of the Cu $1s^1d^{10}L$ configuration, and the single shake-up satellite with energy 7.8 eV relative to the main line reflects the density of the Cu $1s^1d^9$ state of symmetry x^2-y^2.

3. The x-ray Cu K absorption spectrum of the impurity electron states of $La_{2-x}Sr_xCuO_4$ corresponds to the triplet ground state and reflects the density of both the main line (Cu $1s^1d^{10}LL$ configuration) and two shake-up satellites corresponding to the states $d^9L(x^2-y^2)$ and $d^9L(z^2)+d^8$.

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