Role of anisotropy in the spin-dimer compound BaCuSi$_2$O$_6$

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We present results of magnetization and electron paramagnetic resonance experiments on the spin-dimer system BaCuSi$_2$O$_6$. Evidence indicates that the origin of anisotropic terms in the spin Hamiltonian lies in magnetic dipolar interactions. Axial symmetry breaking is on a very small energy scale of $\leqslant 11$ mK, confirming Bose-Einstein condensation critical scaling over an extended temperature range in the vicinity of the quantum critical point.

A field-tuned quantum critical point (QCP) separates the low-field quantum paramagnetic phase in spin-dimer compounds from the magnetically ordered phase in high magnetic fields. The *XY* antiferromagnetic ordered state of these compounds corresponds to a Bose-Einstein condensate (BEC) in the absence of axial symmetry breaking. To ascertain the extent of the BEC universal region in each spin-dimer material therefore, it is vital to identify the nature and size of any anisotropic terms that may be present in the Hamiltonian.[1] In order to observe BEC critical scaling, any anisotropic terms must be small enough that the universal region is at least a decade in reduced field. Anisotropic terms may be directly measured by means of electron paramagnetic resonance (EPR), which has revealed, for example, in the prototypical spin-dimer compound TlCuCl$_3$ (triplon bandwidth ~1 meV),[2–6] staggered Dzyaloshinskii-Moriya (DM) terms on the order of 0.1 meV.[7] In this report, we discuss the size and role of anisotropy in the spin-dimer compound BaCuSi$_2$O$_6$.[8–11]

A first approximation to the equivalent magnetic lattice corresponding to the room temperature tetragonal body-centered BaCuSi$_2$O$_6$ lattice[12] is the isotropic spin Hamiltonian

$$\mathcal{H} = \sum_i J\mathbf{s}_{i,1} \cdot \mathbf{s}_{i,2} + \sum_i \sum_\nu J'\mathbf{s}_{i+\hat{e}_\alpha,\nu} \cdot \mathbf{s}_{i,\nu} + \sum_i J_f \mathbf{s}_{i+\hat{e}_\beta,1} \cdot \mathbf{s}_{i,2}$$
$$- g_\theta \mu_B \sum_{i,\nu} H s^z_{i,\nu}. \tag{1}$$

An antiferromagnetic (AF) exchange constant $J>0$ couples each pair of Cu^{2+} $s=\frac{1}{2}$ spins within vertical spin dimers on Cu$_2$Si$_4$O$_{12}$ layers (where i is the index of the dimer, and $\mathbf{s}_{i1}$ and $\mathbf{s}_{i2}$ are the two spins that form the pair i). Intralayer (J') and interlayer (J_f) AF exchange constants couple nearest neighboring spin dimers on the lattice, indexed by $\hat{e}_\alpha = \{\hat{x}, \hat{y}\}$, $\hat{e}_\beta = \{\hat{z} \pm \hat{x}/2 \pm \hat{y}/2\}$ as defined in the high-temperature structure.[13] For an $s=\frac{1}{2}$ system, energy levels corresponding to the isotropic Hamiltonian are a groundstate singlet, and three degenerate triplet excited states, separated from the ground state by the spin gap Δ. An applied magnetic field H introduces a Zeeman splitting term in the Hamiltonian, scaled by the g factor g_θ, corresponding to the

orientation of H. Experimental results reveal a critical magnetic field $H_{c1} \sim 23.5$ T at which the system orders for $H \| c$, and comparison of the measured phase boundary with the model Hamiltonian in Eq. (1) gives values of $J=4.45$ meV, $J'=0.51$ meV, and an even smaller value of J_f.[9,10]

The above description neglects anisotropic exchange interactions which can reduce the symmetry of the ordered state. In the more general spin Hamiltonian, the bilinear spin term $\mathbf{s}_i \cdot \mathbf{s}_j \equiv \mathbf{s}_i \mathbf{I} \mathbf{s}_j$ in Eq. (1) is replaced by the exchange interaction $\sum_{i,j=1}^3 \mathbf{s}_i \overleftrightarrow{T}_{i,j} \mathbf{s}_j$, where

$$\overleftrightarrow{T}_{i,j} = 3T_s + \overleftrightarrow{T}_{as} + \overleftrightarrow{T}_{sm}, \tag{2}$$

$$\overleftrightarrow{T}_{as} = \sum \frac{1}{2}(T_{i,j} - T_{j,i})(\mathbf{e}_i \times \mathbf{e}_j), \tag{3}$$

$$\overleftrightarrow{T}_{sm} = \frac{1}{2}(T_{i,j} + T_{j,i})_{i \neq j}. \tag{4}$$

