Competing magnetic interactions in the extended Kagomé system YBaCo$_4$O$_7$

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YBaCo$_4$O$_7$ belongs to a new class of geometrically frustrated magnets like the pyrochlores, in which Co spins occupy corners of tetrahedra. The structure can be viewed as an alternating stacking of Kagomé and triangular layers. Exactly half of the triangular units of the Kagomé plane are capped by Co ions to form columns running perpendicular to the Kagomé sheets. Neutron powder diffraction reveals a broad temperature range of diffuse magnetic scattering, followed by long-range magnetic ordering below 110 K. A unique low-temperature magnetic structure simultaneously satisfies an $S=0$ arrangement in the uncapped triangular units and antiferromagnetic coupling along the columns. A spin reorientation above 30 K tracks the relative strengths of the in-plane and out-of-plane interactions.

Magnetic frustration has attracted considerable interest over the last 50 years.[1–3] Whether the frustration arises from competing exchange interactions or the peculiar geometry of the spin lattice, it invariably leads to unconventional magnetic states at low temperatures. Frustrated systems commonly exhibit the persistence of strong spin fluctuations at low temperatures and at least partial suppression of the magnetic order. Various spin states can be stabilized below the cooperative paramagnetic regime, such as a spin liquid, spin glass or spin ice. In some cases, long-range magnetic order is established, either by structural distortions that lift the ground-state degeneracy, or by the "order-by-disorder" mechanism.[4] Kagomé antiferromagnets have been widely studied, in particular because a spin-liquid state is predicted at low temperatures for the $S=1/2$ Heisenberg system. However, real Kagomé lattices display either spin-glass behavior or long-range order with the well-known propagation vectors $k=0$ and $k=(\frac{1}{3},\frac{1}{3})$ [often referred to as $k=(\sqrt{3},\sqrt{3})$] structures.[5,6] More exotic ground states, including incommensurate spin-density waves and cycloidal structures, have been found in related lattices such as the so-called Kagomé staircase.[7]

Recently, a new class of geometrically frustrated magnets, with formula RBaCo$_4$O$_7$ ($R=$Y,rare-earth ion) has been reported.[8–10] The crystal structure is built up of alternating Kagomé and triangular cobalt lattices, in a similar way as SrCr$_{9x}$Ga$_{12-9x}$O$_{19}$,[11] but with magnetic Co^{2+}/Co^{3+} ions in a 3:1 ratio on both crystallographic sites ($S=1.625$ on average). The magnetic network in RBaCo$_4$O$_7$ is reminiscent of that of hexagonal ice $1h$,[12] but with one important difference: here, half of the triangles in the Kagomé sheets are *bicapped* by Co atoms of the adjacent triangular layers, providing magnetic superexchange interactions along the third direction. An added element of interest is that this network is built of corner-sharing CoO$_4$ tetrahedra, as opposed to the more common octahedral or pyramidal arrangement of other frustrated magnetic oxides. The ground state of this new topology is yet unknown, although one would suspect that the interplanar coupling in the third direction might play an important role in lifting the geometrical frustration. Recently,

Valldor[10] reported magnetic susceptibility measurements of YBaCo$_4$O$_7$ that indicate strong antiferromagnetic (AFM) interactions, with an extracted Curie-Weiss temperature $\Theta=-907$ K, and a spin-glass transition $T_f=66$ K, yielding a "frustration index" $\Theta/T_f\sim14$. More recent single-crystal neutron diffraction measurements by Soda *et al.*[13] have identified the presence of diffuse magnetic scattering at low temperatures, suggesting short-range magnetic correlations. Broad magnetic scattering below 105 K is observed at two inequivalent positions in reciprocal space, which is interpreted as arising from *independent* short-range ordering of both triangular and Kagomé lattices.

In a previous paper on isostructural YbBaCo$_4$O$_7$, we have established a clear link between oxygen content and magnetic properties, showing that only N$_2$-annealed samples display long-range magnetic order.[14] However, the details of the spin ordering pattern are difficult to establish for the Yb compound, due to the presence of two distinct propagation vectors and strong microstructural effects. In this Brief Report, we report that an *oxygen-stoichiometric* sample of YBaCo$_4$O$_7$ undergoes a transition to a long-range-ordered magnetic state below 105 K, with a single propagation vector $k=0$. Using neutron powder diffraction data, we have determined the complex spin arrangement that results from the competition between in-plane interactions in the Kagomé lattice, and AFM interactions along the c axis. The magnetic structure is strongly temperature dependent, with a gradual spin reorientation above 30 K, indicating the comparable strengths of the in-plane and out-of-plane interactions. Short-range magnetic correlations are present in an extended temperature range above 110 K, associated with a magnetic susceptibility behavior typical of frustrated systems.

