Structure-property relationships in GdCuX corresponding hydrides (X= Si, Al)

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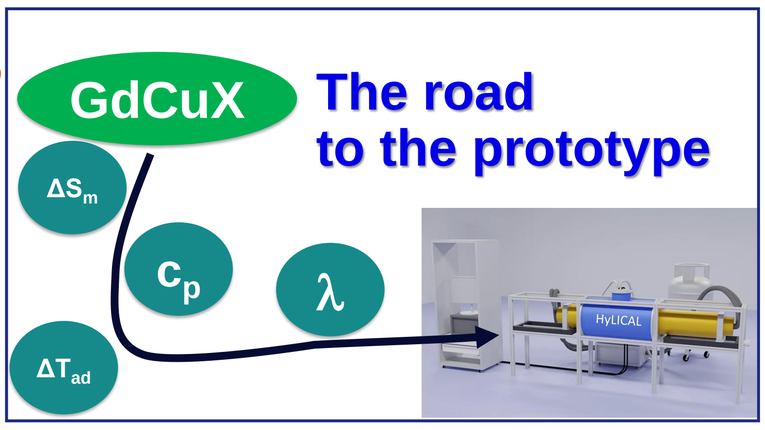
Motivation and objectives

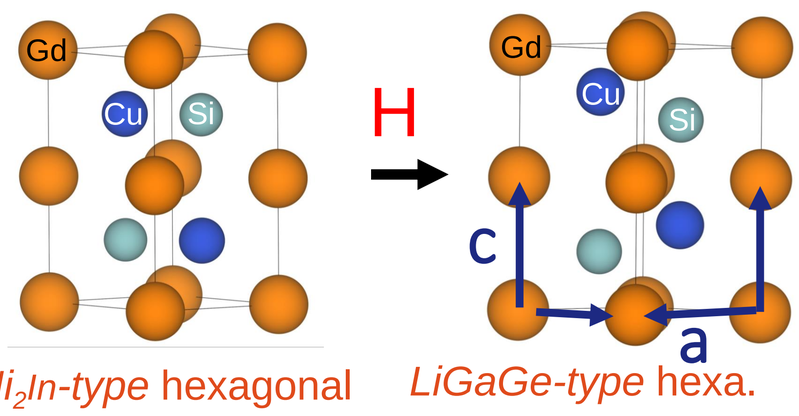
- Magnetocaloric hydrogen liquefaction aims to replace the cryogenic part of the hydrogen liquefaction cycle (77-20 K), which is energy-intensive [1].
- GdCuX (where X=Si,Al) exhibit magnetic transition temperatures close to, or within the desired ranges for LH_2 [2,3].



- This study provides fundamental structure –magnetic property relationships in **GdCuAl**, **GdCuSi** and their **hydrides** to **guide composition design** of magnetocaloric materials for H_2 liquefaction towards prototypes.
- Such fundamental relationships enable a better understanding of **Gd-Gd** interactions, responsible for the magnetic properties in the studied GdCuX (X=Si,Al) compounds.

GdCuSi and hydride

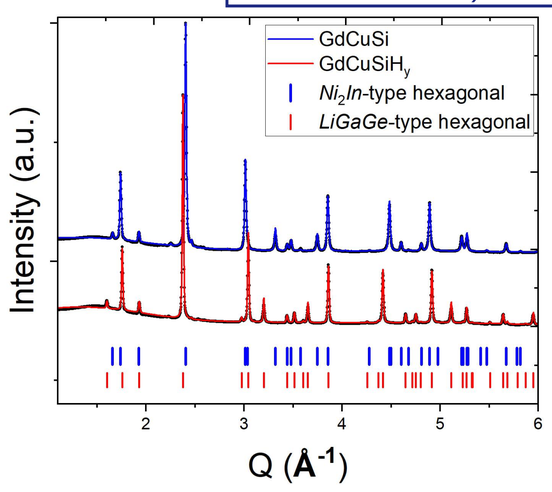
Structural properties



Ni_2In-type hexagonal → *LiGaGe-type* hexa.

