Magnetic-Field-Induced Condensation of Triplons in Han Purple Pigment BaCuSi$_2$O$_6$

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Besides being an ancient pigment, BaCuSi$_2$O$_6$ is a quasi-2D magnetic insulator with a gapped spin dimer ground state. The application of strong magnetic fields closes this gap, creating a gas of bosonic spin triplet excitations. The topology of the spin lattice makes BaCuSi$_2$O$_6$ an ideal candidate for studying the Bose-Einstein condensation of triplet excitations as a function of the external magnetic field, which acts as a chemical potential. In agreement with quantum Monte Carlo numerical simulations, we observe a distinct lambda anomaly in the specific heat together with a maximum in the magnetic susceptibility upon cooling down to liquid helium temperatures.

About 2000 years ago, early Chinese chemists synthesized barium copper silicates for the first time, and used them as pigments for pottery and trading as well as for large empire projects such as the Terracotta Warriors [1–3], preceding even the invention of paper and the compass. BaCuSi$_2$O$_6$, also known as Han Purple [1], is then possibly the first man-made compound containing a metallic bond. In its layered crystallographic structure, pairs of Cu^{2+} ions form dimers arranged in a square lattice, with Cu-Cu bonds projected normal to the planes [4]. Neighboring Cu bilayers are weakly coupled, i.e., the magnetic system is quasi-two dimensional [5]. Applied magnetic fields in excess of 23.5 T suppress the spin singlet ground state in BaCuSi$_2$O$_6$, giving rise to a bosonic gas of triplet dimers.

At low temperatures, an ideal gas of bosons undergoes a phase transition into a condensate with macroscopic occupation of the single-particle ground state. A great deal of interest in this phenomenon was triggered by the discovery of the anomalous behavior of liquid helium. Upon cooling, liquid ^{4}He exhibits a λ transition in the specific heat at 2.17 K that signals the onset of a zero-viscosity superfluid state [6]. Superfluidity arises from the macroscopic fraction of He atoms that occupy the single particle ground state. Within the last decade, Bose-Einstein condensation (BEC) was also realized for dilute clouds of atoms at temperatures lower than ten millionths of a degree Kelvin [7]. The possibility of producing BEC with quantum spin magnets [8] has stimulated considerable experimental effort to find the candidate materials [9].

Spin-dimer systems such as SrCu$_2$(BO$_3$)$_2$ [10] and TlCuCl$_3$ [11] have recently become of interest owing to the ability of strong magnetic fields to generate a gas of

$S^z = 1$ spin-triplet states moving in a non-magnetic background. These triplets can be regarded as bosonic particles with hard core repulsions that carry a magnetic moment, but no mass or charge. The external field plays the role of a chemical potential in controlling the number of particles. The Ising component of the inter-dimer exchange interaction generates an effective repulsion between neighboring bosons.

Upon cooling, the gas of triplets can either crystallize or condense in a liquid state, depending on the balance between the kinetic energy and the repulsive interactions [9]. In particular, if the kinetic energy dominates and the number of triplets (or total magnetization) is a conserved quantity, the system undergoes BEC corresponding to the coherent superposition of $S^z = 1$ spin-triplet and $S = 0$ singlet states on each and every dimer. The BEC of triplets was proposed to occur in TlCuCl$_3$ [11–13] and KCuCl$_3$ [14,15]. However, recent data suggest that the anisotropic crystal structure of these spin-ladder systems breaks the U(1) rotational invariance that is required to have gapless Goldstone modes [16]. Consequently, the Goldstone modes or *triplons* [17] acquire a finite gap or mass. In this Letter we introduce a new system whose bilayer structure provides a realization of a quasi-two-dimensional gas of triplet dimers.

