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Abstract

A complete investigation of the complex magnetic behaviour of Gd$_5$Ge$_4$ by means of linear thermal expansion and magnetostriction measurements (5–300 K, 0–120 kOe) has been carried out. Our results support the suggested existence in this system of a coupled crystallographic–magnetic transition from a Gd$_5$Ge$_4$-type *Pnma* (antiferromagnetic) to a Gd$_5$Si$_4$-type *Pnma* (ferromagnetic) state. Strong magnetoelastic effects are observed at the field-induced first-order magnetic–martensitic transformation. A revised magnetic and crystallographic H–T phase diagram is proposed.

1. Introduction

Gd$_5$(Si$_x$Ge$_{1-x}$)$_4$ is a unique class of materials where many important properties and exotic behaviour have been recently discovered [1]. Among the most relevant we can highlight: the giant magnetocaloric effect [2, 3], strong magnetoelastic effects [4, 5], giant magnetoresistance [6, 7], unusual Hall effect [8], and spontaneous generation of voltage [9]. All this behaviour has been associated with the intrinsically layered crystallographic structure combined with a magnetic–martensitic first-order phase transformation [10]. The coupled magnetic–crystallographic transition can be induced reversibly by changing external parameters such as temperature, an external magnetic field or hydrostatic pressure [1–5]. Therefore, these alloys are attractive for their potential applications in magnetic refrigeration and/or as magnetostrictive/magnetoresistive transducers.

The phase relationships, crystallography and magnetic phase diagram were initially proposed in [11] and recently revised [12]. A total of three extended solid solution regions were confirmed: the Si-rich solid solution, $0.575 \leqslant x \leqslant 1$, has the orthorhombic Gd$_5$Si$_4$-type structure [O(I)] belonging to the *Pnma* space group, the intermediate phase $0.4 < x \leqslant 0.503$ has a room temperature monoclinic (M) structure, space group $P112_1/a$, and the Ge-rich

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region, $0 \leqslant x \leqslant 0.3$, crystallizes into the Gd_5Ge_4-type structure [O(II)], also in the orthorhombic *Pnma* space group. All three structures are composed of identical two-dimensional (2D) sub-nanometre-thick layers (slabs) interconnected via partially covalent inter-slab X–X bonds (X = Si, Ge). In the O(I) structure, all the slabs are interconnected by X–X bonds; half of these bonds are broken in the M structure and none remain in the O(II) structure. The magnetic–crystallographic transition involves breaking and reforming specific covalent X–X bonds [10] and the low-temperature ground state for all compositions $0 < x \leqslant 1$ is always ferromagnetic (FM) with all the slabs being interconnected, i.e. with the O(I) structure [5, 10].

The magnetic ground state of the parent Gd_5Ge_4 alloy has been reported to be a simple antiferromagnet (AFM) with a Néel temperature of $\sim$15 K [13], but recent electrical resistivity, heat capacity and magnetization measurements clearly demonstrated that Gd_5Ge_4 orders antiferromagnetically at $\sim$130 K, and that no FM phase is observed in zero magnetic field down to the lowest measured temperature of $\sim$1.8 K [14, 15]. This is in sharp contrast with the magnetic behaviour of the Ge-rich compounds with $0 < x \leqslant 0.3$, see e.g. $x = 0.08$ [16] or 0.1 [5]. Furthermore, this system presents a very complex magnetic field–temperature (H–T) phase diagram, see figure 4 in [15]. Details about these intriguing and unexpected magnetic phenomena are described in detail in [14]. Briefly, above a critical field of $\sim$18 kOe at 4.3 K an irreversible first-order AFM $\rightarrow$ FM transition takes place (i.e. when the magnetic field is removed, the entire volume of the sample remains in the FM state), which becomes completely reversible above $\sim$20 K. It has been proposed [14, 15] that this AFM $\rightarrow$ FM metamagnetic transition is accompanied by a field-induced O(II) $\rightarrow$ O(I) crystallographic transformation, although no direct confirmation exists so far.

The research reported in this paper is a complete investigation of this complex magnetic behaviour of Gd_5Ge_4 by means of linear thermal expansion (LTE) and magnetostriction measurements. Our study supports the suggested existence of a coupled magnetic–crystallographic transition in this system, resulting in strong magnetoelastic effects. A revised H–T phase diagram is proposed.

