Spin-gap behavior in the two-leg spin-ladder $BiCu_2PO_6$

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We present magnetic susceptibility and heat capacity data on a new $S=1/2$ two-leg spin ladder compound $BiCu_2PO_6$. From our susceptibility analysis, we find that the leg coupling J_1/k_B is ~80 K and the ratio of the rung-to-leg coupling $J_2/J_1 \sim 0.9$. We present the magnetic contribution to the heat capacity of a two-leg ladder. The spin-gap $\Delta/k_B=34$ K obtained from the heat capacity agrees very well with that obtained from the magnetic susceptibility. Significant interladder coupling is suggested from the susceptibility analysis. The hopping integrals determined using the *N*th order muffin-tin-orbital based downfolding method lead to ratios of various exchange couplings in agreement with our experimental data. Based on our band structure analysis, we find the interladder coupling in the *bc* plane J_3 to be about $0.75J_1$ placing the compound presumably close to the quantum critical limit.

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INTRODUCTION

Following the discovery of high-temperature superconductivity (HTSC) in the cuprates,[1] there has been an increased focus on the properties of low-dimensional antiferromagnetic systems. This is due to the innate exotic properties of these magnetic systems themselves and their supposed connection with HTSC. Significant work has taken place recently elucidating the properties of $S=1/2$ and 1 Heisenberg chains and their response to impurity substitutions. Whereas quantum fluctuations prevent long-range order (LRO) in one-dimensional (1D) Heisenberg systems, three-dimensional (3D) systems exhibit conventional LRO. On the other hand, in two-dimensional (2D) systems where the strength of magnetic interactions and quantum fluctuations can be comparable, one might expect competing ground states and a quantum critical point separating them. Spin-ladders serve as a bridge between one-dimensional (1D) and two-dimensional (2D) magnetic systems and it is believed that an improved understanding of spin-ladders will lead to a better understanding of magnetism in the 2D systems. A major step was taken in this direction with the prediction of spin gaps in even-leg ladders and their absence in odd-leg ladders,[2] followed by experimental verification in $SrCu_2O_3$ (two-leg ladder) and $Sr_2Cu_3O_5$ (three-leg ladder).[3] However, in spite of the large experimental effort, only a small number of gapped ladders have been synthesized and studied. Of these, only two ($LaCuO_{2.5}$ and $Sr_{14}Cu_{24}O_{41}$) could be doped significantly with holes of which only the latter becomes superconducting.[4] Some other compounds which have been investigated are $(C_5H_{12}N)_2CuBr_4$ (Ref. 5), $Cu_2(C_5H_{12}N_2)_2Cl_4$ (Ref. 6), and $Cu_2(C_5H_{12}N_2)_2Br_4$ (Ref. 7) which have substantially smaller spin gaps. There is continued effort to synthesize and study new low-dimensional systems since they provide a rare opportunity to elucidate the significance of low-dimensionality, spin gap, etc. to HTSC as also allow one to examine impurity and doping effects in a strongly correlated cuprate.

In this Brief Report, we report on the preparation and properties of a cuprate which, we demonstrate, can be modeled as a two-leg ladder system with significant interladder coupling in the *bc* plane and negligible interplanar coupling. The spin gap, as determined from our susceptibility and heat capacity measurements is about 34 K while the intraladder leg coupling is about 80 K. Our electronic structure calculations within the framework of the *N*th order muffin-tin-orbital (NMTO) downfolding method[8] yield hopping integrals between various Cu atoms. Using the NMTO downfolding method, we calculate the Wannier-like effective orbitals which illustrate the shape and extent of the active Cu orbitals and therefore indicate the exchange pathways which lead to the ladder topology. From a practical standpoint, the estimated $J/k_B \approx 80$ K provides a unique opportunity to examine the excitations of the coupled ladder system at temperatures ranging from well above J/k_B to well below J/k_B. Impurity substitutions will then allow us to probe the nature of magnetic effects thus induced, in a wide temperature range.

