P H Y S I C A L R E V I E W L E T T E R S

Molecular Engineering of Antiferromagnetic Rings for Quantum Computation

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The substitution of one metal ion in a Cr-based molecular ring with dominant antiferromagnetic couplings allows the engineering of its level structure and ground-state degeneracy. Here we characterize a Cr_7Ni molecular ring by means of low-temperature specific-heat and torque-magnetometry measurements, thus determining the microscopic parameters of the corresponding spin Hamiltonian. The energy spectrum and the suppression of the leakage-inducing S mixing render the Cr_7Ni molecule a suitable candidate for the qubit implementation, as further substantiated by our quantum-gate simulations.

Because of their relative decoupling from the environment and of the resulting robustness, electron spins in solid-state systems are currently considered among the most promising candidates for the storing and processing of quantum information (QIP) [1]. In this perspective, an increasing interest has recently been attracted by a novel class of molecular magnets, including both ferromagnetic [2] and antiferromagnetic (AFM) [3] systems. In the latter case the quantum hardware is thought as a collection (e.g., a planar array) of coupled molecules, each corresponding to a different qubit. A major advantage with respect to analogous schemes based on single-spin encodings would arise from the larger dimensions of the physical subsystem, and from the resulting reduction of the spatial resolution which is required for a selective addressing of each qubit by means of local magnetic fields. A detailed, system-specific investigation is, however, mandatory in order to verify the actual feasibility of this approach, and to suitably engineer the intra- and intercluster interactions, the coupling between the computational and the environmental degrees of freedom, as well as the gating strategy.

It is the purpose of the present Letter to argue the suitability of Cr-based AFM molecular rings for the qubit implementation on the basis of a detailed theoretical and experimental investigation of its wave functions and energy levels, and of its simulated time evolution as induced by sequences of pulsed magnetic fields. Molecular rings [4] are characterized by a cyclic shape and by a dominant antiferromagnetic coupling between nearest neighboring ions. In the absence of applied fields and for even numbers of spin centers, their energy spectrum typically consist in a singlet ground state and in characteristic rotational excitations [5]. The recently demonstrated substitution of a Cr^{3+} ion with a divalent transition metal [6] provides an extra spin to the otherwise fully compensated molecule: this may in turn result in the formation of a ground state doublet energetically separated from the higher energy levels, i.e., in a suitable level structure for the qubit implementation.

In the octanuclear heterometallic ring of our present concern, one of the Cr^{3+} ($s = 3/2$) ions is substituted by a Ni^{2+} ($s = 1$) one. The cyclic molecule, with a diameter $d \sim 1$ nm, is characterized by a planar arrangement; we thus define θ to be the angle between the static magnetic field $\mathbf{B}_0$ and $\hat{\mathbf{z}}$, the latter being perpendicular to the ring plane. The spin Hamiltonian corresponding to the single molecule reads [7]

$$\mathcal{H} = \sum_{i=1}^{8} J_i \mathbf{s}_i \cdot \mathbf{s}_{i+1} + \sum_{i=1}^{8} d_i [s_{z,i}^2 - s_i(s_i + 1)/3]$$
$$+ \sum_{i<j=1}^{8} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j + \mu_B \sum_{i=1}^{8} g_i \mathbf{B} \cdot \mathbf{s}_i, \quad (1)$$

where the first term accounts for the dominant isotropic exchange interaction, while the second and third ones describe the anisotropic local crystal field and the intra-cluster dipole-dipole interaction, respectively; isotropic g factors are assumed for the last, Zeeman term. The anisotropic part of $\mathcal{H}$ does not commute with the squared total-spin operator $\mathbf{S}^2$, and thus mixes subspaces corresponding to different values of the total spin (S mixing). Because of its reduced symmetry, $\mathcal{H}$ can no longer be independently diagonalized within each $(2S + 1)$-dimensional block: an efficient solution scheme, based on an irreducible tensor operator formalism, is thus required (see Ref. [7], and references therein).

