

## Quantum Oscillations of the Total Spin in a Heterometallic Antiferromagnetic Ring: Evidence from Neutron Spectroscopy

S. Carretta,<sup>1</sup> P. Santini,<sup>1</sup> G. Amoretti,<sup>1</sup> T. Guidi,<sup>2,3,\*</sup> J. R. D. Copley,<sup>2</sup> Y. Qiu,<sup>2,4</sup>  
R. Caciuffo,<sup>5</sup> G. Timco,<sup>6</sup> and R. E. P. Winpenny<sup>6</sup>

<sup>1</sup>*Dipartimento di Fisica, Università di Parma, I-43100 Parma, Italy*

<sup>2</sup>*NIST Center for Neutron Research, Gaithersburg, Maryland 20899, USA*

<sup>3</sup>*Dipartimento di Fisica, Università Politecnica delle Marche, I-60131 Ancona, Italy*

<sup>4</sup>*Department of Materials Science and Engineering, University of Maryland, Maryland 20742, USA*

<sup>5</sup>*European Commission, JRC-ITU, Postfach 2340, 76125 Karlsruhe, Germany*

<sup>6</sup>*Department of Chemistry, University of Manchester, Manchester M13 9PL, United Kingdom*

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Using inelastic neutron scattering and applied fields up to 11.4 T, we have studied the spin dynamics of the Cr<sub>7</sub>Ni antiferromagnetic ring in the energy window 0.05–1.6 meV. We demonstrate that the external magnetic field induces an avoided crossing (anticrossing) between energy levels with different total-spin quantum numbers. This corresponds to quantum oscillations of the total spin of each molecule. The inelastic character of the observed excitation and the field dependence of its linewidth indicate that molecular spins oscillate coherently for a significant number of cycles. Precise signatures of the anticrossing are also found at higher energy, where measured and calculated spectra match very well.

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Magnetic molecules have of late become the focus of intense research activity because of their remarkable and fascinating spin dynamic properties at the crossover between the classical and quantum regimes [1–3]. Many nanoscopic clusters have been synthesized and identified as promising candidates for the macroscopic observation of quantum phenomena such as the resonant tunneling of the magnetization between quasidegenerate levels in molecular nanomagnets [4–6] and the coherent Néel vector tunneling (NVT) in antiferromagnetic (AF) rings [7]. These phenomena are interesting from a fundamental point of view since a detailed understanding of their properties will shed light on the transition from classical to quantum behavior. In addition, the identification of model systems displaying quantum coherence is crucial for the implementation of qubits [8]. Magnetic molecules are very promising systems for the study of quantum coherent phenomena because they have well-defined structures and magnetic properties. In fact, their magnetic dynamics can usually be modeled with an outstanding degree of accuracy. A straightforward amplification of the single-molecule signal is naturally provided by single crystals, which may be considered as macroscopic ensembles of identical weakly interacting magnetic units [3]. Another advantage of magnetic molecules is their high degree of tunability; indeed, it is often possible to chemically engineer molecules for specific purposes. In particular, AF rings have attracted considerable interest since they were suggested as promising candidates for the observation of NVT [7,9]. In the ideal NVT scenario, the tunnel frequency may be tuned using an applied magnetic field, and it is much greater than the decoherence frequency. Unfortunately, the low-energy dynamics of AF rings is only very approximately characterized by NVT [9]. We recently proposed a different

quantum coherent phenomenon that might characterize the microscopic spin dynamics of AF heterometallic (HM) rings, i.e., quantum oscillations of the total spin [10,11]. Whereas in nanomagnets the total spin  $S$  of each molecule is almost a good quantum number, the molecular ground state of a HM AF ring can be rendered a superposition of two different total-spin states by the application of a suitable magnetic field (see Fig. 1). In this case the total spin of each molecule oscillates longitudinally (along the direction of the field) between  $S$  and  $S + 1$ . These zero-temperature oscillations are absent in the classical version of the model. Interestingly, our calculations indicate that the frequency of these quantum oscillations can be tuned

