

## Spin Chirality in a Molecular Dysprosium Triangle: The Archetype of the Noncollinear Ising Model

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Single crystal magnetic studies combined with a theoretical analysis show that cancellation of the magnetic moments in the trinuclear  $Dy^{3+}$  cluster  $[Dy_3(\mu_3-OH)_2L_3Cl(H_2O)_5]Cl_3$ , resulting in a nonmagnetic ground doublet, originates from the noncollinearity of the single-ion easy axes of magnetization of the  $Dy^{3+}$  ions that lie in the plane of the triangle at  $120^\circ$  one from each other. This gives rise to a peculiar chiral nature of the ground nonmagnetic doublet and to slow relaxation of the magnetization with abrupt accelerations at the crossings of the discrete energy levels.

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Molecular nanomagnetism has provided benchmark systems to investigate new and fascinating phenomena in magnetism [1] like high spin clusters showing magnetic memory at the molecular level [2], quantum tunneling of the magnetization [3,4] or destructive interferences in the tunneling pathways [5]. More recently antiferromagnetic clusters, rings or triangles [6,7], have attracted increasing interest for their possible use in quantum computation, thanks to the longer decoherence time induced by weaker intercluster dipolar interactions. We have recently synthesized a trinuclear  $Dy^{3+}$  cluster  $[Dy_3(\mu_3-OH)_2L_3Cl(H_2O)_5]Cl_3$  (where L is the anion of ortho-vanillin) [8], hence abbreviated as  $Dy_3$ , which seems to combine for the first time both types of features, i.e., a system with almost nonmagnetic moment showing the slow magnetic relaxation typical of some high spin clusters. Preliminary powder magnetic measurements revealed an unprecedented magnetic behavior where the magnetization vs field curve at low temperature is almost flat, suggesting a nonmagnetic ground state. It suddenly increases to its saturation value [8] in contrast to the common multistep behavior of antiferromagnetic triangular clusters [9]. A possible explanation lies in the almost trigonal ( $C_{3h}$ ) symmetry of the molecule (see Fig. 1 and EPAPS for more information) [10] combined with the large Ising anisotropy of  $Dy^{3+}$  ions [11]. With this molecular symmetry, if the single-ion easy anisotropy axes are in the  $Dy_3$  plane and not perpendicular to it, they must be at  $120^\circ$  from one another, as represented in the scheme of Fig. 1. In that case, an antiferromagnetic interaction among the  $Dy^{3+}$  would result in a nonmagnetic ground state characterized by a vortex spin-chirality.

In this work we show that  $Dy_3$  is an unprecedented experimental realization of this simple but fascinating spin structure, which represents the archetype of noncollinear spin systems. Moreover thanks to its rich magnetization dynamics, with quantum acceleration at the level

crossings, it represents a new type of magnetic memory despite the nonmagnetic ground state.

To verify our hypothesis larger crystals (of size *ca.* 1 mm<sup>3</sup>) were grown through very slow evaporation of the solvent [8]. This allowed an accurate face indexing of the crystal on the x-ray diffractometer and the investigation of the magnetic anisotropy by using a horizontal sample rotator in the SQUID magnetometer (see EPAPS for experimental details) [10]. Scans in different crystallographic planes allowed us to determine the three magnetic anisotropy axes, denoted as X, Y, and Z. The two structurally equivalent  $Dy_3$  molecules in the unit cell have the  $Dy_3$  planes almost perpendicular to Z and one side of the triangle parallel to Y (see Fig. 1). Magnetization vs field curves along these axes are given in Fig. 2(a). Along X and Y a sudden jump around 8 kOe is observed while an almost linear but weaker magnetization is observed along Z. In Fig. 2(b) the temperature dependence of the magnetization along the three axes measured at 1 kOe, and thus before the