CRYSTAL STRUCTURE AND MEASUREMENTS

Our measurements are on single phase, polycrystalline $BiCu_2PO_6$ samples (space group *Pnma* with lattice parameters $a=11.776$ Å, $b=5.1776$ Å, and $c=7.7903$ Å).

A schematic diagram of the structure is shown in Fig. 1. The unit cell contains four formula units, with two inequivalent Cu (Cu1 and Cu2) sites and four inequivalent O (O1-O4) sites. The characteristic feature of the structure are CuO_5 distorted square pyramids, with a Cu^{2+} ion at the center of the fivefold oxygen coordination. Two such pyramids share an edge formed from a pair of basal oxygens (O2) to give rise to a Cu dimer with an intradimer distance of 2.8 Å. Along the *b* axis, each dimer connects two others by its four O1 corners resulting in a zigzag double chain (ladder) running along the *b* axis (see Fig. 1). The interdimer cohesion is further strengthened by PO_4 tetrahedra that connect two consecutive dimers by O2 corners. The Bi ions are positioned between two ladders. The Cu-O-Cu angle along the leg is about 112° and that along the rung is about 92°. In Fig. 1, various exchange couplings (J_1, J_2, etc.) and hopping integrals (t_1, t_2, etc.) have been indicated.

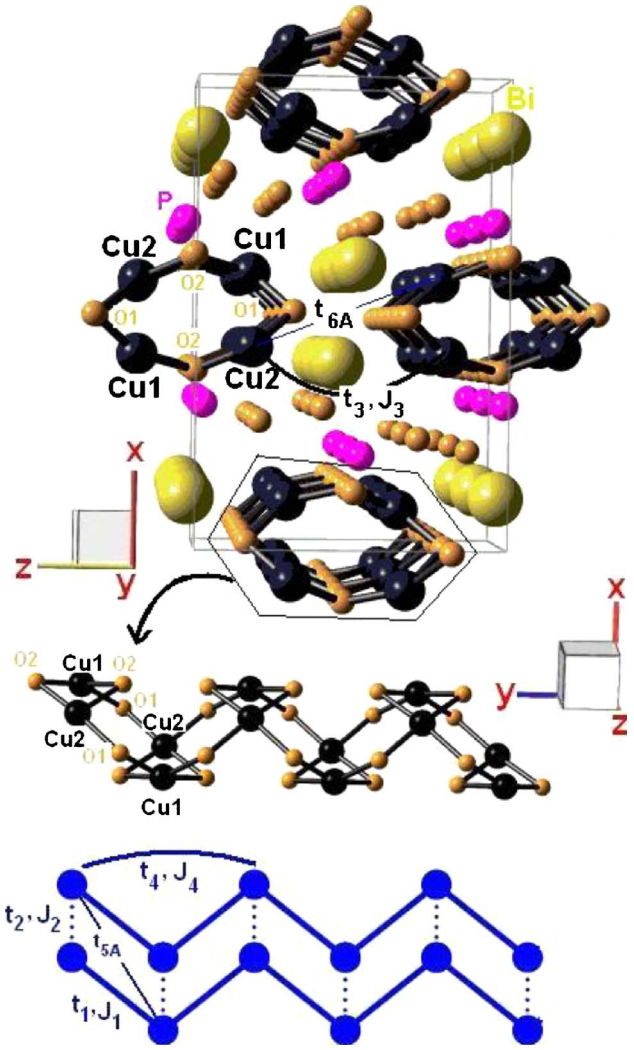

FIG. 1. (Color online) A schematic of the $BiCu_2PO_6$ crystal structure is shown. It can be seen that two-leg ladders run along the crystallographic b direction. The two-leg ladder is separately shown for clarity. Also shown are the various significant hopping parameters and exchange couplings between Cu atoms.

