Magnetic Phases of the Spin-1/2 Triangular-Lattice Antiferromagnet Ba$_3$CoSb$_2$O$_9$

G. Koutroulakis, T. Zhou, C. D. Batista, Y. Kamiya, J. D. Thompson, S. E. Brown, and H. D. Zhou

1 Condensed Matter and Magnet Science, MPA-CMMS, Los Alamos National Laboratory, Los Alamos, NM 87545
2 Department of Physics & Astronomy, UCLA, Los Angeles, CA 90095
3 Theoretical Division, T-4 and CNLS, Los Alamos National Laboratory, Los Alamos, NM 87545
4 Department of Physics & Astronomy, University of Tennessee, Knoxville, TN 37996

The magnetic phases of the spin-1/2 triangular-lattice antiferromagnet Ba$_3$CoSb$_2$O$_9$ are identified and studied using $^{135,137}$Ba nuclear magnetic resonance (NMR) spectroscopy in magnetic fields ranging to 12T, oriented parallel and near perpendicular to the crystallographic ab-plane. Notably, the NMR spectra provide microscopic evidence for the stabilization of an up-up-down (UUD) spin configuration for in-plane fields, which gives rise to an one-third magnetization plateau. The results are compared to expectations obtained from a semi-classical energy density modeling, in which quantum effects are mimicked by including a phenomenological biquadratic coupling. The interlayer coupling plays a significant role in the outcome.

PACS numbers: 75.10.Jm,75.25.-j,76.60.-k

The study of frustrated quantum magnets has constituted a central problem in condensed matter physics over the past decades \[1\]. In these systems, quantum fluctuations lift the accidental degeneracy of the classical Hamiltonian, resulting in a breadth of exotic ground states and associated excitations. A characteristic example of a geometrically frustrated quantum system is that of the two-dimensional spin-1/2 Heisenberg antiferromagnet on a triangular lattice (TLHAF), which is known to order in a 120° state in the absence of a magnetic field \[2\]. A hallmark of the TLHAF’s quantum character is the prediction for the stabilization of an up-up-down (UUD) spin configuration at \( T = 0 \) for a finite field range \[3\], which corresponds to a magnetization plateau at one-third of the saturation value \( M_{sat} \).

Experimentally, there is a dearth of results on the magnetically ordered states of TLHAFs, mainly due to the difficulty of growing regular triangular-lattice materials. In fact, the only spin-1/2 system for which a difficulty of growing regular triangular-lattice materials.

Moriya interaction is key for the details of the magnetization process \[2\]. A hallmark of the TLHAF’s quantum character is the prediction for the stabilization of an up-up-down (UUD) spin configuration at \( T = 0 \) for a finite field range \[3\], which corresponds to a magnetization plateau at one-third of the saturation value \( M_{sat} \).

Weak interlayer couplings make for long-range order at finite temperature \[12\].

\( M_{sat} \) for in-plane fields \( 10T \) to \( 15T \), associated with a UUD spin structure \[11,14\]. It has thus become clear that Ba$_3$CoSb$_2$O$_9$ can serve as both a contrast to the quantum disordered candidate systems with Cu, Ni magnetic ions, and an excellent, prototypical TLHAF. Nevertheless, taking into account the interlayer coupling is necessary for a complete description. Nuclear magnetic resonance (NMR) spectroscopy poses as an ideal technique for the investigation of this system, since it can provide a local map of the magnetically ordered states.

In this Letter, we describe results from $^{135,137}$Ba NMR measurements, carried out to determine the detailed spin configuration and phases at field \( B \leq 12T \), which was oriented in the \( ab \)-plane (\( \theta = \pi/2 \)), and closer to the \( c \)-axis (\( \theta = 0.26 \), or 15°). Our results for the phase transition lines in the magnetic field-temperature plane agree quantitatively with previous magnetization and specific heat experiments \[11,17\]. In addition, the NMR probe provides direct microscopic evidence for the transition...
to the incompressible UUD phase for \( \mathbf{B} \perp \hat{c} \) at fields \( B > B_{c1\perp} \sim 10T \). The lower field phase is identified as coplanar to the \( ab \)-plane, with spin configurations in adjacent layers characterized by a reflection symmetry about the field direction. The NMR spectra are consistent with an ‘umbrella’ phase for low fields and \( \mathbf{B} \parallel \hat{c} \). Due to the \( \theta = 15^\circ \) off- \( c \)-axis alignment, precursor effects of a higher field phase (\( B \geq 12T \)) are clearly resolved, although this phase could not be reached in the field strength available. Finally, the experimental results are found to be in excellent agreement with the predictions of a relevant mean-field model.