T_s is a scalar, while the antisymmetric term $\overleftrightarrow{T}_{as}$ of the form $\mathbf{D} \cdot [\mathbf{s}_i \times \mathbf{s}_j]$, and the traceless symmetric term $\overleftrightarrow{T}_{sm}$ of the form $\mathbf{s}_i \overleftrightarrow{\Gamma} \mathbf{s}_j$ mix spin components.[14] The DM interaction arising from the spin-orbit coupling is antisymmetric in nature, leading to singlet-triplet (ST) mixing to the lowest order of perturbation. Magnetic dipolar interactions, however, belong to the traceless symmetric category. Terms of this nature lead to intratriplet matrix elements entering at the lowest order of perturbation, but ST mixing at higher orders of perturbation only for H oriented away from the dipole vector. An additional possible source of anisotropic exchange interactions is the reduced symmetry of the BaCuSi$_2$O$_6$ lattice at low temperatures (recent structural analysis has revealed a weak orthorhombic structural transition at ~100 K, accompanied by an incommensurate lattice modulation[15]).

An applied magnetic field with a component perpendicular to either the DM or dipolar vector would result in spin nonconservation due to mixing of singlet and triplet energy levels with inequivalent S_z. The symmetry of the Hamiltonian would therefore reduce from rotational invariance [U(1)] to the discrete Z_2 group, resulting in a magnon spectrum in the ordered phase with a finite gap to the minimum,

rather than a gapless Goldstone mode. The extent of symmetry breaking, however depends on the order of perturbation at which spin-nonconserving terms enter the spin Hamiltonian; it is therefore important to identify the origin of any anisotropic interaction in the Hamiltonian. Previous measurements[10,11] of a BEC critical exponent in $BaCuSi_2O_6$ down to 0.03 K provide empirical evidence for the absence of U(1) symmetry-breaking terms down to this energy scale for $H\|c$. In this Rapid Communication, we discuss more direct experimental evidence that estimates the size of any axial symmetry breaking due to anisotropic exchange terms in the spin Hamiltonian.

Single crystals were grown using the slow cooling flux technique. Polycrystalline $BaCuSi_2O_6$ precursor was synthesized by a solid state reaction of $BaCO_3$, SiO_2, and CuO between temperatures of 900 and 1050 °C in flowing oxygen, with repeated regrinding. Single crystals up to 1 g were grown by heating a 2:1 molar mixture of ground polycrystalline material and $LiBO_2$ flux in a platinum crucible to 1000 °C in air, followed by slow cooling to 875 °C and decanting by centrifuge.

EPR measurements were performed for a range of frequencies between 26 and 660 GHz for both $H\|c$ and $H \perp c$. At elevated temperatures, population of the Zeeman split triplet states results in intratriplet transitions, observed as sharp dips in the transmission through a microwave cavity [Fig. 1(a)]. At the highest temperatures, a single EPR peak is observed, corresponding to the degenerate transitions between triplet levels (in the absence of anisotropic terms). The intensity (integrated area under the peak) diminishes rapidly upon reducing the temperature below $\sim$30 K [Fig. 1(c)], as the triplet states depopulate. A residual intensity can be observed to persist, and even grow, at the lowest temperatures, exhibiting hyperfine splitting (into four distinct peaks). The four-peak pattern is consistent with hyperfine coupling associated with a localized $s=\frac{1}{2}$ and a lone Cu nucleus $(I=\frac{3}{2})$. From fits to the temperature dependence of the total integrated intensity [Fig. 1(c)], we conclude that the central portion of the spectrum observed below about 5 K is dominated by a small concentration [0.5(1)%] of isolated paramagnetic Cu^{2+} defects $(s=\frac{1}{2})$ in agreement with estimates from dc magnetic susceptibility $(\chi=m_z/H)$ measurements of the same sample made using a superconducting quantum interference device SQUID magnetometer [Fig. 1(b)]. Since the hyperfine splitting has the same g factor and anisotropy as the lattice, the associated Cu^{2+} defects likely correspond to singly occupied dimers. Perhaps the most important feature in the data is the appearance of distinct, albeit weak, shoulders which split from the central peak at low temperatures [dashed lines in Fig. 1(a)]. The vanishing intensities of these peaks as $T\rightarrow 0$ indicate that they involve EPR transitions within the triplet state.