In order to estimate the parameters entering the above spin Hamiltonian, we measure the heat capacity C as a function of the temperature ($0.4 < T < 10$ K) and of the magnetic field ($0 < B_0 < 7$ T) [6]. The sample we investigate is a 2 mg bulk crystal, consisting of an ensemble of independent, iso-oriented, and identical rings. In fact, the synthesis procedures developed in supramolecular chemistry allow the engineering of regular arrays, as required (together with an intercluster coupling) by the long-term goal of scaling up the quantum hardware. The experimental details

and the method are described in Ref. [7], while the synthesis [6] and a systematic study of the thermodynamic properties of $[\{(CH_3)_2NH_2\}\{Cr_7MF_8[O_2CC(CH_3)_3]_{16}\}]$ (in short Cr_7M, with $M =$ Fe, Co, Ni, Mn, Cd) will be reported elsewhere. In Fig. 1 we show $C(T; B_0)$, normalized to the gas constant R, for five different values of B_0. The typical low-T Schottky anomaly appears upon application of the magnetic field and is shifted towards higher temperatures as B_0 increases. The overall specific heat $C(T; B_0)$ arises from two distinct contributions: one is a lattice-related Debye term, $C_{latt}/R = 234rT^3/(\Theta_D + \lambda T^2)^3$, where $r = 298$ is the number of atoms per molecule, $\Theta_D = 158 \pm 10$ K, and $\lambda = 0.42 \pm 0.02$ K^{-1}; the other, C_m, depends on the spin degrees of freedom and is responsible for the Schottky anomaly. The dependence of C_m on the energy eigenvalues ϵ_i of $\mathcal{H}$ reads

$$C_m = R\beta^2 \frac{\sum_i \epsilon_i^2 e^{-\beta\epsilon_i} \sum_i e^{-\beta\epsilon_i} - (\sum_i \epsilon_i e^{-\beta\epsilon_i})^2}{(\sum_i e^{-\beta\epsilon_i})^2}, \quad (2)$$

with $\beta = 1/k_B T$. The best fit of the specific-heat temperature dependence at different values of B_0 (solid lines in Fig. 1) provides the following set of values for the microscopic physical parameters: $J_{Cr}/k_B = 17 \pm 0.5$ K, $J_{Ni}/J_{Cr} = 0.9 \pm 0.1$, $|d_i|/k_B = 0.3 \pm 0.15$ K (for all the spin sites), and $g_{Ni} = 2.2 \pm 0.1$; $g_{Cr} = 1.98 \pm 0.02$ was determined from previous measurements on Cr_8. The sign of the anisotropies d_i needs to be independently determined by means of torque-magnetometry measurements. In the inset of Fig. 1 we report an angular scan of the torque signal, measured at $T = 2$ K and $B_0 = 2$ T. The torque exerted, e.g., for slightly off-perpendicular magnetic-field orientations ($\theta \sim 90°$) tends to align the ring plane to the direction of $\mathbf{B}_0$. For symmetry reasons, the doublet ground state gives no contribution to the torque, and the first excited multiplet ($S = 3/2$, see below) is the only one meaningfully populated at $T = 2$ K: the above behavior therefore shows that the $S = 3/2$ manifold has an easy-plane anisotropy, which implies $d_i < 0$. Results independently obtained by high-field torque measurements and inelastic neutron scattering (INS) confirm the above findings [8].

We are now able to include the microscopic parameters in $\mathcal{H}$ and accordingly draw the pattern of the low-lying energy levels ϵ_i as a function of $\mathbf{B}_0 = B_0\hat{z}$ (Fig. 2). At zero field the ground state is a degenerate doublet ($\epsilon_{0,1}$), with a largely dominating ($\gtrsim 99\%$) total-spin component $S = 1/2$; the first excited states (ϵ_{2-5}), instead, belong to a typical rotational band, with $S \simeq 3/2$. Noticeably enough, these low values of the S mixing allow us to consider the total spin as a good quantum number for the lowest eigenstates of the Cr_7Ni molecule. As discussed in more detail in the following, two other physical quantities play a crucial role in the perspective of a QIP implementation. The first one is the energy difference between the ground-state doublet and the higher-lying levels, i.e., $\Delta \equiv \epsilon_2 - \epsilon_1$: in fact, Δ determines to which extent the ring behaves as an effective two-level system, i.e., a meaningful population of any state but $|0\rangle$ and $|1\rangle$ can be avoided throughout the molecule manipulation. The second one is the splitting between the two $S = 1/2$ states, $\delta \equiv \epsilon_1 - \epsilon_0$: δ fixes the temperature the system has to be cooled at in order for it to be initialized to its ground state. Likewise the same existence of a ground-state doublet and the suppression of the S mixing, the large energy separation from the higher states in the present molecule, $\Delta(0) \simeq 13$ K, is a nontrivial result of the system engineering. Besides, the magnetic field allows a further tuning of the molecule's level structure. In particular, it increases δ, whereas it decreases the energy difference $\Delta(B_0)$ between $|1\rangle \simeq |S = 1/2, M = 1/2\rangle$, and $|2\rangle \simeq |3/2, -3/2\rangle$. The achievement of the best trade off between the conflicting requirements of maximizing δ and Δ therefore determines the optimal value of the field, which we identify with $B_0 = 2$ T (see the discussion below). As a consequence, the achievable temperature required for the system initialization to the $|0\rangle$ state is

