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Nuclear-spin relaxation in magnetic rings

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In magnetic rings of transition-metal ions, electron-spin correlations are found to exhibit rather unusual dynamical features, as a result of a subtle interplay between finite-size effects and magnetic interactions distinctly smaller than the dominant Heisenberg exchange Hamiltonian. These findings, mostly obtained by a mode-coupling approach, are shown to have important consequences on the nuclear-spin (proton) relaxation rates T_1^{-1} as measured in two specific rings, comprising six Cu or six Fe ions (respectively, ferromagnetic and antiferromagnetic). In both systems the magnetic-field and temperature dependence of the theoretical results is found to compare rather well with the experimental findings. [S0163-1829(98)04002-8]

I. INTRODUCTION

In recent years, much attention has been devoted to mesoscopic clusters of transition-metal ions and to their implications in fundamental physics.[1] In this respect, magnetic rings are particularly interesting because of their ‘‘bridge’’ character between low-dimensional bulk magnetism (e.g., magnetic chains) and zero-dimensional microscopic magnetism. On the experimental side, the rather unusual spin dynamics of these rings can be detected indirectly by taking advantage of the hyperfine interaction between the electronic spins of the ions and the nuclear spins (typically, ^{1}H) present in the compound. As a result, a measurement of the proton spin-lattice-relaxation rate T_1^{-1} by standard NMR techniques is expected to yield important pieces of information on the peculiar magnetic features of the rings.

In this work we address two quite different systems:

(i) an antiferromagnetic ring of six iron ions with a nonmagnetic ($S_{\rm tot}=0$) ground state: $[\mathrm{NaFe_6(OCH_3)_{12}(C_{17}H_{15}O_4)_6}]^+\cdot \mathrm{ClO_4^-}$ (hereafter referred to as Fe6),[2] and

(ii) a ferromagnetic ring of six copper ions with a magnetic ($S_{\rm tot}=3$) ground state: $[\mathrm{(PhSiO_2)_6Cu_6(O_2SiPh_6]\cdot 6EtOH}$ (hereafter referred to as Cu6).[3]

For Fe6, a qualitative account of the temperature dependence of T_1^{-1} has been reported elsewhere[4] on the basis of a very simplified scheme of the energy levels as deduced by exact calculations. The agreement was satisfactory in the low-temperature region, where it is essential to take into account the quantum character of the system. The goal of the present paper is to establish a sound theoretical interpretation of the data[4,5] for both Fe6 and Cu6 at intermediate and high temperatures. To be satisfactory, such a theory should explain a number of experimental findings, such as the observed dependence of the relaxation rate T_1^{-1} on the magnetic field at room temperature, and the different temperature dependence of T_1^{-1} in the two compounds as detected in the range 100–300 K.

The required theoretical framework comprises two basic steps. The first step, to establish the connection between the measured nuclear relaxation rate and the electron-spin time-dependent correlations, makes use of well-known perturbative results,[6] and is in principle straightforward. The second step, namely the spin dynamics of the magnetic ions, is much more demanding. We shall adopt a mode-coupling approach,[7–10] a self-consistent semiclassical method which in one-dimensional magnetic chains was shown to be reliable at all but the lowest temperatures.[11] Even for our systems, the dynamical events occurring at low temperatures (for example, at $T<100$ K) cannot be accounted for owing to the increasing role of quantum effects. However, this inherent limitation does not prevent the consideration of a number of peculiar effects, the most striking of which being related to the relatively small number of magnetic ions in the ring ($N=6$). In particular, irrespective of their range, the two-spin time correlation functions (CF's) are found to approach, as $t\to\infty$, a finite asymptotic value which depends only on N and on T.

The ultimate consequences of the above *plateau* on the nuclear-spin relaxation are found to be important, although not so dramatic as one would have anticipated. Indeed, to make a real contact with the magnetic rings probed in the experiments, we should allow for the additional presence of several ‘‘cutoff’’ mechanisms such as nonsecular intraring dipolar terms, inter-ring dipolar or exchange interactions, anisotropic terms in the spin Hamiltonian, etc.,[12–14] Although the magnitude of these extra contributions is considerably smaller than that of the dominant exchange interaction, they have the effect of restoring the ergodicity of the CF’s and to produce their final decay to zero. In practice, the effect of the additional interactions can be accounted for by assuming a long-time decay of the CF’s with a rate proportional to their intensity, which can be readily estimated.[15] At the very end, we find that the predicted relaxation rates in the two compounds agree rather well with the corresponding experimental findings, including the two particular sets of data mentioned above.

The paper is organized as follows. In Sec. II, after a brief account of the systems under investigation, we report the basic experimentals about the nuclear-spin relaxation measurements. Section III deals with the mode-coupling results for the two-spin time correlation functions at different temperatures for both Fe6 and Cu6. In Sec. IV we recall the basic results of relaxation theory, discuss how the peculiarities of the spin dynamics affect the relaxation rate, and finally compare the predictions with the experimental data. Some concluding remarks are made in Sec. V. Finally, the Appendix is devoted to a brief review of the mode-coupling framework as applied to magnetic rings.

II. EXPERIMENT

A detailed account of the structure of Fe6 has already been reported.[2] Here we briefly summarize the basic results important for our purposes. The six iron (III) ions are arranged in a nearly coplanar way at the vertices of an almost regular hexagon with an alkali metal ion in the center. Their magnetic properties are dominantly ruled by a nearest-neighbor antiferromagnetic exchange Hamiltonian

$$\mathcal{H}=-J\sum_{i=1}^{6}\mathbf{S}_i\cdot\mathbf{S}_{i+1}, \qquad (1)$$

where $\mathbf{S}_7=\mathbf{S}_1$ and $S_i=5/2$. The exchange integral J/k_B is estimated to be -28.6 K.[2] The ground state is a nonmagnetic singlet with total spin $S_{\mathrm{tot}}=0$ and the energies of the lowest-lying exchange multiplets obey a Landé’s interval rule.

