Interplay and competition of magnetism and ferroelectricity in cupric oxide

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Cupric oxide is multiferroic at unusually high temperatures. From density functional calculations we find that the low-T magnetic phase is paraelectric and the higher-T one ferroelectric, with a size and direction of polarization in good agreement with experiment. By mapping the *ab initio* results onto an effective spin model we find that in the high-T magnetic state non-collinearity and inversion symmetry breaking stabilize each other via the Dzyaloshinskii Moriya interaction. This leads to a novel mechanism for multiferroicity, with the particular property that non-magnetic impurities enhance the effect.

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In multiferroics the simultaneous presence of electric and magnetic ordering is particularly intriguing when the magnetic ordering triggers the ferroelectric polarization, as was observed for the first time by Kimura and coworkers in $TbMnO_3$ [1]. Since then, several so-called type-II multiferroics [2] have been discovered in which *magnetic order causes ferroelectric order*. Although plenty of potential applications are envisioned, in random access memory devices for instance, the small values of the induced polarization as well as a low transition temperature in most type-II multiferroics hinder practical applications. The very recent discovery that cupric oxide (CuO) is a type-II multiferroic with a high antiferromagnetic transition temperature T_N of 230 K changed this situation drastically and opened the perspective to room-temperature multiferroicity [3, 4]. The discovery is even more intriguing considering that CuO is closely related to the family of copper-oxide based materials displaying High-T_c superconductivity.

From a theoretical point of view, it is not very clear yet how multiferroicity appears in CuO from a microscopic perspective, particularly because its type-II behavior is apparently not a groundstate property: it is only present at finite temperatures, between ∼210 and 230 K, disappearing above and below. Here we clarify the mechanism for the observed finite temperature multiferroicity in CuO.

To elucidate this point we have investigated the electronic structure of CuO with density functional calculations for the different magnetically ordered phases. These calculations confirm, as we will see, the presence of magnetically induced ferroelectricity in CuO and we find a polarization that agrees with experiment. A subsequent investigation of the stability of magnetic phases at finite temperatures using classical Monte-Carlo simulations shows that the experimental ground state at low temperature can be well understood by mapping the magnetic interactions onto a Heisenberg Hamiltonian with *ab initio* derived exchange constants. The microscopic model shows that multiferroicity in CuO arises from a new mechanism in which spin canting and polarization mutually stabilize each other, crucially involving the Dzyaloshinskii-Moriya interaction.

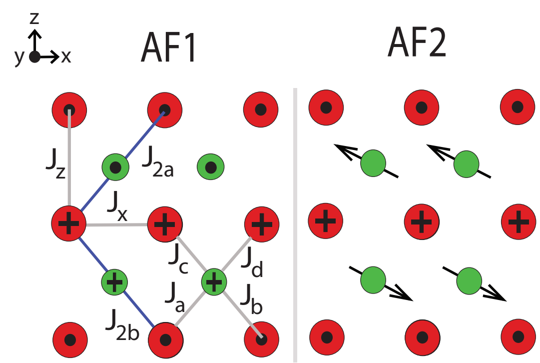

FIG. 1: (Color online) Schematic view of AF1 and AF2 magnetic states. Cu ions belong to different plane along $y = 0$ (red/big circle, termed even plane in the text) and $y = 1/2$ (green/small circle, termed odd plane in the text). Dot (cross) refers to spin pointing along the positive (negative) y axis. We have neglected the tilting of the monoclinic structure.