The measurements were carried out on a 30mg single crystal of \( \text{Ba}_3\text{CoSb}_2\text{O}_9 \) synthesized by the traveling-solvent floating-zone method, as for previous thermal and neutron scattering experiments [11]. Approximate dimensions were \( 4mm^2 x 1.2mm \) thickness. The crystal was placed inside an NMR coil wound for this purpose, and the assembly was mounted on a single axis piezo-driven rotator (Attocube ANRv51/RES). Relative rotation was obtained by observing the angle variation of the rotation axis was determined using a resistive sensor built into the rotator, and complementary absolute information was obtained by observing the angle variation of the NMR transition frequencies [19]. The rotation axis was lying \( 15^\circ \) out of the \( ab \)-plane; consequently, the angle closest to \( \mathbf{B} \parallel \hat{c} \) was also \( \theta_{\text{min}} = 15^\circ \).

There are two crystallographically inequivalent Ba sites, hereafter referred to as \( \text{Ba}(1) \), \( \text{Ba}(2) \), both with uniaxial symmetry. The \( \text{Ba}(1) \) location is between Co ions of adjacent layers, at \( (0,0,1/4), (0,0,3/4) \). The \( \text{Ba}(2) \) site is equidistant from three Co ions in a layer, but offset \( 1.3\AA \parallel \hat{c} \). Since the isotopic concentrations are 11% and 6% for \( ^{137}\text{Ba} \) and \( ^{135}\text{Ba} \), respectively, we mostly confined our measurements to the more abundant species, for which the gyromagnetic ratio is \( ^{137}\gamma/2\pi = 4.73158\text{MHz/T} \) and the nuclear spin is \( I = 3/2 \). Labeling of the various NMR transitions and extraction of the NMR parameters are outlined in the Supplemental Material.

As a way of introducing the problem, we present Fig. 1 which summarizes the outcome of a semi-classical mean-field theory at \( T = 0 \), assuming TLHAF with a small easy-plane anisotropy. Specifically, the expression for the six-sublattice energy density is

\[ E_{\text{MF}} = \frac{1}{2} \sum_{\mu=e,o,n=1;2;3} \left[ J S^2 \left( \Delta_1 s_{\mu,n}^x s_{\mu,n+1}^x + s_{\mu,n}^y s_{\mu,n+1}^y \right) + s_{\mu,n}^x s_{\mu,n+1}^x + J_Q s_{\mu,n}^x s_{\mu,n+1}^x \left( s_{\mu,n} \cdot s_{\mu,n+1} \right)^2 \right] + \frac{J'}{3} \sum_{n=1;2;3} \left( \Delta_2 s_{c,n}^z s_{c,n}^z + s_{c,n}^x s_{c,n}^x + s_{c,n}^y s_{c,n}^y \right) - \frac{h}{6} \sum_{\mu=e,o,n=1;2;3} s_{\mu,n} \right] \]

where \( \mu = e,o \) stands for even and odd layers, \( 1 \leq n \leq 3 \) is the sublattice index on each layer, and\( s_{\mu,n} = \left( s_{\mu,n}^x, s_{\mu,n}^y, s_{\mu,n}^z \right) \) is the classical spin of unit length. \( J \) and \( J' \) are the intra- and inter-layer exchange constants respectively, \( \Delta_1, \Delta_2 \) parameterize the exchange anisotropy, and \( h = q u \mu S \mathbf{B} \) is the reduced applied field. \( J'/J = 0.025 \) and \( \Delta_1 = \Delta_2 = 0.95 \) are chosen as deduced by ESR [17]. The quantum effects, responsible for removing the accidental degeneracy by favoring collinear states, are mimicked by the phenomenological ferro-biquadratic coupling \( J_Q < 0 \) [4, 20]. While ideally \( J_Q \) is chosen depending on the magnitude of quantum fluctuations (e.g., \( J_Q \rightarrow 0 \) close to the saturation field), we fix \( J_Q S^2/J = -0.032 \), which opens a gap in the linear spin-wave spectrum for the UUD state of similar size to that given by a Hartree-Fock approximation of the original TLHAF [21]. Since the main role of \( J_Q \) is simply to lift the degeneracy, its exact magnitude is not crucial, as long as one assumes a small value, especially in the low-field regime which is the focus of the present work (the experimental results are limited to 12T, and therefore extend to magnetizations of the order of \( M_{sat}/3 \)).

