Brinkman-Rice transition driven by interatomic repulsion in hexagonal copper oxides

M. E. Simón and A. A. Aligia

Centro Atómico Bariloche and Instituto Balseiro, Comisión Nacional de Energía Atómica, 8400 Bariloche, Argentina

M. D. Núñez Regueiro*

European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble Cedex, France

We propose an effective one-band Hamiltonian to describe the low-energy physics of $R\mathrm{CuO}_{2+\delta}$ delafossites, assuming that the relevant states are predominantly Cu $3d_{3z^2-r^2}$ and O p_z. Due to geometrical factors, the effective hopping between Cu sites is nearly 16 times smaller than in superconducting cuprates. As a consequence, when the effective Hamiltonian is treated in slave-boson mean-field theory, a moderate interatomic repulsion drives a localization transition in the structure proposed for oxygen content 8/3. Experimental evidence suggests that $\mathrm{La_2CuO_{2.66}}$ and $\mathrm{Y_{0.99}Ca_{0.01}CuO_{2.66}}$ are near the localization transition but on opposite sides of it.

The basic structural feature of copper oxide superconductors are the $\mathrm{CuO_2}$ planes, in which the Cu ions lie on a square lattice (if small distortions are neglected). Recently Cava *et al.*[1] have succeeded in oxidizing the ordinary delafossite compounds, in which the Cu ions lie in a hexagonal planar arrangement. This opened the possibility to study CuO arrangements with a different geometry, but a similar doping level as the high-T_c superconductors. The physical properties turned out to be quite different.[1,2] Measurements of specific heat, magnetic susceptibility and resistivity suggest that $\mathrm{Y(Ca)CuO_{2+\delta}}$ and $\mathrm{LaCuO_{2+\delta}}$ with $\delta \sim \frac{2}{3}$ are near to a ferro- and antiferromagnetic instability, respectively, while the doping level is such that the formal valence of Cu is near 2.33. The resistivity of the Y compound displays a variable-range hopping, behavior typical of localized states. While both systems exhibit large susceptibility enhancements, only the La compound shows a comparable specific-heat mass enhancement.[2] Curiously it is difficult to obtain a sample with $\delta = 0.5$; O content is always greater than 2.5, inhibiting the obtention of a state which allows to study $\mathrm{Cu^{2+}}$ in a triangular lattice exactly equivalent to that of the square-lattice Cu oxides.[1] For these doping values, $\delta \sim \frac{1}{2}$, the resistivity shows an activated temperature dependence.

An important difference between high-T_c compounds and delafossites is pointed out by the band-structure calculations:[3] while in the former the important Cu orbitals are the $3d_{x^2-y^2}$, the density of states of the latter at the Fermi level is predominantly composed of $3d_{3z^2-r^2}$. An estimate of the relative magnitude of the effective hopping between two of these orbitals (via $2p$ orbitals of intermediate O atoms, see Fig. 1 for $\delta = \frac{2}{3}$) can be made assuming that the hopping integral $(pd\sigma)$ is smaller than the energy Δ necessary to transfer a hole from a Cu d to an O p orbital. In this limit the effective hopping in high-T_c systems is $t = (pd\sigma)^2/\Delta$. In delafossites, there is a factor $\frac{1}{3}$ due to the different d orbital involved, a factor $\frac{1}{2}$ because of the angle Cu-O-Cu of 120° in delafossites (see Fig. 1), and finally, since the Cu-Cu distance is similar in both types of compounds and the Cu-O distance is $2/\sqrt{3}$ larger in delafossites,

this introduces a factor $(\sqrt{3}/2)^7$. Thus the effective hopping is expected to be about 16 times smaller in delafossites in comparison with high-T_c compounds. Similarly, the effective exchange interaction between Cu atoms J scales approximately as t^2, and is expected to be two orders of magnitude smaller in delafossites, in quantitative agreement with the estimate based on measurements of magnetic susceptibility.[1]

Due to the small magnitude of the effective hopping t, one expects that the holes brought by the inclusion of O atoms in the structure remain localized near the added $\mathrm{O^{2-}}$ ions because of the Coulomb attraction with them. This is probably the case for $\delta \sim 0.55$. However for $\delta = \frac{2}{3}$, the structural studies[1,4] suggest a hexagonal $H(\sqrt{3} \times \sqrt{3})$ superstructure in which all Cu atoms are equivalent (any Cu atom can be mapped into any other one by a symmetry operation of the space group, see Fig. 1) and this argument is not valid. Band-structure calculations[3] have shown that, in the absence of strong electronic correlations, these materials are expected to be metallic conductors, particularly near this stoichiom-
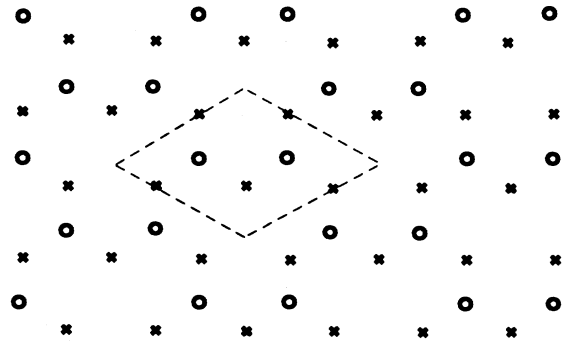

FIG. 1. Structure of the $\mathrm{CuO_{2/3}}$ planes (Refs. 1 and 3) of $\mathrm{La_2CuO_{8/3}}$. Crosses denote Cu atoms and open circles represent O atoms. The dashed line indicates a possible choice of unit cell.

