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A 2D Layered Lanthanide Hydroxide Showing Slow Relaxation of Magnetization – $Dy_8(OH)_{20}Cl_4\cdot 6H_2O$

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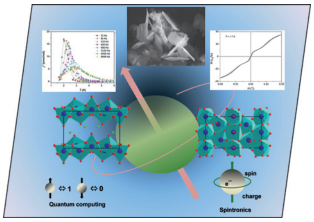

COVER PICTURE

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The magnetic properties of the layered lanthanide hydroxide $Dy_8(OH)_{20}Cl_4\cdot 6H_2O$ were studied. Below 5 K, slow magnetic relaxation was observed even in the absence of an external field, with a blocking temperature of 3 K and an energy barrier of 36.1 K, a behavior characteristic of single-molecule magnets.

Introduction

Layered double hydroxides (LDH), also known as anionic clays or hydrotalcite-like compounds, are nanostructured materials represented by the general formula $[\mathrm{M^{II}}(1-x)\mathrm{M^{III}}x(\mathrm{OH})_2]\mathrm{An}^{-x}\cdot n\mathrm{H_2O}$, where $\mathrm{M^{II}}$ and $\mathrm{M^{III}}$ include d-block transition metals and An^- might be any organic and/or inorganic anion, intercalated between the hydroxide layers by anion exchange or direct synthesis.[1] This class of ionic lamellar solids finds a wide range of applications, namely as polymer stabilizers, catalyst supports, electroactive and photoactive materials.[2] Particularly for lanthanide elements, from La through Lu, including the congener Y, there is a high potential for different technological applications such as luminescent devices,[3] high-performance magnets, catalysts, and other functional materials.[4]

The magnetic properties of LDHs with d-block transition metals have already been studied,[5] but those based on rare earths have been largely overlooked. A recent study refers to a LDH directly coated on a magnetic medium to form a magnetic carrier system, $(Mg_2Al_{0.95}Eu_{0.05})$Fe–IBU (IBU = ibuprofen), which has a superparamagnetic behavior with saturation magnetization of 1.86 emu/g. These magnetic properties are similar to those of pure Fe_3O_4, although with lower saturation magnetization (1.86 emu/g vs. 73 emu/g).[6] Superconductivity and magnetism were also reported in other lamellar hybrid materials with compositions $[Zn_{0.66}Al_{0.33}(OH)_2][TaS_2]$ and $[Ni_{0.66}Al_{0.33}(OH)_2][TaS_2]$, the last one with ferromagnetic Ni–Ni interactions through the hydroxido bridges.[7]

Recently, a family of nine layered lanthanide hydroxides (LLH) with composition $Ln_8(OH)_{20}Cl_4\cdot nH_2O$ (Ln = Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, and Y) were synthesized through homogeneous precipitation of $LnCl_3\cdot nH_2O$ and NaCl in the presence of hexamethylenetetramine (HMT).[8] This is an isostructural series of compounds in which the layered structure is slightly contracted with the increase in atomic number of the rare-earth atom, as a result of lanthanide contraction. The layered structure is stabilized by water molecules directly coordinated to the lanthanide centers in a fixed position.[9]

It is now already established that, because of their large spin–orbit coupling and potentially significant magnetocrystalline anisotropy, compounds with f-elements present attractive features for the development of single-molecule quantum magnets (SMMs) with high energy barriers.[10] Indeed, the slow relaxation of magnetization below a certain blocking temperature has more recently been observed in several f-element compounds, either with chain structures or composed of an assembly of discrete single ions. In the case of lanthanides (Ln), a wide number of recent publications have revealed slow magnetic relaxation in mononuclear Ln compounds,[11] but also in systems with different reduced nuclearities, with di-,[12] tri-,[13] tetra-,[14] and higher numbers of metal centers[15] up to 12 atoms, which have been recently reviewed.[16] Many lanthanide compounds can now be designed to have a combination of different properties such as luminescence and SMM behavior; however, so far SMM behavior has not been observed in systems with higher dimensionality. In this paper we report single-molecule magnetic behavior in a layered type of dysprosium hydroxide $Dy_8(OH)_{20}Cl_4\cdot 6H_2O$ (Dy–LLH).