We have studied the electronic structure of CuO by performing calculations using the PAW method as implemented in VASP [5]. To take into account the Coulomb interactions between the Cu $3d$ electrons we employ SGGA+U [6–8] and hybrid functional (HSE) [9] schemes for $U_{eff} = U - J_H$ ranging between 3.5 and 7.5 eV, and fraction of Hartree-Fock (HF) exchange (α) between 0.15 and 0.25. In the experimental structure of CuO (C2/c space group No. 15), Cu ions are arranged as corner and edge-sharing square-planar CuO_4s, in which Cu ions lie in a plane formed by oxygen neighbors forming

	J_z	J_x	J_{2a}	J_{2b}	$J_a = J_d$	$J_b = J_c$	J_y
U_{eff}=5.5	107.76	-15.76	6.89	16.18	7.98	15.82	-21.48
α=0.15	120.42	-24.33	4.99	14.27	4.19	13.17	-23.02

TABLE I: Exchange coupling parameters (meV) calculated within SGGA+U and hybrid functional calculations. The structure allows for $J_a \neq J_d$ and $J_b \neq J_c$ but we take them equal for simplicity. This is inessential for our conclusions. We keep the same notation of reference [16].

O-centered tetrahedra [10]. The low temperature magnetic structure (AF1) with Cu magnetic moments aligned collinearly along the y axis and ordered antiferromagnetically along z and ferromagnetically along the x direction (see Fig. 1 (a)) is found to be the ground state in agreement with the neutron diffraction study[11] and other ab-inito calculations [16, 17]. The high Neel temperature suggests the presence of strong exchange interactions [12] and the quasi-one-dimensional antiferromagnetism of CuO is suggested by experiments[13, 14]. The energy gap of 1.4 eV [15] is recovered using U_{eff}=5.5 eV or an exact-exchange fraction as $\alpha = 0.15$ [16]. The Cu and O spin moments are 0.6 μ_B and 0.1 μ_B respectively, in good agreement with the results of neutron diffraction experiments [11].

We analyze the exchange interactions using the Heisenberg Hamiltonian $H_M = \sum_{ij} J_{ij}\, \mathbf{S}_i \cdot \mathbf{S}_j$. The parameters J_{ij}, reported in Table I, are calculated from total energy differences of different magnetic configurations within a unit cell containing 32 Cu sites. The strongest interaction is $J_z \sim 100$ meV in good agreement with the optical experiments of Ref. [14]. The magnetic structure within a constant-y plane can be viewed as chains running along z with dominant interaction J_z and moderate interchain interactions J_x, J_{2a} and J_{2b}. Hereafter we will term the planes with $2y$ odd (even) as odd (even) planes. J_y couples planes of the same kind (separated by $\Delta y = \pm 1$). Finally J_a, J_b, J_c and J_d couple nearest neighbor (nn) planes of different kind.

Remarkably the classical coupling energy among unlike planes vanishes when the chains are assumed to be aligned AF. Indeed J_y favors a ferromagnetic staking of planes of the same kind. A close examination of the structure shows that the pattern of couplings among the plane at $y = 1/2$ and the plane at $y = 1$ is identical to the one of Fig. 1 but with the exchanges $J_a \leftrightarrow J_d$ and $J_c \leftrightarrow J_b$. It is easy to check that this symmetry makes the classical energy of the model independent of the angle between the magnetization in even and odd planes, and the ground state is infinitely degenerate. This degeneracy will play an important role for the multiferroic mechanism. Within the DFT calculations including spin-orbit (SO) coupling we find that AF1 is the ground state with the easy-axis along y. The energy difference of 2.2 meV per Cu atom between AF1 and AF2 can be attributed to small anisotropies and charge and lattice relaxation, and can be modelled via biquadratic or anisotropic-exchange terms in the spin Hamiltonian.

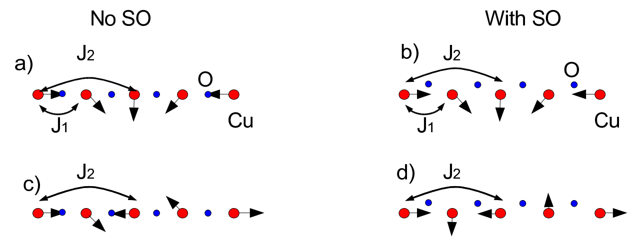

FIG. 2: (Color online) (a) Schematic mechanism of multiferroic effect in 1D. a) and b) standard cycloid scenario as in Ref. [18]. In c) $J_1 = 0$ and the system separates into two interpenetrating sublattices. The angle between the magnetic moments of the different sublattices is undefined. d) SO interaction stabilizes both the angle and the finite polarization.

