

Crystal Electric Field Level Scheme Behind Giant Magnetocaloric Effect for Hydrogen Liquefaction

1. Introduction

Magnetic refrigeration, which is known as a cooling method using a magnetic field, has been actively researched so far mainly for application to near room temperature or extremely low temperatures below 1 K [1]. On the other hand, recently, magnetic refrigeration in the intermediate temperature range (on the order of several tens of K) has been attracting attention as a new cooling method for efficiently cooling liquid hydrogen [2]. Magnetic refrigeration for the purpose of hydrogen liquefaction requires efficient cooling in the temperature range from the hydrogen liquefaction temperature of 20 K to around 77 K (assuming precooling with liquid nitrogen). In magnetic refrigeration, the magnetic entropy change (ΔS_M) of a magnetic material when a magnetic field is excited or demagnetized is an important factor in developing an efficient magnetic refrigeration system.

For the purpose of obtaining high performance MCE materials, heavy rare earth compounds become the most promising candidates. Because, as a potential maximum magnetic entropy is defined as $S_M = R \ln(2J + 1)$, where R is the gas constant and J is total angular momentum quantum number. However, in most of the cases, such potentially large S_M does not exist at several tens degrees of Kelvin temperature range that could be useful for hydrogen liquefaction, due to the crystal electric field reducing the large entropy even in zero magnetic field condition. Such temperature range of several tens degrees of Kelvin is generally comparable to the crystal electric field (CEF) energy levels for heavy rare earth ions (schematic illustration is presented in Fig. 1). Magnetic entropy change (ΔS_M) strongly depends on the degeneracy of the 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.

2. Inelastic neutron scattering of HoB₂

In inelastic neutron scattering (INS) experiments, the energy levels of the CEF can be determined by measuring the energy spectrum of the purely paramagnetic phase, because there is no internal magnetic field induced by ferromagnetic long-range order. As an

example, we selected the MR material HoB₂ with a huge MCE to evaluate the CEF energy level scheme. HoB₂ was recently discovered to exhibit a very large $|\Delta S_M|$ value near the hydrogen liquefaction temperature [2]. INS experiments were performed using the High-Resolution Chopper Spectrometer (HRC) beamline. The experimentally determined CEF level scheme shown in Fig. 2(a) was illustrated, which reproduces the experimental INS 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)).

Here, we discuss how the CEF states of the obtained HoB₂ affect the magnetic entropy change ΔS_M when a magnetic field is applied. When the temperature of the system is assumed to be 20 K, the energy gap between the ground state (Γ_1^B) and the excited states Γ_6^C and Γ_6^B can be considered pseudo-degenerated with respect to the system temperature. When applying magnetic fields along a principal axis, the pseudo-degeneracy is lifted, leading to such a large $|\Delta S_M|$ (Fig. 2(d)).

3. Mean-field calculation with CEF and exchange parameters

We also calculated the ideal CEF level scheme for general heavy rare earth ions with site symmetries, cubic O_h and hexagonal D_{6h} by using mean-field calculations. Figure 3(a) shows one example, crystal field parameter dependence of $|\Delta S_M|$ (5 T, 20 K) for cubic O_h.

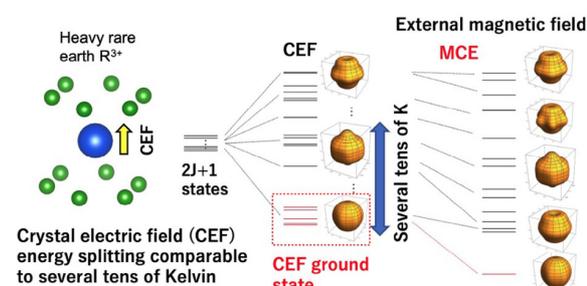


Figure 1. Schematic illustration of complicated crystal electric field (CEF) energy level splitting in heavy rare earth ions (with schematic drawings of electrons wave functions in each energy level), and Zeemann splitting of the CEF levels resulting in a large magnetocaloric effect. For several tens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

