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Incommensurate spin correlation driven by frustration in $BiCu_2PO_6$

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The magnetic properties of $BiCu_2PO_6$ have been analyzed by means of magnetic-susceptibility and inelastic neutron-scattering measurements on powder samples by evaluating the spin-exchange interactions on the basis of density-functional calculations and by simulating the inelastic neutron scattering in terms of spin-exchange parameters. $BiCu_2PO_6$ exhibits magnetic properties described by the two-leg spin ladder with strong spin frustration along each leg chain and has a gapped quantum singlet ground state with excited magnetic states, showing an incommensurate dispersion arising from frustration.

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Frustrated antiferromagnets have received much attention due to the possibility of finding unconventional ground states with novel "quantum order.[1]" The geometric spin frustration in these magnetic systems arises mostly from the competition between nearest-neighbor (NN) and next-nearest-neighbor (NNN) exchange interactions. For a number of simple spin-lattice systems, theoretical analyses have shown that NNN exchanges play a decisive role in determining the nature of the magnetic ground state. For example, for a spin-1/2 Heisenberg chain with antiferromagnetic NN and NNN exchanges J_{NN} and J_{NNN}, respectively, a quantum dimer order is stabilized when $J_{NNN}/J_{NN} > \sim 0.2411$.[2,3] In a two-leg spin ladder, another archetypal one-dimensional (1D) antiferromagnet, NNN exchanges can induce several phase transitions from the rung-dimer ground state to other exotic quantum states.[4] For a two-dimensional (2D) square antiferromagnetic lattice, strong NNN interactions are suggested to prevent the classical long-range antiferromagnetic order and possibly lead to a homogeneous spin liquid state.[5] However, it has been rare to find real low-dimensional magnetic materials possessing such unusual ground states as predicted by theory[6,7] because they generally undergo a phase transition to a classical long-range-ordered Néel state at low temperature due to extra exchange interactions neglected in theoretical prediction.

In this Rapid Communication, we show that $BiCu_2PO_6$ (Refs. 8 and 9) exhibits a gapped quantum singlet ground state with an incommensurate dispersion driven by magnetic frustration. This is a coupled quasi-1D Heisenberg two-leg ladder frustrated by strong NNN interactions along the legs. Our conclusion is supported by performing magnetic-susceptibility and inelastic neutron-scattering (INS) measurements by evaluating the spin-exchange parameters on the basis of first-principles density-functional theory (DFT) calculations and simulating the INS in terms of spin-exchange parameters.

In $BiCu_2PO_6$, the Cu^{2+} ($S=1/2$) ions are arranged in zigzag ladders along the b axis (Fig. 1) and are interconnected by diamagnetic Bi^{3+} and PO_4^{3-} groups (not shown in Fig. 1 for simplicity). The spin-exchange interactions necessary for describing the magnetic properties of $BiCu_2PO_6$ include the NN exchanges along the leg and rung of the geometrical ladder (J_1 and J_3, respectively), the NNN exchanges along the leg (J_2 and J_2'), the interchain exchange between the ladders (J_4), the diagonal exchanges (J_5 and J_5') in each rectangle formed by J_1 and J_3, and the diagonal exchanges (J_6 and J_6') in each rectangle formed by J_1 and J_4. Here J_1 and J_3 are Cu-O-Cu superexchanges (SEs), but all others are Cu-O…O-Cu supersuperexchanges (SSEs). The SE J_3 is expected to be weak because the associated ∠Cu-O-Cu bond angle is close to 90° (i.e., 92°).[10] In contrast, the SSE J_4 is anticipated to be substantial because the ∠Cu-O…O-Cu dihedral angle is nearly zero (i.e., ~1°) and the O…O contact distances (2.746 Å) are within the van der Waals distance.[11]

We evaluated these exchange parameters on the basis of DFT calculations using the Vienna *ab initio* simulation package,[12] the generalized gradient approximations (GGA)