Also the structure of Cu6 has been reported.[3] In this compound, the six copper (II) ions exhibit a distorted tetragonal pyramidal coordination and the symmetry of the metal array approximates the 6/*mmm* one. As a result of the geometry at the bridging siloxanolate oxygens, the Cu ions are ferromagnetically coupled with a Hamiltonian (1) where $J/k_B=60.4$ K and $S_i=1/2$. At low temperatures, the presence of spin-spin contributions causes a zero-field splitting of the ground $S_{\mathrm{tot}}=3$ spin state.[3]

The ^{1}H pulsed NMR experiments were performed by using a Stelar Spinmaster Broadband pulse Fourier transform spectrometer with an electromagnet able to work from ^{1}H NMR frequencies $\nu_n=7$ MHz to $\nu_n=60$ MHz. The temperature was varied between 4 and 295 K using an Oxford CF1200S flux cryostat. The spin-lattice relaxation time T_1 and the NMR spectra were obtained by using standard pulse sequences.[16] Further details on the experimental settings and the line shapes can be found in Ref. 4 (Fe6) and Ref. 5 (Cu6).

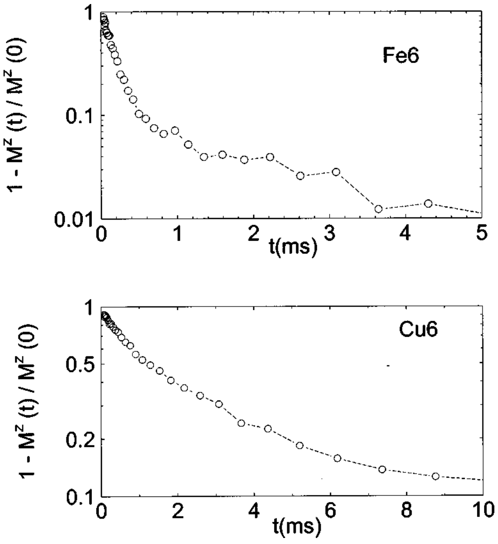

FIG. 1. Recovery curves of the nuclear magnetization $M^z(t)$ experimentally measured by the NMR technique at room temperature in the Fe6 and Cu6 clusters, respectively. The data (open circles) were taken at $\nu_n=14.1$ MHz. The dashed lines are guides to the eye.

In both Fe6 and Cu6, as a result of the multitude of nonequivalent protons (21 for Fe6 and 32 for Cu6), the recovery of the nuclear magnetization is found to deviate from a strict exponential behavior (see Fig. 1). The data can, however, be simply analyzed in terms of an average T_1 obtained from the tangent at the origin of the recovery plot of the nuclear magnetization. Proceeding in such a way, one finds the experimental data for the relaxation rate T_1^{-1} reported in Figs. 2 and 3 for Fe6 and Cu6 at different temperatures. After an initial nearly exponential increase of the relaxation rate at very low T, both compounds exhibit a maximum at a temperature independent of the magnetic field. The subsequent

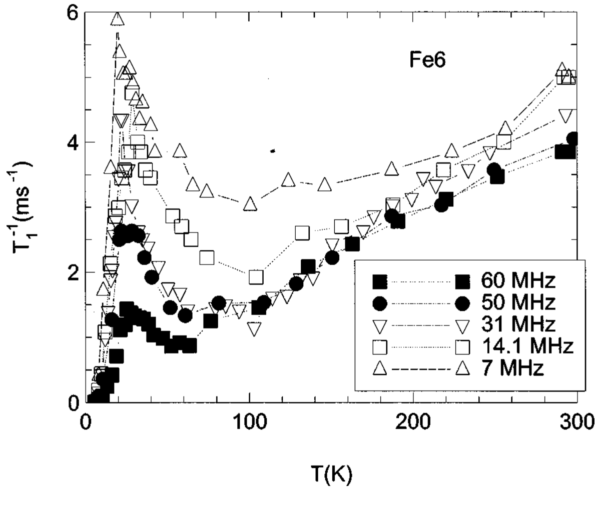

FIG. 2. Temperature dependence of the spin-lattice relaxation rate T_1^{-1} measured in the Fe6 cluster at selected values of the magnetic field, or NMR frequency $\nu_n=\gamma_n H_0$ (symbols). The lines are guides to the eye.

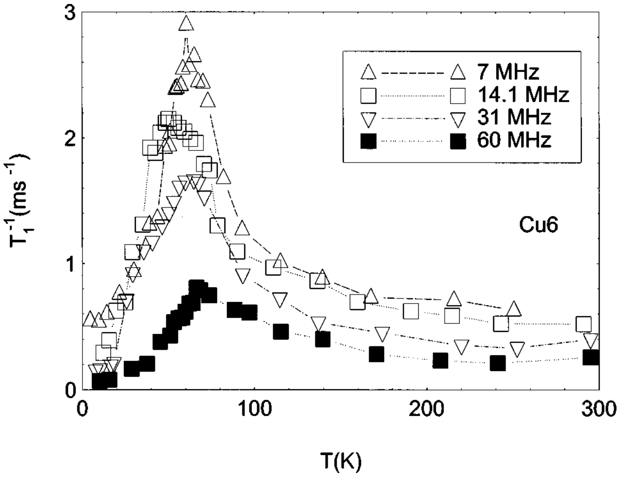

FIG. 3. The same as in Fig. 2, but for the Cu6 cluster.

behavior of T_1^{-1} in the range 100–300 K (the one explicitly addressed in this work) is different in the two compounds, being almost constant in Cu6 and linearly increasing with T in the Fe6 case. Finally, the field dependence of the relaxation rate at room temperature is reported in Fig. 4: in both systems, T_1^{-1} is found to decrease smoothly at increasing fields.

III. MODE-COUPLING RESULTS FOR THE SPIN-CORRELATION FUNCTIONS

Mode-coupling approaches are widely used for the dynamics of several condensed systems. Their self-consistent character makes them particularly attractive in magnetism, and in fact there are several applications of these techniques for the evaluation of time-dependent spin correlations in Heisenberg systems.[7–10] The numerical work involved in these calculations is usually rather heavy, but a considerable simplification occurs at temperatures such that $T > |J| S(S+1)$. In this range, whichever its dimensionality, the system is in a ''disordered'' phase and, owing to the isotropy of the spin CF's, one has to solve a single integrodifferential equation for both ferro- and antiferromagnets. In the cases of our interest, we assume to deal with such a ''high-temperature'' regime; details about the approach and the numerical procedure are reported in the Appendix.

