PHYSICAL REVIEW B **83**, 014404 (2011)

Low-frequency spin dynamics and NMR spin-lattice relaxation in antiferromagnetic rings

T. Itou,[*] T. Sagane, A. Oyamada, and S. Maegawa
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

S. Igarashi[†] and Y. Yukawa
Department of Environmental Science, Faculty of Science, Niigata University, Niigata 950-2181, Japan

(Received 17 July 2010; revised manuscript received 22 November 2010; published 10 January 2011)

We develop a general theory of the spin dynamics of Heisenberg antiferromagnetic rings (HAFRs) that explains the mechanism of NMR spin-lattice relaxation at low temperatures. In HAFRs, the imaginary parts of the q-summed dynamic spin susceptibilities parallel and perpendicular to an applied static field, $\chi''_{\mathrm{sum}\parallel}(\omega)$ and $\chi''_{\mathrm{sum}\perp}(\omega)$, are composed of the sum of many slightly broadened δ-functional modes at many frequencies. The NMR relaxation is caused by the quasielastic mode in $\chi''_{\mathrm{sum}\parallel}(\omega)$ at around zero frequency. This quasielastic mode is characterized by two physical quantities, intensity $P_{0\parallel}$ and frequency width $\Gamma_{0\parallel}$. Although $P_{0\parallel}$ has to date been assumed to be identical to the uniform static susceptibility, we point out that the two quantities are not identical. Without making this unreliable assumption for $P_{0\parallel}$, we demonstrate experimentally how $P_{0\parallel}$ and $\Gamma_{0\parallel}$ behave, by analyzing the NMR relaxation rates of two different nuclei, ^{1}H and ^{13}C, in a real HAFR. This analysis is more rigorous and thus can be used to estimate $\Gamma_{0\parallel}$ and $P_{0\parallel}$ more precisely than previously possible. We find that the temperature dependence of $P_{0\parallel}$ exhibits activation-type behavior reflecting the first excitation gap. We also find that $\Gamma_{0\parallel}$ decreases monotonically on cooling but saturates to a nonzero value at zero temperature. This strongly suggests that $\Gamma_{0\parallel}$ is dominated not only by the electron-phonon interactions but also by internanomagnet dipole interactions, which have been neglected to date.

DOI: 10.1103/PhysRevB.83.014404 PACS number(s): 75.50.Xx, 75.75.−c, 76.60.−k

I. INTRODUCTION

The dynamics of mesoscopic systems, which contain a limited number of atoms, has a completely different nature from that of bulk systems and is an important challenging issue in modern physics. A fascinating example of mesoscopic systems is single-molecular nanomagnets composed of a limited number of magnetic ions, which have become famous in the last decade for their peculiar magnetic features.[1] One of the most peculiar features is that they generally exhibit slow electron-spin dynamics at low temperatures.[1,2] This low-frequency spin dynamics remains an important issue and has been studied using several experimental techniques. For example, the dynamics causes a curious enhancement of the nuclear magnetic resonance (NMR) relaxation.[2] Since understanding the mechanism of the NMR relaxation will open the way to understanding the peculiar spin dynamics of nanomagnets, the relaxation has been intensively studied and has been subject to considerable debate. However, such an understanding is still lacking, even though researchers have proposed several phenomenological models that could explain the relaxation in single-molecular nanomagnets.[2]

