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Spin fluctuations and covalence in the half-filled narrow-band Hubbard model

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We calculate the spin density within the widely accepted model for the insulating parents (La_2CuO_4 and $YBa_2Cu_3O_6$) of the superconducting cuprates, namely, the half-filled narrow-one-band Hubbard model as mapped from the three-band model for the CuO_2 planes. The result, which includes quantum spin fluctuations and covalence simultaneously, disagrees strongly with neutron-diffraction results. Possible remedies are discussed. A reinterpretation of the neutron data on these insulators gives considerable, but insufficient, improvement.

Over the past several years, extensive literature has developed a picture of the electronic structure of the high-T_c superconducting oxides that is widely believed to provide satisfactory understanding, at least for the insulating "parents," La_2CuO_4 and $YBa_2Cu_3O_6$.[1-3] On the contrary, the present work demonstrates that neutron-diffraction results disagree sharply with this picture in even the simplest case, the insulating ground state. We discuss some possible ways to overcome the difficulty.

The most common picture[1-3] of these materials is that they are antiferromagnetic (AF) Mott insulators. The electrons that give rise to the low-lying excitations are localized around the Cu^{2+} ions, the site spins (spin $\frac{1}{2}$) are governed predominantly by the nearest-neighbor Heisenberg model, the corresponding orbitals being Cu $3d$ states covalently mixed with the nearby oxygen p states. Furthermore, the calculation of the ordered AF spin in the Heisenberg-model ground state is also generally agreed upon.[4-6] The existence of a problem with this picture *vis-à-vis* experimental results was recently pointed out.[7] Namely, the ordered moment at low temperature as found by magnetic neutron-Bragg-scattering experiments,[8-11] which is widely accepted,[1,2,12] agrees closely with theory[4-6] based on the Heisenberg model. This theory gives a large reduction (about 40%) from the nominal $1\mu_B$, due to zero-point spin fluctuations. *However,* this agreement is misleading because it leaves no room for the large additional reduction expected from the covalence.[7,13] The fact that such a problem exists is made more difficult to understand by the fact that many other properties of these materials are well explained by the Heisenberg model.[1-3] Our claim that such a difficulty exists was strengthened by recent neutron-diffraction studies of the closely related material La_2NiO_4, which indeed found very large covalent effects.[14]

Using the same data and essentially the same theory, Tranquada *et al.* concluded that covalent contributions to the ordered moment (in $YBa_2Cu_3O_6$) are negligible.[8] Here, we show that present theory based on Hubbard-type models implies the existence of a *very large* covalent contribution to the ordered moment.[15]

We noted[7] a possible solution to the above problem that involved an unorthodox idea[16] concerning the relation between the order parameters m and m_0 in the broken- and unbroken-symmetry ground states of the spin Hamiltonian, and this remains viable.[17] Here we look in another direction, partially motivated by the fact that previous work treated spin fluctuations[4-6] and covalence[13] *separately,* whereas the two should of course be treated together. We calculate the spin density, which determines the neutron-Bragg-scattering cross section, within the single-band Hubbard model with the band half filled and narrow. As far as we know, this is the first such calculation (although it is related to a recent simulation,[18] as discussed below).

We find a covalence contribution in $O(t^2/U^2)$, t and U being the usual Hubbard-model parameters. This, which we call d-d covalence,[19] is different from the usual d-p covalence of Hubbard and Marshall[13] (HM). We also incorporate the d-p covalence by choosing the Wannier function that underlies the one-band Hubbard model in the spirit of the HM approach, namely a Cu d orbital of the appropriate symmetry mixed with neighboring oxygen p orbitals. This is also in the spirit of the mapping of the well-known three-band model on to the one-band case.[20] We find that both types of covalence introduce a modification of the ordered moment; on using common values of the parameters in the three-band model, we find the modification to be a large additional reduction to that from spin fluctuations, as we had expected.[7] In other words, given the commonly used reduction from spin fluctuations,[4-6] *our calculation produces an ordered moment that is much smaller than the one extracted from the neutron experiments.*

We also find that the d-p covalence dominates the large covalent moment reduction (it is of the same order of magnitude found[14] in La_2NiO_4), the d-d covalence being negligible compared to the $\approx 50\%$ effects we are concerned with. This has the consequence that the large physical effects come from a relatively simple theory (the ground state to *zero* order in t/U). The rather more complicated perturbation calculation described below is needed only for the negative, but important, conclusion that the d-d covalence is negligible. Finally, we point out that the interpretation of the neutron-Bragg-peak intensities, used by all the groups to come up with a value of the ordered moment, is not optimum, given the available information; and we give an alternate procedure based on the result obtained here. This interpretation gives a much more reasonable picture, but, unfortunately, a serious problem remains. Other possibilities for solving this problem are mentioned.

