Unconventional Nonequilibrium Dynamics in Ni_{10} Magnetic Molecules: Evidence from NMR

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Crystals containing Ni_{10} magnetic molecules display an unprecedented form of out-of-equilibrium behavior of the bulk magnetization M at temperatures as high as 17 K. We have performed ^1H NMR measurements to probe the local Ni magnetic moments and their dynamics. It is apparent that no freezing of the Ni moments occurs, in striking contrast to what is observed in blocked superparamagnetic systems. The average local moments display the same behavior as M, thus unambiguously demonstrating the intrinsic character of the phenomenon. This result supports the hypothesis that the slowing down of M is due to a resonant phonon trapping mechanism which prevents the thermalization of M but not the fast spin flippings of the individual molecular moments. Indeed, the measured nuclear spin-lattice relaxation rate points to fast single-molecule dynamics at low temperature.

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Understanding relaxation mechanisms of the magnetization (M) in crystals containing magnetic ions or molecules is of paramount importance in fundamental physics and for the envisaged applications of magnetic molecules as classical or quantum bits. A class of materials showing slow relaxation of M is formed by single-molecule magnets (SMMs) [1], for which the nonequilibrium behavior is due to the presence of an energy barrier associated with uniaxial anisotropy. This leads to a blocking of M at temperatures which may reach a few degrees Kelvin. Spin-phonon interactions provide the relevant mechanism for relaxation of M, with phonons behaving as a heat bath. Indeed, phonon bottleneck effects are relevant only at a very low temperature, i.e., $T \leq 1$ K. It should be stressed that in crystals of SMMs the dynamics is blocked on all length scales, from the bulk magnetization M down to the magnetic moment of each individual molecule. This implies that local probes such as nuclear magnetic resonance (NMR), Mossbauer, or μSR detect sizable static fields on the target site. This property characterizes other well-known systems displaying slow magnetic dynamics such as blocked nanoparticles, spin glasses, or ferromagnetic domains.

It has recently been discovered that a growing family of molecular crystals containing noninteracting magnetic Ni_{10} [2–4] and Co_{10} [5] molecules is characterized by slow relaxation of M at temperatures as high as 17 K. Ni_{10} and Co_{10} are not conventional SMMs, since in the lack of an anisotropy barrier the slow relaxation cannot be explained in the framework of phonon-assisted relaxation. It has been proposed that the peculiar dense spectrum of magnetic low-energy excitations in Ni_{10} creates the conditions for an unprecedented form of resonant phonon trapping resulting in a breakdown of the heat-bath assumption for phonons [3,6]. Within this framework, a slow relaxation of macroscopic observables occurs in the presence of fast single-molecule dynamics, differently from blocked superparamagnets or spin glasses.

The purpose of this Letter is the investigation by ^1H NMR of the local spin dynamics in Ni_{10} in the temperature (T) and magnetic field (H) range where slow relaxation of M occurs. The analysis of NMR spectra and of the nuclear spin-lattice relaxation time confirms the intrinsic character of the out-of-equilibrium behavior and shows that no freezing of local moments takes place, as expected from the proposed mechanism.

In the Ni_{10} family of compounds, the magnetic core consists of 10 Ni^{2+} ions arranged on a supertetrahedron [see Fig. 1(b)]. The cores are well separated and embedded in crystalline-ordered molecular structures, where the molecular and crystal symmetries are dictated by the specific organic ligands used [2–4]. Magnetic [3] and neutron-scattering [7] measurements demonstrate the presence of a hierarchy of values for the exchange constants within each molecule. Indeed, the six Ni ions bisecting the edges of the supertetrahedron [gray spheres in Fig. 1(b)] can be divided into three pairs, each pair being connected by a linear Ni-O-Ni superexchange bridge passing through the

