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

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We present results of magnetisation 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 is from magnetic dipolar interactions. Axial symmetry-breaking is on a very small energy scale of $\leq 11$ 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, it is vital to identify the nature and size of any anisotropic terms that may be present in the Hamiltonian $\hat{H}$. 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 TiCuCl$_3$ (triplon bandwidth $\sim 1$ meV) [2, 3, 4, 5, 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$_6$ [2, 3, 4, 5, 6].

A first approximation to the equivalent magnetic lattice corresponding to the room temperature tetragonal body-centered BaCuSi$_2$O$_6$ lattice [2, 3] is the isotropic spin Hamiltonian:

$$\mathcal{H} = \sum_i J \mathbf{s}_i \cdot \mathbf{s}_i + \sum_i \sum_{\nu} J_\nu \mathbf{s}_i + \mathbf{e}_\nu \cdot \mathbf{s}_i + \sum_i \sum_{\nu} J_\nu \mathbf{s}_i + \mathbf{e}_\nu - g_\mu B \sum_i \mathbf{H} \mathbf{s}_i$$

An antiferromagnetic (AF) exchange constant $J > 0$ couples each pair of Cu$^{2+}$ spin $\mathbf{s}_i = \frac{1}{2} \mathbf{s}$ within vertical spin dimers on the Cu$_2$Si$_2$O$_{12}$ layers (where $i$ is the index of the dimer, and $\mathbf{s}_1$ and $\mathbf{s}_2$ are the two spins that form the pair $i$). Intra-layer ($J'$) and inter-layer ($J_f$) AF exchange constants couple nearest neighbouring spin dimers on the lattice, indexed by $\mathbf{e}_\nu = \{\hat{x}, \hat{y}\}$, $\mathbf{e}_\beta = \{\hat{z} \pm \hat{x}/2 \pm \hat{y}/2\}$ as defined in the high-temperature structure [4]. For an $s = \frac{1}{2}$ system, energy levels corresponding to the isotropic Hamiltonian are ground-state singlet, and three degenerate triplet excited states, separated from the groundstate by the spin gap $\Delta$. An applied magnetic field $H$ introduces a Zeeman splitting term in the Hamiltonian, scaled by the $g$-factor $g_\theta$, 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 $H \parallel c$, and comparison of the measured phase boundary with the model Hamiltonian in Eqn. 1 gives values of $J = 4.45$ meV, $J' = 0.51$ meV, and an even smaller value of $J_f$.

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 $\mathbf{s}_i \cdot \mathbf{s}_i \equiv s_i \mathbf{I} \mathbf{s}_i$ in Eqn. 1 is replaced by the exchange interaction $\sum_{i,j=1}^3 s_i \bar{T}_{i,j} s_j$, where

$$\bar{T}_{i,j} = 3T_s + \bar{T}_{as} + \bar{T}_{sm}$$

$$\bar{T}_{as} = \sum_i \frac{1}{2} (T_{i,j} - T_{j,i}) (\mathbf{e}_i \times \mathbf{e}_j)$$

$$\bar{T}_{sm} = \frac{1}{2} (T_{i,j} + T_{j,i}) \delta_{i,j}$$

$T_s$ is a scalar, while the antisymmetric term $\bar{T}_{as}$ of the form $\mathbf{D} \cdot [\mathbf{s}_i \times \mathbf{s}_j]$, and the traceless symmetric term $\bar{T}_{sm}$ of the form $\mathbf{s}_i \bar{T}_{s} \mathbf{s}_j$ 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 intra-triplet matrix elements entering to the lowest order of perturbation, but ST mixing to 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 $\sim 100$ 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 non-conservation due to mixing of singlet and triplet energy levels with inequivalent $S_z$. The symme-
sociated with a localized 4-peak pattern is consistent with hyperfine coupling as-
hibiting hyperfine splitting (into 4 distinct peaks). The states depopulate. A residual intensity can be observed below
the temperature below the area under the peak) diminishes rapidly upon reducing
absence of anisotropic terms). The intensity (integrated
the degenerate transitions between triplet levels (in the
structures, a single EPR peak is observed, corresponding to
Zeeman split triplet states results in intra-triplet transi-
tions, observed as sharp dips in the transmission through
and
H

2

3

1

H

3

O

6

3

1

6

2

5

1

\text{emu/mol Oe})

\mu_B T

\mu_B g \theta

\delta = \frac{1}{2} D(3 \cos^2 \theta - 1)/\mu_B g \theta

FIG. 1: [Colour online] (a) EPR spectrum measured at different T for H\parallel 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\parallel 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\parallel c. Solid lines in panels (b) and (c) show fit to isolated dimer model including a Curie term to account for paramagnetic impurities.

involves 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 by the frequency dependent measurements for H \parallel c, i.e. the splitting (\delta) is field-independent. The field orientation dependence of the splitting can be fit by the equation:

