Band-theoretical study of magnetism in Sc_2CuO_4

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Self-consistent, spin-polarized calculations were performed for Sc_2CuO_4. Both ferromagnetic and antiferromagnetic ground states were investigated and found to be unstable. Magnetic form factors were calculated and are discussed in view of experiments on La_2CuO_4 and the applicability of band theory.

INTRODUCTION

The discovery of antiferromagnetism in slightly oxygen-deficient La_2CuO_{4-y} (Refs. 1–4) has added to the developing school of thought which is considering antiferromagnetic spin interactions rather than phonons as a possible mechanism for superconductivity in the new copper-oxide based high-T_c materials.[5] In most of these theories the starting point is a Hubbard-like Hamiltonian, with on-site Coulomb repulsion playing the key role. The difficulty in performing accurate analytical or numerical calculations for general versions of these model Hamiltonians has hindered a quantitative comparison with the growing amount of experimental information. Band-theoretical calculations have been criticized for such systems because of their inaccurate treatment of on-site Coulomb correlation. On the other hand, band-theoretical methods allow precise numerical calculations and have been very successful in the last ten years in the evaluation of the parameters governing conventional superconducting properties. Indeed, band-theoretical methods have recently been applied to the $La_{2-x}Sr_xCuO_4$ system to evaluate the electron-phonon coupling and the transition temperature, with results in reasonable agreement with experiment.[6] It is therefore of interest to further test the band theoretical approach by evaluating the magnetic properties. To this end we have used a first-principles linear combination of atomic orbitals (LCAO) method to study both the ferromagnetic and antiferromagnetic response of Sc_2CuO_4. The Sc compound was chosen for the majority of the calculations in this paper because of the fewer number of core electrons (compared to La) which greatly facilitated calculations using the LACO codes. As discussed below, the Sc and La potentials have a similar effect on the occupied band structure of these compounds, so that the conclusions we obtain with regard to the Cu-O interactions should be common to both materials.

METHOD

For the tight-binding or LCAO code used in these calculations the radial part of the atomic basis functions are represented by a series of Gaussian functions. The potential, charge, and spin densities are also expanded about atomic sites in a series of Gaussian functions.[7] We have used this method recently to successfully calculate the electronic structure and total energies of Si,[8] Nb and Mo,[9] and AlN.[10] In addition, we have tested the spin polarized version of the codes and obtained results in excellent agreement with calculations on Ni (Ref. 11) and Cr (Ref. 12). For the spin-dependent local-density approximation to the exchange correlation potential we have used the von Barth–Hedin form[13] as modified by Moruzzi *et al.*[14] Besides the core states, the atomic basis consisted of 4*s*, 4*p*, and 3*d* functions on Sc; 2*s*, 2*p* functions on O; and 4*s*, 4*p*, and 3*d* functions on Cu. The lattice constants as measured by neutron scattering for La_2CuO_4 were taken from Jorgenson *et al.*[15] With these lattice constants it was found that the lowest Sc 3*d* band remained unoccupied but dropped below the highest Cu-O antibonding band (at the *X* point in the tetragonal structure). This was the only significant difference with the band structure of La_2CuO_4. The lower Sc 3*d* band is related to the smaller ionic radius of the Sc atom compared to La. By decreasing the Sc-O distance along the axis perpendicular to the plane (this changed the lattice constant for the long axis from 25.045 to 24.000 a.u.) we found that the Sc-O interaction mimicked the La-O interaction. That is, the bottom Sc 3*d* band was raised so that the modified Sc_2CuO_4 bands closely resemble the La_2CuO_4 bands. The rest of the calculations on Sc_2CuO_4 were made with this modification of the lattice constants. The Cu-O in-plane separations were kept the same for both compounds.

RESULTS

The band structure for Sc_2CuO_4 in the tetragonal phase (one formula unit per cell) is shown in Fig. 1. The bands are very similar to those reported for La_2CuO_4.[16,17] The Fermi energy cuts a single band at the top of the Cu 3*d* and O 2*p* complex of 17 bands having a total width of about 10 eV. The Cu 3*d*-like character is spread throughout the bands in this energy range with the lowest band at the *X* point consisting of bonding states between the Cu $3d_{x^2-y^2}$ orbital and the nearest-neighbor, in-plane, O $2p_x$ and $2p_y$ orbitals. The corresponding antibonding band is at the top of the complex and is half occupied. The calculated Fermi surface is in good agreement with that reported by Xu *et al.*[18] which differs only slightly from that of Mattheiss.[17]

