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Double-exchange driven ferromagnetic metal-paramagnetic insulator transition in Mn-doped CuO

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Employing *ab initio* self-interaction-corrected local-spin-density calculations, we explain the nature of the ferromagnetic, metallic phase of Mn-doped CuO (an antiferromagnetic insulator when undoped), and of its concurrent transitions to a paramagnetic, insulating phase. Mn-induced donor levels enable conduction through ferromagnetically aligned Mn centers and ferromagnetic CuO planes via double exchange. In the paramagnetic insulating phase, a polaron hopping mechanism consistent with the experiments is envisaged. Our results suggest the intriguing possibility of designing double-exchange driven ferromagnetic cuprates.

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The physics of diluted magnetic semiconductors[1] (pushed by the interest in "spintronic" functionalities of electronic devices) and the time-honored research on cuprate compounds (fueled by the interest in their high-T_c superconducting members) would appear to be quite distinct topics at first glance. However, the recent successful magnetic doping of an antiferromagnetic (AFM) insulating cuprate, CuO,[2,3] and the ensuing perspective of robust ferromagnetic (FM) ordering and large local moments, have revealed yet another intriguing facet of magnetic cuprates amenable to manipulation and design. In this perspective, here we explore the basic mechanisms of the prototypical case of Mn doping of AFM CuO, explaining the nature of the low-temperature ferromagnetic metallic phase, and of the concurrent transitions to a paramagnetic and insulating phase.

Bulk CuO, a robust *A*-type AFM insulator with critical temperature 212 K,[4] has been shown[3] to become FM upon Mn doping within a large concentration range (3.5%–15%), and to revert to paramagnet above $T_c=80$ K (with average magnetization $\sim 1.5\mu_B$/Mn). The temperature dependence of the resistivity indicates a metal-insulator transition at the same critical temperature: above T_c the resistivity obeys the exponential Mott law of variable-range hopping[5] as modified by a Coulomb gap at the Fermi energy;[6] below T_c the resistivity has a metallic behavior, but is quite high ($\sim 2\times 10^4$ Ω cm for $x=0.15$ at $T=0$), and increases rapidly as the Mn concentration decreases (while T_c is unchanged). Finally, despite apparent analogies with typical colossal magnetoresistive (CMR) behavior,[7] no appreciable shift of T_c with applied magnetic field is observed.

Among the questions that are so far unanswered: How does Mn inclusion turn AFM CuO into a ferromagnet? What is the relation of the metal-insulator and FM-paramagnetic transitions? What is the nature of the metallic but highly resistive, and the insulating but hopping-conductive phases? A sound interpretation of this delicate system requires a first-principles theory describing properly the individual phases involved as well as their relation. Standard density-functional approaches have difficulties in this context[8,9] (e.g., CuO is described as a nonmagnetic metal), so we apply the pseudo-SIC method[10] based on a self-interaction corrected[11] (SIC) single-electron Hamiltonian that is free of ad-hoc parameters and preserves the feasibility of standard density functional theory calculations. The method has been successfully applied to a number of correlated oxides,[12] and in particular to bulk CuO, whose electronic and magnetic properties are described correctly and accurately (see Ref. 13). For Mn-doped CuO we employ ultrasoft pseudopotentials[14] with 30 Ryd cutoff energies, and up to 900 special k points for density of states (DOS) calculations. Supercells of 16, 32, and 64 atoms corresponding to $1\times1\times1$, $2\times1\times1$, and $2\times1\times2$ symmetries, and Mn concentrations between $x=12.5\%$ and $x=3.1\%$ are used.

The AFM CuO structure, shown in Fig. 1 (left) is monoclinic,[15] and made by 8 formula units. The Cu sublattice is a distorted fcc, while each O has four first-neighbor Cu arranged on a distorted tetrahedron, with z-parallel Cu-O-Cu angles ($\sim 146°$) larger than in-plane Cu-O-Cu angles ($\sim 108°$). In Fig. 1 (right) some Cu's are substituted by Mn with the same spin orientation. We restrict to this case in the following, since other possibilities (e.g., Mn with spin opposite to that of replaced Cu, or interstitial Mn) are found to be highly unfavorable energetically and can be discarded.

