# TAILORING STRUCTURAL AND MAGNETIC PROPERTIES OF $R_5(SI,GE)_4$ COMPOUNDS WITH R = Gd AND Tb

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## Motivation

In the past few years, at IFIMUP-IN (Porto) we have been focusing our efforts into the understanding of the physical mechanisms that rule the magnetocaloric effect on the $R_5(Si,Ge)_4$ compounds. Namely, we have identified some features that contribute in a critical way to the performance of these magnetocaloric materials, such as: **the tunning of the magnetic and structural transitions**, **the quality of the samples** and the **correlation of these two effects**. Therefore, in order to study these features we have used three different tools: **chemical substituion**, **application of high-magnetic fields** and **thermal treatments**. Particularly, here we present four different studies that can be identified as follows:

Understanding the role played by Fe on the tuning of magnetocaloric effect in $Tb_5Si_2Ge_2$;
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Tailoring Magnetism of $Tb_{1-x}La_xSi_2Ge_2$ Compounds by La Substitution;
**Paper submitted to Physical Review B**

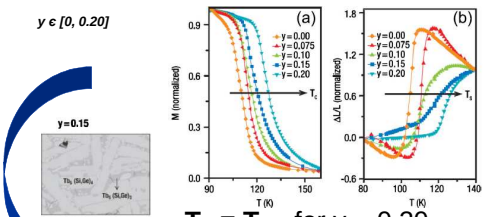
Unveiling the (De)coupling of magnetostructural transition nature in magnetocaloric $R_5Si_2Ge_2$ (R = Tb, Gd) materials **Applied Physics Letters 99, 132510 (2011)**

Phase control studies in $Gd_5Si_2Ge_2$ Giant Magnetocaloric compound;
**Under preparation**

## Understanding the role played by Fe in the MCE of $Tb_5Si_2Ge_2$

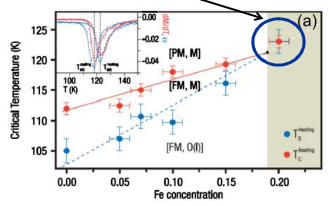
### Chemical substitution [Ge → Fe]: $Tb_5Si_2Ge_{2-y}Fe_y$ system

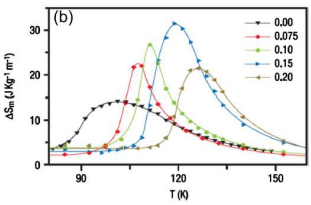
*y ϵ [0, 0.20]*



Fe is predominantly in the $Tb_5(Si,Ge)_3$ phase. This phase is responsible for interfacial strain between 5:4 and 5:3 phases, mimicking the external pressure effect.

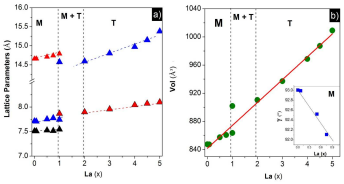
$T_S = T_C$ , for y = 0.20

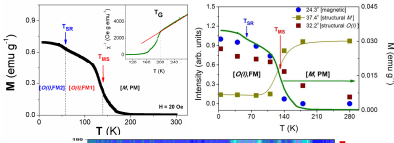


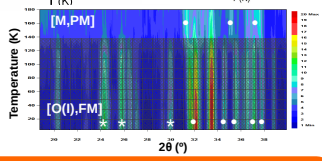


## Tailoring the magnetism of $Tb_{5-x}La_xSi_2Ge_2$

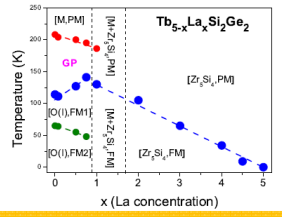
### Chemical substitution [Tb → La] , x ϵ [0, 5]→complete series







