

Formation of an Fe-H complex anion in YFe₂: adjustment of imbalanced charge by additional Li as an electron donor

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Supporting information

Experimental procedures

Synthesis of the complex hydride YLiFeH₆

A button ingot of YFe₂ was prepared by arc-melting high-purity metals Y and Fe (99.9% and 99.5%, respectively, Nilaco Corporation, Japan) under Ar. After the ingot was pulverized and sieved (100–300 μm), the powder was mixed with LiH (99.9%, Aldrich Co. Ltd.) in the molar ratio of 1:1 by mechanical milling at 400 rpm using a planetary Fritsch P7 with 20 steel balls (7 mm in diameter) in a hardened steel vial (30 cm³ in volume) for 2 h under 0.1 MPa Ar. We used LiH instead of Li because ductile Li is unsuited for use in mechanical milling. The hydrogenation was conducted for the mixed powder in the temperature range of 873–1073 K at the hydrogen pressure of 6 GPa for 2–12 h with a cubic anvil-type high pressure apparatus in a similar manner as described previously.^{S1}

Structural characterizations

The products recovered at ambient temperature and pressure were characterized by powder X-ray diffraction (XRD) measurements on a PANalytical X'Pert diffractometer with Cu-Kα radiation and a semiconductor detector for high-speed measurement and a high-resolution synchrotron x-ray powder diffractometer (SR-XRD, monochromatized 20 keV x-rays, λ = 0.61993 Å) constructed in the BL22XU at SPring-8, Japan, and by Raman spectroscopy using a Nicolet Almega-HD spectrometer equipped with color-CCD and 532-nm laser with back scattering geometry.

Theoretical procedures

All calculations were performed using a plane-wave basis and projector augmented wave (PAW) method^{S2} within the generalized gradient approximation (GGA) with exchange and correlation functional of Perdew, Burke, and Ernzerhof (PBE),^{S3} as implemented in Vienna Ab-initio Simulation Package (VASP).^{S4} Well converged plane-wave basis sets, cutoff energy of 800 eV, were employed. The Brillouin zone sampling was performed using the special k points method^{S5} with a 8 × 8 × 8 mesh.

Detailed electronic structure of YLiFeH₆

We first checked for the magnetic solutions, but found a non-spin-polarized structure is the most stable, reflecting the octahedral ligand coordination for the only magnetic constituent Fe, which stabilizes the non-spin-polarized configuration. Figure S1 shows (a) the calculated band structure for 9 atom primitive cell of YLiFeH₆ along the high-symmetry line in the Brillouin zone, and (b) the corresponding electronic density of states (DOS). Roughly speaking, the valence bands are comprised of six H 1s derived and three Fe 3d derived bands, making up an 18 electron count as in most of the complex hydrides with a K₂PtCl₆ structure such as Mg₂FeH₆.^{S6} The H 1s derived bands provide the DOS from -7.8 eV to -1.9 eV which is divided into two branches. The lower branch extends from -7.8 eV to -5.5 eV is a one-fold *a*_{1g} band which is hybridized with the Fe 4s state, as may be seen from the moderate Fe 4s character in the corresponding DOS. The higher bands lie from -4.7 eV to -1.9 eV are three-fold and two-fold degenerated *t*_{1u} and *e*_g combination hybridized with the Fe 4p and Fe 3d states, respectively. The Fe 3d states are split into the lower-lying *t*_{2g} bands, which give rise to the DOS peak just below the Fermi level, and the higher-lying *e*_g branches, which form the bottom of the conduction bands, providing a band-gap of 1.7 eV. Thus the valence bands consist of six formally bonding H *s*-Fe *d* combinations, *a*_{1g}, *t*_{1u} and *e*_g, and three formally nonbonding *t*_{2g} bands, providing the thermodynamically stable complex hydride due to the absence of any anti-bonding H *s*-Fe *d* occupations. Since there is modest contribution of Y 5*sp* and Li 2*sp* states (see Fig. 5 in the text) to the valence bands, Y and Li can be thought as the trivalent Y³⁺ and Li⁺ which donate a total of four electrons to the FeH₆ unit, pointing to the charge state Y³⁺Li⁺[FeH₆]⁴⁻.

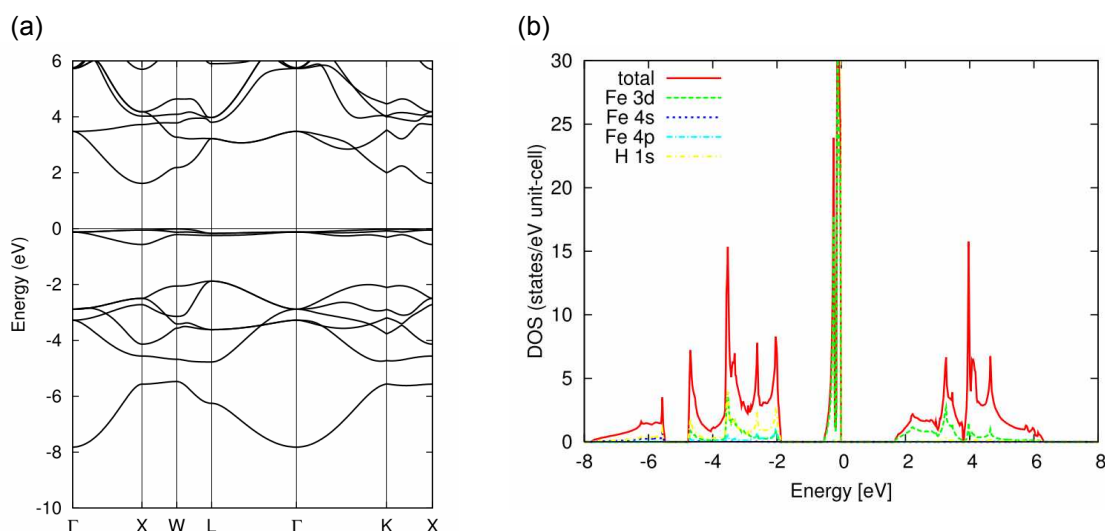


Figure S1. (a) Calculated band structure along the high-symmetry line in the Brillouin zone and (b) electronic density of states and H 1s, Fe 3d, Fe 4s and Fe 4p projections of relaxed 9 atom primitive cell of YLiFeH₆. The energy zero is set at the valence-band maximum.

References

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