For the moment, we highlight the model response to a magnetic field for \( \theta = 0, \pi/2 \) (\( \mathbf{B} \parallel \hat{c} \) and \( \mathbf{B} \perp \hat{c} \), respectively), with the latter being the easy-plane condition. At zero field, we start with the 120° easy-plane spin configuration, and adjacent layers are presumed antiferromagnetically coupled [12, 17]. The UUD phase occurs for \( \theta = \pi/2 \), and the LFC/UD, UUD/HFC1

FIG. 1. Magnetic field orientation vs. strength phase diagram, obtained from the mean-field analysis described in the text (center). \( \theta = \pi/2 \) corresponds to the field directed in the easy-plane condition, \( \mathbf{B} \perp \hat{c} \). The sublattice spin configurations for specific parameters \( (B, \theta) \), indicated by the cross symbols, are shown above and below the main panel. 1-3-4-6 refer to the the spin sublattices in adjacent (even, odd) layers [12]. The labeling is as follows: LFC, UUD, HFC, UM, FP corresponds to Low-Field Coplanar, Up-Up-Down (plateau), High-Field Coplanar, UMBrella, and Fully Polarized.
transitions are continuous at the mean-field level (Fig. 1). Note that, interestingly, the model also predicts the HFC1/HFC2 first-order phase transition inducing a discontinuous change of the relative orientation between the even and odd layer spins [2], which may correspond to the one seen in magnetization measurements at $M \sim 3/5M_{\text{sat}}$ [17]. For $\theta=0$, upon increasing the field, the spins cant in the field direction, with a 120° degree structure in the transverse components, so we refer to this specific configuration as the umbrella phase. Varying the field direction as $\pi/2 \rightarrow 0$ causes a continuous distortion between LFC→UM, resulting in a non-coplanar state for $\theta \neq \pi/2$. One such example is highlighted in Fig. 1 for a case similar to the one of Fig. 3 i.e. $\theta = 15^\circ$.

![Diagram](image)

**FIG. 2.** (a) Field evolution of the Ba(1) hyperfine frequency shifts (see text) for $\theta = 90^\circ$ at $T = 1.6K$. The dashed line shows the paramagnetic phase spectrum at $T = 6K$ for comparison. (b) Experimental phase diagram for $\mathbf{B} \perp \hat{c}$, after Ref. [11]. The vertical dashed line corresponds to the field range and temperature in (a). (c) Magnetization vs. magnetic field. The solid, dashed lines are from magnetization results, and the model of Eq. (1) respectively. The data points are derived from the NMR spectra: circles are the first moment that scales quantitatively with the average moment/Co. Evidently, the first moment of the full absorption spectrum for the Ba(1) central transition follows the average magnetization previously measured, and this is reproduced well by the model results.

The temperature dependence of the ordered moment amplitudes in the UUD phase was measured at $B = 11.5T$, as denoted by the horizontal cut (dashed line) through the phase diagram in Fig. 2c). The results are summarized in the inset of Fig. 2c, which shows the scaled hyperfine field splitting between the two Ba(1) local environments vs. temperature. As expected for an incompressible phase, there is little variation at low temperatures, but it drops suddenly for $T > 5K$. Further measurements will be necessary to establish whether this is a first-order transition, as might be described by the three-state Potts model in three dimensions. For the moment, we comment only that the onset coincides with the thermodynamic results [11].

![Diagram](image)

Not shown are spectra recorded within the UUD part of the phase diagram, but near to the point ‘A’ in Fig. 2b). These display a complex distribution of hyperfine fields at the Ba(1) sites, indicating either phase inhomogeneity, possibly with domain walls, or incommensurate spin structures.

