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M. Roger and J. M. Delrieu

Dph. G. SPSRM- CEA CENS, 91191 Gif sur Yvette Cedex, France

Abstract. – Taking into account the small energy difference of conducting holes between Cu and O sites and large on-site energy for double occupancy which prevents holes from crossing on the same site, we prove that cyclic four hole exchange *via* intermediate O sites is dominant in the 2D CuO_2 square lattice, like in hard core solid ^3He. Some experimental discrepancies are resolved by this model.

1. Introduction

The presence of two dimensional conducting CuO_2 planes with a square lattice of copper atoms connected through oxygen is essential for the physics of most high T_c superconductors. The most common current picture is a Hubbard Hamiltonian on copper sites with transfer energy t_{Cu_Cu} and on-site repulsion U_{Cu}. However it comes out from experiments [1] that: i) U is very large ($\sim$ 8 to 10 eV) ii) The energy difference for a hole occupying a Cu or O site is relatively weak ($\varepsilon \sim 0.4$ eV), and thus the intermediate configuration O^- is much more likely than Cu^{+++}. Consequently, new correlations involving intermediate oxygen sites should lead to original experimental properties.

A generalized Hubbard Hamiltonian [1, 2] seems to be more realistic:

$$\mathcal{H} = \varepsilon_\alpha \sum_i n_{i\sigma} + t \sum_{i,j} c^+_{i\sigma} c_{j\sigma} + V \sum_{i<j} n_{i\sigma} n_{j\sigma'} + U_\alpha \sum_i n_{i\downarrow} n_{i\uparrow} \quad (1)$$

where $c^+_{i\sigma}, c_{i\sigma}, n_{i\sigma}$ represent respectively the creation, annihilation and number operators for holes on Cu or O sites. ε_α are on-site energies for single hole occupancy, depending on O ($\alpha = \mathrm{p}$) or Cu ($\alpha = \mathrm{d}$) site. t is the hopping frequency. U_α are on-site energies for double occupancy of holes. V is the Coulomb repulsion between first neighbors holes.

In the large U limit, exchange processes between holes should be very similar to that occuring in hard core quantum fluids as solid ^3He. The large U energies prevent two holes from crossing on the same site as shown in figure 1a; but four holes can exchange cyclically through eight successive hops *via* intermediate O sites (Fig. 1b), involving lower potential barriers ($V \sim 2$ eV, $\varepsilon \sim 0.4$ eV).

Similar multiple exchange processes account for all unusual magnetic properties of bcc ^3He [3, 4]. From simple steric arguments we predicted dominant three particle exchange in triangular geometry leading to fermagnetism [3], which was confirmed experimentally in hcp ^3He five years later, (currently admitted theories (like superexchange) expected antiferromagnetism!).

In this paper, we prove that with one hole per Cu site and in the large U_α limit, the Hamiltonian (1) reduces to an effective spin exchange model with dominant four holes interactions. We investigate some physical and compare with experimental results.

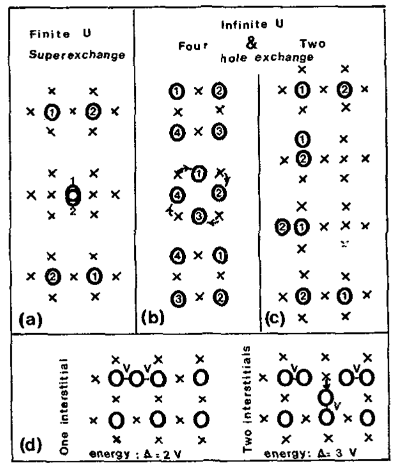

Fig. 1.

By doping, additional holes are introduced on the O sites and the system becomes a delocalized Fermi liquid. If the effective Coulomb repulsion between holes is short range, as assumed in (1), we prove that two intersticial holes bind together as shown in figure 1 to decrease the first neighbor repulsion. Such a mechanism as recently proposed for finite U_α [2, 6], could lead to a large effective attaction of order $V \sim 2$ eV explaining high T_c superconductivity.

2. Four spin Hamiltonian. Some properties

In order to show the new correlations neglected in the simple Hubbard model, we take $U_\alpha/t \to \infty$ in (1) and use general perturbation in powers of t/V, $\varepsilon/V < 1$ to derive an effective spin Hamiltonian. Since, in this limit, superexchange is suppressed, spin exchange terms only appear at 8th order. Figure 1b shows 8 successive hops *via* intemediate O sites on a square, leading to the cyclic exchange of four holes. Two hole exchange can also occur at the same order through 8 hops *via* neighboring O site, as illustrated in figure 1c. The effective exchange Hamiltonian is:

$$\mathcal{H}_{\text{ex}} = -J\sum_{i<j} P_{ij} - K \sum_{i<j<k<1} \left(P_{ijkl} + P_{ijkl}^{-1}\right) \quad (2)$$

where P_{ij} and P_{ijkl} are two and four spin permutation operators;

$$J = -16t^8/(\varepsilon+V)\left[(\varepsilon+V)(\varepsilon+2V)(2\varepsilon+V)\right]^2;$$

$$K = \frac{-4t^8}{(\varepsilon+V)^4(3\varepsilon+V)^2(2\varepsilon+V)^2}\times$$

$$\times\left(\frac{(6\varepsilon+5V)^2}{\varepsilon} + \frac{(4\varepsilon+3V)^2(3\varepsilon+4V)^2}{(\varepsilon+2V)^2(\varepsilon+V)}\right)$$

