Magnetic Ordering under Strain and Spin-Peierls Dimerization in $GeCuO_3$

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(Received 19 October 2006; published 8 May 2007)

Studying from first principles the competition between ferromagnetic (FM) and antiferromagnetic (AF) interactions in the charge-transfer-insulator $GeCuO_3$, we predict that a small external pressure should switch the uniform AF ground state to FM, and estimate (using exchange parameters computed as a function of strain) the competing AF couplings and the transition temperature to the dimerized spin-Peierls state. Although idealized as a one-dimensional Heisenberg antiferromagnet, $GeCuO_3$ is found to be influenced by nonideal geometry and side groups.

DOI: 10.1103/PhysRevLett.98.196403 PACS numbers: 71.30.+h, 71.15.Mb, 71.20.−b, 75.25.+z

Cuprates are a challenge to modern condensed matter science. Highly complex physics—from high-T_c superconductivity to exotic magnetic phenomena—occurs in the CuO_2 plaquettes, stripes, or planes characterizing many of their structures, especially those with low effective dimensionality. CuO and $YBa_2Cu_3O_{6+x}$ are examples of effectively 3D and 2D compounds. A candidate for the starring role among 1D cuprates is $GeCuO_3$, a charge-transfer type, weakly (Neél temperature ~ 80 K) antiferromagnetic (AF) insulator, structurally characterized (Fig. 1) by narrow quasi-one-dimensional (1D) CuO_2 stripes connected by Ge-O "side groups." It is considered a nearly ideal experimental realization of a 1D Heisenberg antiferromagnet [1]. At low temperature (14 K) $GeCuO_3$ undergoes a so-called spin-Peierls transition [2–4] to an AF state with a gapped excitation spectrum, exhibiting a subtle structural and magnetic dimerization.

This Letter presents a first-principles study of the competition of AF and ferromagnetic (FM) order in $GeCuO_3$. We (a) directly calculate the AF exchange interaction for the uniform phase to be 90 K; (b) we predict that an external pressure of order 1 GPa switches the magnetic ordering of uniform $GeCuO_3$ from AF to FM; (c) we estimate alternating first-neighbor couplings of $J_1 = 115$ K and $J_2 = 66$ K in the experimental dimerized spin-Peierls geometry [3], which (within the alternating 1D-AF Heisenberg linear-chain model [5]) correspond to a spin-Peierls transition temperature $T_{sp} \sim 20$ K, close to the experimental 14 K. Finally, (d) we give an orbital-physics-based rationale for magnetism and its dependence on structural changes, singling out the role of the structural motifs (stripe geometry and side groups) of the real material.

Theoretical method, structure, and electronic properties.— Any parameter-independent prediction on complex materials such as $GeCuO_3$ exacts the use of fully *ab initio* methods. However, state-of-the-art density-functional theory (DFT) calculations [in typical approximations such as the local-spin density approximation (i.e., LSDA)] incorrectly describe most magnetic cuprate insulators [6], including $GeCuO_3$ [7], as nonmagnetic metals. Here we employ the DFT-based pseudo-self-interaction-correction (pseudo-*SIC*) method, which includes an approximate self-interaction correction within the single-particle LSDA approach, and has been successfully applied to study correlated materials [8]. For $GeCuO_3$, it provides a quantitative description of magnetic ordering and electronic structure.

