Tuning order-by-disorder multiferroicity in CuO by doping

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The high Curie temperature multiferroic compound, CuO, has a quasidegenerate magnetic ground state that makes it prone to manipulation by the so called “order-by-disorder” mechanism. First principle computations supplemented with Monte Carlo simulations and experiments show that isovalent doping allows to stabilize the multiferroic phase in non-ferroelectric regions of the pristine material phase-diagram with experiments reaching a 250% widening of the ferroelectric temperature window with 5% of Zn doping. Our results allow to validate the importance of a quasidegenerate ground state on promoting multiferroicity on CuO at high temperatures and open a path to the material engineering of new multiferroic materials.

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I. INTRODUCTION

The prospect of magnetoelectric coupling in spintronic devices, enabling the magnetic ordering to be controlled by an electric field and the ferroelectric ordering to be controlled by a magnetic field, has been a strong driving force in the research on multiferroic materials [1]. This class of materials is characterized by the simultaneous presence of two or more order parameters of different nature (like electric and magnetic). The high transition temperatures and the unusual sequence of the magnetic and multiferroic phases [2] have been strong motivations for experimental and theoretical investigations on CuO. Recent experiments report electric field control of the ferroelectric moment. Indeed, the correct value of the transition itself is not essential to explain the magnitude of the spin alignment, the spins form a long wavelength spiral [6–8].

Cupric oxide crystallizes in a monoclinic structure with space group C2/c (No 15). The only point group symmetry is inversion. The lattice can be divided into two interpenetrating sublattices, one residing on planes with integer Wyckoff position along the [010]-direction (z-axis), hereafter termed “even planes” and one residing on planes with half-integer Wyckoff position along y, termed “odd planes” (Fig. 1). The dominant magnetic interaction $J_z \sim 100$ meV produces an antiferromagnetic alignment of spins within one sublattice along [101] while other weaker interactions tend to align same sublattice spins ferromagnetically in the [101]-direction and y-direction. The ground state (AF1) spin configuration is a collinear ordering with the y-direction as easy axis and ordering vector $q_{AF1} = (0.5, 0, -0.5)$ (r.l.u.). The multiferroic phase, AF2, occurs above the first order phase transition at $T_N1 = 213$ K and ranges up to a subsequent weakly first order phase transition at $T_N2 = 230$ K. The magnetic structure within one sublattice is similar as in the AF1 phase, but the spins on nearest neighbor planes are nearly perpendicular to each other. On top of this, the spins form a long wavelength spiral [6–8].

At the classical Heisenberg level, neglecting the small incommensuration, the Weiss field acting on spins of one sublattice due to the spins in the other sublattice cancel [Fig. 1(a)], leading to a degenerate state with an undefined angle between the spins on different sublattices [9]. Thus state selection occurs through small perturbations [9, 10] like magnetic anisotropies, biquadratic terms in the Hamiltonian [11], the order-by-disorder mechanism [12] and competing interactions [13]. Monte Carlo computations have shown that presence of the spiral is essential to stabilize the nearly perpendicular configuration of spins in different sublattices [10] as proposed by Yablonski long ago [12].

The aim of the present study is to explore how the multiferroic properties of CuO can be tuned by isovalent doping in the Cu site (i.e. Cu$_{1-x}$M$_x$O with M a metal ion). Henley’s arguments [12] suggest that impurities will stabilize the multiferroic AF2 phase as schematically shown in Fig. 1(b) (hereafter “first-rank Henley effect”). In the presence of an impurity (non-magnetic in the ex-
ample) inversion symmetry is locally broken (dashed vs. full orange bond) and the cancellation of the Weiss field at atom 1 is no longer valid. Random fields appear which are parallel to the spins on even planes and act on the spins in odd planes (and vice versa). This leads to a stabilization of the AF2 phase by a mechanism analogous to the one by which the spins of an ordinary AF point in a direction approximately perpendicular to an external field \[ \mathbf{H}_{\text{ext}} + \mathbf{H}_{\text{bg}} + \mathbf{H}_{\text{ani}} \]