Finally, the monotonically reduced hyperfine splitting for $B < B_{c1\perp} \approx 10T$ indicates a continuous transition from the low-field coplanar (LFC) phase. The NMR spectra in this phase are consistent with spin configurations in adjacent layers related by a reflection symmetry about the field direction (see Fig. 1a), as predicted by the model set out in Eq. (1). Other, slightly different, proposals for
In particular, the specific non-coplanar configuration realized in this case (see Fig. 1) leads to two separate local field environments for the Ba(1) nuclear sites, and hence broadening of the NMR line. In Fig. 3c, the evolution of the hyperfine fields is plotted and compared with that produced by the model of Eq. 1 for a similarly aligned magnetic field. As shown, the development of inequivalent Ba(1) sites thus occurs only on approaching the actual (first-order) phase transition, in both the experiment and the model. That is, the distortions are nonlinear.

In presenting the results for \( \theta = 15^\circ \), we have suggested that so far as the magnetic field vs. temperature phase diagram is concerned, not much is changed from \( \theta = 0 \), save for the distortion which becomes more severe as the first order transition at \( B \sim 12T \) is approached. In Fig. 3c, the solid square data points were derived from measurements of the spin-lattice relaxation rate \( T_1^{-1}(T) \). The temperature dependence, covering the transition, is shown in Fig. 4. We take the sharp drop upon cooling as the indicator for the first order transition \( T_N(B) \) at each of the measured fields, and otherwise note that very little increase in rate is observed as \( T_N \) is approached from higher temperatures. Below the ordering temperature, the drop in relaxation rate occurs quite fast. In fact, it is indistinguishable from an activated form with \( \Delta \sim 11K \), though the excitation spectrum could be expected to be gapless. With anisotropic contributions to the hyperfine coupling, two-magnon processes are possible and lead to \( 1/T_1 \sim T^d \), with \( d \) the dimensionality. We acknowledge that some caution is warranted here, since the variation of the temperature relative to the ordering is limited.

Next, we turn to fields applied close to the \( c \)-axis. The phase diagram used for comparison is derived from magnetization measurements with \( B \parallel \hat{c} \), and is shown in Fig. 3a. As noted above, we were not aligned along \( \hat{c} \), but instead we report the results for \( \theta = 15^\circ \). While we presume that many aspects of the \( B - T \) phase diagram obtained from \( B \parallel \hat{c} \) still apply, there were nevertheless additional features observed in the Ba(1) spectra due to the deviation from \( c \)-axis that we describe below.

The Ba(1) central nuclear transition spectra are shown in Fig. 3a for \( \theta = 15^\circ \) at \( T = 1.7K \). On increasing the applied field from 4.5T, a single line is observed until the field reaches \( \sim 10T \). Further increase in the magnetic field leads to line broadening, and subsequently a double-peak structure is evident. The single line spectrum reflects the UM phase, with the angle of the umbrella closing for increasing field towards its direction. The line splitting, which occurs at the same field independent of temperature as illustrated in Fig. 3a, is the result of the spin structure’s distortion from UM when moving off \( c \)-axis.

In concluding, we have carried out \(^{135,137}\)Ba NMR measurements on the easy-plane triangular lattice antiferromagnet Ba\(_3\)CoSb\(_2\)O\(_9\) to fields up to 12T, whereas the saturation field is approximately 30T. Within that field range, we have identified the low-field phases up to and including the plateau UUD phase, and these are consistent with what is predicted from a classical mean-field model that incorporates a term reproducing quan-
tum fluctuation effects. An interesting but so far unexplored line of phase transitions is also predicted, between two compressible coplanar phases that we have labeled HFC1 and HFC2 in Fig. 1. This phase transition may have been detected in previously reported magnetization measurements [17].

The research reported here was supported by the National Science Foundation under grant no. DMR-1105531 (UCLA). Work at LANL was performed under the auspices of the U.S. DOE through the Laboratory Directed Research and Development program. G.K. acknowledges support from the LANL Seaborg Institute.