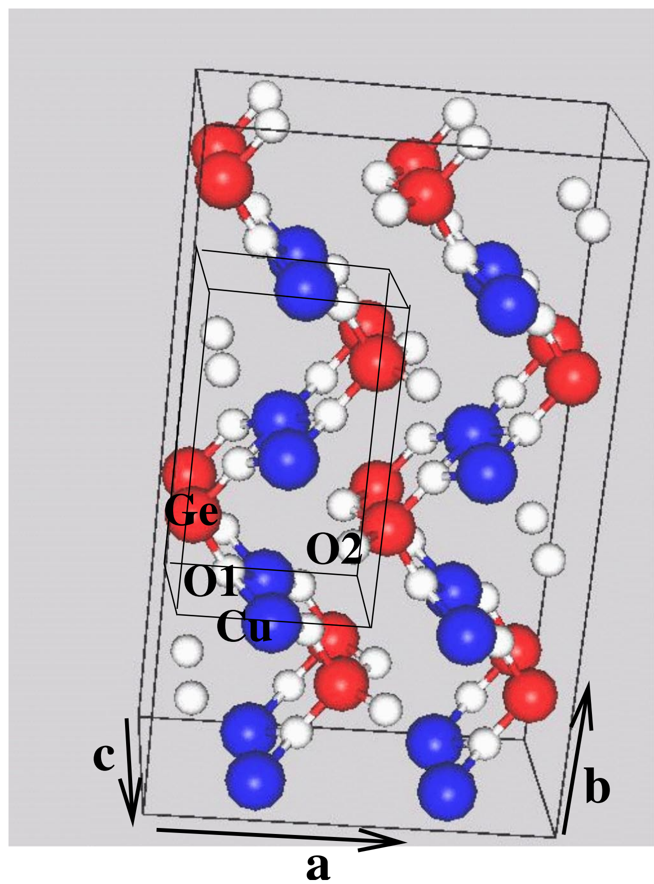

FIG. 1 (color online). Structure of *Pmma* AF $GeCuO_3$. Dashed line: nonmagnetic unit cell (2 f.u.); AF cell is doubled along c. Internal parameters [10]: $x_1(\mathrm{Ge}) = 0.0743$, $x_1(\mathrm{O2}) = 0.87$, $x_1(\mathrm{O1}) = 0.2813$, $x_2(\mathrm{O1}) = 0.0838$.

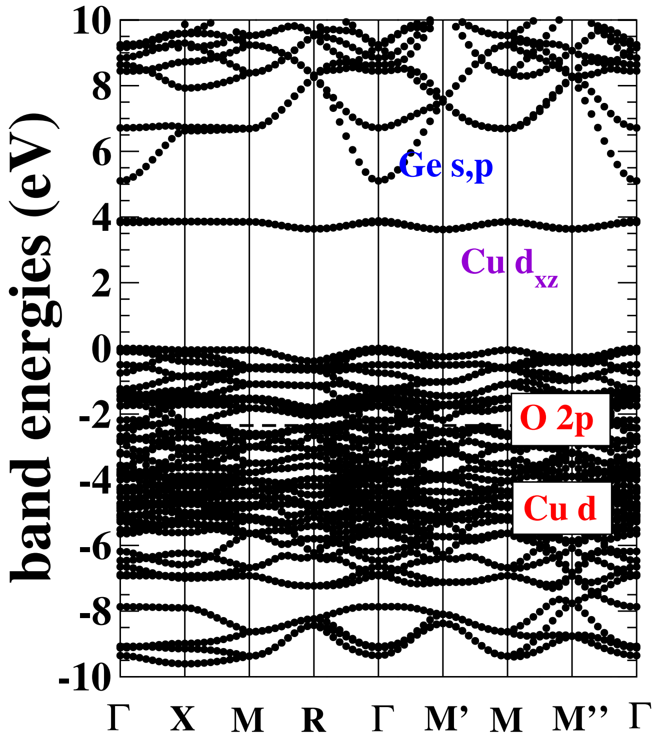

FIG. 2 (color online). Band energies of AF $GeCuO_3$. K points: $X = [1/2, 0, 0]$, $M = [1/2, 1/2, 0]$, $R = [1/2, 1/2, 1/2]$, $M' = [0, 1/2, 1/2]$, $M'' = [1/2, 0, 1/2]$ in units of $2\pi/a$, $2\pi/b$, $2\pi/c$. Energy zero is the valence band top.