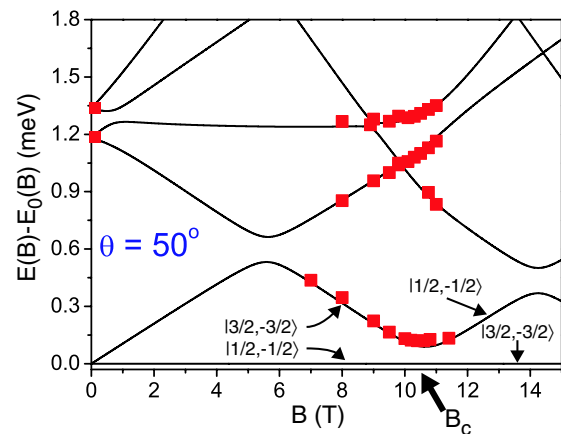


FIG. 1 (color online). Calculated field dependence of the low-lying energy levels of Cr<sub>7</sub>Ni for  $\theta = 50^\circ$ , relative to the ground-state energy. Points indicate the positions of the observed INS peaks. Kets indicate the leading  $|S, M_S\rangle$  component of the corresponding level.

from zero to several tenths of GHz simply by changing the direction of the applied field. Hence the study of these oscillations also offers the possibility to address the cross-over between the coherent and incoherent regimes. To date, this phenomenon has only been indirectly probed, studying its implications for the field dependence of static observables such as magnetic torque and specific heat [10]. Up to now we have had no direct, model-independent information on the value of the quantum oscillation frequency, nor whether these oscillations are coherent for a sizeable number of cycles.

In this Letter we describe inelastic neutron scattering (INS) measurements on a Cr<sub>7</sub>Ni single crystal which establish that quantum oscillations of the total spin indeed characterize the low-frequency dynamics of HM AF rings, and that these oscillations are coherent over many cycles. In addition, we argue that these quantum coherent oscillations could be detected by direct real-time magnetization measurements or by parallel electron paramagnetic resonance (EPR) experiments. We also determine the magnetic-field dependence of the energy of low-lying levels of Cr<sub>7</sub>Ni. The results are in very good agreement with calculations based on the microscopic spin Hamiltonian determined from zero-field experiments.

Each Cr<sub>7</sub>Ni molecule is described by the spin Hamiltonian [12]

$$H = \sum_i J_i \mathbf{s}(i) \cdot \mathbf{s}(i+1) + \sum_i d_i [s_z^2(i) - s_i(s_i+1)/3] + \sum_{i>j} \mathbf{s}(i) \cdot \mathbf{D}_{ij} \cdot \mathbf{s}(j) + \mu_B \sum_i g_i \mathbf{B} \cdot \mathbf{s}(i), \quad (1)$$

where  $\mathbf{s}(i)$  is the spin operator for the  $i$ th ion in the molecule [ $\mathbf{s}(9) \equiv \mathbf{s}(1)$ ]. The first term is the dominant nearest neighbor isotropic Heisenberg exchange interaction ( $J_i = J = 1.46$  meV for  $i = 1, \dots, 6$ ;  $J_i = 1.16$  J for  $i = 7, 8$ ). The second and third terms describe uniaxial local crystal fields and anisotropic intracluster spin-spin interactions (the  $z$  axis is perpendicular to the ring plane). The last term is the Zeeman coupling with an external field  $\mathbf{B}$  [10,12]. While the Heisenberg term conserves the length  $|\mathbf{S}|$  of the total-spin  $\mathbf{S} = \sum_i \mathbf{s}_i$ , the anisotropic terms do not conserve this observable. Nevertheless, since the Heisenberg contribution is usually largely dominant,  $|\mathbf{S}|$  is nearly conserved, and the energy spectrum of  $H$  consists of a series of level multiplets with an almost definite value of  $|\mathbf{S}|$  [ $=\sqrt{S(S+1)}$ ]. Thus quantum fluctuations of  $|\mathbf{S}|$ , associated with the mixing of states with different values of the quantum number  $S$  (“ $S$ -mixing” [13]), are usually neglected. Within this approximation the lowest-lying states of Cr<sub>7</sub>Ni for  $B = 0$  are a ground  $S = 1/2$  doublet and an  $S = 3/2$  quartet at about 1.2 meV (Fig. 1), but if  $B$  is large enough one of the  $S = 3/2$  levels comes very close to the ground state and an avoided level-crossing (AC) occurs. The AC gap  $\Delta_{AC}(\theta)$  is due to the anisotropic interactions in Eq. (1), and it is maximum (of the order of  $10^{-1}$  meV) when the angle  $\theta$  between  $\mathbf{B}$  and  $z$  is  $45^\circ$ , and vanishes for