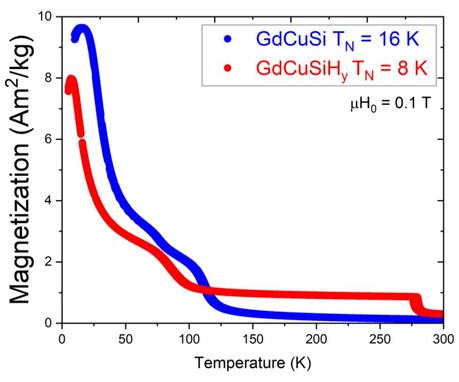
- **a contraction, c expansion** after hydrogenation as evidenced by Bragg peaks shifting left and right (see below);
- Cu and Si sublattices are no longer coplanar after hydrogenation (possible insertion in trigonal bipyramidal sites)

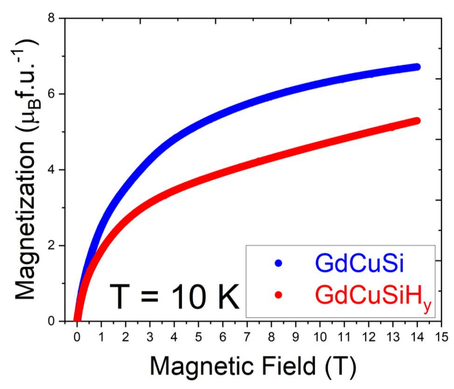
Sample	GdCuSi	$GdCuSiH_y$
Space Group	$P6_3/m\ m\ c$	$P6_3mc$
d_{Gd-Gd} in **a** axis (Å)	4.171(1)	4.130(2)
d_{Gd-Gd} in **c** axis (Å)	3.786(2)	3.925(2)
Volume (Å^3)	114.09	115.988
Volume expansion (%)	1.66	



Magnetic properties

- AFM behavior (cusp at 16 and 8 K);
- Indication of a ferro-magnetic impurity at T~125 and 100 K.



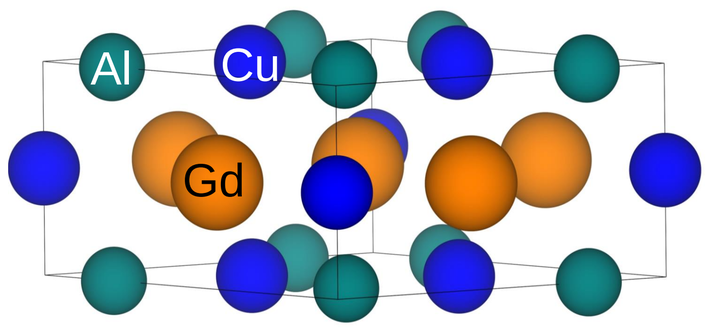


- Saturation magnetization (M_S) in GdCuSi reaches ~6.7 μ_b/f.u., close to free Gd^{3+} moment (7.94 μ_b);
- M_S reaches 5.3 μ_b/f.u. in GdCuSi hydride;

