High-$T_c$ ferroelectricity emerging from magnetic degeneracy 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 show that the system has a manifold of almost degenerate ground states. 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 multiferros 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 ThMnO$_3$ [1]. Since then, several so-called type-II multiferros [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 multiferros 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, the microscopic mechanism of multiferroicity in CuO is not clear yet, particularly because its type-II behavior is apparently not a groundstate property: it is only present at finite temperatures, between $\sim 210$ 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 the ground state is almost degenerate so phase selection occurs through small terms. We show that multiferroicity in CuO arises from a new mechanism in which spin canting and polarization mutually stabilize each other, crucially involving phase selection through the Dzyaloshinskii-Moriya interaction.

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 ($\alpha$) 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$_4$S, in which Cu ions lie in a plane formed by oxygen neighbors forming O-centered tetrahedra [10]. The low temperature magnetic structure (AF1) with Cu magnetic moments aligned collinearly along the $y$ axis and ordered antiferromagnet-
TABLE I: Exchange coupling parameters (meV) calculated within SGGA+U and hybrid functional calculations. The structure allows for $J_x \neq J_y$ and $J_d \neq J_c$, but we take them equal for simplicity. This is essential for our conclusions. We keep the same notation of reference [18].

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

On a first sight one would expect that the incommensurate spiral is crucial to obtain a finite polarization, as in the standard cycloid scenario [4, 20, 21]. However the commensurate state closest to the incommensurate spiral, labeled AF2 in Fig. 1 has spin canting which can produce a finite polarization. Indeed, taking into account spin-orbit coupling, we evaluate the electronic contribution to the polarization $P$ using the Berry phase (BP) method [22] on the commensurate AF2 state and we obtain $P_{AF2} \sim 0.02 \mu C/cm^2$ along $y$ axis, in overall good agreement with the experimental value. Thus the incommensurate state is not crucial but canting clearly is. The perpendicular configuration ensures that AF2 state has maximal spin current $j_{1,2} = \langle S_1 \times S_2 \rangle$ among nn planes of different kind. We will show that this is a fingerprint of the proposed scenario.

While canting and spin orbit coupling are standard ingredients of the cycloid scenario causing the multiferroicity [4, 20, 21], the situation in CuO is subtly different. In order to explain the difference and similarities we illustrate the two mechanisms in the one-dimensional (1D) model [23] 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 [24, 25] and elastic contributions read:

$$H_{DM} = \sum_n \lambda (u_{n+1/2} \times e_{n,n+1}) \cdot (S_n \times S_{n+1}), \quad (1)$$

$$H_E = \sum_n \frac{k}{2} |u_{n+1/2}|^2.$$
form classical Monte-Carlo simulations on the following plane of Cu atoms shown in Fig. 1.

by replacing each magnetic site in Fig. 2 by a constant-y pressure to the order by disorder mechanism, and tend to suppression which favor a collinear configuration, according to the 1D model. This is done by replacing $J_i \mathbf{S}_i \cdot \mathbf{S}_j$ by $J_z \mathbf{S}_i^z \mathbf{S}_j^z + (1 + \gamma) \mathbf{S}_i^y \mathbf{S}_j^y + \mathbf{S}_i^z \mathbf{S}_j^z$ 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 $\sim 2.15$ 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 \[26\]. In order to simplify the Monte Carlo computation we consider only 4 possible states at $90^\circ$ for the spin variables. Figure 3(a) shows the phase 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 $T_N \sim 250$K. Presence of a small $D$ opens a narrow window near $T_N$ where AF2 is stabilized. A large external field eventually drives the groundstate 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 $p_y/D_y$ for small $D_y$. 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. Assuming classical lattice displacements they can be integrated out of the partition function leading to a quadratic effective interaction among spin currents so $H_{DM} + H_E$ is replaced by $H_{DME} = -\langle J_z^2/2\rangle \sum_{i,j} (\mathbf{S}_i \times \mathbf{S}_j)^2$. 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 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. This is similar to the physics of quantum critical points relevant to heavy fermion compounds [27] where 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.

As mentioned above thermal and quantum fluctuations tend to suppress $\chi_{jj}$ 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 and enhance the polarization [28] which opens a new way to engineer high-$T_c$ multiferroic materials. Non-magnetic impurities, vacancies or magnetic impurities with a different spin will lead to this effect. In addition our results suggest to search for other materials where two subsystems have negligible interactions by symmetry but strong interactions within one subsystem as a recipe 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. Our results open new routes for the material design of multiferroics.

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During the completion of this manuscript we became aware of Ref. [28], 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. [28].

![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 $p_y/D$. Within linear response one should take the limit $D \rightarrow 0$ corresponding to the upper curves.](image-url)