[1] P. W. Anderson, Mater. Res. Bull. 8, 153 (1973)
[2] L. Balents, Nature 464, 199 (2010).
[3] eds. C. Lacroix, P. Mendels, and F. Mila, Introduction to Frustrated Magnetism (Springer-Verlag, 2011).
[4] D. A. Huse and V. Elser, Phys. Rev. Lett. 60, 2531 (1988).
[5] T. Jolicoeur and J. C. Le Guillou, Phys. Rev. B 40, 2727 (1989).
[6] H. Nishimori and S. Miyashita, J. Phys. Soc. Japan 55, 4448 (1986).
[7] A. V. Chubukov and D. I. Golosov, Journal of Physics: Condensed Matter 3, 69 (1991).
[8] T. Ono, H. Tanaka, H. Aruga Katori, F. Ishikawa, H. Mitamura, and T. Goto, Phys. Rev. B 67, 104431 (2003).
[9] N. A. Fortune, S. T. Hannahs, Y. Yoshida, T. E. Sherline, T. Ono, H. Tanaka, and Y. Takano, Phys. Rev. Lett. 102, 257201 (2009).
[10] Y. Shirata, H. Tanaka, A. Matsuo, and K. Kindo, Phys. Rev. Lett. 108, 057205 (2012).
[11] H. D. Zhou, C. Xu, A. M. Hallas, H. J. Silverstein, C. R. Wiebe, I. Umegaki, J. Q. Yan, T. P. Murphy, J.-H. Park, Y. Qiu, J. R. D. Copley, J. S. Gardner, and Y. Takano, Phys. Rev. Lett. 109, 267206 (2012).
[12] Y. Doi, Y. Hinatsu, and R. Ohyama, Journal of Physics: Condensed Matter 16, 8923 (2004).
[13] H. D. Zhou, E. S. Choi, G. Li, L. Balicas, C. R. Wiebe, Y. Qiu, J. R. D. Copley, and J. S. Gardner, Phys. Rev. Lett. 106, 147204 (2011).
[14] J. G. Cheng, G. Li, L. Balicas, J. S. Zhou, J. B. Goodenough, C. Xu, and H. D. Zhou, Phys. Rev. Lett. 107, 197204 (2011).
[15] The crystal structure, with emphasis on the relative positions of the Co ions and the Ba nuclear spin sites, is provided in the Supplemental Material.
[16] A. Abragam and Bleaney, Electron paramagnetic resonance of transition ions (Oxford University Press, 1970) p. 751.
[17] T. Susuki, N. Kurita, T. Tanaka, H. Nohjiri, A. Matsuo, K. Kindo, and H. Tanaka, Phys. Rev. Lett. 110, 267201 (2013).
[18] Our present NMR results clearly indicate that the UUD phase occurs for $B \perp \hat{c}$, consistent with the findings of Ref. [17] but opposite to those of Ref. [11].
[19] see Supplemental Material.
[20] T. Yildirim, A. B. Harris, and E. F. Shender, Phys. Rev. B 58, 3144 (1998).
SUPPLEMENTAL MATERIAL: CRYSTAL STRUCTURE AND $^{135,137}$ BA NMR PARAMETERS

Figure 5 depicts the crystal structure of Ba$_3$CoSb$_2$O$_9$. It represents a highly symmetric hexagonal structure, space group $P6_3/mmc$, with lattice constants $a = b = 5.8562$ Å and $c = 14.4561$ Å. For clarity, the oxygen atoms of the corner-sharing CoO$_6$ octahedra and the face-sharing Sb$_2$O$_9$ biotahedra are not shown. Layers of regular magnetic triangular lattices are formed parallel to the $ab$-plane by the Co$^{2+}$ ions (blue), which carry effective spin $S = 1/2$. The different Co sublattices are denoted by 1-3, and 4-6 on even, odd layers, respectively. There are two inequivalent, uniaxially symmetric Ba sites in the unit cell, referred to as Ba(1) (dark green) and Ba(2) (light green).

The full NMR hamiltonian for a nucleus of spin $I \neq 1/2$ and gyromagnetic ratio $\gamma$, sitting on an axially symmetric site, is given by

$$\mathcal{H} = -\gamma \hbar I \cdot (\mathbf{I} + \mathbf{K}) \cdot \mathbf{B} + \frac{\hbar \nu Q}{6} \left[ 3I_z^2 - I(I + 1) \right],$$

where $\mathbf{B}$ is the applied magnetic field, $\mathbf{K}$ is the NMR shift tensor, and $\nu Q$ is the nuclear quadrupole frequency $[2]$. For $I = 3/2$, three NMR lines occur, corresponding to the nuclear transitions $(m_I \leftrightarrow m_I - 1)$. There are two NMR active Ba isotopes, $^{135}$Ba with $^{135}\gamma/2\pi = 4.2295$ MHz/T and $^{137}$Ba with $^{137}\gamma/2\pi = 4.73158$ MHz/T, both with $I = 3/2$. Their respective abundances are 6% and 11%. Thus, in Ba$_3$CoSb$_2$O$_9$ where there are two crystallographically inequivalent Ba sites, four sets of three lines are expected in the NMR spectrum. Figure 6 shows the NMR spectrum in the paramagnetic state for $\mathbf{B} \parallel \hat{c}$, with the various lines labeled accordingly. The corresponding values of $\nu Q$ are listed in Table I.