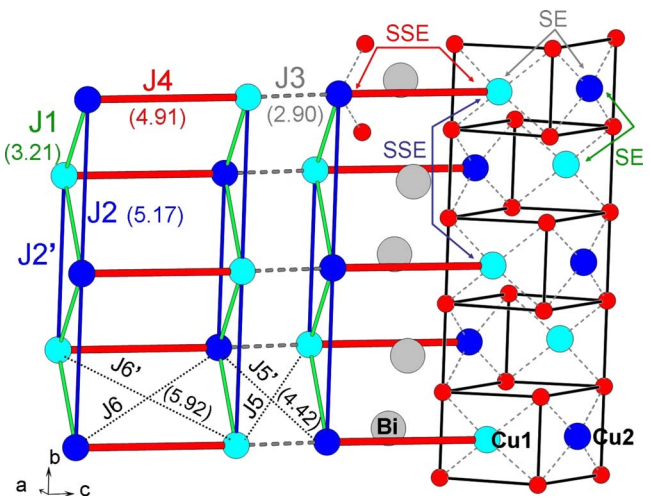

FIG. 1. (Color online) Schematic representation of the Cu^{2+} ion arrangement and the SE/SSE spin-exchange paths in $BiCu_2PO_6$. The two crystallographically nonequivalent copper atoms are indicated by blue and cyan circles, and the oxygen atoms by red circles.

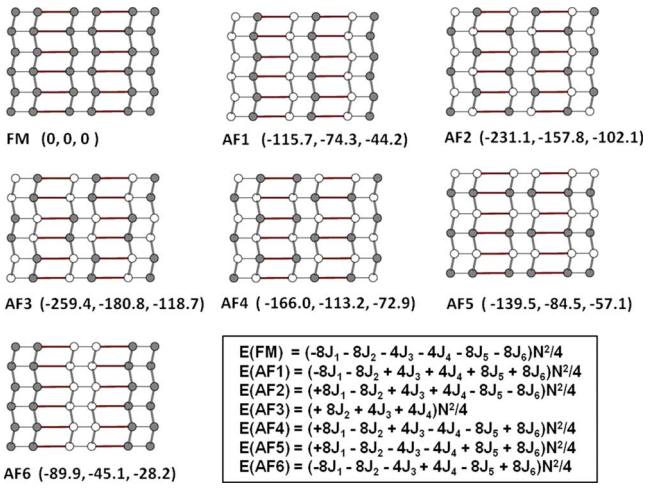

FIG. 2. (Color online) Seven ordered spin states (i.e., FM, AF_1, AF_2, AF_3, AF_4, AF_5, and AF_6) of $BiCu_2PO_6$ employed to extract the six spin-exchange parameters J_1-J_6 and their total spin-exchange energies in terms of J_1-J_6. Only the Cu^{2+} sites are shown for simplicity, and the up-spin and down-spin Cu^{2+} sites are represented by filled and empty circles, respectively. For each ordered state, the three numbers in the parenthesis, from left to right, refer to the relative energies obtained from the GGA+U calculations with U=4, 6, and 8 eV, respectively.

for the exchange and correlation corrections,[13] the plane-wave cutoff energy of 400 eV, 196 k points for the irreducible Brillouin zone, and the threshold of 10^{-6} eV for the self-consistent-field convergence of the total electronic energy. To properly describe the electron correlation of the Cu 3d states, the GGA plus on-site repulsion U (GGA+U) method[14] was employed with an effective U=4, 6, and 8 eV on the Cu atom. It will be assumed that $J_2'=J_2$, $J_5'=J_5$, and $J_6'=J_6$ since their geometrical parameters are similar. To determine the six parameters J_1-J_6, we perform GGA+U calculations for seven ordered spin states depicted in Fig. 2 and also express their total spin-exchange interaction energies in terms of the spin Hamiltonian, $\hat{H}=\Sigma_{i<j}J_{ij}\hat{S}_i\cdot\hat{S}_j$, where J_{ij} is the spin exchange between the spin sites i and j, i.e., $J_{ij}=J_1-J_6$. The total spin-exchange energies of the seven ordered spin states per unit cell (i.e., per four formula units) are summarized in the Fig. 2, where N is the number of unpaired spins at each spin site (i.e., N=1 in the present case). Thus, in mapping the relative energies of the seven ordered spin states determined from the GGA+U calculations (listed in Fig. 2 under each state) onto the corresponding energies obtained from the total spin-exchange energies (Fig. 2), we find the values of J_1-J_6 summarized in Table I.