Our results of the susceptibility χ_{meas} (magnetization M divided by applied field H) as a function of temperature T using a vibrating sample magnetometer (VSM) of a physical property measurement system (PPMS) from Quantum Design are plotted in Fig. 2. As seen, χ_{meas} has a broad maximum around 57 K (indicative of a low-dimensional magnetic system) below which it drops rapidly (suggestive of a spin gap). A very weak low-temperature upturn is seen below 6.5 K, likely due to extrinsic paramagnetic impurities and/or natural chain breaks in our polycrystalline sample. We now analyze these data quantitatively.

An analytical solution for the spin-susceptibility of two-leg ladders in the full T-range is not known. However, Johnston, based on extensive quantum Monte Carlo (QMC) simulations[9] has proposed an equation which accurately reproduces the QMC-determined susceptibilities at discrete temperatures. This equation (not reproduced here since it is unwieldy) is useful for determining the exchange couplings

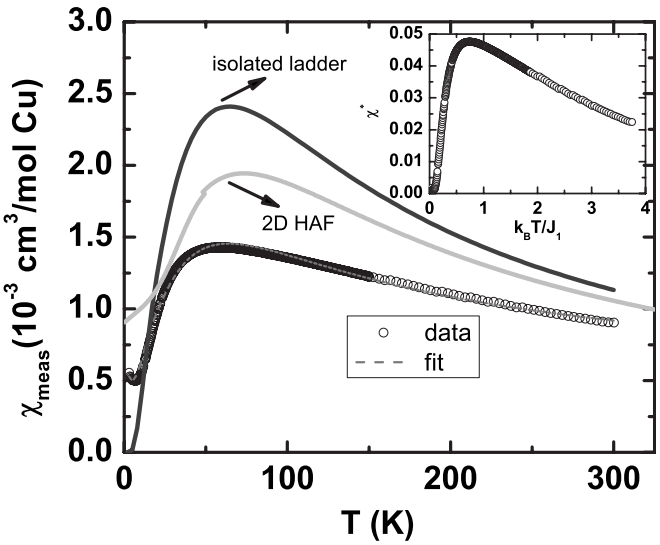

FIG. 2. Magnetic susceptibility ($\chi_{meas}=M/H$) vs temperature T for $BiCu_2PO_6$ in an applied field of 5 kG. The open circles represent the raw data and the dashed line is a fit (see text). Also shown are simulated curves for the isolated ladder (dark gray line) and for the 2D HAF (gray line). The inset shows the dependence of χ^* on k_BT/J_1 (see text).

by fitting the measured susceptibility data and has been used to analyze such data in the two-leg ladder $SrCu_2O_3$. We then fit (dashed line in Fig. 2) χ_{meas} to $\chi_o+C/(T-\theta)+m\chi_{ladder}(T)$ where the fitting parameters are χ_o, C, θ, J_2/J_1, J_1, and m. Here $\chi_{ladder}(T)$ is the χ of isolated ladders as given by Johnston.[9] In the absence of a generic fitting function which can take into account arbitrary interladder interactions, we attempt to do so using the parameter m. With m as a variable, the obtained parameters are $\chi_o=(4.4\pm0.1)\times10^{-4}$ cm^3/mol Cu, $C=(3.0\pm0.2)\times10^{-4}$ cm^3 K/mol Cu, $\theta\sim0$ K, $J_2/J_1=0.87\pm0.05$, $J_1/k_B=(80\pm2)$ K, and $m=0.41\pm0.02$. The value of the spin gap using[9] $\Delta/J_1=0.4030\left(\frac{J_1}{J_2}\right)+0.0989\left(\frac{J_1}{J_2}\right)^3$ is about 34 K. The Curie constant corresponds to less than 0.1% of isolated $S=1/2$ impurities. This value is comparable to typical parasitic Curie terms found in single crystals, indicating the very high quality of our samples. Since the core-diamagnetic susceptibility[10] χ_{core} is -0.6×10^{-4} cm^3/mol, $\chi_o-\chi_{core}$ yields the Van Vleck susceptibility $\chi_{VV}=5\times10^{-4}$ cm^3/mol which is somewhat higher than χ_{VV} of other cuprates. We show in Fig. 2 the curve for isolated two-leg ladders (with $J_1/k_B=80$ K). We also show the simulated curve for a uniform, 2D $S=1/2$ HAF with $J/k_B=80$ K where the high-T behavior is generated using the series expansion given by Rushbrooke and Wood.[11] Also, Johnston[12] parametrized the low-T $\left(\frac{k_BT}{J}\leqslant1\right)$ simulations of Takahashi[13] and Makivic and Ding,[14] which we use. The experimental data are lower than both the 2D HAF curve and the isolated ladder susceptibility. This behavior points to the importance of a next-nearest-neighbor (NNN) interaction along the leg (which might be expected due to the zigzag nature of the leg) which might be frustrating and might even enhance the spin gap. In a latter section, based on our band-structure calculations, we actually find significant

