

CuO chains and carrier statistics in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$

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The electronic states in Cu–O chains are analyzed in Emery's model. The separation of the spin and charge degrees of freedom is studied. A new representation of the Hamiltonian of the model is proposed. A flow of charges between chains of various lengths and from chains to planes is discussed. Correlations among the structural, antiferromagnetic, and metal–insulator transitions in YBaCuO are also discussed.

The CuO chains play an important role along with the CuO_2 planes in YBaCuO ; in particular, they serve as a reservoir that furnishes carriers to the planes.¹ The one-dimensional problem of a CuO chain is naturally much simpler than the corresponding three-dimensional problem, which is far from solution. In the present letter we first analyze the electronic states of a CuO chain and then use these states to describe the statistics of holes in YBaCuO . Under certain assumptions regarding the length distribution of the chains, it becomes possible to explain the following points in a unified way: (1) why all the phase transitions occur at approximately the same values of x (Refs. 2 and 3) and (2) why the flow of holes from chains to planes and the suppression of antiferromagnetism begin sharply as x is increased, in a narrow concentration interval near $x_0 \approx 0.4$ (Refs. 3 and 4).

THEORY OF A CuO CHAIN

The bridge oxygen atoms which connect the chains to the planes contribute little to the hole states,⁵ so a chain of alternating copper and oxygen atoms is a good model. We will discuss it within the framework of Emery's model,⁶ with oxygen p orbitals and copper d orbitals (the latter are lower in energy, $\epsilon \equiv \epsilon_p - \epsilon_d > 0$, and cannot be doubly occupied: $U_d \rightarrow \infty$). Under these conditions the Hamiltonian of the system can be put in the form

$$\begin{aligned} H = & t \sum_{\sigma, \sigma'} \sum_{m=1}^{N-1} [a_{m\sigma}^+ (2\vec{S}_{m+1} \vec{\sigma}_{\sigma\sigma'} + \frac{1}{2} \delta_{\sigma\sigma'}) a_{m+1\sigma'} + \text{h.c.}] \\ & + \tau \sum_{\sigma\sigma'} \sum_{m=1}^N a_{m\sigma}^+ [2(\vec{S}_m + \vec{S}_{m+1}) \vec{\sigma}_{\sigma\sigma'} + \delta_{\sigma\sigma'}] a_{m\sigma'} \\ & + J \sum_{m=1}^N (2\vec{S}_m \vec{S}_{m+1} + \frac{1}{2}) (1 - a_{m\uparrow}^+ a_{m\uparrow}) (1 - a_{m\downarrow}^+ a_{m\downarrow}), \end{aligned} \quad (1)$$

This expression describes a system of localized copper spins \vec{S}_m ($S_m = 1/2$) which are

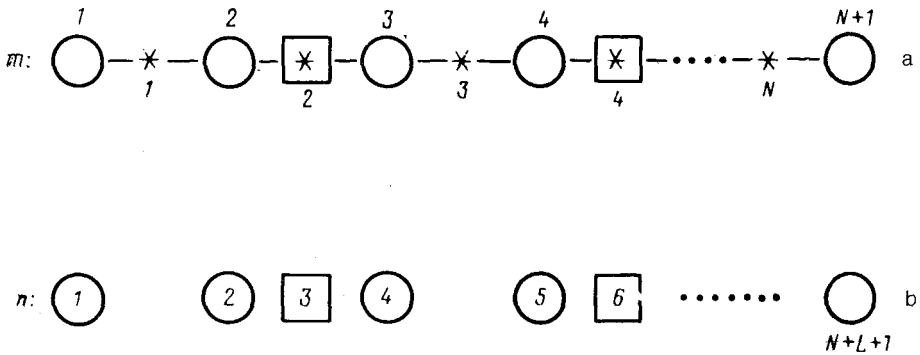


FIG. 1. a: Numbering of the sites in a CuO chain and initial variables. \circ —Copper site with a spin (Cu^{2+}); \ast —oxygen site (O^{2-}); \ast —oxygen site with a hole (O^{1-}). b: Internal variables. Here L is the number of holes.

interacting with each other (by virtue of the superexchange J) and with holes ($a_{m\sigma}^+, a_{m\sigma}$) which are moving along oxygen atoms. Figure 1a explains the numbering of the sites. We assume a Hubbard repulsion U_p at the oxygen which is strong (but finite, in contrast with U_d), so Hamiltonian (1) is projected onto the lower Hubbard oxygen subband. We need to bear in mind that a double occupation is forbidden. A systematic derivation of (1) from Emery's model leads to $t \sim t_{pd}^2/\epsilon$, $\tau \sim t_{pd}^2/(\epsilon + U_p)$, and $J \sim t_{pd}^4/[\epsilon^2(\epsilon + U_p)]$. For $t_{pd} \ll \epsilon \ll U_p$ we thus have

$$J \ll r \ll t. \quad (2)$$

When we incorporate the interaction at sites other than nearest sites, we obtain a renormalization of t , r , and J , so these quantities can conveniently be treated as independent parameters.