The range of fields and temperatures required to obtain a BEC of triplets in BaCuSi$_2$O$_6$ creates a unique situation from the experimental standpoint: the triplons dominate the thermodynamics in a very simple and predictable fashion. The simplicity of BaCuSi$_2$O$_6$ is best described by a spin Hamiltonian that includes only the nearest-neighbor Heisenberg antiferromagnetic exchange couplings. The Cu^{2+} ions and the SiO$_4$ tetrahedra in BaCuSi$_2$O$_6$ are arranged in layers parallel to the (001)

crystallographic plane, as shown in Fig. 1(a). Within each Si-O-Cu layer, the Cu^{2+} ions form a square lattice bi-layer of $S = 1/2$ spins [4]. The relevant Heisenberg exchange couplings within the bilayers are the intra-dimer interaction, J, and an inter-dimer nearest-neighbor interaction J' [Fig. 1(a)]. The different bilayers are antiferromagnetically coupled via the effective exchange constant J''. The resulting spin Hamiltonian is

$$H_s = J\sum_{\mathbf{i}}\mathbf{S}_{\mathbf{i},1} \cdot \mathbf{S}_{\mathbf{i},2} + J'\sum_{\mathbf{i},\alpha,\beta}\mathbf{S}_{\mathbf{i},\beta} \cdot \mathbf{S}_{\mathbf{i}+\hat{e}_\alpha,\beta}$$
$$+ J''\sum_{\mathbf{i}}\mathbf{S}_{\mathbf{i},1} \cdot \mathbf{S}_{\mathbf{i}+\hat{z},2} - g_\parallel\mu_B H\sum_{\mathbf{i},\beta}S^z_{\mathbf{i},\beta} \quad (1)$$

where $\alpha = \{1, 2\}$ is the direction index, $\beta = \{1, 2\}$ is the layer index, $\hat{e}_1 = \hat{x}$, $\hat{e}_2 = \hat{y}$ and $\hat{z}$ are unit vectors along the crystallographic axes, and $g_\parallel = 2.306 \pm 0.008$ is the component of the gyromagnetic tensor along the c axis, which is the direction of the applied magnetic field H. The value of $J = 4.5$ meV is known from inelastic neutron scattering studies [5], which also show that $J'' \ll J' \ll J$. Precise values of J' and J'' are determined from the experiments described below.

In the limit $J' = J'' = 0$, the ground state of H_s is a product of local singlet-dimer states: $|\Psi_0\rangle = \otimes_{\mathbf{i}}|\phi^s_{\mathbf{i}}\rangle$, where $|\phi^s_{\mathbf{i}}\rangle$ is the singlet state between two spins on a dimer $\mathbf{i}$. $J = 4.5$ meV is the energy gap for a spin triplet excitation in a single isolated dimer [5]. This gap decreases linearly with an applied magnetic field as shown in Fig. 1(b). Since J'', $J' \ll J$, the spectrum is dominated by the two low energy states of the isolated dimer (the $S = 0$ singlet and the $S^z = 1$ triplet) once $g_\parallel\mu_B H$ becomes of the order of J. By projecting H onto this low energy subspace, we derive an effective Hamiltonian, H_{eff}, in which each dimer is represented by one effective site with two possible states. In this way, we are neglect-

ing the effect of the high energy triplet states and, therefore, the highest order terms of H_{eff} are linear in J' and $J'' = 0$ (first order perturbation theory). A similar procedure was used before by Mila [18] to describe spin ladders in a magnetic field. We associate the two low energy states with the two possible states of a hard core boson on a lattice [5] [see Fig. 1(c)]. The empty site corresponds to the singlet state $|\phi^s_{\mathbf{i}}\rangle$, while the site occupied by the hard core boson represents the $S^z = 1$ triplet state: $|\phi^s_{\mathbf{i}}\rangle \rightarrow |0\rangle_{\mathbf{i}}$, $|\phi^t_{\mathbf{i}}, S^z = 1\rangle \rightarrow b^\dagger_{\mathbf{i}}|0\rangle_{\mathbf{i}}$, where $|0\rangle_{\mathbf{i}}$ represents the empty state at the site $\mathbf{i}$. In this language, the effective low energy Hamiltonian is

$$H_{\text{eff}} = t\sum_{\mathbf{i},\alpha}(b^\dagger_{\mathbf{i}+\hat{e}_\alpha}b_{\mathbf{i}} + b^\dagger_{\mathbf{i}}b_{\mathbf{i}+\hat{e}_\alpha}) + t'\sum_{\mathbf{i}}(b^\dagger_{\mathbf{i}+\hat{z}}b_{\mathbf{i}} + b^\dagger_{\mathbf{i}}b_{\mathbf{i}+\hat{z}})$$
$$+ V\sum_{\mathbf{i},\alpha}n_{\mathbf{i}}n_{\mathbf{i}+\hat{e}_\alpha} + V'\sum_{\mathbf{i}}n_{\mathbf{i}}n_{\mathbf{i}+\hat{z}} + \mu\sum_{\mathbf{i}}n_{\mathbf{i}}, \quad (2)$$