FIG. 1. Specific heat C/R of a single Cr_7Ni crystal as a function of the temperature (T) and of the magnetic field (B_0). We attribute the slight discrepancy between the theoretical curve and the experimental data at $B_0 = 0$ and low T to an experimental artifact. Inset: torque signal measured on a $0.7 \times 1 \times 0.5$ mm^3 Cr_7Ni crystal at $T = 2$ K and $B_0 = 2$ T. In our experimental setup the rotation and torque direction is perpendicular to $\mathbf{B}_0$ and a positive torque induces a rotation of a negative θ.

FIG. 2. Energy levels of the Cr_7Ni molecule as a function of a static magnetic field applied along the z axis. At zero field the ground-state doublet is energetically well separated from the higher states $[\Delta(0) \simeq 13$ K$]$, thus representing a suitable choice for the qubit encoding.

$T \ll \delta/k_B \simeq 2.4$ K, whereas $\Delta(B_0) \simeq \Delta(0) - 2g\mu_B B_0 \simeq$ 9.4 K. On the grounds of the above results, the Cr_7Ni molecule can be considered as an effective $S = 1/2$ spin cluster, and the information states $|0\rangle$ and $|1\rangle$ safely identified with its ground-state doublet. Such a conclusion is unaffected by the uncertainty on $\Delta(0)$ (resulting from that on the microscopic parameters), which is of the order of that on J_{Cr} [9].

The time simulation of the quantum gates provides an important feedback for the optimization of the physical parameters. The general unitary transformation applied to the computational space can be decomposed into a sequence of elementary gates, such as the $SU(2)$ rotations of the single-qubit and the controlled NOT (or equivalent two-qubit gates) [10]. We start by considering the former, which can be obtained as a combination of three rotations about any two orthogonal axes, e.g., $U(\alpha, \beta, \gamma) = \exp(-i\alpha\sigma_y)\exp(-i\beta\sigma_x)\exp(-i\gamma\sigma_y)$, being $\sigma_{x,y}$ the Pauli matrixes. Transitions between the $|0\rangle$ and $|1\rangle$ states, i.e., rotations about the x and y axes, can be induced by means of resonant, in-plane electromagnetic pulses $B_1(t)\cos\omega t$, where $B_1(t) \ll B_0$ represents the slowly varying envelope. In the present case, however, the transverse magnetic field also couples the $|0\rangle$ and $|1\rangle$ states to the higher-lying ones, thus inducing a population loss (*leakage*) during gating, quantified by $L = 1 - [|\langle 0|\psi(t)\rangle|^2 + |\langle 1|\psi(t)\rangle|^2]$. More specifically, the possible occurrence of such unwanted transitions is due to the S mixing and to possible intracluster inhomogeneities in the magnetic fields (or, equivalently, in the ion g factors): both result in nonvanishing matrix elements $\langle 0, 1|\mathcal{H}_{op}|i \geq 2\rangle$, with $\mathcal{H}_{op} = \mu_B\Sigma_{i=1}^8 g_i\mathbf{B}_1 \cdot \mathbf{s}_i$. Together with a molecular engineering aimed at the suppression of the S mixing, the minimization of L can be achieved by the use of "soft" enough pulses, i.e., by keeping the pulse spectral dispersion $\Delta\omega < (\Delta - \delta)/\hbar$. Being $\Delta\omega \sim 1/\tau_g$, such inequality gives a lower bound to the ratio τ_g/τ_d that can in principle be achieved ($\tau_{g,d}$ are the gating and decoherence time, respectively).

