Conclusions

This Ph.D. Thesis has been devoted to the preparation and characterisation of bulk $Gd_5(Si_xGe_{1-x})_4$ alloys and to the study of both the magnetocaloric effect and the first-order magnetostructural transition appearing in these compounds. In this final section, we summarise the most relevant results and the main conclusions obtained from this research. Some recommendations for further work are also included.

Summary and conclusions

- Bulk $Gd_5(Si_xGe_{1-x})_4$ samples with $0 \leq x \leq 0.5$ have been successfully prepared by using our home-made arc-melting furnace. All characterisation techniques show the good quality of the samples. SEM and electron-beam microprobe analyses show that the main 5:4 phases with the desired x are obtained. Ac susceptibility shows the magnetic transitions occurring in these alloys, while XRD detects the crystallographic structures corresponding to the phases at room temperature. $M(H)$ at 5 K show the presence of secondary Gd(Si,Ge) (1:1) and $Gd_5(Si,Ge)_3$ (5:3) phases in all samples. This presence is confirmed by XRD and e-beam microprobe, which also detect residual 5:4 phases with an x value different from that of the main phase. DSC shows that all samples present the first-order transition, and that secondary phases do not affect the latter. The heat treatments favour the segregation of these secondary phases [$M(H)$, XRD, SEM and microprobe], but also reduce the spread in the x value (ac susceptibility and DSC) and remove 5:4 residual phases with very different x values (as susceptibility and microprobe). Therefore, a trade-off between phase segregation and removal of x spread is desirable. A treatment at 920°C for 4 hours in a 10^{-5} mb vacuum furnace enables such a trade-off.

- A new differential scanning calorimeter (DSC) has been developed. The equipment features a high sensitivity down to 10 K and operates under applied magnetic fields of up to 5 T and within the temperature range 10-300

K. The device may be used to study first-order solid-solid phase transitions in the presence of magnetic fields. It has also been shown that this calorimeter enables an accurate determination of the entropy change associated with the magnetostructural phase transition of alloys exhibiting giant magnetocaloric effect. The transition can be induced by sweeping either T or H. Therefore, this kind of measurements clarifies the controvertial issue of the actual value of the entropy change at a first-order transition.

- The magnetocaloric effect arising from a field variation $0 \rightarrow H_{max}$, in a system which presents a first-order field-induced phase transition, can be properly evaluated through the entropy change obtained from the Maxwell relation, even when an ideal first-order transition takes place. When the Maxwell relation is evaluated over the whole field range, the T and H dependences of the magnetisation in each phase outside the transition region yield an additional entropy change to that associated with that of the actual first-order transition. It has also been shown, from both experimental data and phenomenological models, that the Maxwell relation, the Clausius-Clapeyron equation and the calorimetric measurements yield the entropy change associated with the first-order magnetostructural transition, ΔS, provided (i) the Maxwell relation is evaluated only within the field range over which the transition takes place, and (ii) the maximum applied field is as high as to complete the transition. The transition temperature must significantly shift with the applied field, in order to achieve a large MCE taking advantage of the entropy change associated with the first-order transition. This is relevant for the understanding of the thermodynamics and MCE of first-order magnetostructural transitions.

- DSC under H has been successfully used to measure ΔS associated with the first-order magnetostructural phase transition for $Gd_5(Si_xGe_{1-x})_4$, $x \leq 0.5$. We have shown that the transition entropy change scales with T_t. The scaling of ΔS is a direct consequence of the fact that T_t is tuned by x and H and it is thus expected to be universal for any material showing strong magnetoelastic effects, yielding a field-induced nature of the transition. ΔS is expected to (i) go to zero at zero temperature, (ii) tend asymptotically to zero at high temperature since the latent heat is finite, and (iii) display a maximum at a temperature for which both ΔM is maximised and T_t shows the minimum field dependence. The specific shape of ΔS *vs.* T_t will depend on the details of the phase diagram, $T_t(x)$. Finally, the scaling of ΔS shows the equivalence of magnetovolume and substitution-related effects in $Gd_5(Si_xGe_{1-x})_4$ alloys.

- The variation of the transition field with the transition temperature, dH_t/dT_t, has been studied in $Gd_5(Si_xGe_{1-x})_4$ for all the range of compositions where the first-order transition occurs, $0 \leq x \leq 0.5$. Taking into account the behaviour of dH_t/dT_t as a function of x and ΔM decreasing monotonously with T_t, it is shown that dH_t/dT_t governs the scaling of ΔS with T_t, giving further evidence that the origin of this scaling is the magnetoelastic nature of the transition. Moreover, two distinct behaviors for dH_t/dT_t have been found on the two compositional ranges where the magnetostructural transition occurs, thus showing the difference in the strength of the magnetoelastic coupling in this system.

- It has been shown that an unreported field-induced magnetic phase transition exists from the AFM phase to a phase which presents short-range correlations (SRAFM). The results suggest that the transition results from the breaking of the long-range AFM correlations when a magnetic field is applied, which leads to competing FM and AFM short-range correlations. FM correlations are also relevant in the whole long-range AFM phase. The expected transition from the SRAFM to the PM phase takes place at ~240 K at zero field, being widened and smoothed under applied field. This findings contribute to the understanding of the rich and complex magnetic behaviour of Ge-rich $Gd_5(Si_xGe_{1-x})_4$ alloys, which arises from the competition between the intraslab FM interactions and the interslab AFM interactions.

- The study of dynamics of the first-order transition in $Gd_5(Si_xGe_{1-x})_4$ alloys has unveiled a very interesting behaviour. On one hand, our DSC under field has revealed that the entropy change associated with the transition is different when it is field- or thermally-induced, evidencing that the initial and final states are different because the transition is not ideal. On the other hand, a cycling study shows that the field-induced entropy change increases during the first cycles, then reaching a stationary value. This behaviour is related to the avalanche distribution, which also evolves with cycling. The structure of avalanches becomes repetitive after a few cycles tending towards a power-law distribution, unveiling the athermal character of the transition.

Future perspectives and recommendations

The magnetocaloric effect (MCE) has promising applications to magnetic refrigeration. Magnetic refrigeration, which shows a high efficiency and is environment-friendly, is a serious alternative to the conventional gas-compression technology. Therefore, the search for new materials showing MCE is of great interest.

In this work, we have shown that $Gd_5(Si_xGe_{1-x})_4$ alloys present a giant MCE due to a variety of properties, mainly related to the first-order field-induced magnetostructural phase transition occurring in this system. An interesting research line would be the study of other materials showing a transition with similar properties, in order to be applied to magnetic refrigeration. In fact, after the discovery of the giant MCE in $Gd_5(Si_xGe_{1-x})_4$ alloys, new works on MCE have been focused in MnAs-based and $La(Fe,Si)_{13}$ intermetallic systems.

Concerning the $Gd_5(Si_xGe_{1-x})_4$ alloys, a lot of effects remain to be explained in this exciting system. Although the microscopic mechanisms of the transition begin to be understood, other essential questions are still opened. The actual magnetic structure in the various magnetic phases present in the system is a relevant one. The dynamics of the first-order transition, which we have just begin to face, is another open question. The competition between AFM and FM interactions in Ge-rich alloys is another unsolved problem that we have also contributed to understand.

Finally, we would like to remark that MCE can be studied in a large variety of materials. We also remark that $Gd_5(Si_xGe_{1-x})_4$ alloys offers a very rich and complex magnetic and structural behaviour. We hope that the present thesis has helped to unveil and understand the properties of this system a litte bit more.