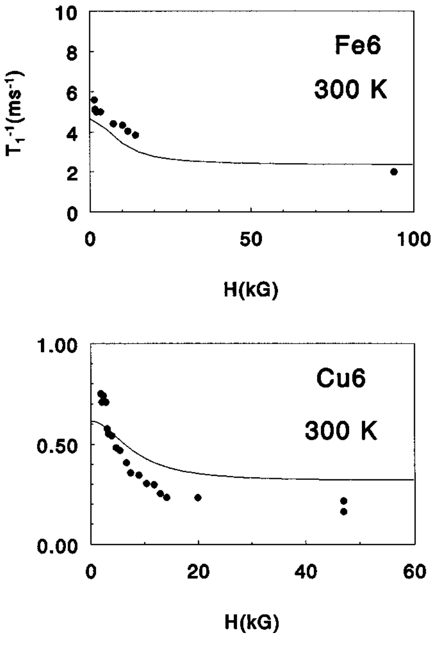

FIG. 4. Field dependence of the spin-lattice relaxation rate at room temperature for the Fe6 and Cu6 clusters, respectively. Symbols: experimental data. Full lines: theoretical results.

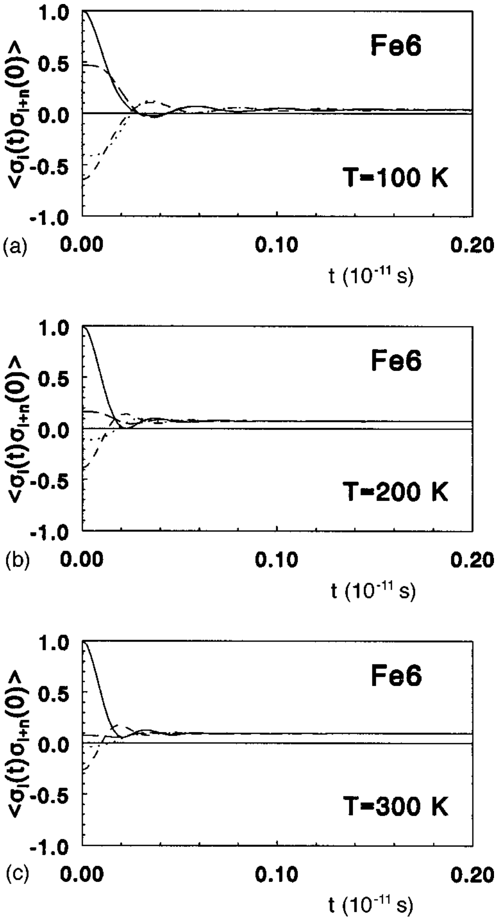

FIG. 5. Time-dependent two-spin-correlation function, as calculated in the framework of mode-coupling theory for antiferromagnetic Fe6 ($J = -28.6$ K) at three selected temperatures: 100, 200, and 300 K. Full, short-dashed, long-dashed, and dotted lines denote auto, first, second, and third neighbor correlations, respectively. The calculated asymptotic values for $k_N(T)$ are, respectively, (a) 0.039 at $T = 100$ K; (b) 0.075 at 200 K; (c) 0.096 at 300 K.

To begin with, we assume that both systems under investigation are dominantly ruled by the Hamiltonian (1). The results obtained for the two-spin time correlation functions are conveniently expressed in the following ''normalized'' form:

$$\langle \sigma_i(0)\sigma_{i+n}(t)\rangle = \frac{\langle S_i^\alpha(0) S_{i+n}^\alpha(t)\rangle}{\frac{1}{3}S(S+1)}, \tag{2}$$

where $\alpha = x,y,z$ owing to spatial isotropy and $n = 0,\cdots,N-1$ denotes the spatial range of the CF.

The calculated correlation functions are reported in Figs. 5 and 6 (referring to Fe6 and Cu6, respectively) at three selected temperatures (100, 200, and 300 K). In both sys-

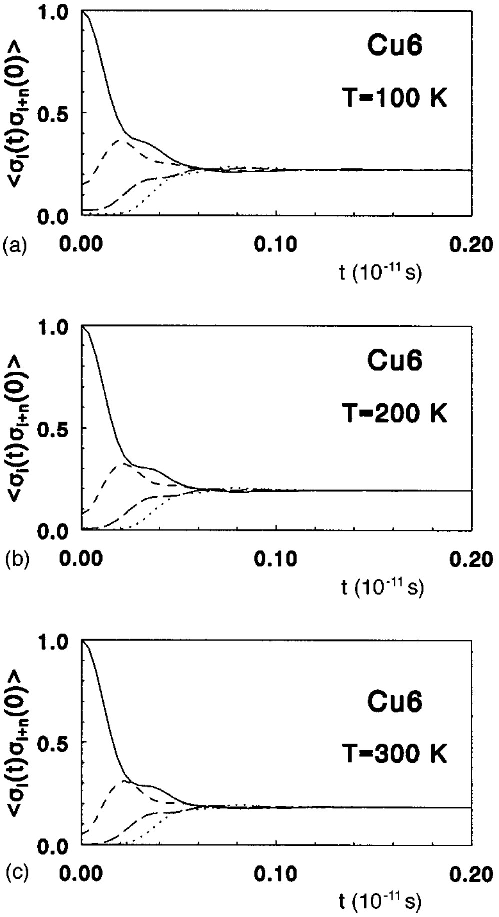

FIG. 6. The same as in Fig. 5, but for ferromagnetic Cu6 ($J=60.4$ K). The calculated asymptotic values for $k_N(T)$ are respectively: (a) 0.225 at $T=100$ K; (b) 0.194 at 200 K; (c) 0.184 at 300 K.

tems, after a fast initial decay, the CF's are seen to approach a finite asymptotic value $k_N(T)$

$$\lim_{t\to\infty}\langle\sigma_i(0)\sigma_{i+n}(t)\rangle=k_N(T),\qquad\forall n \tag{3}$$

independent of the ''spatial range'' index n, but dependent on the number N of spins in the ring and on the temperature T.