In this work, we aim to reach a comprehensive understanding of the NMR relaxation and low-frequency spin dynamics of Heisenberg antiferromagnetic rings (HAFRs), an important class of single-molecular nanomagnets. We develop a more general theory of HAFRs at low temperatures than in previous works.[2–4] In HAFRs, the imaginary parts of the q(wavenumber)-summed dynamic spin susceptibilities parallel and perpendicular to an applied static field, $\chi''_{\mathrm{sum}\parallel}(\omega)$ and $\chi''_{\mathrm{sum}\perp}(\omega)$, are composed of the sum of many slightly broadened δ-functional modes at many frequencies. The NMR relaxation is caused by the quasielastic mode in $\chi''_{\mathrm{sum}\parallel}(\omega)$ at around zero frequency. One of our important findings is that the intensity of the quasielastic mode is not identical to the uniform spin susceptibility, in contrast to what was believed in previous works. The authors of previous works have estimated and discussed the characteristic time scale of the spin dynamics, that is, the frequency widths of the quasielastic mode. However, these estimations were not completely accurate because they were based on the assumption of the intensity and susceptibility being identical. We have performed a full analysis of the NMR data without this assumption, by measuring the NMR relaxations of two different nuclei. Our rigorous analysis details the behavior of the intensity and frequency width of the quasielastic mode more precisely than in previous works and thus provides a conclusive insight into the low-frequency spin dynamics of HAFRs at low temperatures.

II. GENERAL FORMALISM

The NMR spin-lattice relaxation rate T_1^{-1}, reflecting low-frequency spin dynamics, is related to the imaginary part of the dynamic spin susceptibility through the fluctuation-dissipation theorem. For finite temperatures $k_{\mathrm{B}}T \gg \hbar\omega_n$, where ω_n is the NMR frequency, typically about 1 mK, the theorem gives

$$T_1^{-1} = \frac{2\gamma_n^2 k_{\mathrm{B}} T}{(\gamma_e \hbar)^2} \times \sum_q \left[|A_{\mathrm{od}}(q)|^2 \frac{\chi''_\parallel(q,\omega_n)}{\omega_n} + |A_\perp(q)|^2 \frac{\chi''_\perp(q,\omega_n)}{\omega_n} \right], \tag{1}$$

where $\chi''_{\parallel,\perp}$ are the imaginary parts of the dynamic spin susceptibilities parallel and perpendicular to the applied static uniform magnetic field, respectively.[5] Note that $\chi_{\parallel,\perp}$ indicates the susceptibilities under the applied magnetic field, different from those under zero magnetic field.[6] The coefficients $A_{\mathrm{od},\perp}(q)$ are the q (wavenumber)-dependent hyperfine form factors: $A_\perp(q)$ reflects the hyperfine tensor elements perpendicular to the applied field and $A_{\mathrm{od}}(q)$ reflects the off-diagonal elements of the hyperfine tensor between the parallel and perpendicular directions.

For simplicity, we consider a case where the q dependence of the hyperfine coupling can be neglected. In this case, introducing the q-summed susceptibility χ_{sum}, which describes the response to a spatially δ-functional magnetic field $[\Delta B(r) = \delta(r)]$, we can reduce Eq. (1) as follows by using the relation $\chi_{\mathrm{sum}}(\omega) = \sum_q \chi(q,\omega)$:

$$T_1^{-1} = \frac{2\gamma_n^2 k_{\mathrm{B}} T}{(\gamma_e \hbar)^2}\left[|A_{\mathrm{od}}|^2 \frac{\chi''_{\mathrm{sum}\parallel}(\omega_n)}{\omega_n} + |A_\perp|^2 \frac{\chi''_{\mathrm{sum}\perp}(\omega_n)}{\omega_n}\right]. \tag{2}$$

We consider now T_1^{-1} for HAFRs with an even number N of spins, described by the following spin Hamiltonian with periodic boundary conditions:

$$H = \sum_{a=1}^{N} J\, \mathbf{s}_a \cdot \mathbf{s}_{a+1} - g\mu_{\mathrm{B}} B S_z, \tag{3}$$

where $\mathbf{s}_a$ are spin operators of the ath magnetic ion in HAFRs, and $S_z = \sum_a s_{az}$ is the total spin component along an applied magnetic field B.

While bulk systems have dense states with continuous energy levels and thus continuous energy dissipation $\chi''_{\mathrm{sum}}(\omega)$, the most striking feature of ideal single-molecular nanomagnetic spin systems with no external interactions is that $\chi''_{\mathrm{sum}}(\omega)$ is composed of the sum of δ functions [see Fig. 1(a)] because the energy dissipation is caused by transitions between eigenstates with discrete energy levels. Thus, $\chi''_{\mathrm{sum}}(\omega)$ can become nonzero only when $\omega = (E_i - E_j)/\hbar$ is satisfied, where E_i and E_j are the energies of the ith and jth eigenstates ($|i\rangle$ and $|j\rangle$), respectively.

