Lanthanide Anisotropy

DOI: 10.1002/anie.201204838

Differentiation of Highly Anisotropic Tb^{III} and Dy^{III} with ^{57}Fe Mössbauer Spectroscopy**

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The magnetocrystalline anisotropy of many lanthanides makes them suitable for incorporation into molecular magnets, as witnessed in recent years by the use of lanthanides to modulate the properties of transition-metal magnetic materials, resulting in the rapid expansion of the field of 3d–4f coordination compounds.[1] The first lanthanide single-molecule magnets to be identified were a series of sandwich-shaped mononuclear complexes with phthalocyanine.[2] The oblate electron density distributions of Dy^{III} and Tb^{III} ions promote strongly axial single-ion anisotropies, which makes compounds in this type of environment function as single-molecule magnets. Although both ions have very similar anisotropy shapes, the terbium complex shows the highest anisotropy barrier.[2] This is because the sandwich structure of these compounds provides a crystal-field environment with a high axial symmetry, which leads to maximization of the anisotropy for Tb ions in comparison to dysprosium ions. This result does not make dysprosium ion less attractive in molecular magnetism: it is more flexible than terbium regarding interaction between the single-ion electron density and the crystal-field environment, and it is a Kramers ion for which the doubly degenerate m_J ground state is ensured. Although an appropriate design of the ligand-field anisotropy makes it possible to design and control the magnetic anisotropy of some lanthanides,[3] the anisotropy and its orientation for the Dy^{III} ion is still hard to predict using simple geometric considerations. Experimentally, however, using angle-resolved single-crystal magnetometry, it was possible to obtain the orientation of the principal axes of the magnetization of a Dy^{III} ion in a low-symmetry environment,[4] which could also be confirmed by ab initio calculations.

Although ^{57}Fe Mössbauer spectroscopy is still a qualitative approach in spotting lanthanide anisotropy,[5] it could nevertheless offer an useful alternative in iron-containing systems for angle-resolved magnetometry, which has stringent requirements in terms of crystal system, with the "difficult" triclinic system favored with just one molecule per unit cell.[4] Furthermore, this method has been shown to be applicable for studying polynuclear coordination clusters and does not require single crystals.

Herein it is shown how ^{57}Fe Mössbauer spectroscopy can easily assess the difference between anisotropy of Dy^{III} and Tb^{III} ions. A series of coordination cluster molecules with different topologies and Fe/Ln ratios[5,6] (Figure 1) has been studied, from which only Dy and Tb derivatives are analyzed in terms of spotting the difference between their anisotropies.

The first examples are two tetranuclear complexes $[Fe^{III}_3(Tb/Dy)O_2(CCl_3COO)_8H_2O(THF)_3]$, denoted **$Fe_3Ln$**.[6a] These isostructural molecules have a "butterfly" core consisting of two $Fe_2Ln(\mu_3\text{-}O)$ triangular "wings" which share a common Ln–Fe "body". The antiferromagnetic coupling within the Fe_3 cluster was confirmed by the opposite trend of the field dependence of the two Fe_{wing} sextets as compared with the third sextet of the Fe_{body}. The spectra at 3 K in zero

