Observation of a Griffiths-like Phase in the Magnetocaloric Compound $Tb_5Si_2Ge_2$

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The onset of a Griffiths-like phase has been observed in $Tb_5Si_2Ge_2$ ($T_C = 110$ K) by means of magnetic susceptibility and small-angle neutron scattering experiments. We show the growth of a ferromagnetic cluster system characterized by an inverse susceptibility exponent lower than unity at $T_C < T < T_G \approx 200$ K. We suggest that the Griffiths-like state is originated by local disorder within the crystallographic structure, stabilized and enhanced by competing intralayer and interlayer magnetic interactions. Both factors thus promote segregation of nanometric regions with ferromagnetic interactions.

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The observation of Griffiths singularities [1] in materials presenting notably complex magnetic interactions has lately excited significant scientific interest. Recent works on colossal magnetoresistive (CMR) $LaMnO_3$-based oxides [2–5], $4f$-type strong correlated systems presenting a non-Fermi liquid behavior (NFL) [6,7], or spin glass systems [8] have been proven to show the features of a Griffiths phase. The Griffiths model accounts for a magnetic system in which a random distribution of the magnetic interactions given by disorder sets in such a way that different values for the exchange constant can be assigned randomly to the different sites of the lattice [1,9,10]. In this context, the thermodynamical functions become unanalytical in $T_C < T < T_G$, where T_C is the proper ordering temperature of the system (given by complete randomness in the distribution of magnetic interactions), and T_G accounts for the complete absence of disorder. In the temperature range $T_C < T < T_G$, the disordered system is between the conventional paramagnetic (PM) phase and the ordered ferromagnetic (FM) state. This intermediate regime is called the Griffiths phase, and is microscopically characterized by a clusterlike system induced by this disordered state. Experimentally this is signaled by anomalies in the magnetic susceptibility, specific heat, or transport properties [3,6,7]. Although the macroscopic manifestation of the classical Griffiths phase is theoretically weak [11,12], it has been observed in several materials. For example, the existence of the cluster distribution of a Griffiths phase has been claimed to be responsible for the CMR in the $LaMnO_3$-based perovskites [2–5]. Quite recently, observation of a Griffiths phase at fairly large temperatures, $T \sim 260$ K, in the paramagnetic phase of $La_{1-x}Sr_xMnO_3$ has also been reported [13]. Burgy *et al.* have argued that the coexistence of two competing ordered phases stabilizes and enhances the FM Griffiths-like effects, this state becoming observable [2]. Therefore, a fundamental ingredient in the onset of a Griffiths phase is the competition between magnetic interactions. The existence of magnetic anisotropy and the intrinsic disorder that is inherent to real materials also play a key role in the physical realization of a Griffiths phase in a magnetic system.

The rare-earth intermetallic system $R_5(Si_xGe_{1-x})_4$ (R = rare earth) might be a serious candidate to host a Griffiths-like phase. These alloys, especially the $R = Gd$ family, are known for being the paradigm of magnetocaloric materials due to the discovery of the giant magnetocaloric effect [14] associated with a simultaneous magnetic and structural transformation, which can be induced by the change of external parameters such as temperature, magnetic field, or pressure [15–17]. The physical properties of these systems are strongly determined by their intrinsically layered crystallographic structure, and the strong interplay between the magnetic and structural degrees of freedom. The crystal structure is conformed by the stacking of rigid two-dimensional layers (*slabs*) of R and $T = Si/Ge$ atoms. The actual crystallographic phase and the nature of the magnetic interactions are controlled by the number of interlayer covalentlike T-T bonds connecting the slabs [15], as in these alloys two different magnetic interactions are playing part: the intralayer interaction ruled by the conventional $4f$-$4f$ Ruderman-Kittel-Kasuya-Yosida indirect exchange, and the interlayer interactions, strongly influenced by an additional R-T-T-R superexchange interaction via the existing T-T bonds [18]. Microscopic experimental evidence has been reported supporting the picture that the intralayer magnetic structure is essentially FM, whereas the interlayer coupling tends to be either FM or antiferromagnetic (AFM), depending on the number of interslab pairs which are covalently bonded [19]. In the case of $Tb_5Si_2Ge_2$, the high-temperature PM state crystallizes in a monoclinic $P112_1/a$ structure (M), characterized by the existence of half of the possible interlayer bonds. On cooling, this compound experiences a second-order transition to a FM state at $T_C = 110$ K, anomalously decoupled from the structural $M \rightarrow O(\mathrm{I})$ transformation taking place at $T_t = 100$ K [19,20]. In this Letter, we experimentally demonstrate the existence of a Griffiths-like phase in $Tb_5Si_2Ge_2$ through the existence of an