We note that, in Heisenberg spin systems (or, more generally, in systems where the total spin component along an applied magnetic field, S_z, is a good quantum number), the matrix elements $\langle i|s_{a\pm}|j\rangle$ $(i \neq j)$ can be nonzero between two eigenstates with $\Delta S_z = \pm 1$ and thus $\chi''_{\mathrm{sum}\perp}$ arises from the transitions with $\Delta S_z = \pm 1$. By contrast, the matrix elements $\langle i|s_{az}|j\rangle$ can be nonzero between two eigenstates with $\Delta S_z = 0$ and thus $\chi''_{\mathrm{sum}\parallel}$ results from the transitions with $\Delta S_z = 0$. It is important to note that some of these paired eigenstates with $\Delta S_z = 0$ have the same energies $(E_i = E_j)$ because of the high-symmetric structures of HAFRs. Transitions between these degenerate eigenstates cause the quasielastic mode at zero frequency in $\chi''_{\mathrm{sum}\parallel}$ (off-diagonal quasielastic mode), because $(E_i - E_j)/\hbar = 0$. As for the diagonal terms, whereas $s_{a\pm}$ always has zero diagonal matrix elements, s_{az} can have nonzero diagonal matrix elements; $\langle i|s_{az}|i\rangle$ can be nonzero. This also causes the quasielastic mode in $\chi''_{\mathrm{sum}\parallel}$ (diagonal quasielastic mode).[4,7]

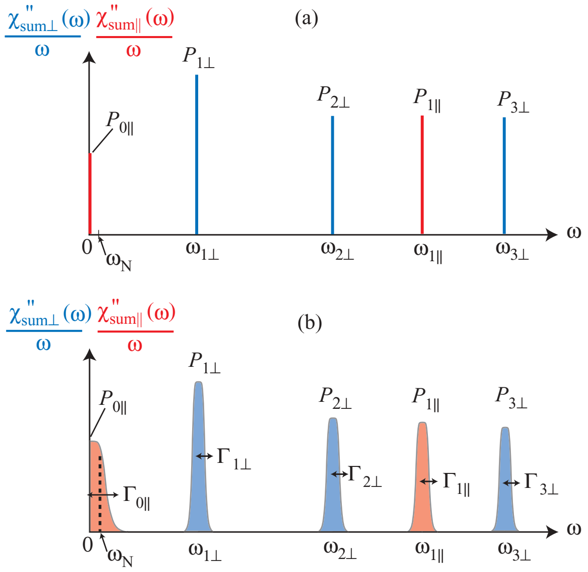

FIG. 1. (Color) Imaginary parts of the dynamic spin susceptibilities over ω at low temperatures for an HAFR under an applied static field. Blue and red indicate directions perpendicular and parallel to the applied field, respectively. (a) The case of an ideal HAFR with no external interactions; (b) the case of a real HAFR with finite lifetimes of its eigenstates. The values $P_\parallel$ and $P_\perp$ are the strengths of each mode, defined by the integrated areas in this graph. The values $\Gamma_\parallel$ and $\Gamma_\perp$ in (b) are the widths of each mode, defined by the half width at half maximum.

We can see from Fig. 1(a) that spin-lattice relaxation, which is proportional to $\chi''_{\mathrm{sum}}(\omega_n)/\omega_n$, does not occur in the ideal HAFR spin system. Thus, the actual spin-lattice relaxation observed in real HAFR systems is caused by broadening of the energy levels, as shown in Fig. 1(b). The finite lifetimes of the eigenstates due to external interactions give rise to uncertainty in their energies and result in broadening of the δ functions in $\chi''_{\mathrm{sum}}(\omega)$. This broadening is generally described by the Lorentzian function,[4,8] that is,