\delta = \frac{1}{2} D(3 \cos^2 \theta - 1)/\mu_B g \theta

where \theta is the angle between H and the vector between the intra-dimer Cu^{2+} sites (i.e. the c-axis). One possible source of such an angular dependence is a symmetric anisotropic interaction (Eqn. 4) in the Hamiltonian of the form DS^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(2) K. Similar shoulders have been observed in Ref. 15, and the angle dependence of the shoul-

of the Hamiltonian would therefore reduce from rotacional invariance (U(1)) to the discrete Z_2 group, result-
ing in a magnon spectrum in the ordered phase with a finite gap to the minimum, rather than a gapless Gold-
stone mode. The extent of symmetry breaking, however
depends on the order of perturbation at which spin non-
conserving terms enter the spin Hamiltonian; it is there-
fore important to identify the origin of any anisotropic interaction in the Hamiltonian. Previous measurements of a BEC critical exponent in BaCuSi_2O_6 down to 0.03 K [10] provide empirical evidence for the absence of U(1) symmetry-breaking terms down to this energy scale for H\parallel 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 the central portion of the spectrum observed below about 51 K is dominated by a small concentration (0.091(3) K. Similar shoulders have been observed in Ref. 15, and the angle dependence of the shoul-

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ders fit 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, zfs 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-factor of $g_{\parallel} = 2.307(3)$ and $g_{\perp} = 2.057(3)$, in excellent agreement with susceptibility and X-band EPR data [17].

The observed zfs is consistent with either an antisymmetric DM interaction (Eqn. 9), with $D \parallel c$ [15] and $|D| = 4.8(2)$ K or a symmetric dipolar intra-dimer interaction. A DM interaction would mix singlet ($S$) and triplet $S_{\parallel} = 0$ ($T_0$) states for $H \parallel c$ to lowest order - which although not U(1) symmetry-breaking, would allow a significant EPR transition between the $S$ and triplet $S_{\perp} = -1$ ($T_-$) states (labelled ST in Fig. 1). Simulations which include an antisymmetric anisotropy predict similar intensities for the triplet transition (labelled R1 and R2 in Fig. 1) and the high-field ST transition at 6 K. In contrast, for $H \perp c$, an ST EPR transition is forbidden by symmetry for an intra-dimer dipolar interaction, and would be negligibly small due to higher order mixing of the $S$ and $T_-$ states for an inter-dimer 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 inter-dimer dipolar processes. Therefore, the DM interaction would lead to significant non-linear field-dependence of the intra-triplet 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 intra-triplet 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$_2$O$_6$. The magnetic lattice comprises closely spaced pairs of Cu$^{2+}$ ions ($r_{\parallel} = 2.74$ Å intra-dimer 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 $\mu_s^2/16\pi r_{\parallel}^3(2g_{\parallel}^2 + g_{\perp}^2)\mu_B^2$, which has the value 0.113 K for $r_{\parallel} = 2.74$ Å. This is remarkably close to the measured zfs $\sim 0.1$ 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 $[3(s_1 \cdot \hat{z})(s_2 \cdot \hat{z}) - (s_1 \cdot s_2)]$. 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 co-flipping between neighboring dimers of opposing spin projection. As more triplets are excited, such co-flipping 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 inter-dimer). 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 fur-
ther narrowing of the spectrum at higher $T$ (not shown), which has also been observed in Ref. 17.

![Graph](image)

FIG. 4: [Colour online] Magnetisation measured as a function of $H$ up to 40 T. The applied field $H \parallel c$ and $H \perp c$ ($g_\parallel = 2.31, g_\perp = 2.05$) is represented as an equivalent energy $E = \mu_0 H g_\parallel H / \mu_B$ meV on the lower $x$-axis, such that both orientations share the same axis. The upper $x$-axis shows $H$ along the $c$-axis.

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 $H \parallel c$ (shown in Figure 3B) 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 $g_\parallel = 2.31(5)$ in agreement with EPR results, where $\parallel$ 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 $H_{\perp}$ with $g_\parallel$.

High field magnetisation 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 magnetisation ($m_\parallel$) of BaCuSi$_2$O$_6$ as a function of field for $H \parallel c$ and $H \perp c$. The value of $m_\parallel$ for both directions of $H$ has been normalised by $2/g_\parallel$ at 40 K so that the saturation value is $1 \mu_B$/Cu. The upturn in $m_\parallel$ measured at 0.5 K occurs at $H_{\perp}$, at which magnetic ordering takes place. Linear extrapolation of $m_\parallel$ is used to determine the value of $\Delta = g_\parallel \mu_B H_{\perp}$ for $H \parallel c$ and $H \perp c$. The value of spin gap thus extracted is $\Delta = 3.2(1)$ meV for $H \parallel c$ and $H \perp c$. As expected, the values of $H_{\perp}$ and $m_\parallel$ scale with $g_\parallel$ for $H$ along different crystal axes. The effect of the anisotropy in $g$ appears only in the Zeeman term in Eqn. 4 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 intra-dimer symmetry-breaking is of the order of $|D|J'/J = 11$ mK only for $H \perp c$, whilst of the order of $(\Delta J'/\Delta J = 0.7$ mK for all $H$ due to inter-dimer dipolar interaction. Indeed, the family of spin-dimer compounds is distinct from other XY antiferromagnets due to the small size of $J'/J$ and $r_{\parallel}/r_{\perp}$, 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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