Origin of ferroelectricity in high-$T_c$ magnetic ferroelectric CuO

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Cupric oxide is a unique magnetic ferroelectric material with a transition temperature significantly higher than the boiling point of liquid nitrogen. However, the mechanism of high-$T_c$ multiferroicity in CuO remains puzzling. In this paper, we clarify the mechanism of high-$T_c$ multiferroicity in CuO, using combined first-principles calculations and an effective Hamiltonian model. We find that CuO contains two magnetic sublattices, with strong intrasublattice interactions and weakly frustrated intersublattice interactions, which may represent one of the main reasons for the high ordering temperature of the compound. The weak spin frustration leads to incommensurate spin excitations that dramatically enhance the entropy of the multiferroic phase and eventually stabilize that phase in CuO.

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“Magnetic ferroelectric” materials, in which ferroelectricity is induced by magnetic ordering, have attracted intense interest [1, 2]. The strong magnetoelectric (ME) coupling in these materials opens a new path to the design of multifunctional devices that allow the control of charges by the application of magnetic fields or spins through applied voltages. However, nearly all current magnetic ferroelectric materials are strongly frustrated magnets [2], with very low ordering temperatures ($\sim 30 - 40$ K), several times lower than the temperatures expected from the strengths of their spin interactions. Low critical temperature is one of the major factors that limit the application of these important materials. Therefore, a new mechanism that allows high-temperature magnetic ferroelectricity is highly desirable.

Recently, CuO has been found to be multiferroic at $T_c=230$ K, which is much higher than the critical temperatures of any other magnetic ferroelectric materials [3]. CuO undergoes two successive magnetic phase transitions when it is cooled from room temperature to a temperature near zero. Neutron scattering experiments [4] have shown that at temperatures below $T_{N1}=213$ K, the spin structure is collinear antiferromagnetic (AFM1) [see Fig. 1(a)]. Between $T_{N1}$ and $T_{N2}=230$ K, the spin structure becomes non-collinear and slightly incommensurate (AFM2) [see Fig. 1(b)], with a modulation vector of $Q = (0.006, 0, 0.017)$. An electric polarization of 160 $\mu$C m$^{-2}$ along the b axis also develops in the AFM2 phase. Elucidation of this unusual high-temperature multiferric behavior may provide useful information in the search for novel room-temperature magnetic ferroelectric materials. However, the mechanism that stabilizes the multiferricity in CuO is still not understood, and it remains the subject of significant debate [5, 6]. The phase diagram of CuO has been studied via a phenomenological approach by Tolédon et al. [6], which based on symmetry considerations only, could not reveal the microscopic mechanism that stabilizes the multiferric phase in CuO. Giovannetti et al. performed Monte Carlo simulations on an effective Hamiltonian model of CuO [6]. However, in the simulation the spins were artificially constrained into only four possible directions, which dramatically changes the free energy of the system and misses important physics in CuO.

In this work, we clarify the mechanism of high-$T_c$ multiferroicity in CuO using combined first-principles calculations and simulations based on an effective Hamiltonian model. We find that CuO contains two magnetic sublat-
tices, with strong intrasublattice interactions and weakly frustrated intersublattice interactions, which might represent one of the main reasons that the compound exhibits a high ordering temperature. The weak spin frustration leads to incommensurate spin excitations that dramatically enhance the entropy of the AFM2 phase and eventually stabilize the multiferroic phase. This mechanism is novel and differs from previously proposed mechanisms \[5\]. This work suggests that high-\(T_c\) magnetic ferroelectric materials can be sought in weakly frustrated magnets similar to CuO.

The crystal structure of CuO is monoclinic and contains four chemical units per unit cell. The AFM1 spin structure is composed of two antiferromagnetic (AFM) spin sublattices, shown in two different colors in Fig. 1(a), in which Cu ions have the same \(b\) values in each sublattice. The spin chains along the [101] direction are antiferromagnetic, and are labeled chain I and chain II for the two sublattices, whereas the chains along the [101] direction are ferromagnetic. In the AFM1 phase, all spins are ferromagnetic, and are labeled chain I and chain II for the ferromagnetic chain I to chain II.