The rapid initial decrease of the autocorrelation function $\langle\sigma_i(0)\sigma_i(t)\rangle$ reflects a microscopic spin dynamics directly associated with the exchange constant $|J|$. If this decay were the full story, the time dependence of the CF's would be characterized[6,17] by a rate $\omega_{\mathrm{exch}}\simeq\sqrt{\frac{4}{3}S(S+1)}|J|/\hbar$, i.e., $\simeq 13\times10^{12}\mathrm{s}^{-1}$ for Fe6, and $\simeq 8\times10^{12}\mathrm{s}^{-1}$ for Cu6.

However, from Figs. 5 and 6 it is apparent that for times long enough that $\omega_{\mathrm{exch}}t\gg1$, the CF's approach a nonzero asymptotic limit. It is readily seen that this peculiar behavior is a consequence of the finite value of N, the number of magnetic ions. Indeed, in the absence of any external dissipative mechanism, after a sufficiently long time the initial ($t=0$) correlations tend to be equally distributed among the different spins of the ring. As a result, for $t\to\infty$, the CF's exhibit the same asymptotic behavior irrespective of their (finite) range n. The common limiting value is easily found in the $T\to\infty$ case, where all cross correlations vanish and $\langle\sigma_i(0)\sigma_{i+n}(0)\rangle=\delta_{n,0}$ for both the ferro- and antiferromagnetic case. Thus, at temperatures $T\gg|J|S(S+1)$ one finds

$$\lim_{t\to\infty}\frac{1}{N}\sum_{n=0}^{N-1}\langle\sigma_i(0)\sigma_{i+n}(t)\rangle=\frac{1}{N}\sum_{n=0}^{N-1}\langle\sigma_i(0)\sigma_{i+n}(0)\rangle=\frac{1}{N}$$
$$=k_N(T\to\infty). \tag{4}$$

The result (4) agrees with the one obtained in the theory of discrete random walk,[18] as expected, since the latter approach becomes appropriate at very high temperatures.

The attainment of a finite asymptotic value for finite rings should be contrasted with the corresponding long-time results obtained in an infinite magnetic chain. In the latter system, the CF's were found to exhibit a ''tail'' associated with the spin-diffusion constant $\mathcal{D}$. In particular, mode-coupling approaches predict[9] an asymptotic behavior of the form $\langle\sigma_i(0)\sigma_{i+n}(t\to\infty)\rangle=(1/\sqrt{4\pi\mathcal{D}t})e^{-(n^2/4\mathcal{D}t)}$, which was in fact revealed by NMR measurements in the quasi-one-dimensional antiferromagnet TMMC at room temperature.[19]

It is crucial to note that the temperature dependence of the asymptotic value $k_N(T)$ is ruled by the sign of J. Namely, whereas in the ferromagnetic ring $k_N(T)$ is found to decrease smoothly with increasing temperatures, in the antiferromagnetic case $k_N(T)$ exhibits a marked and approximately linear increase with T.

This different behavior can be understood by noting that at finite temperatures the CFs $\langle\sigma_i(0)\sigma_{i+n}(0)\rangle$ are positive whatever the ''spatial'' range n for the ferromagnet, while they alternate in sign as $(-1)^n$ for the antiferromagnet. Consequently, the asymptotic value $k_N(T)$ is expected to be larger or smaller than $1/N$ depending if we deal with a ferro- or an antiferromagnetic ring. For high temperatures, $T\gg|J|S(S+1)$, the CF's must approach the common asymptotic value $k_N(T\to\infty)=1/N$ irrespective of the sign of the exchange interaction.

In the following section we will show that this opposite behavior implies a quite different temperature dependence of T_1^{-1} in Fe6 and Cu6, as indeed observed experimentally.

IV. THEORY OF NUCLEAR-SPIN RELAXATION

Let us briefly summarize the basic steps by which one arrives at an expression of the relaxation rate T_1^{-1} in terms of the electron-spin CF's. In both compounds under investigation (Fe6, Cu6) NMR probes the protons present in the rings, characterized by a nuclear spin $I=1/2$. In the presence of a static magnetic field H_0, the combined system of nuclear and electron spins is ruled by an ''unperturbed'' Hamiltonian $\mathcal{H}_0=\mathcal{H}_n+\mathcal{H}_e$, where

$$\mathcal{H}_n=-\hbar\gamma_n\mathbf{I}\cdot\mathbf{H}_0, \tag{5a}$$

$$\mathcal{H}_e=-J\sum_{l<l'}\mathbf{S}_l\cdot\mathbf{S}_{l'}-\hbar\gamma_e\mathbf{H}_0\cdot\sum_l\mathbf{S}_l. \tag{5b}$$

In Eq. (5), γ_n and γ_e denote the proton and the electron gyromagnetic ratios, respectively. The approach of the nuclear system to thermal equilibrium is dominantly ruled by their interaction with the electronic spins $\mathbf{S}_j$. In our case, the hyperfine interaction $\mathcal{H}'$ has a dipolar origin:

$$\mathcal{H}'=\gamma_e\gamma_n\hbar^2\sum_j \frac{1}{r_j^3}\left[(\mathbf{I}\cdot\mathbf{S}_j)-3\frac{(\mathbf{I}\cdot\mathbf{r}_j)(\mathbf{S}_j\cdot\mathbf{r}_j)}{r_j^2}\right], \tag{6}$$

where r_j denotes the separation between the proton and the jth electronic spin. To see the effect of $\mathcal{H}'$, it is convenient to adopt an ''interaction picture'' in which the nuclear and the elctronic spins evolve in time with $\mathcal{H}_n$ and $\mathcal{H}_e$, respectively. As a result of the evolution of $\mathbf{S}_j$, the interaction $\mathcal{H}'$ acquires a time dependence which modifies the local magnetic field at the proton site, and is ultimately able to cause transitions between the nuclear-spin states. A perturbative calculation at leading order in $\mathcal{H}'$ yields the following result[6] for the transition probability at time t:

$$W_1(t)=\frac{1}{6}(\gamma_e\gamma_n\hbar)^2 S(S+1)\sum_{jj'}\frac{1}{(r_j r_j')^3}\left\{\alpha_{jj'}\int_{-t}^{t}dt'\cos(\omega_n t')\langle\sigma_j^z(0)\sigma_{j'}^z(t')\rangle + \frac{1}{4}\beta_{jj'}\int_{-t}^{t}dt'\cos(\omega_e t')[\langle\sigma_j^+(0)\sigma_{j'}^-(t')\rangle+\langle\sigma_j^-(0)\sigma_{j'}^+(t')\rangle]\right\}. \tag{7}$$