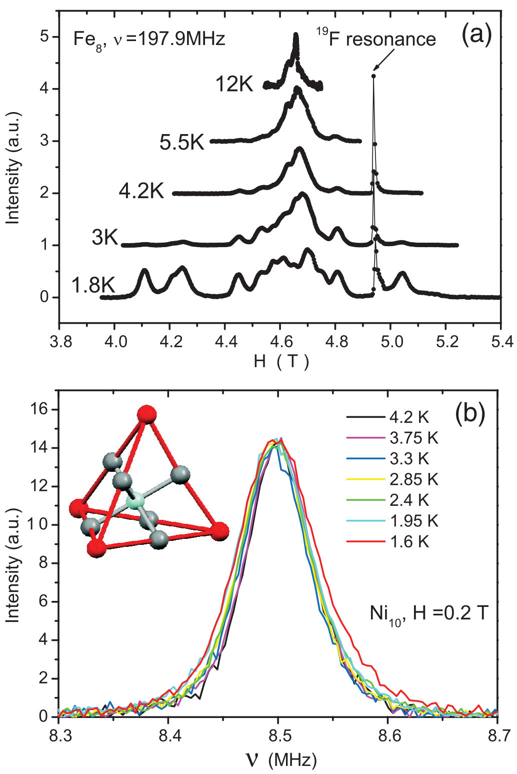

FIG. 1 (color). (a) Temperature evolution of the proton NMR spectra in Fe$_8$ obtained by sweeping the field at constant frequency $\nu = 197.9$ MHz. The huge broadening of the spectra and their structuring reflect the blocking of the molecular magnetization and can be approximately reproduced by considering the nuclear-electron dipolar interaction [9]. This broadening is not due to a trivial field-induced paramagnetic shift but to the local static fields associated with the blocked state of Fe$_8$. Indeed, a similar degree of broadening occurs in zero external field [9]. (b) Temperature evolution of the proton NMR in Ni$_{10}$ obtained by sweeping the frequency at constant field. To compare the two figures, one can use Larmor's relation for ^{1}H: $\nu = 42.57$ MHz/T. Hence, the maximum broadening in (b) (95 kHz for $T = 1.6$ K) corresponds to about 0.002 T, 3 orders of magnitudes smaller than the maximum broadening in (a). Note that in Ni$_{10}$ we have investigated a broad frequency window (about 2.5 MHz), finding no additional signal. Hence, the whole absorption takes place in the narrow frequency range of panel (b). Inset: Magnetic core of [Ni$_{10}$(O)(thme)$_4$(dbm)$_4$(O$_2$CPh)$_2$(EtOH)$_6$] (red and gray: Ni; cyan: O). More than 20 variants having different ligands exist. Only the spin degrees of freedom of the four external Ni ions (red spheres) are relevant at low T.

central oxygen ion [cyan sphere in Fig. 1(b)]. This leads to a strong antiferromagnetic (AF) interaction of about 15 meV within each pair, while other superexchange interactions are much weaker, of the order of 1 meV. Hence, at low T the spins of the six central Ni ions are nearly frozen in a singlet state, and each molecule behaves as a tetrahedron of weakly coupled spins associated with the four external Ni ions. Overall magnetic anisotropy is rather large but nearly tetrahedral, with no associated energy barrier for the reversal of M.

The resulting 81 low-energy levels span the energy window below about 1 meV and cause a continuous phonon absorbance for $E \lesssim 1$ meV. In the proposal of Ref. [3], low-E phonons experience trapping within the crystal and do not act as a heat bath anymore. A slow and many-time-scales nonequilibrium dynamics results for the statistical distribution of the joint spin-phonon system, while the expected equilibrium behavior is progressively recovered as the applied field strength increases [3]. In this proposal, each molecule undergoes frequent phonon emission and absorption processes; thus, local fluctuations remain *ample* and *fast* in spite of statistical populations (and hence bulk observables) being slow.

If the proposed resonant phonon trapping mechanism is correct, one expects to observe no freezing of the local magnetic moments μ_i of individual molecules, as observed instead in traditional SMMs with anisotropy barrier [8]. ^{1}H NMR experiments provide a unique tool to probe the local spin dynamics via measurements of the proton line width and of the nuclear spin-lattice relaxation time T_1. The linewidth reflects the values at target nuclei of hyperfine fields produced by nearby electronic moments. If these freeze, a large broadening or even a structuring of the nuclear ^{1}H absorption line occurs. T_1 provides information on the time scales characterizing temporal fluctuations of these local hyperfine fields, which in turn reflect fluctuations of the magnetic moment μ of the molecule to which the nucleus belongs. Hence, NMR T_1 measurements are complementary to bulk measurements (e.g., ac susceptibility) in two ways: On the one hand, single-molecule (instead of total) fluctuations of the magnetization are sensed. On the other hand, the probed time scales are much shorter and of the order of dozens of nanoseconds.