We perform ab initio calculations on CuO, with non-collinear spin-polarized local density approximation (LSDA) implemented in the Vienna ab initio simulations package (VASP) \[7\]. The on-site Coulomb interactions \(U=7.5\) eV are included for Cu ions in a rotationally invariant scheme \[3\]. The spin-orbit coupling is considered in the calculation unless otherwise noticed. To accommodate the spin structures, we use a \(2\times1\times2\) CuO supercell that contains 32 atoms. For the AFM2 structure, we neglect the small incommensurate component of the spin structure [i.e., we set \(Q=(0, 0, 0)\)], and rotate the spin directions of chain II \(90^\circ\), so that it lies in the \(ac\) plane. The spins form cycloidal spirals along both the \(a\) and \(c\) axes in the AFM2 phase. The incommensurate component of the magnetic modulation vector \(Q\) is extremely small, and it should not affect the calculated electric polarization because \(P \propto S_i \times S_j\) \[10\]. More details of the first-principles calculations can be found in Ref. \[11\].

We first determine the crystal structure of CuO under the AFM1 spin configuration. The room temperature crystal structure is monoclinic and of space group \(C2/c\), with inversion symmetry. However, the magnetic structure of the AFM1 phase only has \(P2_1/c\) symmetry. Therefore, after relaxation, the crystal structure is also reduced to \(P2_1/c\) symmetry because of “exchangestriction” effects \[12\]. Further analyses \[12\] show that the Cu and O ions deviate from their high symmetry sites by approximately \(10^{-3}\) Å. This distorted structure preserves the inversion symmetry; therefore it has no net polarization. The inversion center is shown in Fig. 1(a). An inversion operation about the inversion center changes spin chain I to chain II.

We then fix the spin orientations to the AFM2 configuration and relax the crystal structure again to obtain the crystal structure of the AFM2 phase. It turns out that the AFM2 configuration is a local minima of the total energy. The results change little if the spins are let free to rotate after the initial spin configuration is set to the AFM2 phase. The calculated total energy of the AFM2 phase is greater than that of the AFM1 phase by approximately 0.33 meV per atom, which is consistent with experiments that have shown the AFM2 phase to appear at a higher temperature than that at which the AFM1 phase appears \[4, 13\]. Before structural relaxation, the total energy of the AFM2 phase is approximately 0.08 meV per atom higher than that of the AFM1 phase. This energy difference is primarily attributed to the spin anisotropy energy, which can be observed when the spin-orbit coupling is turned off, which reduced the energy difference between the two phases to 0.03 meV per atom. The remaining difference of 0.25 meV per atom exists because the ionic distortion in the AFM1 phase is substantially larger than that in the AFM2 phase, as shown below.

The AFM2 spin structure exhibits \(P2_1\) space group symmetry, to which the rotation of spin chain II does not give inversion symmetry, as can be seen in Fig. 1(b). The crystal structure is distorted by the Dzyaloshinskii-Moriya (DM) interaction \[15\], which breaks the inversion symmetry. When compared with the high symmetry structure, all the oxygen ions are shifted in the \(+b\) direction by approximately \(7\times10^{-5}\) Å, whereas all Cu ions are shifted in the \(-b\) direction by a similar amount. The ionic distortion in the AFM2 phase is approximately two orders of magnitude smaller than that driven by the “exchangestriction” effects in the AFM1 phase.

Next, we calculate the electric polarization using the Berry-phase theory of polarization \[15\]. The calculated total polarization is approximately 90 \(\mu\)C m\(^{-2}\) in the \(-b\) direction, which is somewhat smaller in magnitude than the experimental value of 160 \(\mu\)C m\(^{-2}\) along the \(b\) axis. The agreement between the theoretical calculations and experimental values is reasonable, given that the current functionals are not adequate to treat the subtle correlation effects in magnetic ferroelectric materials \[15\].

