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Oxygen vacancies and antiferromagnetism in La_2CuO_4

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Self-consistent spin-polarized band-structure calculations have been carried out on stoichiometric La_2CuO_4 and two ordered oxygen-vacancy supercells corresponding to $La_2CuO_{3.75}$. Both the tetragonal and orthorhombic structures are considered. No stable antiferromagnetic moment is found and the presence of oxygen vacancies appears to further reduce any tendency to antiferromagnetic ordering. Ba and Sr doping are also shown to reduce antiferromagnetism.

A number of recent experiments[1-3] have found antiferromagnetic ordering in orthorhombic La_2CuO_{4-x} that is very sensitive to the degree of oxygen deficiency. The stoichiometric compound ($x=0$) appears to be nonmagnetic, but a small number of oxygen vacancies (0.01–0.03) leads to antiferromagnetism.[3] In view of the fact that the same compound, when doped with barium or strontium is a high-temperature superconductor, the occurrence of antiferromagnetism in the undoped compound lends support to the idea that superconductivity in these systems may be due to magnetic interactions,[4-6] rather than the conventional electron-phonon mechanism.

It is clearly of great interest to understand the origin and nature of this antiferromagnetic state. Leung, Wang, and Harmon[7] have performed spin-polarized local-density band-structure calculations on the related compound Sc_2CuO_4 and find that the calculated ground state is nonmagnetic. They conclude that some form of correlation beyond the local-density approximation is necessary to give a realistic description of the system. We have carried out similar calculations for the La_2CuO_4 system which basically confirm their results.

Kasowski, Hsu, and Herman[8] have proposed that the presence of the oxygen vacancies may alter the band structure sufficiently to favor antiferromagnetism. We have tested this proposal by carrying out super-cell calculations for two different arrangements of the oxygen vacancies and find that the calculated ground state is always nonmagnetic. Furthermore, while the stoichiometric compound shows some tendency towards antiferromagnetism, even this is destroyed in the presence of the O vacancy.

The calculations have been carried out using the linear muffin-tin-orbital (LMTO) method[9] within the local spin-density approximation.[10] The basis set included up to *f* orbitals on the La sites and up to *d* orbitals on all other sites. The La 5*p* and O 2*s* core states are treated as band states and allowed to relax self-consistently. At first, the linear tetrahedron method[11] was used to perform the Brillouin-zone summations; however, we found that this gave a small antiferromagnetic moment in the stoichiometric compound which reduced as the number of *k*-points was increased. On changing to a special *k*-point method with a small thermal broadening, the sensitivity to the number of *k* points was eliminated and no antiferromagnetism was found.

We have considered both tetragonal and orthorhombic structures, taking the lattice parameters from Jorgensen *et al.*[12] Antiferromagnetic calculations for the stoichiometric compound were carried out on a 14-atom one-face-centered orthorhombic unit cell both with and without the orthorhombic distortions and the rotation of the oxygen octahedra. The oxygen-vacancy calculations were carried out on two 28-atom unit cells, formally corresponding to $La_2CuO_{3.75}$. In the first case, the 7-atom tetragonal unit cell is doubled in the Cu—O plane and again in the perpendicular direction to give a simple orthorhombic unit cell. An oxygen atom in one of the Cu—O planes is then removed to create the vacancy. This structure then has two distinct Cu—O layers, one of which has O vacancies, the other being stoichiometric. The orthorhombic distortion of the unit cell is included in this calculation. The second vacancy structure is produced by doubling the tetragonal unit cell in both directions in the Cu—O plane, then removing an in-plane oxygen atom. For simplicity, the orthorhombic distortion is not included here, but this is not a serious error since the results for tetragonal and orthorhombic calculations on the stoichiometric compound are so similar. This second structure is the same as that considered by Kasowski *et al.*[8]