Results and Discussion

$Dy_8(OH)_{20}Cl_4\cdot 6H_2O$ (Dy–LLH), as a polycrystalline sample consisting of platelike crystals with typical size $0.1\times 0.5\times 1\ \mu m^3$ (Figure 1), was obtained by following a previously described procedure,[8] and its composition and

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purity were confirmed by X-ray diffraction and thermogravimetry (see Supporting Information). The temperature dependence of the magnetic susceptibility was measured in the temperature range 2–300 K under applied fields up to 1 kOe, showing a perfect overlap of zero-field-cooled (ZFC) and field-cooled (FC) measurements with no indication of any ordering. At room temperature, the χT value (χ is the paramagnetic susceptibility and T the absolute temperature) is 111.5 emu K mol^{-1} (Figure 2), slightly smaller than that expected (113.36 emu K mol^{-1}) for eight non-interacting Dy^{III} ions (S = 5/2, L = 5, J = 15/2, $^6H_{15/2}$, and g = 4/3). Upon cooling, χT is first essentially temperature-independent in the range 300–100 K, then slightly decreases smoothly down to 107 emu K mol^{-1} at 19 K, then slightly rises, reaching a maximum at 5.5 K, and finally decreases to 92.5 emu K mol^{-1} at 1.8 K. This initial decrease can be understood as resulting from a progressive depopulation of excited Stark sublevels due to the ligand field,[17] the Dy–Dy interactions being negligible at higher temperatures.[11d,15a] However, the irregular evolution of χT upon cooling with the increase from 19 to 5.5 K denotes the existence of dominant ferromagnetic interactions between the Dy ions.

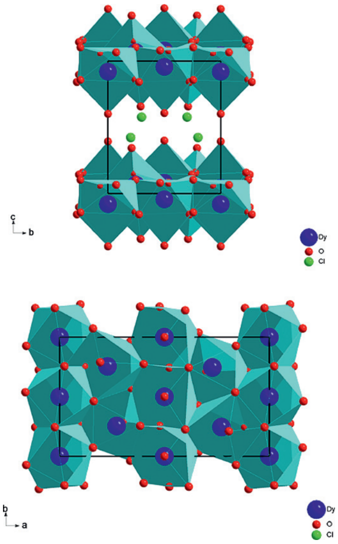

Figure 1. The $Dy_8(OH)_{20}Cl_4 \cdot 6H_2O$ unit cell viewed along the a axis (top) and c axis (bottom).[8]

The existence of non-negligible Dy–Dy interactions is not surprising in view of the crystal structure, because the unit cell contains three crystallographically distinct Dy atoms connected by different types of contacts. These Dy–Dy contacts are bridged by oxygen atoms, each hydroxy group acting as a μ_3-bridge, and in three cases the distances are very short (Dy1–Dy1 at 3.818 Å, Dy1–Dy2 at 3.891 Å, and Dy2–Dy3 at 3.616 Å), denoting possible direct Dy–Dy interactions.

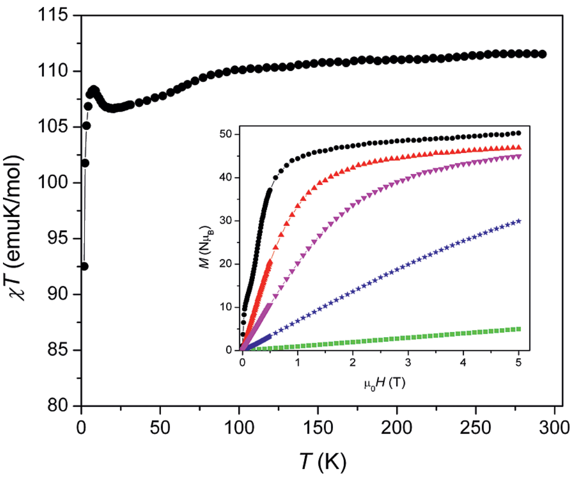

Figure 2. Temperature dependence of the χT product at 1 kOe. Inset: Field dependence of the magnetization at several temperatures, 1.7 (circles), 5 (red triangles), 10 (purple triangles), 30 (stars), and 200 K (squares).