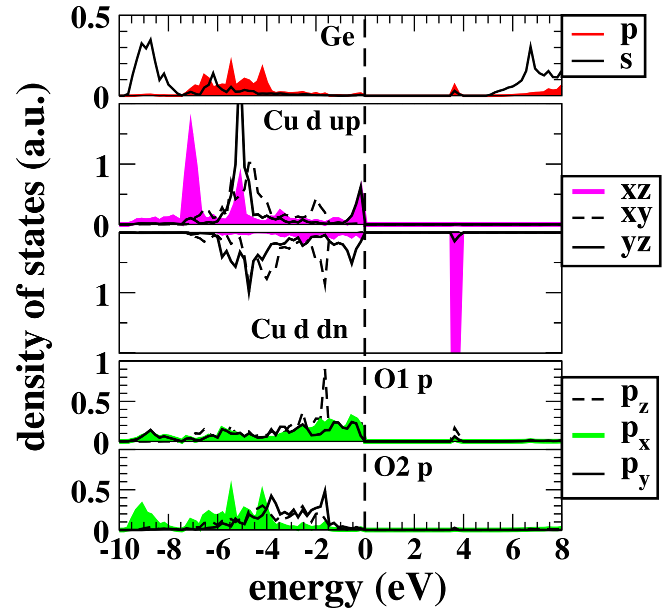

FIG. 3 (color online). Orbital-resolved DOS of AF $GeCuO_3$. For clarity, only d t_{2g} orbitals are shown for Cu (the e_g's are localized and lie 4 to 6 eV interval below E_F).

We use plane-wave basis and ultrasoft pseudopotentials [9] with 35 Ryd cutoff, $6 \times 6 \times 6$ k-point grids [250 special k points and tetrahedron interpolation for density of states (DOS)].

The orthorombic uniform structure of $GeCuO_3$ (Fig. 1) features CuO_2 stripes along c (or z) with slightly nonideal Cu-O-Cu angle, connected by $Ge^{4+}O^{2-}$ units in an alternate-tilt stacking along b (or y). The slanted stripe stacks are only weakly coupled along a (or x). CuO_2-stripe oxygens are labeled O1, those bound to Ge only are O2. Calculated lattice parameters are $a = 4.85$ Å, $b = 8.89$ Å, $c = 2.97$ Å (+ 0.8, +4.9, −1% from experiment [10]).

Figures 2 and 3 show the band structure and orbitally resolved DOS for AF $GeCuO_3$ calculated within pseudo-*SIC*. The calculation assumes AF ordering along Cu chains (c direction) as well as along b (4 f.u./cell). The conduction band bottom (CBB) is a flat, spin-polarized state, of almost exclusive Cu d_{xz} character, derived from the two up-polarized Cu atoms in the cell. The valence band top (VBT) is mainly of O1 (i.e., on-stripe) p character, partially hybridized with Cu d_{xz} and d_{yz} lying somewhat lower in energy. Both the O p VBT and Cu d CBB are flat in k_x and k_y (Γ to M); i.e., these orbitals are basically uncoupled along both x and y. Thus, Cu and O orbitals on each CuO_2 stripe are effectively isolated; adjacent stripes only interact through Ge-centered tetrahedra. In agreement with x-ray photoemission [11,12], this is a charge-transfer insulator. The calculated energy gap (3.60 eV) and magnetic moment ($0.76\mu_B$) compare favorably with experiment (3.7 eV [11] and $0.7\mu_B$[13]). The magnetization (Fig. 4, top view along b) is primarily d_{xz} like and centered on alternating Cu sites consistently with calculated AF ordering and band character.

As mentioned, LSDA fails to produce a fundamental gap in $GeCuO_3$ [7,14]. An LDA + U band calculation [14] finds a gap, but the CBB has Ge character heavily admixed into the Cu CBB, whereas we find them well separated. The on-site energy parameter used, $U = 9.66$ eV, is consistent with our spin splitting of $\simeq 10$ eV for Cu d_{xz} (Fig. 3). Hartree-Fock [15] bands have a purely Mott-type gap between Cu-d like states, at variance with our results and with experiment.

