Magnetic order of the rare earth sublattice in *h*-$YbMnO_3$

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^{170}Yb-Mössbauer spectra have been recorded for *h*-$YbMnO_3$ over the temperature range of 1.5–40 K. A rapid increase in the Yb 2*a*-site magnetic hyperfine field and electronic ground state fluctuation time provides microscopic evidence for long-range magnetic order of the Yb 2*a*-site sublattice below $T_{N_2} \approx 5$ K. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3068011]

I. INTRODUCTION

The hexagonal manganites are currently of interest because of their multiferroic behavior and geometrical frustration, both of which are associated with the Mn sublattice. The Mn sublattice first orders ferroelectrically at $T_C = 993$ K and then antiferromagnetically at $T_{N_1} = 89$ K.[1] However, experimental evidence suggests that the Yb sublattice orders at a much lower temperature. Anomalous paramagnetic susceptibility behavior has been observed for $YbMnO_3$ at approximately 4 K (Ref. 2) and its low temperature residual magnetization was reported to fall to zero just above 3 K.[3] In a previous Mössbauer investigation,[4] we interpreted a single 4.5 K ^{170}Yb-Mössbauer spectrum in terms of the superposition of a "static" magnetic subspectrum for the Yb 4*b*-site and a motionally narrowed subspectrum for the Yb 2*a*-site. For each case, these were attributed to hyperfine interactions with a well-isolated, fluctuating, Kramers doublet ground state. In line with similar behavior observed elsewhere for $Yb_2Ti_2O_7$,[5] the static subspectrum was assumed to be the result of fluctuation slowing caused by a nonzero exchange interaction. Diviš *et al.*[6] interpreted their optical spectroscopy data in terms of a Mn–Yb exchange that is reported to act only at the 4*b*-site. In this present work, a more extensive set of ^{170}Yb-Mössbauer spectroscopy data has been employed to test this interpretation and to monitor the onset of magnetic order for the Yb sublattice.

II. EXPERIMENTAL DETAILS

The single-phase specimen of *h*-$YbMnO_3$ was prepared by the repeated solid state reaction (in air at 1250 °C) of an initial stoichiometric mix of Yb_2O_3 (99.9%) and $MnCO_3$ (99.9%). ^{170}Yb-Mössbauer spectra were then recorded over the temperature range of 1.5–40 K with both the source and the absorber ($\approx$490 mg cm^{-2} of specimen material) mounted vertically inside a helium-flow cryostat. The 20 mCi ^{170}Tm source was prepared by neutron activation of $\approx$25 mg of Tm (10 wt %) Al and the Mössbauer drive was calibrated using an optical interferometer.

III. RESULTS AND DISCUSSION

The ^{170}Yb-Mössbauer spectra are presented in Fig. 1. The spectrum recorded at the base temperature of 1.5 K was able to be fitted in terms of two static, five-line, magnetically split subspectra with intensities in the ratio of 2:1 as expected for the relative occurrence of the Yb 4*b*- and 2*a*-sites. Because of the small quadrupole interaction, it was not possible to determine the alignment of the magnetic hyperfine fields B_{hf} with respect to the principal axes of electric field

