Anisotropic Cascade of Field-Induced Phase Transitions in the Frustrated Spin-Ladder System BiCu₂PO₆

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(Received 17 July 2012; published 17 October 2012)

 $BiCu_2PO_6$ is a frustrated two-leg spin-ladder compound with a spin gap that can be closed with a magnetic field of approximately 20 T. This quantum phase transition and its related phase diagram as a function of magnetic field and temperature (H, T) are investigated up to 60 T by means of specific heat, magnetocaloric effect, magnetization, and magnetostriction measurements. In contrast to other gapped quantum magnets, BiCu₂PO₆ undergoes a series of unexpected first- and second-order phase transitions when an external magnetic field is applied along the crystallographic c axis. The application of a magnetic field along the b axis induces two second-order phase transitions. We propose that the anisotropy and complex phase diagram result from the interplay between strong geometrical frustration and spin-orbit interaction necessary for the description of this fascinating magnetic system.

DOI: 10.1103/PhysRevLett.109.167204

PACS numbers: 75.10.Jm, 75.40.Cx, 75.50.-y

Materials with a spin gap have recently attracted intense theoretical and experimental interest due to the occurrence of field-induced exotic ground states and unconventional (H, T) phase diagrams [1–6]. In BiCu₂PO₆, a spin energy gap between the singlet ground state and the first excited triplet states opens upon cooling because of singlet correlations forming between pairs (dimers) of Cu^{2+} ions with S =1/2. This spin gap can be closed by applying a magnetic field $H = H_c$, hence inducing a quantum phase transition (QPT), resulting in the generation of a macroscopic number of triplet states (triplons) that occupy the Cu dimers in the crystal lattice. The triplet excitations, because of interactions with next-nearest neighbors and beyond, are dispersive and hence can propagate throughout the lattice. In the language of hard-core bosons [7], the triplons have kinetic energy from their mobility in the lattice and potential energy given by their interactions. Depending on the balance between the potential and the kinetic energy of the triplons, the fieldinduced ground states can be described as a Bose-Einstein condensate with uniform staggered order [1,2], as a Mottinsulating state with superlattice order [4], or even as a supersolid phase [8]. The kinetic energy of the triplons is strongly reduced by geometrical frustration, and frustration can lead to various exotic ground states.

The magnetic Cu^{2+} ions in the related quasi-2D system SrCu₂(BO₃)₂ are arranged in a Shastry-Sutherland frustrated lattice, which to date is the only material where a superlattice structure of triplets has been investigated in depth [3,4]. An important step in this topical area of condensed matter physics is to find alternative systems to test theoretical approaches in different limits. In this Letter, we report the first observation of a cascade of phase transitions through magnetization, specific heat, and magnetostriction measurements as a function of magnetic field, resulting in an anisotropic (H, T) phase diagram for the frustrated twoleg ladder spin-gap system BiCu₂PO₆ under fields up to 60 T. The results are discussed in the context of potential magnetic-field-induced superstructures of triplons and transitions between phases with different (commensurate or incommensurate) magnetic order.

BiCu₂PO₆ crystallizes in the orthorhombic Pnma structure and is composed of zigzag two-leg Cu ladders along the crystallographic b axis [9]. Along the rung direction (c axis), the CuO₄ plaquettes share corners and induce the rung coupling, J_{Rung}, mediated by Cu-O-Cu superexchange interaction [10]. These rungs are stacked along the b axis, forming zigzag two-leg ladders and leading to geometrical frustration between the nearest-neighbor leg coupling J_{Leg} and the next-nearest-neighbor leg coupling J_{NNN} . Bi cations are positioned between each ladder, but spin interaction between ladders, J_{II} , is possible due to Cu-O-Cu superexchange paths [10]. The *bc* planes are separated by PO₄ tetrahedra, and interactions between the planes are believed to be very weak [10,11].

The exchange interactions in BiCu₂PO₆ have recently been studied in detail by inelastic neutron scattering and magnetic susceptibility measurements on powder samples, and by numerical calculations, and are estimated to be $J_{\rm Leg} = 137.8$ K, $J_{\rm NNN} = 73.3$ K, and $J_{\rm Rung} = 58.4$ K, respectively [11]. The potentially strong frustration between J_{Leg} and J_{NNN} suggests that the gapped spin-singlet ground state has an incommensurate dispersion [11,12]. NMR data were used to estimate the spin gap $\Delta_s/k_B \approx 38.3$ K [13], which is consistent with the critical field $\mu_0 H_c \approx 22 \text{ T}$ estimated from magnetization measurements in a polycrystalline sample [10]. J_{IL} cannot be accurately estimated because numerical simulations show it to be very sensitive to the choice of the other stronger exchange parameters [10,11]. This leads to some controversy regarding the fieldinduced ground state and the dimensionality of the spin system. Tomonaga-Luttinger liquid [10] and Ising ground states [12] have been predicted but remain an open question in BiCu₂PO₆.