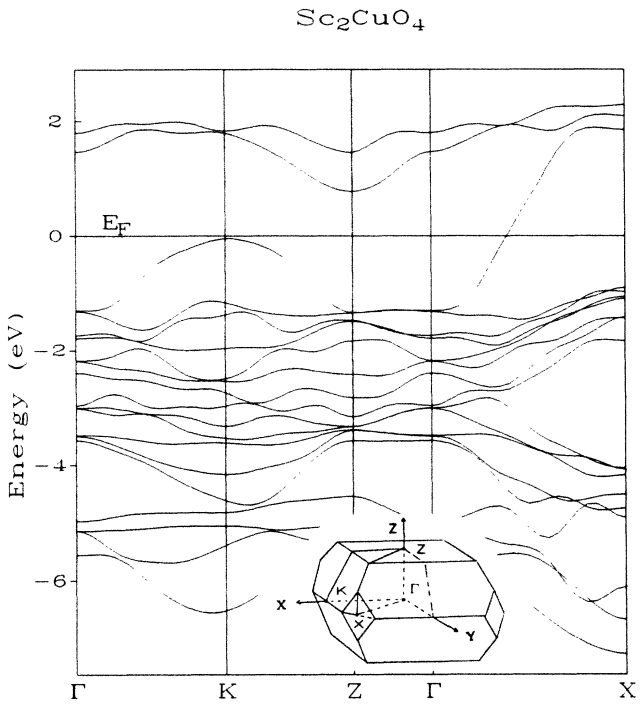

FIG. 1. The self-consistent band structure of Sc_2CuO_4 in the tetragonal phase.

An important quantity in the discussion of the magnetic properties is the generalized susceptibility

$$\chi(\mathbf{q})=\sum_{\mathbf{k}}\frac{f(\mathbf{k})[1-f(\mathbf{k}+\mathbf{q})]}{E(\mathbf{k}+\mathbf{q})-E(\mathbf{k})},$$

which is shown in Fig. 2 for $\mathbf{q}$ along the [110] direction. The wave vector corresponding to the observed antiferromagnetic ordering occurs in this direction at the zone boundary X point.[2] The calculated $\chi^0(q)$ for the partially occupied band is very similar to that reported for La_2CuO_4 by Xu *et al.*[18] The magnitude of $\chi^0(q=0)=\frac{1}{2}N(E_F)=5.6$ states/(Ry cell) is somewhat smaller than the 7.3 states/(Ry cell) of Xu *et al.* for La_2CuO_4 and our own value of 6 states/(Ry cell) for La_2CuO_4. The value of $\chi^0(q=X)$ is 11.7 states/(Ry cell) or more than double the $\chi^0(q=0)$ value.

We first consider the ferromagnetic response corresponding to $q=0$. The unenhanced Pauli susceptibility is $\mu_B^2N(E_F)=2.6\times10^{-5}$ cm^3/mol. To calculate the enhancement we performed self-consistent spin-polarized calculations with an applied field created by shifting the spin-up (down) bands by -2 ($+2$) mRy. These calculations were made for Sc_2CuO_4 in the tetragonal structure with 20 k points sampled in the irreducible $\frac{1}{16}$th of the Brillouin zone.[19] The band splitting, $\Delta E(k)=I(k)$ m, was found to be nearly uniform near the Fermi level and gave an average value for I of about 0.030 Ry cell. Thus the Stoner enhancement $S=[1-IN(E_F)/2]^{-1}\sim1.2$ is not very large, and indicates the ferromagnetic ground state is not stable. Indeed, whenever we released the applied field during our calculations the moment quickly decayed to zero in a few iterations. It is difficult to extract an experimental value for the Pauli susceptibility of

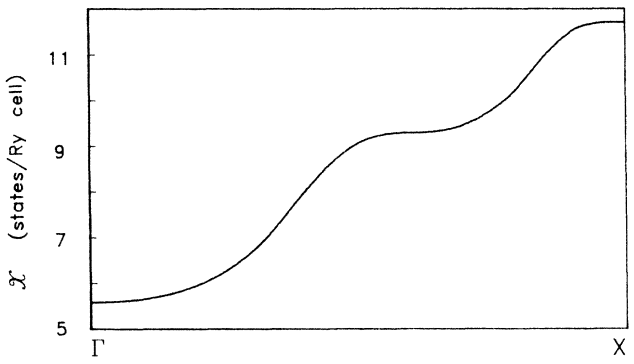

FIG. 2. The generalized susceptibility for Sc_2CuO_4 along the [110] direction. Contributions only from band 17, which cuts the Fermi level, are included.