We have performed ^{1}H NMR measurements in a polycrystalline Ni$_{10}$ sample with a Fourier transform (FT) pulse spectrometer. Since the magnetic response of Ni$_{10}$ is nearly isotropic and since there are many inequivalent protons in each molecule, NMR spectra for polycrystalline and single crystal samples are the same. For linewidths below 150 kHz, the spectrum was acquired by FT of half of the echo after a standard Hahn echo pulse sequence with a $\pi/2$ pulse length of 3 μs. The temperature evolution of the ^{1}H NMR spectrum for Ni$_{10}$ is compared in Fig. 1 with that of Fe$_8$, which is a prototype SMM [1,9]. For Fe$_8$, the broadening of the line and the appearance of a very wide structure in the spectrum are a direct signature for freezing of the local moments μ_i, which causes the blocking of M [8,9]. On the contrary, in Ni$_{10}$ no sizable broadening occurs in the T and H range in which blocking of M is observed in magnetization measurements ($T \lesssim 8$ K for $H = 0.1$ T and $T \lesssim 5$ K for $H = 0.2$ T; see Fig. 2). This lack of broadening and structuring of the line also rules out that the blocking of M arises from the onset of magnetically ordered or spin-glass phases, which would imply sizable static local moments well below the transition temperature. These mechanisms were already considered to be extremely unlikely given the structural and magnetic properties of the Ni_{10} family [3,4] and are definitely ruled out by the present results.

The proton linewidth results from the combination of an H- and T-independent contribution due to nucleus-nucleus dipolar interactions and a contribution associated with the dipolar hyperfine coupling of the different protons with the neighboring local magnetic moments at the Ni^{2+} sites, typically belonging to the same molecule (the minimum Ni-H distance is on average several Angstroms; hence, contact hyperfine terms are negligible). This produces a proton-site-dependent shift of the Larmor frequency. In the usual Gaussian approximation for the line shape, the linewidth is proportional to the square root of the second moment, which in turn is given by the sum of the second moments due to the two interactions described above:

$$\Delta\nu_{\mathrm{tot}}^2 = \Delta\nu_d^2 + \Delta\nu_m^2, \tag{1}$$

where $\Delta\nu_d^2$ is the intrinsic second moment due to nuclear dipolar interactions and $\Delta\nu_m^2$ is the second moment of the local frequency-shift distribution (due to nearby electronic moments) at the different proton sites of all molecules. $\Delta\nu_d^2$ can be determined by calculating the statistical distribution of nuclear dipolar fields on ^{1}H nuclei produced by other ^{1}H nuclei. By using the x-ray determined positions of ^{1}H atoms [2], we obtain $\Delta\nu_d = (\Delta\nu_d^2)^{1/2} \approxeq 16$ kHz. Thus, the electronic contribution can be directly extracted from the measured linewidths (Fig. 2). The link between $\Delta\nu_m^2$ and the local Ni moments is given by

$$\Delta\nu_m^2 = \sum_R \sum_{i\in R} (\langle \nu_{R,i} - \nu_0 \rangle_{\Delta t})^2 / N, \tag{2a}$$

where R labels different molecules, $\nu_0 = \gamma H$ is the bare Larmor frequency, N is the number of probed protons, and $\nu_{R,i}$ is the resonance frequency of the ith protons of molecule R. The difference between the two resonance frequencies represents the shift for nucleus i due to the local field generated by the nearby moments j:

$$\sum_{i\in R} (\langle \nu_{R,i} - \nu_0 \rangle_{\Delta t})^2 \simeq \gamma^2 \sum_{i\in R} \Bigg[\sum_{j\in R} \frac{A(\theta_{i,j})}{r_{i,j}^3} \langle m_{z,j} \rangle_{\Delta t} \Bigg]^2. \tag{2b}$$

Here j spans the four external Ni ions within molecule R (the six core Ni ions are nearly nonmagnetic; see above), $A(\theta_{i,j})$ is the angular-dependent dipolar coupling constant between nucleus i and moment j, and $r_{i,j}$ the corresponding distance. $\langle m_{z,j} \rangle_{\Delta t}$ is the component of the Ni moment j in the direction of the applied field (z), averaged over the NMR data acquisition time scale (of the order of 10 μs). Because of anisotropy, even if the field is along z, $\langle m_{x,j} \rangle_{\Delta t}$ and $\langle m_{y,j} \rangle_{\Delta t}$ do not vanish in general and might contribute. However, for Ni_{10} the off-diagonal magnetic response is significantly smaller than the diagonal one, and therefore x-y contributions can be neglected in (2b).

