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The Smallest Compass

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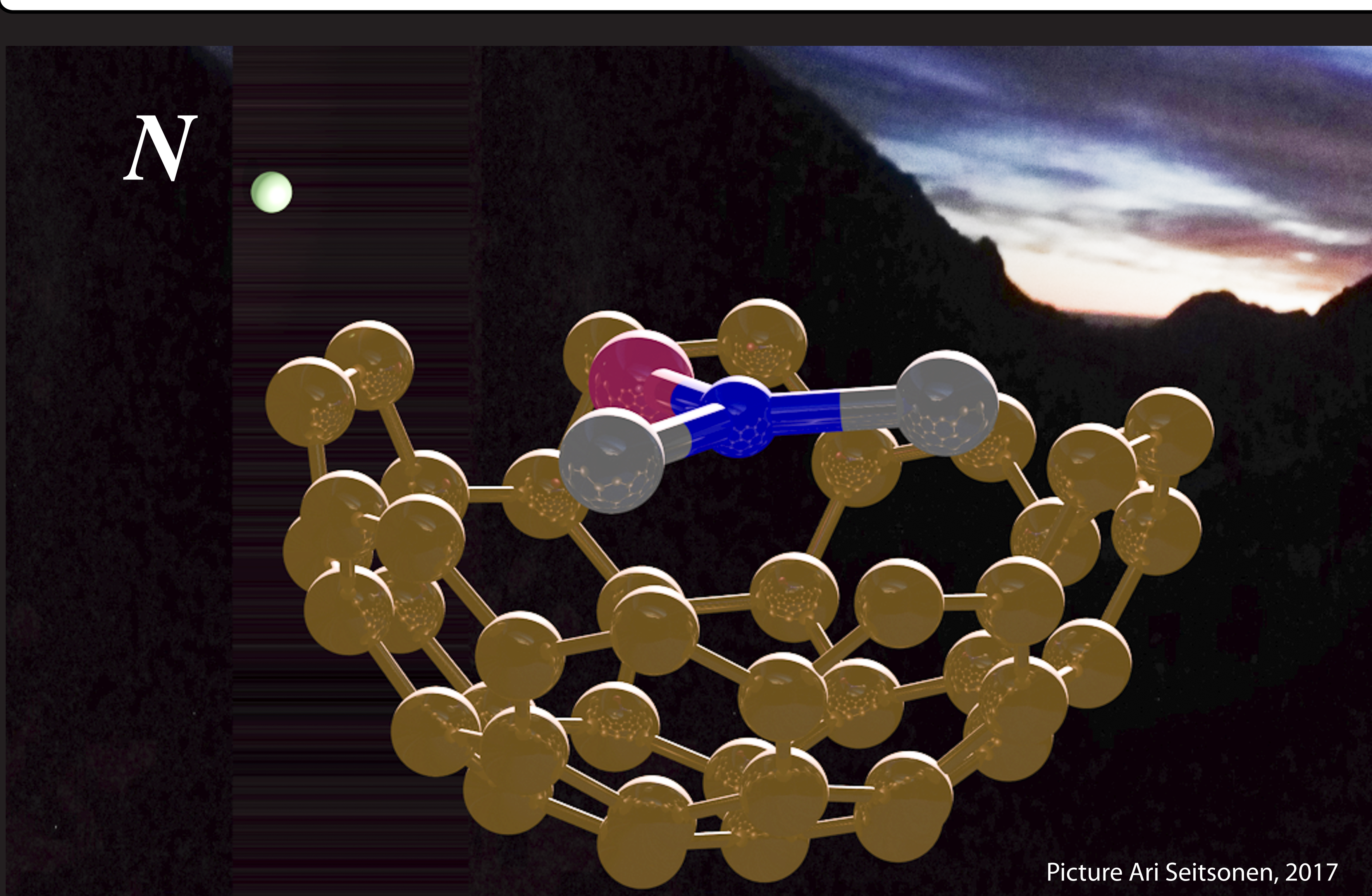
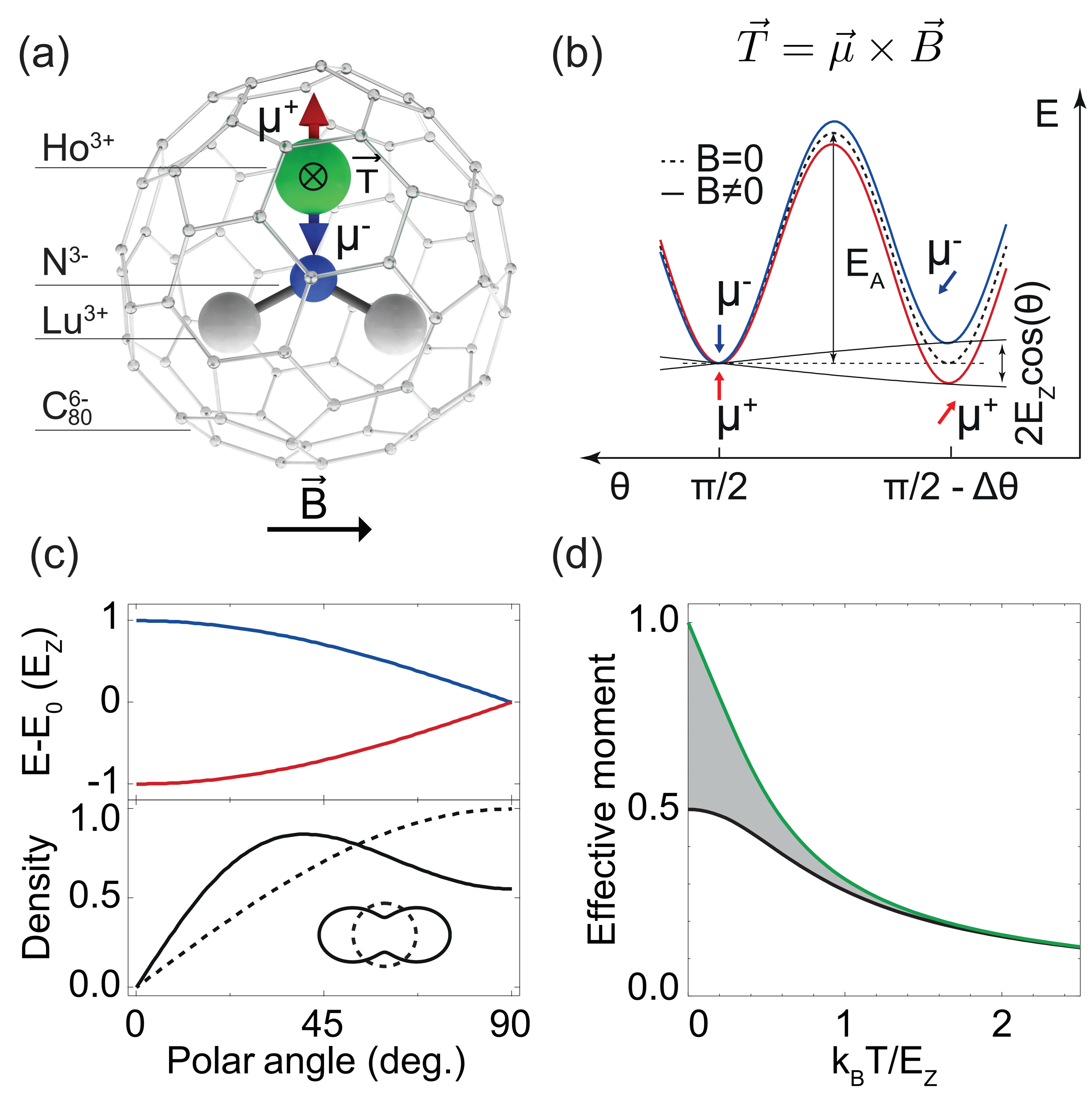