Equation (7) shows that the effects of the perturbation comprise both radial and angular contributions, with the latter depending on combinations $\alpha_{jj'}$, $\beta_{jj'}$ of direction cosines.[6] In a typical NMR experiment, for $H_0=10$ kG, the nuclear and electronic frequencies are $\omega_n\equiv\gamma_n H_0\simeq 10^8$ s^{-1} and $\omega_e\equiv\gamma_e H_0\simeq 10^{11}$ s^{-1}, respectively. On the other hand, the times t at which one looks at the effects of $\mathcal{H}'$ is of the order of some 10^{-4} s, i.e., a time scale where usually the electron-spin correlation functions have already decayed to zero. In such a case, one can safely let $t\rightarrow\infty$ in Eq. (7) and the transition probability $W_1(t)$ becomes a genuine relaxation rate T_1^{-1} proportional to the time Fourier transform of the electron-spin correlation functions.

In the case of finite rings, however, the presence of an asymptotic *plateau* makes the dynamics of the CF's appear quite unusual,[14,18] and the above statements of the conventional theory of relaxation need a critical examination. In fact, if the real evolution of the CF's at long times were the one illustrated in Figs. 5 and 6, one may even question the existence of a ''relaxation time,'' and the recovery of the nuclear magnetization would exhibit a highly nonexponential behavior. In practice, however, the model of magnetic rings adopted in Sec. III is somewhat idealized. Even if the exchange interaction, Eq. (1), is by far the dominant one, in a real ring one always deals with minor additional contributions which at sufficiently long times have the effect of modifying the ideal finite-size asymptotic behavior, and ultimately of causing the CF's to vanish. This ''cutoff'' effect is provided, in principle, by any magnetic interaction which, in contrast with $\mathcal{H}_e$, does not conserve the total spin components. In practice, such ''minor'' contributions stem from a variety of mechanisms, including intraring dipolar and anisotropic exchange interactions, single-ion anisotropies, interring dipolar or exchange interactions, etc.,[12–14]

In view of all this, it is important to ascertain which mechanism is relevant in the systems under investigation. In the case of Fe6, the compact hexagonal clustering of the magnetic ions in the ring enhances the importance of dipolar intraring interactions. On the basis of the Fe-Fe distances (at 298 K, $a_1=3.215$ Å, $a_2=5.563$ Å and $a_3=6.425$ Å for first, second, and third neighbors respectively[2]), it is possible to estimate the ''cutoff frequency'' ω_c such that the CF's exhibit a substantial decay from the *plateau* value at times $t\gg 1/\omega_c$. For the dipolar intraring mechanism relevant in Fe6 we find that

$$\omega_c\simeq\hbar(\gamma_e S)^2\left[\frac{2}{a_1^3}+\frac{2}{a_2^3}+\frac{1}{a_3^3}\right]=1.54\times10^{11}\mathrm{s}^{-1}. \tag{8}$$

On the other hand, in Cu6 there is evidence[3] for an anisotropic (exchange + dipolar) contribution to the interaction between nearest-neighbor spins:

$$\mathcal{H}_{\mathrm{anis}}=\sum_{i=1}^{6}\mathbf{S}_i\cdot\mathbf{D}_{i(i+1)}\cdot\mathbf{S}_{i+1}. \tag{9}$$

The elements of the tensor in Eq. (9) are estimated to be of the order of $D_{12}/k_B\simeq 1.44$ K,[20] so that in the case of Cu6 the ''cutoff frequency'' ω_c can be roughly estimated to be (with $S=1/2$):

$$\omega_c\simeq\frac{D_{12}}{\hbar}S(S+1)=1.41\times10^{11}\quad\mathrm{s}^{-1} \tag{10}$$

i.e., of the same order as in Fe6.

Thus, according to the different regimes it is convenient to split the integration limits in Eq. (7) into two intervals:

(i) a microscopic domain in which the CF's undergo a fast decay ruled by ω_{exch}, until at a time t_1 of the order of $10\omega_{\mathrm{exch}}^{-1}$ they attain the asymptotic value $k_N(T)$, and (ii) a long-time domain ($t\geqslant t_1$) in which owing to the above cutoff mechanisms, the CF's exhibit an exponential decay such that $\langle\sigma_j^\alpha(0)\sigma_{j'}^\alpha(t)\rangle\simeq k_N(T)e^{-\omega_c t}$. At times much longer than $t_c=1/\omega_c$ all the CF's have vanished, and we are justified in letting $t\rightarrow\infty$ in Eq. (7), and in identifying the transition probability $W_1(t\rightarrow\infty)$ with a relaxation rate T_1^{-1}.