$$\frac{\chi''_{\mathrm{sum}\parallel}(\omega)}{\omega} = \frac{\Gamma_{0\parallel}}{{\Gamma_{0\parallel}}^2 + \omega^2}\frac{2P_{0\parallel}}{\pi} + \sum_{\alpha=1} \frac{\Gamma_{\alpha\parallel}}{{\Gamma_{\alpha\parallel}}^2 + (\omega - \omega_{\alpha\parallel})^2}\frac{P_{\alpha\parallel}}{\pi},$$

$$\frac{\chi''_{\mathrm{sum}\perp}(\omega)}{\omega} = \sum_{\alpha=1} \frac{\Gamma_{\alpha\perp}}{{\Gamma_{\alpha\perp}}^2 + (\omega - \omega_{\alpha\perp})^2}\frac{P_{\alpha\perp}}{\pi}, \tag{4}$$

where P and Γ are the strength and width of each mode, respectively.

Except around level-crossing fields where one of the $\omega_{\alpha\perp}$ values drops to zero, the low-energy dynamics in the NMR frequency at low temperatures includes contributions only from the quasielastic mode in $\chi''_{\mathrm{sum}\parallel}$. This is because $\omega_{\alpha\parallel}$ and $\omega_{\alpha\perp}$, or differences in the energy levels, are dominated by J and are typically of the order of a kelvin and thus are much larger than the NMR frequency, which corresponds to about 1 mK. Then, Eq. (2) can be written as

$$T_1^{-1} = \frac{4\gamma_n^2 k_{\mathrm{B}} T}{\pi(\gamma_e \hbar)^2}|A_{\mathrm{od}}|^2 \frac{\Gamma_{0\parallel}}{{\Gamma_{0\parallel}}^2 + \omega_n^2} P_{0\parallel}. \tag{5}$$

This form is the starting point for discussing the mechanism of T_1^{-1}. The remaining problem is to establish how $\Gamma_{0\parallel}$ and $P_{0\parallel}$ behave.

III. RELATION BETWEEN $P_{0\parallel}$ AND $\chi'(0,0)$

Equation (5) resembles the phenomenological model for HAFRs postulated by the Borsa group, where T_1^{-1} is proposed to be proportional to $\chi'(0,0)k_{\mathrm{B}}T\,\Gamma_{0\parallel}/({\Gamma_{0\parallel}}^2+\omega_n^2)$.[2–4] If it is assumed that $P_{0\parallel}$ is identical to the static uniform susceptibility $\chi'(0,0)$, our general form reduces to their phenomenological model. Here we show, however, that this assumption is not entirely true.

One way to consider the relation between $P_{0\parallel}$ and $\chi'(0,0)$ is to use the general Kramers-Kronig relation. The only thing that can be definitively determined from the Kramers-Kronig relation $[\int_0^\infty \chi''_{\mathrm{sum}\perp,\parallel}(\omega)/\omega\, d\omega \propto \chi'_{\mathrm{sum}\perp,\parallel}(0)]$ is that the summation of all the mode strengths ($\sum_\alpha P_{\alpha\perp,\parallel}$) is proportional to $\chi'_{\mathrm{sum}\perp,\parallel}(0)$, which is equal to the q-summed susceptibility $\sum_q \chi'_{\perp,\parallel}(q,0)$. Thus, the only trivial relation is $\sum_\alpha P_{\alpha\parallel} \propto \sum_q \chi'_\parallel(q,0)$. Hence, the relation between $P_{0\parallel}$ and $\chi'(0,0)$ cannot be simply derived from the general Kramers-Kronig relation, because the dynamic susceptibility of HAFRs has many modes at many frequencies and also has a q dependence.