The magnetic field dependence of the magnetization (inset of Figure 2) at 2 K reaches, above 20 kG, a saturation value of 50.32 μ_B, which is far from the saturation value expected for eight uncorrelated spins (80 μ_B). This difference has also been observed in several Dy cluster compounds[11b,12] and has been assumed to be the result of magnetic anisotropy and/or crystal field effects (low-lying excited states) in the system.[11b,14b] The curve of the magnetic field dependence of the magnetization at 1.7 K shows a rather unusual two-step shape with hysteresis as shown in Figure 3. The first step, which reaches a magnetization of approximately 10 μ_B at 500 G, is followed by a second step, which rapidly increases to 35 μ_B at 5 kG and finally reaches 50.3 μ_B at 50 kG. This feature is reminiscent of metamagnetism or a spin-canting process, as commonly observed in layered materials. However, similar steps in the magnetization curves have been found in other Dy^{III} complexes[13a,15b] and attributed instead to quantum tunneling effects.

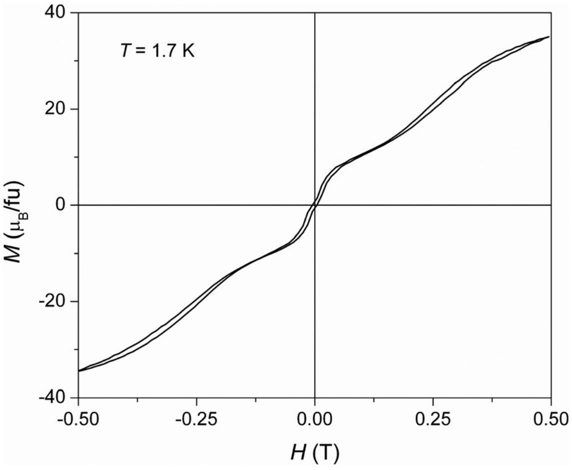

Figure 3. Magnetic field dependence of magnetization M for Dy–LLH at 1.7 K measured at 1.2 T/min.

Further information on the irreversibility and the relaxation of the magnetization was further probed by AC susceptibility measurements at low temperatures with an AC field of 5 Oe. Both the real, χ', and imaginary, χ'', components of the AC susceptibility below 5 K exhibit, even under zero static field, a strong frequency dependence (Figure 4), maxima shifting to higher temperatures with increasing frequencies, following a behavior characteristic of slow magnetic relaxation.[18] These measurements revealed a significant slow magnetic relaxation in the absence of an external DC field, which might be the signature of a SMM behavior. The maximal relative shift of χ' and χ'' per decade of frequency is $\phi = \Delta T_{max}/T_{max}\Delta(\log\omega) = 0.17$, higher than the typical shift obtained for a spin glass system ($\phi = 0.01$), and is comparable to the values obtained for other Ln compounds with SMM behavior.[11b,11c]

