Temperature dependence of induced Ni^{2+} moment fluctuations in the Eu_2BaNiO_5 Haldane system

C. J. Voyer
Centre for the Physics of Materials, Department of Physics, McGill University, Montréal, Quebec HSA 2T8, Canada

J. van Lierop[a)]
Department of Physics and Astronomy, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

D. H. Ryan
Centre for the Physics of Materials, Department of Physics, McGill University, Montréal, Quebec HSA 2T8, Canada

J. M. Cadogan
School of Physics, The University of New South Wales, Sydney, New South Wales 2052, Australia

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^{151}Eu and ^{153}Eu Mössbauer spectroscopies have been used to study the magnetism of the Ni^{2+} moments in Eu_2BaNiO_5 by way of the exchange-induced Eu^{3+} moments. These independent and complementary probes indicate that at high temperatures all of the moments in the Haldane quantum spin chains are paramagnetic. On cooling below 25 K, fluctuations of ~90% of the Ni^{2+} moments slow down, while the remaining 10% remain paramagnetic (indicating the presence of chain defects). Both ^{151}Eu and ^{153}Eu Mössbauer measurements yield the same Ni^{2+} moment. Furthermore, below 5 K, the 90% chain component becomes static and ordered, in excellent agreement with the ordering temperature expected from the rare-earth exchange energy. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2165609]

I. INTRODUCTION

The linear chain rare-earth nickelates, R_2BaNiO_5, are unique model systems of Haldane-gap quantum spin chains.[1,2] The $S=1$ Haldane subsystem is composed of Ni^{2+} ion chains that undergo a strong and essentially isotropic nearest-neighbor antiferromagnetic exchange interaction with a 10-20 meV Haldane energy gap.[1] At temperatures of some tens of kelvin, three-dimensional long-range antiferromagnetic order in the rare-earth ion (R^{3+}) sublattice occurs in concert with the one-dimensional antiferromagnetically coupled Ni^{2+} chains, creating an effective staggered exchange field on the Ni^{2+} chains. The size of the staggered exchange field can be tuned using either the R^{3+} moment size or temperature. The metamagnetic ordering temperature T_M of the rare-earth ions has been observed to track the estimated R^{3+} spin component (ignoring crystal-field effects).[3] Furthermore, since the R^{3+}-R^{3+} interaction is minor in comparison to the R^{3+}-Ni^{2+} interaction, one would expect that T_M increases with the R moment. Indeed, this trend is by and large observed (see the inset in Fig. 1).

Interestingly, for R=Eu with what should be a zero effective magnetic moment ($J=0$), initial optical spectroscopy studies suggested magnetic ordering around 20 K,[4] a temperature considerably higher than the scaling of T_M with R would indicate. In addition, recent ^{151}Eu Mössbauer measurements[5] on Eu_2BaNiO_5 have been interpreted as giving $T_M=30$ K, well above anything expected from the R^{3+}-to-Ni^{2+} interaction dependence on T_M and inconsistent with the linear dependence of T_M with the rare-earth exchange energy.[5]

Recent inelastic neutron-scattering experiments on R_2BaNiO_5 (Refs. 1 and 2) have shown that there are substantial dynamic magnetic interactions between the Ni^{2+} quantum spin chains and the R^{3+} subsystem, in addition to the expected static interactions. Since the optical measurements are sensitive to dipole transitions that occur on a time scale of $10^{-7}-10^{-9}$ s, it is possible that the optically determined T_M of Ref. 4 may simply be an effective dynamical freezing temperature of the moment fluctuations probed on a nanosecond time scale, and that the true, static transition occurs at a significantly lower temperature. Similarly, ^{151}Eu Mössbauer measurements[5] were interpreted in terms of a static distribution of Eu^{3+} hyperfine fields induced via the Ni^{2+} chain moments, however, static disorder and dynamic effects can yield very similar Mössbauer patterns and a unique separation is challenging.[6] The temperature evolution of the ^{151}Eu Mössbauer spectra in Ref. 5 has all the earmarks of moments undergoing magnetic relaxation effects, so that the observed T_M may also be a dynamical effect.

