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Electronic properties of oxygen vacancies in La_2CuO_{4-y}

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The electronic properties of oxygen vacancies in chemically pure La_2CuO_4 have been investigated by the *ab initio* pseudofunction method using a supercell geometry. Oxygen vacancies alter the electronic structure significantly, breaking up the 2-eV-wide partially filled conduction band into narrower bands, which are only about 0.1 eV wide in $La_2CuO_{3.75}$. Our results suggest that vacancy-induced narrow bands near the Fermi level could lead to the antiferromagnetic state observed in some nonstoichiometric La_2CuO_4 samples.

La_2CuO_4 exhibits a wide variety of interesting physical properties depending on how the samples are prepared.[1-8] La_2CuO_4 is metallic at room temperature and above.[1,2] At low temperatures, La_2CuO_4 is variously found to be the following: (a) metallic down to 4 K,[1] (b) semimetallic down to about 30 K, where the conduction electrons appear to become localized,[3] (c) semiconducting and weakly paramagnetic with the formation of a spin density wave around 250 K,[4] (d) magnetic, with a localized magnetic moment above 200 K which vanishes smoothly below 200 K,[5] (e) antiferromagnetic with a Néel temperature between 240 and 290 K,[6-8] and (f) superconducting below 40 K.[9,10]

Leaving aside deliberate doping, oxygen vacancies appear to be the most important variable controlling the final properties. For example, long-range antiferromagnetic order in oxygen-deficient La_2CuO_{4-y} is closely correlated to the value of y.[11] In this paper we will study the electronic properties of oxygen vacancies theoretically and discuss their possible relationship to T_c and antiferromagnetism in the La_2CuO_{4-y} system.

In recent theoretical studies,[12,13] we demonstrated that the orthorhombic phase of La_2CuO_4 is metallic, with a highly anisotropic band structure. The metallic character arises from the fact that the highest occupied and lowest unoccupied bands touch at certain points and along certain surfaces of the reduced zone. Elsewhere in the zone these bands are separated by a gap. In contrast to statements by earlier workers,[3,14,15] we suggested that the orthorhombic phase of La_2CuO_4 could be the host of superconductivity in doped as well as undoped samples under suitable conditions. These predictions have subsequently been confirmed experimentally,[9,10,16-19] as has our further prediction that at very low temperatures La_2CuO_4 becomes a semiconductor due to an orthorhombic-to-monoclinic structural phase transition.[20]

Since all band-structure calculations to date indicate that La_2CuO_4 has broad bands crossing the Fermi level, the main paradox conceptually is the occurrence of localized moments and an antiferromagnetic ground state. The broad bands should preclude the existence of a magnetic ground state since the usual models of magnetism, such as the Hubbard and Anderson models, require narrow bands and large correlation energies.

In this paper we will show theoretically that oxygen vacancies alter the electronic structure significantly, breaking up and narrowing the broad conduction bands of the stoichiometric compound in the neighborhood of the Fermi level. The vacancy-induced narrow band (in $La_2CuO_{3.75}$) is only 0.1 eV wide and so could conceivably support localized moments as well as an antiferromagnetic ground state. The narrow band obtained here is consistent with the earlier conclusion reached by one of us that O vacancies along one-dimensional Cu—O chains in $YBa_2Cu_3O_{7-x}$ can break the broad conduction bands at E_F into several narrow bands.[21]

To study the effect of oxygen vacancies on the electronic properties of La_2CuO_4, we constructed a supercell of four tetragonal unit cells of La_2CuO_4, i.e., 28 atoms. We used atomic coordinates appropriate for tetragonal La_2CuO_4 for ease of computation. The supercell was formed by doubling the tetragonal unit cell in the two planar directions. Body-centered tetragonal symmetry is preserved for this configuration. We then removed 1 of the 16 O atoms in the supercell from the 2D Cu—O network. The only remaining point symmetry is inversion. The separation between adjacent vacancies is 7.6 Å, and this proves to be sufficiently large to avoid significant intervacancy interactions.

We calculated the energy bands for this structure, formally $La_2CuO_{3.75}$, using the pseudofunction method.[22] Identical calculations were also carried out for the same structure but with the vacancy occupied. Although the actual symmetry is much higher now, we continued to use the lower symmetry of the 27-atom case as a numerical check. Our results for the 28-atom case (no vacancy) closely resemble published band structures for tetragonal La_2CuO_4 (Refs. 14 and 15), thus increasing our confidence in the adequacy of our ordered vacancy calculation.