Before approaching the doped compound, an accurate description of the undoped compound was desired as a reference. Therefore a parametrization to a magnetic Hamiltonian in the undoped phase has been performed which is treated semiclassically at finite temperatures in Monte Carlo simulations. This extends previous computations \[ J_{ij} = J_{ij}^0 + \frac{1}{2} K_{ij} (S_i \cdot S_j)^2 + \frac{1}{2} \sum_{i,j} S_i J_{ij}^\text{ani} S_j \]

II. UNDOPED CuO

A. Model Hamiltonian

Total energies were calculated with density functional theory (DFT) for 39 collinear spin configurations, from which a magnetic Hamiltonian,

\[ \mathcal{H}_M = \mathcal{H}_{\text{exch}} + \mathcal{H}_{\text{bg}} + \mathcal{H}_{\text{ani}} \]

\[ J_{ij} = J_{ij}^0 + \frac{1}{2} K_{ij} (S_i \cdot S_j)^2 + \frac{1}{2} \sum_{i,j} S_i J_{ij}^\text{ani} S_j \]

was parametrized and expressed in terms of classical spin variables \( S_i \) of length 1/2.

For the DFT calculations we have used the VASP software \[ 17, 18 \] with a GGA+U functional \[ 19 \] in the PBE parametrization \[ 20, 21 \]. The calculations were performed for a 64 atom cell with the lattice vectors \( a' = 2a, b' = 2b, c' = 2c \) with the experimental \[ 22 \] atomic positions and lattice vectors \( a = (4.6837, 0, 0), b = (0, 3.4226, 0) \) and \( c = (0.85005, 0, 5.0579) \). Convergence was obtained for a cutoff of 400 eV for the augmented plane wave basis set and a \( 2 \times 2 \times 2 \) \( \Gamma \)-centered \( k \)

FIG. 1. Spheres represent Cu atoms in even planes (orange), odd planes (red) or impurities (black). Brown arrows represent spins. (a), Low-temperature AF1 state. We also show some of the exchange interactions considered. \( J_a, J_b, J_c, J_d \) connect sites defined as “first neighbors”. Bonds of the same color are equivalent and have the same exchange. Because the Cu ion is at an inversion center in the undistorted structure the Weiss field due to the orange Cu’s on the red Cu cancels (and vice versa). More interactions are shown on Fig. 2. (b) First-rank Henley effect. In the presence of an impurity (non-magnetic in the example) inversion symmetry is locally broken (dashed vs. full orange bond) and the cancellation of the Weiss field at atom 1 is no longer valid. (c) Second-rank Henley effect. If the wave-function at atom 1 is perturbed due to the impurity, all the intersublattice interactions indicated by thick bonds get affected. Weiss fields parallel to the odd spin magnetization appear also in all second neighbors of the impurity (defined as the first neighbors of the first neighbors excluding the impurity, e.g. atom 2) leading again to the stabilization of AF2.

In order to explore the relevance of quenched disorder effects on CuO we first use first-principle computations to derive a generalized Heisenberg model of the magnetic degrees of freedom (Sec. III A) and use classical Monte Carlo computations to show that it can describe correctly the undoped phase (Sec. III B) including the subtle incommensurate spiral. This is supplemented by an analytical computation of the pitch of the spiral (Appendix A). Then we use again first principle computations to study systematically the effects of different impurities on stabilizing the multiferroic phase (Sec. III A). Monte Carlo simulations confirm that indeed impurities stabilize the ferroelectric phase respect to the collinear magnetic phase (Sec. III B). Finally experiments using Zn and Co as dopants confirm the theory prediction (Sec. III C). We conclude in Sec. IV.
The system for the configuration where computed not including spin orbit change interaction. The total energies of the 39 spin that positive numbers refer to an antiferromagnetic ex-
solution was obtained minimizing the least mean-square
6.166 Å