Like in a compass, magnetic moments of single atoms may be oriented in an external magnetic field and if the torque is transferred to the surrounding of the moment, molecule or macroscopic rotation may result. In order to search for this orientation effect in the single atom limit the ratio X between Zeeman energy and thermal energies $\mu_B B/k_B T$ has to be considered.

Here we report the alignment of the endohedral unit of $HoLu_2N@C_{80}$ (Figure 1(a)) in an externally applied magnetic field B [0]. The endohedral unit is subject to thermally activated hop-rotation between equivalent low energy conformations [1, 2], way below the freezing temperature of the carbon cages in a solid, which is 250 K for the case of solid C_{60} [3]. The external magnetic field imposes a bias in the endohedral hop-rotation via the torque on the Ho^{3+} ion that is transferred on the endohedral unit because of the magnetic anisotropy, i.e. the alignment of the Ho magnetic moment in the strong ligand field [4].

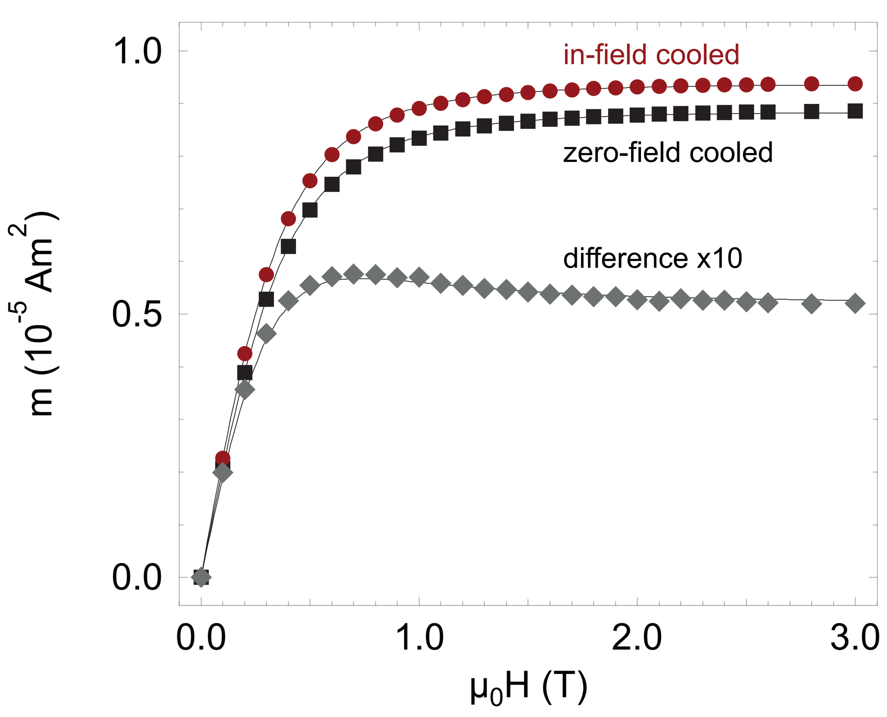
$HoLu_2N@C_{80}$ endofullerenes were produced by arc-discharge synthesis using corresponding metal oxides and guanidine thiocyanate as the nitrogen source followed by several extraction and separation processes. The sample used for this work contained 20% of diamagnetic $Lu_3N@C_{80} - I_h$ [1].