The crystal orientation was verified by mapping the oxygen atoms (blue), which carry $9\alpha$ bioctahedra and the $9\beta$ ions (oxygen atoms not shown). Layers of regular magnetic triangular lattices are formed parallel to the $ab$-plane by the Co$^{2+}$ ions (blue), which carry effective spin $S = 1/2$. The different Co sublattices are denoted by 1-3, and 4-6 on even, odd layers, respectively. There are two inequivalent, uniaxially symmetric Ba sites in the unit cell, referred to as Ba(1) (dark green) and Ba(2) (light green).

FIG. 5. Chemical unit cell of Ba$_3$CoSb$_2$O$_9$ (oxygen atoms not shown).

The crystal orientation was verified by mapping the oxygen atoms (blue), which carry $9\alpha$ bioctahedra and the $9\beta$ ions (oxygen atoms not shown). Layers of regular magnetic triangular lattices are formed parallel to the $ab$-plane by the Co$^{2+}$ ions (blue), which carry effective spin $S = 1/2$. The different Co sublattices are denoted by 1-3, and 4-6 on even, odd layers, respectively. There are two inequivalent, uniaxially symmetric Ba sites in the unit cell, referred to as Ba(1) (dark green) and Ba(2) (light green).

FIG. 6. Ba$_3$CoSb$_2$O$_9$ NMR spectrum for $\mathbf{B} = 8.4524$ T, $\mathbf{B} \parallel \hat{c}$ at $T = 6$ K. For each Ba site/isotope, the spectrum is composed of three quadrupole transition lines (Eq. 2), the central $(1/2 \leftrightarrow -1/2)$ and the two satellites $(\pm 3/2 \leftrightarrow \pm 1/2)$. The difference in frequency between the two satellites is equal to $\nu Q$ $(2\nu Q)$ for $\mathbf{B} \parallel \hat{c}$ ($\mathbf{B} \perp \hat{c}$).

FIG. 7. NMR frequency of the $^{137}$Ba(2) central transition vs. $\theta$ for $B = 8.4524$ T and $T = 6$ K.

The paramagnetic shifts $K_a$ are given by $K_a = K_0 + A_{\alpha\alpha} \chi_{\alpha}$, where $\alpha$ denotes the field orientation, $K_0$ is the orbital contribution, and $A_{\alpha\alpha}$ are the diagonal components of the hyperfine coupling tensor. Thus, $A_{\alpha\alpha}$ can be deduced from the slope of a $K - \chi$ plot, for which the implicit parameter is temperature. The results are shown in Fig. 8 and the relevant values for $A_{\alpha\alpha}$ are listed in Table I.
**FIG. 8.** $K - \chi$ plots for both Ba sites at $B = 8.4524T \parallel, \perp \hat{c}$.

**TABLE I.** NMR parameters for the Ba nuclear sites/isotopes.

| Nuclear site | $\nu_Q$ (MHz) | $A_{\parallel c}(G/\mu_B)$ | $A_{\perp c}(G/\mu_B)$ |
|--------------|---------------|-----------------------------|--------------------------|
| $^{137}$Ba(1) | 2.72          | -156                        | -612                     |
| $^{137}$Ba(2) | 15.4          | -1313                       | -752                     |
| $^{135}$Ba(1) | 1.75          | -156                        | -612                     |
| $^{135}$Ba(2) | 9.8           | -1313                       | -752                     |

[1] Y. Shirata, H. Tanaka, A. Matsuo, and K. Kindo, Phys. Rev. Lett. **108**, 057205 (2012).

[2] A. Abragam and Bleaney, Electron paramagnetic resonance of transition ions (Oxford University Press, 1970) p. 751.