The strengths of the calculated spin exchanges decrease in the order $J_4>J_1>J_2>J_3\gg J_5$, J_6, which shows that J_1 and J_4 form a two-leg spin ladder with significant spin frustration in each leg chain due to the NNN exchange J_2. Such frustrated two-leg spin ladders interact through the inter-spin-ladder exchange J_3, so that the spin lattice of $BiCu_2PO_6$ has a 2D character. The three leading exchanges give rise to the $J_1-J_2-J_4$ frustrated spin ladder model for $BiCu_2PO_6$, which differs from that presented by Koteswarao *et al.*,[15] who described $BiCu_2PO_6$ in terms of the two-leg spin ladder defined by J_1 and J_3. In the following, we establish that the simplest spin lattice needed to describe the magnetic properties of $BiCu_2PO_6$ is the $J_1-J_2-J_4$ frustrated spin ladder model.

TABLE I. Spin exchange parameters J_1-J_6 (in meV) of $BiCu_2PO_6$ obtained from the GGA+U calculations (the numbers in parentheses are the relative values with respect to the strongest exchange parameter).

	U=4 eV	U=6 eV	U=8 eV	Ref. 16
J_1	31.87 (0.82)	21.01 (0.94)	14.37 (1.00)	(1.00)
J_2	21.49 (0.55)	16.20 (0.72)	11.40 (0.79)	(0.34)
J_3	13.06 (0.34)	14.47 (0.64)	7.98 (0.56)	(1.00)
J_4	38.76 (1.00)	22.43 (1.00)	14.34 (1.00)	(0.74)
J_5	−0.08 (0.00)	0.06 (0.00)	0.02 (0.00)	(0.04)
J_6	3.10 (0.08)	0.07 (0.00)	−0.13 (−0.01)	(0.03)

That $BiCu_2PO_6$ has a nonmagnetic ground state has been known from neutron-diffraction (D2b diffractometer, Grenoble, France) measurements, specific heat[15] and magnetic susceptibility.[9] Indeed, these last measurements show that this material has a Δ=2.9 meV spin gap. Koteswarao *et al.*[15] analyzed the magnetic susceptibility $\chi(T)$ of $BiCu_2PO_6$ in terms of a non-spin-frustrated (J_2=0) spin ladder model,[16] to find that the $\chi(T)$ data can be reasonably fitted only if they reduce the susceptibility $\chi_{\text{ladder}}(T)$ calculated for the spin ladder by factor of m=0.41(2), namely, $\chi(T)=\chi_o+C/(T-\theta)+m\chi_{\text{ladder}}(T)$, where χ_o is the temperature-independent susceptibility, and the $C/(T-\theta)$ term takes care of a trace amount of paramagnetic impurities. The use of such a scaling factor m is highly unphysical. It is interesting to probe whether the $J_1-J_2-J_4$ spin-frustrated spin ladder model can fit the $\chi(T)$ data. Our data collected at 500 Oe have been analyzed in terms of the extended Hamiltonian $\hat{H}_{\text{ex}}=\Sigma_{i,j=1}^{N}J_{ij}\hat{S}_i\cdot\hat{S}_j+g\mu_B\Sigma_{i=1}^{N}\hat{S}_i\cdot\vec{H}$, where $J_{ij}=J_1$, J_2, or J_4. We determined the matrix representation of this Hamiltonian by using a double ring made up of 12 spin-1/2 sites (i.e., each leg chain forms a ring of six spin sites) and then diagonalize the resulting matrix to find the magnetic states of the system and hence adjust the magnetic susceptibility by using the program SPIN.[17] Then, the susceptibility $\chi_{1-2-4}(T)$ calculated for the $J_1-J_2-J_4$ frustrated spin ladder model describes the observed susceptibility well, i.e., $\chi(T)=0.0408(5)\frac{g^2S(S+1)}{4T}+\chi_{1-2-4}(T)$, with $J_1/k_B\approx-137.8(8)$ K, $J_2/k_B\approx-73.3(1)$ K, $J_4\approx-58.4(1)$ K, and g=2.1(2). The good qualitative agreement between the experimental and the calculated susceptibility curves [Fig. 3(a)] supports our view that the spin frustration associated with J_2 is essential. Interestingly, the J_2/J_1 and J_4/J_1 ratios deduced from the fitting analysis are somewhat smaller than their calculated counterparts; $(J_2/J_1)_{\text{fit}}$=0.53 vs $(J_2/J_1)_{\text{calc}}$=0.55–0.79, and $(J_4/J_1)_{\text{fit}}$=0.42 vs $(J_4/J_1)_{\text{calc}}$=1.00–1.19 (see Table I). This discrepancy is due in part to the neglect of the interladder interaction J_3 in the $J_1-J_2-J_4$ frustrated spin ladder model. The coupling of the $J_1-J_2-J_4$ spin ladders via J_3 leads to a 2D character, for which a reduction in the spin gap Δ is expected.[7,18] Furthermore, we checked that the spin gap Δ calculated from the $J_1-J_2-J_4$ frustrated spin ladder model