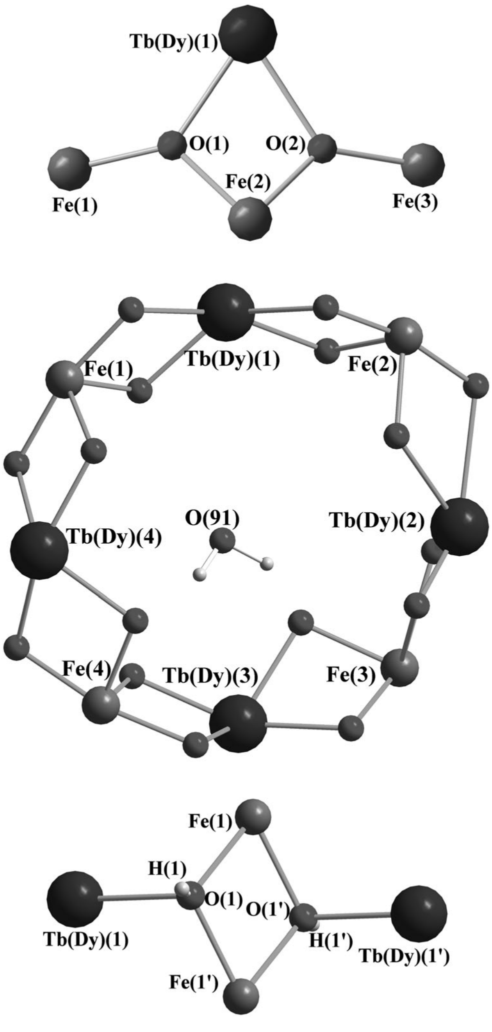

Figure 1. The cores of Fe-Ln compounds discussed herein: **Fe_3Ln** (top),[6a] **Fe_4Ln_4** (middle),[6b] and **Fe_2Ln_2** (bottom).[5]

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[**] This work was supported by the DFG-funded transregional collaborative research center SFB/TRR 88 "3MET". The author also thanks Prof. Annie K. Powell for her support.

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and weak applied external magnetic field are clearly resolved into three subspectra with relative intensities of 1:1:1. For the higher intensity subspectrum, the total field at the nucleus $H_{eff} = H_{appl} + H_{hf}$, which is the sum of the applied (H_{appl}) and magnetic hyperfine fields (H_{hf}), decreases with increasing H_{appl}, and the sextets move inwards indicating a negative magnetic hyperfine interaction for Fe_{wing} atoms. On the other hand, the magnetic hyperfine interaction for the Fe_{body} atoms in the lower-intensity subspectrum is positive and the sextet moves outwards. The observed changes in the internal magnetic field values are consistent with the effect of local spin polarization along the applied magnetic field direction. Mössbauer spectra (MS) in an applied field were obtained in a field oriented perpendicular to the γ-radiation direction and parallel to sample holder. For applied magnetic fields in **Fe_3Tb** with $H_{appl} \geq 1$ T, the $\Delta m = 0$ lines (second and fifth) of the sextets become more intense, indicating that the nuclear spin moments of the iron centers tend to orient parallel to the applied field, thus demonstrating that under applied external magnetic field the angle between H_{eff} and direction of γ-rays also changes, as would be physically expected.

Whereas the total evolution of the MS for **Fe_3Dy** (Figure 2, bottom) in magnetic field is similar to that of **Fe_3Tb**, there is nevertheless a small but important difference. The MS for **Fe_3Dy** shows rather minor or negligible changes in the intensities of the second and fifth absorption lines, and this demonstrates a clear resistance of Fe magnetic moments to align themselves along the applied field direction. The reason for such different behavior in applied magnetic field lies in the large and specific anisotropy of Dy and Tb ions. The anisotropy of the ground state of both ions depends on the crystal field acting on the orbital moment. It appears that the type of crystal field around these two ions in these two compounds leads to an anisotropic ground state for Dy ion, which is not the same as that of the Tb ion. Although the Tb ion is also strongly anisotropic in certain crystal field environments, being a non-Kramers ion the anisotropic ground state requires that a more exact axial symmetry be preserved, which is not the case in present two compounds. It seems that when an external magnetic field is applied to these two compounds, the nuclear spin moments of iron ions in **Fe_3Tb** compound align along the direction of the applied magnetic field, whereas in case of **Fe_3Dy** compound their preferred direction is dictated by the anisotropy of the Dy ions. For the Dy^{III} ions, even applied fields of several Tesla are insufficient to turn their moments significantly away from their local quantization axes, which suggests that the observed stiffness of the Fe^{III} moments originates in fact from the interaction of Fe^{III} with the Dy^{III} ions in the molecule. Given that high-spin Fe^{III} is a relatively isotropic ion, this suggests that the major contribution to the magnetic anisotropy is induced in **Fe_3Dy** by the Dy^{III} ions, and that these also dictate the easy axis of the molecular magnetization and the direction of the iron nuclear spin moments. Being non-anisotropic in actual crystal field, the Tb ions have a minor influence on the Fe^{III} moments and thus the MS show a behavior typical for isotropic ions.