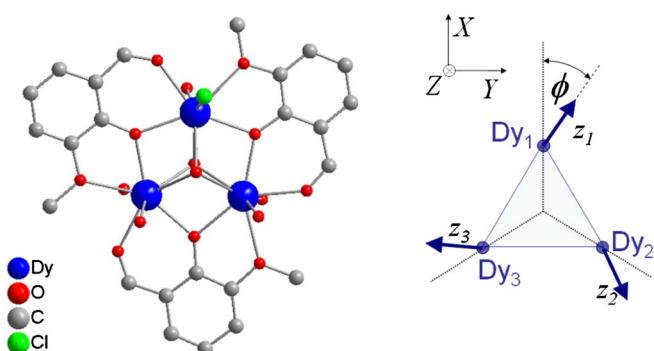


FIG. 1 (color online). Left: View of the molecular structure of  $Dy_3$  cluster where the hydrogen atoms, the chloride counter-anions and the solvent molecules of crystallization have been omitted. Right: Schematic view of the spin structure of the  $Dy_3$  triangular cluster and of the local easy axes orientation in respect of the laboratory XYZ reference frame.

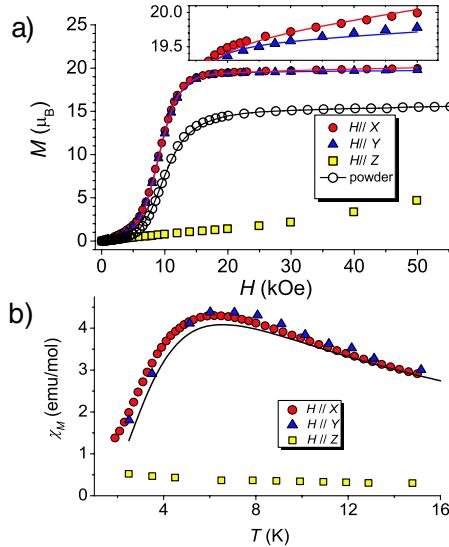


FIG. 2 (color online). (a) Field dependence of the magnetization measured along the  $X$ ,  $Y$ , and  $Z$  axes at  $T = 1.9$  K. In the inset a magnified view of the high field region is reported. (b) Temperature dependence for the susceptibility along  $X$ ,  $Y$ , and  $Z$  axes with an applied field of 1 kOe. The solid lines represent the calculated values with Eq. (2) and the best-fit parameters discussed in the text.

jump to saturation, are shown. The in-plane  $X$  and  $Y$  directions are very similar and  $M$  tends to zero at low temperatures, confirming a nonmagnetic ground state, while a weaker signal is observed along  $Z$ .

The observed behavior has been modeled with the canonical formalism of the statistical thermodynamics by taking into account that intermolecular interactions can be neglected [8] and that  $Dy^{3+}$  ions have a very large magnetic single-ion anisotropy due to the crystal field splitting of the  $^6H_{15/2}$  ground state. In a first approximation each  $Dy^{3+}$  ion, which is supposed to have the doublet ground state well separated in energy from the other excited Stark sublevels, can be represented by an effective spin  $S = 1/2$  and the  $Dy_3$  system can be modeled by an Ising Hamiltonian:

$$H = - \sum_{i,k=1,2,3}^{i>k} j_{zz} S_{z_i} S_{z_k} - \mu_B \sum_{i=1,2,3} g_z H_z S_{z_i} \quad (1)$$

where for each  $Dy^{3+}$  ion the  $z_i$  local axis is considered to be in the plane of the triangle at  $120^\circ$  one from each other as schematized in Fig. 1. The basis set of the full system consists therefore of 8 vectors:  $|\uparrow\uparrow\rangle$ ,  $|\downarrow\downarrow\rangle$ ,  $|\uparrow\downarrow\rangle$ ,  $|\uparrow\downarrow\rangle$ ,  $|\downarrow\uparrow\rangle$ ,  $|\downarrow\downarrow\rangle$ ,  $|\uparrow\uparrow\rangle$ ,  $|\downarrow\downarrow\rangle$ , where, however, up and down refers to the local  $z$  axes. Actually, these vectors are already the eigenvectors of (1). The best-fit parameters of the powder data are  $j_{zz}/k_B = 10.6(4)$  K and  $g_z = 20.7(1)$ . This last value confirms that the ground doublet for the  $Dy^{3+}$  ions is well described by  $|J = 15/2, m_J = \pm 15/2\rangle$ . In fact  $J = 15/2$  results from the coupling of  $L = 5$  and  $S = 5/2$  and thus

$g_J = 4/3$ , which, for  $m_J = \pm 15/2$ , gives an effective gyromagnetic factor of 20.