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even and odd
of 146
large strength is explained by the Cu-O-Cu bond angle
lizes the AFM chains running along [10 \bar{1}]
neighbor couplings
Bonds of the same color are equivalent. Notice that the ori-
FIG. 2. The exchange couplings used in the calculations.
image
point mesh. For the Cu atoms the Hubbard constant
$U_{\text{eff}} = 5.5 \text{ eV}$ was used. This resulted in a magnetic
moment of $\mu_{\text{Cu}} = 0.62 \mu_B$, corresponding well to the
experimental value of 0.65 $\mu_B$.
A set of 10 effective $J_{ij}$ ranging up to a distance of
6.166 Å were considered (See Table I and Fig. 2). Note
that positive numbers refer to an antiferromagnetic ex-
change interaction. The total energies of the 39 spin
configuration where computed not including spin orbit
coupling (SOC), rendering an overdetermined equation
system for the $J_{ij}$. For each configuration we defined
the error as the difference in energy between the result
of the model and the DFT computation. An optimum
solution was obtained minimizing the least mean-square
error with respect to the exchange couplings $J_{ij}$.

The strongest coupling is $J_z$ (c.f. Fig. 2) and stabi-
lizes the AFM chains running along [101] direction. The
large strength is explained by the Cu-O-Cu bond angle
of 146° close to 180°. For $J_x$ the corresponding bond
angle is 109°. The closeness to 90° leads to a FM cou-
pling according to Goodenough-Kanamori rules $^{22,24}$. Along
the $y$-direction a coupling $J_y$ was considered to
account for the effective exchange between Cu atoms on
planes separated by $\Delta y = \pm 1$, i.e. a coupling between
neighboring even planes or neighboring odd planes.

The four couplings with the shortest distances link the
even and odd $y$-planes. The linked atoms are defined
"nearest neighbors" in Fig. 1. Even though the $J_a$ and
$J_d$ couplings have the same distance, close examination
of the structure shows that they can have different val-
ues. Despite that, in order to simplify the computations,
we assumed the same value $J_a = J_d$. An analytic
computation shows that this approximation does not affect
the pitch of the spiral (see Appendix A).

Within constant $y$-planes the exchange couplings $J_x$, $J_z$, $J_e$, and $J_f$ were considered. Going two steps along $J_a$, $J_b$, $J_c$ and $J_d$ the couplings $J_{a2}$, $J_{b2}$, $J_{c2}$, $J_{d2}$ are
introduced with $J_{b2} = J_{c2}$ by symmetry. $J_{d2}$ was assumed
to be zero after a close examination of potential exchange
paths.

The effective biquadratic $K_{ij} = -K$ interaction acts
among classical neighboring spins on different sublattice
in the spirit of Ref. $^{27}$ and takes into account charge
relaxation effects. Such interaction, which for spin-half
systems has not an obvious quantum counterpart $^{27}$, describes the effect of relaxation of charge degrees of
freedom in stabilizing the AF1 configuration with respect to
the AF2 phase. It was determined by rotating the spins
on the even plane to be perpendicular to the spins on the
odd plane. For simplicity we restrict the biquadratic
interaction to the 8 bonds connecting spins on different
sublattices (the bonds bridged by $J_a$, $J_b$, $J_c$ and $J_d$)
and assume all the bonds have the same constant $K_{ij} = -K$.

When allowing the charge to relax in the DFT calcula-
tions we find that at zero doping the AF2 phase is higher
in energy with respect to the AF1 phase by $\Delta E(0) = 2.15 \text{ meV/Cu}$. The energy splitting is parametrized as
$\Delta E(0) = 4K_S^4$ with $S = 1/2$, for the Cu spin and
$K = 8.61 \text{ meV}$.

Contributions to symmetric anisotropic exchange was
determined by including SOC in the calculation and
from Ref. $^{3}$. We assign anisotropic interactions to the
strongest magnetic bond so that $J_{ani}^{j} \neq 0$ only for bonds
bridged by $J_z$. Inclusion of spin-orbit interaction in the
calculation reveals that the $y$ direction ([010]) acts as an
easy axis with $J_{ani}^{jyz} = 0.145 \text{ meV}$. In order to repro-
cduce correctly the orientation of the spins in the AF2
phase a more precise description of anisotropic exchange
is necessary. Following $^{24}$ we use $J_{ani}^{jyz} = 0.53 J_{ani}^{jyz}$ and
$J_{ani}^{jxz} = 0.42 J_{ani}^{jxz}$ with the Cartesian $x$-axis coinciding
with the [100] direction.