To definitively understand the physics of the interactions between the Eu^{3+} ions and the Ni^{2+} quantum spin chains, we have performed basic magnetic characterization in addition to ^{151}Eu and ^{153}Eu Mössbauer spectroscopies on a powder sample of Eu_2BaNiO_5. Using both Eu Mössbauer isotopes allows us to precisely probe the magnetism of the Eu^{3+} ions in an independent and complementary manner and provide a measure of the Ni^{2+} moments in the quantum spin chains by way of the exchange-induced Eu^{3+} moments. We find that

a)Electronic mail: johan@physics.umanitoba.ca

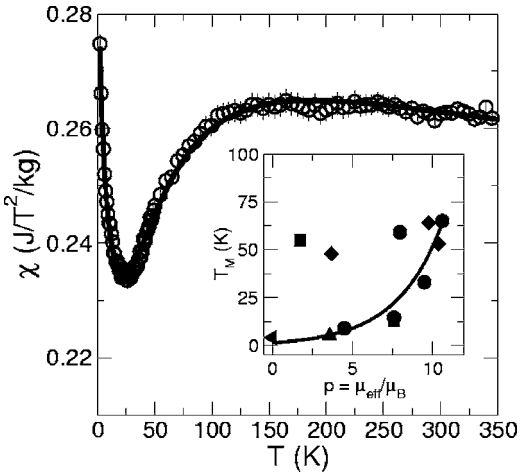

FIG. 1. dc susceptibility (χ) as a function of temperature for the Eu_2BaNiO_5 sample. The solid line is a fit in the text. Inset: Ordering temperature T_M as a function of rare-earth moment size p in R_2BaNiO_5. The solid line is a guide to the eye.

the broad hyperfine field distribution apparent in the earlier work is entirely due to the dynamic effects of moment fluctuations. Both ^{151}Eu and ^{153}Eu Mössbauer measurements yield the same Ni^{2+} moment size. Furthermore, the Eu moments become static and ordered below $T_M=5$ K, in excellent agreement with the ordering temperature measured via the static susceptibility and in agreement with the rare-earth exchange energy. This provides strong evidence that the R^{3+}-Ni^{2+} interaction governs the rare-earth exchange energy.

II. EXPERIMENTAL METHODS

Eu_2BaNiO_5 was prepared by mixing stoichiometric amounts of Eu_2O_3 (REacton, 99.9% pure), $BaCO_3$ (Aldrich, 99.999% pure), and NiO (Aldrich, 99.99% pure) and heating in air to 1170 K for 24 h. The powder was then pressed into a pellet and fired in air at 1270 K for 24 h. The pellet was then ground, pressed, and fired at 1370 K until all x-ray-visible impurities disappeared. Cu K_α x-ray diffraction showed the expected orthorhombic crystal structure (space group *Immm*) with cell constants $a=3.7992(6)$ Å, $b=5.8488(9)$ Å, and $c=11.4961(19)$ Å.[1] Basic magnetic characterization was carried out on a commercial susceptometer/magnetometer. ^{151}Eu transmission Mössbauer spectra were collected on a constant-acceleration spectrometer using a 4 GBq $^{151}SmF_3$ source. The spectrometer was calibrated using ^{57}Co and α-Fe. ^{153}Eu transmission Mössbauer spectra were collected on a laser-calibrated spectrometer operated in sine mode using a 1 GBq $^{153}Sm_2O_3$ source that was obtained by neutron-irradiating $^{152}Sm_2O_3$ (98%+ pure isotope). All spectra were collected in a helium-flow cryostat. Source linewidths for the ^{151}Eu($\Gamma_{nat}=1.337\pm0.006$ mm/s) and ^{153}Eu($\Gamma_{nat}=0.627\pm0.002$ mm/s) Mössbauer sources were determined using a $Eu_3Fe_5O_{15}$ standard.

