

Origin of superhyperfine interactions in the antiferromagnetic ring Cr₇Ni

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W-band pulsed ESR measurements on the antiferromagnetic ring Cr₇Ni reveal that the spin-lattice relaxation time is $T_1 = 5.3 \pm 0.2 \mu\text{s}$ at $T = 4.0 \text{ K}$, and decreases strongly with increasing temperature. The phase coherence time is determined to be $T_M = 357 \pm 10 \text{ ns}$. Pulsed W-band ENDOR measurements quantify the superhyperfine coupling of the electron spin to the proton nuclear spins. Calculating the dipolar contribution of all the protons to the hyperfine splitting, in the point-dipole approximation, gives a good simulation of the experimental data, demonstrating that magnetic dipole interactions between electron and nuclear spins are the origin of the superhyperfine interaction.

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Molecular nanomagnets (MNMs) are molecular clusters of paramagnetic transition-metal ions, bridged by simple ligands. Intermolecular superexchange interactions result in a well-defined ground spin state with a gap to the first excited spin state. Quantum coherence in MNMs has recently attracted a great deal of attention for three reasons.¹⁻⁵ First, MNMs are promising candidates for spin-based qubits, because they can be easily and extensively modified through established methods of chemical synthesis, enabling the development of large scalable arrays of MNMs.⁶ Second, the excited spin states may be used to implement two-qubit gates.⁷ Finally, MNMs are ideal model systems to investigate the mechanisms of decoherence in mesoscopic systems, furthering the understanding of the transition from the quantum to classical world. The facile chemical modification of MNMs allows judicious tuning of geometric and electronic structure, as well as insertion or elimination of electron or nuclear spins.

In these investigations,¹⁻⁵ pulsed electron-spin resonance (ESR) demonstrated that the quantum coherence times of MNMs are in the microsecond range at temperatures around 5 K. These measurements also showed that (super)hyperfine coupling of the electron spin to nuclear spins in the molecule or in the surrounding matrix are the main cause of decoherence. Thus replacing protons by deuterium atoms in Cr₇Ni resulted in a sixfold increase in T_M ,¹ while removing the nuclear spins from the frozen solvent matrix increased T_M by a factor of 2 in an Fe₄ MNM.⁴ However, no quantitative estimate of the superhyperfine coupling strength has been reported to date and also the origin of the reported hyperfine coupling has not yet been resolved. Understanding the origin of decoherence in MNMs is critically important for improvement of their coherence times, enabling the development of viable qubits based on MNMs.

Here we present W-band pulsed ESR studies on the antiferromagnetic ring Cr₇Ni. Furthermore, pulsed W-band ENDOR measurements enabled us to extract an estimate of the superhyperfine coupling strength of the electron spin to proton nuclear spins. The Cr₇Ni cluster itself consists of an almost regular octagon formed by seven chromium (III) and one nickel (II) ion [Fig. 1(a)]. Intramolecular antiferromagnetic exchange

interactions result in an $S = \frac{1}{2}$ ground state for this cluster, which has been extensively studied by both CW and pulsed ESR.^{1,8,9}

The compound $(\text{Me}_2\text{NH}_2)^+[\text{Cr}_7\text{NiF}_8\text{Piv}_{16}]^-$ (Cr₇Ni), where Me = methyl and Piv⁻ is pivalate, was synthesized as previously published.⁸ Pulsed ESR and pulsed electron-nuclear double resonance (ENDOR) spectra were recorded on frozen solutions of Cr₇Ni in toluene (0.2–1.0 mg ml⁻¹) on a Bruker Elexsys E680 W-band ESR spectrometer equipped with a helium flow cryostat. Dilution below 1.0 mg ml⁻¹ did not increase spin-relaxation times, proving that dipolar intermolecular interactions can be neglected in the measurements presented here. Phase coherence times T_M were determined by a modified Hahn echo sequence $\frac{2}{3}\pi - \tau - \frac{2}{3}\pi - \tau - \text{echo}$, where the use of $\frac{2}{3}\pi$ pulses rather than the more usual $\frac{\pi}{2}$ and π pulses increases the echo intensity.¹⁰ We note that the relaxation time thus measured is not the real spin-spin relaxation time (T_2) but a lower limit denoted T_M .¹⁰ Spin-lattice relaxation times T_1 were determined by recording the echo intensity as a function of τ in the inversion recovery sequence $\pi - \tau - \frac{2}{3}\pi - \tau_{\text{fix}} - \frac{2}{3}\pi - \tau_{\text{fix}} - \text{echo}$, with $\tau_{\text{fix}} = 256 \text{ ns}$ and $\frac{2}{3}\pi$ pulse length 40 ns. Pulsed ENDOR spectra were recorded by using the Mims sequence $\frac{\pi}{2}(\text{MW}) - \tau_{\text{fix}} - \frac{\pi}{2}(\text{MW}) - \frac{\pi}{6}(\text{RF}) - \frac{\pi}{2}(\text{MW}) - \tau_{\text{fix}} - \text{echo}$, with $\frac{\pi}{2} = 44 \text{ ns}$, $\tau_{\text{fix}} = 256 \text{ ns}$, and $\frac{\pi}{6}(\text{RF}) = 5 \mu\text{s}$. A limited turning angle for the rf pulse was chosen in view of the short T_1 time of Cr₇Ni. Heating effects were avoided by using long shot repetition times of $t_{\text{rep}} \geq 15 \text{ ms}$, above which no change in echo intensity was observed. Echo decay curves were fit by monoexponential functions to extract relaxation times. Pulsed ESR- and ENDOR-spectra were simulated by using the Easyspin package.¹¹