J is expected to be one order of magnitude smaller than K. To fix the ideas with $\varepsilon \sim 0.4$ eV, $V \sim 1.5$ eV, $t \sim 0.6$ eV, we obtain $\mid K \mid \sim 0.045$ eV ~ 500 K; $\mid J \mid \sim 0.006$ eV. For comparaison a superexchange process involving four hops and double occupancy of one O site with $U = 10$ eV (Fig. 1a) would lead to a pair exchange frequency $\mid J_{se} \mid \sim 4t^4/U(\varepsilon+V)^2 \sim 0.014$ eV, three times smaller.

All eigenstates of Hamiltonian (2) have been calculated exactly by computer for small systems of $N = 4$ to 16 spins with periodic boundary conditions. The ground states of larger systems (N = 18, 20) have been determined by Lanczos method. We used the methods decribed in [7, 8] to extrapolate energies and spin correlations at $N \to \infty$ through plots as a function of $1/N$. With pure four spin exchange ($J = 0$), the mean field AF state has four sublattices with orthogonal magnetization ($\uparrow$, $\rightarrow$, $\downarrow$, $\rightarrow$), (two spin exchange gives an ordinary two sublattice AF order ($\uparrow\downarrow$)). For both kind of order we have estimated the staggered magnetization as defined in [7, 8], taking into account a correcting factor $\sqrt{3}$ (see Ref. [9]). The four sublattice orthogonal magnetization extrapolates to zero at $N \to \infty$. In contrast, the two sublattice alternate magnetization extrapolates to a finite value of $\sim 0.4 M_0$, M_0 beeing the saturation magnetization. This is not surprising, since the exact ground state energy is far from mean field. Taking the value 1.12 μ_B for Cu^{++} magnetic moment one predicts an order parameter of $\sim 0.45\ \mu_B$ in fair agreement with neutron data [1].

We determine the susceptibility $\chi(T)$ by fourth order high temperature series expansions (down to θ) and complete diagonalization of the Hamiltonian for 4 to 16 spin clusters. As already observed in 3D ^{3}He [3], four spin exchange enhance the susceptibility. The large deviation (-25 %) from Curie-Weiss law at $T \sim -\theta$ observed in the 2D Heisenberg model is suppressed and $\chi(T)$ obeys Curie Weiss law down to $\sim -\theta$. At lower temperatures χ further increases up to ~ 1.5 to 2 times the Curie Weiss value $\chi_{CW}(-\theta)$, for $T \to 0$. In contrast, the 2D Heisenberg susceptibility presents a broad maximum just below θ with $\chi \sim 0.75\ \chi_{CW}$. Estimations of exchange frequencies from susceptibility measurements, assuming a Heisenberg Hamiltonian lead to $\theta \sim 800$ to 1 000 K for both La_2CuO_4 [10] and $YBa_2CU_3O_6$ [11] families. They are appreciably smaller than the values of $\theta \sim 1$ 500 K obtained from two-magnon Raman spectra [5]. From the same susceptibility data, estimation of K, using a four spin exchange Hamiltonian leads to larger values $\theta \sim 1$ 500 K, scaling as the susceptibility ratios between both models. Such values fully agree with Raman data.

3. Properties with intersticial holes

By doping La_2CuO_4 with Sr, or increasing from O_6 to O_7 the oxygen content in Y-Ba-Cu-O, additional holes are introduced on O sites in the 2D planes. With infinite U, in order to move, an interstitial has to push away a neigboring hole (like for two particle exchange) and this reduces its mobility. Hence, we expect a Fermi liquid behaviour with T_F of the same order as exchange frequencies [1].

An isolated intertitial increases the energy by $2V$; if we consider a pair of interstitials they tend to bind together as shown in figure 1d, with a repulsive shift of a neigboring Cu hole. The pair energy is thus $3V$ instead of $2\times 2V$. This strong attraction of order V, can induce superconductivity. This type of attracting process has been previously proposed for finite U_α [2, 6], it is also relevant in the infinite U limit. It is however important to determine the limits for localisation of such pairs as a function of t, ε, V.

For $U \to \infty$, the extended Hubbard Hamiltonian (1) can lead to antiferromagnetism and superconductivity and gives new insight in both new superconductors and quantum hard core fluids as ^{3}He.

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