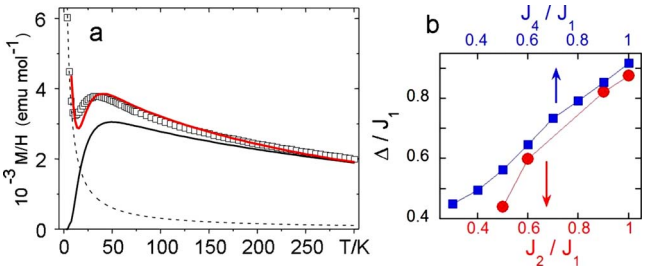

FIG. 3. (Color online) Analysis of the magnetic susceptibility and spin gap of $BiCu_2PO_6$ using the $J_1-J_2-J_4$ frustrated spin ladder mode: (a) experimental (circles) and fitted (red line) magnetic susceptibility. The typical gapped behavior (black solid line) is shown after removing the paramagnetic contribution (black dotted line). (b) Evolution of the normalized spin gap Δ/J_1 as a function of the frustration ratio J_2/J_1 (with J_4/J_1 fixed at 0.25) and the rung to leg ratio J_4/J_1 (with J_2/J_1 fixed at 0.50).

increases with increasing J_2 and J_4 [Fig. 3(b)]. It follows that the fitted J_2/J_1 and J_4/J_1 ratios are underestimated due to the effect of J_3 in the real system.

To further probe the spin frustration in $BiCu_2PO_6$, we carried out INS measurements for powder samples of $BiCu_2PO_6$ using the thermal and cold triple axis spectrometers at the LLB-Orphee reactor. Use of powder samples leads to a partial loss of the anisotropic information about the dispersion of magnetic excitations. The intensity of neutron scattering, proportional to a powder averaged spin-spin correlation function, gives a measure of the density of state. A $\omega-Q$ mapping of the low-temperature ($T=11$ K) INS intensity obtained by constant-energy scans is presented in Fig. 4(a), the most prominent features of which are the opening of a spin gap and the two maxima observed at 4 and 6 meV. These peaks are magnetic in nature because they vanish above 50 K. The lowest excitation energy centered at 4 meV is consistent with the spin gap $\Delta=2.9$ meV deduced from $\chi(T)$. The $\omega-Q$ mapping of Fig. 4(a) clearly indicates a significant dispersion of the first magnetic excitation, with minimum at $Q\approx 1$ Å^{-1}. The Q dependence at energy just above the spin gap is also of great interest. This is illustrated in Fig. 4(b), which presents a constant-energy scan taken at $\omega=4$ meV and $T=1.7$ K. The corresponding structure factor exhibits a maxima centered at $Q=1$ and 2 Å^{-1} followed by a number of small subsequent oscillations.