Thus we need to consider the microscopic details in determining the relation between $P_{0\parallel}$ and $\chi'(0,0)$. One clue is the fact that, in a certain basis of the eigenstates, all the eigenstates of HAFRs under a magnetic field, $|i\rangle$, can be written as uniformly magnetized states ($\langle i|s_{az}|i\rangle = 1/N\langle i|S_z|i\rangle$). Under this basis of the eigenstates, the diagonal quasielastic mode is completely described by ferromagnetic fluctuations and thus the intensity of the diagonal quasielastic mode is identical to $\chi'(0,0)$, as discussed in Ref. 4. However, we must remember that degeneracy exists in the excited states of HAFRs because of their high symmetry. Thus $P_{0\parallel}$ is attributed not only to the diagonal mode but also to the off-diagonal mode due to transitions between the degenerate eigenstates ($E_i = E_j, i \neq j$). These transitions are related to nonzero-q fluctuations. Therefore, nonzero-q fluctuations also contribute to $P_{0\parallel}$, and as a result $P_{0\parallel}$ is not identical to $\chi'(0,0)$. The contributions from this off-diagonal quasielastic mode were not accounted for in the previous discussion in Ref. 4. (In other words, we can choose another basis of the eigenstates of HAFRs, where some of the excited states can be expressed as nonuniformly magnetized states, which are composed of the linear combinations of the uniformly magnetized eigenstates with the same energy in the original basis. Under this revised basis, the diagonal quasielastic mode directly contains nonzero-q fluctuations.)

IV. SCOPE OF PRESENT WORK

Although $P_{0\parallel}$ has to date been assumed to be identical to $\chi'(0,0)$, this assumption is not completely true, as explained in the previous section. Analyses in previous NMR studies[2–4] on HAFRs were based on this assumption. It is necessary to perform a full analysis of the NMR data of HAFRs without making this assumption.

We therefore explored experimentally how $\Gamma_{0\parallel}$ and $P_{0\parallel}$ behave, without making this assumption. To obtain these two unknown quantities, we need information on T_1^{-1} at two different frequencies, because a two-variable problem requires two simultaneous equations. One may think, at first glance, that this can be realized by measuring T_1^{-1} at two different magnetic fields, which give two different resonant frequencies. However, the spin dynamics, or $\chi''_{\mathrm{sum}}(\omega)$, is itself influenced by an applied field. Indeed, we will show that $P_{0\parallel}$ at low temperatures is dominated by the first excitation gap, which clearly has field dependence. Hence, we need to obtain information on T_1^{-1} at two different frequencies *under the same applied field*. We acquired this information by measuring NMR relaxations for two different nuclei. This rigorous analysis of the NMR data gives a more precise estimation of $\Gamma_{0\parallel}$ and $P_{0\parallel}$ than has previously been obtained.

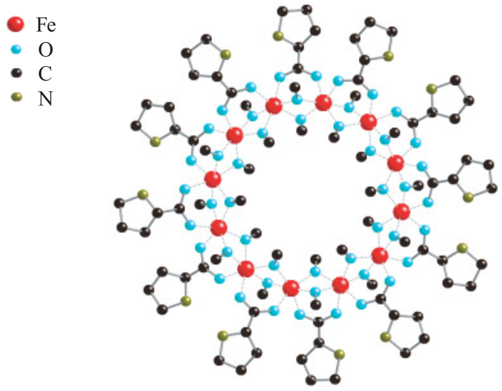

FIG. 2. (Color online) Structure of the wheel ring in Fe12, excluding H atoms. The ClO_4 anions, separating the rings, are not displayed here.

V. EXPERIMENT

As a subject material we choose $[Fe(OCH_3)_2(C_5H_9NO_2)]_{12}(ClO_4)_{12}$ (abbreviated as Fe12), which has an antiferromagnetic exchange interaction between $s = 5/2$ spins arranged in a wheel ring, as shown in Fig. 2.[9] The exchange interaction between neighboring $s = 5/2$ spins is an isotropic Heisenberg interaction with $J \sim 23$ K, leading to an $S = 0$ ground state.[9,10] We measured T_1^{-1} of ^{1}H and ^{13}C, giving information on two different frequencies. The measurements were performed under an applied field of 2.99 T for powder samples using the echo method. Since the natural abundance of ^{13}C is only 1.1%, it is difficult to measure T_1^{-1} of ^{13}C at high temperatures and thus we performed the measurements only below 50 K. The typical pulse widths were sufficiently smaller than the inverse of the spectral widths, and thus the pulses could cover the whole NMR spectra. The spin-lattice relaxation curves were obtained from the integrated spin-echo intensity after a time delay following saturation of the comb pulses. Because there are numerous nonequivalent ^{1}H and ^{13}C sites in the crystal and powder distribution, the relaxation curves were nonsingle exponential. We define T_1 as the initial slope of the relaxation curves. This value measures the weighted average of the relaxation rates of all the nuclei. In this case, the hyperfine coupling in Eq. (5) should also be treated as the weighted average value. Since there are numerous sites for both ^{1}H and ^{13}C, the q dependencies of the hyperfine couplings of ^{1}H and ^{13}C are averaged and consequently almost vanish. Thus, it is a good approximation that the q dependencies of the averaged hyperfine couplings can be neglected.