The Hubbard Hamiltonian is

$$H=\sum_{ij} t_{ij}a_{i\sigma}^{\dagger}a_{j\sigma}+U\sum_{i} n_{i\uparrow}n_{i\downarrow}\,, \qquad (1)$$

where $a_{i\sigma}^{\dagger}$ creates a fermion in the (one-particle) state $w_{i\sigma}=w_i(\mathbf{r})\alpha_\sigma$ and $n_{i\sigma}=a_{i\sigma}^{\dagger}a_{i\sigma}$. $w_i(\mathbf{r})=w(\mathbf{r}-\mathbf{R}_i)$ is the Wannier function at site $\mathbf{R}_i$ and α_σ is the spin state $(\sigma=\pm 1)$. The w_i form an orthonormal set, they are real and have the site symmetry of the lattice considered; we assume the usual condition, $t_{ij}=t=t^*$ when i and j are nearest neighbors, zero otherwise; and $U>0$. We take the external field to be zero, except insofar as a staggered field is understood for purposes of spontaneous symmetry breaking.

We seek the expectation value of the spin density (Fourier transform),

$$s(q)=\frac{1}{2}\sum_{ij\sigma} f_{ij}(q)\sigma a_{i\sigma}^{\dagger}a_{j\sigma}\,, \qquad (2)$$

in the ground state of (1). Here

$$f_{ij}(q)=\int \exp(i\mathbf{q}\cdot\mathbf{r})w_i(r)w_j(r)d^3r\,.$$

This approach differs slightly from (and is simpler than) that of Ref. 7, where we calculated $\langle s(q)s(-q)\rangle$. For the broken-symmetry state we expect $\langle s(q)s(-q)\rangle=|\langle s(q)\rangle|^2$ in the thermodynamic limit, for $\mathbf{q}$ corresponding to a Bragg peak (see Ref. 16 for discussion).

Hirsch and Tang[18] calculated

$$S(q)=(4/N)\sum \exp[i\mathbf{q}\cdot(\mathbf{R}_i-\mathbf{R}_j)]\langle S_i^z S_j^z\rangle\,,$$

with $S_i^z=\frac{1}{2}(n_{i\uparrow}-n_{i\downarrow})$. Writing (2) as $s(q)=s_D(q)+s_{0D}(q)$, s_D containing only the terms with $i=j$, one sees that $\langle s_D(q)s_D(-q)\rangle=N|f_w(q)|^2S(q)$, where

$$f_w(q)=\int \exp(i\mathbf{q}\cdot\mathbf{r})w(r)^2d^3r\,. \qquad (3)$$

Thus we are calculating the same thing, aside from the factor $|f_w(q)|^2$, provided s_{0D} is neglected, and we use the relation $m/m_0=\sqrt{3}$ assumed[16] in Ref. 18. It turns out[21] that for the antiferromagnetic Bragg peaks $(q=q_{\mathrm{AF}})$, s_{0D} does not contribute (although it will for ferromagnetic Bragg peaks, which occur on application of a uniform field; and s_{0D} will contribute to diffuse scattering). Besides these in-principle relationships between our work and theirs, we also note that for the large U of interest, their simulation has large numerical uncertainty.[18] This suffices to motivate the present calculation; the unsatisfactory situation in the literature discussed above makes the calculation even more desirable.

The treatment of (1) when the hopping term is small is well known.[22] The low-lying energy eigenvalues are those of the spin Hamiltonian[22]

$$H_s=\sum J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j+O(t^4/U^3)\,, \qquad (4)$$

where $\mathbf{S}_i$ is the spin at site i, and $J_{ij}=2t_{ij}^2/U$ is the exchange parameter for the Heisenberg Hamiltonian. We calculated the ground-state expectation of (2) to $O(t^2/U^2)$; the contributions to the Bragg peaks are[21]

$$\langle s(q)\rangle=mf_w(q)[1-2Z\gamma(t/U)^2]F(q)\,. \qquad (5)$$

Here $m=\langle S_n^z\rangle_{sp}$, the average in the (broken-symmetry) ground state of (4), $F(q)=\sum\exp[i(q-q_{\mathrm{AF}})\cdot R_j]$ is the structure factor that gives Bragg peaks at the antiferromagnetic wave vectors q_{AF}, Z is the number of nearest neighbors, and $\gamma=\frac{1}{4}-3\langle\mathbf{S}_n\cdot\mathbf{S}_m\rangle_{sp}$, where n,m are nearest neighbors.

