PHYSICAL REVIEW B **76**, 060406(R) (2007)

Thermodynamics of the up-up-down phase of the $S=\frac{1}{2}$ triangular-lattice antiferromagnet Cs_2CuBr_4

H. Tsujii,[1,2] C. R. Rotundu,[1,*] T. Ono,[3] H. Tanaka,[3] B. Andraka,[1] K. Ingersent,[1] and Y. Takano[1]
[1]*Department of Physics, University of Florida, P. O. Box 118440, Gainesville, Florida 32611-8440, USA*
[2]*Department of Physics, Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan*
[3]*Department of Physics, Tokyo Institute of Technology, Meguro-ku, Tokyo 152-8551, Japan*
(Received 16 May 2007; revised manuscript received 31 July 2007; published 21 August 2007)

The specific heat and magnetocaloric effect are used to probe the field-induced up-up-down (UUD) phase of Cs_2CuBr_4, a quasi-two-dimensional spin-$\frac{1}{2}$ triangular antiferromagnet with near-maximal frustration. The transitions between the commensurate UUD phase and the incommensurate phases adjacent to it are clearly first order, at least at low temperatures. The shape of the magnetic phase diagram shows that the UUD phase is stabilized by quantum fluctuations, not by thermal fluctuations as in the corresponding phase of classical spins. The magnon gaps determined from the specific heat are considerably larger than those expected for a Heisenberg antiferromagnet.

DOI: 10.1103/PhysRevB.76.060406 PACS number(s): 75.30.Kz, 75.40.Cx, 75.50.Ee

The interplay between geometric frustration and quantum fluctuations in small-spin antiferromagnets provides fertile ground for observation of new phenomena. The prime example is a spin $S=\frac{1}{2}$ antiferromagnet on a triangular lattice, which has been intensively studied since Anderson's conjecture of a resonating-valence-bond ground state.[1] The zero-field ground state of the nearest-neighbor Heisenberg model has been shown to be weakly ordered with a 120° spin arrangement.[2] However, the magnons suffer from unusual two-particle decay processes and display significantly renormalized dispersion[3] with rotonlike minima at the zone boundaries.[4,5] Experimentally, observation of unusual dynamics in the spin-$\frac{1}{2}$ triangular antiferromagnet Cs_2CuCl_4 (Ref. 6) has led to proposals of nearby spin-liquid states.[7,8]

The frustration-fluctuation interplay in $S=\frac{1}{2}$ triangular antiferromagnets also manifests itself in a magnetization plateau at 1/3 of the saturation value in both Heisenberg and *XY* nearest-neighbor models.[9] Any magnetization plateau must arise from an energy gap in the low-lying magnetic excitations. Since such a gap is a consequence of the ground state maintaining the continuous rotational symmetry of the Hamiltonian, a magnetization plateau indicates that the ground state is a spin liquid, a collection of spin multimers, or an ordered state that is collinear with the magnetic field. Moreover, the ground state must be commensurate with the underlying crystal lattice, unless it is a spin liquid.[10] In spin-$\frac{1}{2}$ Heisenberg and *XY* antiferromagnets on a triangular lattice, the plateau arises from a collinear up-up-down (UUD) phase,[9] in which up spins parallel to the magnetic field form a honeycomb sublattice and the down spins form a triangular sublattice comprising the centers of the hexagonal honeycomb cells.

Among the known spin-$\frac{1}{2}$ triangular-lattice antiferromagnets, Cs_2CuBr_4 is the only one exhibiting a magnetization plateau indicative of the UUD phase.[11–13] The compound has an orthorhombic crystal structure with space group *Pnma*.[14] The magnetic Cu^{2+} ions are located within distorted $CuBr_4^{2-}$ tetrahedra, which form a triangular lattice in the *bc* plane. At the magnetization plateau with $\boldsymbol{H}\|\boldsymbol{c}$, the *b* component of the order vector detected by neutrons agrees within the experimental uncertainty with the wave number $k_0=2/3$ of the UUD phase.[12] The ^{133}Cs NMR spectra for $\boldsymbol{H}\|\boldsymbol{b}$ provide further evidence for this phase.[15]