In magnetic ferroelectric materials, the transition temperatures are predominantly determined by the magnetic exchange interactions \[3\]. We extract the superexchange interactions \(J_{ij}\) of CuO using a Heisenberg model, \(H_M = -\sum_{ij} J_{ij} S_i \cdot S_j - \sum_{i} (\mathbf{K} \cdot \mathbf{S}_i)^2\) from the calculated total energies of the different spin configurations in the symmetrized \(C2/c\) crystal structure with spin-orbit coupling. \(\mathbf{K}\) is the anisotropic energy due to spin-orbit coupling. There are seven \(J\) values in total, which are shown in Fig. 1(c). Among them, \(J_1\) is the exchange interaction between nearest-neighbor Cu atoms along the [101] direction, \(J_2\) is the interaction between nearest-neighbor Cu atoms along the [101] direction, \(J_3\) is the interaction between the nearest-neighbor spins of the same sublattice along the \(b\) direction, and \(J_4\) and \(J_5\) are the intersublattice exchange interactions. The fitted value of \(J_1=\)
The fitted inter-sublattice coupling value \( J \) as asymmetric. Interaction \( J \) is essentially determine the ground state spin structure, AFM1. The \( J_3 \) next-nearest-neighbor interactions further favors the antiferromagnetic spin chain along the [10 1] direction, whereas, \( J_6 \) only adds a small frustration to this configuration. The major competing interactions are those of the inter-sublattice interactions, \( J_3 \) and \( J_4 \). The weak incommensurateness of the spin spiral caused by the frustrated exchange interactions \( J_3 \), \( J_4 \) is consistent with that effect in this material, because the spin competition is small. We calculate the ordering temperature of the Heisenberg model by a Monte Carlo simulation, in which all exchange interactions are forced to be ferromagnetic and we obtain \( T_c = 311 \) K \( \text{[22]} \). This temperature is only about 1.5 times greater than the \( T_c \) value of the AFM1 phase, (in RMnO\(_5\) \( \text{[28]} \), the ratio is approximately 3 - 4.), which also indicates that the spin frustration is weak in CuO.

The lack of strong competing interactions in this compound may explain the high spin-ordering temperature of CuO.

To study the multiferroic phases of CuO, we simulate the full Hamiltonian model with spin-lattice interactions, 
\[
H = H_{\text{ph}} + H_{\text{M}} + H_1 + H_{\text{DM}},
\]

where,
\[
H_{\text{ph}} = E_0 + \sum_k \frac{1}{2} m_1 \omega_1^2 u_1^2(k) + \frac{1}{2} m_2 \omega_2^2 u_2^2(k),
\]

\[
H_1 = \sum_{i,j} J_{ij} u_1(k) S_i \cdot S_j,
\]

\[
H_{\text{DM}} = \sum_{i,l>0} D[u_2(i)b \times e_{i,i+l}] \cdot (S_i \times S_{i+l}).
\]