Pure CuO is mainly characterized[13] by the presence of a single unpaired Cu d_{z^2} states favoring AFM superexchange along the z axis through σ-type Cu($d_{z^2}^{\uparrow}$)-O($p_z^{\downarrow}$,$p_z^{\uparrow}$)-Cu($d_{z^2}^{\downarrow}$) coupling. Within the (x,y) plane the main coupling is

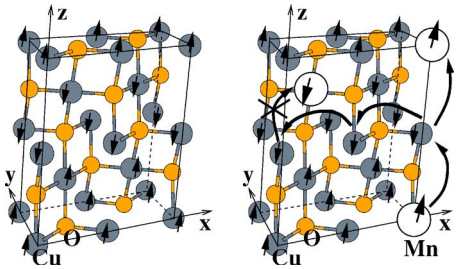

FIG. 1. (Color online) Left-hand side: unit cell of monoclinic CuO. Small arrows show spin orientation on Cu atoms within the ground-state AFM ordering. Cell parameters are $a=6.346$ Å, $b/a=0.5387$, $c/a=1.18$, $\beta=\hat{xz}=99.54°$ (Ref. 15). Right-hand side: some Cu are substituted by Mn (indicated by larger white balls) with same spin orientation of replaced Cu. Long arrows show patterns of electron conduction (see the text).

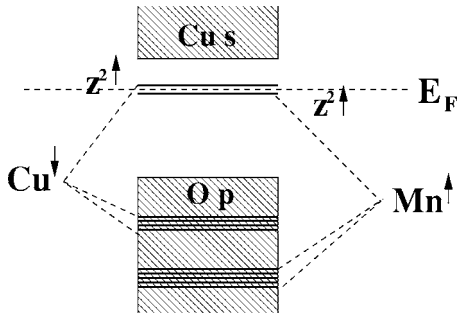

FIG. 2. Sketch of d orbital energies for an up-polarized substitutional Mn^{2+} ion and a down-polarized Cu^{2+} ion resulting from our band energy calculations. Each Mn induces a shallow $d\ z^2$ donor just below the empty Cu $d\ z^2$ conduction bottom.

through two different O p orbitals, that is π-type Cu($d_z^{2\uparrow}$)-O($p_x^{\downarrow}$,$p_y^{\downarrow}$)-Cu($d_z^{2\uparrow}$) interactions. By Hund's rule the double oxygen polarization favors parallel p_x, p_y alignment, thus FM Cu-O-Cu ordering prevails.

The effect of Mn doping on the CuO electronic structure is sketched in Fig. 2, showing majority d levels of $Cu^{+2}d^9$ and Mn^{2+} d^5 ions with antiparallel spins (this is the case of two contiguous Mn and Cu ions along z). We take Cu down polarized, so its only empty d orbital is $d_{z^2}^{\uparrow}$, i.e., the conduction band bottom (CBB) of pure CuO. Not surprisingly, we find substitutional Mn to be in a Mn^{+2} d^5 configuration. While the four lowest Mn d states lie well within the bulk CuO valence manifold, the highest $d_{z^2}^{\uparrow}$ nearly touches the Cu $d_{z^2}^{\uparrow}$ CBB. Thus, a single substitutional Mn introduces an energetically very shallow donor level in the CuO gap. For appreciable Mn concentrations, a defect band is envisaged, nearly overlapping the Cu derived CBB.

Figure 3, left-hand panel, shows the calculated band structure for a substitutional Mn in a 16-atom cell, i.e., $x=12.5\%$. At this concentration the Mn distribution, on average, forms alternating $Mn^{\uparrow}$-O-$Cu^{\downarrow}$-O chains along z, and FM $Mn^{\uparrow}$-O-$Cu^{\uparrow}$-O chains along x. The system is FM overall, with a net magnetic moment per Mn equal to $4\mu_B$ since each