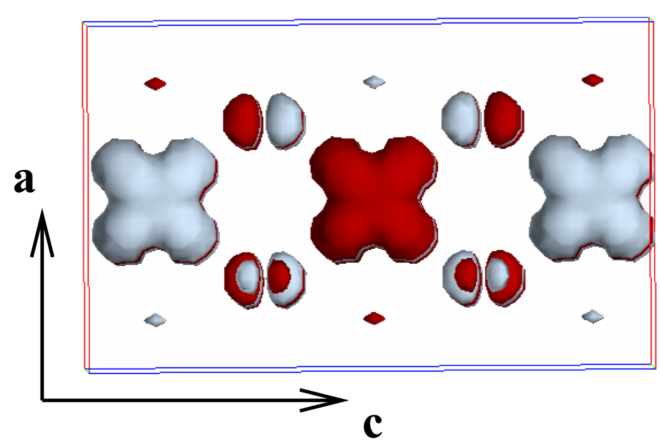

FIG. 4 (color online). Hole magnetization in $GeCuO_3$ in a 4 eV energy interval above E_F. Cyan (light) and red (dark) isosurfaces: magnetization density $\pm 0.027/\mathrm{Bohr}^3$, respectively.

Energetics under strain.—The energy competition of AF and FM ordering within the CuO_2 stripes is unusually tight. Figure 5(a) displays the total-energy difference δE of the AF and FM states vs Cu-O-Cu angle. At the theoretical equilibrium structure, the AF alignment is favored, and the calculated nearest-neighbor coupling in the spirit of the 1D Heisenberg model is $J_c = \delta E/2 = 10.5$ meV or 90 K, close to the value obtained by a susceptibility data [2] fit with the same model [4]. The calculated Cu-O-Cu angle $\theta_0 = 97.7°$ (vertical line in Fig. 5) is close to the experimental 98.2°. Based on Goodenough-Kanamori-Anderson (GKA) rules [16], FM ordering would be expected to prevail. Yet $GeCuO_3$ happens to fall on the AF side of the phase diagram, and in fact nearly by accident, witness the tiny AF-FM energy difference and the crossover point just below θ_0 at $\sim 95°$. This subtle competition involves structural details of the Cu-O1-Cu angle and Ge-O side groups. Our finding, and the discussion below, agree qualitatively with many-body calculations [17] based on GKA rules extended to side groups.

We analyze the exchange interaction within CuO_2 stripes under two structural distortions. The first and most relevant is a pure shear strain in the CuO_2 plane changing the Cu-O-Cu angle θ at fixed atomic distances. It is realized by a c-axis strain, and by a simultaneous shift along a of the O1-Ge-O2 block on each stripe so that atomic distances are unchanged as θ varies. Upon distortion, the exchange coupling $J_c(\theta) = \delta E/2$ [Fig. 5(a)] is nearly linear for $\theta = \theta_0 \pm 10°$, and follows the superexchange trend of increasing AF character at large angles.

In Fig. 5(a) we also report the magnetic stress $\sigma_M = 0.25\partial(\delta E)/\partial\theta$, defined [18] as the stress excess per bond caused by a spin flip inverting the alignment of two magnetic centers. At θ_0, $\sigma_M < 0$, hence an AF to FM spin flip induces a tensile stress relieved by a negative strain (a decrease of θ). Since $\sigma_M < 0$ in the relevant region near equilibrium, AF (FM) alignment always tries to increase (decrease) θ. Near equilibrium, $\delta\theta = \delta c/[d\cos(\theta_0/2)]$, with d the Cu-O distance, $\delta\theta$ and δc the shear-angle and Cu-Cu-distance changes. In the uniform phase, a spin-alignment switch can then be obtained by the small compressive stress $P = (abd\cos\theta_0/2)^{-1}\partial(\delta E)/\partial\theta|_{\theta=\theta_0} \simeq 1.14$ GPa.

