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Vacancies as dopants in high-temperature superconductors

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Abstract. The shift in the Fermi energy E_F and the modification of the density of states $\rho(E)$ have been calculated for oxygen vacancies in $La_{1.85}Sr_{0.15}CuO_{4-y}$ and $YBa_2Cu_3O_{7-y}$ and for lanthanum vacancies in $La_{2-x}CuO_4$. Oxygen vacancies are found to act as donors in every case, and La vacancies as acceptors. These conclusions are in accord with the well known observations that oxygen vacancies decrease T_c, and with the suggestion that the superconductivity of nominally pure La_2CuO_4 could be due to La vacancies.

The discovery of high-temperature copper oxide superconductors [1, 2] has led to many investigations of the structure and properties of these materials. Stoichiometry has been found to play a critical role in several different respects.

The transition temperature of $La_{2-x}M_xCuO_4$ is optimised by doping with Sr at $x = 0.15$, yielding $T_c \simeq 38$ K [3]. The superconducting properties are highly sensitive to the oxygen content, with the highest T_c resulting from full oxygen occupancy [3, 4]. Excess Sr doping with $x > 0.15$ apparently leads to charge compensation through the formation of oxygen vacancies, with a depression of T_c [4–6]. Annealing under high oxygen pressure suppresses the formation of oxygen vacancies, and allows superconductivity at $T_c \simeq 36$ K in $La_{2-x}Sr_xCuO_4$ up to $x = 0.24$ [7]. However, the transition temperature decreases for $x > 0.24$, with no superconductivity observed beyond $x = 0.32$, although metallic conductivity persists [7].

The undoped material La_2CuO_4 exhibits superconductivity of a filamentary nature. The small volume fraction (much less than 1%) of the superconducting region was attributed to either excess oxygen or lanthanum vacancies within the material [8]. The lanthanum-deficient material $La_{2-x}CuO_4$ shows a sharper resistive transition and a greater diamagnetic susceptibility than the nominal La_2CuO_4 superconductor [9], indicating that La vacancies can indeed contribute to the superconductivity.

The 93 K superconductor $YBa_2Cu_3O_7$ is found to have an orthorhombic structure characterised by planes of CuO_2 stacked with one-dimensional chains of CuO [10–14]. A high-temperature orthorhombic-to-tetragonal phase transition near 700 °C in $YBa_2Cu_3O_7$ is found to be an order–disorder transition in which the O(1) oxygen atoms in the CuO chains are disordered onto the normally vacant adjacent sites [15]. A decrease in the oxygen stoichiometry is found to introduce vacancies on the same O(1) chain sites [16]. These oxygen vacancies lead to a depression of T_c from above 90 K to about 55 K

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for $0.1 \leq y \leq 0.5$, and a loss of the superconductivity and even metallic conductivity for $y > 0.5$ [17, 18].

Here we consider the changes in electronic structure that result from vacancies in these original copper oxide superconductors, using a tight-binding model that was developed to study such effects [19]. We neglect local strains and the small changes in the lattice constants that occur as vacancies are introduced. For simplicity, we use the BCT structure [20] for $La_{1.85}Sr_{0.15}CuO_4$, neglecting the small orthorhombic distortion that doubles the unit cell below 200 K [21]. For $YBa_2Cu_3O_7$, the observed orthorhombic structure [10] is used. The change in the density of states is computed with a standard Green's function technique.

The unperturbed Green's function has the spectral representation

$$G_0(E) = \sum_{k,n} w_k \frac{\psi(\boldsymbol{k}, n)\psi^*(\boldsymbol{k}, n)}{E - E(\boldsymbol{k}, n) + i\delta} \tag{1}$$

where $E(\boldsymbol{k}, n)$ and $\psi(\boldsymbol{k}, n)$ are the electronic energy and wavefunction (in a tight-binding representation) for the nth band and one of the N sample wavevectors $\boldsymbol{k}$ (with weight w_k) within the irreducible part of the Brillouin zone. In the present calculations, $N = 24$ for the BCT structure and 64 for the orthorhombic. A finite value $\delta = 0.2$ eV was used to smooth the results. The local density of states for both spins is given by