Here \( E_0 \) is the energy of the high-symmetry structure without magnetic interactions. Since the symmetry-lowering displacement is extremely small, we treat this displacement in the AFM1 (AFM2) phase as the nonpolar (polar) phonon mode \( u_1 \) \( \text{[23]} \). \( u_1(k) \) and \( u_2(k) \) are the phonon modes in the \( k \)th unit cell, and \( m_1 \) \( m_2 \) and \( \omega_1 \) \( \omega_2 \) are the reduced mass and frequency of the non-polar modes (polar modes), respectively. For simplicity, we neglect the phonon dispersion in the simulation, which has little effect on the results \( \text{[23]} \). \( H_1 \) is the isotropic spin-lattice interaction caused by exchange striction effects, \( J_{ij} = \frac{\partial^2 E}{\partial u^2_{kl}} \). In CuO, only \( J_3 \) and \( J_4 \) are involved in the nonpolar lattice distortion, and all other \( J_5 \)'s are canceled out by symmetry. \( H_{\text{DM}} \) is the DM interaction term, which sums over the nearest neighbor spin \( l \) along the \( a \) and \( c \) axes, where \( b \) is the unit vector along the \( b \) (polar) axis and \( e_{i,i+l} \) is a unit vector connecting the \( i \)-th and the \( i + l \)-th Cu atoms. Unlike the model in Ref. \( \text{[3]} \), our model explicitly includes the lattice degree of freedom, especially the non-polar modes, which are missing in the model of Ref. \( \text{[3]} \).

For simplicity, we redefine \( u_1 \) \( u_2 \) to be a dimensionless parameters that takes the value of unity at the low-symmetry state of the AFM1 (AFM2) phase, and we assign spin moments \( |S_i|=1.0 \). All parameters in the model can be obtained by fitting to the total energies of the first-principles calculations \( \text{[22]} \). We use \( J_3'=J_4'=0.35 \) meV, which is approximately 1.5 times greater the values obtained by first-principles calculations \( \text{[24]} \). To obtain the correct ground state, we reduce the values to \( J_3=2.45 \) meV, and \( J_4=3.5 \) meV, which are approximately half of the fitted values. \( m_1 \omega_1^2=0.4, m_2 \omega_2^2=0.49D \). \( D_c=0.8723 \) meV is the critical value at which the energies of AFM1 and AFM2 phases are degenerate. Our main results are valid in a reasonable range of the values of parameters for the model Hamiltonian, provided \( J_3' \) and \( J_4' \) are larger than 0.27 \( J_3 \) (to ensure that the ground state is in the AFM1 phase) and \( J_3 \) and \( J_4 \) are larger than half of the fitted values.

We simulate the effective Hamiltonian model in the temperature range from 29 to 387 K, using a replica-exchange Monte Carlo method \( \text{[23]} \). We perform the Monte Carlo simulations on the \( n \times n \times n \) lattices \( (n=12 - 72, m=2 - 12) \) with periodic boundary conditions. The electric polarization \( P = \langle u_2 \rangle \). Typical simulation re-
experimental value of zero \[\text{see Fig. 3(b)}\], which slightly underestimates the \(T\) tric (PE) to ferroelectric transition clearly occurs near \(T\) scaling for agreement with experiments. Fourier analyses of the spin tem enters the AFM1 phase. This result is in excellent non-polar lattice distortion, which indicates that the sys-

results for the \(n=12\) lattice are shown in Fig. 2. There is no stable AFM2 phase, even with a large DM interaction, \(D=0.5D_c\). If we artificially constrain the spin to only four possible directions at 90°, as was done by Giovannetti at al. \[5\], we obtain a weak AFM2 phase at approximately 300 K, as shown in Fig. 2 that is similar to the one obtained by Giovannetti et al. \[5\]. The above results suggest that the DM interaction alone cannot stabilize the AFM2 phase in CuO.

Surprisingly, if the simulation lattice size is increased to \(n>32\), a well defined AFM2 phase is obtained. The simulation results of a \(48\times4\times48\) lattice with a small \(D=0.066\) \(D_c\), are presented in Fig. 3 a). A paraelectric (PE) to ferroelectric transition clearly occurs near \(T_2=180\) K. At \(T_1=125\) K, the polarization suddenly drops to zero, accompanied by the appearance of the non-polar lattice distortion, which indicates that the system enters the AFM1 phase. This result is in excellent agreement with experiments. Fourier analyses of the spin structures \[23\] also confirm the above results. A finite size scaling for \(T_2\) with \(m\) gives \(T_2=192\) K as \(1/m\) approaches zero [see Fig. 3 b)], which slightly underestimates the experimental value of \(T_2=230\) K \[3\].