At low T the uniform Cu chain becomes dimerized [3]: adjacent Cu atoms along c alternatively shrink and stretch their mutual distances, opening a spin gap in the otherwise continuum magnetic excitation spectrum. Correspondingly, the magnetic susceptibility suddenly drops to zero below T_{sp}. We note that the measured dimerization [3] implies an alternating change in θ along the chain by $\pm 0.7°$ (for unchanged O-Cu bond lengths). From our calculated, monotonically decreasing $J_c(\theta)$, we estimate the change of θ due to the dimerization to cause a coupling variation of ∓ 2.8 meV. The resulting AF couplings are therefore $J_1 = 13.3$ meV $= 115$ K for increased angle (farther Cu atoms) and $J_2 = 7.7$ meV $= 66$ K for reduced angle (closer Cu atoms; at variance with a conventional Peierls distortion, in the spin-Peierls the closer Cu pairs are *less* coupled). Now, following the Duffy and Barr [5] treatment of the 1D-alternating-AF Heisenberg chain model, the ratio $\alpha_A = J_2/J_1 = 0.58$ corresponds to a susceptibility onset at $\simeq 0.13|J_1|$, or $\simeq 20$ K in our case. Thus, the appearance of alternating AF intrachain couplings due to dimerization (interchain effects, discussed next, are minor) and their first-principles estimated values, are internally consistent with the measured transition at 14 K to the spin-Peierls phase. Pressure effects on the dimerized phase [19] will be studied in future work.

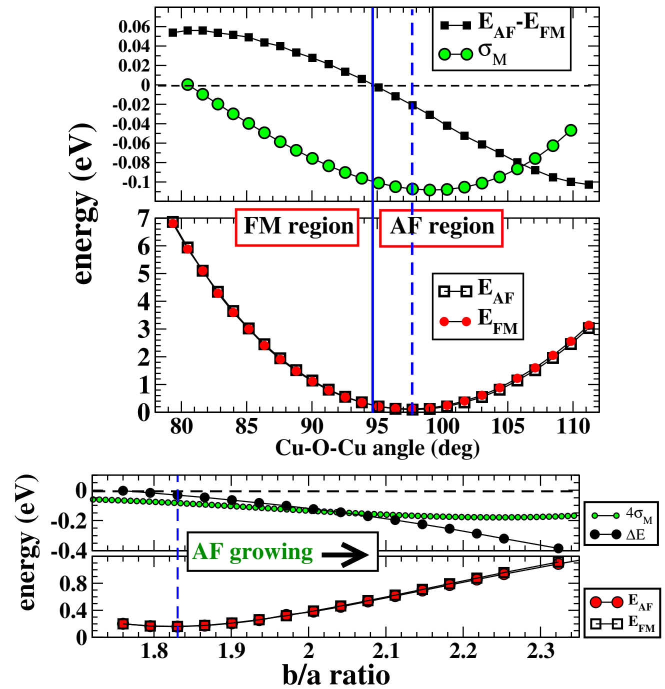

FIG. 5 (color online). Panel (a) (upper): AF-FM energy difference per cell $\delta E = 2 \times J_c$, magnetic stress σ_M, and raw FM and AF energies vs Cu-O1-Cu angle. Vertical lines: FM-AF crossover (solid) and theoretical equilibrium (dashed). Panel (b) (lower): same, vs b/a ratio. See text for discussion.

The second distortion is a longitudinal strain along the b axis, changing the distance between adjacent CuO_2 stripes so as to partially decouple them from Ge-O2 side groups, but keeping the Cu-O1 relative positions unchanged. In a low-dimensional model decoupling the CuO_2 units from "side groups", the intrachain Cu-Cu J_c coupling may be expected to be unchanged by this strain. However, Fig. 5(b) shows it to change as significantly as for the intrachain shear strain [Fig. 5(a)]. Once again tensile strains (i.e., increasing chain distances) stabilize the AF phase. Conversely, from the magnetic stress we find that a mere $\simeq 0.5$ GPa *compression* along the b axis switches the ordering from AF to FM. Together with the earlier shear-strain result, this means that hydrostatic compressions of order 1 GPa should turn $GeCuO_3$ into an insulating ferromagnet. Figure 5(b) shows that a b-axis shortening would reduce interchain coupling, reinforcing our previous argu-