Figure 2(a) reports the echo intensity recorded after an inversion recovery pulse sequence at different concentrations and temperatures. In all cases, single-exponential decay is observed. At a concentration of $c = 1 \text{ mg ml}^{-1}$, and a temperature of $T = 5.0 \text{ K}$, the spin-lattice relaxation time is found to be $T_1 = 2.0 \pm 0.1 \mu\text{s}$. The same T_1 was found in measurements on a fivefold diluted solution ($c = 0.2 \text{ mg ml}^{-1}$), indicating that the spin dynamics is not

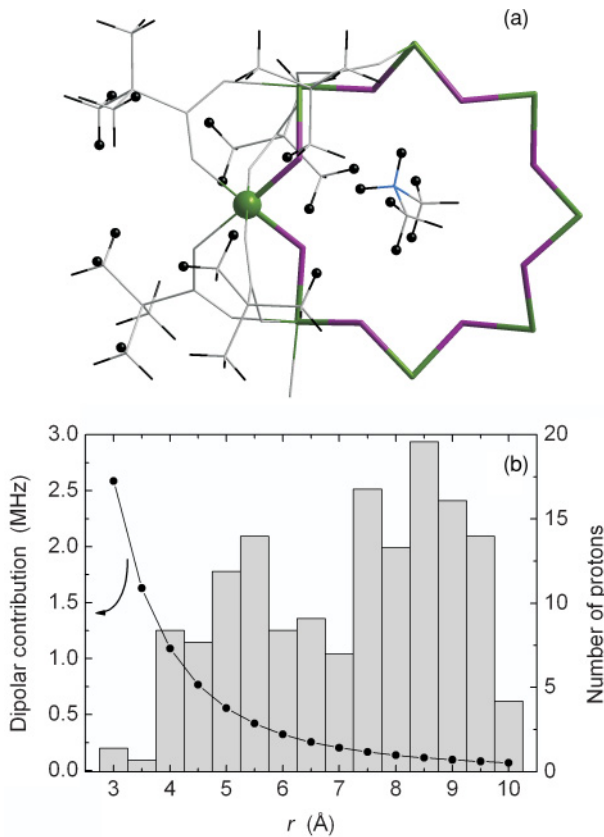


FIG. 1. (Color online) (a) Partial molecular structure of Cr_7Ni . The thick lines indicate the ring formed by alternating chromium (III) and fluoride ions, with one chromium ion shown as a large sphere. The molecule in the middle of the ring is the Me_2NH_2^+ cation. The thin lines on the left of the ring depict the pivalate ligands that have at least one hydrogen atom within 5 Å of the chromium ion indicated by a sphere. All hydrogen atoms within that distance are shown as small spheres. All other pivalate ligands have been omitted. (b) Histogram of the distribution of the distance r between the chromium ion indicated in the top panel and all hydrogen atoms of one Cr_7Ni molecule and its Me_2NH_2^+ cation. The symbols indicate the expected dipolar contribution (A^{dip}) to the superhyperfine splitting with principal elements ($-A^{\text{dip}}$, $-A^{\text{dip}}$, $+2A^{\text{dip}}$). The line is a guide to the eye.