The two crystals we investigated, oxygen-deficient $La_2CuO_{3.75}$ and stoichiometric La_2CuO_4, bracket the undoped material $La_2CuO_{3.88}$, whose structure has been

studied by neutron diffraction.[3] These studies clearly indicated that all the O vacancies occur in the Cu—O plane, as assumed in our theoretical model.

We used an ordered-vacancy supercell approach because we believe that this approach should provide accurate local information on the electronic structure of isolated oxygen vacancies. Moreover, none of presently available first-principles self-consistent band-structure computational methods can deal with disordered vacancies realistically. Since we found considerable changes in the electronic structure as the self-consistent iteration proceeded, we would expect simplified non-self-consistent methods such as empirical tight-binding calculations to miss many of the essential physical features of the (ordered or disordered) oxygen vacancy problem.

Our principal results are presented in Fig. 1. The bottom panel shows the energy bands for the 28-atom model (no vacancies), and the top panel the energy bands for the 27-atom (one O vacancy) model. It is readily apparent that, on the average, there is only one unfilled band for the 27-atom case and two for the 28-atom case. Apart from this feature, which is dictated by the different number of electrons and available orbitals, the bandwidths are strikingly different in the two cases. While there is a broad band roughly 2 eV wide crossing E_F for the 28-atom case, in agreement with previous studies of stoichiometric La_2CuO_4 by ourselves[12] and others[14,15], the bands for the 27-atom case are considerably narrower, having been broken up by the ordered vacancy superlattice.

In contrast to textbook pictures of energy bands that are perturbed slightly only near the reduced zone boundaries by superlattice periodicity, the superlattice splitting extends throughout the reduced zone in the present instance. In fact, a band gap opens over a substantial part of the reduced zone between the 79th and 80th bands. Combined with the change in the number of filled bands (79 rather than 80), the oxygen vacancies create a very narrow band in the neighborhood of E_F whose width is about 0.1 eV. This narrow band forms the valence band edge and is highlighted in Fig. 1(a). Our result therefore

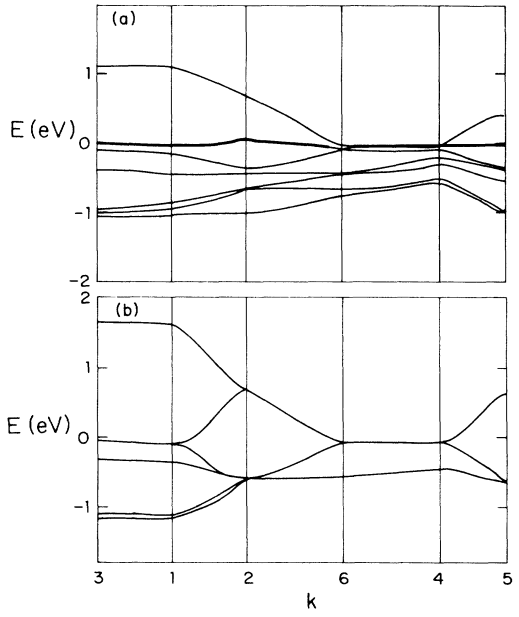

FIG. 1. Band structures of La_2CuO_{4-y}. (a) $y=0.25$ (with O vacancies) and (b) $y=0$ (without O vacancies). The **k** points labeled 1–6 along the horizontal axis are $3=(0.0,0.0,0.2878)$, $1=(0.0,0.0,0.0)=\Gamma$, $2=(0.25,0.0,-0.0179)$, $6=(0.25,0.25,-0.1438)$, $4=(0.25,0.25,0.2438)$, and $5=(0.0,0.25,-0.0179)$. Narrow band at $E_F(=0$ eV) is highlighted.

suggests that *nonmagnetic* $La_2CuO_{3.75}$ could have considerably higher density of states at E_F than stoichiometric La_2CuO_4. However, we believe $La_2CuO_{3.75}$ is likely antiferromagnetic and may not exhibit such a high density of states as suggested by Fig. 1(a).