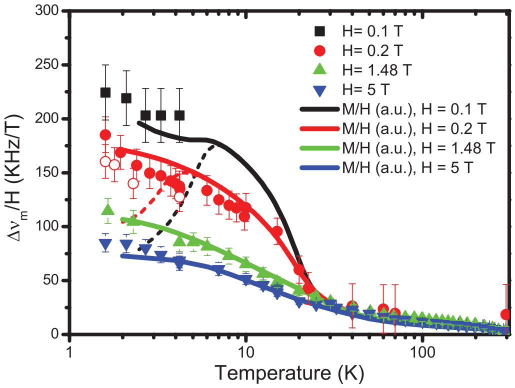

FIG. 2 (color online). Comparison between the temperature dependence of $\Delta\nu_m/H$ [from Eq. (1)] and the macroscopic susceptibility obtained with SQUID. The latter has been rescaled by a common factor so as to match NMR data in the high temperature range. Open and closed circles at 0.2 T refer to ZFC and FC measurements, respectively. The large nonlinearity of M and $\Delta\nu_m$ with respect to H is a signature of nonequilibrium behavior.

Both field-cooled (FC) and zero-field-cooled (ZFC) measurements were performed. The strong preparation dependence observed in M has not been found in NMR linewidths. Only for $H = 0.2$ T, ZFC widths are slightly smaller than FC ones for low T, in the range where the bulk magnetization shows a strong preparation dependence (see Fig. 2). As it is evident in Fig. 2, the behavior of $\Delta\nu_m = (\Delta\nu_m^2)^{1/2}$ measured with the FC protocol closely recalls that of the bulk magnetization M measured on the same sample, and, in particular, it displays the same large and highly unusual nonlinearity with respect to H. In typical slowly relaxing systems such as molecular nanomagnets, blocked superparamagnetic particles, or spin glasses, for small H, $\Delta\nu_m$ and M do not behave in the same way as local moments are frozen and randomly oriented for times much longer than the intrinsic NMR time scale. The fact that here $\Delta\nu_m$ and M behave in the same way implies that the following three conditions are simultaneously satisfied for the FC protocol. (i) The dependence of $\langle m_{z,j} \rangle_{\Delta t}$ on j is weak and can be neglected in (2b). In this case $\langle m_{z,j} \rangle_{\Delta t} \simeq \frac{1}{4} \langle \mu_{z,R} \rangle_{\Delta t}$, $\mu_{z,R}$ being the total magnetic moment of the molecule at site R. This is reasonable in view of the lack of a privileged axis for magnetic anisotropy. (ii) The average molecular magnetization over Δt is nearly homogeneous; i.e., $\langle \mu_{z,R} \rangle_{\Delta t}$ is weakly dependent on R, and therefore $N_A \langle \mu_{z,R} \rangle_{\Delta t}$ practically coincides with the bulk magnetization M, N_A being the number of Avogadro. If both (i) and (ii) hold, then (2a) can be written as

$$\Delta\nu_m^2 = \gamma^2 \sum_R [\langle \mu_z \rangle_{\Delta t}]^2 A/N = BM^2, \tag{3}$$

where A and B are positive coefficients. It is evident that (i) and (ii) have to be supplemented by (iii): Bulk magnetization and NMR linewidths are determined by the same set of electronic moments. This directly and definitely rules out an impurity origin of the observed nonequilibrium behavior, which had already been shown to be very unlikely on the basis of indirect lines of reasoning [4].