anomalous behavior of the magnetic susceptibility, and the observation by small-angle neutron scattering (SANS) of a system of nanometric FM clusters in the PM regime within the M phase.

The polycrystalline alloy of nominal composition $Tb_5Si_2Ge_2$ employed in this work was the same used in previous works [19,20]. Low-field dc magnetization measurements were carried out using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer. The SANS experiments were performed on the D16 instrument ($\lambda = 4.54$ Å, 0.03 Å $< q <$ 0.65 Å, $\Delta q = 0.005$ Å^{-1}), at the Institute Laue-Langevin (ILL) (Grenoble, France), the neutron spectra being collected in the temperature range 10–300 K, and in magnetic fields up to 50 kOe.

The existence of a Griffiths-like phase in $Tb_5Si_2Ge_2$ in the form of a FM cluster system within a PM matrix is first indicated by macroscopic magnetization experiments [3]. In Fig. 1, we present the inverse dc magnetic susceptibility (χ^{-1}) as a function of temperature on heating in low magnetic fields. This picture clearly illustrates the anomalous behavior of χ^{-1} that represents the fingerprint of a Griffiths phase. In the conventional PM regime ($T >$ 200 K), the effective paramagnetic moment is $9.8(1)\mu_B$/Tb, independent of the specific field value, which perfectly agrees with the theoretical value of $\mu_{\text{eff}} = 9.72\mu_B$/Tb. However, below 200 K, a dramatic stairlike fall of χ^{-1} is evident at very low fields (<100 Oe), the different plateaux corresponding to different FM cluster sizes. On further increasing the magnetic field, only one plateau is observed, and the magnetic susceptibility at $H \geq 500$ Oe becomes nearly indistinguishable from the high-temperature range values within the experimental error. This might indicate that the clusterlike FM component is masked at high fields by the linear increase of the PM contribution of the matrix [13] or the magnetic-field-induced disappearance of the intermediate cluster system for the benefit of the PM state. In all cases, the smoothness of the curve points to a complex microscopic structure that could be explained in terms of a very diluted system of FM clusters, where the total contribution to the magnetization of the FM particles is small with respect to the PM matrix, or in terms of larger typical cluster size with weaker magnetic correlations and low magnetic moment [21]. Both possibilities would match the physical picture of a Griffiths phase. It has been shown that the Griffiths phase is univocally characterized by a magnetic susceptibility exponent lower than unity, i.e., $\chi^{-1} \propto (T - T_C)^{1-\lambda}$, where $0 \leq \lambda < 1$ [6]. We have fitted the logarithmic representation of χ^{-1} (see inset in Fig. 1) obtaining clearly different values for the exponent λ depending on whether we refine it in the anomalous region of χ^{-1} [125 K $< T <$ 165 K, $\lambda_G \cong 0.31(1)$ at 1 Oe] or in the conventional PM phase [$T >$ 200 K, $\lambda_{\text{PM}} \cong 0.064(3)$ at 1 Oe]. At high field, the values of the exponent remain far from zero value, e.g., $\lambda_G(1500\ \text{Oe}) \cong 0.25(1)$, so the Griffiths-like state remains at fields higher than 1 kOe. Thus, the magnetic-field suppression of the anomaly displayed by χ^{-1} should be explained in terms of the masking of the FM signal by the rising PM background, as already proposed by Deisenhofer *et al.* in manganite systems [13]. In contrast, λ_{PM} remains very small, $\lambda_{\text{PM}}(1500\ \text{Oe}) \cong 0.040(1)$, indicating that the Griffiths phase does not extend to temperatures higher than ~200 K.