Charge density plots are useful for understanding the bonding qualitatively. In Fig. 2 we have plotted the total pseudofunction charge density for the 28- and 27-atom cases. We see that the charge density contours around the

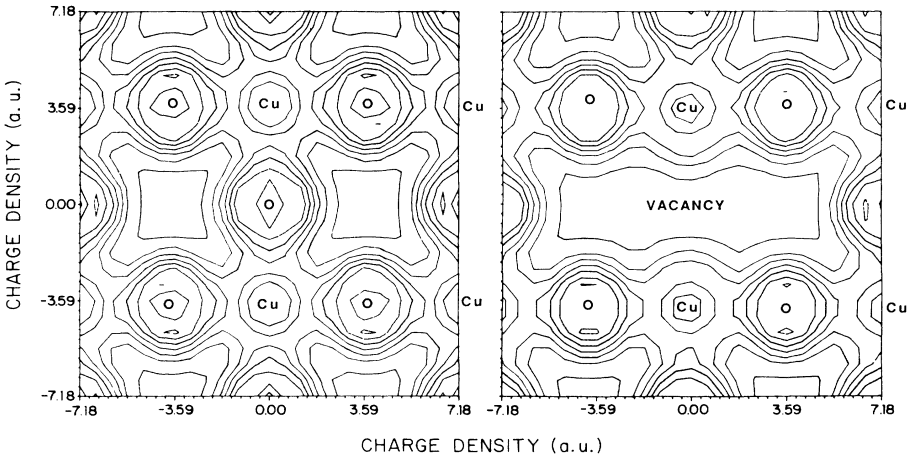

FIG. 2. Pseudofunction charge density for La_2CuO_{4-y}: left panel is for $y=0$ (without O vacancies) and right panel is for $y=0.25$ (with O vacancies).

Cu and O atoms are quite similar, whether or not the O vacancy is present. The removal of an O atom thus has only a minor effect on neighboring atoms. Since there is very little rearrangement of electronic charge, it is as if a neutral O atom is plucked out of the lattice. The effect of removing the O atom is screened within a short distance, as is usually the case in covalent materials. Since the screening length is so short, adjacent vacancies do not interact with one another, suggesting that the present model describes the neighborhood of a vacancy realistically, assuming that lattice relaxation effects can be neglected.

In real oxygen-deficient compounds, the O vacancies are arranged at random, so that superlattice band gaps are not actually formed. Nevertheless, we would expect the electronic density of states in real materials to reflect the changes that occur in exaggerated form in our ordered vacancy model. That is to say, we would expect randomly arranged O vacancies to induce deep minima rather than absolute band gaps in the electronic density of states. So we will continue to speak of vacancy-induced narrow bands though we realize that these bands have smeared-out rather than sharply defined band edges.

In view of the narrow bands in our 27-atom model, and the fact that Cu $3d$ atomic orbitals contribute strongly to the crystal wave functions near E_F, we would expect this model to support Hubbard-type antiferromagnetism. We hope to carry out spin-polarized band calculations at a later date. If the above ideas are correct, we expect to find a nonmagnetic ground state for the 28-atom structure and an antiferromagnetic ground state for the 27-atom structure.

Our conclusions should also apply to the lower symmetry orthorhombic phase because the crucial conduction bands under consideration are of the same width, about 2 eV, for both materials. In addition, spin-polarized band splitting, if it occurs in tetragonal La_2CuO_{4-y}, would occur more easily in the orthorhombic phase due to the preexistence of energy gaps in substantial portions of the reduced zone.

Emery[23] and Harrison[24] have concluded independently that pure La_2CuO_4 is an antiferromagnetic semiconductor at low temperature. Both use model Hamiltonians with electron-electron repulsion $U=6.0$ eV. In their models a large U is necessary because the bands at E_F are very broad. Our calculations suggest that the presence of O vacancies leads to a reduction in the effective widths of energy bands near E_F, requiring smaller (and possibly more realistic) values of U for antiferromagnetic behavior. In any event, the pure stoichiometric compound should not be an antiferromagnetic semiconductor in view of the broad energy band.

The relationship between band narrowing and O vacancies should also play an important role for $YBa_2Cu_3O_{7-y}$. Depending on the conditions under which O is removed, $YBa_2Cu_3O_{7-y}$ $(0.5 < y < 1)$ can be either a superconductor or a semiconductor. We believe this is related to whether O atoms are removed from the dimpled Cu—O planes or not. Semiconducting samples probably would have substantial O vacancies in those planes whereas superconducting samples would have less vacancies.

In summary, our calculations indicate that O vacancies tend to break up the broad conduction band in La_2CuO_4 into much narrower bands in the neighborhood of E_F, increasing the likelihood of antiferromagnetic behavior.

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