In CuO, an incommensurate phase (AF2) with magnetic modulation vector Q=(0.506, 0, 0.517) has been reported [3, 11, 12]: the effect of increasing temperature T is to order spins along y axis and in xz plane as shown schematically in Fig. 1 (b). Experimentally, a small electric polarization P ($\sim$0.01 $\mu C/cm^2$) is found along y axis[3].

Using the commensurate state closest to the incommensurate spiral, schematically shown in Fig. 1 (labeled AF2), and taking into account spin-orbit coupling we evaluate the electronic contribution to the polarization P using the Berry phase (BP) method [20] and we obtain $P_{AF2} \sim 0.02$ $\mu C/cm^2$ along y axis, in overall good agreement with the experimental value. The perpendicular configuration ensures that AF2 state has maximal spin current $\mathbf{j}_{1,2} \equiv \langle \mathbf{S}_1 \times \mathbf{S}_2 \rangle$ among nn planes of different kind. This is what one expect on the basis of the standard cycloid scenario[4, 18, 19] causing the multiferroicity. However, we will show that in CuO the situation is subtly different – in fact here the mechanism for multiferrocicty is new. The maximum spin current appears naturally from this new scenario.

In order to explain the difference and similarities with the standard cycloid scenario we illustrate the two mechanisms in the one-dimensional (1D) model [18] depicted in Fig. 2. Consider an hypothetical Cu-O chain with Hamiltonian $H = H_M + H_{DM} + H_E$. For the purely magnetic part H_M we assume there is a nearest neighbor AF interaction J_1 and a next nearest neighbor AF interaction J_2. The Dzyaloshinskii-Moriya (DM) interaction [22, 23] and elastic contributions read:

$$H_{DM} = \sum_n \lambda(\mathbf{u}_{n+1/2} \times \mathbf{e}_{n,n+1}).(\mathbf{S}_n \times \mathbf{S}_{n+1}), \quad (1)$$

$$H_E = \sum_n \frac{k}{2} |\mathbf{u}_{n+1/2}|^2.$$

Here $\mathbf{u}$ are the oxygen displacements and $\mathbf{e}_{n,n+1}$ is a unit vector joining nearest neighbors atoms. Treating the spin classically for $J_2 > J_1/4$ one finds that the ground state is a spiral with a pitch angle given by $\cos\theta = -J_1/4J_2$ and a finite spin current $\mathbf{j} = \langle \mathbf{S}_n \times \mathbf{S}_{n+1} \rangle$. SO interaction is not necessary to stabilize this state [Fig. 2(a)]. In the presence of SO coupling the free energy per site due to uniform O's displacements u, perpendicular to the chain and to $\mathbf{j}$ is given by $\delta F_{DM} = \lambda u j + \frac{k}{2}u^2$. Minimizing one obtains a polarization $P = \delta q u = -\delta q j/k$ [Fig. 2(b)].

In the case $J_1 = 0$ [(c) and (d)] the system separates into two interpenetrating sublattices analogous to the odd and even planes of CuO. Without SO coupling the angle between the magnetic moments of the different sublattices is arbitrary and the ground state is infinitely degenerate (c). This degeneracy can be broken by the DM interaction. The free energy per site can be expanded as: $\delta F = \frac{1}{2}\chi_{jj}^{-1} j^2 + \lambda u j + \frac{k}{2}u^2$. Here χ_{jj} is the spin current susceptibility defined for H_M alone. δF has to be minimized with respect to *both* j and u since H_M does not determine the spin current. Minimizing with respect to u one obtains $\delta F = \frac{1}{2}(\chi_{jj}^{-1} - \lambda^2/k) j^2$. When