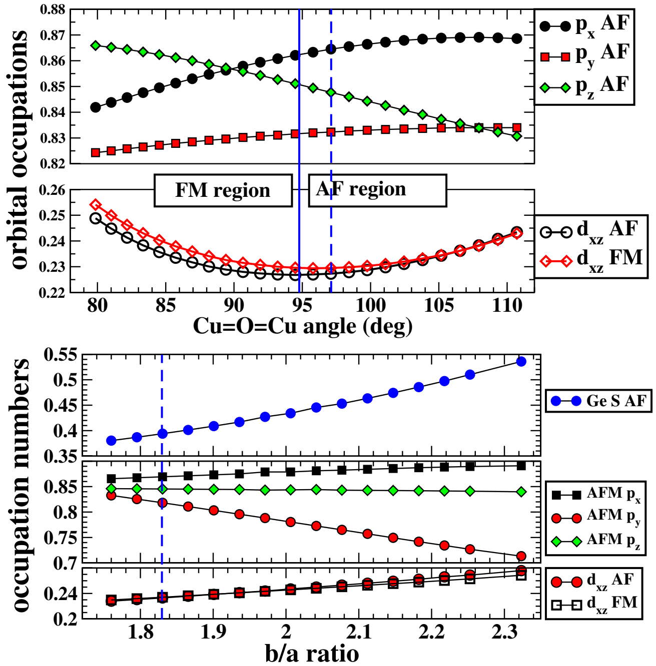

FIG. 6 (color online). Panel (a) (upper): orbital occupations of O1 p_x,p_y,p_z, minority Cu d_{xz} vs Cu-O1-Cu angle. Panel (b) (lower): same, plus Ge s, vs b/a ratio. See text for discussion.

ment on the spin-Peierls distortion. However, the observed [3] b decrease in the spin-Peierls phase is tiny (0.01%) and energetically immaterial.

As a microscopic-level rationale of exchange interactions, Fig. 6(a) show orbital occupations for Cu minority d_{xz} and O1 p vs θ. The former has a quadratic minimum around 95°. At large θ, O p_z, and Cu d_{xz} tend to overlap; hence, overlap and hybridization increase, and charge flows from p_z (whose occupation decays linearly) to d_{xz}. As expected, this enhances the AF contributions. The same displacement simultaneously reduces the hybridization of p_x and p_y with d_{xz}, so charge flows from Cu towards ligand O1. By charge conservation, $\delta d_{xz} \sim -(\delta p_x + \delta p_y + \delta p_z) \sim \theta^2$. Over the chosen range of θ, the occupations of O1 p_x, p_y, and p_z change by ~3.5%, 1%, and 5%, respectively. Since p_x changes mostly at small θ as its overlap with d_{xz} increases, and p_y (nearly orthogonal to the Cu-O1-Cu plane) is almost constant throughout, p_z dominates the AF-FM competition vs θ. Thus, p_z-d_{xz} overlap may be considered an order parameter of the FM-AF transition vs changes in angle θ.

Finally, we consider the chain-decoupling distortion. While the relative Cu-O1 positions are unchanged, Cu d_{xz} and O1 p occupations change considerably, as shown in Fig. 6(b). Decoupling the chains, charge leaves the CuO_2 units, and moves almost entirely to the Ge s orbital (the stretch makes Ge more free-atom like). This strongly suggests that the chemistry of stripes and side groups are tightly related, and should not be arbitrarily decoupled.

In summary, we analyzed the low-dimensional cuprate $GeCuO_3$ within a fully first-principles pseudo-*SIC* approach. AF and FM ordering compete closely, and a moderate (~ 1 GPa) hydrostatic stress turns the compound into a ferromagnet. The dimerizing spin-Peierls distortion causes an alternance of antiferromagnetic couplings ($J_1 = 13.3$ meV and $J_2 = 7.7$ meV), whose ratio $\alpha_A \simeq 0.58$ corresponds to an estimated transition temperature of $\simeq 20$ K to the spin-Peierls phase of $GeCuO_3$, in good agreement with experiment. O p_z-Cu d_{xz} overlaps determine the AF-FM competition; CuO_2 chains are nonideal and appreciably coupled to Ge side groups.

Partial support by MiUR (PON Cybersar, PRIN 05, project "Rientro Cervelli"), Fondazione Banco di Sardegna, CASPUR Rome.

Note added.—During review we were informed that [20] reports an AF-FM transition of the undimerized state under pressures with upper bound 4 GPa. This is quite compatible with our results.

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