affected by intermolecular dipolar interactions. On decreasing the temperature, T_1 increases strongly to $T_1 = 2.9 \pm 0.1 \mu\text{s}$ at $T = 4.5 \text{ K}$, and $T_1 = 5.3 \pm 0.2 \mu\text{s}$ at $T = 4.0 \text{ K}$. Figure 2(b) displays the echo intensity recorded on a frozen solution of Cr_7Ni in toluene ($c = 0.2 \text{ mg ml}^{-1}$) at $T = 5.0 \text{ K}$ after the echo sequence $\frac{2}{3}\pi - \tau - \frac{2}{3}\pi - \tau$ -echo. By fitting the exponential decay function $Ae^{-2\tau/T_M}$ to the data, a phase coherence time of $T_M = 357 \pm 10 \text{ ns}$ was obtained. A very similar T_M of $T_M = 379 \text{ ns}$ was obtained from X-band measurements at 4.5 K.¹ The phase coherence time of this molecule was reported to be limited by superhyperfine coupling to the proton nuclear spins of the ligands, which agrees with the observed lack of field dependence of T_M . No modulation of the echo intensity due to electron-spin envelope modulation (ESEEM) effects was observed in the present W-band measurements, in contrast to what was reported for X-band measurements. ESEEM effects give information on the nature of any nuclear

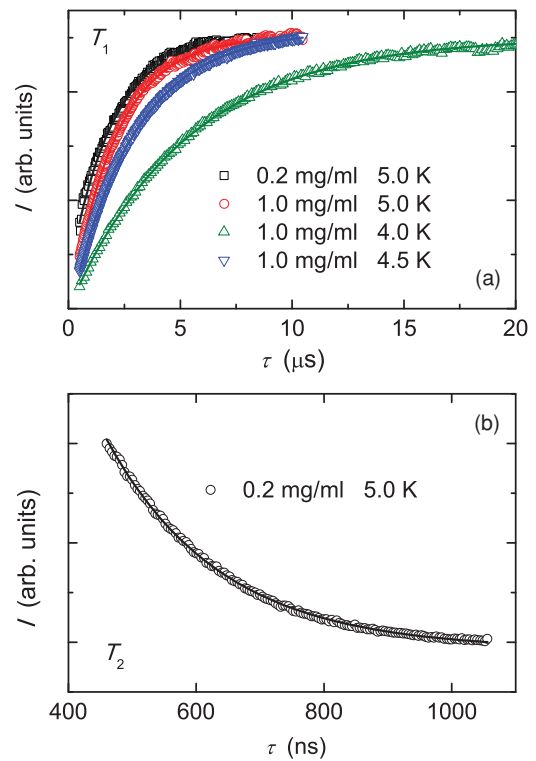


FIG. 2. (Color online) (a) Echo intensity measured after the inversion recovery pulse sequence $\pi - \tau - \frac{2}{3}\pi - \tau_{\text{fix}} - \frac{2}{3}\pi - \tau_{\text{fix}}$ -echo, as a function of delay time τ , measured on solutions of Cr_7Ni in toluene, with an external field of $B_0 = 3.85 \text{ T}$, at a microwave frequency of $\nu = 94.26 \text{ GHz}$ and at different concentrations and temperatures as indicated. Solid lines are fits to monoexponential decay functions. (b) Echo intensity measured after the Hahn echo sequence $\frac{2}{3}\pi - \tau - \frac{2}{3}\pi - \tau$ -echo, as a function of delay time τ , measured on a 0.2 mg ml^{-1} solution of Cr_7Ni in toluene at 5.0 K , with an external field of $B_0 = 3.85 \text{ T}$, and at a microwave frequency of $\nu = 94.26 \text{ GHz}$. The solid line is a fit to a monoexponential decay function.

spin that the electron spin is coupled to. The lack of ESEEM in the W-band measurements is due to the fact that the ESEEM intensity, expressed as the modulation depth parameter k , decreases strongly with external field B_0 ($k \propto B_0^{-2}$),¹⁰ and thus no pronounced ESEEM is expected. However, electron-nuclear double resonance (ENDOR) is excellently suited to the study of electron-nuclear-spin coupling in high magnetic fields.¹⁰

We have measured pulsed ENDOR spectra, using a modified Mims ENDOR pulse sequence, on a 1 mg ml^{-1} solution of Cr_7Ni in toluene (Fig. 3). The data clearly show an ENDOR signal consisting of two branches centered around 164 MHz, which is very close to the ^1H Larmor frequency ν_L at the employed field of $B_0 = 3.85 \text{ T}$ ($\nu_L = 163.92 \text{ MHz}$). In spectra measured at the higher field of $B_0 = 3.885 \text{ T}$, the center of the observed signal shifts to 165.4 MHz, proving the ENDOR origin of the signal. No ENDOR signal was observed around the Larmor frequency of ^{19}F , which agrees with the fact that no ESEEM due to that nucleus was observed at the X band.¹ Both branches are asymmetric which suggests the presence of anisotropy in the superhyperfine interaction. In addition, the high-frequency branch has a slightly lower intensity