It is interesting to focus on the energy of the eight eigenstates of the Hamiltonian (1) as a function of the applied magnetic field in the  $Dy_3$  plane, as shown in Fig. 3. At zero field two states with a zero net magnetic moment, are degenerate with energy equal to  $-3j_{zz}/4$ , whereas the other 6 states are also degenerate with energy equal to  $j_{zz}/4$ . In an applied magnetic field the energy of the last six levels depends on the angle the magnetic field forms with the local easy  $z$  axes. Let us suppose that the field is applied along one bisector of the triangle as shown in Fig. 3. Two limiting scenarios can be observed depending whether the local easy axes are along the edges of the triangle [Fig. 3(a)] or along the bisectors [Fig. 3(b)]. A jump to saturation magnetization at the first level crossing,  $H_1$ , is expected in both cases, as indeed observed in  $Dy_3$ . In general, thanks to the structural noncollinearity of the easy axes, the two states of the ground doublet have opposite vortex chirality, with clockwise or anticlockwise rotation of the spins.

This simple model cannot however reproduce the weak linear increase in the magnetization above the step, visible in the inset of Fig. 2(a). We have therefore formulated a new Hamiltonian model by considering that for each  $Dy^{3+}$  the ground state doublet is  $|J = 15/2, m_J = \pm 15/2\rangle$  and that the first excited doublet is  $|J = 15/2, m_J = \pm 13/2\rangle$ . These states can be efficiently admixed by the  $J_+$  and  $J_-$  operators of the Zeeman interaction. To avoid overparameterization we have limited the treatment to the first

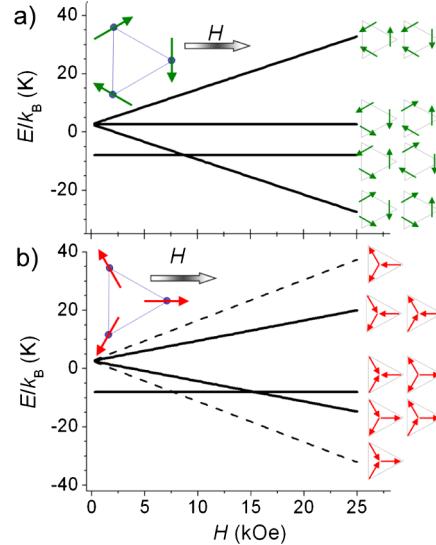


FIG. 3 (color online). (a) Zeeman splitting of the levels due to the application of the field along the  $X$  axis (bisector) calculated with the Spin Hamiltonian (1) and the parameters indicated in the text, assuming  $\phi = 90^\circ$ . (b) Same diagram calculated with  $\phi = 0^\circ$ . The spin structure for each state is schematized by the arrows. The nondegenerate states are highlighted by dashed lines.

excited doublet. The expression for the new Hamiltonian is

$$H = -j \sum_{\alpha_i, \alpha_k}^{i,k=1,2,3; i>k} \cos(\hat{\alpha}_i, \hat{\alpha}_k) S_{\alpha_i} S_{\alpha_k} - g \mu_B \sum_{\alpha_i}^i H_{\alpha_i} S_{\alpha_i} + \frac{\delta}{14} \sum_i \left( \left( \frac{15}{2} \right)^2 - S_{z_i}^2 \right), \quad (2)$$