The frequency and field orientation dependences of the split shoulders are displayed in Fig. 2. The splitting suggests an anisotropic zero-field-splitting (ZFS) interaction in the spin Hamiltonian, as confirmed from the frequency-dependent measurements for $H\|c$, i.e., the splitting (δ) is field independent. The field orientation dependence of the splitting can be fitted by the equation
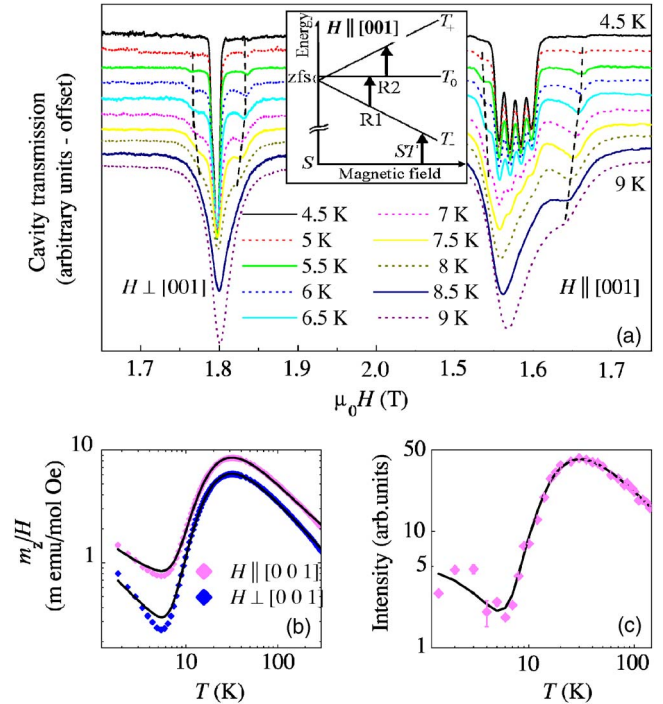

FIG. 1. (Color online) (a) EPR spectrum measured at different T for $H\|c$ and $H \perp c$ using a resonant frequency of 51.8 GHz. For clarity, data for different T have been offset. Weak shoulders appear and split from the central EPR peak upon reducing the temperature (see dashed lines and main text for explanation). The central peak also exhibits hyperfine splitting for $H\|c$ (see main text). The inset shows a schematic of the possible transitions between different spin states. (b) Temperature dependence of the magnetic susceptibility for a field of 5000 Oe aligned parallel and perpendicular to the crystalline c axis. (c) Measured temperature dependence of the integrated EPR intensity for $H\|c$. Solid lines in (b) and (c) show fit to isolated dimer model including a Curie term to account for paramagnetic impurities.

$$\delta = \frac{1}{2}D(3\cos^2\theta - 1)/\mu_B g_\theta \qquad (5)$$

where θ is the angle between H and the vector between the intradimer Cu^{2+} sites (i.e., the c axis). One possible source of such an angular dependence is a symmetric anisotropic interaction [Eq. (4)] in the Hamiltonian of the form $D\hat{S}_z^2$, where S is the total spin ($=$1) of the dimer and $D=\Gamma_{zz}$. The value of the anisotropic parameter D is found from the angle dependence to be 0.091(3) K. Similar shoulders have been observed in Ref. 17, and the angle dependence of the shoulders was fitted to $D\sim 0.1$ K. A more direct measure of the anisotropic parameter involves a determination of the ZFS of triplet levels by extrapolating the frequency dependence to zero field (Fig. 2). By this method, ZFSs of 1.8(3) GHz [0.09(1) K] and 2.1(1) GHz [0.10(1) K] are obtained, in agreement with the value from the angle dependence. We note also that fits to the central high-temperature peak yield extremum values for the g factors of $g_\|=2.307(3)$ and $g_\perp =2.057(3)$, in excellent agreement with susceptibility and X-band EPR data.[17]
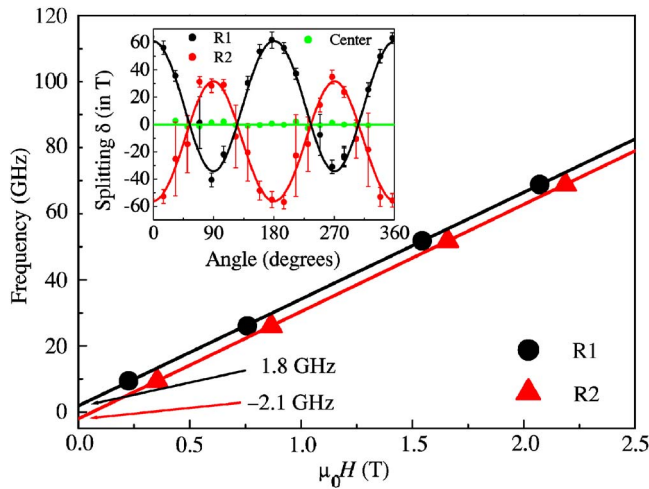
FIG. 2. (Color online) Magnetic field dependence of experimentally measured intratriplet splitting (labeled $R1$ and $R2$ following Fig. 1) for $H \| c$. The solid lines are linear fits to the intratriplet splitting as a function of magnetic field, extrapolated down to zero magnetic field. The inset shows the angular dependence of this splitting measured using a resonant frequency of 51.8 GHz at a temperature of 6 K. The solid lines show a fit to Eq. (5) with D =0.091 K.