The SANS instrument D16 is adequate to accurately probe the existence of FM clusters and characterize their properties, size and temperature and magnetic-field evolution. To treat the data, we consider an Ornstein-Zernike form for the magnetic correlations $\langle M(0)M(r)\rangle \approx [\exp(-r/\xi)]/r$, where ξ is the correlation length, and r is the distance between two spins. From this analytical expression, the deduced SANS intensity should present a Lorentzian dependence of ξ, $I = I_0/[q^2 + (1/\xi)^2]$ [22]. All the SANS spectra have been fitted with the help of this

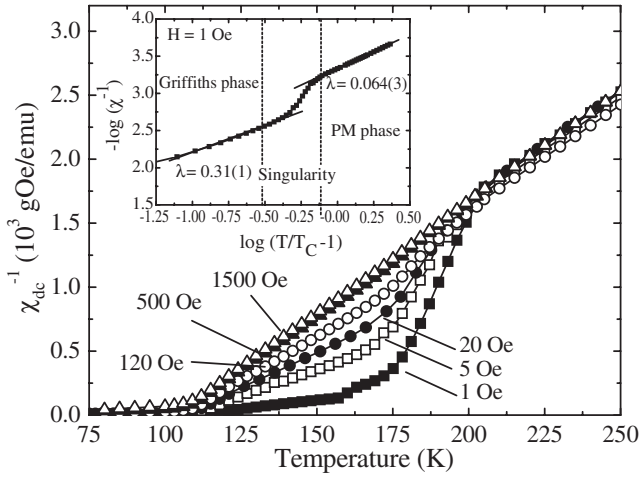

FIG. 1. Temperature dependence of χ^{-1} as a function of magnetic field, measured on heating. The inset shows fits at 1 Oe in the Griffiths and PM phases, respectively.

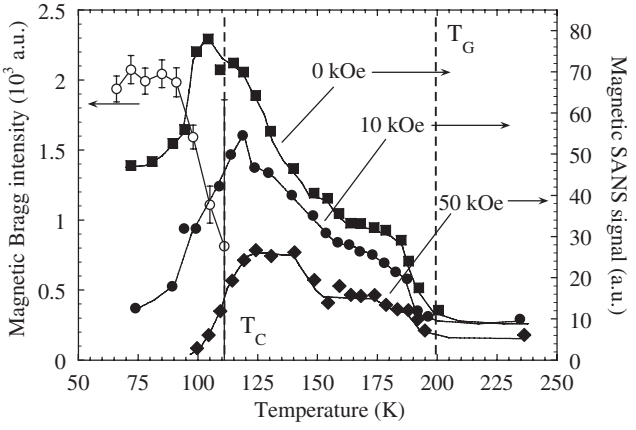

FIG. 2. Temperature dependence of the magnetic SANS intensity collected in D16 at $q = 0.1$ Å^{-1} in different magnetic fields (filled symbols), in comparison with the intensity of a magnetic Bragg peak extracted from Ref. [19] (empty symbols).

expression, thus obtaining the dependence of the correlation length with temperature and applied magnetic field.

The temperature dependence on cooling of the SANS intensity as a function of magnetic field, and at $q = 0.1$ Å^{-1}, which is a typical intermediate value in the range of transferred momentum within the resolution of the instrument, is shown in Fig. 2. As a comparison, the intensity of a long-range FM Bragg peak growing at $T_C = 110$ K is also included from Ref. [19]. First, a remarkable increase of the SANS signal is observed from 200 to 175 K, this step being followed by a small plateau that extends down to ~150 K. This intermediate saturation discards a superparamagnetic origin of the described phenomena, as in that situation the intensity should increase in a Curie-Weiss-type fashion. This anomalous contribution in the temperature range 150–200 K could be related with the nucleation of FM clusters within the PM region of $Tb_5Si_2Ge_2$. Below $T \approx 150$ K, a huge increase of the signal is found associated with a strong rise of magnetic correlations in the vicinity of the Curie temperature of a second-order FM transition. A double peak is seen, at $T_C = 115$ K and $T_t = 105$ K, which is likely associated with the decoupled magnetic-crystallographic transformation [20]. Upon application of a magnetic field, the decrease of the SANS intensity in the whole temperature range is considerable. In fact, at 50 kOe the magnetic signal obtained from the subtraction of the nuclear part is small and in most of the temperature range, can be considered negligible within the experimental error. The large anomaly associated with the main magnetic transition is shifted to higher temperatures, as can be expected from the results seen in previous experiments. The double peak structure is still observable at 10 kOe, although at 50 kOe both peaks should have merged due to the recoupling of the crystallographic and magnetic transformations [20]. It is worth noting that the SANS intensity is proportional to the number of scattering centers [23], and therefore, a strong decrease in the magnetic contribution should be indicative of a reduced amount of magnetic clusters.