We first report results for the stoichiometric compound. We find that nonmagnetic ground states are favored over ferromagnetic and antiferromagnetic states in both the tetragonal and orthorhombic structures. Leung *et al.*[7] showed in their calculations on the related compound Sc_2CuO_4 that an antiferromagnetic state can be constrained in this case by using the magnetic moment to split a doubly degenerate band which lies at the Fermi surface and preferentially occupying only the lower of these two bands. We have performed a similar calculation by using an antiferromagnetic moment on the Cu atoms to split this degenerate band and then occupying only the lowest 53 bands at each *k* point for the 14-atom unit cell, thereby disregarding the fact that, since the bandwidth is larger than the antiferromagnetic splitting, the Fermi energy should really cross both bands. These bands are the planar Cu—O antibonding bands, so, in a crude way, this mimics the introduction of a large Hubbard *U* term on the Cu atoms which is expected to increase the splitting and narrow the width of the *d* bands. On iterating to self-consistency in this way, we find an antiferromagnetic moment of $0.145\mu_B$ on the copper atoms in the tetragonal structure, reducing to $0.139\mu_B$ when the orthorhombic distortion is included. Antiferromagnetism splits the doubly degenerate bands by 0.1 eV in both cases which is significantly smaller than the bandwidths of 0.46 eV and 0.42 eV, respectively. All of this agrees well with Leung *et al.*'s results[7] once the differences between lanthanum and scandium are taken into account.

One might expect that increasing the lattice constants would favor an antiferromagnetic state, since the dispersion of the bands decreases as the interatomic spacing increases and once this dispersion becomes comparable to the exchange splitting, antiferromagnetism would be stabilized. In fact, the bandwidth is almost independent of the lattice constant. At a 3% increase in lattice parameters, the system is still nonmagnetic, though a moment can be stabilized using the procedure described above. The moment increases by only 4% while both the splitting and the bandwidth are essentially unchanged, indicating that the experimentally observed antiferromagnetism cannot be explained in terms of a more or less uniform relaxation of the Cu—O planes in the presence of oxygen vacancies. The insensitivity of the bandwidth to lattice constant is due to the fact that changes in the ionicity of the system counteract the reduction in the overlap of the orbitals.

In the superconducting compound, where Ba or Sr is substituted on the La site, no antiferromagnetism has been observed. Since Ba and Sr have one less valence electron than La and the lanthanum bands lie far away from the Fermi energy, we can mimic this doping by changing the number of electrons in the unit cell. The highest T_c occurs around $La_{1.85}Ba_{0.15}CuO_4$, which we model by removing 0.3 electrons from the 14-atom unit cell. On performing another self-consistent spin-polarized calculation for this case, we find that an antiferromagnetic moment cannot be sustained, even when we constrain the occupation of the bands as described above. This indicates that only the states very close to the Fermi energy can support the antiferromagnetic splitting and that the magnetic ordering is destroyed when the Fermi energy is moved by a small amount.

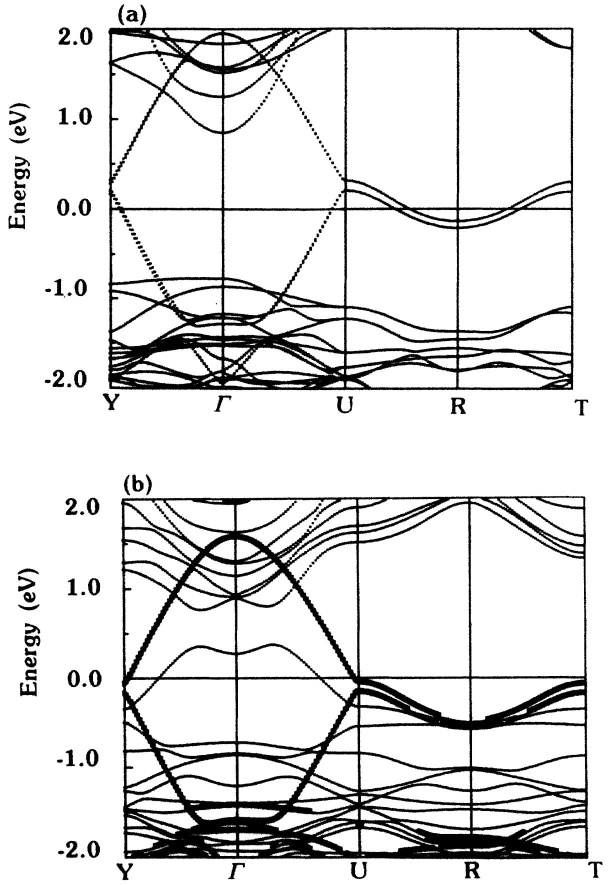

FIG. 1. Band structures of La_2CuO_{4-x} near the Fermi energy in the first vacancy structure. (a) $x=0$, no oxygen vacancies; (b) $x=0.25$, oxygen vacancies present. The Fermi energy is taken as the zero of energy in both cases.