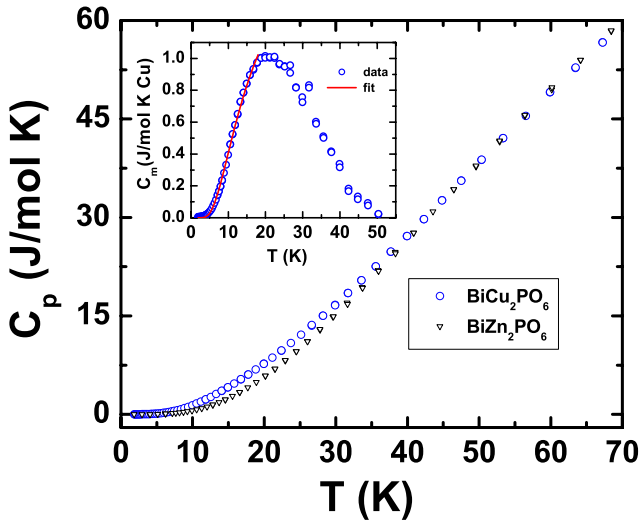

FIG. 3. (Color online) The measured heat capacity as a function of T for $BiCu_2PO_6$ and $BiZn_2PO_6$. Inset: the magnetic specific heat of $BiCu_2PO_6$ along with a fit (see text).

NNN as also interladder couplings. The absence of LRO in spite of these deviations from the isolated ladder picture should motivate the theorists to refine their models of such systems. In the inset of Fig. 2, we plot the normalized susceptibility $\chi^*(T)=\chi_{spin}(T)J_1/(Ng^2\mu_B^2)$ [where $\chi_{spin}(T)=\chi_{meas}-\chi_o-C/T$] as a function of k_BT/J_1. We find $\chi^{*,\max}$ (i.e., χ^* at the broad maximum) to be about 0.05 which is lower than the expected value for isolated ladders of about 0.12.

To further confirm the spin-gap nature of $BiCu_2PO_6$, we did heat capacity C_p measurements. Since the lattice C_p dominates the data, it has so far not been possible to experimentally determine the magnetic contribution to C_p in any spin-ladder compound unambiguously. In the present case, we are fortunate to have a nonmagnetic analog of $BiCu_2PO_6$ in $BiZn_2PO_6$. We have then determined the magnetic heat capacity C_M of $BiCu_2PO_6$ by subtracting the measured C_p of $BiZn_2PO_6$ from that of $BiCu_2PO_6$ (see Fig. 3 inset). The data are fit to[9] $C_M(T)=\frac{3}{2}Nk_B\left(\frac{\Delta}{\pi\gamma}\right)^{1/2}\left(\frac{\Delta}{k_BT}\right)^{3/2}\left[1+\frac{k_BT}{\Delta}+0.75\left(\frac{\Delta}{k_BT}\right)^2\right]\exp\left(\frac{-\Delta}{k_BT}\right)$ shown by the solid line (Fig. 3 inset). From the fit, the spin gap $\frac{\Delta}{k_B}\sim 34$ K, in excellent agreement with our susceptibility results.