YBaCo$_4$O$_7$ was synthesized from high-purity Y$_2$O$_3$, BaCO$_3$, and Co$_3$O$_4$. Repeated firing in air at 1150 °C yielded an oxygen hyperstoichiometric compound YBaCo$_4$O$_{7+x}$, with $x\sim0.2$, as determined by thermogravimetry. X-ray diffraction shows this to be biphasic, containing oxygen-rich and oxygen-poor phases. Treating this as-made material in nitrogen at 900 °C removed the excess oxygen to produce a single-phase material with $x=-0.05(5)$, as we recently showed for the Yb analog.[14] Magnetic susceptibility was col-
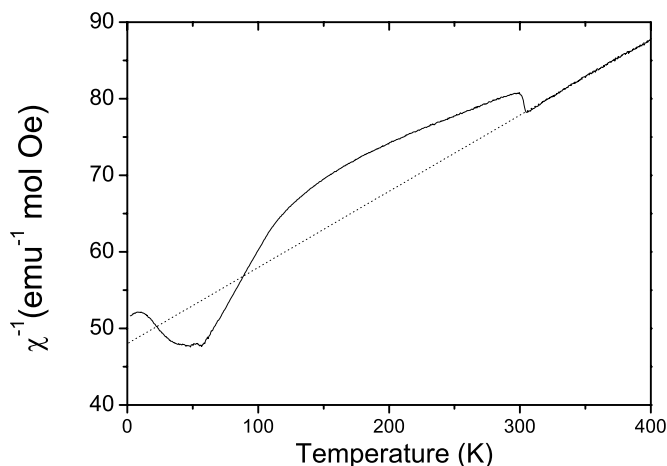
FIG. 1. Inverse magnetic susceptibility of $YBaCo_4O_7$ collected at 1000 Oe. The dotted line is a fit of the high-temperature data with a Curie-Weiss law.

lected under a magnetic field of 1 T, on warming between 2 and 300 K at a sweep rate of 2 K/min, using a vibrating sample magnetometer (Quantum Design, PPMS). Medium-resolution neutron powder diffraction data were collected on warming using the GEM diffractometer of the ISIS facility (Rutherford Appleton Laboratory) equipped with a He cryostat. Additional high-resolution diffraction patterns were recorded on the HRPD diffractometer and the long-wavelength OSIRIS diffractometer. Rietveld analysis was carried out using the FULLPROF software.[15] High-resolution neutron patterns were used to determine the ordered magnetic structures. A simulated annealing procedure[15] including 134 integrated intensities, regrouped in 36 clusters of overlapping reflections, was employed to explore the possible spin arrangements.

The reciprocal magnetic susceptibility, reported in Fig. 1, shows a Curie-Weiss behavior above 313 K, with a Curie constant $C = 10.08$ emu mol^{-1} K^{-1} and a Weiss temperature $\Theta_{CW} = -508$ K indicating dominant antiferromagnetic interactions. In the linear high-temperature region the system is best described by a cooperative paramagnetic regime down to $T \ll \Theta_{CW}$, a signature of geometrically frustrated systems.[2] The effective moment per formula unit is $8.9\mu_B$, in good agreement with the calculated spin-only value of $8.3\mu_B$ considering a mixture of $3Co^{2+}$-$1Co^{3+}$. Below 313 K an abrupt jump in the magnetic susceptibility is observed (Fig. 1) as a result of a first-order structural phase transition, as in the Yb analog.[14] High-resolution neutron diffraction data confirm that $YBaCo_4O_7$ has trigonal symmetry (space group $P31c$) at high temperature and undergoes a structural phase transition to orthorhombic symmetry, space group $Pbn2_1$ with an $(a, \sqrt{3}a, c)$ supercell, below $T_s = 313$ K. The transition occurs as a response to a strongly underbonded Ba ion and does not appear to involve charge ordering on the Co ions.[14] At low temperatures, $YBaCo_4O_7$ displays a slight monoclinic distortion, as clearly evidenced by our high-resolution neutron data (see below) as well as by preliminary synchrotron data.[17] A detailed study of these phase transitions, outside the scope of this Brief Report, will be presented elsewhere. We note, however, that the structural transition directly influences the
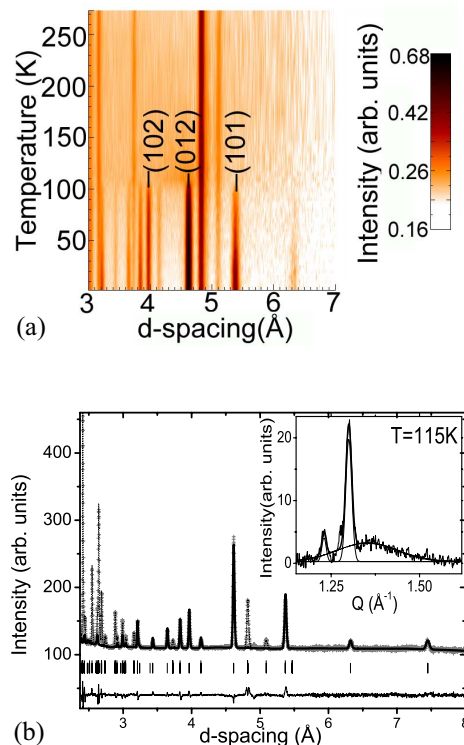