As discussed above, m will be reduced from its mean-field value of $\frac{1}{2}$ due to zero-point spin fluctuations. The additional reduction in $\langle s(q)\rangle$ seen in (5), of $O(t^2)$ and q independent, can be understood physically through the (unrestricted) Hartree-Fock approximation to the ground state of (1): Taking the occupied orbitals for the A sites to have spin up, with the B sites down, and allowing the spatial part of each state to be a linear combination of the $w_i(r)$,[23] we recover (5) provided m and γ have their mean-field values, $\frac{1}{2}$ and 1. To the order of the calculation, an A-site state, e.g., is $[w_i-(t/U)\sum w_j]\alpha$, the sum going over nearest neighbors. Thus the up (down) electron spreads out onto the neighboring down (up) sites, thereby lowering the ordered moment. Although this reduction is not due to the same covalence effect discussed previously,[13,14] which involves interplay between paramagnetic and diamagnetic ions, the effect here is very similar. This plus an effect contained in $f_w(q)$ depending on d-d overlap [see Eq. (7)], we call d-d covalence [Hirsch and Tang[18] call the effect excluding $f_w(q)$ charge fluctuations].

For (5) to be correct to $O(t^2)$ one must keep the terms of $O(t^4)$ in (4). We write $m=m_{\mathrm{Heis}}+\delta m=m_{\mathrm{Heis}}(1+\xi t^2/U^2+\cdots)$. Thus[24]

$$\langle s(q)\rangle=m_{\mathrm{Heis}}f_w(q)[1-(2Z\gamma-\xi)(t/U)^2]F(q)\,. \qquad (5')$$

From the known ground-state energy[4,5] we get $\gamma=1.26$. To estimate ξ we follow Takahashi[22] and treat the spin Hamiltonian through $O(t^4/U^2)$ in the spin-wave approximation (SWA). We find $\xi=4.23$. Since both the energy and the order parameter are given very well in the SWA,[4,5] we expect this to be a reasonable estimate.

For $t/U\leq\frac{1}{8}$ (5′) gives the term in square brackets very close to ($<5\%$ above) the Hartree-Fock value $1-8t^2/U^2$. This is consistent with Hirsch and Tang's result that m is close to what they called HF×SW.[18] In fact, taking $m/m_0=\sqrt{3}$ as they do, our result suggests that theirs is somewhat low for large U (see the inset of Fig. 3 in Ref. 18).

To compare our result with neutron experiments we need explicit Wannier functions w_i. It is therefore convenient to work in terms of unit-cell type of localized functions $u(r-R_i)$ which are not in general orthogonal. This allows one to use explicit Cu and O wave functions (which are ordinarily not orthogonal at different sites). We assume $u(r)$ has the symmetry of $w(r)$. As long as the overlap integral Δ between neighboring u functions is small, our perturbation theory remains justified. For bipartite lattices one finds[21] to $O(\Delta^2)$

$$f_w(q_{\mathrm{AF}})=f_u(q_{\mathrm{AF}})(1+Z\Delta^2/2)\,, \qquad (6)$$

where $f_u(q)$ is the Fourier transform of $u(r)^2$. To summarize, we have

$$\langle s(q)\rangle=m_{\mathrm{Heis}}f_u(q)[1+Z\Delta^2/2-(2Z\gamma-\xi)(t/U)^2]F(q)\,. \qquad (7)$$