Single crystals of BiCu₂PO₆ were grown by the traveling solvent-floating zone technique in an image furnace (Model FZ-T-10000-H-VI-VP, Crystal System, Inc., Japan) using four 300 W halogen lamps as heat sources, as described before [9]. Specific heat (C_p) and magnetocaloric effect (MCE) measurements were performed in a 35 T dc magnet. C_p vs T was obtained using both thermal relaxation time and dual slope techniques [14]. Specific heat capacity as a function of H was measured using an ac technique, simultaneously collecting the MCE data [15]. The magnetic contribution to the specific heat, C_M , was obtained by subtracting the lattice contribution determined in its nonmagnetic analog BiZn₂PO₆ [16]. Longitudinal magnetostriction (MS) measurements were performed by using a fiber optic strain gauge in a 60 T pulsed magnet [17]. Magnetization measurements were performed in a magnetic field up to 60 T [10]. The magnetic moment of the sample was obtained by integration of the voltage induced in a compensated pickup coil system surrounding the sample. Details of the experimental procedure are described elsewhere [10]. The field dependence of the magnetization M(H) was calibrated with low field magnetization data measured through NMR (see, for instance, Kodama et al. [18] for a detailed discussion of how NMR data can be used to quantify magnetic moments in frustrated magnets) and a Quantum Design® Vibrating Sample Magnetometer.

Magnetization data for three different magnetic-field orientations, i.e., parallel to the main crystallographic axes, are shown in Fig. 1. Depending on the field orientation, the magnetization data show a finite slope at low magnetic fields. Upturns corresponding to the closure of the spin gap are observed at $\mu_0 H_c = 23$, 21, and 20 T for magnetic fields applied along the *a*, *b*, and *c* axes, respectively, in good agreement with $\mu_0 H_c \approx 22$ T measured on a polycrystalline sample [10]. For H//a, a smooth magnetization curve is observed above H_c within the noise



FIG. 1 (color online). Magnetization M vs H for H//a [light gray (red) line], H//b [dark gray (blue) line], and H//c (black line). Inset: M vs H for H//c measured at different temperatures (the experimental data are vertically displaced for clarity).

level of our measurement. On the other hand, for fields applied along the *b* and the *c* axes, the M(H) curves show unexpected transitions at $\mu_0 H \approx 36$ T, ≈ 34 T, and ≈ 40 T, respectively.

The relative crystal length changes in the *a*, *b*, and *c* axes $(\Delta L/L)$ are shown in Figs. 2(a)–2(c), respectively. When a



FIG. 2 (color online). Magnetostriction $\Delta L/L$ vs *H* for (a) H//a, (b) H//b, and (c) H//c. For clarity, the data at different temperatures were shifted vertically.

magnetic field is applied parallel to the c axis, $\Delta L/L$ shows a sharp increase at H_c and two additional steps at higher fields. These steps persist up to 5.7 K and are similar to the M(H) curves at the corresponding temperatures (see the inset of Fig. 1). Below 6 K, MS measurements detect that both high-field anomalies display strong hysteresis as a function of field, suggesting first-order phase transitions. Accordingly, MCE measurements in dc fields detect an irreversible heat release on both field up- and down-sweep, as shown by the thick (orange) curve in Fig. 3(a). The observed heating reveals the presence of dissipation and/or irreversibility, which can be the signature for first-order phase transitions [15,19]. Taken together, hysteresis in $\Delta L/L$ and irreversible heating in MCE provide firm evidence that the anomalies correspond to first-order phase transitions. When a magnetic field is applied along the a and b axes, the $\Delta L/L$ curves exhibit broad structures. For H//b, two broad anomalies can be seen at H_c and at $\mu_0 H \approx$ 35 T. The broad anomaly at higher field (indicated by an arrow) seems to be connected to the observed magnetization



FIG. 3 (color online). Magnetic phase diagram for (a) H//c and (b) H//b deduced from the C_p (circles), MS (squares), and MCE (triangles) measurements taken at various temperatures and as a function of magnetic field. The error bars are evaluated from the size of the hysteresis and the width of the peaks. The light gray (orange) curves correspond to MCE data measured in a 35 T dc magnet. (a) The MCE traces have been multiplied by a factor of 10. (b) MCE traces for H//b have been multiplied by 100 (at 1.3 K) and 50 (at 0.7 K), respectively.

steps. Accordingly, it appears where the MCE data show heating and cooling, as seen in Fig. 3(b). Symmetric MCE curves are typically seen at second-order phase boundaries.

Figures 4(a) and 4(b) show the magnetic contribution to the specific heat, $C_M(T)$ for H//b and H//c, respectively. Above H_c , $C_M(T)$ exhibits λ -type anomalies for both H//cand H//b. Sharp anomalies are characteristic of longrange magnetic ordering, rather than a crossover expected for low-dimensional systems [6]. When a magnetic field is applied along the *b* axis, the peak position in temperature and the size of the anomaly monotonically grow with increasing field. On the other hand, for H//c, the peak position in temperature first increases and then splits into two peaks above 33 T. Figures 4(c) and 4(d) show the magnetic-field dependence of C_M for H//c and H//b, respectively. In the spin-gapped region, $H < H_c$, $C_M(H)$ monotonically increases as the magnetic field increases.