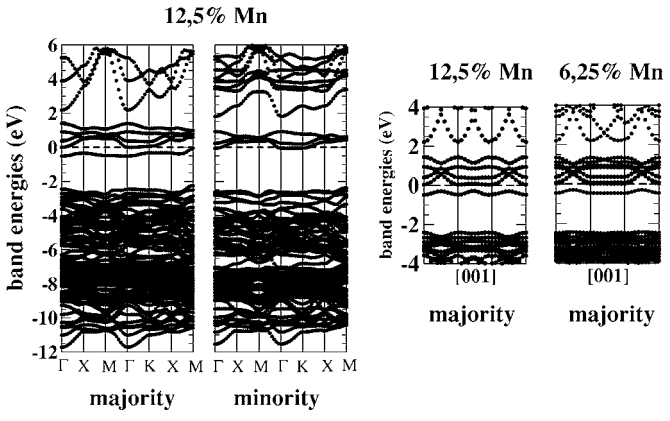

FIG. 3. Left-hand side: band energies of Mn-doped CuO within a 16-atom unit cell. Right-hand side majority band energies of the 16-atom ($x=12.5\%$) and 32-atom ($x=6.25\%$) unit cells. Along [001] ($\Gamma-K$ on the left-hand side; middle segment on the right-hand side) CBB bands are visibly flatter than elsewhere.

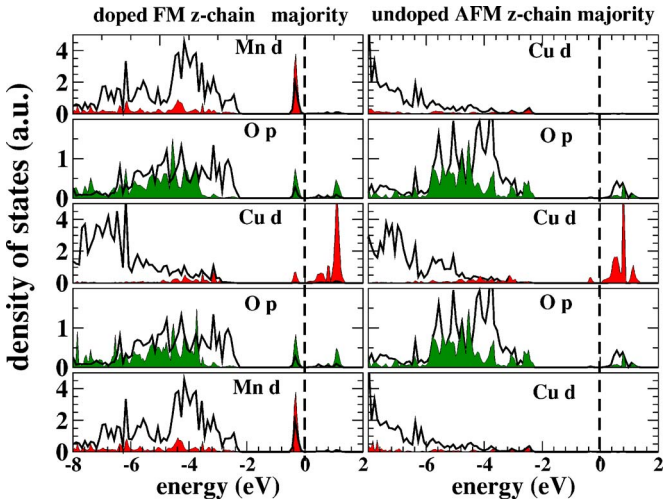

FIG. 4. (Color online) Orbital-resolved DOS of the 16-atom unit cell with one Mn (12.5% concentration). Panels are vertically ordered according to the atomic positions along z chains. Left-hand side, chain with Mn; right-hand side, chain undoped. For Mn or Cu the filled red (dark gray) line represents $d\ z^2$ and the solid black line is sum of all other d contributions. For oxygens the filled green (dark gray) line is p_z, and the solid black line p_x+p_y. Only majority DOS are considered.

Cu-Mn substitution adds five Mn μ_B and subtracts one Cu μ_B to the AFM host. An energy gap of a few meV is visible between the Mn donor band and the CBB in the majority band manifold (since Mn is up polarized), while the lower four Mn d occupied bands are within the valence band manifold. The Mn d empty bands lie in the upper side of the minority manifold, strongly admixed with empty Cu s and p bands. In the 16-atom cell there are four down polarized and three up polarized Cu's, so we see four and three d_{z^2} empty bands in the majority and minority manifolds, respectively. In the right-hand panel of Fig. 3 we blow up the band energies around E_F for $x=12.5\%$ and 6.25% (one Mn in a 16 and 32 atom cell). The CBB Cu band dispersion is clearly flatter along [001] (Γ-**K**) than in-plane, so that a large transport anisotropy is expected. The donor band dispersion along [001] is quite sensitive to concentration changes (neighboring Mn's couple mainly by hybridization along z). The visible band flattening as x decreases agrees with the rapid growth in resistivity for decreasing concentrations observed in Ref. 3.

In Fig. 4 the atom-resolved density of states (DOS) for $x=12.5\%$ is shown. Consider first the DOS for the z chain without Mn (right-hand panel): this is quite similar to the DOS of bulk CuO, which[13] is a charge-transfer insulator with an energy gap of 2.2 eV between the mainly O p-like valence band and a CBB well localized on Cu $d_{z^2}^{\downarrow}$ orbitals (and residually also on the on-top O p). The d_{z^2} orbital undergoes a large spin splitting ($\sim$10 eV), providing a $0.72\mu_B$ magnetic moment per Cu atom. Now, the introduction of Mn dramatically changes the picture (Fig. 4, left-hand panel): the $d_{z^2}^{\uparrow}$ DOS introduced by each substitutional Mn nearly lines up to the same state of the oppositely polarized Cu, inducing a visible peak of p_z DOS on the bridging O. This $d_{z^2}^{\uparrow}$ DOS

spreads through the whole cell in the z direction, and activates a double-exchange channel mediated by $d^{\uparrow}_{z^2}$-p_z-$d^{\uparrow}_{z^2}$ interactions (Mn d_{xy} orbitals contribute also, since Mn-O segments are not exacly parallel to $\hat{z}$). The Mn-centered and Cu-centered $d^{\uparrow}_{z^2}$ DOS are ~0.5 eV and 2 eV wide, respectively. Furthermore in the Cu $d^{\uparrow}_{z^2}$ band a Coulomb gap[6] (induced by the repulsive correlation between filled and empty localized defects) $E_{gap} \simeq 50$ meV is present, consistently with the exponential decay of the resistivity vs T observed in the paramagnetic phase.