III. RESULTS AND DISCUSSION

The temperature dependence of the susceptibility $\chi(T)$ of the Eu_2BaNiO_5 sample is shown in Fig. 1. The experimental data have been corrected taking into account a paramagnetic

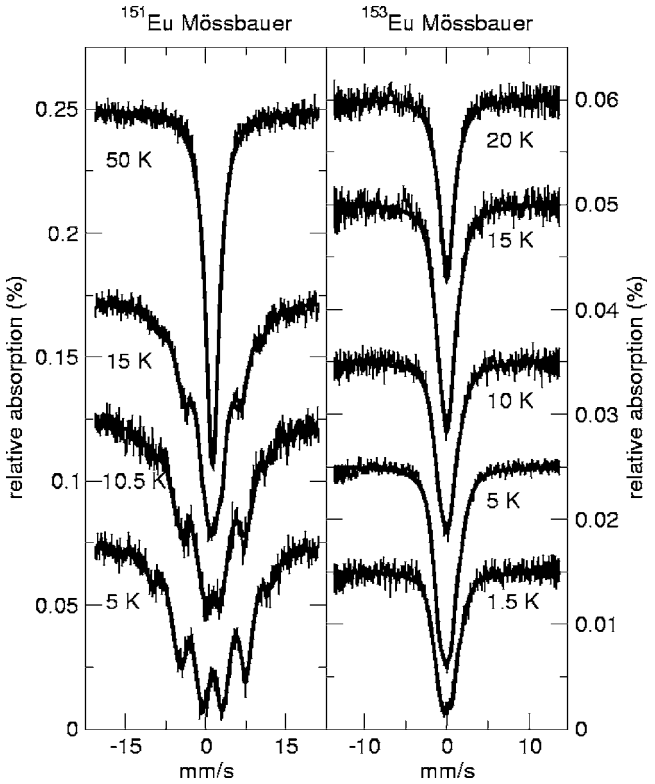

FIG. 2. Typical ^{151}Eu (left panel) and ^{153}Eu (right panel) transmission Mössbauer spectra of Eu_2BaNiO_5.

contribution that is typical of powder R_2BaNiO_5.[6,7] The impact of the Haldane gap on $\chi(T)$ is clearly seen by way of the exponential susceptibility. The Curie-law behavior of $\chi(T)$ at $T<25$ K has been observed in other R_2BaNiO_5 systems[1,6,7] and indicates that the low-lying excited states of Eu with nonzero J are being coupled to by the Ni^{2+} quantum spin chains, resulting in an effective Eu moment. $\chi(T)$ of a one-dimensional quantum spin chain ladder has been shown to follow $T^{-1/2}\exp(-\Delta/k_BT)$,[8] from which follows the phenomenological description of $\chi(T)$ in R_2BaNiO_5 (Ref. 7),

$$\chi(T)=\chi(0)+\frac{C}{T+T_M}+\frac{a}{\sqrt{T}}\exp\left(-\frac{\Delta}{k_BT}\right), \tag{1}$$

where $\chi(0)$ is a constant part of the susceptibility, C is a Curie-Weiss term, a is a fitting constant, Δ is the energy gap of the one-dimensional quantum spin chain, k_B is Boltzmann's constant, and T is the temperature. A nonlinear least-squares fit of Eq. (1) (solid line in Fig. 1) gives $T_M=4\pm1$ K and $\Delta/k_B=100\pm5$ K. T_M is in good agreement with the expected increase with the R moment (◀ in Fig. 1 inset), and Δ is in excellent agreement with the inelastic neutron-scattering measurements of the Haldane-gap energy in other R_2BaNiO_5 systems.[1]

The temperature evolution of the magnetism in Eu_2BaNiO_5 is shown by representative ^{151}Eu and ^{153}Eu transmission Mössbauer spectra in Fig. 2. These independent and complementary measures of the induced Eu moment by the Ni ions is a firsthand probe of the Ni quantum spin chain magnetism. Spectra were fitted using a modified two-level magnetic relaxation Blume-Tjon formalism[9,10] with the correct hyperfine parameters for ^{151}Eu and ^{153}Eu and line inten-

sities proportional to the appropriate Clebsch-Gordan coefficients[12] (solid lines in Fig. 2). The lowest-temperature spectra (5 K for the ^{151}Eu data and 1.5 K for the ^{153}Eu data) were used to determine the linewidth Γ, isomer shift IS, quadrupole shift QS, and magnetic hyperfine field B_{hf}. The temperature evolution of the spectra was described entirely by the fluctuation rate of the Eu moment, ν. $\Gamma = 1.3(3)$ mm/s for the 5 K ^{151}Eu spectrum and $\Gamma = 0.63(7)$ mm/s for the 1.5 K ^{153}Eu spectrum are in excellent agreement with the experimentally determined source linewidths (see above). Two subspectra were required to fit the base-temperature spectra. ~90% of the spectral area required a combination of quadrupole and magnetic interactions, while the remaining 10% showed only a quadrupole interaction. The 10% nonmagnetic contribution is consistent with the paramagnetic fraction of the sample seen in $\chi(T)$. Furthermore, this paramagnetic component indicates the presence of Ni^{2+} chain defects.[1,5] Finally, the fitted IS ~1.2 mm/s is consistent with the nonmagnetic $^{151}Eu^{3+7}F_0$ ground state.[11]

