Experimental report

04/09/2023

Proposal: **5-31-2908** **Council:** 4/2021

Title: Influence of magnetic disorder on the Griffiths-like phase of magnetocaloric Tb5Si2Ge2 promoted by minute La substitutions of Tb ions

Research area: Physics

This proposal is a resubmission of 5-31-2807

Main proposer: **Noelia MARCANO AGUADO**

Experimental team: Andreas MICHELS
Mathias BERSWEILER
Elizabeth MARTIN JEFREMOVAS

Local contacts: Nina-Juliane STEINKE

Samples: $Tb_{4.925}La_{0.075}Si_2Ge_2$
$Tb_{0.5}La_{0.5}Si_2Ge_2$

Instrument	Requested days	Allocated days	From	To
D33	2	2	22/09/2021	24/09/2021

Abstract:

The Griffiths-like phase (GP) is a singular feature related to the formation of random magnetically ordered regions within the paramagnetic phase, at temperatures above that of long-range magnetic ordering. The existence of GP is found in materials with quenched disorder and /or competing magnetic interactions, as in the family of giant magnetocaloric materials $R_5(Si_yGe_{1-y})_4$ (R = rare earth). Very recently, our detailed AC-susceptibility measurements on La-diluted system $Tb_{5-x}La_xSi_2Ge_2$ revealed that we are able to tune in the formation of short-range ferromagnetic (FM) clusters in the GP in the parent compound $Tb_5Si_2Ge_2$. The measurements reveal that minute La-substitutions promote a drastic change in the magnetic response of clusters. Here, we would extend the study at the magnetic nanoscale to disclose the size/number of the GP clusters for different levels of La doping and the relation to magnetic disorder. SANS is the ideal probe since it is able to measure magnetic correlations on the relevant length scales. Magnetic field is required to extract the nuclear and magnetic scattering and the field evolution of GP-like clusters.

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The strong correlation between structural and magnetic properties may result in the appearance of exotic regimes. One of such striking behaviors is that related to the existence of Griffths-like phases (GP). The fascination stems from the fact that magnetic order appears in the paramagnetic state. Thus this phase may be understood as a precursor of magnetic order in some specific systems and explain broad physical phenomena in which order is achieved by percolation of an increasing number of magnetic clusters. GP are then characterized by the pre-formation of ferromagnetically ordered nanometric clusters at some temperature T_G, much above the true long-range ferromagnetic (FM) ordering at the Curie temperature T_C [1, 2]. To date, the existence of GP has been shown in a limited number of materials but with a high technological potential as the *magnetocaloric* intermetallics of the $R_5(Si_yGe_{1-y})_4$ type (R = Gd, Tb, Dy or Ho) [3, 4, 5, 6], object of this work. The onset of GP within the $R_5(Si_yGe_{1-y})_4$ family was first reported in $Tb_5Si_2Ge_2$ by means of low-dc magnetic susceptibility ($\chi_{dc}(T)$) and SANS experiments in D16 (ILL). These studies revealed the formation of nanometric regions with FM interactions in the PM regime (and a spin-spin correlation length of $\xi \sim 0.5$ - 8 nm) below $T_G = 200$ K, well above $T_C = 110$ K [4]. These small clusters give rise to the characteristic downward deviation of the reciprocal susceptibility $\chi_{dc}^{-1}(T)$ from the Curie-Weiss predictions below T_G that represent the fingerprint of a GP.

Further work by Marcano et al [7] showed that the substitution of Tb magnetic ions by La (nonmagnetic), ***even with a small amount of La (x = 0.075), promotes a drastic change*** in the formation of short-range FM clusters in the GP of the non-diluted compound $Tb_5Si_2Ge_2$ ($x = 0$). The simultaneous detection of linear and nonlinear AC susceptibility $\chi_{AC}(T, f)$ revealed a **novel cluster-glass state** within the GP in the x = 0.075 compound. The great sensitivity of the nonlinear susceptibility allowed to detect two-closely related magnetic processes that were not fully resolved by the linear susceptibility. In particular, the nonlinear response revealed that ferromagnetic-like correlations were built up at around $T_G^* \sim 155$ K, which became frozen at a lower temperature ~ 140 K [7], thus in analogy with a **reentrant spin glass behavior**.

This unusual reentrant behavior in the GP was not detected in the non-diluted compound $Tb_5Si_2Ge_2$ (x = 0) since the magnetic signal coming from the short-range FM clusters in the GP was much weaker. Such a drastic weakening of the magnetic response of the GP clusters over the PM matrix could be connected to a smaller cluster size and/or a smaller number of clusters in the non-diluted compound relative to the diluted compound, x = 0.075. These findings make these $Tb_{5-x}La_xSi_2Ge_2$ alloys with minute La-substitutions a unique playground to unveil unambiguously the relation of magnetic disorder with the percolation of GP-like clusters and the mechanism of the cluster glass state.