We now turn to the first of the two vacancy calculations. This structure has two inequivalent Cu—O planes, only one of which has O vacancies. As in the stoichiometric compound, self-consistent spin-polarized calculations lead to a nonmagnetic ground state. When we use the procedure described above to try to stabilize an antiferromagnetic moment by occupying only the lowest bands at each k point, we find that the two planes behave very differently. The vacancy plane shows only a very small Cu moment ($0.004\mu_B$) while the stoichiometric layer retains a moment of $0.136\mu_B$, very similar to that found in the vacancy-free case. A comparison of Fig. 1(a) and Fig. 1(b) clearly indicates the effects of the vacancy. Figure 1(a) shows the band structure of the vacancy-free system in this 28-atom unit cell. The flattish Cu—O bands crossing the Fermi energy along the U-R-T directions are split by the antiferromagnetic moment which is stabilized by occupying only the lowest of the two bands. The splitting here is purely due to the antiferromagnetism. By looking at the character of the wave functions we can determine which bands reside on vacancy-copper-oxygen layer and which are related to the stoichiometric plane. The highlighted bands in Fig. 1(b) belong to the stoichiometric Cu—O layer. Here, once again, we see the antiferromagnetic splitting of the bands in the U-R-T direction and the more highly dispersive Cu—O bands along Y-Γ-U. We also see flatter, less dispersive bands which derive from the Cu—O layer with the vacancy. The bands on the vacancy-free layer are essentially identical to those of the stoichiometric system while the layer with the vacancy shows a narrowing of the Cu—O bands and a splitting at U and T which is caused not by an antiferromagnetic moment, since the vacancy layer is essentially nonmagnetic, but by the change in the potential produced by the O vacancy.

Another consequence of the vacancy is to produce an upward shift of the Fermi energy. This can be understood quite easily if we assume that the oxygen is present as an O^{2-} ion. Removing an oxygen atom will then leave two electrons which must be accommodated in some way, leading to the increase in the Fermi energy. We have seen that antiferromagnetism is destroyed by lowering the Fermi energy by Ba or Sr doping, and we expect the same thing to happen when the Fermi energy is raised, since we then have to occupy states which contribute predominantly up-spin density on the down-spin Cu atoms and down-spin density on the spin-up Cu sites, so reducing the moment. This correlates well with the observation that Fermi-surface nesting occurs for the stoichiometric compound where the antibonding Cu—O band is exactly half filled.[13] Moving the chemical potential then reduces the tendency of this nesting feature to produce antiferromagnetism. This is the main cause of the reduction in antiferromagnetism, but there are other effects which may play a greater or lesser role. First we note that the superexchange interaction between the Cu atoms on either side of the O vacancy will be affected, reducing the antiferromagnetic coupling between them, though correlation can still be maintained in this case through interactions with other neighboring sites. Second, the perturbation produced by the vacancy changes the character of the wave functions in the band crossing the Fermi energy along the *U-R-T* directions, lifting the degeneracy in the states near the Fermi energy. The response to an antiferromagnetic field will then be reduced since this degeneracy has already been lifted. Competing with this is the fact that the vacancy can make the Cu wave functions more localized, hence favoring the formation of a local magnetic moment. All of these effects are small, however, compared to the upward shift of the Fermi energy.

In the second vacancy calculation, all Cu—O layers are the same and one oxygen in eight is removed from the Cu—O plane. In this case, no stable antiferromagnetic moment was found, either with or without the constraint on the occupation of bands. The band structure of the stoichiometric compound is shown (without the antiferromagnetic splitting) in Fig. 2(a) and the vacancy calculation is presented in Fig. 2(b). This time, all the bands are strongly affected by the vacancy. The fourfold degeneracies at *a* and *b* are completely lifted, splitting the bands over a range of 0.7–0.9 eV, and the flattish Cu—O band crossing the Fermi energy in the *a*-Γ-*b* direction is strongly hybridized with the other more highly dispersive Cu—O bands in this direction. This flattish band is, in fact, related to the *U-R-T* bands in Fig. 1 and is folded back onto *a*-Γ-*b* in this second vacancy structure. It is also clear that once again the relative position of the Fermi energy has been raised on removing the oxygen atom.