where the chemical potential is $\mu = J - g_\parallel\mu_B H$, $t = V = J'/2$, and $t' = V' = J''/4$. Eq. (2) describes a gas of hard core bosons with nearest-neighbor hopping and repulsive interactions. For H less than a critical field H_{c1} ($g_\parallel\mu_B H_{c1} = J - 2J' - J''/2$), the ground state of H_{eff} is completely empty, i.e., all dimers are spin singlets, because the chemical potential, μ, is large and positive. A finite concentration of particles $\rho = m$ (m is the magnetization per site) emerges in the ground state only when H exceeds H_{c1}. Because the condition $V \leq 2t$ is not fulfilled, the triplets or hard core bosons never crystallize for any concentration $\rho < 1$.

The single crystal samples used in this study were prepared using the floating-zone technique. $BaCO_3$, CuO, and SiO_2 were used as starting materials and the powders of stoichiometric compositions were mixed and sintered at 700 °C for 15 h. The sintered powder was reground and molded into a rod under a pressure of 400 kg/cm² for about 10 min. The rod is sintered between 1000 °C and 1100 °C for about 100 h. The sintered rod is then used for the floating zone method [22]. The floating zone growth was done twice. In the first run the speed of the growth was set to 50 mm/h, and in the second run to ~0.5 mm/h, both in an O_2 flow of ~200 cc/min. The purple color and texture of our single crystal sample is appreciated in a picture taken in transmission (backlight) mode [Fig. 1(d)]. Figure 2(a) shows the magnetization versus field data obtained in capacitor-driven pulsed magnetic fields [19]. The magnetization increases continuously between the critical field $H_{c1} = 23.5$ T and the saturation field $H_{c2} = 49$ T at $T = 0.4$ K. The nearly linear slope of the magnetization contrasts sharply with the staircase of plateaus observed in $SrCu_2(BO_3)_2$, where the gas of triplets is known to crystallize in a structure that is commensurate with the underlying crystallographic lattice [9,10]. Pulsed magnetic field experiments on $BaCuSi_2O_6$ were repeated at different temperatures up to 40 K and cross calibrated against low-field SQUID magnetometer data [5]. The structure observed around
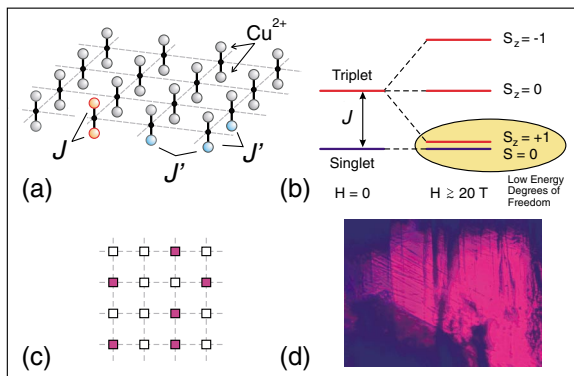

FIG. 1 (color online). (a) Cu^{2+}-dimer plane in $BaCuSi_2O_6$ in a square lattice arrangement. J and J' are the intradimer and interdimer exchange constants. (b) Evolution of the isolated dimer spin singlet and triplet with an applied magnetic field H. (c) Partially occupied hard core boson lattice. Occupation (chemical potential) is given by the external magnetic field. (d) Transmission-light picture of a $BaCuSi_2O_6$ single crystal.
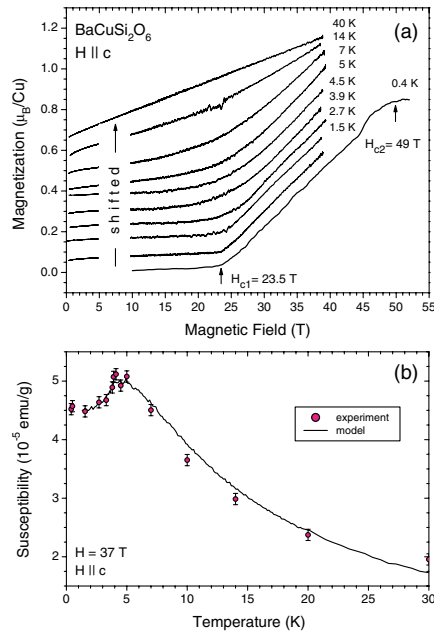
FIG. 2 (color online). (a) Magnetization vs field at different
temperatures from 0.4 to 40 K, measured in both 65 T short-
pulse and 45 T midpulse capacitor driven pulsed magnets.
(b) Magnetic susceptibility vs temperature from measurements
in (a), and from our model using a quantum Monte Carlo
algorithm.