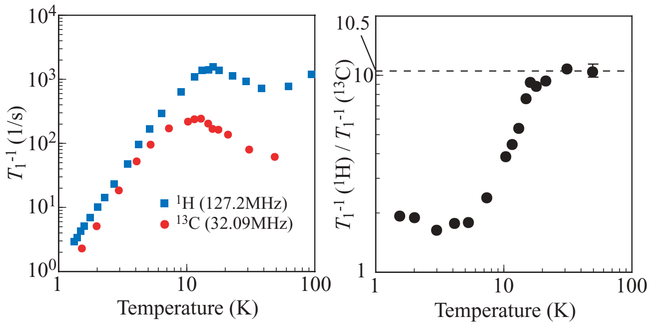

FIG. 3. (Color online) Left: Temperature dependence of ^{13}C and ^{1}H nuclear spin-lattice relaxation rates for Fe12. Right: Temperature dependence of their ratio.

VI. RESULTS AND DISCUSSION

The left panel of Fig. 3 shows the temperature dependence of T_1^{-1} of ^{1}H and ^{13}C. In order to evaluate $\Gamma_{0\parallel}$ by eliminating $P_{0\parallel}$ from these data, we plot the ratio, R, in the right panel of Fig. 3:

$$R = \frac{T_1^{-1}(^1\mathrm{H})}{T_1^{-1}(^{13}\mathrm{C})} = \left(\frac{\gamma_\mathrm{H}|\overline{A_{\mathrm{od\,H}}}|}{\gamma_\mathrm{C}|\overline{A_{\mathrm{od\,C}}}|}\right)^2 \frac{{\Gamma_{0\parallel}}^2 + \omega_\mathrm{C}^2}{{\Gamma_{0\parallel}}^2 + \omega_\mathrm{H}^2}, \qquad (6)$$

where ω_H (=127.2 MHz) and ω_C (=32.09 MHz) are the NMR frequencies of ^{1}H and ^{13}C under the present applied field 2.99 T, respectively. The value of $\Gamma_{0\parallel}$ is expected to increase with rising temperature, because excited phonons make the eigenstates unstable.[3,4,11] At sufficiently high temperatures, $\Gamma_{0\parallel}$ is expected to be much greater than ω_C and ω_H. Then, R asymptotically approaches a constant value $(\gamma_\mathrm{H}|\overline{A_{\mathrm{od\,H}}}|/\gamma_\mathrm{C}|\overline{A_{\mathrm{od\,C}}}|)^2$. Our experimental results indeed show that R takes a constant value of 10.5 ± 0.5 above about 30 K, i.e., $(\gamma_\mathrm{H}|\overline{A_{\mathrm{od\,H}}}|/\gamma_\mathrm{C}|\overline{A_{\mathrm{od\,C}}}|)^2 = 10.5 \pm 0.5$.

