High frequency EPR on dilute solutions of the single molecule magnet Ni₄

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Dilute frozen solutions of the single molecule magnet Ni₄ ($S=4$) have been studied using 130 GHz electron paramagnetic resonance (EPR). Despite the random orientation of the molecules, well defined EPR absorption peaks are observed due to the strong variation of the splittings between the different spin states on magnetic field. Temperature dependent studies above 4 K and comparison with simulations enable identification of the spin transitions and determination of the Hamiltonian parameters. The latter are found to be close to those of Ni₄ single crystals. No echo was detected from Ni₄ in pulsed experiments, which sets an upper bound of about 50 ns on the spin coherence time. © 2008 American Institute of Physics. [DOI: 10.1063/1.2834447]

Single molecules magnets (SMMs) have been suggested as candidates for qubits in quantum processors.¹ However, the coherence time (T_2) of high-spin molecules has not yet been determined. Quantum tunneling of magnetization (QTM) has been widely studied in SMMs.^{2–4} A recent focus is on coherent QTM in which the tunneling rates may be faster than the rate of decoherence.^{5–7} Due to inhomogeneous broadening, only a lower bound (≈ 0.5 ns on most of the measured SMMs) of T_2 can be extracted. Furthermore, in SMM crystals the strong dipolar interactions between the molecules (separated by ≈ 1 nm) is expected to drastically reduce the coherence time. In order to determine the latter (e.g., through spin echo) and to coherently manipulate the magnetization with microwave pulses in SMMs, it thus may be necessary to work with dilute ensembles of molecules.

SMMs may be diluted in solvents. The drawback of such a method is that the molecules are randomly oriented. However, magnetometry⁸ and EPR experiments⁹ on randomly oriented powder have been successfully performed. Only recently have dilute frozen solutions been studied by high frequency (HF) techniques. Frequency domain spectroscopy showed that the zero field splitting (ZFS) parameters of Mn₁₂ clusters diluted in a frozen solvent were almost the same as in the crystal form.¹⁰ Even more interesting, standard microwave pulse experiments have determined a long intrinsic coherence time (few μ s at 2 K) in doped antiferromagnetic wheels (low spin).¹¹

In this paper we present continuous wave (cw) HF EPR experiments performed on dilute frozen solutions of the SMM Ni₄ ($S=4$) as a function of temperature between 6 and 30 K. Well defined transitions are observed in the 0–7 T range at $f=130$ GHz. Simulations using ZFS parameters close to the ones determined from single crystals¹² and D and g strains qualitatively reproduce the spectra measured. No spin echo from the Ni₄ clusters was observed in pulse experi-

ments, which sets an upper limit for T_2 of about 50 ns.

[Ni(hmp)(dmb)Cl]₄, henceforth referred to as Ni₄, is a particularly clean SMM with no solvate molecules present in its crystal phase and only 1% (natural abundance) of nuclear spins on the transition metal sites.¹³ This results in narrower EPR peaks than in many SMMs.¹² The spin Hamiltonian of Ni₄ is to first approximation,

$$\mathcal{H} = DS_z^2 + BS_z^4 + C(S_+^4 + S_-^4) + \mu_B \mathbf{H} \cdot \hat{\mathbf{g}} \cdot \mathbf{S}, \quad (1)$$

where the first term is the uniaxial anisotropy, the second and third terms are fourth-order anisotropy terms, and the last term is the Zeeman energy. The $S=4$ ground state at low temperature is the consequence of ferromagnetic exchange interactions between the four Ni^{II} ($S=1$) ions. The uniaxial anisotropy leads to a large energy barrier $|D|S^2 \approx 12$ K to magnetization reversal between states of projection $S_z = \pm 4$ along the easy axis of the molecule. The ZFS parameters have been measured on single crystals using HF EPR.¹² In particular, the strong C -term (≈ 10 MHz) explains the fast tunneling observed at zero field,¹⁴ and a recent analysis shows that the fourth-order terms in Eq. (1) may result from a finite ratio of the (second order) single ion anisotropies to exchange constant.¹⁵