B_{hf} for the 90% magnetic components in the ^{151}Eu [15.25(7) T] and ^{153}Eu [15.2(5) T] Mössbauer spectra are in excellent agreement, a clear indication that the same Eu^{3+} moments are being measured. At high temperatures, the spectra for both Eu Mössbauer isotopes show a single broad line (Fig. 2). However, upon cooling, the spectra evolve such that the hyperfine field appears to become larger as the spectral linewidth narrows, until at the lowest temperatures (bottom spectra in Fig. 2) where the full set of lines can be resolved and fitted with the source Γ_{nat}.

This development of the spectra on cooling is entirely described by a single fitted parameter ν that represents the Eu^{3+} moment fluctuation rate.[10] Figure 3 shows the fitting results of $\nu(T)$. At high temperatures, the exchange-induced Eu^{3+} moment [from the Ni ions in the one-dimensional (1D) quantum spin chains] oscillates rapidly and time averages to $B_{hf} \sim 0$ T so that a single broad spectral line is observed (Fig. 2). $\nu(T)$ decreases on cooling and the time-averaged B_{hf} becomes larger, which is mirrored in the resolution of the spectral lines. Finally, by ~5 K the Ni^{2+} are static and $\nu = 0$. Independent fits of the ^{151}Eu and ^{153}Eu spectra provide exactly the same $\nu(T)$ behavior (Fig. 3), a clear evidence of the correctness of our description of the physics of magnetism during the ordering process of this R^{3+}-Ni^{2+} Haldane quantum spin chain system. Further corroboration is provided by the T_M determined from the Mössbauer fits being in excellent agreement with the T_M determined from fitting $\chi(T)$.

This T_M is in good agreement with the ordering temperature expected from the rare-earth exchange energy and provides strong evidence that the R^{3+}-Ni^{2+} interaction governs this exchange energy. ^{151}Eu and ^{153}Eu Mössbauer isotopes are sensitive to different time scales,[11] and both probes of the Eu^{3+}-Ni^{2+} magnetism present the same ν. This result establishes that the effective staggered magnetic field on the Ni^{2+} spin chains from the Eu ions results in moments undergoing time-dependent fluctuations that dynamically freeze and become static at a temperature determined by the R^{3+}-Ni^{2+} interaction energy.

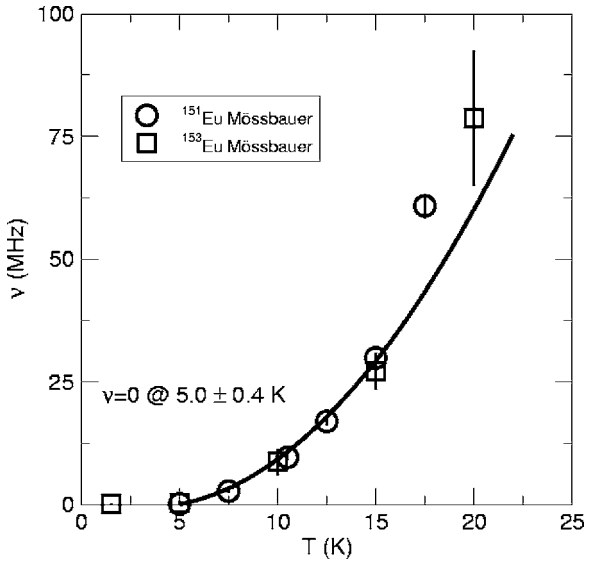

FIG. 3. Eu^{3+} moment fluctuation rate as a function of temperature determined from the fitted ^{151}Eu and ^{153}Eu Mössbauer spectra. The solid line is a fitted exponential that indicates a $T_M \sim 5$ K.

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