Hubbard and Marshall considered paramagnetic cations involving unfilled $3d$ shells surrounded by diamagnetic anions (O^{2-} or F^-); the interaction between the magnetic ions occurs via the intervening anions, direct cation-cation overlap being considered negligible. Thus they chose the u function associated with a cation as

$$u(r)=C\left[d(r)-A\sum p_j(r)\right], \tag{8}$$

the sum going over the nearest-neighbor-anion p states appropriate to the point symmetry of the magnetically active cation d state (u, d, and p_j are normalized). For simplicity we discuss this for CuO_2 planes; then there is only one active $3d$ orbital. Following HM,[13] we first assume small A (weak covalence) and neglect overlap between anion orbitals. We find

$$f_u(q_{AF})=f_d(q_{AF})(1-Z_{ca}A^2) \\ -2A\sum_j [f_{dp_j}(q_{AF})-f_{dp_j}(0)f_d(q_{AF})], \tag{9}$$

where $Z_{ca}=4$ (number of anion neighbors of a cation), $f_d(q)$ and $f_{dp}(q)$ being the Fourier transforms of $d(r)^2$ and $d(r)p(r)$, respectively. Due to the AF order, the contributions from the $p_j(r)^2$ cancel at $q=q_{AF}$.[13] In fact, if we replace the square-bracketed factor in (7) by 1, and take the mean-field value of m_{Heis}, we obtain HM's theory. Further, neglect of the correction terms in the square-bracketed factor *is correct* in the following context: From (8) we see that for small A the nearest-neighbor u-u overlap, $\Delta=O(A^2)$, and therefore t is also $O(A^2)$; so these correction terms are $O(A^4)$, whereas those *kept* are $O(A^2)$. HM refer to $1-Z_{ca}A^2$ in Eq. (9) as the effective moment per magnetic ion (in units of $g\mu_B$) seen in Bragg scattering, with the second term giving a change in *shape* from the usual $3d$ form factor, $f_d(q)$. From (7) and (9) we see that in the proper generalization of weak covalence theory[13] to include spin fluctuations, one is to identify

$$g\mu_B m_{Heis}(1-Z_{ca}A^2)=M_{ord} \tag{10}$$

as the ordered AF moment or effective moment for Bragg scattering [note that the second term on the right-hand side of (9) vanishes at $q_{AF}=0$]. This definition is sensible physically: *The integral of the spin density* $s(\mathbf{r})$, whose Fourier transform is given by (7) with (9), *over the Wigner-Seitz cell surrounding an up-spin Cu* [which is a nodal surface of $s(\mathbf{r})$], *is* $M_{ord}/g\mu_B$, as can be shown.[21] Allowing for stronger covalence, where $Z_{ca}A^2$ is not $\ll 1$, but where the correction terms in the square brackets of Eq. (7) are $\ll 1$ (of interest, as seen below) the ordered AF moment is, within this one-band model

$$M_{ord}=g\mu_B m_{Heis}[1+Z_{ca}A^2/(1-2Z_{ca}AS)]^{-1}. \tag{10'}$$

Neglect of the corrections in the square brackets in Eq. (7) leads directly to the problem discussed earlier.[7] Namely, M_{ord} found experimentally (in units of μ_B) is very close to the theoretical value,[4,5] 0.64 ± 7%, of gm_{Heis} (with[25] $g=2.2$), whereas the covalent reduction $\approx Z_{ca}A^2$ is expected to be large. (A statistical factor was included in the error estimate.) We now argue that for parameter values thought to be appropriate for the cuprates, $Z_{ca}A^2$ *is* large; also that the corrections in the square brackets of Eq. (7) are small.

For the CuO_2 planes $d(r)$ is the "x^2-y^2" e_g state;[1] neglecting O-O overlap, (8) gives, to lowest order, $\Delta=2AS-A^2$, where $S=\int d(r)p(r)\,d^3r>0$. To estimate A we use the result[26] that a hole in the insulating ground state of the three-band model has 80% Cu, 20% O character, referring, of course, to Wannier functions w_j for the Cu and O sites. Thus if we write our unit-cell function $u=\bar{C}(w_{Cu}-\bar{A}\sum_i w_{Oi})$, then $\bar{C}^2=0.8$, and thus $\bar{A}=0.25$. Rewriting u in terms of the nonorthogonal orbitals $d(r)$ and $p_i(r)$ we find $A=\bar{A}+S$. We estimate $S\approx0.1$ to 0.2 (e.g., from the theory for the Ni compound,[14] $S=0.17$ there). Thus we obtain $A=0.35$ to 0.45; the uncertainty in this for given S is $\approx 10\%$, namely, that quoted[26] for the three-band-model parameters. Interestingly, the value 0.35 of A is just that found[14] for La_2NiO_4. Of the various estimates of A and S discussed, the smallest covalent reduction occurs for $A=0.35 \pm 10\%$, $S=0.1$; this gives a value for the square bracket in (10′) of ≈ 0.6, with corresponding uncertainty $\approx \pm 20\%$, a large covalent reduction indeed.