Other examples analyzed herein are two octanuclear complexes $[Fe^{III}_4(Tb/Dy)_4(teaH)_8(N_3)_8(H_2O)]$ (teaH = triethanolamine), denoted **Fe_4Ln_4**.[6b] The structure of these two isostructural compounds is based on a ring-like $\{Fe_4Ln_4\}^{24+}$ core with alternating Fe^{III} and Ln^{III} centers. Magnetic susceptibility data show ferromagnetic interaction between the Fe and the Ln^{III} centers. For a polycrystalline sample, the type of magnetic ordering can be determined from measurements of MS in external magnetic fields. For a ferromagnetic material, an alignment of the magnetic moments along the external field H_{appl} with a concomitant rotation of the internal field is expected so as to reduce the nuclear hyperfine field. As seen from the Mössbauer spectra at 3 K in external fields of 3 and 5 T (Figure 3), an additional magnetic splitting does not occur (as in case of **Fe_3Ln**), but the positions of the peaks shift slightly inwards, that is, the hyperfine field is slightly reduced.

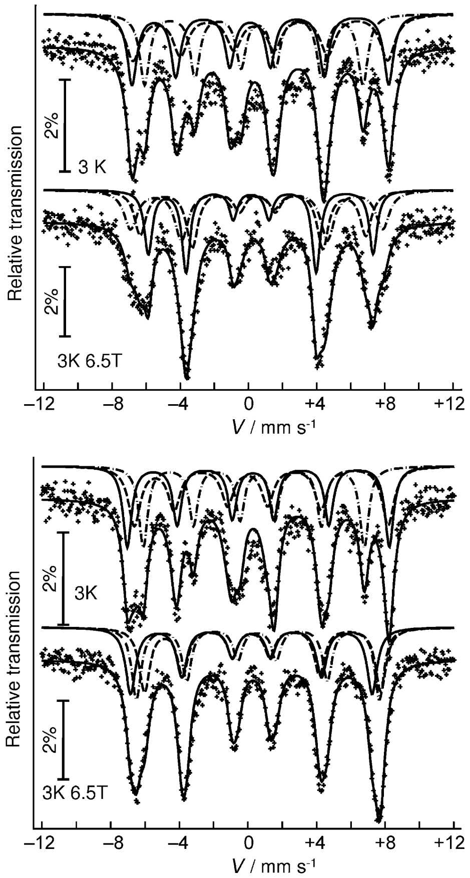

Figure 2. Mössbauer spectra of **Fe_3Tb** (top) and **Fe_3Dy** (bottom) at 3 K without and with an applied field.

Although the spectrum for **Fe_4Dy_4** has been fitted with one sextet, the fit for **Fe_4Tb_4** was only possible with two sextets having almost the same value for δ, but different quadrupolar shifts, ε, and hyperfine fields. Having the same environment, but different anisotropy of the ground state, it would be expected that a different direction of the easy axes of magnetization on Dy^{III} and Tb^{III} ions would be observed, which in turn will influence the ^{57}Fe Mössbauer hyperfine parameters (especially the quadrupole splittings, which depend on the orientation of the electric field gradient, dictated by the lattice, relative to the magnetization direction)