SANS experiments make possible to investigate the role of *La* dilution in the concentration/size of FM clusters within the PM matrix. SANS allows *to extend the study at the magnetic nanoscale to disclose the size/number of the GP clusters* in the magnetic response and to establish the magnetic correlation lengths among these randomly arranged entities for different levels of La doping. Moreover, the evolution of the SANS contribution with temperature above T_C provides unique information about the moment coupling in the re-entrant cluster-glass state within the GP.

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To this aim, we have focused our efforts on polycrystalline $Tb_{4.925}La_{0.075}Si_2Ge_2$ (disk-shaped). Three sample-detector distances, 2.3, 7.8 and 12.8 m, were used in order to extend the range of accessible scattering vectors (0.00353 $Å^{-1}$< q< 0.2644 $Å^{-1}$), using a wavelength of 4.6 $Å^{-1}$. Data were taken from 90 to 250 K at several magnetic fields (H_{dc} = 0, 0.05, 2T). It is worth commenting the fact that it was a fully remote experiment (COVID).
Fig. 1a shows the SANS intensity as a function of the momentum transfer *q* (log-log scale) under no applied magnetic field ($\mu_0 H$ = 0) for seven temperature values below T_G, T = 90, 100, 135, 140, 150, 155 and 180 K. The nuclear contribution to the SANS has been subtracted from the SANS pattern measured at 250 K (paramagnetic region). To ease the understanding, we have included at the bottom of Fig. 1a simple sketch indicating the temperature-dependent regions of interest of the alloy. Accordingly, all the measured temperatures included in Fig. 1a correspond to the Griffiths-like phase (GP) region.

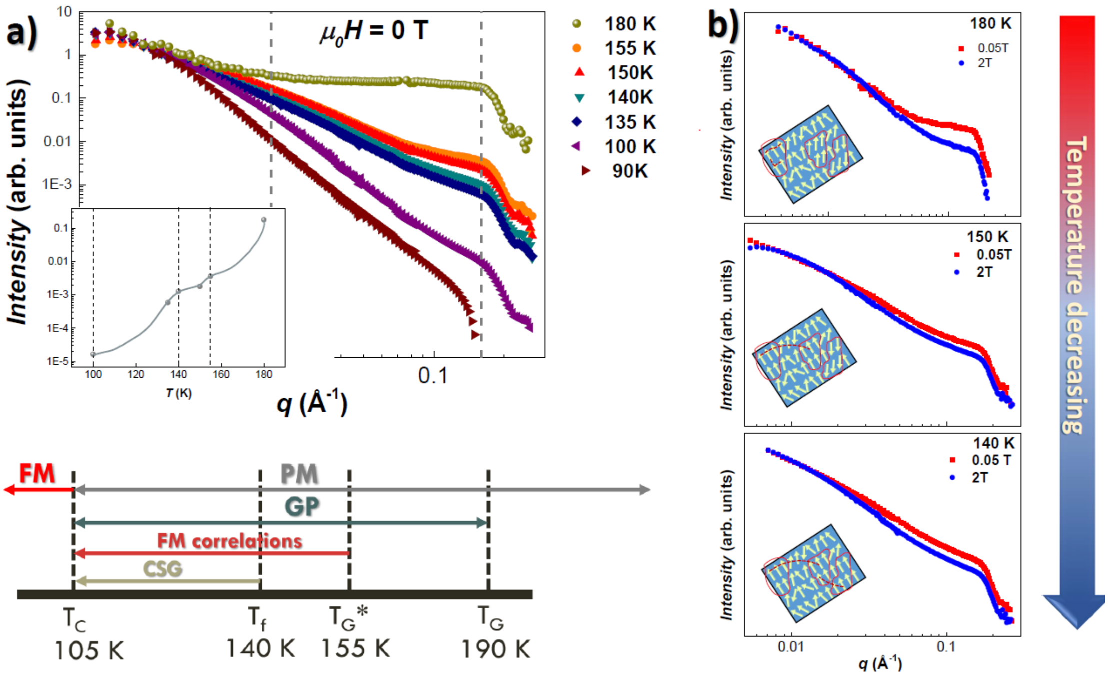

Figure 1.- Small-Angle Neutron Scattering (SANS) intensity as a function of the momentum transfer q (log-log scale) measured for $Tb_{4.925}La_{0.075}Si_2Ge_2$ at a) temperature values between 90 and 180 K under no applied magnetic field, and b) at fixed temperature (180, 150 and 140 K, top to bottom) and 0.05 and 2 T magnetic external applied field. Inset in a) shows the intensity of the peak (log scale) located at q = 0.160 $Å^{-1}$ as a function of the temperature (line is a guide for the eyes). A sketch in the bottom of the different magnetic regions is provided. Fig 1b includes different sketches for the GP clusters and the onset of inter-cluster FM interactions.