The Mn-O-Cu-O alignment along z builds up an orbital ordering analogous to that in $La_{1-x}Ca_xMnO_3$ perovskites, where double exchange is activated in the FM planes by alternately filled and empty e_g orbitals. In the present case, an electron placed on the Mn-derived $d^{\uparrow}_{z^2}$ orbital can hop—by double exchange with the bridging-O p orbitals—to the empty $d^{\uparrow}_{z^2}$ Cu orbital, following the pattern drawn on the right-hand panel of Fig. 1, *provided* that Mn and Cu ions have spins antialigned. Conversely, double exchange is shut down through spin-aligned Mn-Cu or spin-antialigned Cu-Cu segments. The narrow $d^{\uparrow}_{z^2}$ DOS channel suggests a low carrier mobility, consistently with the large resistivity observed in the metallic phase.

Of course, the Mn distribution considered so far, with alternating Mn and Cu ions along z, is just one particular case. Nevertheless, double exchange can indeed justify metallicity in general. Indeed, due to the CuO AFM ordering, in-plane Cu $d^{\uparrow}_{z^2}$ orbitals are all spin-paired. Thus, spin-polarized carriers derived by Mn donors can freely move within the FM planes through spin-paired Cu-O-Cu segments, while the previously discussed spin-antiparallel Mn-O-Cu unit is only needed to jump through adjacent planes.

This provides a mechanism for long-range conductivity even at low doping concentration: in order to have conduction, a regular Mn-O-Cu-O alternance along z is not necessary, since carriers can freely move within a plane until a favorable on-top Mn (i.e., with spin antiparallel to the Cu of this layer) is found. As in ordinary double exchange, the described mechanism nicely correlates conductivity to the FM ordering of Mn: due to the AFM topology of CuO, *carriers can only flow through a Mn with same spin polarization of the Mn previously visited* (see Fig. 1). So, this double exchange across two Mn works just like ordinary double exchange, except that it is mediated by a whole portion of CuO lattice rather than by a single O, and is therefore indirect and doping induced.

Our results provide a sound interpretation of the observed metal-insulator transition: the metallic regime is always possible in the presence of spin-aligned Mn, even in the limit of small Mn concentration (i.e., in the limit of isolated Mn impurities). Each couple of misaligned Mn generates instead a depletion of the $d^{\uparrow}_{z^2}$ DOS and a confining wall for the electron mobility. Thus, as soon as the thermal fluctuations of Mn polarization are such as to overcome the percolation threshold[4,16]—i.e., at the FM-paramagnetic phase transition—double exchange becomes hindered and the system behaves as insulating.

Even then, however, the localized charge can still undergo phonon-assisted hopping across forbidden space regions giving rise to the observed variable-range hopping conduction regime (see Ref. 16 for a quantitative description of polaron hopping). In Fig. 5 a schematic one-dimensional picture of this mechanism for several Mn distributions and concentrations is shown. Case (a) corresponds to the optimal double-exchange conducting regime along z: in one dimension this is the only possible metallic case. In cases (b), (c), and (d) a polaron with magnetization $M=3\mu_B$ is trapped in a 3-atom Cu-O-Cu space region, so that only hopping conduction is possible. The actual DOS of arrays (b) and (c), calculated using 64-atom supercells, are reported in Fig. 6. In both cases the doping carriers are confined within a single Cu-