We observed a decrease in R below 20 K, which shows that $\Gamma_{0\parallel}$ decreases to the NMR frequency scale on cooling. We calculated the temperature dependence of $\Gamma_{0\parallel}$ using the observed R value and relation (6), as shown in Fig. 4, which exhibits a monotonic decrease in $\Gamma_{0\parallel}$. This monotonic decrease is consistent with the idea that $\Gamma_{0\parallel}$ is dominated by excited phonons via the spin-phonon interaction.[3,4,11] Importantly, however, our analysis also suggests that $\Gamma_{0\parallel}$ saturates to a nonzero value below 5 K. This saturation indicates that $\Gamma_{0\parallel}$ is dominated not only by excited phonons but also by an interaction that works even at zero temperature. The saturated value of $\Gamma_{0\parallel}$ at low temperatures is about 50 MHz, corresponding to about 2.5 mK. This value is of the same order as the inter-ring dipole interactions estimated from the inter-ring distance of about 8 Å. Therefore, we consider that they contribute to $\Gamma_{0\parallel}$ and cause the saturation in the low-temperature limit. Such interactions have been neglected so far only because they are much smaller than the main intra-ring exchange interaction. However, our analysis clearly reveals that such small interactions play an important role for the spin dynamics of HAFRs at low temperatures.

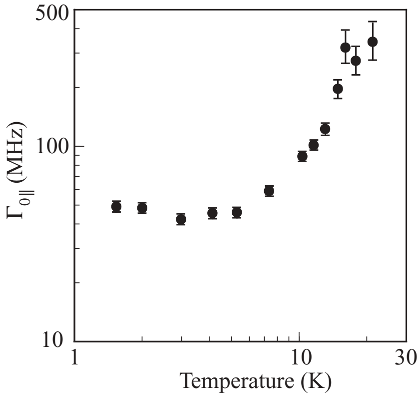

FIG. 4. Temperature dependence of $\Gamma_{0\parallel}$ derived from ^{13}C and ^{1}H nuclear spin-lattice relaxation rates.

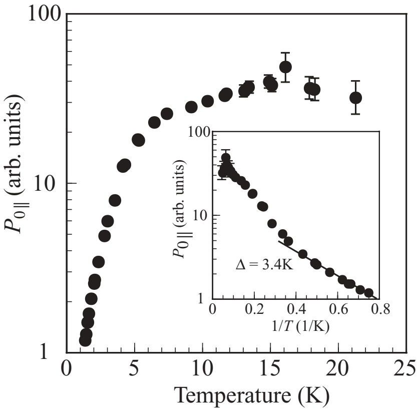

FIG. 5. Temperature dependence of $P_{0\parallel}$ derived from ^{13}C and ^{1}H nuclear spin-lattice relaxation rates. The inset shows the Arrhenius plot.

Lastly, we discuss the temperature dependence of $P_{0\parallel}$. Several studies have reported that in HAFRs, the temperature dependence of T_1^{-1} at low temperatures shows activation behavior, reflecting the first excitation gap.[10,12,13] Since T_1^{-1} in nanomagnets is dominated by the two parameters $P_{0\parallel}$ and $\Gamma_{0\parallel}$, it is an open issue which parameter causes the activation behavior. The temperature dependence of $P_{0\parallel}$ for the present system, shown in Fig. 5, is obtained from T_1^{-1} of ^{1}H and ^{13}C, by substituting previously solved values of $\Gamma_{0\parallel}$ into Eq. (5). As seen in the inset, $P_{0\parallel}$ shows an activation behavior with a gap of 3.4 K. This is considered to be the gap between the ground state with $(S,S_z) = (0,0)$ and the first excited state with $(S,S_z) = (1,-1)$. The present result gives a reason for the activation-type behavior in T_1^{-1}; namely, it is the intensity $P_{0\parallel}$ that gives rise to the activation-type temperature dependence, and not the frequency width $\Gamma_{0\parallel}$.