La_2CuO_4 since many samples have some oxygen vacancies and order antiferromagnetically with T_N as high as 290 K.[1] Since the measured susceptibility above T_N is not Curie-Weiss–like and seems to be similar for samples with various values of T_N, there may be some justification in making a comparison between our calculated value and the high temperature susceptibility. The measured χ at 500 K is about 5×10^{-5} cm^3/mol and rises gradually to $\sim7\times10^{-5}$ cm^3/mol at 750 K.[1] This is a factor of 2 larger than our calculated $\chi_p=3.0\times10^{-5}$ cm^3/mol. (The theoretical temperature dependence is small and amounts to less than 10% at 600 K.)

A potentially more informative measure of the ferromagnetic response would be the induced magnetic form factor as measured by neutron scattering. This is *not the same* as the form factor measured for the antiferromagnetic ordered state, but rather is a measure of the induced ferromagnetic spin density arising in response to an applied field. The applied field shifts the spin-up and spin-down bands only slightly, and the repopulation of states near the Fermi energy results in an induced spin density corresponding to the charge density for states on the Fermi surface:

$$S(\mathbf{r})=2\mu_B^2\oint_{E=E_F}\frac{ds}{|\nabla_k E|}|\psi_k(\mathbf{r})|^2.$$

As discussed above, the states at E_F are predominantly an antibonding combination of $d_{x^2-y^2}$ orbitals on Cu with p_x and p_y orbitals on O. This means that unlike the antiferromagnetic case described below, each in-plane oxygen site has a fairly large moment (55% that of the Cu moment) and contributes substantially to the form factor. If band theory was incorrect and the moments were isolated on the Cu sites, the measured form factor would resemble an ionic Cu form factor. The calculated form factor is shown in Fig. 3 and differs from the Cu ionic form factor for reflections which involve destructive interference from the oxygen moment. Since the Fermi energy lies well above the center of the Cu d and O p bands and below the Sc of La d bands we do not expect a significant van Vleck orbital contribution to the form factor. Likewise the spin-orbit coupling for Cu is not strong enough to add more than a few percent of or-

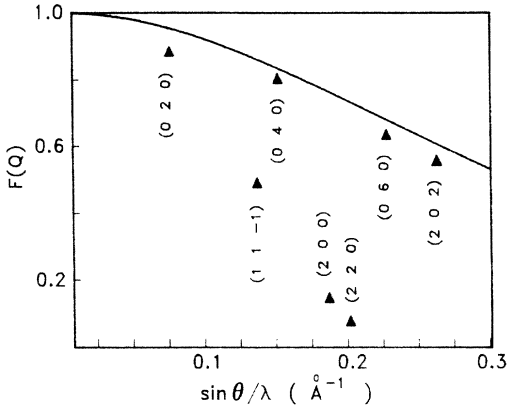

FIG. 3. The induced magnetic form factor normalized to the total moment. The reflections are labeled with respect to the orthorhombic structure and $(\sin\theta)/\lambda$ values are for the La_2CuO_4 lattice constants (see Ref. 2). The ionic Cu^{2+} form factor is shown for comparison.

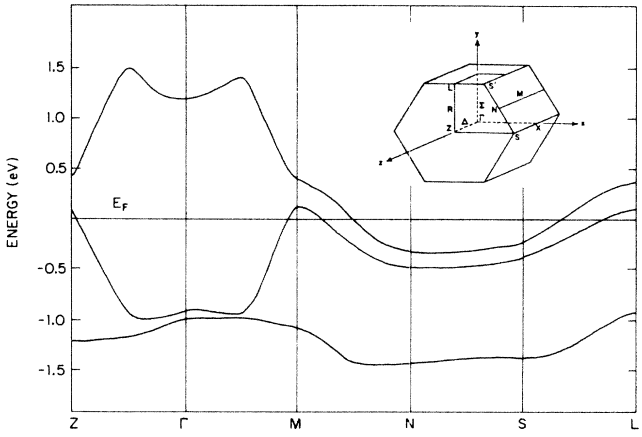

FIG. 4. The bands near the Fermi level for Sc_2CuO_4 in the orthorhombic structure with an applied staggered field corresponding to $0.5\mu_B$ per Cu site. The splitting along *MNSL* on the zone boundary is entirely due to the antiferromagnetic field.