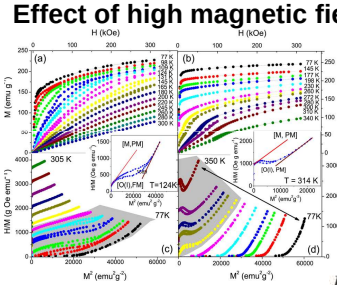
- ***x < 1: Monoclinic* structure (** P1121/a space group)
- ***x > 1: Tetragonal* structure** (P41212 space group)

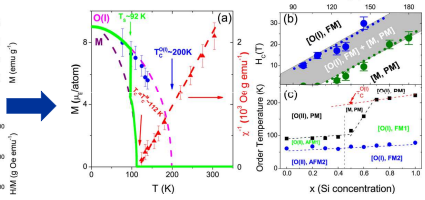


La critically influences structure and magnetism:
- Increase of $T_C$ for x < 1;
- Change in Magnetocrystalline competition;
- Suppresion of Griffiths-like phase;
- Coupling of structural and magnetic transitions;

## Unveiling the (De)coupling of magnetostructural transition

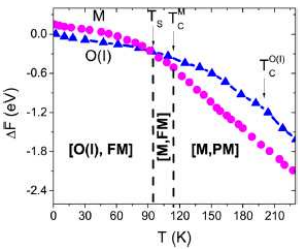
### Effect of high magnetic fields in $R_5Si_2Ge_2$ *R = Gd* and *Tb*





**Experimental determination of $T_C$ for O(I) and M structures**

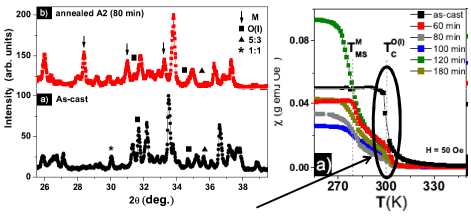
$$F(T,\sigma) = U_{lat} - \boxed{HgJ\sigma} - \frac{3}{2}\frac{J}{J+1}k_BT_C\sigma^2 - TS_M - TS_{lat}$$



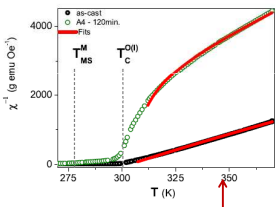
- Magnetic field decreases the free energy in a more significant way for structures with higher $T_C$;
- $T_S < T_C^M < T_C^{O(I)}$ → decoupled transitions;
- $T_C^M < T_S < T_C^{O(I)}$ → coupled transitions;
- MCE should be maximum when $T_S = T_C^M$

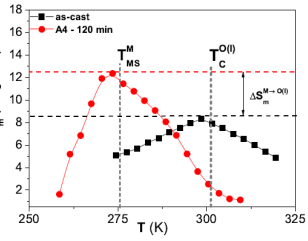
## Phase control studies in $Gd_5Si_2Ge_2$ GMC compound

### T = 1473K for t ϵ [0, 180 min], followed by $N_2$ quenching;



- **High amount of O(I) phase in the as-cast sample;**
- **Conversion of the O(I), Gd:(Si,Ge) = 5:3, 1:1 into M phase;**





- Conversion achieved, resulting in > 65 % M;
- **50% enhancement of the MCE;**
- Optimal annealing time: [60, 120] min
- Efficient alternative method to extract M and O(I) phase amounts through $\chi^{-1}$ (T) Fit;

## Conclusions

- Chemical substitution of both Rare Earth and Transion Metal elements is a very usefull tool in order to tune the spin lattice coupling thus improving the magnetic properties ($T_C$, ΔSm, $T_S$ );
- Strain caused by secondary phases promotes coupling between structural and magnetic phase transitions (similarly to the effect of external pressure);
- High Magnetic field magnetization measurements is an effecient technique to deepen the studies on the main mechanisms that rule the magnetostructural phase transition;
- Thermal treatments can significantly improve the MCE of a $Gd_5Si_2Ge_2$ as-cast sample (up to ~50%).

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