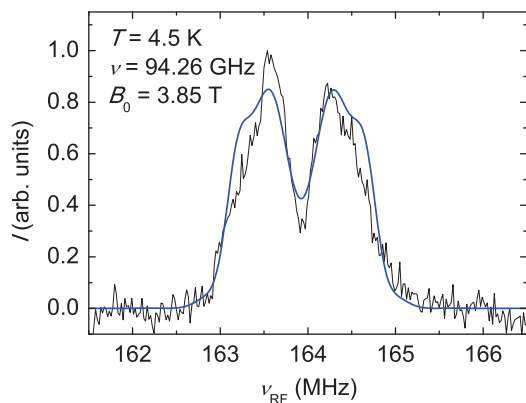


FIG. 3. (Color online) Experimental pulsed ENDOR spectrum, measured by using the pulse sequence given in the text, on a 1-mg ml⁻¹ solution of Cr₇Ni in toluene at 4.5 K, with an external field of $B_0 = 3.85$ T, and at a microwave frequency of $\nu = 94.26$ GHz. The smooth, solid line is a simulation of the ENDOR data, using the superhyperfine parameters calculated by using the point-dipolar approximation, distances obtained from the crystal structure, and a linewidth of 0.19 MHz.

than the low-frequency branch. The molecule possesses 144 hydrogen atoms, at different distances from the metal ions. Furthermore, the protonated amine counter ion in the solid as well as solvent molecules in frozen solution may approach the metal ions closely. Clearly, a model which considers all the different hydrogen superhyperfine interactions as free parameters would be hugely overparametrized. However, we can calculate the magnetic dipolar contribution to the hyperfine coupling, where the tensor is expected to have the principal values $(-A^{\text{dip}}, -A^{\text{dip}}, +2A^{\text{dip}})$.¹² Under this assumption, we can simulate the ENDOR spectrum in the following manner. From the separation between the hydrogen atoms and the metal ions in the crystal structure we can estimate the strength of the dipolar hyperfine coupling, according to¹⁰

$$A^{\text{dip}} = \sum_i \frac{\mu_0 \mu_B \mu_N g g_N}{4\pi h r_i^3}, \quad (1)$$

where the μ_0 is the vacuum permeability, μ_B is the Bohr magneton, μ_N is the nuclear magneton, g is the electron g factor ($g = 1.77$),⁸ g_N is the nuclear g factor of hydrogen, h is Planck's constant, and r_i is the distance between the chromium ion and a proton nucleus. The summation is over all the proton nuclei in the molecule and its counterion. Figure 1(b) shows a histogram of the distances of the hydrogen atoms to one of the chromium (III) ions, derived from the reported crystal structure.⁸ It is noteworthy that the hydrogen atoms that approach the metal ions most closely are the ones of the protonated amine cation. With these distances, A^{dip} can be calculated for each of the distances in the histogram [Fig. 1(b)]. Simulating the pulsed ENDOR spectra with these A^{dip} values, for each of the sets of hydrogen atom distances, multiplying by the number of atoms at that distance, and finally summing the spectra gives a result that matches the experimental spectrum very well (Fig. 3). Note that apart from the linewidth there are no free parameters in this calculation. Closer lying protons contribute to the outlying part of the spectrum, while protons that are further away from the electron spin contribute to the region closer to the center of the spectrum. Discrepancies between experimental and simulated spectra may be due to the fact that the simulation assumes ideal (i.e., infinitely short) pulses, which is clearly not the case here ($\frac{\pi}{2} = 44$ ns, while $\tau_{\text{fix}} = 256$ ns). The good match between experimental data and simulated spectrum indicates that the predominant origin of the superhyperfine coupling in Cr₇Ni is the magnetic-dipolar interaction between the electron spins on the metal ions and the proton nuclear spins.

In conclusion, we have obtained a quantitative estimate of the superhyperfine coupling between the electron spin and the hydrogen nuclear spins, by using pulsed ENDOR. The superhyperfine splitting was shown to be mainly due to magnetic dipole interactions between the electron and nuclear spins.

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