Endohedral ordering in a B-field



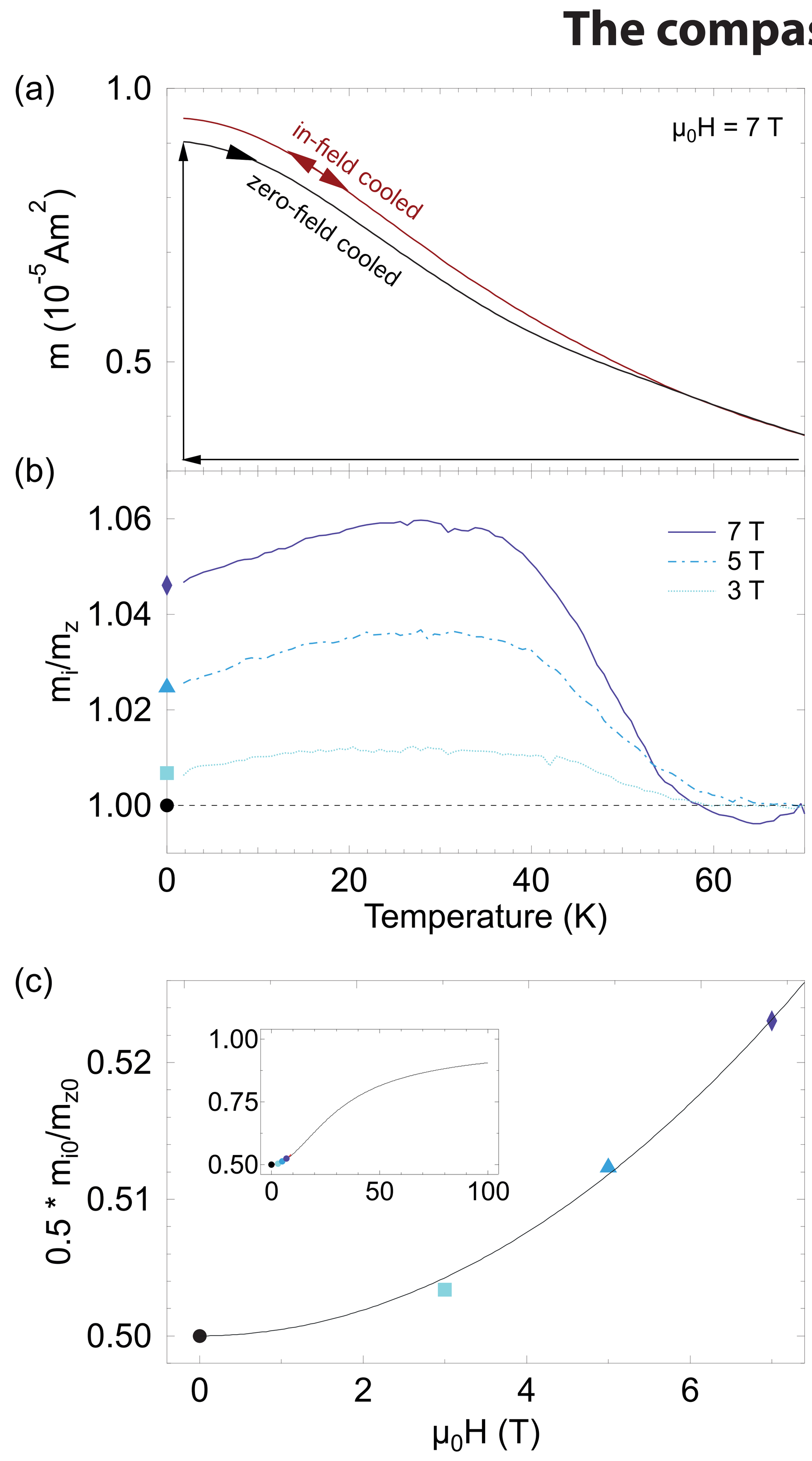
(a) A magnetic field B exerts a torque T on Ho magnetic moment μ. (b) The energy barrier E_A separates preferred orientations. The Zeeman energy imposes a bias for magnetic moments parallel to the B field. (c) (top) Zeeman splitting and (bottom) Equilibrium angular density distribution for E_Z = 0 (dashed line) and k_BT/E_Z = 1/2 (solid line). (d) Effective magnetic moment in thermal equilibrium vs. k_BT/E_Z for freely rotating endohedral units (green) and for frozen, isotropically distributed magnetic moments (black). The effect of in-field cooling should lie within the green and the black curves in the shaded area.

Magnetization curves



Magnetization m (raw data) vs externally applies magnetic field μ_0H at 1.8 K. Both data from zero-field (black squares) and in-field 7 T (red circles) cooled sample were fitted (solid lines) simultaneously with a model of isotropically (randomly) oriented Ho magnetic moments and an equilibrium distribution with a freezing temperature T_F. The fits yield N = $2\cdot10^{17}$ Ho atoms, 9.55 μ_B for the Ho magnetic moment and a T_F of 52.3 K for B = 7 T and $\beta = 5\cdot10^{-4}$ K/s. Grey diamonds are the difference between zero-field and in- field cooled. The solid line is the difference of the corresponding fits.