**B. Finite temperature simulations**

We have performed Monte Carlo Metropolis (MC) sim-
ulations of the above Hamiltonian. To improve the con-
vergence and determine accurately the transitions tem-
peratures the parallel tempering scheme $^{28}$ was used.
Cell size for the phase diagram was chosen not too large
to avoid the exponential critical slowing down typical
of first-order phase transitions (see Ref. $^{28}$ and Ap-
pendix B). The magnetic ordering has been studied by
computing the static structure factor $S(q)$, calculated as
the Fourier transform of the spatial displaced equal time
spin-spin correlation function

$$S(q) = \frac{1}{2\pi} \int dr \, e^{-i\mathbf{q} \cdot \mathbf{r}} \langle \mathbf{S}(\mathbf{r}) \cdot \mathbf{S}(\mathbf{r}') \rangle.$$  (2)
TABLE I. Heisenberg exchange couplings. Positive numbers refer to an antiferromagnetic exchange interaction. By symmetry $J_0 = J_e$ and $J_{a2} = J_{e2}$. Analyzing the exchange paths we assume $J_{a2} = 0$.

| Label | $J_a$ (meV) | $J_b$ (meV) | $J_c$ (meV) | $J_d$ (meV) | $J_e$ (meV) | $J_f$ (meV) | $J_{a2}$ (meV) | $J_{e2}$ (meV) |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|--------------|--------------|
| Dist (Å) | 2.90 | 3.08 | 2.90 | 3.17 | 3.42 | 3.75 | 4.68 | 5.12 |
| Strength (meV) | 5.83 | -2.04 | 5.83 | -4.24 | -1.90 | 120.00 | -2.61 | 16.10 |

Here $\langle \ldots \rangle$ indicate an average over the N Cu sites in the simulation cell and over time.

The ferroelectric properties of the system were investigated by sampling the average polarization [30]

$$\mathbf{P} = \frac{\gamma}{N} \sum_{(ij)} \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$$

with the sum running over the first neighbors defined in Fig. 1. $\mathbf{e}_{ij}$ is a vector in the direction of the bond and $\gamma = 894 \mu C/m^2$ has been determined by matching the electronic DFT polarization in the AF2 state at $T = 0$ K and without impurities [9].

C. Results

We use the peak value of the structure factor $S(\mathbf{q})$ as a function of momentum as the square of the order parameter for the two magnetic phases. The corresponding momentum is commensurate for the AF1 phase, $\mathbf{q}_{AF1} = (0.5, 0, -0.5)$, and incommensurate for the AF2 phase, $\mathbf{q}_{AF2} = (0.528, 0, -0.472)$ in excellent agreement with the experimental [4] value $\mathbf{q}_{AF2} = (0.506, 0, -0.483)$. A close by value can be obtained analytically providing a stringent test for the model (See Appendix A).

In Fig. 3 we see that a first order transition occurs at $T_{N1} = 165$ K. Above this temperature and below $T_{N2} = 178$ K (determined from the anomaly in the specific heat $C_V$) the incommensurate AF2 phase appears. Above $T_{N2}$ the system becomes paramagnetic. In Refs. 4, 11 an electron-phonon coupling was deemed necessary to stabilize the AF2 phase. With our present, more accurate parameter set and MC simulation, we find that AF2 is stable even without coupling to the lattice, in agreement with Ref. 4, 13. In addition, the temperature dependence of the structure factor is in good agreement with neutron scattering experiments [31].

Between $T_{N1}$ and $T_{N2}$ also the chiral symmetry is spontaneously broken and the system acquires a net polarization due to the inverse Dzyaloshinskii-Moriya mechanism [31] as shown in Fig. 3. While in principle it is possible that the polarization becomes finite above the temperature at which the magnetic ordering sets in, we do not find evidence of such “chiral liquid” phase or the AF3 phase of Ref. 3, although we can not exclude them due to size limitations.

