Comment on "High-T_c Ferroelectricity Emerging from Magnetic Degeneracy in Cupric Oxide"

The origin of the multiferroicity in cupric oxide was addressed in a recent Letter [1], in which Giovannetti *et al.* performed classical Monte Carlo simulations on a 3D Hamiltonian to estimate the spin-current susceptibility χ_{jj} for the CuO structure. However, they used incorrect exchange parameters J_{ij} as inputs. Giovannetti *et al.* [2] have done the following. (i) They introduced a new ferromagnetic (FM) J parameter, namely, J_y, but neglected an important antiferromagnetic (AFM) supersuperexchange interaction with a dihedral Cu-O-O-Cu angle of 0°, previously defined as J_{nnn} in Ref. [3] and J_{2a} in Ref. [4]. (ii) They mentioned that they used the notations of Ref. [4], which is not true and leads to severe confusions. In particular, they interchanged J_a with J_b, J_{2b} with J_{2a}, and J_{2c} with J_{2b}. (iii) They used incorrect coefficients for their J_b parameter in their energy expressions (twice too much). (iv) They performed their mapping analysis such that the number of equations is equal to the number of unknown parameters, which does not guarantee the robustness of the so-obtained J parameters.

We used for our total energy calculations the same conditions as specified in Ref. [1]. However, we considered 23 different magnetic states and a least-squares fit procedure and not only a minimal set of equations as in Ref. [1]. The discussion in the present Comment is based on the notations previously defined in Refs. [4,5].

As shown in Table I, the J values (fit#1) obtained using a similar strategy as Giovannetti *et al.*, i.e., with only their 8 revised energy expressions and neglecting J_{2a}, are very close to the values reported in Ref. [1], except for J_a, i.e., their J_b parameter, due to the coefficient correction. However, the J values (fit#2), deduced from 23 equations and including all the reported J_{ij} parameters, differ significantly from the values of Ref. [1], except for J_z. For instance, it clearly appears from fit#2 that J_{2c} (i.e., J_{2b} in Ref. [1]) and J_y are insignificant in contrast to their high values proposed in Ref. [1] and fit#1.

More dramatically, as shown in Fig. 1, the mapping with only 8 equations (fit#1) does not guarantee that other magnetic states can be properly described, in contrast to the mapping with 23 equations (fit#2). Using the J values from fit#2, we could accurately reproduce the energy of the 23 magnetic states with a standard deviation of only 0.6 meV, instead of 5.2 meV when using the J values from fit#1.

TABLE I. Exchange-coupling parameters (meV) calculated using DFT + U calculations.

Refs. [4,5]	J_z	J_x	J_a	J_b	J_{2a}	J_{2b}	J_{2c}	J_y
Ref. [1]	J_z	J_x	J_b	J_a	⋯	J_{2a}	J_{2b}	J_y
$d_{\mathrm{Cu-Cu}}$ (Å)	3.748	3.173	2.901	3.083	5.801	5.129	4.684	3.423
J_{ij} fit#1	99.53	−13.04	23.13	5.07	⋯	6.23	14.80	−19.42
J_{ij} fit#2	107.12	−3.65	8.32	−2.92	20.05	10.11	−1.04	0.77

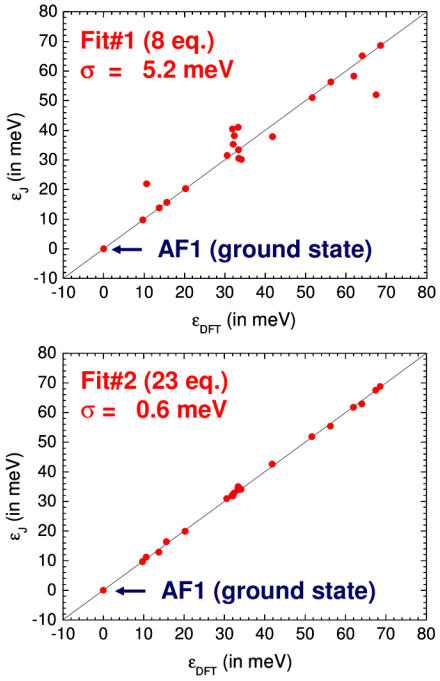

FIG. 1 (color online). Graphical representation of fit#1 and fit#2 results. $\varepsilon_{\mathrm{DFT}}$ and ε_J are, respectively, the relative energies (with respect to the ground state, labeled "AF1" in Ref. [1]) deduced from the density-functional theory (DFT) calculations and the J parameters.

To conclude, Giovannetti *et al.* have missed the second-most-important J parameter in their mapping analysis, which leads to very different values for the other J values, except for J_z. In particular, the second-strongest coupling, namely, the one between the even planes ($\Delta y = \pm 1$), is a strong AFM coupling (J_{2a} in the revised notation) and not a strong FM coupling (J_y) as suggested in Ref. [1]. Therefore, it will be necessary to redo the Monte Carlo simulations using the corrected J_{ij} input parameters of the 3D spin Hamiltonian, in order to properly simulate the phase diagram and polarization of CuO.

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