$\theta = 0$  and  $\theta = 90^\circ$  due to the axial character of  $H$ . Near the AC the  $S$  mixing is very large, and right at the AC the ground and first excited states are very close to

$$|\psi\rangle_{\pm} = \frac{1}{\sqrt{2}} \left( \left| \frac{1}{2}, M_S = -\frac{1}{2} \right\rangle \pm \left| \frac{3}{2}, M_S = -\frac{3}{2} \right\rangle \right), \quad (2)$$

where  $S$  in  $|S, M_S\rangle$  is the total-spin quantum number and  $M_S$  is its component along the direction of  $\mathbf{B}$ . Equation (2) implies that at the AC the total spin  $S$  experiences quantum oscillations between  $1/2$  and  $3/2$  with frequency  $\Delta_{AC}(\theta)/\hbar$ . (In contrast, the magnetization tunneling in nanomagnets such as Fe<sub>8</sub> is a total-spin reversal with no change in length; i.e.,  $S$  is constant and  $M_S$  oscillates between  $S$  and  $-S$ .) The magnetic anisotropy also causes ACs involving pairs of excited states (see, e.g., the one at  $\sim 5.5$  T in Fig. 1) which, however, do not contribute to the  $T \rightarrow 0$  quantum dynamics. In order to demonstrate that this picture is appropriate, and, in particular, that the dynamics implied by Eq. (2) are not washed out by dephasing and/or decoherence, the spin dynamics should be directly probed in the time or frequency domain. INS can directly probe the AC gap through the magnetic cross section [9,14]: the observation of an *inelastic* (resonant) peak will demonstrate that the associated oscillations occur coherently for many cycles, the energy of the peak will yield the oscillation frequency, and its width will provide information about the damping. 3.75 g of the deuterated microcrystalline compound (C<sub>2</sub>D<sub>5</sub>)<sub>2</sub>NH<sub>2</sub>Cr<sub>7</sub>NiF<sub>8</sub>[O<sub>2</sub>CC(CD<sub>3</sub>)<sub>3</sub>]<sub>16</sub> [in short “Cr<sub>7</sub>Ni”, space group  $P4$ , with magnetic ions at Wyckoff positions (4d)] were prepared as in [12]. After many attempts, two large crystals finally grew from solution following very slow evaporation of the solvent at room temperature over a period of three months. One of the crystals,  $11 \times 13 \times 2$  mm<sup>3</sup> (0.4 g), was sealed in a preservative THF/MeCN (1:2) atmosphere within a copper sample holder designed to hold it in the desired orientation with respect to the vertical  $\mathbf{B}$  field. A dilution refrigerator was used to cool the crystal to 66 mK, to ensure that only the ground state was occupied and to suppress phonon-induced damping. Measurements were performed using the time-of-flight Disk Chopper Spectrometer [15] at the NIST Center for Neutron Research. Figure 2 shows the field dependence of the lowest energy transition, clearly demonstrating that the AC occurs at the critical field  $B_c \simeq 10.5$  T. The peak is *inelastic*, and near the AC it is centered at about 0.12 meV and its intensity is minimum. This behavior is in agreement with calculations [see Figs. 1 and 3(a)]. The measured peak width decreases near the AC, where it reaches the experimental resolution. The broadening away from the AC might originate either from the interaction with phonons and nuclei or from a distribution of parameters in Eq. (1) resulting from some local disorder (e.g., “ $J$ ” or “ $d$  strain”). Phonons lead to energy levels with finite lifetimes which we have calculated by modeling the spin-phonon interaction as in [16], assuming the same coupling as in the Cr<sub>8</sub> parent com-