Overall the magnetic phase diagram is in good accord with experiment. We remark that we have not made any fitting of the exchange constants to reproduce the experimental Néel temperatures. Probably our exchange constants are underestimated leading to both $T_{N1}$ and $T_{N2}$ being 23% lower than the experimental values. Qualitatively similar results were obtained using the parameters of Refs. 3 and 15 except that they have stronger frustration leading to spirals with a shorter periodicity.

III. DOPED CuO

A. DFT calculations

As mentioned in Sec. II doping is expected to reduce the energy gap between AF2 and AF1. The magnitude of this effect depends on details such as how much the local interactions are modified by the impurities, their magnetic moment, etc. To estimate these effects we use DFT computations to compute the energy gain of the AF2 phase respect to the AF1 phase due to different dopants. For simplicity we neglect the small incommensurability and spin-orbit coupling. These effects will be restored below. We have replaced up to 3 out of the 32 Cu atoms in the cell with impurities. In the case of magnetic impurities Hubbard constants have been used, with values...
taken from the literature; for Co, $U_{\text{eff}} = 3.3$ eV [32], and for Ni, $U_{\text{eff}} = 7.05$ eV [19]. The resulting magnetic moments [32] reported on the inset of Fig. 4 are in good agreement with published values [33, 34].

As expected, we find that for each of the impurity elements the energy difference per Cu among the two states, $\Delta E$, decreases monotonically with the impurity concentration (c.f. Fig. 4). Up to ~6% doping the decrease in the energy gap is linear. For higher doping the non-linear behavior indicates that impurities start to interact with each other.

In order to understand the energy gain it is useful to separate the energy difference between the two phases in two contributions

$$\Delta E = \Delta E_{\text{bq}} + \Delta E_{\text{Hen}}. \quad (4)$$

The first term is due to the local change of the interactions which contribute to $\Delta E$ in the undoped case. This can be obtained by computing the energy in a configuration in which different sublattice spins in the AF2 phase are constrained to be exactly at right angles. In this case the contribution of classical Heisenberg interactions cancels and only biquadratic and spin-orbit terms contribute. We checked that the latter makes a negligibly doping-dependent contribution (on the order of 2 $\mu$eV at 3% doping) therefore this part of the energy is referred to as “dilution in the biquadratic interaction” ($\Delta E_{\text{bq}}$).

In the case of non-magnetic impurities and assuming that the biquadratic interactions do not change around the impurities one obtains $\Delta E_{\text{bq}}(x) = \Delta E(0)(1 - 2x)$. We find that this formula overestimates the DFT doping induced dilution energy gain for Zn and Mg and works much better for Cd. We attribute this discrepancy to local rearrangements of the biquadratic interactions on the sites neighboring the impurity.

The second term in Eq. (4) is Henley relaxation energy ($\Delta E_{\text{Hen}}$) which is the energy gain obtained from the previous configurations allowing the spins to relax in the transverse direction. The DFT Henley relaxation energy is shown at 6.250% doping by the arrows in Fig. 4 and accounts for around 40% of the gap reduction for Zn and Mg, while it dominates the doping induced energy gain for Cd. As expected, the transverse relaxation is negligible in the AF1 configuration so the effect reported is due to the transverse relaxation of the magnetization in the AF2 configuration.

From a rough estimate, the conventional Henley mechanism which we call “first-rank” [Fig. 1(b)], leads to an energy gain of order $\Delta E_{\text{Hen}} \sim -x J_1^2/J_2 \sim -x 0.09$ meV with $J_1 \sim 3$ meV of the order of the intersublattice exchanges and $J_2 \sim 100$ meV of the order of the intrasublattice exchange. This is much smaller than $\Delta E_{\text{bq}}$. The sizable Henley relaxation found is due to higher-rank Henley effect. Figure 4(c) shows schematically an example of second-rank Henley effect which comes into play to the disturbance of the spin and charge density beyond the first shell of neighbors of the impurity. For the atom labeled 2 the Heisenberg interac-

![FIG. 4. DFT computation of the stabilization of the ferroelectric phase with different impurities. We show the energy difference per Cu atom between the AF1 and the AF2 configurations as a function of doping for different dopants. The arrows show the magnitude of Henley relaxation energy at 6.250% doping for (from left to right) Mg, Zn and Cd. The legend reports the magnetic moment we find at the impurity site in the DFT computations.](image)

**B. Finite temperature simulations**

Since non-magnetic impurities show the largest stabilization effect of the AF2 phase, we concentrate on those. It is expected that the ordering temperature will be determined mainly by the intrasublattice interactions so $T_{N2}$ will be depressed by dilution. On the other hand, once the system orders, the width in temperature of the multiferroic phase will be determined by the relative stability among the phases.