To prepare dilute solutions of Ni₄, dried crystals were dissolved in a 1:1 mixture of toluene and dichloromethane. This glass was chosen due to solubility constraints. ¹HNMR spectra were collected for [Ni(hmp)(dmb)Cl]₄ and the analogous complexes [Ni(hmp)(CH₃OH)Cl]₄ and [Ni(hmp)(CD₃OD)Cl]₄, as well as the free ligand 2-hydroxymethylpyridine (hmpH). The proton signals for the bound hmp[−] ligand were positively identified through comparison of the [Ni(hmp)(CH₃OH)Cl]₄ and deuterated [Ni(hmp)(CD₃OD)Cl]₄ complexes. Comparison of the [Ni(hmp)(dmb)Cl]₄ and free hmpH spectra confirmed that no free ligand is present, and, thus, the [Ni(hmp)(dmb)Cl]₄ complex is intact in solution. Most of our EPR experiments

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FIG. 1. (Color online) EPR spectrum of a 10 mg/ml Ni_4 solution at $f = 130$ GHz and $T = 5.5$ K. The dashed and solid lines are, respectively, the absorption and dispersion channels (a 12 $\text{G}_{\text{p-p}}$ field modulation is used). The spurious signal at low field was also observed without Ni_4 molecules in the 1:1 mixture of toluene and dichloromethane.

were carried out on a 10 mg/ml solution, corresponding to an average distance of 6 nm between molecules.

D -band (130 GHz) EPR spectra were acquired on a spectrometer capable of working in cw and pulse modes. The quadrature detection microwave bridge was designed and built by HF EPR Instruments, Inc. (V. Krymov, New York). During the acquisition in cw mode, a field modulation of 12 $\text{G}_{\text{p-p}}$ is generated at 100 kHz by a coil surrounding the cavity, and the dispersion and absorption channels¹⁶ are recorded as a function of the external field, generated by a 7 T superconducting magnet. Figure 1 shows the result of such an experiment performed at 5.5 K on a 10 mg/ml Ni_4 solution contained in a quartz capillary tube (active volume of 0.2 μl). Large absorption peaks (labeled α to ζ with decreasing field) can be observed above 2.5 T. They are attributed to transitions between spin states of the dissolved Ni_4 molecules. The narrow signal around 4.6 T ($g \approx 2$) and the spurious absorption at low field were also measured without Ni_4 clusters in the solvent, in contrast to the high field peaks. These do not affect the high field part of the spectrum, and we will not discuss them further.

To address the origin of the transitions observed in Fig. 1, we discuss the dependence of the EPR signal on temperature and the comparison with simulations, shown in Figs. 2(a) and 2(b), respectively. The latter were performed using the EasySpin toolbox,¹⁷ which allows calculation of EPR spectra¹⁸ and provides the visualization tools used in Fig. 3. $2^\circ \times 2^\circ$ cells in one octant of the upper hemisphere were used to perform the powder average. First, we used the ZFS parameters of Ni_4 single crystal [$D = -0.748(5)$ K, $B = -6 \times 10^{-3}$ K, $C = \pm 2.9 \times 10^{-4}$ K, $g_x = g_y = 2.23$, $g_z = 2.3$],^{12,14} and a convolution by a Gaussian of width of 0.1 T [dashed curve on Fig. 2(b) at 6 K]. The position of the high field peaks is slightly offset with respect to the data, and a large absorption peak close to zero field is calculated, but not detected.

To improve the position of the calculated peaks, we used slightly different D and B parameters [$D = -0.746(5)$ K, $B = -9 \times 10^{-3}$ K] and introduced D and g strains ($\sigma_D = 0.11|D|$ and $\sigma_g = 0.02\hat{g}$), which wash out the low field transitions and lead to an overall better fit to the spectrum. It is known that D and g strains influence the line shapes in SMM single crystals.¹⁹ Random dipolar fields, also expected to play a role, should be less important in dilute solutions due to the

FIG. 2. (Color online) (a) EPR signal vs temperature. (b) The dashed curve is the simulation at 6 K using the ZFS parameters of the single crystal (see text) and a 0.1 T Gaussian broadening. The continuous curves have been calculated using the parameters indicated in the inset, that include D and g strains.

larger average distance between neighboring molecules. The simulations reproduce rather well the dependence of the experimental data on temperature. In particular, the simulations reproduce the global decrease of the absorption and the extinction of the peaks α and β as the temperature increases. This is expected from Boltzmann statistics, since the difference in population between the lowest energy levels decreases exponentially with temperature (note that $f = 130$ GHz corresponds to $T = 6.2$ K). Therefore, α is associated with a transition from the ground state to the first excited state. However, we were unable to reproduce the line shapes and the very intense ϵ peak. We explored the possibility of having two Ni_4 species (dissolved and precipitated¹⁰) in the solution without success. We believe that our dilute solutions are free of precipitate, and it was checked after each experimental run that the dilute solution contained in the quartz tube was still clear. Increase of the D and g strains does not improve the fit either. The values used in the simulations are already larger than the ones fitted on single crystals¹⁹ by a factor of 2–10. This probably results from the variation in the molecular environment of the SMM clusters in the frozen solution. It is known to play a critical role, e.g., in Mn_{12} crystals.²⁰ In solution, the strain could also depart from axially symmetric. E -strain cannot be excluded, as simulations performed with $\sigma_E = 0.05$ K slightly broaden peaks α to γ .