The observed ZFS is consistent with either an antisymmetric DM interaction [Eq. (3)], with $\mathbf{D} \| c$ (Ref. 18) and $|\mathbf{D}|=4.8(2)$ K or a symmetric dipolar intradimer interaction. A DM interaction would mix singlet (S) and triplet $\hat{S}_z=0$ (T_0) states for $H \| c$ to lowest order—which, although not U(1) symmetry breaking, would allow a significant EPR transition between the S and triplet $\hat{S}_z=-1$ (T_-) states (labeled ST in Fig. 1). Simulations that include an antisymmetric anisotropy predict similar intensities for the triplet transition (labeled $R1$ and $R2$ in Fig. 1) and the high-field ST transition at 6 K. In contrast, for $H \| c$, a ST EPR transition is forbidden by symmetry for an intradimer dipolar interaction, and would be negligibly small due to higher-order mixing of the S and T_- states for an interdimer dipolar interaction. For $H \perp c$, the extent of mixing of the S and T_- states [which would break U(1) symmetry] would be considerable for a first-order DM process, but very weak for higher-order intra- and interdimer dipolar processes. Therefore, the DM interaction would lead to significant nonlinear field dependence of the intratriplet transition frequency for fields approaching H_{c1}, whereas the dipolar interaction would not. High-field EPR measurements reveal no sign of ST transitions in the vicinity of H_{c1}, or any unusual behaviour of the intratriplet EPR transitions for $H \perp c$ up to 21.7 T (Fig. 3), strongly indicating that the observed low-temperature EPR splitting arises from dipolar interactions which are symmetric in nature. Furthermore, as we describe below, both the magnitude of the zero-field splitting and its T dependence are consistent with dipolar and not DM interactions.

The dilute concentration of well-separated thermally activated triplets at low T, H provides the ideal conditions to observe the effects of magnetic dipolar interactions in $BaCuSi_2O_6$. The magnetic lattice comprises closely spaced
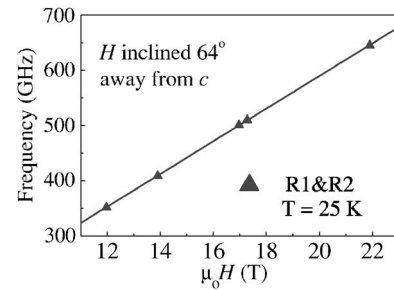

FIG. 3. High-field linear field dependence of the intratriplet Zeeman splitting with H inclined with respect to [001].

pairs of Cu^{2+} ions ($r_\| = 2.74$ Å intradimer spacing at room temperature) which are well separated from each other ($r_\perp = 7$ Å between dimers). The zero-field dipolar splitting of triplets is given by $(\mu_0 / 16\pi r_\|^3)(2g_\|^2 + g_\perp^2)\mu_B^2$, which has the value 0.113 K for $r_\| = 2.74$ Å. This is remarkably close to the measured ZFS ~ 0.1 K, suggesting that the origin is indeed dipolar interactions. The reason for the collapse of the dipolar splitting at higher temperatures can be understood in terms of "exchange narrowing." At low T, the triplets are dilute and long lived on EPR time scales ($\sim 1/f$). The ZFS results from the anisotropic dipolar field that each spin within a dimer experiences due to its pair $[\propto 3(s_1 \cdot \hat{z})(s_2 \cdot \hat{z}) - (s_1 \cdot s_2)]$. However, as T is raised, and more triplets are excited, any given Cu spin will experience strong fluctuations in the local dipolar fields due to the exchange-induced coflipping between neighboring dimers of opposing spin projection. As more triplets are excited, such coflipping leads to faster fluctuations of the local dipolar fields until they are eventually averaged out on EPR time scales, and the dipolar splitting vanishes. In fact, most of the linewidth observed in these experiments can be attributed to nuclear and dipolar spin-spin interactions (both intra- and interdimer). As T is raised, exchange averaging leads to a gradual reduction in the second moment of the dipolar field distribution, and to a narrowing of the spectrum. We do indeed observe a further narrowing of the spectrum at higher T (not shown), which has also been observed in Ref. 17.