First we analyze first-rank Henley effect alone. For this we simply canceled all interactions connecting the impurity site to the rest of the system. Fig. 5(a) shows the polarization from MC simulations as a function of temperature in the doped (dashed line) and undoped case (blue line). In this case we find that $T_{N1}$ and $T_{N2}$ decrease by the same amount so the temperature width of the AF2 phase remains the same. The decrease in the magnitude of the polarization is due to incoherent canting effects induced by the impurity and the shift to lower temperatures is the expected effect of dilution on the intrasublattice interactions.

Since the first-rank Henley relaxation energy is very small in this system, the fact that the temperature width of the AF1 phase remains constant means that the relative stability among the two phases is not affected by
simply dilution effects. Indeed we have mentioned above that dilution penalizes the AF1 energy by a \((1 - 2x)\) factor. The stability of the AF2 phase is due to Yablonskii’s mechanism (Appendix \(\text{A}\) and Ref. [13]), and it is penalized by the same factor, which is a consequence of the pairwise nature of interactions. Thus the internal energy of both phases is penalized in the same way which leads to a crossing of the free energies at a doping-independent temperature distance from the instability of the paramagnet (roughly \(T_{N2}\)). This delicate balance can be altered by the relaxation energies due to higher-rank Henley effects. To demonstrate this we multiply all four intersublattice exchange couplings on the eight Cu atoms that are nearest neighbors to an impurity by the same factor \(\eta\). These interactions are very small (\(\pm \) a few meV) because the exchange paths form an angle close to 90°. As in the case \([36]\) of CuGeO\(_3\) we expect that even weak perturbations of the electronic orbital overlaps (here due to the presence of the impurities) can result in large relative changes of these intersublattice couplings. Henley effects coming from more distant sites are incorporated for simplicity in an effective way in the single effective changes of these intersublattice couplings. Henley effects coming from more distant sites are incorporated for simplicity in an effective way in the single \(\eta\) parameter. For \(\eta = 3\) one obtains a stabilization of the AF2 due to Henley mechanism comparable with DFT for Zn (i.e. -15 \(\mu\)eV to be compared with -32 \(\mu\)eV in DFT for 3.125% doped Zn). In Fig. (a) we show the polarization for the doped \(\eta = 3\) case (red full line). Even if the extra stabilization energy of AF2 is modest, a large increase on the width of the AF2 phase is observed.

\[\text{FIG. 5.} \quad \text{b-axis electric polarization as a function of temperature. (a) Monte Carlo computations for undoped CuO (blue) and for 3.125\% non-magnetic doping without enhancement of interactions (dashed, red line) and with an enhancement factor } \eta = 3 \text{ (full red line). (b) Experiment using the same protocol as in Ref. [2].}\]

C. Experiments

In order to check the theory experiments have been perform. Single crystals of undoped, Zn-doped, and Co-doped CuO were grown under about 8 atm of pure oxygen by the floating zone technique, following Ref. [37]. The grown crystals were oriented using X-ray diffractometers, and cut into thin plates with the widest faces perpendicular to the \(b\) axis.

For the measurements of pyroelectric current, silver electrodes were vacuum-deposited onto the widest faces of the plate-shaped crystals. The electric polarization along the \(b\) axis was obtained from integration of the pyroelectric current over time. Before the respective measurements, poling electric fields were applied to the crystals at the paramagnetic phase. Then the crystals were cooled to the lower boundary of the AF2 phase. After these procedures, the poling electric fields were removed, and the pyroelectric current was measured during the temperature up and down sweeps as in Ref. [2].