bital contributions. Thus, the calculated from factor in Fig. 3 provides a clear theoretical prediction based on the itinerant model and it will be interesting to compare with forthcoming experiments.[20]

We now consider the antiferromagnetic ordering. One might expect pure La_2CuO_4 to be very near an instability since less than 1% oxygen vacancies are required to stabilize the antiferromagnetic ground state. Within the itinerant model this state would be predicted to be stable if $I(q)\chi^0(q) > 1.0$. Assuming for the moment that $I(q=X)=I(q=0)=I$ we find $I\chi^0(q=X)=0.3$, which is far from a magnetic instability. Before accepting this conclusion there are several factors to consider such as the magnitudes of $I(q=X)$ and $\chi^0(q=X)$ as well as the effect of the orthorhombic distortion.

It is possible to make an estimate of $I(q=X)$. First we consider the bands for the observed orthorhombic structure so that there are now two formula units per primative unit cell. As pointed out by Kasowski *et al.*,[21] this distortion leaves the two Cu atoms in the cell equivalent and results in a set of degenerate bands on the surface of the new Brillouin zone. This would indicate that La_2CuO_4 must remain metallic, contrary to experiments.[1,22] Antiferromagnetic ordering does split these degenerate bands (see Fig. 4) and, by applying a staggered field at the Cu sites and calculating the splitting and moment per Cu, we obtain an estimate for $I(q=X)$ of 0.022 Ry cell. This gives $I\chi^0=0.2$ at $q=X$ which is smaller than the previous estimate using the value of I at $q=0$. The main reason I is smaller at $q=X$ is that there is now no moment allowed (by symmetry) on the in-plane oxygen, so that states at E_F which have substantial in-plane oxygen character in their wave functions are missing this contribution (from an oxygen moment) to the splitting.

The magnitude of $\chi^0(q)$ is dominated by the states near the Fermi level separated by wave vector q. If there is a nesting feature in the Fermi surface so that two planar sections are exactly separated by wave vector Q, a logarithmic singularity occurs in $\chi^0(q)$ at Q and the system is unstable. We do not find exact nesting; however it is fair to ask what would happen (i.e., what ground state properties would result) if $\chi^0(q=X)$ were much larger. We have been able to answer this question semiquantitatively by performing self-consistent, spin-polarized calculations for the room-temperature orthorhombic structure (this structure results from a distortion of the tetragonal phase corresponding to the same wave vector, $q=X$, that describes the magnetic ordering). We effectively raise $\chi^0(q=X)$ by including in our sampling mesh k points along the zone boundary where in the absence of a moment bands 33 and 34, which cut the Fermi level, are degenerate. For the k points on the zone boundary we occupy the 33 band but not the 34 which is a way placing the Fermi level in the middle of the antiferromagnetically split bands. This is of course a device to maximize the tendency for the antiferromagnetic state. If the dispersion of these bands were smaller than the splitting, the Fermi level would fall in the gap naturally; however, the dispersion along the zone boundary shown in Fig. 4 for bands 33 and 34 is 0.7 eV while the splitting for any reasonable moment (without an applied field) is less than 0.1 eV. The dispersion is smaller for La_2CuO_4 (0.43 eV) and is reduced 10% further by including the full low temperature orthorhombic distortion, but is still too large relative to the splitting to give a semiconducting gap. Nevertheless, with a fictitious gap forced by constraining the occupation for the zone boundary states, the calculations did proceed to a self-consistent antiferromagnetic ground state which is quite informative.

The calculated moment on the Cu sites was $0.136\mu_B$ with each out-of-plane oxygen site above and below the Cu site having a moment of about 10% of that of Cu and aligned in the direction opposite the copper moment. The average splitting of bands 33 and 34 along *MNSL* on the Brillouin zone surface was 0.04 eV. We also added staggered fields (corresponding to a moment per Cu of up to $0.8\mu_B$) to see if the system might sustain a larger self-consistent moment, but found the moment per Cu to level off at about $0.16\mu_B$ as long as only physi-