To confirm the validity of the leading $J_1-J_2-J_4$ frustrated spin ladder model in $BiCu_2PO_6$, we simulate the powder-INS data[19,20] using MAGPACK,[21] which enables one to compute the structure factor $S(Q,\omega)$ of a magnetic system with up to 14 spins in terms of a Heisenberg spin Hamiltonian. We especially calculate $S(Q,\omega_0)$, where ω_0 is the energy of the lowest excited state. Simple spin-lattice models, such as an isolated dimer (J_3 or J_4) and a non-spin-frustrated chain (J_1), fail to describe the neutron data. Among various 1D spin lattices we tested (i.e., J_1-J_2, J_1-J_3, J_1-J_4, $J_1-J_2-J_3$ or $J_1-J_2-J_4$), only the $J_1-J_2-J_4$ spin ladder model with strong spin frustration reproduces the two experimental maxima at $Q_{max}=1$ and 2 Å^{-1}, as summarized in Figs. 4(b) and 4(c). It should be noted that the $J_1-J_2-J_3$ frustrated spin ladder model does not match the experimental INS data even with a strong frustration J_2/J_1 ratio [Fig. 4(c)].

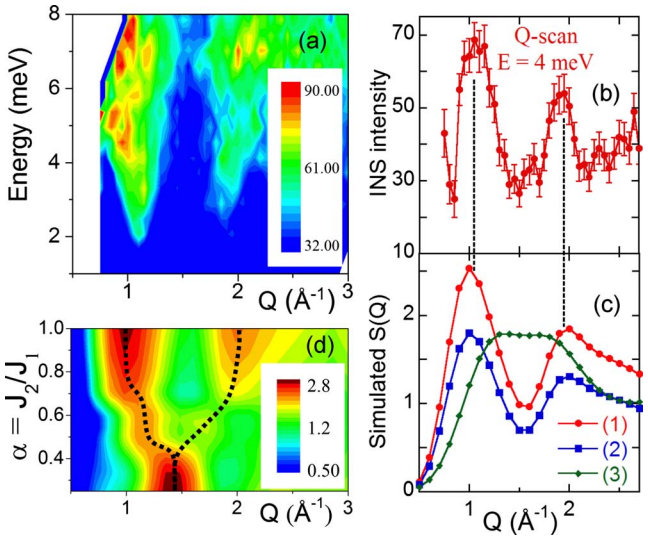

FIG. 4. (Color online) (a) Map of $S(Q,\omega)$ measured for $BiCu_2PO_6$ at 11 K on the three-axis cold spectrometer 4F1 (color online). (b) Experimental Q scan measured at 4 meV; the energy of the lowest magnetic excitation in $BiCu_2PO_6$ at $T=1.7$ K(from the thermal triple axis spectrometer 2T in counts per 2 minutes of acquisition time). (c) Magnetic structure factor $S(Q,\omega_0)$ at the energy ω_0 of the lowest magnetic excitation using the $J_1-J_2-J_4$ and $J_1-J_2-J_3$ frustrated spin ladder models. The curves 1 and 2 are obtained from the $J_1-J_2-J_4$ model and the curve 3 from the $J_1-J_2-J_3$ model (curve 1: $J_4/J_1=1$ and $J_2/J_1=0.75$; curve 2: $J_4/J_1=0.25$ and $J_2/J_1=0.75$; and curve 3: $J_3/J_1=1$ and $J_2/J_1=0.75$). The intensity is in arbitrary units. (d) Mapping of $S(Q,\omega_0)$ as a function of the frustration ratio $\alpha=J_2/J_1$. The color scale represents the amplitude of $S(Q,\omega_0)$.