With the range of A and S values just mentioned, $Z\Delta^2/2$ [in (7)] ranges from 0.1% to 2.5%, much too small to allow solution of this problem. The other term, $-(2Z\gamma-\xi)(t/U)^2$, is $\approx 3\%$, as found using the value[26] $t/U=0.43/5.4$; furthermore, it tends to cancel the Δ^2 term. So it is unlikely that these correction terms (the d-d covalence) will help significantly.

Apparent possibilities for solving this problem[7] are (a) m/m_0 is (appreciably) greater than $\sqrt{3}$,[7,16,17] and (b) the mapping of the three-band model to the one-band model in this half-filled case fails.

We conclude with a discussion of another possibility, which involves the interpretation of the neutron-intensity measurements. Previous results[8–11] were obtained as follows. $g\mu_B\langle s(q_{AF})\rangle$ was measured and was interpreted as $M_{ord}f(q_{AF})$, where $f(q)$ is "the magnetic form factor of a Cu" normalized to 1 at $q=0$. This is consistent with the HM theory [(7), (9), and (10) with small A] provided $f(q_{AF})=f_u(q_{AF})/(1-Z_{ca}A^2)$. Further, the experimentalists[8] understand correctly that the ordered moment can be reduced from the free-ion value by zero-point fluctuations *and* covalence. Since there has been no independent determination of $f(q)$, they[8,10] chose $f(q)$ as that of the essentially isostructural material K_2CuF_4.[27,28] For example, for La_2CuO_4 they[10,11] took the value 0.835 of $f(q)$ appropriate to the (100) peak (at $|q|=1.17$ Å^{-1}), with very similar numbers for the 1:2:3 compound,[8] and this led to the value $0.64\mu_B \pm 6\%$ for M_{ord}, consistent with $f(0)=1$ for the $f(q)$ used (a statistical factor was again included in the error estimate). And the agreement of this moment with spin-wave theory ($0.67\mu_B$ with $g=2.2$) led to the conclusion[8] that there is *no, or negligible, covalent reduction.* Unfortunately, this procedure is quite arbitrary, particularly in light of the fact that K_2CuF_4 is a *ferromagnet.*

An alternate procedure, more reasonable in our opinion, would be to use the form factor that K_2CuF_4 would show *if* it were antiferromagnetically ordered as in La_2CuO_4. The difference is the presence of $p(r)^2$ terms; subtracting those[27] at the $|q|$ of interest yields a value of $f_u(q)$ of 0.735 at the (nonzero) q for this reflection. Note that we obtained $f_u(q)$ rather than $f(q)$, consistent with the fact that after subtraction of the $p(r)^2$ terms, the result is no longer unity at $q=0$. Thus from (7) (with the term in square brackets replaced by 1), division of $\langle s(q_{\mathrm{AF}})\rangle$ by 0.735 yields $g\mu_B m_{\mathrm{Heis}}=0.73\mu_B \pm 6\%$; this is above the theoretical value[4–6] ($0.64\pm 7\%$), but within the error bars. From Ref. 27 we see that $f_u(q_{\mathrm{AF}}=0)$ [as given in (9)] $=0.74$, which is the ratio $M_{\mathrm{ord}}/g\mu_B m_{\mathrm{Heis}}$, as seen from (9) and (10). That is, this procedure gives a *covalent reduction* of about 26%. Thus this interpretation of the data gives appreciable covalence, and a value of m_{Heis} in a range above (but close to) theory, clearly a much more reasonable picture. *However,* the covalence in the oxides should be appreciably larger than that for the fluoride. Judging from the three-band-model mapping above, and from La_2NiO_4,[14] there should be an additional reduction in f_u of at least 15%, leading to gm_{Heis} at least $0.84\mu_B\pm 6\%$, clearly larger than predicted by present theory.[4,5,12] Thus even after a more soundly based interpretation of the data, there seems to remain a serious problem with present theoretical views of these materials. Further investigation, by calculation of the form factor for La_2CuO_4, as well as consideration of the other possibilities noted above, is in progress.

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