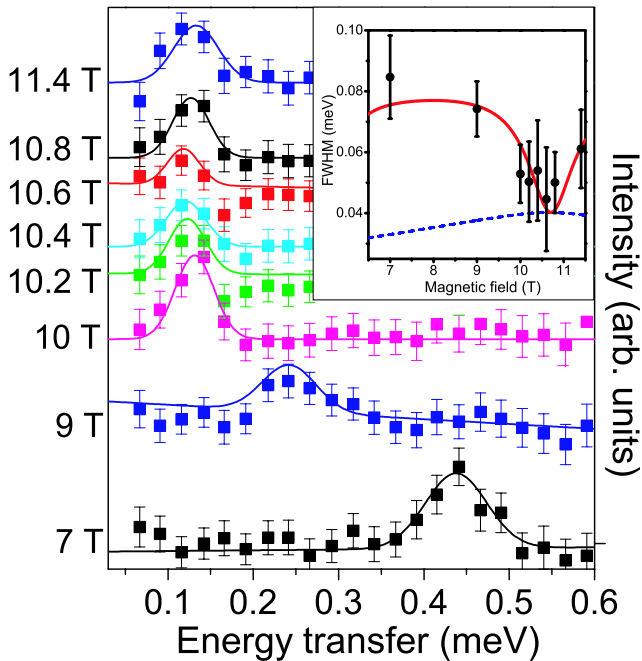


FIG. 2 (color online). High-resolution (FWHM  $\sim 42 \mu\text{eV}$  at the elastic peak) INS data ( $\lambda = 7 \text{ \AA}$ ) for  $\text{Cr}_7\text{Ni}$  at  $T = 66 \text{ mK}$ , for different applied fields at  $50^\circ$  to the ring axis  $z$ . The data are vertically offset for clarity. The background measured at  $B = 0$  was subtracted from the raw data. Lines represent fits to the sum of a Gaussian and a sloping background. The inset shows the field dependence of the experimental peak width (points). The red line is the FWHM of the convolution of the instrumental resolution function and a Gaussian of standard deviation  $\sigma = \sigma_J \partial \Delta_{\text{AC}} / \partial J$ , with  $\sigma_J = 0.025 \text{ J}$ . The dashed blue line shows the instrumental resolution at the peak energy.

pound. The resulting Lorentzian broadening is completely negligible due to the very low temperature. Hence the observed width is not due to phonons. As far as nuclear-induced decoherence is concerned, the observed value of the gap,  $\Delta_{\text{AC}} = 0.12 \text{ meV}$ , implies that the resulting spin dynamics is too fast for the nuclear spins to react. Thus the present phenomenon occurs in the “coherence window” defined in [17]. The vanishing of the observed intrinsic width near the AC strongly suggests a strain mechanism. In particular, a distribution of values of  $J$  leads to a distribution of values of the AC field  $B_c(J)$  centered at the nominal  $B_c$ . The ensuing distribution of the energy gap tracks  $\partial \Delta_{\text{AC}} / \partial J$  and its width vanishes at the AC where  $\partial \Delta_{\text{AC}} / \partial J = 0$  (see Fig. 2 inset). In order to quantitatively fit the observed intrinsic widths we used a Gaussian distribution of exchange integrals centered at the nominal value of  $J$ , with 2.5% standard deviation. This distribution does not lead to finite lifetimes but induces dephasing of the response of an ensemble of molecules. Further support for a  $J$ -strain mechanism is provided by very recent EPR data [18] showing that for small  $B \approx 0.5 \text{ T}$ , where  $J$  strain plays no effect, dephasing effects are very small [19]. Other strain mechanisms that induce dephasing (e.g.,  $g$  strain or  $d$  strain) are expected to produce effects below the experi-