Simple chemical arguments show that the number of oxygen holes in a chain of N oxygen atoms is $L = N - 1$. The total number of holes, i.e., the sum of the number of oxygen holes (L) and the number of holes localized at copper ($N + 1$), is $2N$, i.e., an even number. According to the theorem of Lieb and Mattis,⁷ the ground state of the neutral chain must therefore be a singlet. However, since the holes can flow away from the chains (more on this below), the number L should also be treated as an independent parameter.

We first consider a single hole ($L = 1$). We call the sequence $S_1, S_2, \dots, S_m, \sigma, S_{m+1}, \dots, S_{N+1}$ a "spin configuration." Here S_i is the projection of copper spin i , and σ is the projection of the spin of a hole, which is, by definition, placed at site $m + 1$ if the hole is at site m . In other words, all the spins in this sequence, including the spin of the hole, are numbered from left to right (Fig. 1b). This approach corresponds to introducing "internal" spin variables $S'_1 = S_1, \dots, S'_m = S_m, S'_{m+1} = \sigma, S'_{m+2} = S_{m+1}, \dots, S'_{N+2} = S_{N+1}$. The effect of the first term in (1) reduces to one of interchanging the spin of the hole with the neighboring copper spin, $S_{m+1} \rightleftharpoons \sigma$, with the simultaneous hop of a hole: $m + 1 \rightarrow m$. It is easy to see that the spin configuration is conserved in the process.⁸ In the case of an arbitrary number of holes, we should again number all the spins from left to right, including the hole spins (we recall that

two holes cannot occupy a common site). As a result, with $\tau = J = 0$ we find a system of spin-zero fermions with the Hamiltonian

$$H_c = t \sum_{m=1}^{N-1} (a_m^+ a_{m+1} + a_{m+1}^+ a_m) \quad (3)$$

and a complete degeneracy with respect to spin configurations. To generalize to the case $\tau \neq 0, J \neq 0$, we should introduce internal variables for the fermions also: The "internal coordinate" of a fermion is the number of the spin that corresponds to it in the spin configuration. In terms of these variables, Hamiltonian (1) becomes

$$\mathcal{H} = \mathcal{H}_c + \mathcal{H}_s + \mathcal{H}_{int}, \quad \mathcal{H}_c = t \sum_{n=1}^{N'} (c_n^+ c_{n+1} + c_{n+1}^+ c_n),$$

$$\mathcal{H}_s = J \sum_{n=1}^{N'} (2\bar{S}'_n \bar{S}'_{n+1} + 1/2), \quad \mathcal{H}_{int} = g \sum_{n=1}^{N'} c_n^+ c_n (2\bar{S}'_{n-1} \bar{S}'_n + 2\bar{S}'_n \bar{S}'_{n+1} + 1), \quad (4)$$

where $N' = N + L$, and $g = \tau - J$. The operators c_n^+, c_n describe the fermions in terms of the internal variables. They obey the condition $c_n^+ c_{n+1}^+ \equiv 0$. In other words, they have a hard core which prevents them from occupying neighboring sites. This fictitious interaction arises as a result of the transition to internal variables.

Everything has thus been reduced to a problem of two interacting subsystems: a spin subsystem and a charge subsystem. The role of interaction constant is played by $g = \tau - J$. An exact separation of variables occurs at the microscopic level only in the case $g = 0$. In this case the wave function of the ground state is the product of a fermion part Ψ and a spin part χ , where χ is the Bethe wave function for an antiferromagnetic chain. This result was understood by Emery⁹ as holding in the limit $U_p, U_d \rightarrow \infty$ (i.e., with $\tau = J = 0$). It can be shown, however, that even with $g \neq 0$ the spin subsystem and charge subsystem can nevertheless be separated in first order in τ/t and J/t . Only the exchange is renormalized in this case: $J \rightarrow J_{eff} = J(1 - \rho) + \tau\rho$, where $\rho = L/N$ is the density of holes. The interaction between subsystems arises in *second* order in g/t ; we will study it in a separate paper.