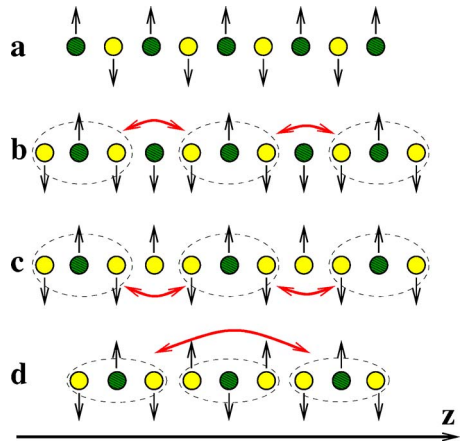

FIG. 5. (Color online) Pictorial representation of the hopping conductivity model proposed in the paper for various Mn distributions. Green (dark gray) and yellow (light gray) balls are Mn and Cu, respectively. (a) Double-exchange metallic-like regime; (b) double-exchange channels are locked by unfavorable spin ordering, thus only hopping conduction is possible. Dashed lines enclose a 3-atom polaron with $M=3\mu_B$. (c) and (d): same as (b) but for lower Mn concentrations.

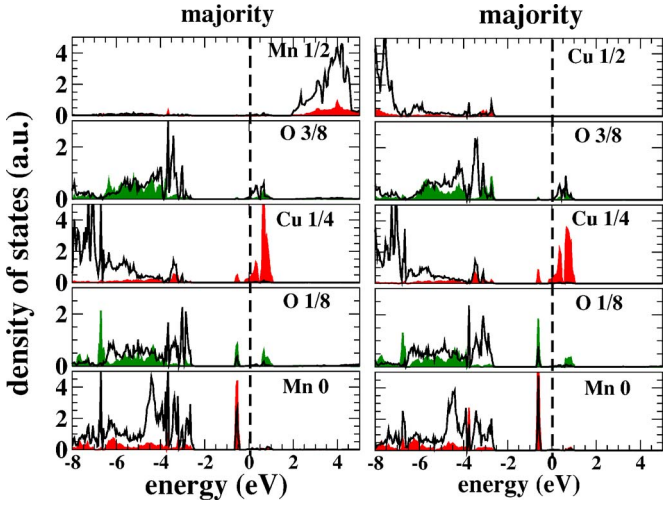

FIG. 6. (Color online) Orbital-resolved DOS for Mn-doping CuO in two different Mn configurations corresponding to (b) (left-hand panel) and (c) (right-hand panel) arrays of Fig. 5. Line code is as in Fig. 4.

Mn-Cu segment parallel to z. The DOS shows a narrower ($\sim$0.24 eV wide) Mn $d^{\uparrow}_{z^2}$ peak and a larger energy gap ($\sim$0.2 eV) compared to case (a), whose DOS is shown in Fig. 4, left-hand panel.

To make it energetically plausible that the Mn:CuO ground state can be FM we calculated the Mn-Mn exchange-interaction parameters for a simplified Mn distribution, with two Mn set apart at two Cu-Cu nearest-neighbor distances (corresponding, on average, to $x=12.5\%$). We indeed obtain ferromagnetic couplings $J_z=28$ meV and $J_x=22$ meV along the $\hat{z}$ and $\hat{x}$ directions, respectively. However, here we are only considering interactions of Mn in the same Cu spin sublattice, while a reliable estimate of average magnetic moments and T_c would require a full calculation within all the possible Mn configurations of Mn-Mn inter- and intra-sublattice interactions, as well as the evaluation of disorder and entropy contributions. Furthermore, the rather low T_c and the magnetic moment of $1.5\mu_B$ found experimentally suggest a rather close competition between FM and AFM Mn-Mn interactions; long-distance Mn-Mn interactions may therefore be essential for a quantitative prediction of the energetics, and as such all the more unreachable by present-day first-principles calculations.

In summary, we have investigated, for the first time by first-principles calculations, the basic chemistry of Mn-doped CuO, showing that substitutional Mn in CuO induces shallow donors with ionization energies ranging between 0.05 and 0.25 eV, depending on the specific Mn spin ordering. We explain the metal-insulating and FM-PM transition in terms of an unconventional double-exchange mechanism, capable of activating electronic conduction in connection with an overall FM ordering. This double exchange is doping induced and long ranged; at variance with the usual double-exchange seen in CMR manganites, it can work even at low doping concentrations. Mn-doped CuO suggests the possibility of producing ferromagnetic insulating cuprates, and can be a useful point of reference for further studies. We emphasize that the qualitative conclusions reached here are arguably valid for the whole cuprate family, which shares with CuO the dominant one-directional AFM coupling, and general similarities of the band structure.

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