VII. CONCLUSION

In conclusion, we have considered a general theory which explains the low-energy spin dynamics, or the NMR spin-lattice relaxation, of HAFRs. The NMR relaxation is dominated by the quasielastic mode in $\chi''_{\mathrm{sum}\parallel}$, which is characterized by two physical parameters, intensity $P_{0\parallel}$ and frequency width $\Gamma_{0\parallel}$. The problem of understanding the NMR relaxation reduces to clarifying the behavior of these two parameters. Although $P_{0\parallel}$ has to date been believed to be identical to the uniform static susceptibility $\chi'(0,0)$, we have shown that $P_{0\parallel}$ and $\chi'(0,0)$ are different quantities. Excluding this assumption $P_{0\parallel} = \chi'(0,0)$, on which previous analyses were based, we have investigated experimentally the behavior of $P_{0\parallel}$ and $\Gamma_{0\parallel}$ for an actual HAFR, by measuring the NMR spin-lattice relaxation rates of two different nuclei. By this rigorous analysis, we clarified the behavior of these two quantities more precisely than previously achieved. The value $P_{0\parallel}$ is found to show activation behavior, reflecting the first excitation gap. We found that $\Gamma_{0\parallel}$ decreases monotonically on cooling, which is consistent with the previously proposed idea that $\Gamma_{0\parallel}$ is dominated by thermally excited phonons. Importantly, we also found that it saturates to a small but nonzero value in the low-temperature limit, indicating that small inter-ring dipole interactions, which have so far been neglected, play an important role in the spin dynamics. As our discussion does not make any nontrivial assumptions, our considerations and experimental clarification provide a conclusive insight into the NMR relaxation mechanism and low-frequency spin dynamics of HAFRs at low temperatures.

---

[*] tetsuaki@staff.mbox.media.kyoto-u.ac.jp

[†] Present Address: Mathematical and Natural Sciences, Faculty of Education, Niigata University, Niigata 950-2181, Japan.

[1] D. Gatteschi, R. Sessoli, and J. Villain, *Molecular Nanomagnets* (Oxford University Press, New York, 2006).

[2] F. Borsa, A. Lascialfari, and Y. Furukawa, in *Novel NMR and EPR Techniques*, edited by J. Dolinšek, M. Vilfan, and S. Žumer (Springer, Berlin, 2006), and references therein.

[3] S. H. Baek, M. Luban, A. Lascialfari, E. Micotti, Y. Furukawa, F. Borsa, J. van Slageren, and A. Cornia, Phys. Rev. B **70**, 134434 (2004).

[4] P. Santini, S. Carretta, E. Liviotti, G. Amoretti, P. Carretta, M. Filibian, A. Lascialfari, and E. Micotti, Phys. Rev. Lett. **94**, 077203 (2005).

[5] T. Moriya, J. Phys. Soc. Jpn. **18**, 516 (1963).

[6] Let us consider a spin system under an applied static uniform field. When an *additional* dynamical staggered field [$\Delta B_\parallel(q,\omega)$ or $\Delta B_\perp(q,\omega)$] parallel or perpendicular to this static uniform field is applied, an *additional* magnetization [$\Delta M_\parallel(q,\omega)$ or $\Delta M_\perp(q,\omega)$] is induced in the system. The dynamic susceptibilities are defined as $\chi_{\parallel,\perp}(q,\omega) = \Delta M_{\parallel,\perp}(q,\omega)/\Delta B_{\parallel,\perp}(q,\omega)$.

[7] A. Würger, J. Phys. Condens. Matter **10**, 10075 (1998).

[8] I. Rousochatzakis, Phys. Rev. B **76**, 214431 (2007).

[9] A. H. Abu-Nawwas, J. Cano, P. Christian, T. Mallah, G. Rajaraman, S. J. Teat, R. E. P. Winpenny, and Y. Yukawa, Chem. Commun. **(2004)** 314.

[10] S. Maegawa, T. Sagane, T. Itou, A. Oyamada, S. Igarashi, and Y. Yukawa, J. Magn. Magn. Mater. **310**, 1441 (2007).

[11] I. Rousochatzakis, A. Lauchli, F. Borsa, and M. Luban, Phys. Rev. B **79**, 064421 (2009).

[12] A. Lascialfari, Z. H. Jang, F. Borsa, D. Gatteschi, A. Cornia, D. Rovai, A. Caneschi, and P. Carretta, Phys. Rev. B **61**, 6839 (2000).

[13] S. Maegawa and Y. Sasaki, J. Phys. Soc. Jpn. **75**, 034710 (2006).