Although in terms of the internal variables the spin subsystem and the charge subsystem can be separated, in terms of the original variables (in terms of which all observable quantities should be expressed) the localized spins are greatly entangled with mobile holes. As an example, we can write the expression for the correlation function of the copper spins, which we have derived by a bosonization method:¹⁰

$$K(m) \equiv \langle \bar{S}_0 \bar{S}_m \rangle \propto (-1)^m |m|^{-(\theta+1/2)} \cos(\pi\rho m), \quad |m| \gg \rho^{-1}, (1 - \rho)^{-1}. \quad (5)$$

At large distances the index¹⁰ $\theta = 1$ acquires an increment of $1/2$; i.e., the correlation function falls off more rapidly when holes are present. As $\rho \rightarrow 0$ (or $\rho \rightarrow 1$), there is an internal region $|m| \ll \rho^{-1}$ [or $|m| \ll (1 - \rho)^{-1}$], in which the fermions are unable to disrupt the correlation, and there is no change in the index θ : $K(m) \propto (-1)^m |m|^{-\theta}$ [or $K(m) \propto |m|^{-\theta}$]. In the latter case the correlation is ferromagnetic, since copper spins alternate with hole spins in the limit $\rho \rightarrow 1$.

STATISTICS OF HOLES

If we ignore τ and J , we can easily find the energy levels for a chain of length N from Hamiltonian (3):

$$\epsilon_{N,K} = 2t \cos(\pi K/N + 1), \quad K = 1, 2, \dots, N. \quad (6)$$

For long chains ($N \gg 1$) there is a 1D band of width $4t$. As $x \rightarrow 1$ (in which case all the chains are long), the holes should flow onto the planes, so the 1D band should overlap with the 2D band of the CuO_2 planes. We can show that there is a threshold $x = x_c$ for the flow of holes to the planes if we assume that the bands overlap by less than 50% (Fig. 2a).

Let us assume that the distribution of chains with respect to length N is described by the function $f(N, x)$. This function does not necessarily have to be a thermodynamic-equilibrium function, particularly at small values of x . It may depend on how the sample is prepared. At small values of x one would expect that the oxygen atoms would be distributed at random, so we would have $f(1, x) \approx x$, $f(N, x) \propto x^N$. As x increases, the average value \bar{N} shifts toward larger N . It is natural to suggest that $\bar{N}(x)$ increases sharply near the structural transition ($x = x_0$; Fig. 2b). A sharp acceleration of the growth of the chains should promote such an increase.¹¹

The energy levels which are occupied in the case of neutral chains are shown in Fig. 2b, but an occupation of this sort does not correspond to a minimum of the energy. The holes must flow in such a manner that they occupy all the levels below the level of the chemical potential, which is found from the condition that the number of holes is conserved (Fig. 2c). At small x the number of all chains with $N > 1$ is small, and all the holes from levels with $\epsilon > 0$ (which are present in chains with $N \geq 4$) drain off onto chains with $N = 1$ (monomers). We find that a few $N_D \approx f(4, x) \sim x^4$, of positively charged chains arise, as does an equal number of negatively charged chains. They have a spin of $1/2$ and differ from neutral chains in that they are paramagnetic centers. The chemical potential is $\mu = 0$, and there is no flow of holes from chains to planes. Working from the analogy with a lightly doped, weakly compensated semiconductor, one can easily show that the Coulomb interaction between charged chains leads to a slight lowering of the chemical potential: $\Delta\mu \propto -x^{1/3}$.

With increasing x , a point is reached at which all the monomers turn out to be charged; at this point, the chemical potential μ begins to increase. This increase becomes sharp near x_0 , and at a certain x_c near x_0 the potential μ reaches the bottom of the 2D band [$\mu(x_c) = \Delta$]. Beginning at $x > x_c$, the redistribution of charge between chains and planes leads to a shift of the bridge oxygen.^{1,4} The holes that have moved to a plane are initially localized. By analogy with LaCuO (Ref. 13), one would expect that a suppression of antiferromagnetism by localized holes and then the holes becoming metallic would occur in a narrow interval $x - x_c \sim 0.05$.