The relative $J_1-J_2-J_4$ values obtained from our GGA$+U$ calculations (typically, $\alpha\equiv J_2/J_1=0.75$ and $J_4/J_1=1$ with $U=8$ eV; see Table I) yields the correct positions for the $S(Q)$ maxima at $Q_{max}=1$ and 2 Å^{-1}. Moreover, $S(Q,\omega_0)$ calculated for $J_4/J_1=1$ shows that the frustration ratio $\alpha=J_2/J_1$ should be in the 0.7–1 range to reproduce the experimental INS data [Fig. 4(d)]. In our $J_1-J_2-J_4$ frustrated spin ladder model, the splitting of the first $S(Q,\omega_0)$ peak occurs above the critical value $\alpha_c\approx 0.5$ [Fig. 4(d)]; this frustration-induced phenomenon is the clear signature of a Lifshitz point, where the $S(Q,\omega_0)$ peak starts moving away from a commensurate Q value.[22,23] This analysis shows that $BiCu_2PO_6$ is located in the incommensurate region of the phase diagram not far from the critical Lifshitz point. In reproducing the $S(Q,\omega_0)$ peaks at 1 Å^{-1} and 2 Å^{-1} in terms of the $J_1-J_2-J_4$ frustrated spin ladder model, the region of the required J_2/J_1 ratio is narrow (i.e., ~0.75) but that of the required J_4/J_1 ratio is rather wide, i.e., $0.25\leq J_4/J_1\leq 1$ [Fig. 4(c)]. This indicates that the spin frustration within each leg chain is largely responsible for the split of $S(Q,\omega_0)$ peaks. It should be noted that for a weakly frustrated ladder system, such as $La_4Sr_{10}Cu_{24}O_{41}$, the observed dispersion is commensurate.[24]

The frustrated spin ladder model for $BiCu_2PO_6$ forms a rich playground for reaching exotic quantum ground states. In the limit of J_1, $J_2\gg J_3$, J_4, the spin lattice becomes a simple frustrated chain, in which the frustration ratio J_2/J_1

induces a quantum phase transition from a gapless spin-fluid phase to a gapped dimer ordered state at the critical ratio $J_2/J_1>0.2411$. In the limit of J_1, J_2, $J_4>J_3$, which describes $BiCu_2PO_6$, a quantum phase transition between three different gapped phases (i.e., the columnar-dimer, the staggered-dimer, and the rung-dimer phases) is expected when the J_4/J_1 ratio is increased.[4] Recent studies on frustrated n-leg spin ladders (with n up to 8) suggest that frustration should induce a transition from a dimer ordered phase at low n to a homogeneous spin liquid state for the infinite n extension.[18] Interestingly, the chemical adaptability of $BiCu_2PO_6$ is such that it may be possible to tune the values of J_1, J_2, J_3, and J_4, for instance, by substituting the VO_4 group for the PO_4 group.[25,26] Thus, solid solutions $BiCu_2P_{1-x}V_xO_6$ may yield promising systems to explore exotic magnetic ground states. A preliminary investigation showed that $BiCu_2P_{1-x}V_xO_6$ decreases its spin gap with increasing x, eventually reaching a gapless state at $x>0.7$, where the crystal structure of $BiCu_2P_{1-x}V_xO_6$ becomes incommensurately modulated.[9]

In conclusion, our work shows that the simplest spin lattice needed for $BiCu_2PO_6$ is a two-leg spin ladder with strong spin frustration along each leg, and this frustration drives $BiCu_2PO_6$ into a gapped quantum singlet ground state with excited magnetic states, showing an incommensurate dispersion.

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[19] To check the validity of our INS simulations, we examined systems, for which exact theoretical results are known. For example, by standard extrapolations to the infinite chain, we obtained the spin gap $\Delta=0.53(3)J$ for the isotropic two-leg spin ladder, which should be compared with the exact value $\Delta=0.51\ J$ (Ref. 20), and the correct evolution of the spin gap for the J_1-J_2 frustrated chain as a function of $\alpha=J_2/J_1$ (Ref. 3). We have also checked that the simulated Q dependence of the first excited state satisfactorily describes the structure factor of the spin 1/2 Heisenberg chain.
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