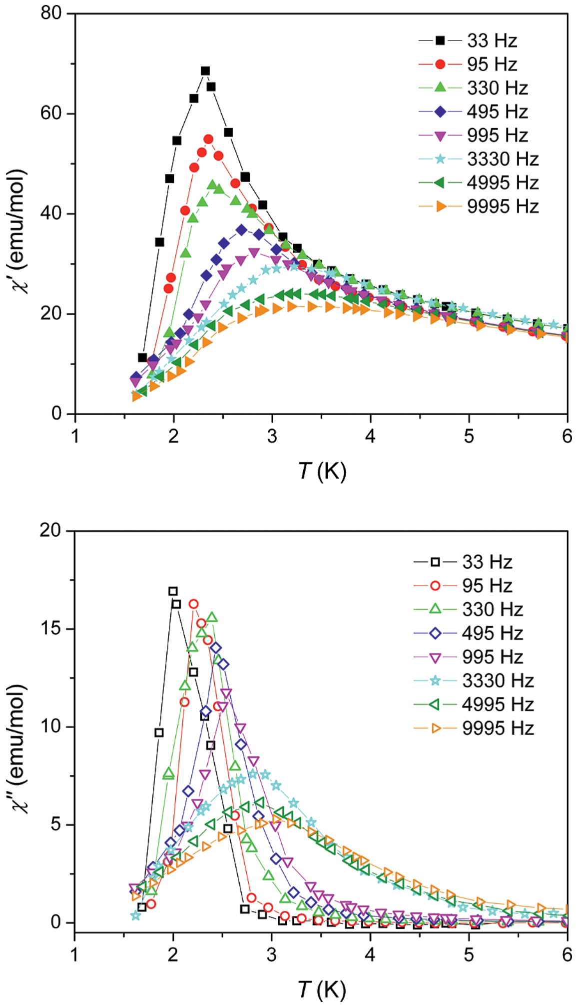

Figure 4. Temperature dependence of the real (χ', top) and imaginary (χ'', bottom) components of the AC susceptibility under zero DC field, collected at different AC frequencies.

The magnetization relaxation rate was analyzed below 5 K according to the Cole–Cole model, which accounts for a distribution of single relaxation processes. At fixed temperatures, χ' and χ'' were measured while the frequency, ω, of the AC field was varied from 10 Hz to 10 kHz in the absence of a static DC field. These data provided Cole–Cole plots (χ'' vs. χ' plots) for those different temperatures, such as that obtained at 3 K shown in Figure 5. The AC susceptibility data show a very good agreement with the generalized Debye model,[19] $\chi(\omega) = \chi_S + (\chi_T + \chi_S)/(1 + i\omega\tau)^{1-\alpha}$, where χ_S and χ_T are the adiabatic and isothermal susceptibilities, respectively, τ is the average magnetization relaxation time, and α is a parameter ranging from 0 to 1 related to the width of the distribution ($\alpha = 0$ corresponds to the ideal Debye model, with a single relaxation time). The fit obtained at 3 K is represented by the solid line giving the parameters $\chi_S = 179.3$ emu/mol, $\chi T = 111.2$ emu/mol, $\alpha = 0.04$, $\tau = 7 \times 10^{-5}$ s. The rather small α value is consistent with only one single magnetization relaxation process with a narrow distribution of relaxation times.

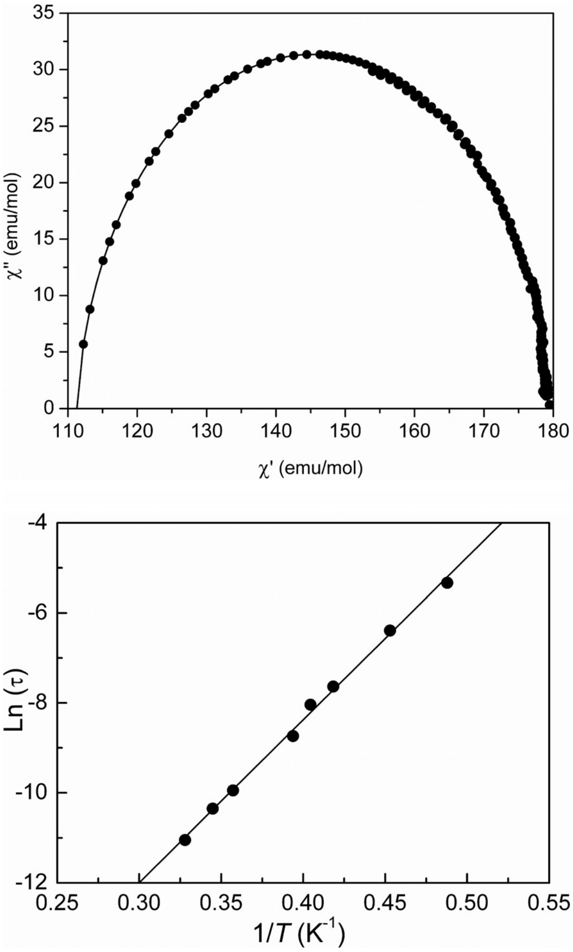

Figure 5. Top: Cole–Cole plot at 3 K. The solid line represents the least-square fits with a generalized Debye model to a distribution of single relaxation modes. Bottom: Plot of ln(τ) vs. T^{-1} with a fit to the Arrhenius law.