In Cs_2CuBr_4, the nearest-neighbor Cu^{2+} exchange J_1 along *b* is greater than J_2 along other principal directions in the *bc* plane. The ratio J_2/J_1 is 0.74, according to a comparison[13] of the wave number k_0 of the incommensurate, cycloidal ordered structure at zero field[12] with results of linked-cluster expansions.[16] Therefore, Cs_2CuBr_4 is much closer to the maximally frustrated limit $J_2/J_1=1$ than is the extensively studied analog Cs_2CuCl_4,[6,17–20] for which $J_2/J_1=0.34-0.37$.[13,18] Numerical diagonalization of finite-size spin-$\frac{1}{2}$ Heisenberg systems predicts that the geometric frustration is sufficient to stabilize the UUD phase only in the range $0.7\lesssim J_2/J_1\lesssim 1.3$,[21] explaining its presence in Cs_2CuBr_4 and absence in the chloride. However, this prediction is challenged by a renormalization-group calculation[22] that finds the UUD phase for infinitesimally small J_2.[23]

In this paper, we report the unique thermodynamic properties of the UUD phase of Cs_2CuBr_4 based on magnetocaloric-effect and specific-heat measurements. We examine in detail the phase diagram, which strongly differs from that of classical spins, to uncover the role of quantum fluctuations in stabilizing this phase. The magnetocaloric effect at $T\leqslant 0.24$ K exhibits unambiguous signatures of first-order transitions between the UUD phase and the adjacent, incommensurate phases, whereas the specific heat reveals dramatic enhancement of the magnon gap, a possible mechanism for which is the presence of a weak Dzyaloshinskii-Moriya (DM) interaction.[24,25] Recently, a novel spin liquid and a weak UUD order have been proposed to occur at 1/3 of the saturation magnetization for $J_2/J_1<1$.[26] The specific-heat data suggest that the UUD phase of Cs_2CuBr_4 is far from such exotic states, at least for the field orientation of the present study. Preliminary results were presented in Ref. 27.

The experiment was performed in magnetic fields applied along the *c* axis. The sample-growth method[11] and the calorimeter[28] have been previously described.

Figure 1 shows the magnetocaloric-effect results, where we swept the magnetic field between 12.5 and 14.6 T at a rate of 0.2 T/min, while continuously measuring the temperature difference between the sample and the thermal res-

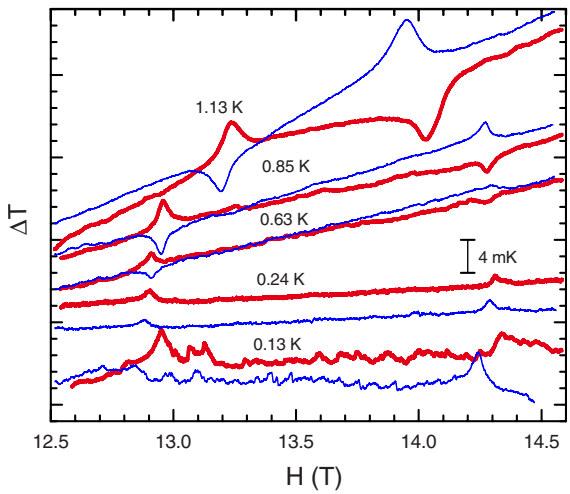

FIG. 1. (Color online) Magnetocaloric effect of Cs_2CuBr_4 in fields along the c axis: temperature difference ΔT between sample and thermal reservoir during 0.2 T/min upward and downward field sweeps (thick and thin lines, respectively). Traces at different temperatures are offset for clarity. The overall separation between up- and down-sweep traces at the lowest temperatures is an uninteresting nuclear-spin effect.