$$\chi_{jj}\frac{\lambda^2}{k} > 1 \tag{2}$$

it is convenient to maximize the spin current $j \propto \sin\phi$ where ϕ is the angle between the magnetization in different sublattices. Thus the energy acquires a term $\delta F \propto -\sin^2\phi$ which favors perpendicular magnetic moments on nearest neighbor sites [Fig. 2(d)]. At the same time this gives rise to a finite polarization as for the cyclic mechanism. Notice however that the spontaneous breaking of symmetry and the spin canting drive each other unlike the cyclic scenario where the spin canting is driven by the magnetic Hamiltonian. From Eq. (2) we see that the multiferroic effect is favored by strong SO coupling, soft lattices and a large spin current susceptibility. This effect competes with thermal and quantum fluctuation which favor a collinear configuration, according to the order by disorder mechanism, and tend to suppress χ_{jj}[21]. Also coupling to other lattice distortions will favor a collinear state and suppress χ_{jj}.

The 1D mechanism can be easily generalized to CuO by replacing each magnetic site in Fig. 2 by a constant-y plane of Cu atoms shown in Fig. 1. In order to estimate χ_{jj} for the CuO structures we perform classical Monte-Carlo simulations on the following 3D spin Hamiltonian:

$$H = H_M + \sum_{(ij)} \mathbf{D}\cdot\mathbf{j}_{i,j} \ . \tag{3}$$

Here, the first term is the magnetic Hamiltonian of CuO and the second term describes the linear coupling of the spin current among unlike planes to an external field $\mathbf{D}$. Summation index (ij) represents inter-plane nearest neighbor bonds indicated as J_a, J_b, J_c and J_d in Fig. 1. We take $\mathbf{D}$ directed along x-axis for all pairs in the unit cell. Rather than measuring the spin current we compute the sum of the relevant components which is proportional to the polarization, $\mathbf{p} = \sum \mathbf{e}_{ij} \times \langle \mathbf{S}_i \times \mathbf{S}_j \rangle$. The desired susceptibility is given by $\chi_{jj} = p_y/D_x$ in the limit of vanishing D_x. When χ_{jj} is large and the condition Eq. (2) is satisfied a spontaneous D and polarization will stabilize each other as explained above. Notice that D breaks inversion symmetry in the system whereas the high temperature structure of CuO has inversion so there is no "permanent" D in the high temperature phase. Of course there will be DM couplings at high-temperatures in the CuO structure but those preserve inversion symmetry and are not related to the appearance of the polarization. For simplicity we neglect these latter couplings.

To lift the degeneracy between AF1 and AF2 in favor of the former we introduce a weak anisotropy in the Heisenberg exchange term. This is done by replacing $J_z \mathbf{S}_i \cdot \mathbf{S}_j$ by $J_z(S_i^x S_j^x + (1+\gamma)S_i^y S_j^y + S_i^z S_j^z)$ in H_M. Other terms like the biquadratic contribution are expected to have a similar effect. We use $\gamma = 0.02$ which translates into an anisotropy energy of $\sim \gamma J_z = 2.15$ meV.

We employ a classical Monte Carlo (MC) technique to explore the competition between different magnetic states at zero and finite temperatures. Given that the CuO is a system with spin 1/2, the quantum effects in this system are unavoidable. Nevertheless the interesting transitions occur at high temperatures where it is safe to assume a classical renormalized regime[24]. In order to simplify the Monte Carlo computation we consider only 4 possible states at 90^0 for the spin variables. Figure 3(a) shows the phased diagram in the T-D plane. In the absence of the external field D, the system undergoes a transition from a paramagnetic (PM) to an AF1 state with $T_N \sim 250K$. Presence of a small D opens a narrow window near T_N where AF2 is stabilized. A large external field eventually drives the groundststate to be AF2 for $D = \gamma J_z/8 \sim 0.27$ meV . The inset of Fig. 3(b) shows the susceptibility computed as the ratio p_y/D_x for small D_x. Remarkably a strong peak appears around the PM to AF1 transition which will favor a spontaneous polarization of the system.