$H \simeq 48$ T at low temperatures, which we could not repro-
duce in later experiments, is likely an artifact caused by
mechanical vibration of the probe. A plot of the slope $\chi =
dM/dH$ of M versus H (magnetic susceptibility) at $H =
37$ T is shown in Fig. 2(b) together with the results of a
Monte Carlo simulation of H_{eff} in a finite lattice of size
L^3, with $L = 12$, performed using the directed-loop al-
gorithm [20,21] with parameters $J = 4.45$ meV, $J' =
0.58$ meV, and $J'' = 0.2 J' = 0.116$ meV. The agreement
between experimental data and model calculations is
remarkable. Notably, the rapid drop of the magnetic sus-
ceptibility below 4 K indicates the onset of an ordered low
temperature state, namely the triplon condensate.

The observation of a phase transition is further con-
firmed by specific heat measurements as a function of
temperature for constant magnetic fields shown in Fig. 3.
This experiment was performed in a calorimeter made
out of plastic materials [23] using both a superconducting
magnet and the 45 T hybrid magnet at the National High
Magnetic Field Laboratory. At zero magnetic field the
specific heat is featureless. As soon as a finite external
field along the c axis is applied the specific heat increases
due to the reduction in the singlet-triplet energy gap
$\Delta(H)$. A small anomaly then develops for
$H = 28$ T at $T \sim 2.7$ K that moves to higher tempera-
tures as the magnetic field is further increased. This
λ-shaped anomaly also grows with magnetic field due to
the increased number of triplets (magnetization). Their
number at low temperatures is roughly proportional to the

magnetic field [see Fig. 2(a)]. Once the middle of the
magnetization ramp is reached at $H = 36 \pm 1$ T, the
transition temperature and the size of the λ anomaly
then start to decrease owing to the reduction in the
availability of singlet dimers. Moreover, the mirror sym-
metry of the phase diagram around this maximal point
(see Fig. 4) offers an experimental confirmation of the
particle-hole symmetry implicit in H_{eff}. No phonon con-
tribution has been subtracted from the specific heat data.
The inset of Fig. 3 displays the data at 37 T after sub-
traction of a small exponential contribution [activated
energy $\Delta(H = 0) = 3.13$ meV] from the $S^z = 0$ triplet
components that becomes apparent only above 8 K. In
addition, a Debye phonon contribution with $\Theta_D = 350$ K
was subtracted. The solid line is the result of our quantum
Monte Carlo calculation for H_{eff} after a finite size scaling
to the thermodynamic limit. The system sizes that were
used for the scaling are $L = 4, 6, 8, 12$.

The phase diagram of Fig. 4 shows all our experimental
data combined, together with some temperature traces
measured while sweeping the magnetic field at a rate of
about 12 T/min, i.e., magnetocaloric effect (MCE) [24].
The left side y axis is for the magnetization versus H
curve. From this curve we obtain $H_{c1} = 23.5$ T and
$H_{c2} = 49$ T. The right side y axis is for the transition
temperature versus field plot obtained from the specific
heat curves (see Fig. 3) and the magneto-caloric effect
measurements. The anomalies in the MCE, observed upon
crossing the phase boundaries in the direction of increas-
ing fields, evidence reduced magnetic entropy within the
critical region consistent with a gas-to-liquid phase tran-
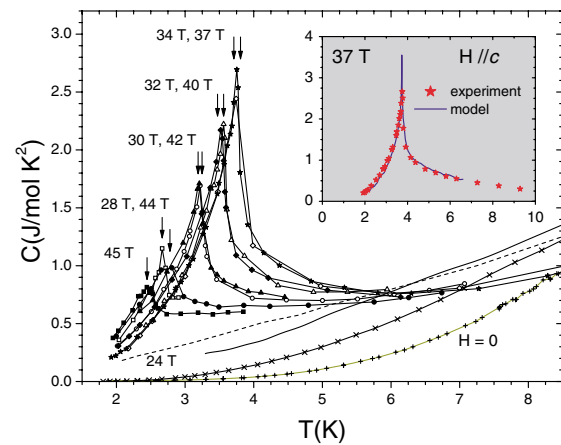sition. Also displayed in Fig. 4 are the transition points