The correlation length extracted from the Lorentzian fits of the SANS spectra as a function of temperature and in different magnetic fields is the final proof of the existence of the FM cluster distribution that characterizes the Griffiths-like phase, and is depicted in Fig. 3. At zero field, measurable correlation lengths (~5 Å) are found around 200 K, its size progressively increasing up to a maximum at around $T_{C1} \approx 165$ K, where the cluster size rises beyond the experimental resolution of the instrument. The same evolution of ξ is observed at 2.5 kOe, with the maximum being shifted to lower temperatures ($T_{C1} \approx 150$ K). Finally, at 10 kOe, a continuous linearlike smooth progress of the correlation length on cooling is found, with no distinct increase above the Curie temperature. These SANS experiments reveal that a new magnetic-field effect is occurring in the Griffiths-like temperature range. In addition to the field-induced suppression of the downturn in dc susceptibility associated with the increase of PM, we observe that a moderate magnetic field seems to hinder the growth of large magnetic clusters within the PM phase, although the anomalous susceptibility exponent suggests the persistence of the clusterlike system. The latter agrees with the microscopic evidence that the magnetic field reduces the size of the clusters, but it does not eliminate the Griffiths-like state.

This suggestion is further supported by SANS isotherms measured in the vicinity of the abrupt increase of ξ. The correlation lengths obtained from these measurements at $T = 165$ and 140 K are represented in Fig. 4. This plot illustrates the effect of saturation that the magnetic field induces in the cluster size; i.e., the correlation length rapidly decreases and remains virtually constant at magnetic fields over 5–10 kOe, reaching minimum values of $\xi \approx 27(1)$ Å and ≈40(2) Å at 165 and 140 K, respectively. Nevertheless, the evolution of the intensity with the magnetic field is not so sharp; see the inset of Fig. 4. The decrease of the SANS intensity at $q = 0.1$ Å^{-1} upon magnetic field shows an approximate linear dependence, with an increasing slope with decreasing temperature, emphasizing the idea of a reduction in the number of scattering centers.

Summarizing the experimental evidence obtained from our study, we can conclude the existence of a system of FM clusters within the M-PM phase of $Tb_5Si_2Ge_2$, which characterize a Griffiths-like phase in the temperature range $T_C < T < 200$ K. The Griffiths temperature, in which the disorder starts to determinate the magnetic interactions of the system giving rise to short-range FM order, should correspond with $T_G \approx 200$ K. This temperature is surprisingly similar to the Curie temperature of the Si-rich range of composition of $Tb_5(Si_xGe_{1-x})_4$, which presents an O(I) crystallographic structure in the whole temperature range below 300 K, ordering ferromagnetically from $T_C(x = 0.7) \cong 205$ K to $T_C(x = 1) \cong 220$ K. In fact, the extrapolation of this transition line would yield an ordering temperature for an O(I) phase with $x = 0.5$ composition of

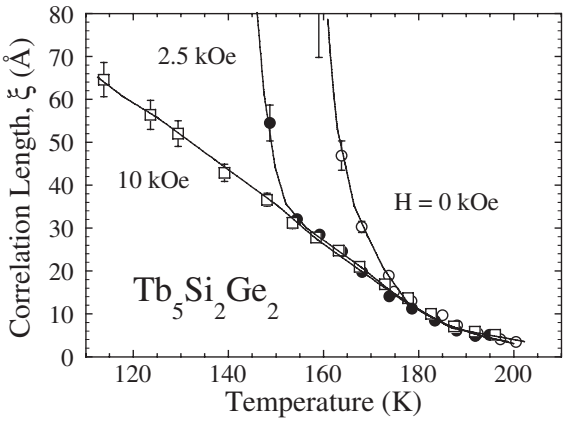

FIG. 3. Temperature and field dependence of ξ calculated from the Lorentzian fits of the SANS spectra.