FIG. 2. (Color online) (a) Thermodiffractogram of $YBaCo_4O_7$ collected on GEM. Data from a bank of detectors situated at $34.96°2\Theta$ are shown. The scattering intensity is color coded and shown on a logarithmic red (gray) scale. (b) Rietveld refinement at 2 K. The gray crosses and dashed solid line represent the experimental data points and calculated diffraction pattern, respectively. The difference is shown at the bottom as a solid line. The row of markers shows the positions of the nuclear and magnetic reflections. The thick solid line represents the contribution from magnetic scattering alone. The inset of (b) displays a section of the neutron diffraction pattern collected at 115 K on GEM showing the coexistence of nuclear Bragg scattering and magnetic diffuse scattering. The solid line is a fit to the data. The diffuse magnetic scattering is modeled by a Lorentzian profile function.

position of oxygens in the crystal and induces a buckling of the CoO_4 tetrahedra in the Kagomé sheets.[14] Since the local environment of the Co ions is only slightly affected, the change of slope in χ^{-1} below T_s is probably not related to an enhancement of the effective moment. Instead, the pronounced curvature below T_s is likely to arise from the onset of short-range correlations, as frustration is lifted by the lowering of symmetry.

A signature of the growing short-range correlations is directly evidenced in the neutron diffraction data. Specifically, magnetic diffuse scattering appears below 250 K (inset of Fig. 2), tracking the pronounced deviation seen in χ^{-1}. This scattering has no counterpart in x-ray synchrotron data,[17] indicating its purely magnetic origin, and is centered at a wave vector $|Q| = 1.35$ Å^{-1}, i.e., the same position as the most intense antiferromagnetic Bragg peak observed at lower temperatures. The exact nature of this broad magnetic feature is uncertain, due to the weakness and breadth of the signal. In particular, it is unclear whether it is two-dimensional (2D) Warren scattering[16] or arises from 3D short-range correla-

tions. Assuming a symmetric profile of the diffuse scattering, modeled by a Lorentzian function, we estimate a correlation length of the short-range order ξ between 10 Å at 200 K and 35 Å at 115 K.

Below 115 K, the diffuse scattering abruptly sharpens, as illustrated in Fig. 2, giving rise to resolution-limited magnetic reflections that can all be indexed at $k=0$ with respect to the primitive orthorhombic cell [or $k=\left(\frac{1}{2},0,0\right)$ in the hexagonal setting]. The appearance of resolution-limited magnetic peaks at a single position in reciprocal space contrasts with recent neutron diffraction experiments on single crystals of YBaCo$_4$O$_{7.2}$,[13] where a broad magnetic response was reported in the entire temperature range. Most likely the discrepancy is attributable to the fact that the single crystal studied by Soda *et al.* is not stoichiometric in oxygen. Indeed, our neutron powder data on an oxygen-rich, biphasic sample of YBaCo$_4$O$_{7.22(2)}$ similarly show broad magnetic scattering at the same multiple Q points. The magnetic structure at 2 K, shown in Fig. 3, corresponds to a simultaneous ordering of Co spins in both the Kagomé planes and triangular layers. Using high-resolution neutron data, we could determine the absolute orientation of the spins with respect to the crystal axes, a crucial element to determine the magnetic symmetry. The magnetic structure can be described in the Shubnikov group $P112'_1$, indicating a loss of both glide planes of the orthorhombic paramagnetic group. Indeed, evidence for a monoclinic distortion [$\gamma=90.135(2)°$] is unambiguously seen in high-resolution data at high Q. Because of this lower symmetry, all the spin configurations are admixtures of two irreducible representations of $Pbn2_1$. The results of simulated annealing runs invariably lead to a supplementary set of constraints that are not imposed by symmetry: (1) all spins lie approximately in the ab plane; (2) spins labeled 1–4 in Fig. 3 are found antiparallel to their primed counterparts (1'–4'). Rietveld refinements with this model fit the data well throughout the entire temperature range from 2 to 100 K.