We also discuss the directional anisotropy in the value of g, which arises from crystal electric field splitting of the Cu^{2+} energy levels in a tetragonal environment, and spin-orbit interactions. The anisotropy in magnetic susceptibility for $H \perp c$ and $H \| c$ [shown in Fig. 1(b)] reflects an anisotropy in g values. Fits to an isolated dimer model using the Bleaney-Bowers equation[16] yield a value of $J=4.40(2)$ meV and values of $g_\perp = 2.03(5)$ and $g_\| = 2.31(5)$ in agreement with EPR results, where $\|$ and $\perp$ refer to H oriented parallel and perpendicular to the c axis. In addition to scaling the low-field susceptibility, the effect of this g anisotropy is to scale the value of H_{c1} with g_θ.

High-field magnetization measurements were performed in pulsed magnetic fields of 500 ms pulse duration up to 40 T. Data were obtained using a wire-wound sample extraction magnetometer in which the sample is inserted or removed from the detection coils *in situ*. Figure 4 shows the uniform magnetization (m_z) of $BaCuSi_2O_6$ as a function of field for $H \| c$ and $H \perp c$. The value of m_z for both directions
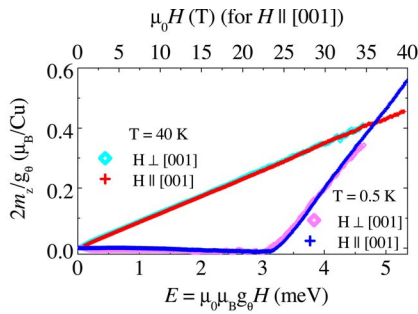
FIG. 4. (Color online) Magnetization measured as a function of H up to 40 T. The applied field $H \| c$ and $H \perp c$ ($g_\| = 2.31$, $g_\perp = 2.05$) is represented as an equivalent energy $E = \mu_0 \mu_B g_\theta H$ meV on the lower x axis, such that both orientations share the same axis. The upper x axis shows H along the c axis.

of H has been normalized by $2/g_\theta$ at 40 K so that the saturation value is $1\mu_B$ per Cu. The upturn in m_z measured at 0.5 K occurs at H_{c1}, at which magnetic ordering takes place. Linear extrapolation of m_z is used to determine the value of $\Delta = g_\theta \mu_B H_{c1}$ for $H \| c$ and $H \perp c$. The value of spin gap thus extracted is $\Delta = 3.2(1)$ meV for $H \| c$ and $H \perp c$. As expected, the values of H_{c1} and m_z scale with g_θ for H along different crystal axes. The effect of the anisotropy in g appears only in the Zeeman term in Eq. (1), indicating that the g tensor is diagonal, and does not lead to mixing of the spin components.

Having carefully examined any possible source of anisotropies in the Hamiltonian describing BaCuSi$_2$O$_6$, we conclude that the dominant effect arises from symmetric dipolar interactions, which lead to U(1) symmetry breaking only to second order. The magnitude of U(1) symmetry breaking due to the intradimer dipolar interaction is of the order of $\sim |D| J'/J = 11$ mK only for $H \perp c$, whilst of the order of $\sim (r_\| / r_\perp)^3 |D| J'/J = 0.7$ mK for all H due to interdimer dipolar interaction. Indeed, the family of spin-dimer compounds is distinct from other XY antiferromagnets due to the small size of J'/J and $r_\| / r_\perp$, which "protect" the U(1) symmetry down to low energy scales in the case of symmetric anisotropies. EPR measurements on BaCuSi$_2$O$_6$ confirm that the correspondence drawn with the BEC universality class is justified in a significant region of criticality near the QCP.

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