where  $\alpha_i$  runs over the local axes of the  $i$  Dy ion ( $\alpha_i = x_i, y_i, z_i$ ). The first term of (2) comes from considering an isotropic (Heisenberg) exchange between two Dy ions, where  $(\hat{\alpha}_i, \hat{\alpha}_k)$  is the angle between the  $\alpha_i$  and  $\alpha_k$  local axes. The latter term describes the single-ion anisotropy and  $\delta$  is the zero field splitting between  $|J = 15/2, m_J = \pm 15/2\rangle$  and  $|J = 15/2, m_J = \pm 13/2\rangle$  states of each  $Dy^{3+}$  ion. The best fit, again performed on the powder data, provided  $j = -0.092(2)$  K,  $g = 1.35(1)$ , and  $\delta = 102(5)$  K. The  $g$  value is now close to  $4/3$  as expected for  $J = 15/2$ . The large separation between the two Kramers doublets is in good agreement with what is reported in the literature for  $Dy^{3+}$  [11,12]. To reproduce the single crystal data the angle  $\phi$  between the  $X$  axis and the local  $z$  anisotropy was allowed to vary freely. The best simulation is obtained with the angles  $\phi = \pm 17(1)^\circ \pm n60^\circ$  ( $n = 0, 1, 2, \dots$ ), where the periodicity results from the symmetry of the cluster. We have also evaluated the intramolecular dipolar contribution to  $j$  as a function of  $\phi$ , and in the most favorable configuration ( $\phi = 90^\circ$ ) it can only account for about half of the observed value.

Susceptibility measurements using standard induction coils in alternating magnetic field allowed us to estimate the relaxation rate from the frequency dependence of the imaginary component of the susceptibility  $\chi''$  assuming that, according to the Debye model, at the maximum of  $\chi''$  vs  $\omega$  curve the simple relation  $\tau = 1/\omega$  is valid (see supplementary material for more details) [10]. When the ac field is applied in the plane of the triangle the relaxation rate decreases on lowering the temperature following an Arrhenius law,  $\tau = \tau_0 \exp(\Delta/k_B T)$ , with  $\tau_0 = 2.5(5) \times 10^{-7}$  s and  $\Delta = 36(2)$  K. At temperatures below ca. 7 K the relaxation increases less rapidly, as shown in Fig. 4.

The Arrhenius behavior of the relaxation time characterizes a class of molecular materials called Single Molecule Magnets, SMMs [13], where the easy axis magnetic anisotropy generates a barrier for the reversal of the magnetization giving rise at low temperature to magnetic bistability and memory effect of pure molecular origin [1,2].  $Dy_3$ , however, represents the first example where such a slowing down of the magnetization dynamics occurs even if the overall magnetization lies in an almost isotropic plane rather than along an easy axis. That is because the system can be better schematized by three interacting SMMs. In the past pairs of weakly coupled  $Mn_4$  clusters have been widely investigated [14,15]. However a fascinating new situation is observed in  $Dy_3$  because the two states of the ground doublet are distinguished by a different

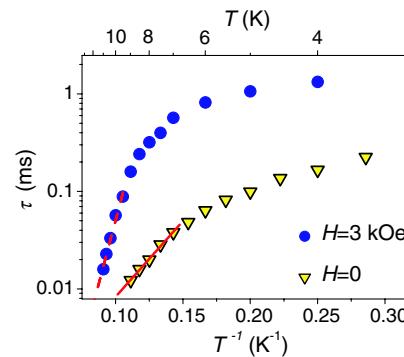


FIG. 4 (color online). Arrhenius plot of the temperature dependence of the relaxation time obtained from the frequency dependence of the ac magnetic susceptibility in zero and applied static field far from a level crossing. The lines represent the linear fit, according to the Arrhenius law, of the highest temperature data.

spin chirality and they cannot be related one to each other by a simple exchange of the magnetic sites. The last is verified even in the special nonchiral case of  $\phi = 0^\circ$ .

One of the striking aspect of SMMs is that relaxation at low temperature can occur through an underbarrier mechanism [1]. The tunneling is particularly efficient close to zero field, where the maximum degeneracy of the states is observed [3,4]. The application of a static field has indeed a strong influence on the dynamics of the magnetization of  $Dy_3$ , as shown in Fig. 5(a) where the real component of the susceptibility,  $\chi'$ , for different frequencies in 1–1000 Hz range is shown as a function of the field. Around zero field and the first level crossing,  $H_1$ , the dynamic susceptibility approaches the equilibrium value, i.e., that obtained from the derivative of the static magnetization curve recorded at the same temperature, while for intermediate fields a strong frequency dependent reduction, arising from the impossibility to follow the oscillating field, is observed. Similar results have been obtained along  $Y$ , as shown in Fig. 5(b) where the field dependence of the relaxation rate at  $T = 7$  K for this orientation is given. The acceleration of the relaxation occurs at a field slightly smaller than that corresponding to the maximum of the static susceptibility, suggesting that only the first crossing is relevant for the dynamics [inset of Fig. 5(b)]. Far from the level crossings, i.e., at  $H = 3$  kOe, the relaxation times, given in Fig. 4, show a significant increase of the barrier to  $\Delta = 120(4)$  K, with  $\tau_0 = 3(1) \times 10^{-10}$  s.