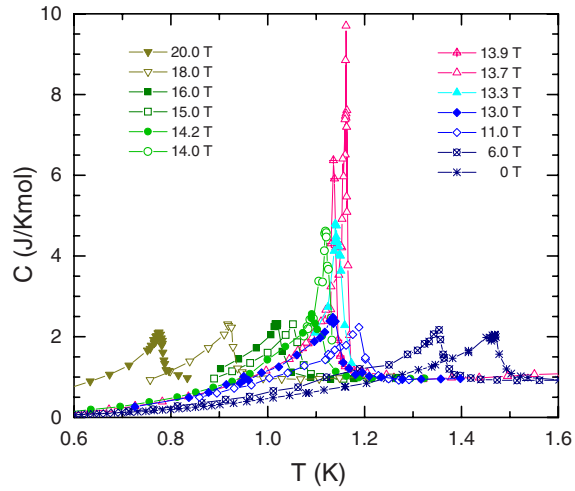

FIG. 2. (Color online) Magnetic specific heat of Cs_2CuBr_4 in zero magnetic field and in fields along the c axis. A small phonon contribution, $7.94T^3$ mJ/K mol, has been subtracted by scaling the specific heat of Cs_2ZnBr_4 (Ref. 13). The lines are guides to the eye.

ervoir. At temperatures $T \leqslant 1.17$ K the transitions between the UUD and other phases, which are incommensurate states according to neutron diffraction[12] and ^{133}Cs NMR,[15] appear as peaks and dips in the temperature traces. At 0.24 and 0.13 K, the two lowest temperatures of the experiment, the transitions become clearly hysteretic: features indicating transitions during up sweeps are shifted relative to those during down sweeps; in addition, all transitions appear as peaks irrespective of the field-sweep direction, indicating heating due to irreversibility. These two signatures of hysteresis unambiguously indicate that the transitions between the UUD and incommensurate phases are first order, as previously suggested by magnetization and elastic-neutron data.[13] No detectable hysteresis exists for $T \geqslant 0.63$ K. One possible explanation is that at these higher temperatures the nucleation rate of a new phase at each transition field exceeds the field-sweep rate.

The transition from the high-temperature, paramagnetic phase to the antiferromagnetically ordered phases appears as a peak in the specific heat at all magnetic fields up to 20 T, the highest field of the present study. As shown in Fig. 2, the peak height at the transition is nearly the same throughout the incommensurate phases, whereas it is larger and strongly field dependent in the UUD phase, reaching a maximum at 13.7 T. The unusually large height and sharp high-temperature edge of the peak at this field suggest that, like the incommensurate-UUD transition, the paramagnetic-UUD transition is first order. The robustness of this transition argues against a proximity of this system to the exotic phases recently proposed.[26]

From the positions of the specific-heat peaks and the sharp features in the magnetocaloric-effect temperature traces, we obtain the magnetic phase diagram shown in Fig. 3. Below 0.7 K, the phase boundaries of the UUD phase are nearly horizontal, indicating (via the magnetic Clausius-Clapeyron relation) a very small entropy difference between this phase and the incommensurate phases. The critical fields extrapolated to $T=0$ are $H_{c1}=12.9$ T and $H_{c2}=14.3$ T, slightly lower than the values 13.1 and 14.4 T obtained from the magnetization curve.[13]

Above 0.7 K, the width of the UUD phase decreases slightly with increasing temperature, indicating that this phase has a smaller entropy than the incommensurate phases. The UUD phase is thus seen to owe its existence to an energy-lowering mechanism rather than to thermal fluctuations, which would decrease the free energy by raising the entropy. That the reduced energy of the UUD state in comparison with the incommensurate phases more than compensates for its slightly lower entropy is confirmed by a bulge of the UUD phase into the paramagnetic phase. According to spin-wave theory,[9] this energy lowering is due to quantum fluctuations. The shapes of the observed phase boundaries