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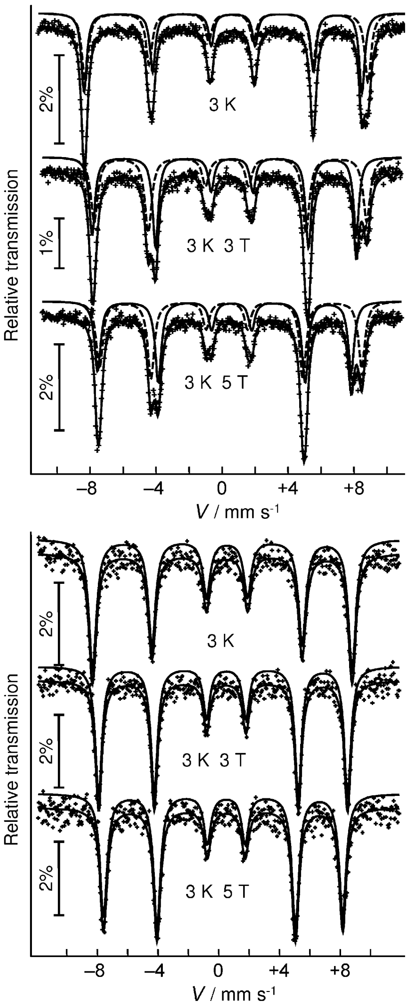

Figure 3. Mössbauer spectra of Fe_4Tb_4 (top) and Fe_4Dy_4 (bottom) at 3 K without and with an applied field.

of the adjacent iron ions. The fact that we observe one sextet in case of $\mathbf{Fe_4Dy_4}$ and two sextets for $\mathbf{Fe_4Tb_4}$ could be explained as follows. As the environments of all four Fe ions are different, different quadrupole splitting (and shifts) and orientations of the electronic spins and thus sextets with different effective magnetic fields are to be expected. This is what we see in case of $\mathbf{Fe_4Tb_4}$. In case of $\mathbf{Fe_4Dy_4}$ due to much stronger anisotropy of Dy ions in the respective crystal environment, the spins of irons are nearly all parallel and their direction is dictated not by the crystal fields, but by the direction of the Dy anisotropy. Given that Tb ions require a more exact axial symmetry to be preserved, they are isotropic in the actual crystal field and have a negligible influence on the Fe^{III} spins, and therefore the MS shows a behavior typical for isotropic ions.

The last two examples are the tetranuclear complexes $[Fe^{III}_2(Tb/Dy)_2(OH)_2(teaH)_2(p\text{-}CN\text{-}C_6H_4COO)_6]$, denoted $\mathbf{Fe_2Ln_2}$.[5] They crystallize in triclinic space groups, with the central cores consisting of a planar Fe_2Ln_2 rhombus (Figure 1, bottom).

The central $\{Fe_2(OH)_2\}$ unit is antiferromagnetically coupled and thus has an $S = 0$ ground state, as determined from MS at 3 K in applied magnetic field on the $\mathbf{Fe_2Tb_2}$ and $\mathbf{Fe_2Dy_2}$ analogues (Figure 4) as well as on the Y^{III} analogue.[5] Remarkable differences are observed at 3 K in zero applied magnetic field. The Mössbauer spectrum of $\mathbf{Fe_2Tb_2}$ is still paramagnetic (doublet; (Figure 4, top), as seen for other reported compounds containing the $\{Fe_2(O)_2\}^{2+}$ core[7] confirming for $\mathbf{Fe_2Tb_2}$, as in case for Fe_2Y_2,[5] the presence of a diamagnetic ground state, $S = 0$, for the central Fe_2 unit), whereas the MS of $\mathbf{Fe_2Dy_2}$ shows a magnetic sextet with hyperfine field of about 20 T at the iron nuclei superimposed on a broad absorption doublet (Figure 4, bottom). This is a huge hyperfine field, which is almost equal to the field provided by two unpaired electrons if we consider values obtained for oxides (ca. 11 T per $S = 1/2$).[8]