mental resolution and could be quantified by a specifically designed experiment (see below). Summarizing, the INS data show that at the AC the total spins of the molecules oscillate coherently for a number of cycles determined by the ratio ( $\gg 1$ ) between the oscillation frequency and the intrinsic width.

Figure 3(b) shows the INS cross section calculated as a function of energy and magnetic field with  $S$  mixing forced to vanish. The main consequence is the disappearance of the AC and the resulting disappearance of quantum oscillations of the total molecular spin. A second qualitative effect appears in the high frequency dynamics. If  $S$  mixing is suppressed, only one peak of sizeable intensity is expected between 0.5 and 1.6 meV for  $B > B_c$ . In this case the ground state is basically  $|\frac{3}{2}, M_S = -\frac{3}{2}\rangle$  and only the transition to the  $|\frac{5}{2}, M_S = -\frac{5}{2}\rangle$  excited state is detectable in the previously mentioned energy range. On the other hand, the mixing of  $|\frac{3}{2}, M_S = -\frac{3}{2}\rangle$  with  $|\frac{1}{2}, M_S = -\frac{1}{2}\rangle$  allows two further sizeable peaks in this energy range [Fig. 3(a)]. Hence, due to the  $S$ -mixing sensitivity of the INS cross section, measurements in this window provide independent proof of the superpositional nature of the ground state. Figure 4 shows shorter wavelength spectra that display three peaks for  $B > B_c$ , proving our picture. Energies and intensities are in remarkable agreement with calculations based on parameters determined from zero-field measurements. The positions of all the observed peaks are reported as points in Fig. 1.

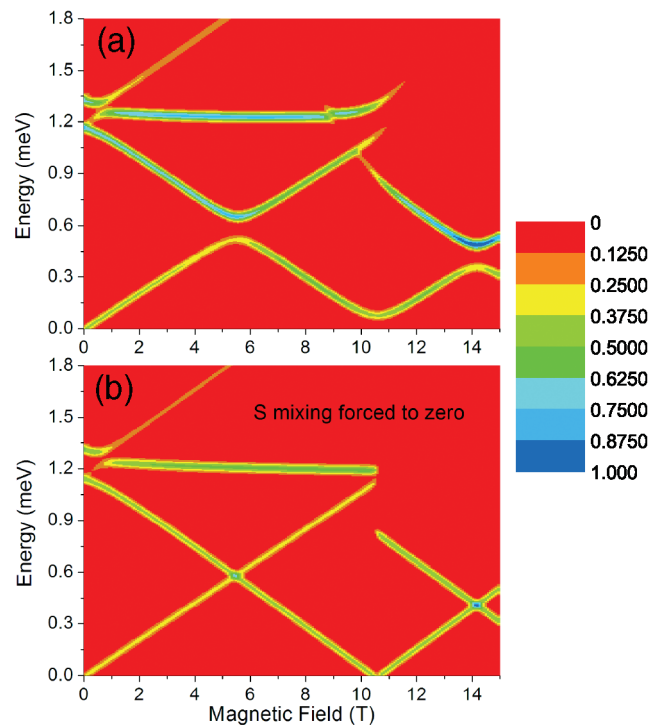


FIG. 3 (color). (a) Intensity plot showing the energy and field dependence of the calculated  $T = 66 \text{ mK}$  INS cross section. (b) Same as (a) with  $S$  mixing forced to zero.

