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Novel lanthanide borohydrides: magnetism of all flavours

<u>W. Grochala</u>¹, T. Jaron¹, W. Wegner², D. Pancerz² ¹Univ. Warsaw, CENT, Warsaw, Poland, ²Univ. Warsaw, Fac. Physics, Warsaw, Poland

The rare-earth metals have high magnetic moments and a diverse range of magnetic structures. However, due to the inner-transition nature of lanthanide elements, the valence f orbitals of their trivalent cations usually do not mix substantially with the ligands' orbitals in the chemical compounds. The majority of lanthanide compounds is thus characterized by a rather ionic metal-ligand bonding and is hosting only weak crystal field effects. Several exceptions known encompass the valence fluctuation systems consisting of Sm, Ey, Tm or Yb combined with less electronegative nonmetal ligands (Si, S, Se, B etc.) or metals (Murani 2003 and references therein). This important class of lanthanide compounds for which crystal field effects are strong includes the classical systems: Yb3Si5 (landelli et al., 1979), YbB12 (Altshuler et al., 1998), and Yb3H8 (Drulis et al., 1999). Even elemental Yb and Eu metals show valence transition at elevated pressure from di- to trivalent (Takemura & Syassen, 1985). These valence fluctuations are typically accompanied by electric resistivity changes: $Ln(2+) \rightarrow Ln(3+) + e-$. Lanthanide borohydrides, Ln(BH4)3, constitute a rather poorly explored and novel group of compounds (Olsen et al., 2014). They are conveniently prepared via mechanochemical synthesis approach (high-energy milling). Quasi-ternary alkali metal-lanthanide borohydrides, MLn(BH4)4, are also available using this synthetic procedure (Wegner et al., 2013 [1] & Wegner et al., 2014 [2]). Here we explore for the first time the magnetic properties of Ln(BH4)3 and MLn(BH4)4 compounds, with particular emphasis on the thermally unstable systems (Ln= Sm, Yb and Eu) as contrasted with the reference case of much more thermally stable derivatives of ordinary lanthanides (Ln = Ho). We show that remarkably strong mixing of Ln(4f) and H(1s) states which causes thermal instability: $Ln(3+) + BH4 \rightarrow Ln(2+) + BH4 \bullet$ leads in some cases to strong magnetic superexchange interactions between Ln(3+) centers [3].

[1] Wegner W, Jaroń T, Grochala W, ACTA CRYST C 69(11): 1289-1291 2013, [2] Wegner W, Jaroń T, Grochala W, submitted 2014, [3] Wegner W, Pancerz D, Jaroń T, Grochala W, submitted 2014

Ln(3+) + BH₄⁻ → Ln(2+) + [BH₄•] lack of thermal stability enhanced magnetic interactions

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