Moreover, we may safely make additional—more trivial—simplifications by noting that in Eq. (7) the isotropic character of the spin CF's implies that $\langle\sigma_j^\pm(0)\sigma_{j'}^\mp(t)\rangle$

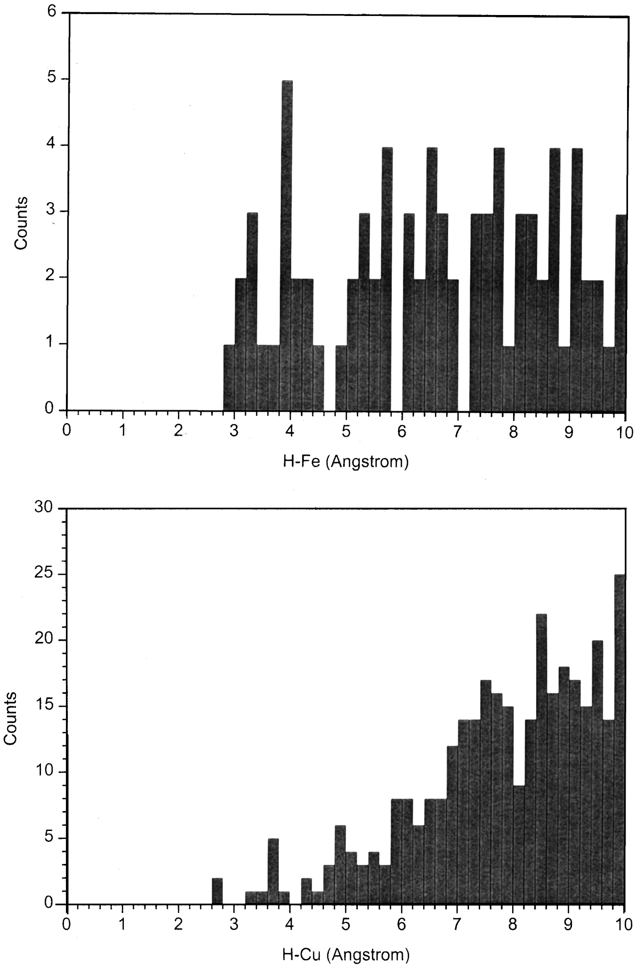

FIG. 7. Calculated distribution of the H-Fe and H-Cu distances for crystallographically independent protons in the crystal lattice of Fe6 and Cu6. Only distances shorter than 10 Å are shown.

$=2\langle\sigma_j^z(0)\sigma_{j'}^z(t)\rangle\equiv 2\langle\sigma_j(0)\sigma_{j'}(t)\rangle$. In addition, since the time range (up to $t\simeq$ some ω_c^{-1}) where the CF's are nonzero is such that $\omega_n t\ll 1$, we may safely set $\cos(\omega_n t)\simeq 1$ in the first term in curly brackets in Eq. (7). Finally, consistently with the treatment of experimental data, the considerable number of nonequivalent protons involved in a ring (21 in Fe6 and 32 in Cu6) justifies an averaging over the relevant separations between the nuclear and electron spins, as well as over the angular variables. Then, the magnitude of the relaxation rate is determined by a prefactor $C\simeq(1/6)(\gamma_e\gamma_n\hbar)^2 S(S+1)\langle f\rangle/\langle r\rangle^6$. The quantity f is a function of the direction cosines entering $\mathcal{H}'$; since it is of order unity and its directional change is not expected[6] to exceed a factor of 2, we set $\langle f\rangle=1$. As for the proton-Fe and proton-Cu distances, their distribution is shown in Fig. 7. The calculation was done on the basis of the known cluster geometry,[2,3] and was limited to $r<10$ Å. It is apparent that the mean proton-Cu distance is greater than the proton-Fe one. This fact, along with the smaller value of S in Cu6 with respect to Fe6, is responsible for the smaller value of T_1^{-1} observed in the former compound. To obtain the curves in Fig. 4, we set $\langle r\rangle=3.2$ Å for Fe6, and $\langle r\rangle=3.4$ Å for Cu6. In fact, owing to the sixth power of $\langle r\rangle$ in the denominator of C, only small distances are expected to contribute significantly in the distribution of Fig. 7.

As a result, Eq. (7) can eventually be rewritten as

$$\begin{aligned}T_1^{-1}\simeq{}& C\sum_{jj'}\int_0^\infty dt'[1+\cos(\omega_e t')]\langle\sigma_j(0)\sigma_{j'}(t')\rangle\\ ={}& C\Bigg\{\sum_{jj'}\int_0^{t_1} dt'[1+\cos(\omega_e t')]\langle\sigma_j(0)\sigma_{j'}(t')\rangle\\ &+N\int_{t_1}^\infty dt'[1+\cos(\omega_e t')]k_N(T)e^{-\omega_c t'}\Bigg\}\end{aligned}\tag{11}$$

It is worthwhile to recall that in the second term in braces, the factor N stems from the common decay rate of any CF in the finite ring for times $t'\gg\omega_{\mathrm{exch}}^{-1}$. In the last step of Eq. (11), the numerical value—hereafter referred to as $g(t_1)$—of the first integral is of the order of t_1 [in this time range, $\cos(\omega_e t')\simeq 1$]. Hence, the dependence of T_1^{-1} on the electronic Larmor frequency (namely, on the external magnetic field) is essentially due to the second term in brackets, i.e., to the one which depends both on the *plateau* value $k_N(T)$ and on the cutoff mechanisms ruled by the frequency $\omega_c\equiv 1/t_c$. Performing a trivial integration, we finally obtain that

$$\begin{aligned}T_1^{-1}={}&C\Bigg\{g(t_1)+Nk_N(T)t_c e^{-\omega_c t_1}\left[1+\frac{1}{1+(\omega_e t_c)^2}\right.\\ &\left.\times[\cos(\omega_e t_1)-(\omega_e t_c)\sin(\omega_e t_1)]\right]\Bigg\}.\end{aligned}\tag{12}$$

The relaxation rate as predicted by Eq. (12) is reported in Fig. 4 for Fe6 and Cu6. It is apparent that the magnitude and the dependence on the magnetic field entering both ω_n and ω_e is fairly well reproduced in the two compounds.

A further check of the theoretical approach is obtained by looking at the temperature dependence of T_1^{-1} predicted by Eq. (12) at constant field, and comparing with the experimental trend reported in Figs. 2 and 3 for the two compounds. Such a comparison is possible at all but the lowest temperatures, where both the shortcomings inherent to mode-coupling approximations and the discreteness of the spin multiplets become apparent. In contrast, in the intermediate and high T regime, the different temperature behavior observed in ferro- and antiferromagnetic rings can be readily understood in terms of Eq. (12). To begin with, at lower T the microscopic time t_1 which accounts for the initial decay of the CF's increases, but in Eq. (12) this has only a marginal effect on the contribution involving $g(t_1)$, which remains quite small anyway. In both systems, the leading contribution to the relaxation rate stems instead from the last integral in Eq. (11), namely from the second term in braces in Eq. (12). In the latter, the dominant temperature dependence is provided by the ''asymptotic'' value $k_N(T)$, which in the range 100–300 K is almost constant in Cu6 and shows a nearly linear increase with T in Fe6. Consequently the same trend is found even in the calculated relaxation rates of the two compounds, shown in Fig. 8, in fair agreement with the experimental data of Figs. 2 and 3.