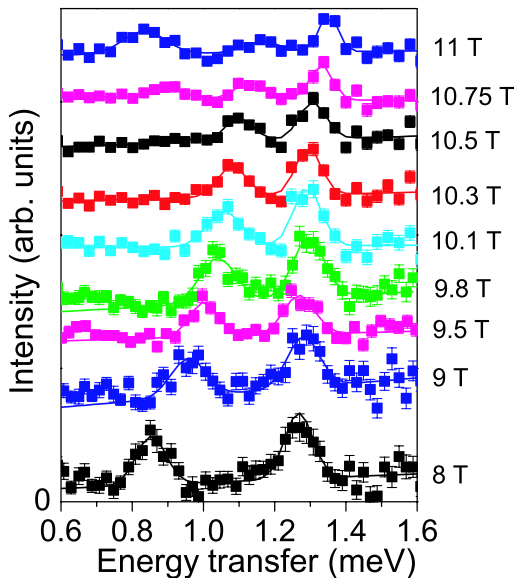


FIG. 4 (color online). INS data with  $\lambda = 5 \text{ \AA}$  at  $T = 66 \text{ mK}$  (FWHM resolution width  $\sim 105 \mu\text{eV}$ ), with  $\theta = 50^\circ$ . The data are vertically offset for clarity. Lines represent fits to a sum of Gaussians and a sloping background.

In summary, we have used INS to establish that by appropriately tuning the applied field  $\text{Cr}_7\text{Ni}$  displays longitudinal quantum oscillations of the total spin with a small degree of dephasing, most likely dominated by  $J$  strain. In principle, a direct real-time observation of these oscillations is possible by performing low- $T$  magnetization measurements at the AC after preparing the system in an eigenstate of  $\mathbf{S} \cdot \mathbf{B}$  by, e.g., a microwave pulse with the oscillating magnetic field polarized along  $\mathbf{B}$ . The difficulty of this approach is the current time-resolution limit of magnetization detection devices. To match the available time resolution the oscillation frequency can be tuned at will by changing the direction of  $\mathbf{B}$ . However, a compromise is needed because oscillations that are too slow will be washed out by decoherence and/or dephasing. A different approach is to use EPR since this technique directly probes the autocorrelation of  $\mathbf{S}$  and the corresponding AC oscillations. The present results indicate that the oscillation frequency for  $\theta = 50^\circ$  is  $\sim 29 \text{ GHz}$ , which is in the range of existing EPR instruments. The measurements have to be performed in a parallel setup, i.e., with the oscillating magnetic field parallel to  $\mathbf{B}$ . A single sizeable sharp peak should be detected at the AC field, with the peak intensity vanishing for large enough  $|B - B_c|$ . The higher resolution of EPR will provide the possibility to study and possibly discriminate between dephasing and decoherence on time scales much longer than those typical of INS.

In conclusion, we have performed high field inelastic neutron scattering measurements on a single crystal of  $\text{Cr}_7\text{Ni}$ . The experiments have provided detailed information regarding the spin dynamics of  $\text{Cr}_7\text{Ni}$  antiferromagnetic rings in the energy window 0.05–1.6 meV and have shown that an anticrossing involving states with different

total-spin quantum numbers occurs. The agreement with calculations for the low-energy transition between the two anticrossing states is very good. The inelastic character of the observed AC excitation and the field dependence of its width indicate that molecules oscillate coherently over a non-negligible number of cycles. Precise signatures of the anticrossing are also found for higher energy transitions as the INS cross section for these transitions is strongly sensitive to the mixed nature of the ground state at the AC. Finally, we have proposed to study finer details of the quantum coherent oscillations of the total spin by direct real-time magnetization measurements or by parallel EPR experiments.

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\*Current address: Hahn-Meitner Institut, Glienicker Strasse 100, 14109 Berlin, Germany.

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