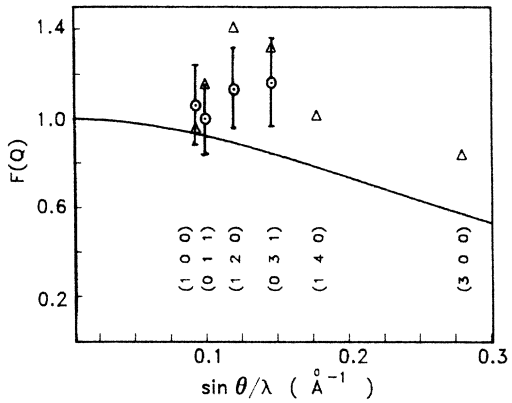

FIG. 5. The magnetic form factor for the antiferromagnetic state as described in the text. The values have been normalized to $1\mu_B$ on the Cu site. The values of $(\sin\theta)/\lambda$ correspond to the lattice constants of La_2CuO_4 in the orthorhombic structure (see Refs. 2 and 15). The experimental data is from Ref. 2 and has been normalized to 1.0 for the second reflection, with error bars from Ref. 24. The line is the Cu^{2+} ionic form factor.

cally reasonable fields were used so that bands 33 and 34 were the only ones involved. In a simple system one might expect a saturation of $1\mu_B$/atom, but here the bands at E_F consist of states with a large amount of wave function character on the in-plane oxygen sites which have an equal amount of spin-up and spin-down density. We calculated the magnetic form factor for the self-consistent ground state and find that the small out-of-plane oxygen contribution interferes with the Cu contribution so that the calculated form factor (shown in Fig. 5) differs noticeably from a Cu ionic form factor. The form factor has been measured experimentally for only four reflections with fairly large error bars (also shown in Fig. 5) and has a shape similar to the theory which suggests a moment on the out-of-plane oxygen may be present.[2] The most important aspect of the experimental measurement is the magnitude which would indicate a moment per Cu of about $0.4\mu_B$. This is well out of the range that can be reached by an itinerant model, and is also far from the $1\mu_B$ one might expect for a localized model.

Calculations similar to those described above were made for the antiferromagnetic state with an 8% larger and an 8% smaller planar lattice area (we assume the effect of pressure on the states near E_F will be dominated by the change of the in-plane lattice constant). Surprisingly the increase in I with pressure was enough to overcome the decrease in χ and a small ($\sim$5%) increase in the antiferromagnetic response in predicted with pressure.

CONCLUSIONS

Although our calculations were made for Sc_2CuO_4, the copper-oxygen geometry was the same as for La_2CuO_4 and the occupied band structure of the two compounds are nearly identical. We therefore expect the calculated physical properties of the two materials to be similar. The spin-polarized calculations indicated little tendency toward ferromagnetic or antiferromagnetic ordering. This is somewhat surprising since less than 1% oxygen vacancies are needed to stabilize the antiferromagnetic state in La_2CuO_4. More significant is the observed semiconducting behavior of pure La_2CuO_4 at low temperatures,[1] while band theory has no energy gap at the Fermi level. A somewhat similar situation occurs in other transition metal oxides such as NiO, FeO, and CoO which are frequently described as Mott insulators. These compounds, however, have the center of the oxygen bands well below the transition metal d bands and it is the d bands which occur at the Fermi level. The antiferromagnetic ground states of these compounds are obtained by band theory, but for FeO and CoO the observed semiconducting state is not obtained.[23] The bands for La_2CuO_4 are quite different in the sense that the center of the oxygen $2p$ and copper $3d$ bands is the same so the width of the band complex ($\sim$9 eV) is determined essentially by the bonding and antibonding states from the Cu-O $pd\sigma$ interaction. This band width means the usual criterion for Mott insulators $W/U \ll 1$ is not well satisfied or is in need of modification for this type of bonding. We suspect the local density functional (LDF) theory is not adequate here and some on-site or intersite (Cu-O) correlation beyond that of the LDF approximation is required for further progress.[23]

If some symmetry breaking in the charge distribution arises so that local moments (ordered or not) can appear on the copper site then the induced magnetic form factor should look quite different than what we have predicted. On the other hand if localized states are present, one might have expected the measured moment in the antiferromagnetic state to be closer to $1\mu_B$/Cu rather than the estimated $0.4\mu_B$.[2] We are presently incorporating a Hubbard like U into a tight-binding Green's function formalism to see if better quantitative agreement with experiment might be obtained.

Note added in proof. We have subsequently calculated both the Van Vleck and diamagnetic susceptibility and find $\chi^{\parallel}_{VV} \sim 4\times10^{-5}$ emu/mole, $\chi^{\perp}_{VV} \sim 1.5\times10^{-5}$ emu/mole, and $\chi_D = -11\times10^{-5}$ emu/mole; so that the total susceptibility within a standard band-theoretical treatment is negative, which we believe is a further indication of strong correlation effects and the need to go beyond band theory.

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