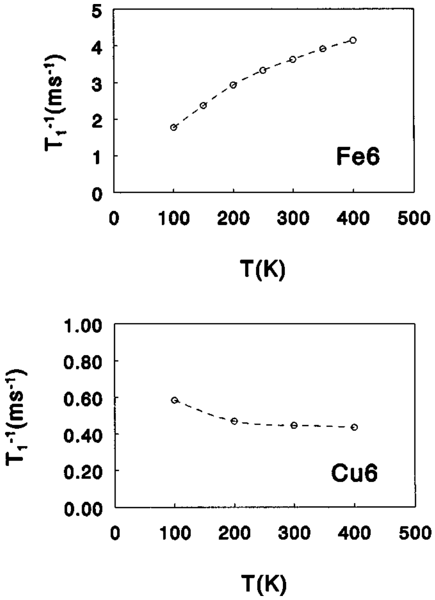

FIG. 8. Temperature dependence of the spin-lattice-relaxation rate at fixed field ($H_0 = 10$ kG) for Fe6 and Cu6, respectively. Open circles: result of numerical calculation. The dashed line is a guide to the eye.

V. CONCLUDING REMARKS

The main purpose of this work is a study of the rather unusual dynamics exhibited by two different finite-size magnetic ''rings,'' implemented with a comparison between the theoretical results and a number of experimental findings which probe this dynamics. The basic results of our investigation, which for the time being is restricted to intermediate and high temperatures, can be summarized as follows. Firstly, owing to the limited number of magnetic ions present in both systems, the spin time correlation functions, after a rapid initial decay, approach—irrespective of their spatial range—a finite temperature-dependent asymptotic value. Secondly, in the two investigated systems minor mechanisms (namely, considerably less important than the dominant exchange interaction) act apparently to restore a ''conventional'' long-time decay to zero of the spin correlations, and must duly be taken into account when comparing with the actual behavior of real magnetic rings. Even so, the peculiar behavior of the idealized model has still some important consequences. This is the case for the NMR relaxation rate of the ring protons, which effectively act as probes of the electron-spin dynamics. In this respect, we have shown that several features present in the experimental data (magnetic field and temperature dependence of the relaxation rates in both systems) can readily be accounted for only by a proper consideration of the unusual aspects of the underlying spin dynamics.

It is worthwhile noticing that the dipolar interactions responsible for the long-time decay of the correlation functions could, in principle, be included in the mode-coupling equations.[21] In such a way, these interactions would be treated on the same footing as the dominant exchange contributions, and there would be no need of introducing a phenomenological relaxation rate such as ω_c. Although undoubtedly more appealing, this more rigorous procedure meets, however, several technical difficulties, mostly connected with the knowledge of the static wave-vector-dependent susceptibilities of the finite system. In the presence of long-range magnetic dipole-dipole interactions, the transfer-matrix method is not very convenient, and one could rather consider the possibility to perform an exact diagonalization of the Hamiltonian in order to obtain temperature- and time-dependent correlations. This could be done for Cu6, since there are only $(2S+1)^N = 2^6$ states available to the copper spins, but for chains with higher values of N and S, the task would be formidable.

In this context, the phenomenological inclusion of the CF's long-time decay in our theory is essentially motivated by the exigence to treat a wide variety of magnetic rings without heavy numerical calculations, yet making the underlying physics clear enough.

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APPENDIX: MODE-COUPLING APPROACH TO TWO-SPIN TIME CORRELATION FUNCTIONS

As is well known, the microscopic dynamics of a magnetic system is usually described in terms of spin time-dependent correlation functions. In the case considered here, one deals with two-spin CF's of the form $\langle S_i^\alpha(0) S_j^\alpha(t) \rangle$, where the suffixes i and j denote two magnetic sites, and $\alpha = x,y,z$. In the particular case of our interest (a magnetic ring where i,j range from 1 to N), the above CF's can be written as $\langle S_i^\alpha(0) S_{i+n}^\alpha(t) \rangle$, where $n = 0,1,\ldots,N-1$, and with the cyclic condition $S_{i+N}^\alpha = S_i^\alpha$.

As is well known, mode-coupling techniques have been found a convenient approximate method to evaluate time-dependent correlation functions in several areas of condensed-matter physics. Originally developed to account for critical slowing down, this ''self-consistent'' framework has subsequently been applied to many other phenomena in which long-lasting events play an essential role. In the time domain, the typical outcome of a mode-coupling formulation is a set of nonlinear integrodifferential equations for the CF's of interest. When applied to magnetic problems, whichever the dimensionality of the system, mode-coupling approaches can, in principle, be used in both the ordered and disordered phases,[7–10] even if the possible presence of magnetic long-range order implies a much more laborious numerical work (three or six coupled integrodifferential equations, depending whether we deal with a ferro- or with an antiferromagnet). In contrast, in the disordered phase, the inherent isotropy of the spin CF's has the effect of leaving us with a single integrodifferential equation both in the ferro- and in antiferromagnetic case. In one-dimensional magnets, mode-coupling techniques have been shown to be accurate at all but the lowest temperatures.[11] When applied to disordered magnetic systems, beside accounting for any long-time ''tails,'' mode-coupling approaches have the further advantage that they happen to provide an approximate description even of the fast initial decay of the CF's, namely of the microscopic events directly associated to the exchange interaction.