FIG. 4 (color online). Specific heat C_M vs T for (a) H//c and (b) H//b. The low temperature upturn in C_M is due to a nuclear Schottky anomaly. C_M vs H for (c) H//c and (d) H//b. The temperature stability was 3% during magnetic-field sweeps.

This tendency is attributed to the increase of triplet excitations, which are activated as the spin gap is closed. At $H = H_c$, a sharp peak emerges, which shifts to higher fields as the temperature increases. The position of the peak at different temperatures is used to construct the (H, T) phase diagram, yielding a very good agreement among the $C_M(T)$, magnetization, MS, and MCE results. When the external magnetic field is applied parallel to the *c* axis, $C_M(H)$ suddenly drops above $\mu_0 H = 32$ T. Below 2 K, a broad anomaly develops around $\mu_0 H \approx 30$ T. The complex shape of $C_M(H)$ reflects the occurrence of a series of field-induced phase transitions. For H//b, a tiny kink was observed below 1.3 K (indicated by an arrow). The kink originates from a second-order phase transition, as indicated by symmetric MCE curves.

Figure 3 summarizes the phase boundaries in $BiCu_2PO_6$ for fields applied parallel to the *b* and *c* axes, constructed from the C_p , MCE, and MS measurements. Open symbols indicate what are likely to be first-order phase boundaries, whereas solid symbols indicate possible second-order phase boundaries. The anisotropy above the QPT at H_c implies that the observed ordered states (II, III, IV, or V) likely have different spin structures.

Field-induced QPTs in gapped quantum spin systems have been studied in a number of compounds, of which the highly frustrated Shastry-Sutherland system $SrCu_2(BO_3)_2$ is a remarkable example. In this material, the transitions at high magnetic fields are accompanied by magnetization steps, evidence of magnetic texture originated in strong geometric frustration. In this Letter, we show for the first time that BiCu₂PO₆, whose backbone is formed by coupled, frustrated spin ladders, also exhibits a series of second- and first-order phase transitions above a fieldinduced QPT. Additionally, as shown in Fig. 1, we observe strongly anisotropic critical fields and a linear magnetization vs field in the spin-gapped region. These indicate that BiCu₂PO₆ has a strong spin-orbital interaction which leads to a Dzyaloshinksy-Moriya term and g-factor anisotropy. Spin-orbital interaction, intrinsically anisotropic, produces off-diagonal Dzyaloshinski-Moriya terms that allow spinlevel mixing and a linear M(H) dependence for $H < H_c$ [10]. The combined effects of strong magnetic frustration and spin-orbital interaction could also account for the anisotropy and for the complexity of the phase diagram displayed by BiCu₂PO₆.

Indeed, geometrical frustration is likely to favor the localization and lead to the formation of magnetic texture and concomitant magnetization plateaus in BiCu₂PO₆. The observed upturns in M(H) (Fig. 1), however, are followed by concave shoulderlike regions between features rather than plateaus expected for an incompressible magnetic state. This important characteristic of the data could be a hint for the formation of a spin supersolid, as proposed by Sengupta *et al.* [8]. However, in addition to the lack of estimation of $J_{\rm IL}$, the geometrical frustration renders it

difficult to apply simple quantum Monte Carlo approaches to BiCu₂PO₆. An alternative scenario may be novel transitions between phases with different commensurate or incommensurate spin structures, similar to those reported in the frustrated quasi-1D quantum spin chain materials Cs₂CuCl₄ [20,21] and BaCu₂Ge₂O₇ [22]. In these systems, the observed anisotropic phase diagrams are likely due to spin-orbital interaction. The magnetization magnitude at the fields where steps occur may also be consistent with this picture. However, it should be pointed out that there is no spin gap in Cs_2CuCl_4 and $BaCu_2Ge_2O_7$. A field-induced anisotropic commensurate-incommensurate transition has not been found in any other spin-gapped ladder systems. The high magnetic fields at which these features are observed make additional experimental studies such as by elastic or inelastic neutron scattering quite difficult.

In conclusion, we present the (H, T) phase diagram of BiCu₂PO₆, a new frustrated gapped quantum magnet, up to 45 T. Anisotropic transitions are observed at high magnetic fields, which have not been reported for other low-dimensional spin-gap systems. The anisotropic and remarkably complex phase boundaries possibly arise from the interplay between spin-orbital interaction and geometric frustration. More theoretical work is needed to be able to fully understand field-induced phase transitions in such frustrated quasi-1D ladder systems. On the experimental side, high-field NMR could be important to elucidate the spin structure of the different regions of the phase diagram.

We thank A. Feiguin and F. Casola for fruitful discussions, Li Gang and E. D. Mun for assistance during experiments, and S. A. Crooker for his contributions and assistance with the optical FBG Magnetostriction measurement. Y. K., A. U., R. D. M., and M. J. were supported by US-DOE, NSF through NSF-DMR-0084173, and the State of Florida. Y. K. was also partially supported by The Institute for Solid State Physics. L. B. is supported by DOE-BES through Grant No. DE-SC0002613. This work was partially supported by the DFG and EuroMagNET II (EU Contract No. 228043). Work in Switzerland was supported by the Swiss NSF under MaNEP and Division II.

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