The most noticeable thing about the band structure in Fig. 2(b) is how close the system is to being a semiconductor. The electron pocket around *b* is compensated by a hole pocket elsewhere in the Brillouin zone, but the overlap is clearly very small. In fact, the accuracy of the LMTO is not sufficient to say definitively whether there is a gap or not and a full potential method would be required to answer that question. However, the LMTO is clearly accurate enough to show that the inclusion of oxygen vacancies will tend to diminish the tendency towards antiferromagnetism, both because of the increase of the Fermi energy and the effect of the vacancy potential on the wave functions.

In their work, Kasowski *et al.*[8] find a very flat band near the Fermi energy in both the stoichiometric and vacancy calculations. This appears to pin the Fermi energy when the O atom is removed and they do not see a significant shift in its position. However, this flat band does not appear in either the published full potential linear augmented-plane-wave method (LAPW)[13] bands or the LMTO bands reported here, which closely resemble the LAPW bands near the Fermi energy. The narrow band which they highlight and propose as a possible source of antiferromagnetism is therefore absent.

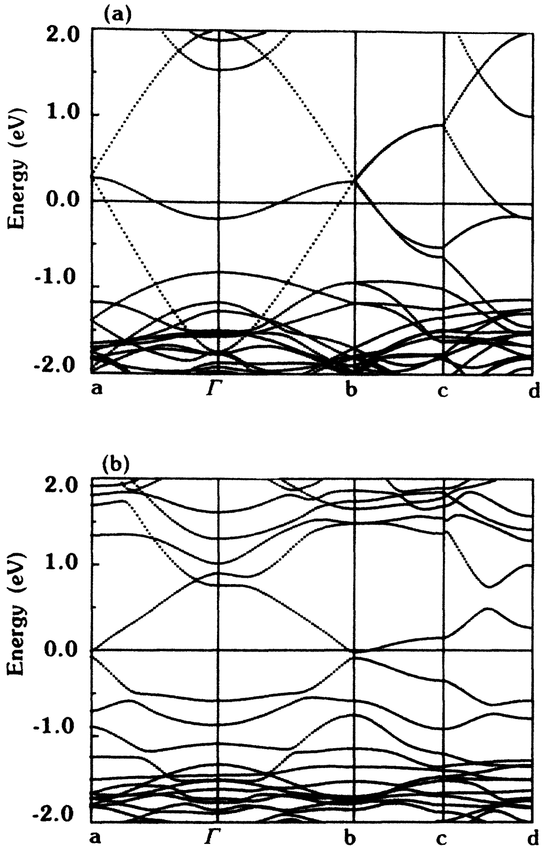

FIG. 2. Band structures of La_2CuO_{4-x} near the Fermi energy in the second vacancy structure. (a) $x=0$, no oxygen vacancies; (b) $x=0.25$, oxygen vacancies present. The Fermi energy is taken as the zero of energy in both cases. The k points are $a=(0.5, -0.5, 0.0)$, $\Gamma=(0,0,0)$, $b=(0.5, 0.5, 0.2863)$, $c=(0.5, 0.0, 0.2863)$, $d=(0.0, 0.0, 0.2863)$ in units of $(2\pi/a)$ where a is the lattice constant of the super cell.

In the calculations reported above, we have ignored the possible influence of relaxation around the vacancy site. Depending on the magnitude of this relaxation, there will certainly be quantitative changes to our results, but we do not believe that the qualitative result will be affected. If the relaxation were strong enough that two electrons were localized on the vacancy site, then the Fermi energy would not be raised and the bands would be less affected, but we do not believe this to be the case. We are therefore forced to the conclusion that oxygen vacancies will always tend to diminish antiferromagnetism. This is in apparent contradiction with experiment[3] which reports that antiferromagnetism increases as the number of O vacancies is increased from 0.0 to 0.03 per unit cell. However, the reported error in the determination of the number of O vacancies is 0.02, so we suggest that, rather than creating vacancies, excess oxygen is being removed from the system and that then the highest moment may actually occur for the stoichiometric compound. Excess oxygen would act rather like Ba doping, reducing the number of electrons in the Cu–O bands and inhibiting antiferromagnetic correlation. Since both excess oxygen and oxygen vacancies will reduce the magnetic interactions, we expect the moment to peak for the stoichiometric compound. The problem then becomes a more familiar one; in common with several other transition metal oxides, the local density approximation does not give an adequate description of the strong local correlations and some approximation beyond the local density approximation is needed to describe the observed antiferromagnetism. This is supported by recent quantum Monte Carlo simulations of an extended Hubbard model for two-dimensional Cu–O lattices[14] which show strong antiferromagnetic correlations using parameters consistent with first-principle calculations.

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