It is initially surprising that the AFM2 phase is not sta-

ble in the small simulation lattice but survives in the large simulation lattice. Fourier analyses of the spin structures suggest that, in the \(n=48\) lattices, many incommensurate spin components are present, which are forbidden in the small (e.g., \(n=12\) ) lattices. The incommensurate spin components are generally known to arise from the frustrated spin interactions, which suggests that the small spin frustration might play an important role in stabilizing the AFM2 phase. We then perform the simulations using the \(48\times4\times48\) lattice, but set the frustrated spin interactions to zero, i.e., \(J_1=J_2=J_3=0\). The results are shown in Fig. 2. Remarkably, the results are very similar to those obtained for the \(n=12\) lattice, and no stable AFM2 phase is found. We also carry out simulations by using the effective Hamiltonian and parameters given in Ref.\[3\] and obtain similar results. This result further confirms the assumption that the weak spin frustration is essential to stabilize the AFM2 phase, and contradicts to previous conclusions \[3, 4\].

To understand why the weak incommensurate spin components can stabilize the AFM2 phase, we calculate the entropy of the system as a function of the temperature using a multihistogram reweighting technique\[25\]. The entropies of the \(48\times4\times48\) lattice with or without spin frustration are compared in Fig. 4. The entropy of the non-frustrated system increases smoothly as temperature increases from 120 K to 130 K. The entropy of the \(n=12\) lattices with frustrated interactions (not shown) exhibits a similar temperature dependence. In contrast, an obvious entropy jump occurs near \(T_1=125\) K in the \(48\times4\times48\) lattice with spin frustration. This increase can be seen more clearly in Fig. 4 (b), which depicts the difference of the system entropies with and without spin frustrations in the temperature range 50 -160 K. Therefore, we conclude that the incommensurate spin excitations caused by the spin frustration greatly enhances the entropy of the system in the AFM2 phase and stabilizes the phase.

To explore the role of the DM interaction in the phase transitions, we tune the DM interaction strength \(D\) from zero to \(D_c\). In the range of \(D < D_c\), transitions from the paramagnetic-PE phase to the AFM2-ferroelectric phase to the AFM1-PE phase are always present. As \(D\) increases, the temperature range of the AFM2 phase also increases. When \(D > D_c\), only the transition from the paramagnetic-PE phase to AFM2-ferroelectric phase exist, and there is no AFM1 phase \[3\]. Interestingly, when we set \(D=0\), we still obtain a stable AFM2-like incommensurate phase, but it has no net electric polarization because there is no unique polarization axis in this case. The DM interaction that breaks the rotational symmetry of the nearly degenerate spin structures in the AFM2 phase and generates the polarization axis \[3\]. However, in the case of a strong magnetic anisotropy, electric polarization is also possible.

Understanding the mechanism of the multiferroicity
in CuO provides important guidance in the search for new high-$T_c$ magnetic ferroelectric materials. We found that CuO contains two magnetic sublattices, with strong intra-sublattice interactions and weakly frustrated inter-sublattice interactions, which may represent one of the main reasons that the compound has a high ordering temperature. Monte Carlo simulations suggest that the incommensurate spin excitations, caused by the weak frustrated interactions dramatically enhance the entropy of the multiferroic AFM2 phase, and they eventually stabilize the phase. The DM interaction break the magnetic rotational symmetry, which causes lattice distortion and lead to electric polarization in the AFM2 phase. This mechanism is distinct from previously proposed mechanisms for CuO. One of the fascinating features of magnetic ferroelectric materials is their rich phase diagrams, which arises from the competing interactions in these materials. However, few reports on the mechanism of these phase transitions at the microscopic level have been published. The methods developed in this work may be useful in elucidating the complex magnetic ferroelectric phase transitions in general magnetic ferroelectric materials.

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