Crystal electric field leading to giant magnetocaloric effect for hydrogen liquefaction

Liquid hydrogen (LH_2) is widely expected to serve as medium for storing renewable energy resources. Although LH_2 can store hydrogen at the highest density in all the media, there is a serious technical bottleneck on cooling method with conventional gas compression technique where the cooling efficiency near hydrogen condensation temperature, 20 K, is much lower than ambient temperature. Recently, magnetic refrigeration (MR) has been extensively studied as an alternative technique to the conventional gas compression cooling in hydrogen liquefaction[1]. The MR materials, which have a large magnetocaloric effect (MCE) identified by magnetic entropy change with the application of magnetic field ΔS_M, are the most important factor in MR cooling system.

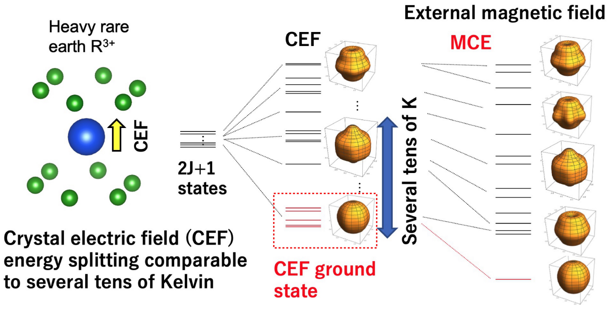

Fig. 1. Schematic illustration of complicated crystal electric field (CEF) energy level splitting in heavy rare earth ions (with schematic drawings of electrons wave functions in each energy level), and Zeemann splitting of the CEF levels giving a large magnetocaloric effect. For several tens of kelvins energy scale, CEF splittings are generally comparable to system temperature in heavy rare earth system.

Heavy rare earth compounds are the most promising MR material candidates. Because, a large magnetic entropy is potentially caused by the large number of states due to the magnetic entropy obeying $S_M = R \ln(2J+1)$, where R is the gas constant and J is total angular momentum quantum number. Unlike MR for extremely low temperature ($T < 1$ K) or for around room temperature range, MR for hydrogen liquefaction is for the target temperature range from 20 K (hydrogen condensation temperature) to 77 K (liquid nitrogen temperature for pre-cooling). Such several tens of kelvin temperature range is generally comparable to the crystal electric field (CEF) energy levels for heavy rare earth ions. (schematic picture is illustrated in Fig. 1) Magnetic entropy change (ΔS_M) is strongly related to degeneracy of CEF ground state, which is lifted by external magnetic field through Zeemann splitting, leading to MCE. In this context, understanding the CEF level scheme for heavy rare earth compounds is important for designing the MR materials for hydrogen liquefaction.

In inelastic neutron scattering (INS) experiment, one can purely see the CEF energy levels by measuring the energy spectrum in the paramagnetic phase due to absence of internal magnetic field induced by the ferromagnetic long-range ordering. As an example, we chose the MR material HoB_2 with giant MCE to evaluate the CEF energy level schame. HoB_2 has been recently discovered to show very large $|\Delta S_M|$ value near hydrogen liquefaction temperature[2]. The INS experiment was carried out with the High Resolution Chopper spectrometer (HRC) beamline. The experimentally determined CEF level scheme shown in Fig. 2(a) successfully explained

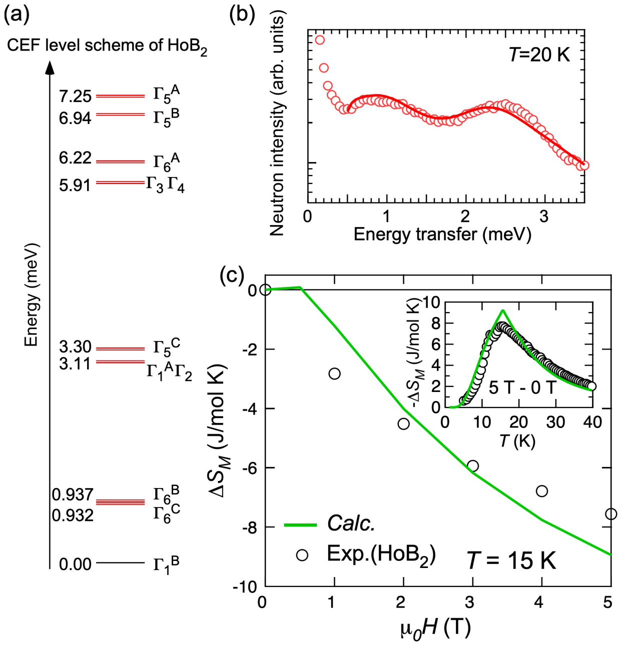

Fig. 2. (a)Crystal electric field (CEF) level scheme in HoB_2 was determined by the present neutron scattering experiment. (b)The neutron intensity (open circle) was successfully explained by theoretical calculation curve (solid line) with the CEF parameters. (c)Magnetic field and temperature dependence of magnetic entropy change (open circle) is roughly consistent with those calculated with the mean-field calculation with the determined CEF parameters. (solid line) The data were taken from Ref. [3].

the measured energy spectrum (Fig. 2(b)). In order to calculate magnetic entropy change with the determined CEF parameters, we conducted the mean-field calculation, which successfully reproduced the ΔS_M, observed in previous magnetization measurement[2](Fig. 2(c)).

We also have calculated the ideal CEF level schemes for general heavy rare earth ions with site symmetries, cubic O_h and hexagonal D_{6h}, to obtain the largest $|\Delta S_M|$ with the applied magnetic field of 5 T at 20 K, by using the mean-field calculations. The calculation results are summarized in Fig. 3. The maximum $|\Delta S_M|$ for Ho^{3+} with the hexagonal symmetry for powder case, corresponding to HoB_2 case, is 10.1 J mol^{-1} K^{-1}, which is 30 % larger than that of HoB_2. We therefore found that there is still room to improve $|\Delta S_M|$ even in one of the largest MCE materials, HoB_2.

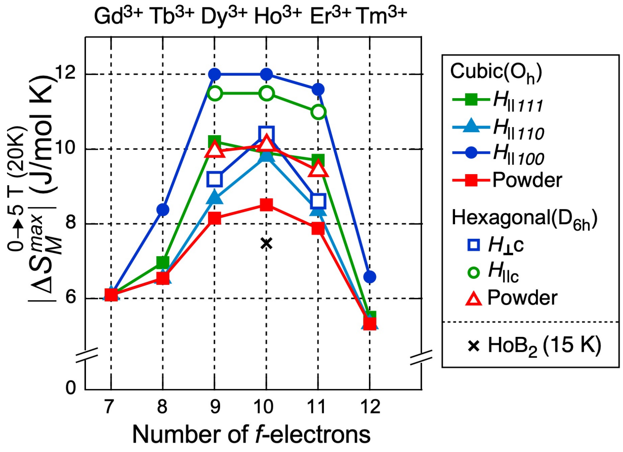

Fig. 3. Heavy rare earth ion dependence of the maximum magnetic entropy change for the cubic (O_h) and hexagonal D_{6h} symmetries. The cross symbol denotes the experimental value of HoB_2. The data were taken from Ref. [3].

Finally, we have studied the CEF level scheme and MCE for the special case of HoB_2 and general heavy rare earth ions, which provided ideal CEF parameters leading to a large ΔS_M. It is hoped that the relationships presented here gives additional guideline for searching compounds with a large MCE and the further MR-materials design.

References

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