To better understand the nature of the transitions involved in the EPR spectrum, Fig. 3(a) shows the energy levels as a function of the angle θ between the easy axis of the

FIG. 3. (Color online) (a) Energy levels for three different angles between the applied field and the molecular easy axis. The transitions corresponding to $f=130$ GHz are shown. The stronger the red color, the larger the matrix element of the transition. (b) Orientations contributing to transitions α and ϵ (cf. Figs. 1 and 2). Note that in (a) and (b), all allowed transitions are displayed without regard to the temperature.

molecules and the magnetic field (the angle ϕ in the hard plane is set to 0°). The well-known diagram is obtained for $\theta=0^\circ$, with the low lying transitions at low field. In our experimental case, the ground state transition ($m=-4 \rightarrow -3$) is not observed because the ZFS of Ni_4 is about 140 GHz, slightly larger than our working frequency. When $\theta=90^\circ$, the ground state transition is on the contrary at the highest field (α in Figs. 1 and 2). For an intermediate angle, the transitions can also be determined by a full diagonalization of the Hamiltonian [Eq. (1)]. As a result of the rapid variation of the splittings with the amplitude and the direction of the applied field, certain subpopulations of molecules are selected, and well defined absorption peaks are observed. Figure 3(b), which shows the orientations contributing to peaks α and ϵ , validates this picture. The influence of the C -term can be seen for the peak α (variation between $\phi=0^\circ$ and $\phi=45^\circ$), for which the easy axis of the contributing molecules almost lie in the plane $\theta=90^\circ$ (the band near $\theta=0^\circ$ is a highly excited transition which does not contribute at low temperature).

Finally, echo experiments ($\pi/2-\tau-\pi-\tau$ -echo high power pulse sequences) were conducted at 5.5 K on several dilutions of Ni_4 (down to 0.5 mg/ml) and on the pure solvent. We did not observe any echo from the Ni_4 molecules. Let us briefly discuss this result. First, the sensitivity of the experimental setup is sufficient to detect echoes with $T_2 > 50$ ns in 200 G broad lines from micromolar solutions (i.e., 10^{11} spins) of $S=1/2$ compounds. Despite the random orientation of the Ni_4 molecules and the broad absorption lines ($\approx 2-4$ kG), the cw EPR data show that a small ($\approx 5\%$) but non-negligible fraction of the molecules contribute to the signal. Taking into account these factors, it is found that there are still about 30 times more spins than needed to detect an echo if $T_2 > 50$ ns for the 10 mg/ml Ni_4 solution. Second, the random orientation makes the intermolecular in-

teraction weak because the effective dilution of the molecules addressed by the microwaves is large. Third, the coupling to nuclear spins can limit the coherence time. However, it can still be larger than 50 ns.¹¹ It is not clear whether the coherence time of spin-state oscillations between excited levels (as $\beta-\zeta$) could be much shorter than the one between the ground state and the first excited states (as α). However, an estimation of the spin-lattice relaxation time from direct spin-phonon process²¹ using a reasonable value for the transverse speed of sound in the frozen solvent (1000 m/s) yields $T_1=40$ ns at $f=130$ GHz and 5.5 K (it increases by a factor 2 at 0 K). This upper bound for T_2 could explain the absence of echo from Ni_4 in our experiments. It is interesting to note that T_1 is a strong function of frequency ($\sim 1/f^3$). For instance, at 10 GHz and 1.5 K we estimate $T_1=60$ μ s.

In conclusion, we have studied dilute frozen solutions of the SMM Ni_4 by HF EPR. The clusters have been found to be stable in solution. Despite the random orientation of the anisotropy axes, it is possible to measure EPR spectra with well-defined transitions and to deduce that the ZFS parameters of the dissolved molecules are close to the ones in the crystal phase. Thus, the behavior of an isolated Ni_4 cluster is essentially the same as that of a single crystal.

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