The relaxation times τ derived from the frequency-dependence measurements between 2 and 5 K present a thermally activated regime following the Arrhenius law, $\tau(T_f) = \tau_0\exp(\Delta/k_B T_f)$, (Figure 5 bottom) where τ_0, Δ, and k_B are the pre-exponential factor, the relaxation energy barrier, and the Boltzmann constant, respectively. From these data, an energy barrier of 36.1 K was obtained, with $\tau_0 = 1.21 \times 10^{-10}$ s. Down to 2 K there are no signs of approaching a temperature-independent regime of the relaxation time of the magnetization, which could be expected to occur at low temperatures as a result of either spin–spin relaxation or quantum tunneling effects.

The slow relaxation of magnetization with SMM behavior now appears to be common feature of many lanthanide[9,15] and actinide compounds.[20] Initially thought to occur as a consequence of multinuclear structure with different magnetic coupling constants between the ions, this behavior has been found more recently in single-ion compounds and therefore interpreted as a consequence of intrinsic ion anisotropy. In this compound, the Dy–Dy interactions cannot be neglected, and, to the best of our knowledge, this layered material is the first compound with a higher-dimensional network of lanthanide ions for which SMM behavior is observed.

In general, magnetic interactions of lanthanide ions with neighboring magnetic species are rather weak because of the inner character of 4f-electrons, and slow relaxation is an intrinsic effect due to single ion anisotropy. In this respect, it is worth noting that the Dy coordination in Dy–LLH is approximately square antiprismatic for the different sites, as in other well-known dysprosium compounds with SMM behavior. However, in this case, in each layer of the structure there is a dense network of Dy–Dy contacts at relatively short distances, either direct or mediated by bridging O atoms, and therefore the magnetic anisotropy may also result from the Dy–Dy interactions. The very large number of different contacts between the three inequivalent Dy atoms in the unit cell makes the analysis of the different types of possible Dy–Dy interactions rather complex. As shown in a recent review,[16] the SMM properties of Dy compounds, namely energy barriers and relaxation time, cannot be easily rationalized in terms of coordination geometry, and often compounds show weaker SMM properties with increasing nuclearity. These results support the idea that the observed slow relaxation probably stems mainly from single ion effects, and Dy–Dy interactions, although non-negligible, play only a secondary role.

Conclusions

This is the first example of single-molecule magnetic behavior in a layered rare earth compound. Up to now the interest in this kind of LLH compounds was mainly focused on their luminescent properties.[3,4] This new feature adds interest to these inorganic solids in molecular magnetism,[21] molecular spintronics,[22] and quantum computing,[23] and can open a new door in the search for new SMMs by suitable choice of LLH intercalation ligands.

Experimental Section

$Dy_8(OH)_{20}Cl_4{\cdot}6H_2O$ (Dy–LLH) was obtained as a polycrystalline powder by following a previously described procedure,[8] and IR spectra, powder X-ray diffraction (Figure S1), and thermogravimetry (Figure S2) confirm the purity and composition of the material. The crystal size and morphology of the samples were examined with a JEOL JSM-7001F field emission scanning electron microscope (Figure S3). Magnetic susceptibility measurements were performed on a polycrystalline sample of about 35 mg by using a 6 Tesla S700X SQUID magnetometer from Cryogenic Ltd. in the range 1.7–300 K, under applied magnetic fields up to 0.1 T. AC magnetic susceptibility measurements were performed with a 12 Tesla multicharacterization system MagLab 2000 (Oxford Inst.) with a typical AC field of 5 Oe in the presence and absence of external DC fields up to 0.1 T, down to a low-temperature limit of 1.5 K. All the data were corrected for diamagnetic contributions from the core diamagnetism estimated by using Pascal's constants as $\chi_D = -361.9\times10^{-6}$ emu/mol (see Supporting Information).

Supporting Information (see footnote on the first page of this article): Sample preparation and characterization data with experimental details.

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