$$\rho_0(E) = -(2/\pi)\,\mathrm{Tr}\,\mathrm{Im}\,G_0(E) \tag{2}$$

where Tr indicates a trace over those orbitals associated with a given site. For an isolated vacancy, the change in the density of states is given by [22, 23]

$$\begin{aligned}\Delta\rho(E) &= -(2/\pi)(\partial/\partial E)\,\mathrm{Im}\log\mathrm{Det}\,G_0^{\mathrm{sub}}(E) \\ &= -(2/\pi)(\partial/\partial E)\tan^{-1}(\mathrm{Im}\,\mathrm{Det}\,G_0^{\mathrm{sub}}(E)/\mathrm{Re}\,\mathrm{Det}\,G_0^{\mathrm{sub}}(E))\end{aligned} \tag{3}$$

where G_0^{sub} refers to the subspace of states associated with the vacancy site. The Fermi energy E_F is calculated by integrating the total density of states up to the number of valence electrons for a given concentration of vacancies.

We consider both oxygen sites in $La_{1.85}Sr_{0.15}CuO_4$ (with O(1) in the CuO_2 planes and O(2) in the LaO layer), and the chain site O(1) in $YBa_2Cu_3O_7$. The calculation neglects the interaction between vacancies. However, for $y = 1$ we have performed an independent calculation with one oxygen vacancy per formula unit, and the change in the density of states is approximately the same.

Figure 1 shows the change in the density of states $\Delta\rho(E)$ for a single oxygen vacancy in $La_{1.85}Sr_{0.15}CuO_{4-y}$. Notice that $\Delta\rho$ has more structure near the Fermi energy for the O(1) site than for the O(2) site, because of the strong pdσ interactions of O(1) p orbitals with copper d orbitals [19]. For both sites, $\Delta\rho$ is negative at the unperturbed Fermi energy. As can be seen in table 1, the density of states at E_F is smaller than the $y = 0.0$ value for $y \leq 0.5$, and E_F monotonically increases for $y \leq 1.0$. Oxygen vacancies thus behave as donors, filling the hole states near the Fermi energy.

For vacancies on the O(2) site, table 1 indicates that $\rho(E_F)$ is smaller than the $y = 0.0$ value for all $y > 0$. The Fermi energy increases somewhat faster for O(2) vacancies, since the more ionic character of the Cu–O(2) bond [19] leaves most of the O(2) states below E_F. These oxygen vacancies are again electron donors.

The change in the density of states of $La_{2-x}CuO_4$ for a single La vacancy is shown in figure 2. The large contribution near $\simeq 5$ eV arises from the unoccupied La d bands. As can be seen table 1, E_F is lowered. Lanthanum vacancies thus donate holes to the

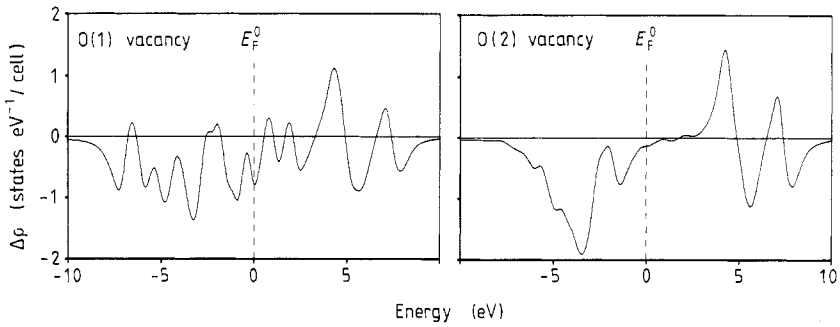

Figure 1. Change in density of states for an isolated oxygen vacancy in $La_{1.85}Sr_{0.15}CuO_{4-y}$. Oxygen site O(1) is in the CuO_2 plane, and O(2) in the La/Sr layer. The zero of energy is the unperturbed Fermi energy E_F^0 of $La_{1.85}Sr_{0.15}CuO_4$.

Table 1. The shift in E_F and density of states for y oxygen vacancies per formula unit. (*a*) Site O(1) in $La_{1.85}Sr_{0.15}CuO_{4-y}$. (*b*) Site O(2) in $La_{1.85}Sr_{0.15}CuO_{4-y}$. (*c*) The La site in $La_{2-x}CuO_4$. (*d*) Site O(1) in $YBa_2Cu_3O_{7-y}$.