In order to check the mechanism we again consider the 3D CuO model with the terms H_{DM} and H_E analogous to the 1D model. We can eliminate the lattice displacements from the problem which lead to a quadratic effective interaction among spin currents so $H_{DM} + H_E$ is replaced by $H_{DME} = -(\lambda^2/2k)\sum_{(ij)}(\mathbf{S}_i \times \mathbf{S}_j)^2$. Fig. 3(c) shows the spontaneous polarization p as a function of temperature for the model defined by $H = H_M + H_{DME}$. As expected one finds that, close to the PM to AF1 transition, H_{DME} induces a phase with broken inversion symmetry and a spontaneous polarization as seen in the experiment. The peak in the polarization is very similar to the experimental observations of a finite electrical polarization between 230K and 213K [3]. If the parameter $\lambda^2/(2k)$ is made too large (> 1 meV) the ferroelectric

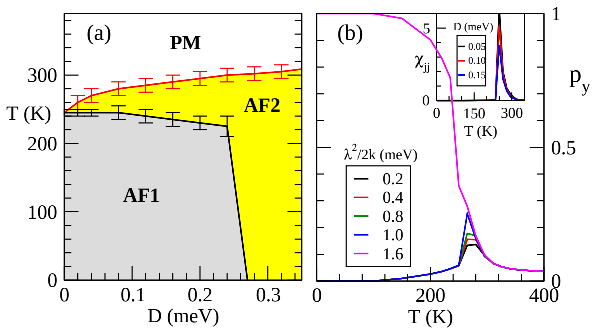

FIG. 3: (Color online) (a) Phase diagram of the magnetic model of CuO with an external field coupling linearly with the spin current. (b) Polarization of CuO model with the addition of a biquadratic spin-current term obtained eliminating the lattice degrees of freedom in the DM coupling. Curves are labeled by the value of $\lambda^2/(2k)$. The inset shows the susceptibility computed as p_y/D. Notice that within linear response we have to take the limit $D \to 0$ which corresponds to the upper curves.

phase extends to zero temperature.

According to our Monte Carlo simulations the main reason for the spontaneous polarization is a strongly enhanced spin-current susceptibility close to the AF1-PM transition. While there is of course a divergent staggered susceptibility when approaching the AF1-PM phase transition the enhancement of the unrelated spin-current susceptibility is not trivial. To some extent this is similar to the physics of quantum critical points relevant to heavy fermion compounds[25]. There close to the quantum transition between a disordered an a magnetically order state a different order appears (superconductivity) which can be attributed to an enhanced pairing susceptibility. The peak of the polarization close to the magnetic transition in the present case is analogous to the enhanced pairing around a QCP.

As mentioned above thermal and quantum fluctuations tend to suppress χ_{jj} and the polarization. On the other hand disorder on the magnitude of the magnetic moments will enhance the tendency to have perpendicular orientations among the sublattices[21]. Non-magnetic impurities, vacancies or magnetic impurities with a different spin will lead to this effect. This opens a new way to engineer high-Tc multiferroic materials. Impurities on CuO can enhance the polarization. In addition search for other materials where two subsystems have negligible interactions by symmetry but strong interactions within one subsystem can open the way to discover new manipulable multiferroics.

To summarize, our density functional calculations confirm the magnetically induced ferroelectricity in CuO with polarization in agreement with experiments. By combining Monte-Carlo analysis with the exchange constants derived by *ab initio* simulations we also confirm the high T_N of this compound. We explain the multiferroic effect as arising from a new mechanism in which spin canting and polarization mutually stabilize each other with a crucial role of Dzyaloshinskii-Moriya interaction. In this new scenario the multiferroicity can be engineered by impurities, opening new routes to material design of multiferroics.

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During the completion of this manuscript we became aware of Ref. [26], presenting results from *ab initio* calculations similar to ours. The mechanism for multiferroicity that we present here, however, is very different from the findings in Ref. [26].

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