First, all patterns above 90 K account for the existence of a magnetic correlation length at q ≈ 0.160(1)$Å^{-1}$, where the scattering intensity drops describing the typical shoulder-like Guinier shape. The position of this signature (q ≈ 0.160(1)$Å^{-1}$) corresponds to a real space distance of ≈ 3.9 nm, and remains almost constant with decreasing temperature (see Fig. 1a) and also, with increasing the magnetic field (see Fig. 1b). On the contrary, the intensity of this signature exponentially decreases with temperature (see inset in Fig. 1a), being severely decreased at T = 100 K, and completely wiped out at *T* = 90 K. Taking

into account the magnetic state of the sample [7], such a correlation length is ascribed to the magnetic moment correlations within the magnetic clusters building up the Griffiths-like Phase state (GP), *i.e.*, the existence of magnetically ordered clusters within the paramagnetic region. Cooling down, the ferromagnetic correlations among the GP (medium-range) get enhanced, coupling a larger number of clusters, ending up in a single global FM state (at T_C = 105 K). It is worth noting that GP correlation length, even if ill-defined, still holds at T = 100 K, close to T_C. This finding, together with the temperature-independent correlation length of the GP clusters, brings light into the mechanism of the underlying magnetic transition. Given that the GP cluster size remains unaffected, FM correlations must be acting on the clusters themselves. Consequently, they are the GP clusters who get progressively FM-coupled upon decreasing the temperature, until the magnetization of all clusters is parallel, and thus, the GP-picture does not hold anymore, and a global FM state is settled.
Fig. 1b evaluates the field dependence (μ_0H = 0.05 and 2 T) corresponding to three temperature values, T = 140, 150 and 180 K. There, it can be seen how the SANS intensity decreases upon increasing the magnetic field, i.e., as the magnetic moments get aligned with the field. It is also worth noting here again that the correlation length of the GP clusters is not altered even at 2T, showcasing the robustness of the GP-coupled entities. The insets sketch the aforementioned alignment mechanism, where the size of the GP clusters remains constant and FM correlations among clusters are promoted while cooling down.

Finally, an additional subtle feature can be observed at $q \approx 0.0260$ Å^{-1} ($\approx$ 24 nm) and T < T_{G*}. This could be indicative of the existence of an additional (longer) correlation length, ascribed to the FM correlations among the GP clusters. According to the size of the GP clusters (~ 4 nm) and this additional FM correlation (24 nm), a supracluster entity, involving up to 6 GP clusters, would get FM aligned. This effect, although subtle, is also detectable in Fig. 1b, where these FM correlations can also be promoted by the magnetic field.
The Cluster Spin Glass (CSG) behaviour, on the contrary, leaves no detectable trace in the SANS. In order to complete the study $X_{AC}(t, T)$ measurements have been conducted. The preliminary results reveal the existence of particular dynamics in this regime.

Finally, it is worth commenting the fact that we were also aiming to measure x = 0.5 sample. However, we decided to better define the subtle changes observed in x = 0.075. Given so, we have focused on x = 0.075 sample, collecting more temperatures.

References

[1] R. Griffiths, *Phys. Rev. Lett.* **23**, 17 (1969); A. J. Bray, *Phys. Rev. Lett.* **59**, 586 (1987).
[2] J. Deisenhofer et al., *Phys. Rev. Lett.* **95,** 257202 (2005); S. Zhou et al., *J. Phys. Chem. C* **115**, 1535 (2011); M. B. Salamon et al., *Phys. Rev. Lett.* **88**, 197203 (2002); S. Guo et al., *Phys. Rev. Lett.* **100**, 017209 (2008).
[3] Y. Mudryk et al., in *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier, 2014), Vol. 44, pp. 283-449.
[4] C. Magén et al., *Phys. Rev. Lett.* **96**, 167201 (2006).
[5] A. M. Pereira et al., *Phys. Rev. B* **82**, 172406 (2010).
[6] J. H. Belo et al., *Phys. Rev. B* **86**, 014403 (2012).
[7] N. Marcano et al., *Phys. Rev. B* **99**, 054419 (2019).