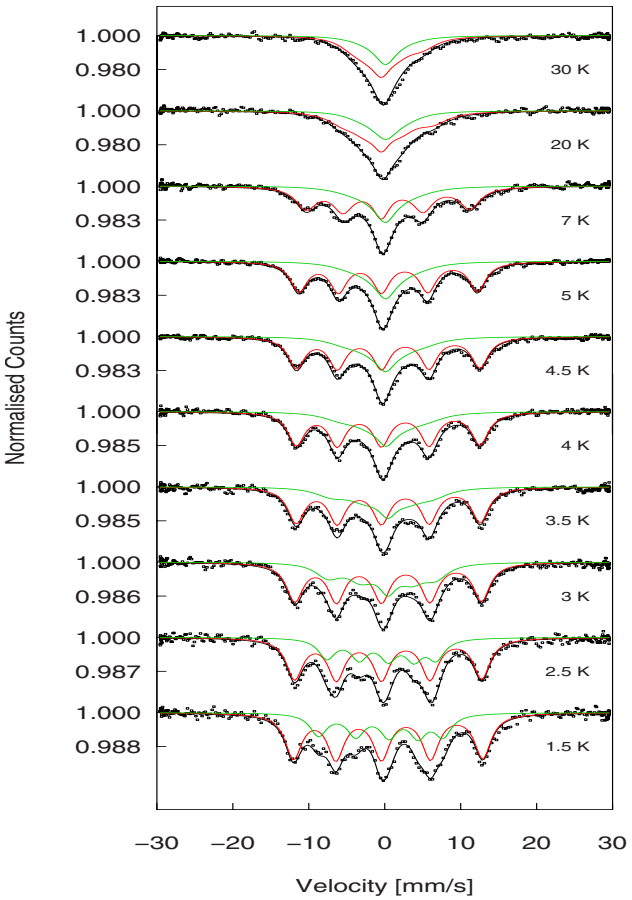

FIG. 1. (Color online) ^{170}Yb-Mössbauer spectra recorded at the indicated temperatures for *h*-$YbMnO_3$. The theory curve through the experimental data is the sum of relaxation subspectra for the Yb 4*b*-site (red) and the Yb 2*a*-site (green).

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TABLE I. Parameters fitted to the static ^{170}Yb-Mössbauer subspectra for h-$YbMnO_3$ at 1.5 K.

Yb site	δ (mm s^{-1})	Γ (mm s^{-1})	B_{hf} (T)	eQV_{zz} (mm s^{-1})
4*b*	+0.0124(1)	2.67(3)	165.9(2)	1.752(2)
2*a*	+0.0124(1)	2.67(3)	109.2(1)	−2.16(1)

gradient acting at the ^{170}Yb nucleus. A simple coaxial model was therefore employed. The fitted parameters are presented in Table I. For the two sites, both B_{hf} and the quadrupole interaction strength eQV_{zz} are significantly smaller than the maximum possible Yb^{3+} "free ion" values of 412.5 T and 55.77 mm/s,[7] respectively. This is in keeping with strong crystal field quenching.

As the temperature is increased, the subspectra are observed to collapse. The 2*a*-site subspectrum is the first to collapse and presents a broad, motionally narrowed line at 5 K. However, a residual magnetic structure persists up to 20 K for the 4*b*-site subspectrum. All of the ^{170}Yb-Mössbauer spectra could be analyzed in terms of a superposition of two relaxation-broadened, magnetic subspectra with integrated intensities in the ratio of 2:1. For the purpose of the analysis, the relaxation model of Wickman *et al.*[8] was employed to represent the expected ground state Kramers doublet fluctuation. In this model, the Kramers doublet's effective spin states $|S_z=+\frac{1}{2}\rangle$ and $|S_z=-\frac{1}{2}\rangle$ are assumed to produce magnetic hyperfine fields of equal magnitude B and of opposite sign at the ^{170}Yb nucleus. At all temperatures, the linewidth Γ, isomer shift δ, and quadrupole interaction strength were fixed at the values obtained for the 1.5 K spectrum. Only τ and B and the Kramers doublet's splitting Δ were allowed to vary.

The fitted τ values are shown in Fig. 2 as a function of temperature. The error bars for τ arise from the lack of sensitivity of the fitting process to the value of Δ and the "trade off" that exists between an increase in Δ/T and a comparatively smaller decrease in τ. It is evident that the fluctuation time is always greater for the 4*b*-site, which is consistent with fluctuation slowing caused by the nonzero Mn–Yb (4*b*) exchange interaction. It also increases gradually over the full temperature range, whereas τ for the 2*a*-site increases much more rapidly below 5 K. This is consistent with the onset of Yb–Yb magnetic order for the Yb 2*a*-site sublattice at $T_{N_2} \approx 5$ K. Fluctuation times $\tau \geq 10^{-7.5}$ s were unable to be quantified because they are well in excess of the Larmor precession times $[(2-4)\times 10^{-9}$ s] and result in static subspectra for the two sites.