FIRST PRINCIPLES STUDY

The local density approximation-density functional theory (LDA-DFT) band structure for $BiCu_2PO_6$ is calculated using the linearized-muffin-tin-orbital (LMTO) method based on the Stuttgart TB-LMTO-47 code.[15] The key feature of the nonspin-polarized electronic structure presented in Fig. 4 is eight bands crossing the Fermi level which are well-separated from the rest of the bands. These bands are predominantly derived from the antibonding linear combination of Cu $d_{x^2-y^2}$ and basal O p_σ states in the local reference frame where the z axis is along the shortest Cu-O bond while the x and y axes point along the basal oxygens O1 and O2. The band structure is 2D with practically no dispersion perpendicular to the ladder plane (along ΓX). The eight band complex is half-filled and metallic as expected in LDA. It lies above the other occupied Cu-d, O-p, and Bi-s character dominated bands. The P (s,p) and Bi (p) derived states are unoccupied and lie above the Fermi level, with the Bi-p states having nonnegligible admixture with the conduction bands. This admixture of the conduction band with Bi-p states is important in mediating the Cu-Cu interladder exchange coupling. Starting from such a density functional input we construct a low-energy model Hamiltonian using the NMTO downfolding technique. This method[8] extracts energy selective Wannier-like effective orbitals by integrating out high energy degrees of freedom. The few orbital Hamiltonian is then constructed in the basis of these Wannier-like effective orbitals. Here, we shall retain only Cu $d_{x^2-y^2}$ orbital in the basis and downfold the rest. The effective Cu $d_{x^2-y^2}$ muffin-tin orbitals generated in the process will be renormalized to contain in their tail other Cu-d, O-p, Bi, and P states with weights proportional to the admixture of these states with Cu $d_{x^2-y^2}$. Fourier transform in the downfolded Cu $d_{x^2-y^2}$ basis gives the desired tight-binding Hamiltonian $\mathcal{H}=\Sigma_{\langle i,j\rangle}t_{ij}(c_j^\dagger c_i+c_i^\dagger c_j)$ in terms of the dominant Cu-Cu hopping integrals t_{ij}. This tight binding Hamiltonian will serve as the single electron part of the many-body Hubbard model relevant for this system and can be mapped to an extended Heisenberg model with the exchange couplings related to the LDA hoppings by $J_{ij}=\frac{4t_{ij}^2}{U_{eff}}$ where U_{eff} is the screened onsite Coulomb interaction. The various hoppings are displayed in Table I and indicated in Fig. 1. The intradimer (rung) hopping proceeds mainly via the edge sharing oxygens while the interdimer interaction (leg hopping) proceeds via the corner sharing oxygens with support from the PO_4 complex. As anticipated in the experiments, we do indeed find that the ratio of the rung hopping to the leg hopping $J_2/J_1\approx 1$. We find that the NNN coupling along the leg J_4 is about 0.3 J_1. Depending on the relative sign of this interaction with respect to that of J_1 one might get significant frustration effects which should also have a bearing on the ground state of the system. We also find an appreciable coupling between the ladders $(J_3/J_1\approx 0.75)$ mediated primarily by the unoccupied Bi-p states. Our conclu-

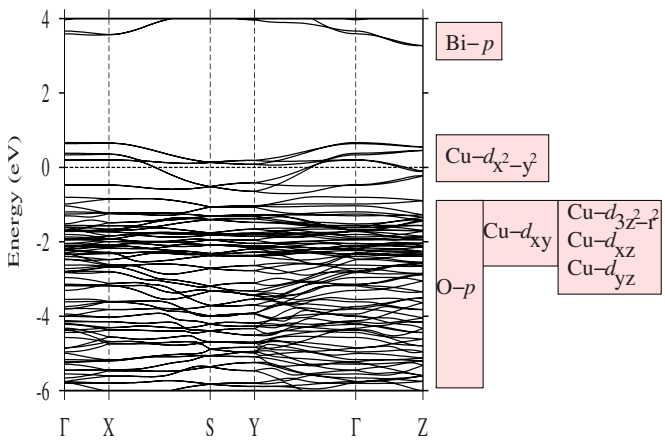

FIG. 4. (Color online) LDA band dispersion of $BiCu_2PO_6$ along various symmetry directions.