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etry where $\frac{2}{3}$ of the available oxygen sites can be filled in the Cu plane in an ordered manner to yield the hoped for two-dimensional fully connected Cu-O array.[5,6] Up to date, however, completely metallic samples have not been synthetized.[5] In this paper we show that in this $H(\sqrt{3} \times \sqrt{3})$ superstructure a modest repulsion V between holes in nearest-neighbor Cu sites can drive a Brinkman-Rice localization of the carries.[7] This possibility was suggested by Ramirez et al.[2] taking into account the Wilson ratio of order unity for the La compound.

The effective one-band Hamiltonian can be constructed following the same procedure as, for example, in Ref. 8. It has the form of a model describing the motion of electrons in Cu orbitals, with in-plane hopping t' between two nearest-neighbor Cu atoms if and only if both Cu atoms have a common nearest-neighbor O atom (see Fig. 1). However, the states with one hole (Cu^{2+}) represent a state which also contains O holes, particularly in the symmetric combination of $2p_z$ orbitals of the two nearest O atoms, which together with the Cu atom, build O-Cu-O sticks perpendicular to the plane.[1,3] Similarly the Cu^{3+} state represents a singlet involving mainly the above-mentioned orbitals. To study the effect of dispersion along the z direction, we add a hopping t_z in that direction, assuming that all the planes can be obtained from one of them by parallel translation along the z direction. This is not true in the real structure of delafossites,[1,3] but the qualitative effects of t_z should be the same. Finally we add a repulsion V between electrons lying in nearest-neighbor Cu atoms in the plane. Thus, the Hamiltonian reads

$$H = -t \sum_{\langle ij \rangle L \sigma}{}' (c_{iL\sigma}^{\dagger} c_{jL\sigma} + \text{H.c.}) - t_z \sum_{iL\sigma} (c_{iL+1\sigma}^{\dagger} c_{iL\sigma} + \text{H.c.})$$

$$+ V \sum_{\langle ij \rangle L} (1 - n_{iL})(1 - n_{jL}), \qquad (1)$$

where $c_{iL\sigma}^{\dagger}$ creates an electron at site i of the plane L, with spin σ under the condition of no double occupancy (we are assuming infinite on-site repulsion U). The prime of the first sum symbol indicates that the sum over nearest neighbors is restricted to only those four "connected" by an O atom. The operator $n_{iL} = \Sigma c_{iL\sigma}^{\dagger} c_{iL\sigma}$ is the number of electrons at site i of plane L, and we denote the respective average hole doping level by $\delta_{iL} = \langle 1 - n_{iL} \rangle$.

To solve the Hamiltonian Eq. (1) we treat the constraint of no double occupancy in the slave-boson mean-field approximation of Kotliar and Ruckenstein.[9] In this approximation, the hopping between two sites $\alpha = i, L$ and $\beta = i', L'$ is reduced by a factor which depends on the respective doping levels:

$$\bar{t}_{\alpha\beta} = \left[\frac{4\delta_\alpha \delta_\beta}{(1 + \delta_\alpha)(1 + \delta_\beta)} \right]^{1/2} t_{\alpha\beta}. \qquad (2)$$

For the interatomic repulsion we use the Hartree approximation:

$$(1 - n_\alpha)(1 - n_\beta) \sim \delta_\alpha(1 - n_\beta) + \delta_\beta(1 - n_\alpha) - \delta_\alpha \delta_\beta. \qquad (3)$$

For large V, one expects that it is convenient to break the symmetry of the system in such a way that $\frac{1}{3}$ of the Cu sites become $+3$, while the rest of the Cu sites are $+2$. This
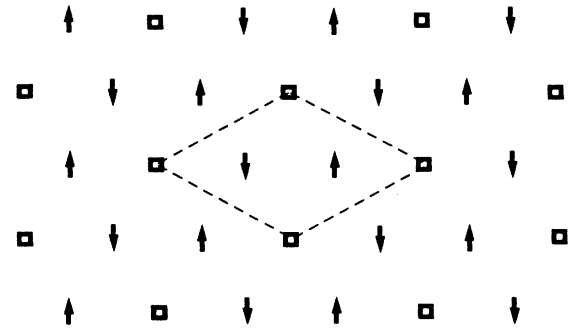