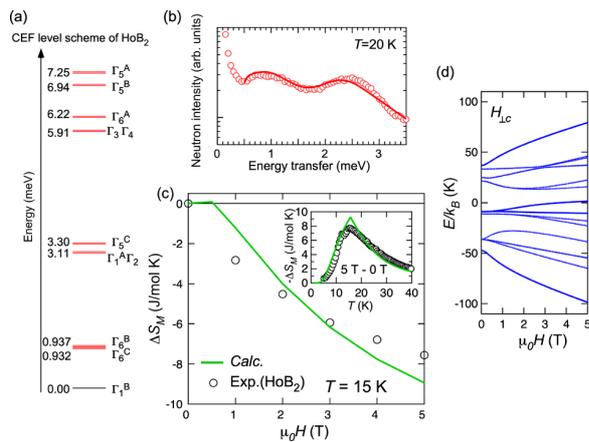


Figure 2. (a) Crystal electric field (CEF) level scheme in HoB_2 was determined by the present neutron scattering experiment. (b) The neutron intensity (open circle) was successfully explained by theoretical calculation curve (solid line) with the CEF parameters. (c) Magnetic field and temperature dependence 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]. (d) Calculated Zeemann splitting for HoB_2 in magnetic field perpendicular to the c -axis.

The $|\Delta S_M|$ influences significantly the crystal field parameters. It is important to note that this does not necessarily show that $|\Delta S_M|$ is largest when the crystal field is zero. In this way, in addition to the degree of degeneracy of the pseudo ground state of the crystal field, the degree of how much the ground state is isolated when a magnetic field is also an important factor in producing a large $|\Delta S_M|$.

The calculation results are summarized in Fig. 3(c). The maximum $|\Delta S_M|$ for Ho^{3+} with the hexagonal symmetry for powder case, corresponding to HoB_2 case, is $10.1 \text{ J mol}^{-1} \text{ K}^{-1}$, 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 .

4. Concluding remarks

The relationship between ΔS_M and crystal field parameters derived in this study provides new guidelines for searching for compounds with larger magnetocaloric effects near the hydrogen liquefaction temperature. Recent advancements in density functional theory

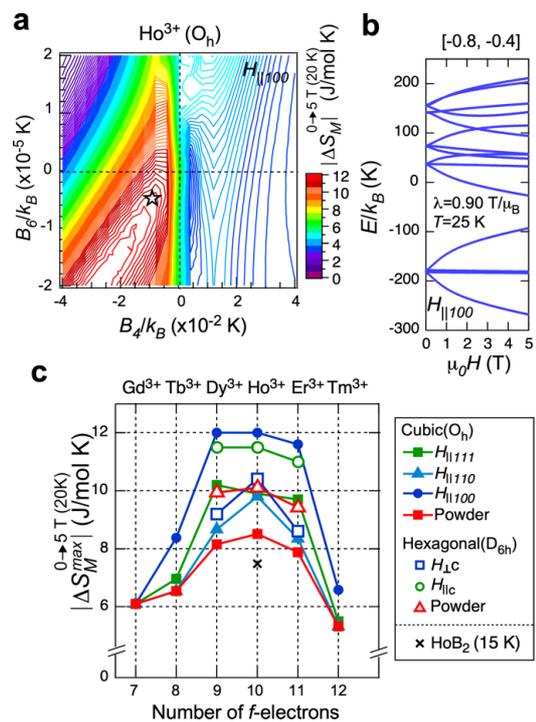


Figure 3. Contour map of magnetic entropy change of Ho^{3+} in the cubic O_h symmetry at $T = 20 \text{ K}$ in magnetic field change from 0 to 5 T along [100] direction. (b) Zeemann splitting in magnetic field along [100] direction at $T = 25 \text{ K}$ for the set of CEF parameters indicated by the star symbol in (a). (c) Heavy rare earth ion dependence of the maximum magnetic entropy change, predicted by the present mean-field calculations for the cubic O_h and hexagonal D_{6h} symmetries. The experimental value of HoB_2 at 15 K is also plotted [3].

calculations have unlocked the possibility of predicting CEF parameters for rare-earth systems based on the crystal information. A combination of DFT calculations and the relationships between $|\Delta S_M|$ and the CEF parameters derived in this study would accelerate the search for compounds with a large MCE and help to design more magnetic refrigeration materials.

References

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