At 2 K, the refined value of the magnetic moment on the triangular layer is $3.49(8)\mu_B$, slightly higher than the expected $3.25\mu_B$ assuming a spin-only contribution from a Co ion with intermediate valence 2.25. In the Kagomé planes, however, the moment [$2.19(4)\mu_B$] is substantially reduced, revealing that a large fraction of the spins remain disordered at low temperatures. Another possibility is that a slight preference for Co^{3+} exists on the apical crystallographic site, as has been suggested by Valldor,[8] although we have found no strong structural evidence for such preference.[14] The three-dimensional magnetic structure can be described as follows. The spins on noncapped triangular units of the Kagomé sheets adopt configurations with total moment $\mathbf{M}_1\simeq\mathbf{0}$, corresponding to one of the negative-chirality arrangements found in the well-known $k=0$ and $k=\left(\frac{1}{3}\frac{1}{3}\right)$ structures. Spins belonging to bi-capped triangular units have a total moment $\mathbf{M}_2\neq\mathbf{0}$, antiparallel to the Co(4) spins capping the triangle above and below, resulting in antiferromagnetic chains running along c. The magnitudes of $\mathbf{M}_2$ and the Co(4) moment are different, implying that each individual column is a ferrimagnetic entity. Globally, the 3D structure does not carry a net moment, as adjacent chains are oriented antiparallel.
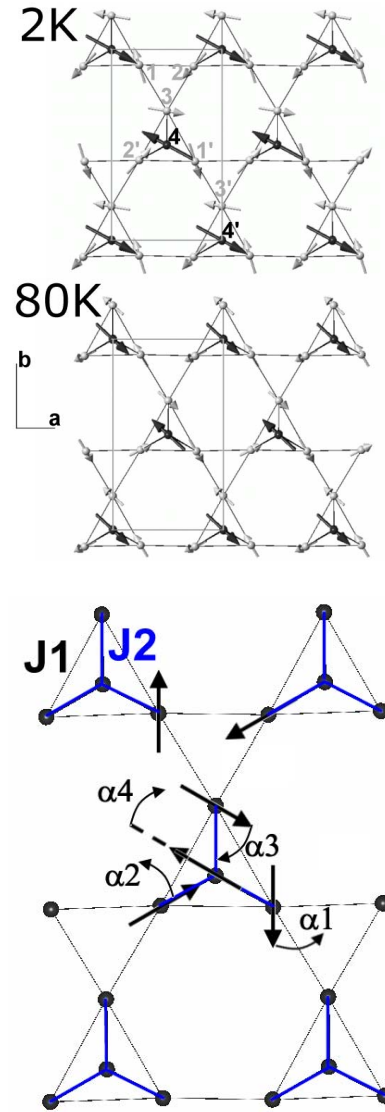

FIG. 3. (Color online) Top: Magnetic structure of YBaCo$_4$O$_7$ projected in the ab plane at 2 (top panel) and 80 K (bottom). The black and gray arrows represent moments on the Co(1) and Co(2) sites, respectively (see text for details). For clarity only one of the two Co(1)/Co(2) layers is shown, i.e., atoms with fractional coordinates $z>0.5$. Magnetic moments on the second layer, not shown, are related by time reversal of the 2_1 symmetry operator. Bottom: Exchange interactions J_1 and J_2 are depicted as black (thin) and blue (thick) lines respectively. The ideal 120° structure is also shown (see text for details).

