Giant Magetic Refrigerant Materials for Hydrogen Liquefaction

Keywords : Magnetic refrigeration, Hydrogen liquefaction, Cluster-glass

Back-ground

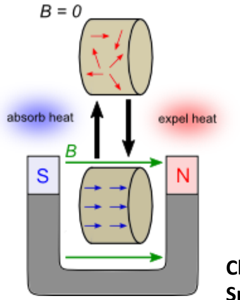
In order to realize the diversification of energy supply in Japan, the high-efficiency hydrogen liquefaction technology is required. The magnetic refrigeration is considered to be one of promising technologies. We are exploring rare-earth intermetallic compounds which show the larger magnetocaloric effect (MCE) in the vicinity of 20 K than reported one in the past. So far, ferromagnets (Fs) with larger MCE have been mainly explored. However, discoveries of antifferomanets (AFs) with giant MCE which had been considered to have less advantage than ferromagnets. Those discoveries indicate expansion of the scope in material search.

Aim

The rare-earth compound Ho5Pd2 has a large relative cooling power (RCP) of 6.32 J/cm3 at around 30K which is close to the boiling temperature 20 K of hydrogen. Our neutron experiments clarified that Ho5Pd2 is a cluster-glass system due to the large number of vacancies. In order to investigate the effect of vacancies on the MCE in Ho5Pd2, we have carried out X-ray diffraction, magnetization, and specific heat measurements in Ho5+xPd2 (-0.4 < x <0.4).

Advanced Research Topics

Principles of magnetorefrigeration and crystal structure of R_5Pd_2



■ Magnetic entropy change : ΔS_m

$$\Delta S_m = \int_0^{B_1} \left(\frac{dM}{dT}\right)_B dB$$

■ Adiabatic temperature change : ΔT_{ad}

$$\Delta T_{ad} = \left[T(S)_B - T(S)_0\right]_s \approx -\frac{T}{C}\Delta S_m$$

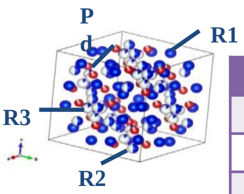
■ Relative cooling power : RCP

$$RCP = -\Delta S_m^{max} \times \delta_{FWHT} \cong \frac{4}{3}Q$$

Chemical formula $R_{2.12}Pd_{0.88}$ ($R_{4.8}Pd_2$)

Space group : Fd-3m

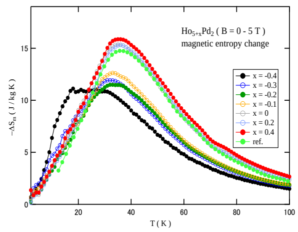
Lattice constant : a = 13.4627 Å (R=Ho)

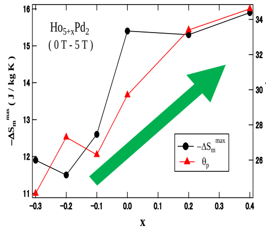


Site		N	Occ.
R1	48f	48	1.0
R2	32e	16	0.5
R3	32e	4	0.125
Pd	32e	28	0.875

Large vacancies

Magnetic refrigeration characters of $Ho_{5+x}Pd_2$





X	$-\Delta S_m^{max}$ (J /kg K)	RCP (J /cm^3)	ΔT_{ad}^{max} (K)
-0.4	10.9	4.7	3.3
-0.3	11.9	5.9	3.5
-0.2	11.5	5.0	3.4
-0.1	12.6	5.3	3.6
0	15.4	6.7	4.6
0.2	15.3	6.9	4.2
0.4	15.9	7.6	4.3
Ref [1]	15	6.3	—

Maximum RCP

Publications

- "A generalized magnetic refrigeration scheme", R. Tamura, T. Ohno, and H. Kitazawa, Applied Physics Letters **104**, 052415-1-4 (2014).
- "Sample dependence of giant magnetocaloric effect in a cluster-glass system Ho_5Pd_2, S Toyoizumi, H. Kitazawa, *et al*., Journal of Applied Physics **117**, 17D101-1-3 (2015).

Summary

- The magnetic entropy change, the adiabatic temperature change, and RCP of $Ho_{5+x}Pd_2$ take a large value at x = 0 - 0:4 for the field change of 5 T. In particular, large $-\Delta S_m^{max}$, RCP value, and ΔT_{ad}^{max} have been observed in $Ho_{5.4}Pd_2$. which is higher value of 20 % than that in Ref.1.
- We could control the magnetic refrigeration efficiency in Ho_5Pd_2 by number of vacancies.

Research outcome

- High-efficiency magnetic refrigeration for the hydrogen liquefaction.
- Storage of helium gas in the helium gas station and helium carrier.

Ref[1]: T. Samanta *et al.*, APL 91 (2007) 082511.

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