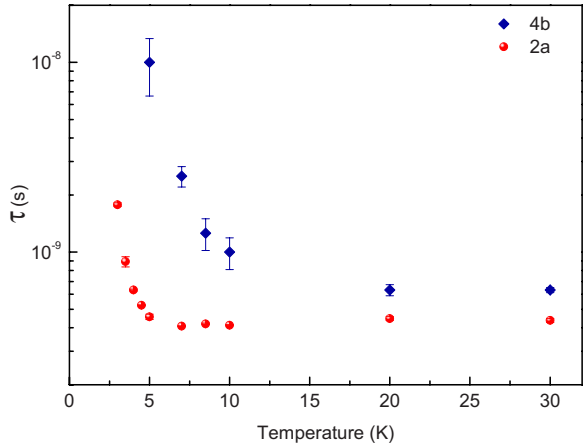

FIG. 2. (Color online) Fluctuation times τ determined for the Kramers doublet ground states at the Yb 4*b*-site (solid diamonds–blue) and the Yb 2*a*-site (solid circles–red) in h-$YbMnO_3$.

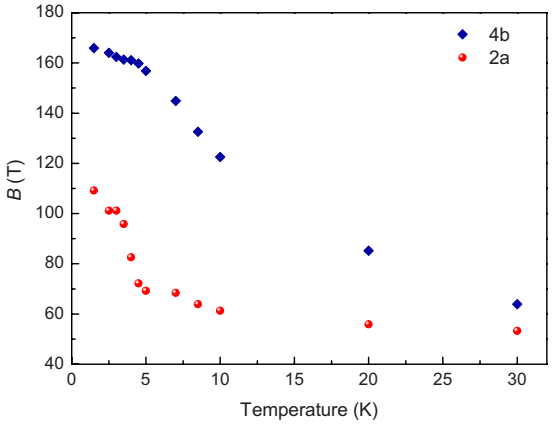

FIG. 3. (Color online) Magnetic hyperfine field B associated with the Kramers doublet's effective spin state $|S_z=+\frac{1}{2}\rangle$ determined as a function of temperature for the Yb 4*b*-site (solid diamonds–blue) and the Yb 2*a*-site (solid circles–red) in h-$YbMnO_3$.

The corresponding B values are presented in Fig. 3 where they are observed to increase with decreasing temperature for both sites. Given that B is not expected to vary with temperature in the context of the Wickman relaxation model, this brings the applicability of the model into question. It is more likely that B represents an average hyperfine field proportional to the local Yb^{3+} moment ($B_{hf} \propto \langle S_z \rangle \propto \langle \mu_z \rangle$) and that the role of the fluctuation model in the spectrum analysis process is to provide the necessary relaxation broadening. If this is the case, then the B (4*b*) data are to be interpreted in terms of a local Yb^{3+} (4*b*) moment that is induced by the nonzero Mn–Yb (4*b*) exchange interaction. Likewise, the relatively steep increase in B (2*a*) below 5 K supports the idea of long-range Yb–Yb magnetic order below $T_{N_2} \approx 5$ K. Despite a small reduction in the rate of increase in B (4*b*) below 5 K, it remains unclear as to whether the Yb 4*b*-site sublattice takes part in this same magnetic ordering process.

IV. CONCLUSION

Rapid increases are observed for the Yb 2*a*-site's ground state fluctuation time and magnetic hyperfine field, thus providing microscopic evidence for the onset of long-range magnetic order of the Yb 2*a*-site sublattice at $T_{N_2} \approx 5$ K.

"Note added in proof." A similar set of ^{170}Yb-Mössbauer spectroscopy data, for which an alternative relaxation model is employed, has since been published (Ref. 9).

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