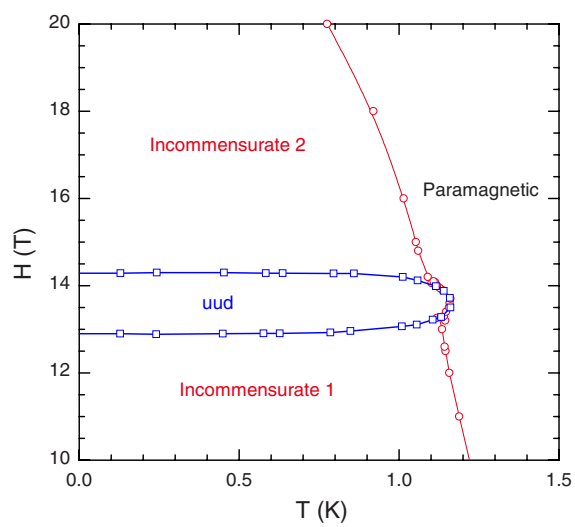

FIG. 3. (Color online) Phase diagram of Cs_2CuBr_4 in magnetic fields along the c axis, as deduced from magnetocaloric-effect (squares) and specific-heat (circles) measurements. Lines indicating the phase boundaries are guides to the eye.

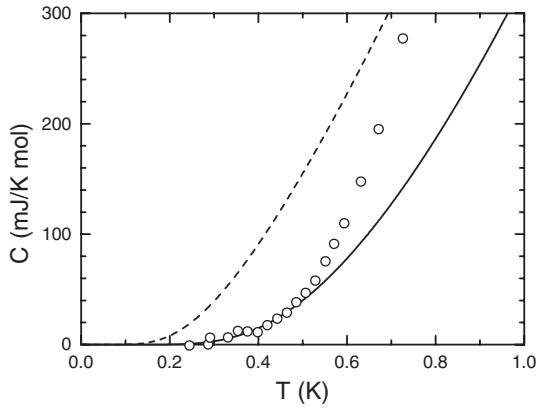

FIG. 4. Magnetic specific heat of Cs_2CuBr_4 in a 13.7 T field along the c axis. The lines are calculations for gapped magnons, as discussed in the text.

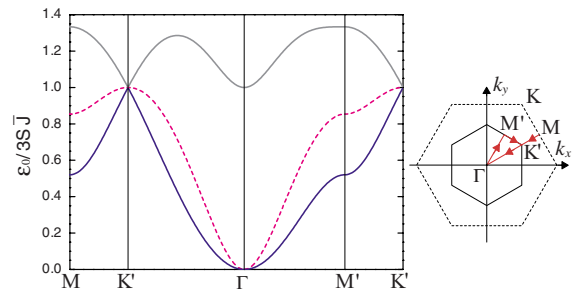

FIG. 5. (Color online) Dispersion $\epsilon_0(\boldsymbol{k})$ of the $S_z=-1$ (solid lines) and $S_z=+1$ (broken line) classical magnon modes in the UUD state of a Heisenberg antiferromagnet on a triangular lattice, along the high-symmetry paths indicated with arrows in the reciprocal space at right. In the reciprocal space, the solid line outlines the first Brillouin zone of the three triangular sublattices, and the broken line that of the full lattice.

are in marked contrast to those of the UUD phase of classical spins.[29,30] Being a single point in the $T=0$ phase diagram, the classical UUD phase becomes stable only at nonzero temperatures, as thermal fluctuations raise its entropy relative to that in either adjacent ordered phase. As a result, the field width of the phase expands with increasing temperature, as observed, for instance, in $RbFe(MoO_4)_2$.[31,32]

The lowering of the energy of the UUD phase explains why the transitions at H_{c1} and H_{c2} are first order. For classical spins, the ground state and, with it, the magnetization evolve continuously with magnetic field, the UUD state being a ground state only at one field. As the energy of this state is preferentially lowered by quantum fluctuations, leaving behind some states over a range of magnetization values, these states lose their ability to be a ground state. Consequently, the wave function and the magnetization of the ground state change discontinuously at the critical fields.

The zero-temperature width of the UUD phase, $H_{c2}-H_{c1}$, is directly related to magnon gaps. In particular, if the spin Hamiltonian commutes with the total spin, the gaps are $g\mu_B(H-H_{c1})$ and $g\mu_B(H_{c2}-H)$ for the $S_z=-1$ and $+1$ magnons, respectively. Here g is the g factor and μ_B the Bohr magneton.