The main experimental result is that the multiferroic window indeed widens with doping. The temperature dependence of the polarization for the doped and undoped compound [Fig. 4(b)] are in good agreement with the theory [Fig. 4(a)]. To the best of our knowledge this is the first verification of Henley’s quenched disorder mechanism at work.
IV. CONCLUSIONS

We have shown theoretically and experimentally that disorder in the form of impurities in CuO can stabilize the ferroelectric phase with respect to the non-ferroelectric collinear magnetic phase. CuO consists of two sublattices with strong intrasublattice interactions and weak intersublattice interactions arranged in such a way that the classical Weiss field of one sublattice on the other cancel. This allows intrasublattice ordering at high temperatures leaving at the same time the possibility to manipulate the relative orientation of the sublattice spins with weak perturbations like a small amount of impurities. This peculiar symmetry and separation of energy scales allows ferroelectricity induced by magnetism at high temperatures as opposed to other frustrated systems which are multiferroic only at very low temperatures \[41\].

Unfortunately impurities affect the intrasublattice interactions which has the unwanted feature to reduce \(T_{N2}\). As mentioned above, in the case of CuO this may be counteracted by chemical pressure.

On a wider perspective we notice that the cancellation of Weiss field is not unique of CuO but can be found in other systems as well \[42\]. Since negative biquadratic terms are the rule (even without invoking quantum and thermal order-by-disorder mechanisms \[12\]), collinear ground states are the most probable outcome. However by the same mechanism shown here, impurities can transform an unsuspected collinear antiferromagnet (possibly using strains and layering to modify the symmetry) into a multiferroic, providing a novel route to search and engineer multiferroics. Particularly interesting in this regard are fcc antiferromagnets \[12\] which also have a quasidegenerate classical ground state as for example MnTe \[43\] or even NiO which has a pristine Néel temperature of 525 K providing a good starting point for engineering of a room temperature multiferroic.

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Appendix A: Stabilization of the AF2 phase by Yablonskii mechanism

As discussed in Sec. II the magnetic structure of CuO can be divided in two sublattices. Within each sublattice spins orient antiferromagnetically in the [10\(\bar{1}\)] direction and ferromagnetically in the \(y\) and [101] directions. Neglecting biquadratic and anisotropic interactions if the spins are collinear within one sublattice, the magnetic ground state is degenerate at the classical level. In this Appendix we show how this degeneracy can be broken by allowing a long wave-length spiral \[13\].

Fig. 7 shows schematically the incommensurate structure present in the AF2 configuration. The experimental periodicity is a factor of 40 longer than what represented. It is easy to check that in the presence of a spiral the spins in the even sublattice produce a Weiss field in the odd sublattice which is perpendicular to the local spin direction in the even sublattice (and vice versa). Thus the long-wave length spiral favors a configuration where locally the spins are nearly perpendicular on different sublattices i.e. the AF2 configuration.

The plane of the spiral is determined by the anisotropies in the system and is defined by the \(b\) axis and a vector \(v\) in the (010) plane. \(v\) is nearly parallel.
FIG. 7. The incommensurate AF2 configuration. Cu ions in an even (odd) plane are represented by orange (red) spheres. Brown arrows represent spins. The pitch of the spiral has been increased by a factor of 40 to allow the visualization of the spin rotations. Q is the ordering wave vector of the spiral distortion.

to the vector Q defined below and shown in Fig. 7. For the present parameter set the direction of v agrees with the experimental one (see below). For the moment we set T = 0 K and neglect the anisotropies taking the direction of v as granted. The spin texture is given by,

$$S(r) = S|\hat{b} \sin(2\pi q_{\text{AF}2} \cdot r) + \hat{v} \cos(2\pi q_{\text{AF}2} \cdot r)|$$  \(A1\)  

with \(q_{\text{AF}2} = q_{\text{AF}1} + Q\). The vector Q is shown schematically in Fig. 7. Notice that the ordering vectors are also in the (010) plane and therefore \(S(r)\) is constant in the b direction.