The ordered moment extracted from Rietveld refinements, shown in Fig. 4(a), varies smoothly with temperature, but the temperature evolution of selected magnetic Bragg peaks [Fig. 4(b)] indicates a gradual reorientation between 30 and 60 K. For example, the (012) peak intensity departs from mean-field behavior at 60 K, correlating with the minimum in χ^{-1}. We have parametrized the spin reorientation by four angles α_i ($i=1-4$), which measure the deviation of individual spins from the ideal 120° structure shown in Fig. 3(b). The low-temperature magnetic arrangement is within a few degrees of the ideal model. On warming above 30 K, the
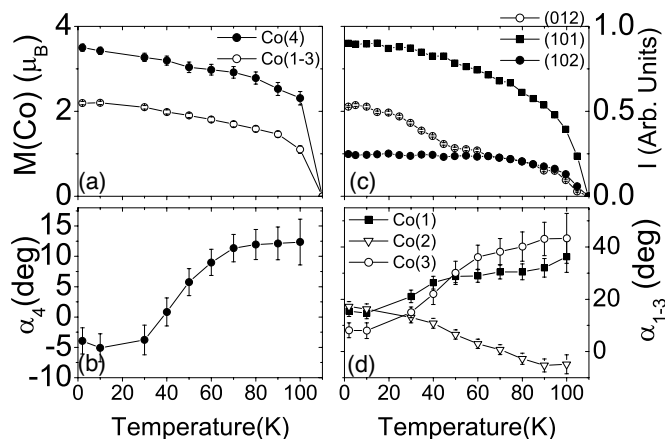
FIG. 4. (a) Temperature dependence of the magnetic moment on the Co(1) and Co(2)–Co(4) sites. (b) Integrated intensities of selected magnetic peaks (labels) versus temperature. (c),(d) Angular deviations from the ideal 120° model for Co ions labeled 1–4 (see Fig. 3 and text for details).

$$E_{HT}(\theta) = -2J_2 S_1 S_2 + (S_1)^2 \sin(\theta)\left(\frac{S_2}{S_1} \cdot J_2 - 2J_1\right), \quad (1)$$

$$E_{LT} = -J_1 S_1^2 - 2J_2 S_1 S_2. \quad (2)$$

At high temperature, the minimum energy configuration is obtained for either a collinear or an anticollinear structure, depending on the ratio $J_1 S_1 / J_2 S_2$. The observed 90° arrangement of the Co(2) spin must therefore involve additional exchange or single-ion anisotropy terms. By varying the ratio S_1/S_2 for a given set of exchange parameters, one finds a crossover between the collinear (or anticollinear) and LT structures.

In summary, a first-order structural phase transition at 313 K relieves the geometric frustration in $YBaCo_4O_7$ giving rise to an extended regime of short-range correlations followed by 3D antiferromagnetic ordering below 110 K. All Co-Co interactions are found to be antiferromagnetic, in agreement with the large negative Weiss temperature. The low-temperature magnetic structure is related to the 120° structures commonly found in Kagomé systems, with $S=0$ arrangement of spins in uncapped triangular units of the Kagomé sheets. Capped triangular units carry a net spin oriented antiparallel to that of the capping Co ions. On warming, spin reorientation leads to progressive loss of the the $S=0$, 120° arrangement, favoring the formation of ferrimagnetic collinear chains along the c axis and suggesting similar energy scales for the competing in-plane and out-of-plane interactions. As the lifting of geometrical frustration is very sensitive to the structural distortion, we suggest that the magnetic phase diagram of $RBaCo_4O_7$ could be tuned by chemical substitutions or the application of external perturbations.

deviation becomes more pronounced with a tendency toward saturation above 60 K. In the high-temperature structure ($T>60$ K), spins on Co(1), Co(3), and Co(4) are essentially collinear whereas the spin on Co(2) becomes approximately orthogonal to the others.

Within the framework of a simple nearest-neighbor isotropic exchange model, the evolution from the 120° to the collinear structures can be understood in terms of competition between the in-plane interaction [J_1 in Fig. 3(c)], which favors the 120° structure, and the out-of-plane interaction J_2, which tends to stabilize collinear AFM chains along the c axis (here $J_1>0$ and $J_2>0$). However, the orthogonal orientation of the Co(2) spin is difficult to reproduce with such a simple model. A straightforward parametrization of the observed high- and low-temperature structure, the former including an angular parameter θ ($\theta = \alpha_2$) to describe the orientation of the Co(2) spin, leads to the energy expressions

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