The present results are well rationalized by the model we have previously developed. The response in the ac field mainly involves transfer of population from (to) the ground doublet to (from) the first magnetic excited state, implying the reversal of one spin inside the triangle. Far from any level crossings this seems to occur through an Orbach process involving the first excited Kramers doublet of each of the  $Dy^{3+}$  ions, and its energy gap  $\delta$ , estimated from the static properties, is found indeed to be in good

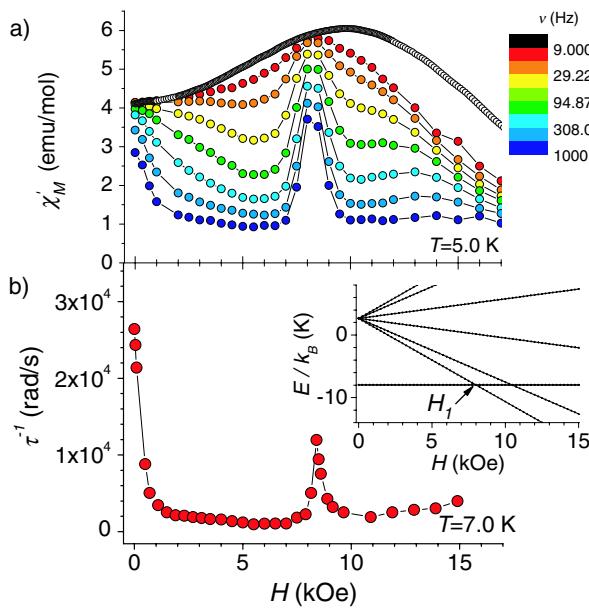


FIG. 5 (color online). (a) Field dependence of the real component at 5 K of the ac susceptibility measured with the field along  $X$  at logarithmic spaced frequencies. The empty circles represent the experimental static susceptibility obtained by derivation of the experimental magnetization curve. (b) Field dependence of the relaxation time measured at  $T = 7$  K with the field applied along  $Y$ . In the inset the Zeeman splitting calculated for  $H$  parallel to  $Y$  with the best-fit parameters discussed in the text.

agreement with the observed activation energy  $\Delta$ . On the contrary, at  $H = 0$  the reduction of the barrier suggests that an alternative mechanism takes place. Tunnelling of the magnetization has already been observed for other lanthanide-based SMMs and is attributed to the admixture in zero external field of the ground Kramers doublet states, made possible by the hyperfine interaction [16,17]. At the first level crossing the situation of zero local field is reestablished for a  $Dy^{3+}$  ion resulting in the observed fast dynamics.

To conclude,  $Dy_3$  has revealed to be a benchmark system to investigate noncollinearity in Ising systems. It is worth stressing that noncollinearity is a key feature of molecular magnetism, where complex building-blocks characterized by low symmetry are assembled in more symmetric architectures.  $Dy_3$  combines the slow dynamics of SMM and the level crossing observed in antiferromagnetic rings [18,19]. Both types of systems are currently being investigated for their potential application in quantum computation [6,7,20,21] and systems with a nonmagnetic nature of the ground doublet state could be used in order to reduce decoherence effects due to the fluctuation of local magnetic fields. The dynamics involving the ground doublet is in principle not directly accessible with magnetometry and requires to be further investigated with more sophisticated

techniques, for instance using local probes like muons or neutrons.

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*Note added in proof*—*Ab initio* calculations on  $Dy_3$ , published after this submission, agree with our interpretation of the experimental data (see [22]).

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