(*a*)	y	ΔE_F (eV)	$\rho(E_F)$ (states eV^{-1}/cell)	(*b*)	y	ΔE_F (eV)	$\rho(E_F)$ (states eV^{-1}/cell)
	0.0	0.00	1.9		0.0	0.00	1.9
	0.1	0.07	1.3		0.1	0.12	1.3
	0.2	0.20	0.73		0.2	0.31	0.74
	0.3	0.44	0.61		0.3	0.60	0.60
	0.4	0.65	1.0		0.4	0.87	0.90
	0.5	0.76	1.5		0.5	1.03	1.4
	0.6	0.83	2.0		0.6	1.14	1.8
	0.7	0.88	2.3		0.7	1.26	1.5
	0.8	0.93	2.3		0.8	1.41	0.94
	0.9	0.97	2.3		0.9	1.66	0.63
	1.0	1.01	2.3		1.0	1.94	0.82

(*c*)	x	ΔE_F (eV)	$\rho(E_F)$ (states eV^{-1}/cell)	(*d*)	y	ΔE_F (eV)	$\rho(E_F)$ (states eV^{-1}/cell)
	0.0	0.00	1.4		0.0	0.00	3.2
	0.1	−0.11	1.9		0.1	0.01	3.1
	0.2	−0.20	1.9		0.2	0.03	3.0
	0.3	−0.29	1.7		0.3	0.05	2.8
	0.4	−0.42	1.2		0.4	0.07	2.7
	0.5	−0.56	1.2		0.5	0.10	2.4
					0.6	0.13	2.2
					0.7	0.16	2.0
					0.8	0.21	1.8
					0.9	0.26	1.6
					1.0	0.31	1.5

material, just as divalent Sr does when substituted for trivalent La. This could explain the occurrence of superconductivity in La_2CuO_4, in that deficiencies of La within the undoped material can provide the required hole carriers. In our calculations, there is an increase in $\rho(E_F)$ for $x \leqslant 0.3$.

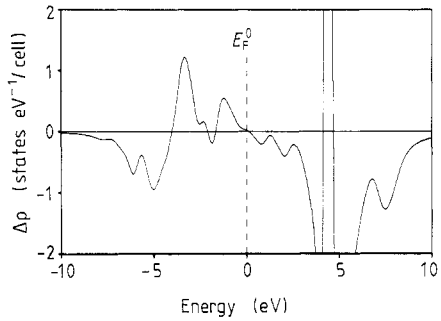

Figure 2. Change in density of states for a lanthanum vacancy in $La_{2-x}CuO_4$.

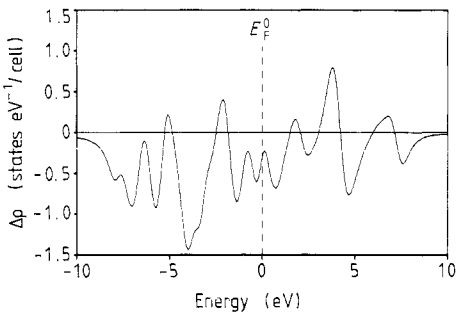

Figure 3. Change in density of states for a single oxygen vacancy on the O(1) chain site in $YBa_2Cu_3O_{7-y}$.

We now consider the electronic effects of oxygen vacancies in $YBa_2Cu_3O_7$. The change in the density of states of $YBa_2Cu_3O_{7-y}$ for an isolated oxygen vacancy introduced on the O(1) site is shown in figure 3. As the number of oxygen vacancies y increases, $\rho(E_F)$ decreases monotonically. Table 1 shows the calculated shifts in E_F and $\rho(E_F)$ for $0.0 \leqslant y \leqslant 1.0$. The removal of oxygen monotonically raises the Fermi level, so the present calculation confirms the expectation that oxygen vacancies act as electron donors in this system. The decrease in the density of states at E_F is consistent with shifts of the valence bands seen experimentally in photoemission studies of oxygen-deficient $YBa_2Cu_3O_{7-y}$ [24].

Since the charge carriers in both $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_7$ are holes [25, 17], the present results are consistent with the large body of experimental studies showing that oxygen vacancies degrade the superconducting T_c and even the metallic conductivity.

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