Sample	Ground state
GdCuSi	AFM
$GdCuSiH_y$	AFM

GdCuAl and hydride

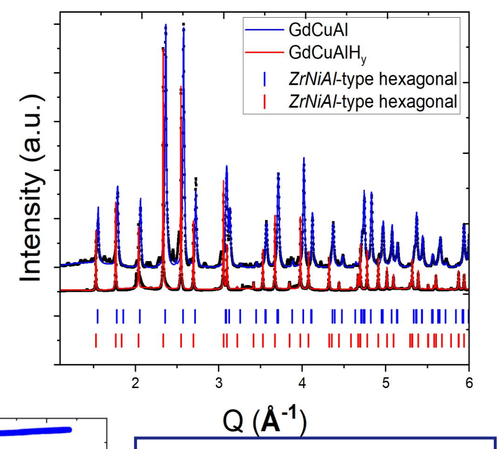
Structural properties



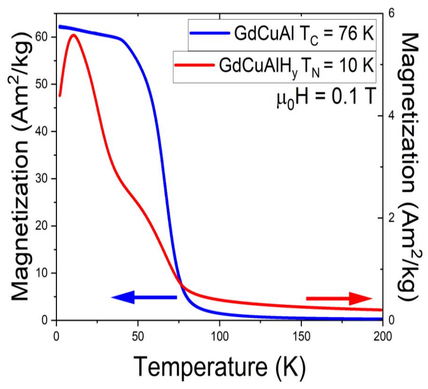
ZrNiAl-type hexagonal

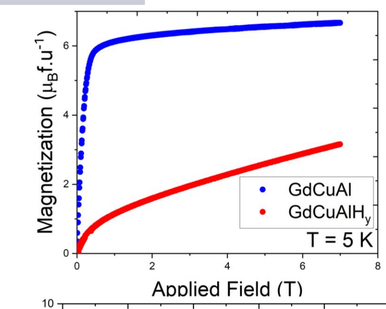
Sample	GdCuAl	$GdCuAlH_y$
Space Group	*P*-62	*P*-62
d_{Gd-Gd} in **a** axis (Å)	3.691(1)	3.735(1)
d_{Gd-Gd} in **c** axis (Å)	4.068(1)	4.114(1)
Volume (Å^3)	176.1	180.9(1)
Volume expansion (%)	2.72	

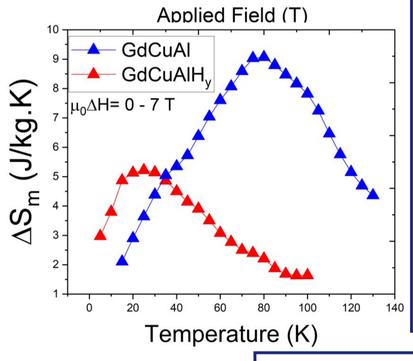
- Isotropic expansion upon hydrogen uptake, as evidenced by the shift of Bragg peaks to the left (see below)



Magnetic properties







- Hydrogen **modifies behavior** from **ferromagnetic to antiferro-magnetic**;
- M_S reaches ~ 6.66 μ_b/f.u. in GdCuAl and 3.15 μ_b/f.u. in hydride;
- Presence of unhydrogenated GdCuAl in M(T) curves;

Sample	Ground state	ΔS_m (J kg^{-1} K^{-1}) $\mu_0\Delta H$= 0 – 7 T
GdCuAl	FM	9.1
$GdCuAlH_y$	AFM	5.2

- GdCuAl showcases broad ferromagnetic transition leading to **large relative cooling power**;
- Hydrogenation lowers entropy change, shifts ΔS_m peak to T~20 K.

Experimental

- Alloys synthesized by arc melting, followed by annealing at 1123 K for 4 days.
- Small ingots were activated up to 573 K under dynamic vacuum, cooled down, then hydrogenated with 30 bar up to 573 K.
- Structural characterization by Synchrotron radiation X-Ray Diffraction at the BM-01 and BM-31 beamline at the European Synchrotron Radiation Facility;
- Magnetic properties measured by a Quantum Design MPMS-3 and PPMS

Conclusion

- GdCuSi has a decrease of T_N upon anisotropic expansion generated by hydrogenation.
- GdCuAl goes from FM to AFM interactions upon a isotropic expansion induced by hydrogenation;
- Decrease in ΔS_m from GdCuAl to $GdCuAlH_y$;
- **Hydrogenation induces weakening of Gd-Gd interactions for GdCuX**

References

[1] Kanoglu, M., Dincer, I. and Rosen, M.A. (2008), Performance analysis of gas liquefaction cycles. Int. J. Energy Res., 32: 35-43.
[2] Gupta, S., Suresh, K.G. & Lukoyanov, A.V. (2015) Effect of complex magnetic structure on the magnetocaloric and magneto-transport properties in GdCuSi. *J Mater Sci* **50**, 5723–5728
[3] P Javorský et al. (1998) Magnetic behaviour of RCuAl compounds, Journal of Alloys and Compounds,Volume 264, Issues 1–2

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