TABLE I. Hopping parameters (t_n) between various Cu's are tabulated along with the corresponding Cu-Cu distances. The hopping paths are indicated in Fig. 1.

Hopping path	Cu-Cu distance (Å)	t_n (meV)	$J_n/J_1 = (t_n/t_1)^2$
Leg (t_1)	3.22	155	1
Rung (t_2)	2.90	154	1
Interladder (t_3)	4.91	133	0.74
NNN in leg (t_4)	5.18	91	0.34
Diagonal (t_{5A})	4.43	30	0.04
Diagonal (t_{6A})	5.81	26	0.03

sion is further supported by the plot of the corresponding Cu $d_{x^2-y^2}$ Wannier function in Fig. 5. We find that each Cu $d_{x^2-y^2}$ orbital in the unit cell forms strong $pd\sigma$ antibonding with the neighboring O-p_x/O-p_y orbitals resulting in the conduction band complex. The Cu ions strongly couple along the leg as well as the rung of the ladder confirming that the hoppings in either direction should be comparable. The O-p_x/O-p_y tails bend towards the Bi atom, indicating the importance of the hybridization effect from the Bi cations and therefore enhances the Cu-Cu interladder exchange interaction (see Table I).

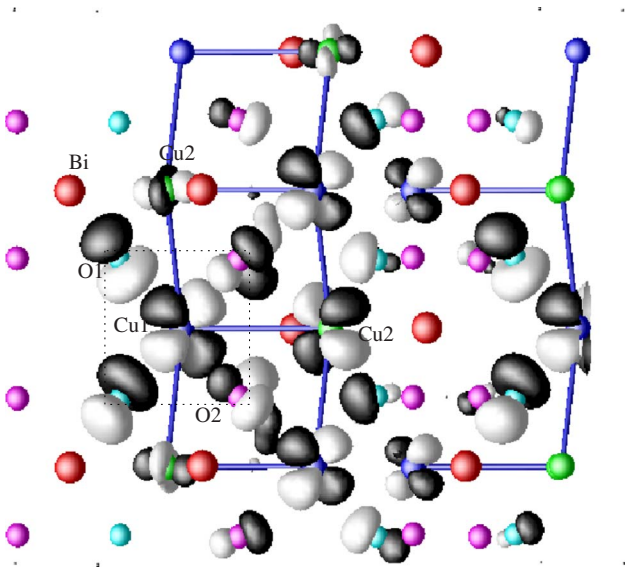

FIG. 5. (Color online) Effective Cu1 $d_{x^2-y^2}$ orbital with lobes of opposite signs colored as black and white. The $d_{x^2-y^2}$ orbital is defined with the choice of the local coordinate system as discussed in the text (height of the isosurface = ±0.09). The spheres represent the ions.

CONCLUSION

In conclusion, we have presented a $S=1/2$ two-leg ladder $BiCu_2PO_6$. From our χ and C_M data we obtain a spin gap $\Delta/k_B \sim 34$ K and a leg coupling $J_1/k_B \sim 80$ K. From our first principles LDA-DFT calculations, we find $J_2/J_1 \sim 1$ and a significant interladder interaction in the corrugated bc plane ($J_3/J_1 \sim 0.74$). Considering that the uniform $S=1/2$ 2D AF system has an ordered ground state, we feel that the strong interladder interaction in $BiCu_2PO_6$ places it close to a quantum critical point. The moderate value of the Δ/k_B in $BiCu_2PO_6$ will allow one to explore the magnetic properties in a large T range, well below and well above the gap temperature, enabling a comparison with and refinement of theoretical models. We feel that there might still be unanticipated features in the physics of low-dimensional magnets and we expect our work to motivate others to carry out numerical simulations and explore the phase diagram of coupled two-leg ladders in the presence of NNN couplings along the leg. We are presently considering doping and substitutions in this two-leg ladder which might be able to tune the interladder exchange and effect a quantum phase transition.

ACKNOWLEDGMENTS

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