The presence of the gaps is evident in the low-temperature specific heat at 13.7 T (roughly the midpoint of the UUD phase) shown in Fig. 4. Here, the nuclear-spin contribution, $21.2(H/T)^2$ μJ/K mol with H in tesla and T in kelvin,[33] has been subtracted along with the insignificant phonon contribution of $7.94T^3$ mJ/K mol. In the nuclear contribution, we have ignored hyperfine interactions and quadrupole interactions. This approximation is justified, since it gives a nuclear specific heat for Cs_2CuCl_4 that agrees to within 23% with the experimental data.[19] We expect the approximation to be considerably better for Cs_2CuBr_4, where the nuclear contribution is dominated by ^{79}Br and ^{81}Br, which have quadrupole moments an order of magnitude smaller than those of ^{35}Cl and ^{37}Cl.[34]

The magnon dispersion of the UUD phase is known for the classical Heisenberg model.[9] Anisotropy may be accounted for by substituting the average exchange $\bar{J}=(J_1+2J_2)/3$ for the isotropic J.[35] As shown in Fig. 5, the two low-energy modes have significantly different dispersions, reflecting the different symmetries of the coplanar phases that occur below and above the field region of the UUD phase. Near the zone center, the dispersion is $\epsilon_{0-}(\boldsymbol{k}) \simeq (3/4)S\bar{J}k^2$ for the lower of two $S_z=-1$ modes and $\epsilon_{0+}(\boldsymbol{k}) \simeq (9/4)S\bar{J}k^2$ for the $S_z=+1$ mode. These classical magnons are gapless, consistent with the collapse of the UUD phase to a single point in the phase diagram at $T=0$. For $S=\frac{1}{2}$, however, quantum fluctuations give rise to gaps at the zone center.[9]

The k dependence of the magnon dispersion is not known for $S=\frac{1}{2}$, but we expect $\epsilon_\pm(\boldsymbol{k})=\epsilon_{0\pm}(\boldsymbol{k})+\Delta_\pm$ to be a good approximation for the low-energy $S_z=\pm 1$ modes, where $\Delta_\pm$ are the gaps. We ignore the higher-energy $S_z=-1$ mode, since its contribution to the specific heat is negligible.

To quantitatively compare the data with a gapped-magnon behavior, we need to know the exchange couplings. These can be determined from J_2/J_1 and from the measured $gH_s \simeq 63$ T, which holds for all three principal field directions despite small variations in g and in the saturation field H_s,[11] combined with the theoretical result $H_s=J_1(2+J_2/J_1)^2/(2g\mu_B)$, which is exact when terms other than J_1 and J_2 are negligible in the spin Hamiltonian. The results are $J_1=11.3$ K and $J_2=8.3$ K,[36] yielding a value $\bar{J}=9.3$ K for substitution into $\epsilon_{0\pm}(\boldsymbol{k})$.

Finally, the magnon specific heat is given by

$$C(T)=\frac{R}{3A_k}\sum_{s=\pm}\int d^2\boldsymbol{k}\left[\frac{\beta\epsilon_s(\boldsymbol{k})}{e^{\beta\epsilon_s(\boldsymbol{k})/2}-e^{-\beta\epsilon_s(\boldsymbol{k})/2}}\right]^2 \qquad (1)$$

at low temperatures, where interactions between magnons can be ignored. Here, R is the gas constant, $\beta=1/k_BT$, and the integral is performed numerically over the first Brillouin zone A_k of the sublattices. As shown by the broken line in Fig. 4, $\Delta_-=g\mu_B(H-H_{c1})$ and $\Delta_+=g\mu_B(H_{c2}-H)$, with $g=2.24$ from electron spin resonance[37] and H_{c1} and H_{c2} taken from the present work, give too large a specific heat in comparison with the data. Surprisingly, the best fit requires gaps that are 2.1 ± 0.1 times these values, as shown by the solid line. According to spin-wave theory,[9] the linear field dependence of the gaps breaks down in spin-$\frac{1}{2}$ XY antiferromagnets, whose Hamiltonian does not commute with the total

spin, giving way to enhanced gaps proportional to $|H/H_{c1,2}-1|^{1/2}$. It is therefore quite possible that a weak DM interaction, which also introduces an easy-plane anisotropy (albeit different from an *XY* type), is responsible for the large gaps found in the specific heat. It is intriguing that, at the same time, this anisotropy destroys the UUD phase when $\boldsymbol{H}\|\boldsymbol{a}$.[13]