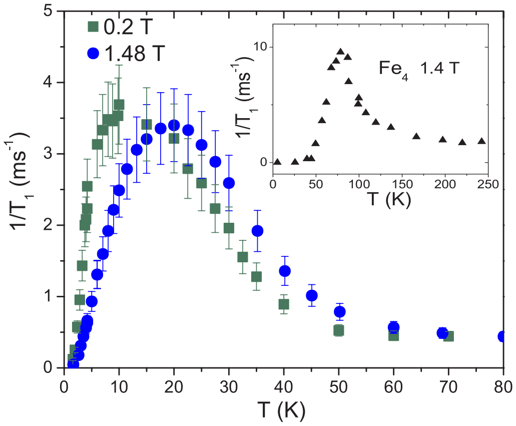

FIG. 3 (color online). Temperature dependence of the nuclear spin-lattice relaxation rate in Ni_{10}. Inset: The same quantity for Fe_4, a prototypical SMM which blocks around 1 K, much below the temperature at which $1/T_1$ peaks [13].

The situation is different for the ZFC protocol as in the T and H range where M shows preparation dependence; the behavior of linewidths measured with the ZFC protocol does not match that of M. Indeed, measured ZFC linewidths are only slightly smaller than FC ones, whereas M is much smaller (see Fig. 2). A likely explanation for this mismatch between global (M) and local (NMR linewidths) probes of molecular moments is that the latter are not uniformly distributed over space; i.e., condition (ii) is not satisfied: Since proton linewidths sense the modulus of the nearby molecular moment $\langle \mu_{z,R} \rangle_{\Delta t}$, it is clear that, if the latter depends on R, the two techniques probe different quantities. This can easily be understood by the simple example of a paramagnet containing inequivalent noninteracting magnetic units. $M(T, H)$ follows a sum of Brillouin laws, but its value ($\sum_i M_i$, with M_i the total moment associated with the ith species of unit) does not track that of the NMR linewidth [roughly proportional to $(\sum_i M_i^2)^{1/2}$]: Only for M_i independent of i does the latter expression track M. Thus, inhomogeneity (in the modulus or the direction of the moments) is a straightforward source of mismatch between M and the linewidth, and we propose it as a plausible explanation of the ZFC data. We have no clear physical picture of this since the model developed in Ref. [3] describes spectral diffusion on average but does not contain spatial information. Including this is an extremely hard task which in light of the present results will deserve further efforts.

In summary, NMR linewidths demonstrate that the nonequilibrium behavior of Ni_{10} is intrinsic and that it cannot be ascribed to common mechanisms responsible for slow magnetic dynamics; i.e., Ni_{10} is neither a nanomagnet nor a spin glass nor a ferromagnet. On the other hand, the present results are compatible with the proposal of Ref. [3]. A peculiar aspect of this proposal is that the macroscopically slow nonequilibrium phase is characterized by fast microscopic single-molecule dynamics, driven by the continuous exchange of phonons with nearby molecules. Besides the lack of structuring of the proton NMR spectrum (Fig. 1), the nuclear spin-lattice relaxation rate $1/T_1$ provides additional evidence that the fluctuation frequency of the molecular magnetization remains fast at low T. In fact, in SMMs, $1/T_1$ peaks when the barrier-climbing Arrhenius process, which becomes very slow at the blocking temperature, reaches a rate matching the Larmor frequency of the target nucleus (42.57 MHz/Tesla). Typically, this occurs at high T (many dozens of degrees Kelvin; see the inset in Fig. 3). Hence, T must be decreased by 50–100 K to make the Arrhenius relaxation rate reduce from the hundreds of megahertz range to the hertz one, where blocking occurs. In Ni_{10}, $1/T_1$ peaks at much smaller temperatures (Fig. 3), much like in fast-dynamics molecules such as AF rings [10,11]. As a consequence, attempts to interpret $1/T_1$ curves in Ni_{10} by a SMM model would inevitably lead to unphysical parameters (e.g., barrier height or spin-phonon coupling constant) [12].

In conclusion, we have performed proton NMR measurements in Ni_{10} as a function of temperature and magnetic field. The results demonstrate that the blocking of M is not associated with freezing of the Ni moments, in striking contrast to what is observed in conventional slowly relaxing systems such as blocked superparamagnets, single-molecule magnets, or spin glasses. This result supports the hypothesis that the slowing down of M is due to a resonant phonon trapping mechanism which prevents the thermalization of M but not the fast spin flippings of the individual molecular moments.

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