Here, by means of a numerical integration of the Schrödinger equation, we calculate the time dependence of $|c_{0,1}|^2 = |\langle 0, 1|\psi(t)\rangle|^2$ and of L corresponding to a π rotation about the x axis, for $|\psi(0)\rangle = |0\rangle$ and $B_0 = 2$ T [see Fig. 3(a)]; the pulsed field is assumed to have a Gaussian profile $B_1(t) = A\exp[-(t - t_0)^2/(2\sigma^2)]$, with $A = 0.1$ T and $\sigma = 150$ ps. To a very large extent the leakage involves the first excited multiplet, and its value remains lower than 10^{-5} throughout the time evolution. Further simulations, performed with more reasonable values of the magnetic field ($A = 0.01$ T) [11], give proportional increases of the pulse duration, with a further suppression of L. We have also investigated the gate robustness with respect to possible spatial inhomogeneities of $\mathbf{B}_1$, generally leading to a larger value of L: even in the worst limiting case of a $\mathbf{B}_1$ which is nonzero only at the Ni-ion site, L remains below the threshold of 10^{-4} ($A =$
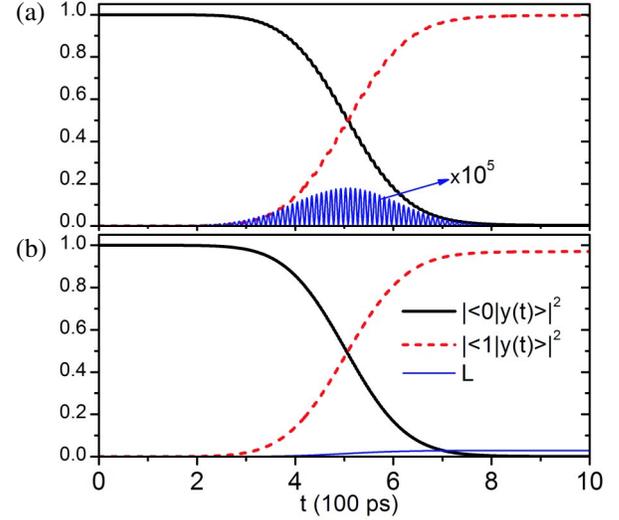
FIG. 3 (color online). Simulated time evolution of the molecular magnet, initially prepared in $|0\rangle$, under the effect of a transverse magnetic field with a Gaussian temporal profile. The black (solid), red (dashed), and blue (lower) lines correspond to $|c_0|^2$, $|c_1|^2$, and L [multiplied by a factor 10^5 in (a)], respectively; the static field is (a) $B_0 = 2$ T and (b) $B_0 = 5.61$ T, whereas $A = 0.1$ T in both cases.

0.15 T, $\tau_g \sim 2\sigma \sim 300$ ps). A larger value of the static field B_0 would polarize nuclear spins, thus reducing the decoherence due to hyperfine field fluctuations (see below). For $B_0 > 5.6$ T, $\epsilon_1 > \epsilon_2$ and $|1\rangle$ can relax into $|2\rangle$ by emitting a phonon (the decay to $|0\rangle$ is practically forbidden, owing to the approximate Kramers-doublet nature of the computational basis). These processes, however, are expected to be completely negligible with respect to other sources of decoherence, due to the small value of $(\epsilon_1 - \epsilon_2)/k_B\Theta_D$. An increase of L might arise, e.g., from a quasidegeneracy between the $0 \rightarrow 2$ and $1 \rightarrow 2$ transitions, as occurs at $B_0 = 5.61$ T: L then rises to .03 [Fig. 3(b)], but it is readily suppressed by small deviations of B_0 from such critical value.