In summary, we have studied the thermodynamics of the UUD phase of the spin-$\frac{1}{2}$ triangular-lattice antiferromagnet Cs_2CuBr_4. The shape of the phase diagram implies that this phase is stabilized primarily by quantum fluctuations. The transitions to the phase from the incommensurate phases and quite possibly from the high-temperature, paramagnetic phase are first order as a result of quantum fluctuations, in contrast to the second-order transitions from the paramagnetic phase to the incommensurate phases. The gaps for the two low-energy magnon modes are considerably larger than expected from the field width of the UUD phase, suggesting gap enhancement by the Dzyaloshinskii-Moriya interaction.

We thank J. Alicea, L. Balents, A. L. Chernyshev, A. V. Chubukov, Y. Fujii, D. L. Maslov, S. Miyahara, J. L. Musfeldt, M. Oshikawa, O. A. Starykh, M. Takigawa, and N. Todoroki for useful discussions, and T. P. Murphy and E. C. Palm for technical assistance. This work was supported by the NSF through Grants No. DMR-9802050 (Y.T.) and No. DMR-0312939 (K.I.), and by the DOE under Grant No. DE-FG02-99ER45748 (B.A.). A portion of the work was carried out at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-0084173 and by the State of Florida.

*Present address: Department of Physics, University of Maryland, College Park, MD 20742-4111, USA.