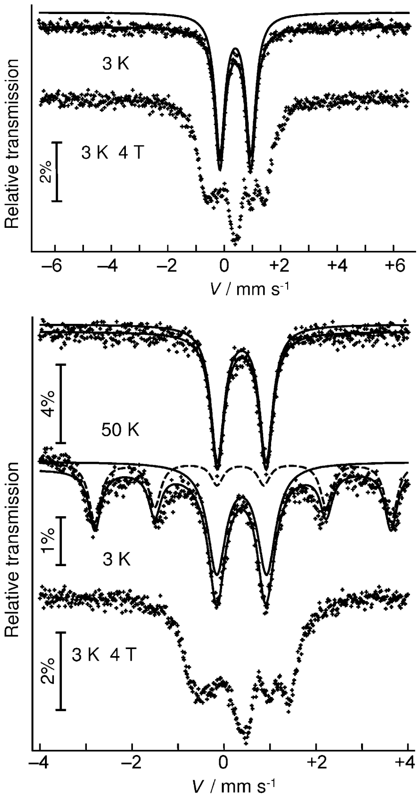

Figure 4. Mössbauer spectra of Fe_2Tb_2 (top) at 3 K and 3 K and applied external field of 4 T (the simulation parameters are $\Delta E_Q = 0.98$ mm s^{-1}, $\delta = 0.40$ mm s^{-1}, and $\eta = 1.0$, assuming an isolated ground state with $S = 0$) and Fe_2Dy_2 (bottom) at 50 K, 3 K without and with applied field (see ref. [5] for hyperfine parameters).

Moreover, if we apply an external magnetic field, the magnetic inset in spectrum of $\mathbf{Fe_2Dy_2}$ vanishes with increasing field[5] and the Mössbauer spectra at high fields exhibit patterns typical of a diamagnetic complex. This raises two questions: Why is the magnetic inset missing in case of $\mathbf{Fe_2Tb_2}$ compound, and why does the magnetic inset in $\mathbf{Fe_2Dy_2}$ spectrum vanish under external field? As in the cases already discussed for the $\mathbf{Fe_3Ln}$ and $\mathbf{Fe_4Ln_4}$ examples, the low-symmetry environment around Dy and Tb ions in these $\mathbf{Fe_2Ln_2}$ examples leads to an anisotropic ground state for Dy ion, but not for Tb. Being anisotropic, the Dy ions interact

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more strongly with the central diamagnetic Fe_2 unit, and a magnetic inset results. On applying an external magnetic field, it appears that the applied field affects the ground state of Dy^{III} by mixing in excited state wave functions into the ground state, thereby lowering the energy of the system and resulting in the change in or a complete quenching of anisotropy direction. This is a quite unusual observation, because to overcome the anisotropic forces in rare earth metal ions usually stronger applied fields would be required.

This study has shown how using ^{57}Fe Mössbauer spectroscopy, microscopic properties of iron ions can be detected when they are affected not only by their electronic structure and coordination environments but also by other delicate effects induced by their nearest neighbors, here lanthanides. We have illustrated how in the same crystal-field environment, Dy and Tb ions show different degrees of anisotropy and how this anisotropy can be qualitatively detected using an indirect method. Another surprising observation is how a weak applied field can destroy the effect of the ligand field responsible for the anisotropic behavior of the dysprosium ions. In spite of the great success obtained with ab initio methods in the calculation of anisotropic magnetic properties,[4] the full theoretical description of the real grounds for the slow relaxation of magnetization and capricious anisotropy of lanthanides is still lacking. We hope that we have given a picture of how ^{57}Fe Mössbauer spectroscopy may complement theoretical and other experimental methods to obtain a consistent picture of the electronic structure of lanthanide based polynuclear systems and to detect the difference between Ln ion anisotropies within the same ligand-field environment. Although the concept of using ^{57}Fe Mössbauer spectroscopy in characterizing magnetic properties of lanthanide ions is not yet an accepted perspective (which is mostly due to lack of new spin-Hamiltonian approach), the unchallenging assessment used herein already provides a consistent and reasonable model interpretation.

Received: June 20, 2012
Published online: September 3, 2012

Keywords: anisotropy · iron · lanthanides · Mössbauer spectroscopy

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