FIG. 3 (color online). Specific heat vs temperature at constant
magnetic fields H. A low temperature λ anomaly is evident at
$H \gtrsim 28$ T. The anomaly first moves to higher temperatures
with increasing magnetic fields, it reaches a maximum at $H =
36 \pm 1$ T, and then decreases for $37 < H < 45$ T. Inset: specific
heat vs T at $H = 37$ T after subtraction of a small contribution
due to the $S^z = 0$ triplet level only relevant at higher tempera-
tures, and phonons. Also displayed is the result of our Monte
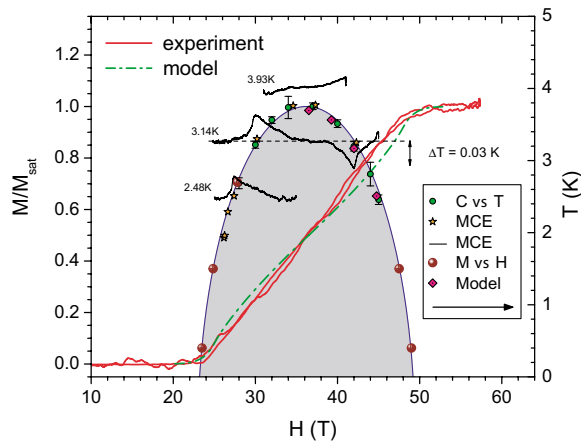Carlo calculation.

FIG. 4 (color online).   Left y axis: magnetization normalized to the saturation value (M/M_{sat}) vs magnetic field along the c axis, measured at 1.5 K (red line). Results for the model discussed in the text (green line). Right y axis: transition temperature from specific heat vs temperature, magnetocaloric effect (MCE) and magnetization vs field data. Black lines are the sample temperature measured while sweeping the magnetic field quasiadiabatically.

calculated with our Monte Carlo algorithm for $L = 12$. The BEC phase is represented by the shaded region whose boundary is intended merely as a guide to the eye. The excellent agreement between experiment and theory is a compelling case for $BaCuSi_2O_6$ being a true realization of a quasi two dimensional BEC of magnetic degrees of freedom.

Early Chinese chemists could not have imagined that $BaCuSi_2O_6$ was not only an attractive purple pigment but also a potential solid state device for exploring the quantum effects of a BEC at liquid ^{4}He temperatures in magnetic fields. Indeed, we show that a minimal Hamiltonian for a lattice gas of hard core bosons describes surprisingly well the magnetization and specific heat of this magnetic system in external magnetic fields. To derive an effective Hamiltonian we simply neglected the high energy triplet states $|\phi_i^t, S^z = 0\rangle$ and $|\phi_i^t, S^z = -1\rangle$. The excellent agreement with the experimental data and the verification of the particle-hole symmetry implicit in H_{eff} validate our approach. However, other physical properties such as the small staggered magnetization that appears in the ab plane, when the triplets condense, would require the inclusion of virtual processes that involve the above mentioned states. It is also important to remark that the phase coherence of the spin BEC requires the conservation of the number of particles that is equivalent to the total magnetization. This condition is fulfilled whenever the crystal has some degree of rotational symmetry about the direction of the applied field like, for instance, a fourfold symmetry axis. Otherwise, the presence of anisotropy terms will significantly reduce the decoherence time of the condensate. Finally, the weakly coupled Cu bilayers in the crystal structure of $BaCuSi_2O_6$

open the door for future studies such as the dimensional crossover of a bosonic gas. By increasing the distance between adjacent bilayers with chemical substitutions the λ-shaped second order phase transition, characteristic of a three-dimensional system, is replaced by a Kosterlitz-Thouless phase transition.

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