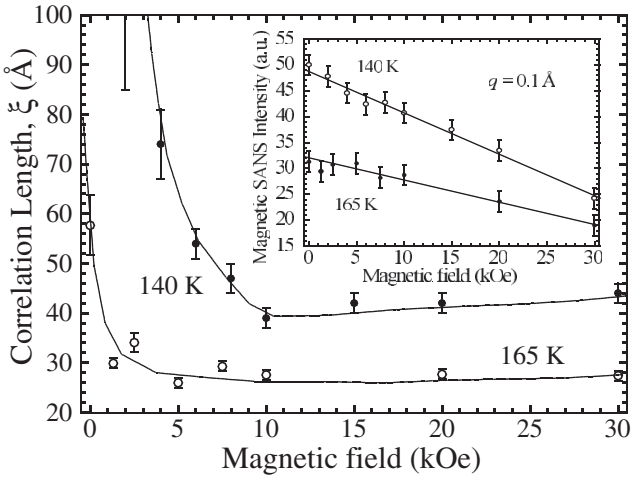

FIG. 4. Magnetic-field dependence of ξ at $T = 140$ and 165 K. The inset displays the isothermal dependence of the SANS intensity as a function of the magnetic field at $q = 0.1$ Å^{-1} for the same temperatures.

~200 K. Disorder within the layered structure is proposed to be responsible for the nucleation and stabilization of the Griffiths phase. For instance, structural defects or small deviations of the stoichiometric proportion of Si/Ge atoms might cause a local Si enrichment of the interslab covalent-like bonds, with the subsequent enhancement of the FM interactions. Choe *et al.* reported the existence of twin boundaries in the microstructure of the monoclinic $Gd_5Si_2Ge_2$ compound, in order to reduce the elastic energy of the system. This gives rise to different, but crystallographically equivalent twins within the crystal [15] separated by twin boundaries induced by stacking faults in the crystal structure. This breaks the periodicity of the consecutive formed/broken bonds between layers in the M phase, giving rise to nanometric regions of orthorhombic character which may serve as nucleation seeds for nanometric-size regions with a higher concentration of bonded pairs, and therefore, stronger O(I) character, and strengthened FM interactions. These nanometric entities with enhanced FM interactions can be interpreted as the FM clusters responsible for the anomalies in the magnetic susceptibility and the strong SANS signal in the PM regime, which would grow in size on cooling as the O(I) phase is more stable at low temperatures [the ground state of the system is O(I)-FM]. This source of disorder is proposed to be a key ingredient for the nucleation of the magnetic clusters and the appearance of a Griffiths-like phase in $Tb_5Si_2Ge_2$. In addition, although inhibition of the growth of FM clusters induced by a magnetic field seems rather counterintuitive, the O(I) structural character of the clusters induced by disorder explains the field evolution of the Griffiths phase in $Tb_5Si_2Ge_2$. Taking into account previous D2B experiments in a magnetic field in the M-PM phase, it is known that the magnetic field produces two effects in this system: first, a PM $\rightarrow$ FM transition on the M phase; second, the appearance of a field-induced O(I) transformed phase. As was reported in Ref. [20], the magnetic field is much more effective inducing the former transition than the latter, so the existence of a M-FM phase is favored. Therefore, we can conclude that the effect of the field on the cluster system is not related to the Griffiths-like nature of the anomaly, but to a particular magnetostructural coupling and the competition between the different structural and magnetic phases, as the application of a magnetic field would favor the M-FM phase to the detriment of the short-range O(I) structure. A similar situation was found in the $Sm_{0.15}Ca_{0.85}MnO_3$ perovskite system [24] where the field and temperature dependencies are explained considering the interplay of both magnetic and structural correlations.

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