The compass effect

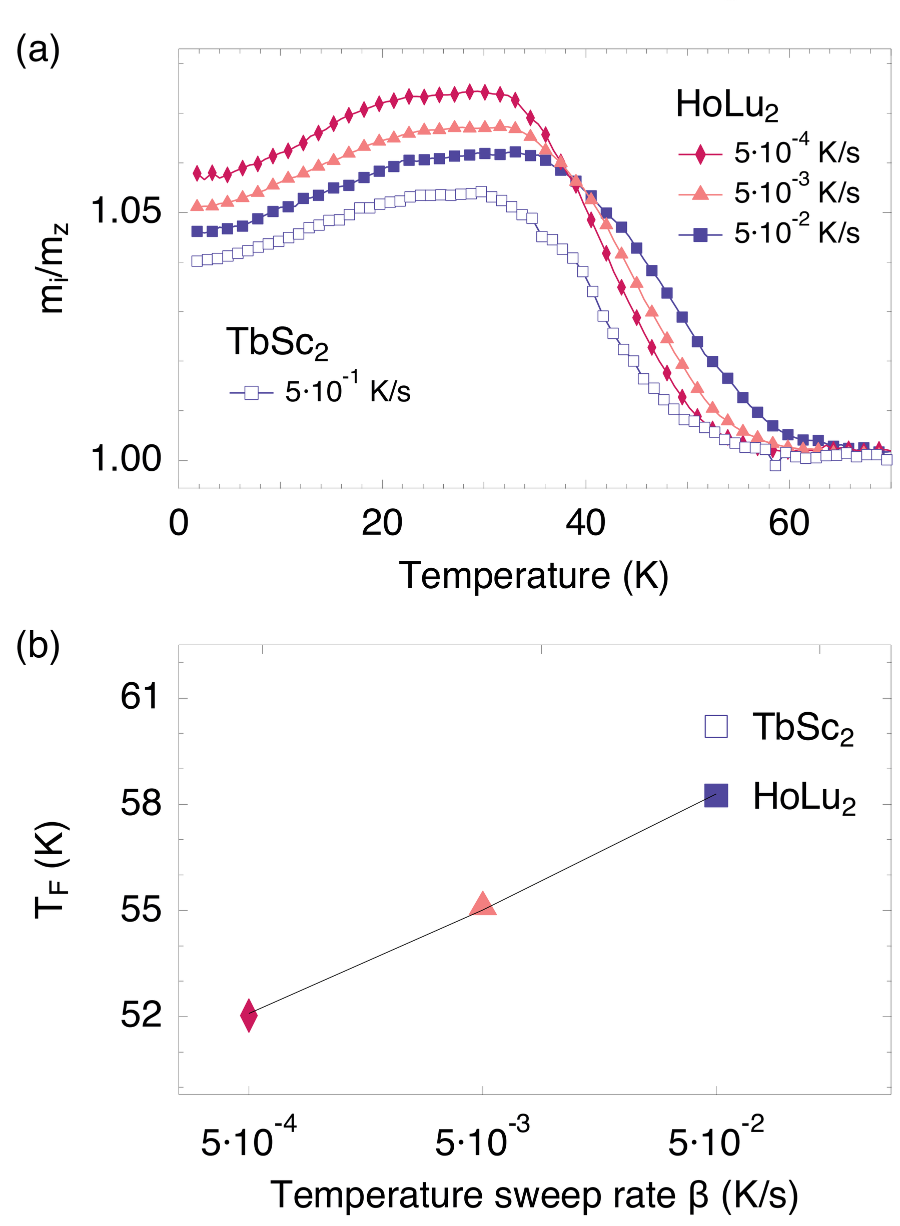


(a) Temperature dependence of the magnetic moment m for zero-field cooled (black) and in-field cooled (red) $HoLu_2N@C_{80}$.

(b) Ratio of the magnetic moment for in-field and zero-field cooled m_i/m_z for different external magnetic fields (7 T, 5 T, 3 T).

(c) $m_{i0}/m_{z0}/2$ extrapolated to 0 K. From the curvature of the parabola the Zeeman energy:k_BT_F ratio is inferred. (inset) Prediction for higher magnetic fields.

Extracting kinetic parameters



(a) Ratio of magnetic moment for in-field and zero-field cooled m_i/m_z

(b) Freezing temperatures $T_F(\beta)$ determined from fits of magnetization curves.

A first order kinetics model with single barrier E_A was used to obtain the kinetic barrier and the attempt frequency ν using the formula: $m(t+\Delta t) = m(t) + \Delta m_E(1-\exp(-\Delta t/\tau))$, $\Delta m_E = m_E(t + \Delta t) - m(t)$. $\tau = (\nu \exp(-E_A/k_BT))^{-1}$

The best fit of first order kinetics barrier height E_A/k_B = (2145 ± 20) K attempt frequency $\nu = 1.8\cdot10^{14\pm0.15}$ s^{-1} for $HoLu_2N@C_{80}$.

References

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