The Weiss field acting on a spin in one sublattice due to the eight neighboring spins in the other sublattice is,

$$h_1(r) = -2J_a \left[ S \left( r + \frac{a + b}{2} \right) + S \left( r - \frac{a + b}{2} \right) \right]$$  

$$- 2J_c \left[ S \left( r + \frac{c + b}{2} \right) + S \left( r - \frac{c + b}{2} \right) \right]$$  

$$= 4S(r) \left[ J_a \sin(\pi Q \cdot a) - J_c \sin(\pi Q \cdot c) \right]$$  \(A2\)  

where we used the translational invariance of the structure along b and defined \(J_{\theta} = (J_a + J_d)/2\). For small Q the Weiss field is linear in Q producing a linear gain in the energy which renders a commensurate structure with the spins perpendicular among different sublattices unstable to spiral formation. It is convenient to parametrize the ordering wave vector in terms of reciprocal lattice vectors, \(Q = \delta_a a^* + \delta_c c^* = (\delta_a, 0, \delta_c)\) r.l.u. Neglecting the anisotropic contributions but restoring the biquadratic interaction the total energy per Cu ion reads,

$$\frac{E_{\text{AF}2}(Q)}{S^2} = -2J_a \sin(\pi \delta_a) + 2J_c \sin(\pi \delta_c) + J_y + J_c \cos(\pi (\delta_a + \delta_c)) - J_c \cos(\pi (\delta_a - \delta_c)) - (J_c + J_{d2}) \cos(2\pi \delta_a)$$  

$$- (J_f + 2J_{d2}) \cos(2\pi \delta_c) - 2KS^2 [\sin^2(\pi \delta_a) + \sin^2(\pi \delta_c)]$$  \(A3\)

Minimization with respect to the ordering wave-vector can be easily done expanding the energy to second order in Q. One finds \(q_{\text{AF}2} = (0.538, 0, -0.466)\) at \(T = 0\) K for the present parameter set. We have also done a few Monte Carlo runs in cells of size 200 × 4 × 200 to increase the momentum resolution yielding \(q_{\text{AF}2} = (0.530, 0, -0.475)\) for \(T_{N1} < T < T_{N2}\). Both results are close to the experimental wave-vector \([6–8]\) and to the incommensurability in the cells used to determine the whole phase diagram.

Taking the commensurate AF2 state as a reference the energy of the AF2 state is,

$$E_{\text{AF}2}(Q) - E_{\text{AF}2}(Q = 0) = -0.23 \text{ meV},$$  \(A4\)

to be compared with the energy of the AF1 state,

$$E_{\text{AF}1} - E_{\text{AF}2}(Q = 0) = -2.15 \text{ meV}.$$  \(A5\)

Thus one finds that at \(T = 0\) K the AF1 state is the ground state, as found experimentally. Notice that the above energies scale as \(S^2\) for the AF2 state and as \(S^4\) for the AF1. At finite temperatures these energies are suppressed in modulus by factors of the form \(\exp(-\Delta E/2kT)\) which is included in good agreement with the experiment \([6–8]\). We have verified in our numerical simulations that the spin configuration is planar, and the vector v is at an angle of 70° to the a-axis when \(J_{d2} = 0\) is included in good agreement with the experiment \([6–8]\).

**Appendix B: Parallel tempering Monte Carlo**

The phase diagrams of the magnetic Hamiltonians has been worked out in classical Monte Carlo simulations combining a parallel tempering scheme \([28]\) with a standard Metropolis local update algorithm. In a typical simulation a set of 64 replicas was used to cover a temperature range of 16 K. The temperatures were uniformly distributed with \(\Delta T = 0.25\) K. For the data presented in Figs. 3 and 5 four non-overlapping temperature brackets
were used, with the endpoint temperatures of the brackets chosen to be away from the phase transitions. Exchange of temperatures were attempted after each 100th Monte Carlo sweep (MCS), and restricted to pairs of neighboring temperatures. As the temperature brackets were rather narrow in comparison with the absolute temperature, only a weak increase in the acceptance rate could be seen for the upper temperatures in a bracket compared with the lower temperatures. For the simulation cells with size $36 \times 4 \times 36$ unit cells, the acceptance rate were in the range 70% to 80%. The simulations were run over $5 \cdot 10^6$ MCS, with the first $5 \cdot 10^5$ MCS used for equilibration.

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