The basic steps of the mode-coupling approach, as applied to the case of our interest, can be summarized as follows. Owing to isotropy, we may omit any reference to the Cartesian index α and introduce space Fourier transforms of the spin operators defined as

$$S_{\mathbf{q}}(t)=\frac{1}{N}\sum_{n=1}^{N} S_n(t)e^{iqan}, \tag{A1}$$

with $qa=2\pi m/N$ $(m=0,1,\cdots,N-1)$ owing to the periodic boundary conditions $(S_{N+1}=S_1)$ imposed by the geometry of the ring. Rather than dealing with the two-spin correlation function $\langle S_{-q}(0)S_q(t)\rangle$, it is convenient to consider the corresponding canonical Kubo's relaxation function[22] $(\beta=1/k_BT)$:

$$(S_{-q}(0),S_q(t))=\int_0^{\beta} d\lambda\langle e^{\lambda\mathcal{H}}S_{-q}(0)e^{-\lambda\mathcal{H}}S_q(t)\rangle \tag{A2}$$

along with its normalized version

$$F_q(t)=\frac{(S_{-q}(0),S_q(t))}{(S_{-q}(0),S_q(0))}, \tag{A3}$$

where $(S_{-q}(0),S_q(0))=\chi_q$ is the wave-vector-dependent static susceptibility. The frequency spectrum $\mathcal{S}(q,\omega)$ of $\langle S_{-q}(0)S_q(t)\rangle$ and the one of $F_q(t)$ are connected by the relation

$$\mathcal{S}(q,\omega)=\frac{\hbar\omega}{1-e^{-\beta\hbar\omega}}\,\chi_qF_q(\omega). \tag{A4}$$

It is easy to show that both $F_q(t)$ and $F_q(\omega)$ are even functions of their arguments. As shown by Mori,[23] in the isotropic phase $F_q(t)$ satisfies the following memory equation:

$$\frac{dF_q(t)}{dt}=-\int_0^t dt'K_q(t-t')F_q(t'). \tag{A5}$$

Here the memory function $K_q(t)=(f_{-q}(0),f_q(t))\chi_q^{-1}$ is defined in terms of a generalized "fluctuating force" $f_q(t)=e^{(1-P)Lt}(1-P)iLS_q(0)$, where $L=i[\mathcal{H},\cdots]$ is the Liouville operator of the system, and the projection operator P projects an arbitrary dynamical variable $A(t)=e^{iLt}A(0)$ over $S_q(0)$ according to

$$PA(t)=(S_{-q}(0),A(t))\chi_q^{-1}S_q(0). \tag{A6}$$

Although exact, Eq. (A5) is of limited use, unless some approximate expression is given for the memory function. Mode-coupling approaches do accomplish this task by means of a number of "reasonable arguments" which can be justified *a posteriori*. In practice, the mode-coupling approximation for $K_q(t)$ is obtained by the following recipes: (i) evaluate the quantity $iLS_q(0)=\dot{S}_q(0)$ appearing in $f_q(t)$; (ii) decouple the resulting four-spin term in $K_q(t)$ into products of two-spin contributions, at the same time ignoring the effects of the projection operator P. In this way one finally arrives at the following integrodifferential equation for the normalized relaxation function[8]

$$\frac{dF_q(t)}{dt}=-\frac{2}{\beta\chi_q}\sum_{q'}(J_{q'}-J_{q-q'})J_{q'}\chi_{q'}\chi_{q-q'}\times\int_0^t dt'F_{q'}(t-t')F_{q-q'}(t-t')F_q(t') \tag{A7}$$

with the initial condition $F_q(0)=1$ and where $J_{\mathbf{q}}=\Sigma_jJ_{ij}e^{i\mathbf{q}\cdot(\mathbf{r}_i-\mathbf{r}_j)}$. In the derivation of Eq. (A7), use has been made of the classical approximation of Eq. (A2), namely $(S_{-q}(0),S_q(t))\simeq\beta\langle S_{-q}(0)S_q(t)\rangle$. In our case of a one-dimensional system with a finite number N of spins and periodic boundary conditions, one has

$$J_q=2J\cos(qa), \tag{A8a}$$

$$\chi_q\simeq\beta\langle S_{-q}(0)S_q(0)\rangle=(2\beta/N)\sum_{n=1}^{N-1}[1-(n/N)]\cos(qan)\langle S_iS_{i+n}\rangle+(\beta/N)\times\langle S_is_i. \tag{A8b}$$

In the classical limit, the static correlation functions $\langle S_iS_{i+n}\rangle$ can be evaluated exactly by a transfer-matrix technique[24]

$$\langle S_i^zS_{i+n}^z\rangle=\frac{1}{Z_N}\sum_{l,m}\lambda_{lm}^n\sum_{l',m'}\lambda_{l'm'}^{N-n}[d_{lm,l'm'}]^2 \tag{A9}$$

where $Z_N=\Sigma_{l,m}\lambda_{lm}^N$ is the partition function and

$$d_{lm,l'm'}=\delta_{m,m'}\int_{-1}^{1}dxx\psi_{lm}^*(x)\psi_{l'm'}(x). \tag{A10}$$

Here, λ_{lm} and $\psi_{lm}(x)$ denote the eigenvalues and eigenvectors of the transfer integral equation[24]

$$2\pi\int_{-1}^{1}dx'e^{\beta Jxx'}I_m[\beta JS(S+1)\sqrt{(1-x^2)(1-x'^2)}]\psi_{lm}(x')=\lambda_{lm}\psi_{lm}(x), \tag{A11}$$

where $I_m(z)$ is the modified Bessel function of order m. An approximate analytic expression for calculating the static correlation functions of classical Heisenberg rings was recently suggested[25,26] by Luscombe *et al.*

Inserting Eqs. (A8b), (A9), and (A10) into the basic mode-coupling result Eq. (A7), it is finally possible to deduce the quantities $F_q(t)$, namely all the required time correlation functions. This has been done at selected values of temperature in the range $T>|J|S(S+1)$. More precisely, starting from the initial condition $F_q(t=0)=1$, we have solved Eq. (A7) by a standard step-by-step integration procedure. In terms of the dimensionless time $\tau=t/t_0$, where $t_0=\hbar/[|J|S(S+1)]^{1/2}$ is the "natural" time unit for the problem, numerical convenience and stability tests showed that the choice $\Delta\tau=0.01$ was satisfactory in all respects.

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