The long-range Coulomb interaction within chains should lead to a "chemical shift" δ_N of the one-particle levels. This shift would depend on N . One might expect that all the energies would shift upward, to an extent which would increase with decreasing N . The chemical shift would lead to an increase in μ at small values of x . If $\mu(0) < \Delta$, there should be no qualitative changes near $x = x_c$. At small values of x , in contrast, the pattern may change: If $\mu(0) \sim t$, the monomers may remain neutral, in

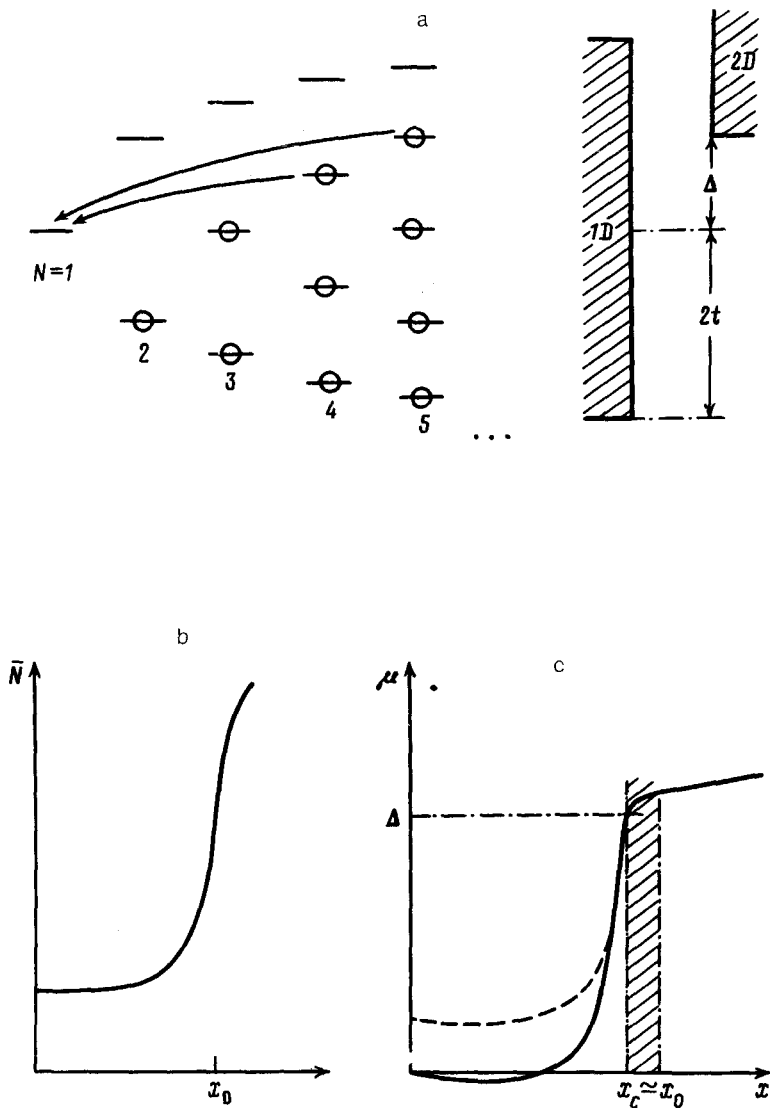


FIG. 2. a: Energy levels for chains of various lengths N . Circles—Levels that are occupied in the case of neutral chains; arrows—flow of holes; Δ —distance from the middle of the 1D band to the bottom of the 2D band. b: Suggested behavior of the average length of the chains as a function of the oxygen concentration; the concentration x_0 corresponds to a structural transition. c: Chemical potential versus the concentration. Dashed line—Shift of μ due to in-chain Coulomb effects; hatching—concentration region in which the holes do penetrate to the planes but remain localized. The suppression of antiferromagnetism occurs in this region.

which case only sufficiently long chains would undergo a change in charge. The case $\mu(0) = \Delta$ might be realized at $\delta_2 > \Delta + t$, but in that case the holes would appear (in a number $\sim x^2$) in planes even at arbitrarily small values of x . This result would seem to contradict experiment.

In summary, the proximity of all the phase transitions can be explained in this model if one assumes (1) that the bottom of the 2D band lies below the top of the 1D band but above its midpoint and (2) that the average length of the chains (and, correspondingly, the chemical potential) increases sharply as $x \rightarrow x_0$.

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