FIG. 2. Structure with three inequivalent Cu atoms per unit cell, denoted by a square, spin up, and spin down, respectively. They correspond in the text to sublattices A, B, and C respectively. For $V > V_c$, the sublattices B and C have one electron per site, while sublattice A is empty. The antiferromagnetic alignment of the electrons on sublattices B and C is expected if the exchange interaction $J \sim t^2/U$ is included in the model.

situation for each plane is illustrated in Fig. 2, where we also show the magnetic order expected when an antiferromagnetic nearest-neighbor exchange interaction J is included in the model. This magnetic order has been previously found theoretically as one of the possible "mixed phases" in systems near the magnetic-nonmagnetic transition.[10] We have looked for self-consistent broken-symmetry solutions in which for the three Cu sites per unit cell $\delta_A \geq \delta_B = \delta_C$. For simplicity we have assumed δ_{iL} independent of L. Since $\delta_A + \delta_B + \delta_C = 1$, the value of δ_A characterizes the solution.

We find only two self-consistent solutions: one symmetric and metallic with $\delta_A = \delta_B = \delta_C = \frac{1}{3}$ and the other semiconducting with $\delta_A = 1$ ($\delta_B = \delta_C = 0$). In this broken-symmetry solution, the effective hopping between any two atoms in the plane $\bar{t}_{\alpha\beta} = 0$ [see Eq. (2)]. This is the situation illustrated in Fig. 2. Only the effective hopping of holes in the t_z direction is different from zero, but this is due to our artificial assumptions about the structure of the system and the symmetry of the ground state in that direction. The energy of this localized solution is $E_l = 0$. If $t_z \neq 0$, it exists only for $V > V_s$, where, for example, $V_s = t/3$ for $t_z = t/2$, $V_s = 2t/3$ for $t_z = t$, and $V_s = 2t_z/3$ for $t = 0$. The energy of the metallic phase E_m is negative for $V = 0$ and increases linearly with V as $(1/3)^2 N_p V$, where $N_p = 3N_s$ is the number of nearest neighbor pairs and N_s is the number of sites. Thus, the critical value of V for which $E_m = E_l = 0$ is determined by E_m for $V = 0$. At this critical value E_c a first-order metal-insulator transition takes place. The resulting values of V_c for several values of t and t_z are listed in Table I.

The value of the effective hopping t depends on the values of the different Cu and O on-site energies, which are

TABLE I. Critical values of the nearest-neighbor interaction V_c at the metal-insulator transition for different values of the in-plane hopping t and the hopping in the perpendicular direction t_z. For $t = 0$, $V_c = 3\sqrt{3}/\pi$ was obtained analytically.

t	1	1	1	1	0
t_z	0	0.5	1	2	2
V_c	2.60	2.62	2.86	3.86	3.31

difficult to estimate. In the cuprates $t\sim 0.4$ eV.[8,11,12] According to the simple estimate made at the beginning of the paper, the order of magnitude of t in the delafossites is approximately 0.06 eV. If instead of using this estimate one uses more accurate expressions for the effective hopping,[8] t turns out to be somewhat larger, but the order of magnitude is still 0.1 eV if the other parameters are similar to those of the cuprates. We expect t_z to be smaller. The bare Coulomb repulsion between two charges at a distance of[1] 3.8 Å is ~ 3.8 eV. Assuming that this value is reduced an order of magnitude by dielectric and electronic screening, it turns out that the system is near the Brinkman-Rice transition (see Table I).[13] The first-order nature of the transition might be an artifact of the Hartree approximation [Eq. (3)]. The quantitative validity of the results is also affected by the slave-boson approximation,[9] but we believe that the order of magnitude of the critical interaction is correct.

In conclusion, due to geometrical factors and the different nature of the d orbitals involved (which are predominantly of $3d_{3z^2-r^2}$ character in delafossites), the effective Cu-Cu hopping is expected to be one order of magnitude smaller in delafossites than in high-T_c compounds. As a consequence a Cu-Cu nearest-neighbor repulsion of magnitude $\geqslant V_c$, where $V_c \sim 0.3$ eV, is enough to localize the carriers in delafossites.

For oxygen content 2.66, on the localized side of the transition and including effective antiferromagnetic interactions, the magnetic configuration shown in Fig. 2 is expected.

Due to the very small value expected for the J/t ratio (of the order of 1/50), a small number of carriers added to the insulator might favor a ferromagnetic alignment of the spins to allow the maximum possible gain in kinetic energy (as in Nagaoka's theorem[14]). This agrees with the ferromagnetic correlations and small mass enhancement observed in $Y_{0.99}Ca_{0.01}CuO_{2.65}$. Instead, the phenomenology of $La_2CuO_{2.64}$ suggests that the system is on the metallic side of the transition, with a significant mass enhancement (~ 5) and strong antiferromagnetic correlations.[1,2,4] This picture is also consistent with the stronger dependence of the resistivity with the oxygen content in the Y compound.[1,5] However, the magnetic behavior and peculiar features of the Y compound might also be due to a slightly different atomic structure than the one we assumed.[4]

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[*]On leave of absence from CONICET, Centro Atómico Bariloche, 8400 Bariloche, Argentina.

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