The experimental demonstration of the intercluster coupling required for the implementation of the two-qubit gates is beyond the scope of the present work: in the following we discuss the present scenario and possible strategies to be pursued in order to achieve the required conditional dynamics. Links between Cr_7Ni rings formed by delocalized aromatic molecules have already been synthesized, and intercluster couplings have been demonstrated in similar systems [12]. The simplest case occurs when the coupling between the rings results from the interaction of the mth spin in molecule I with the nth of II. Within the first-order perturbation theory a Heisenberg interaction $\mathcal{H}_{I,II} = J^*\mathbf{s}_m^I \cdot \mathbf{s}_n^{II}$ can be rephrased as follows in terms of the cluster total spins:

$$\mathcal{H}_{I,II} = J_{eff}\mathbf{S}_I \cdot \mathbf{S}_{II}, \tag{3}$$

where

$$J_{\text{eff}} = 2/3J^*\langle 1/2||s_m||1/2\rangle\langle 1/2||s_n||1/2\rangle \qquad (4)$$

(analogous equations apply to the case of an Ising interaction). In the present molecules the single-cluster reduced matrix element $\langle 1/2||s_{m,n}||1/2\rangle$ has a modulus of the order of unity and alternating positive-negative signs as a function of n and m, whereas it is always negative for the Ni ion. If the interchain couplings are more than one, J_{eff} is given by the sum of the single contributions. Therefore, J_{eff} has the same order of magnitude of the coupling J^* between single spins, whereas its site dependence provides additional flexibility to the implementation scheme [13].

Within the present scenario the intercluster couplings, though engineerable during the growth process, are untunable thereafter. This shortcoming is common to other implementations, and does not in principle prevent one from performing the single- and two-qubit quantum gates. In fact, depending on the form and magnitude of the interchain coupling, different approaches can be adopted. Weak and Ising-like interactions allow the use of the so-called "refocusing techniques," widely developed within the NMR community [14]. Off-diagonal (e.g., Heisenberg) intercluster interactions could instead require either multi-ring encodings of the qubit [15], or the use of interqubit molecules acting as tunable barriers [16].

We finally discuss the decoherence of the cluster-spin degrees of freedom, which is expected to mainly arise from the hyperfine coupling with the nuclear spins. A first estimate can be obtained by considering the dipolar interaction of one Cr ion ($s = 3/2$) with the neighboring F nucleus (natural abundance $\sim 100\%$ of the $I = 1/2$ isotope). Being $g_F = +5.2577$ and the distance of each of the 8 F atoms from the nearest Cr ion $d = 1.91$ Å, the interaction energy corresponds to $E_{\text{hyp}}/k_B = 0.38$ mK. For an octanuclear ring this would give $\tau_d \simeq \hbar/8E_{\text{hyp}} \sim 2.5$ ns, that can be considered as a lower bond for τ_d. Similar τ_d values have been estimated for other molecular magnets [12,17]. Direct measurements of the electron-spin resonance linewidth on a Cr_7Ni crystal (which also includes the effects of possible inhomogeneities, the so-called "dephasing") provides τ_d values 1 order of magnitude larger than the above one [18]. Substantial enhancements of τ_d will result from the suppression of the hyperfine field fluctuations (mK temperatures and few-T static fields) and from the substituting of the F ions with OH groups in the Cr_7Ni compound. Besides, the static field induces a large mismatch between the energy gaps of the nuclear and electronic spins, thus rendering highly inefficient the relaxation processes of the latter. A second potential source of decoherence, the ring-ring dipolar coupling, is characterized by a lower energy scale, $E_{\text{dip}}/k_B \simeq (g\mu_B S)^2/V \sim 0.1$ mK ($S = 1/2$ and $V = 6346$ Å^3), further reducible in diluted Cr_7Ni molecular systems.

In conclusion, the energy spectrum of the investigated Cr_7Ni molecule fully justifies its description in terms of an effective two-level system; besides, the symmetries of the ground-state doublet (S mixing below 1%) suppress the coupling to the higher levels as induced by the transverse magnetic fields which are required for the quantum-gate implementation. In fact, our simulations of the single-qubit gates provide negligible values for the leakage ($L \lesssim 10^{-4}$) even for gating times of the order of 10^2 ps, i.e., well below the tens of nanoseconds estimated for the spin decoherence times. While further work is needed for the engineering of the intercluster coupling, these results strongly support the suitability of the Cr_7Ni rings for the qubit encoding and manipulation.

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