[1] P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973).
[2] B. Bernu, P. Lecheminant, C. Lhuillier, and L. Pierre, Phys. Rev. B **50**, 10048 (1994), and references therein.
[3] A. L. Chernyshev and M. E. Zhitomirsky, Phys. Rev. Lett. **97**, 207202 (2006).
[4] O. A. Starykh, A. V. Chubukov, and A. G. Abanov, Phys. Rev. B **74**, 180403(R) (2006).
[5] W. Zheng, J. O. Fjærestad, R. R. P. Singh, R. H. McKenzie, and R. Coldea, Phys. Rev. B **74**, 224420 (2006); J. O. Fjærestad, W. Zheng, R. R. P. Singh, R. H. McKenzie, and R. Coldea, *ibid.* **75**, 174447 (2007).
[6] R. Coldea, D. A. Tennant, A. M. Tsvelik, and Z. Tylczynski, Phys. Rev. Lett. **86**, 1335 (2001); R. Coldea, D. A. Tennant, and Z. Tylczynski, Phys. Rev. B **68**, 134424 (2003).
[7] S. V. Isakov, T. Senthil, and Y. B. Kim, Phys. Rev. B **72**, 174417 (2005).
[8] J. Alicea, O. I. Motrunich, and M. P. A. Fisher, Phys. Rev. Lett. **95**, 247203 (2005).
[9] A. V. Chubukov and D. I. Golosov, J. Phys.: Condens. Matter **3**, 69 (1991).
[10] M. Oshikawa, Phys. Rev. Lett. **84**, 1535 (2000).
[11] T. Ono, H. Tanaka, H. Aruga Katori, F. Ishikawa, H. Mitamura, and T. Goto, Phys. Rev. B **67**, 104431 (2003).
[12] T. Ono, H. Tanaka, O. Kolomiyets, H. Mitamura, T. Goto, K. Nakajima, A. Oosawa, Y. Koike, K. Kakurai, J. Klenke, P. Smeibidle, and M. Meissner, J. Phys.: Condens. Matter **16**, S773 (2004).
[13] T. Ono, H. Tanaka, T. Nakagomi, O. Kolomiyets, H. Mitamura, F. Ishikawa, T. Goto, K. Nakajima, A. Oosawa, Y. Koike, K. Kakurai, J. Klenke, P. Smeibidle, M. Meissner, and H. Aruga Katori, J. Phys. Soc. Jpn. **74**, Suppl. 135 (2005).
[14] B. Morosin and E. C. Lingafelter, Acta Crystallogr. **13**, 807 (1960); T. I. Li and G. D. Stucky, Inorg. Chem. **12**, 441 (1973).
[15] Y. Fujii, T. Nakamura, H. Kikuchi, M. Chiba, T. Goto, S. Matsubara, K. Kodama, and M. Takigawa, Physica B **346-347**, 45 (2004).
[16] Zheng Weihong, R. H. McKenzie, and R. R. P. Singh, Phys. Rev. B **59**, 14367 (1999).
[17] R. Coldea, D. A. Tennant, R. A. Cowley, D. F. McMorrow, B. Dorner, and Z. Tylczynski, J. Phys.: Condens. Matter **8**, 7473 (1996); Phys. Rev. Lett. **79**, 151 (1997).
[18] R. Coldea, D. A. Tennant, K. Habicht, P. Smeibidl, C. Wolters, and Z. Tylczynski, Phys. Rev. Lett. **88**, 137203 (2002).
[19] T. Radu, H. Wilhelm, V. Yushankhai, D. Kovrizhin, R. Coldea, Z. Tylczynski, T. Lühmann, and F. Steglich, Phys. Rev. Lett. **95**, 127202 (2005).
[20] Y. Tokiwa, T. Radu, R. Coldea, H. Wilhelm, Z. Tylczynski, and F. Steglich, Phys. Rev. B **73**, 134414 (2006).
[21] S. Miyahara, K. Ogino, and N. Furukawa, Physica B **378-380**, 587 (2006).
[22] O. A. Starykh and L. Balents (unpublished).
[23] O. A. Starykh and L. Balents, Phys. Rev. Lett. **98**, 077205 (2007).
[24] I. Dzyaloshinsky, J. Phys. Chem. Solids **4**, 241 (1958); T. Moriya, Phys. Rev. **120**, 91 (1960).
[25] The strength D of the DM interaction in Cs_2CuCl_4 is $0.054J_1$ (Ref. 18). Its strength in Cs_2CuBr_4 has not been determined.
[26] J. Alicea and M. P. A. Fisher, Phys. Rev. B **75**, 144411 (2007).
[27] H. Tsujii, C. R. Rotundu, T. Ono, B. Andraka, H. Tanaka, and Y. Takano, in *24th International Conference on Low Temperature Physics*, edited by Y. Takano, S. P. Hershfield, S. O. Hill, P. J. Hirschfeld, and A. M. Goldman, AIP Conf. Proc. No. 850 (AIP, Melville, NY, 2006), p. 1093.
[28] H. Tsujii, B. Andraka, E. C. Palm, T. P. Murphy, and Y. Takano, Physica B **329–333**, 1638 (2003).
[29] H. Kawamura and S. Miyashita, J. Phys. Soc. Jpn. **54**, 4530 (1985).
[30] S. E. Korshunov, J. Phys. C **19**, 5927 (1986).
[31] L. E. Svistov, A. I. Smirnov, L. A. Prozorova, O. A. Petrenko, A. Micheler, N. Büttgen, A. Ya. Shapiro, and L. N. Demianets, Phys. Rev. B **74**, 024412 (2006).
[32] A. I. Smirnov, H. Yashiro, S. Kimura, M. Hagiwara, Y. Narumi, K. Kindo, A. Kikkawa, K. Katsumata, A. Ya. Shapiro, and L. N. Demianets, Phys. Rev. B **75**, 134412 (2007).
[33] G. C. Carter, L. H. Bennett, and D. J. Kahan, *Metallic Shifts in NMR*, Progress in Materials Science Vol. 20 (Pergamon, Oxford, 1977).
[34] P. Pyykkö, Z. Naturforsch. A: Phys. Sci. **47**, 189 (1992); J. Bieroń, P. Pyykkö, D. Sundholm, V. Kellö, and A. J. Sadlej, Phys. Rev. A **64**, 052507 (2001).
[35] However, the UUD phase ceases to be a classical ground state when J is anisotropic [J. Alicea (private communication)].
[36] The values of J_1 and J_2 given in Refs. 11 and 13 are incorrect due to a numerical error.
[37] H. Nojiri (private communication).