2. Experiment

The alloy with nominal composition Gd_5Ge_4 was synthesized by arc melting of 99.9 wt% pure Gd and 99.9999 wt% pure Ge under a high-purity argon atmosphere. Weight losses during melting were negligible and, therefore, the initial composition was considered unchanged. The quality of the as-cast sample was checked by room-temperature x-ray diffraction. The x-ray pattern confirms the presence of an orthorhombic main phase (*Pnma*) with unit-cell parameters $a = 7.6946(5)$ Å, $b = 14.826(1)$ Å and $c = 7.7814(4)$ Å in good agreement with those reported in [11]. A minor amount ($\sim$6%) of a secondary phase has also been detected and indexed as Gd_5Ge_3. The ac magnetic susceptibility was measured using a commercial (Quantum Design) superconducting quantum interference device (SQUID) magnetometer with an excitation field of 1 Oe (peak value) at frequencies in the range 0.1–10^3 Hz. LTE and magnetostriction measurements were performed using the strain-gauge technique in a superconducting coil that produces a dc magnetic field of up to 120 kOe.

3. Results and discussion

The real part of the ac magnetic susceptibility χ'_{ac} of the Gd_5Ge_4 sample in the temperature range 5–150 K is shown in figure 1. The measurements were carried out while increasing the temperature after the sample had been zero-field cooled down to 5 K (open symbols), and after
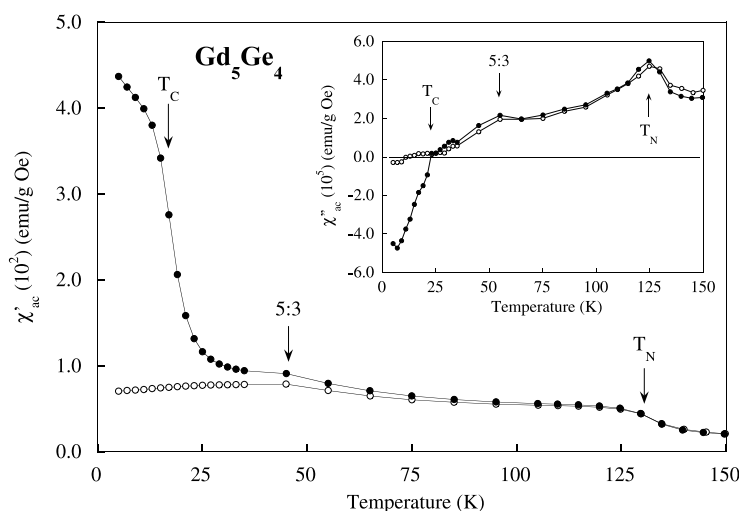
Figure 1. Temperature dependencies of the real part of the ac magnetic susceptibility χ'_{ac} (ac field = 1 Oe, excitation frequency = 500 Hz) of Gd$_5$Ge$_4$. Data were taken on heating in zero dc magnetic field after the sample was zero-field cooled (AFM state at 5 K, $\circ$) and after the sample was zero-field cooled and then a magnetic field of 50 kOe was applied and removed isothermally at 5 K (FM state at 5 K, $\bullet$). The inset shows the temperature dependencies of the imaginary part of the ac magnetic susceptibility χ''_{ac} measured in the same conditions as χ'_{ac}.

applying and removing isothermally a magnetic field of 50 kOe at 5 K (solid symbols). Our results confirm the previously reported magnetic behaviour [14, 15]. In zero field the sample orders antiferromagnetically at $T_N = 130$ K, probably in a magnetic structure (unknown until now) similar to that of Tb$_5$Ge$_4$ [17]. A small anomaly can also be detected at about 45 K that can be attributed to the 5:3 impurity phase present in our sample [18]. In the second heating run, after applying and removing 50 kOe at 5 K, a stable FM phase sets in and remains up to a temperature $T_C = 16$ K, where the reversed FM $\rightarrow$ AFM transition takes place spontaneously. The values of all the transition temperatures have been taken at the maximum dχ'_{ac}/dT values. In the inset of figure 1, the temperature dependence of the imaginary part of the ac susceptibility χ''_{ac} is displayed. It is noteworthy that in the FM state χ''_{ac} is negative, as previously observed in Gd$_5$(Si$_{1.5}$Ge$_{2.5}$) and Gd$_5$(Si$_2$Ge$_2$) below the magnetostructural transition [19]. This unusual magnetic behaviour is thought to be caused by an anomalous relaxation process of the domain-wall oscillations excited by the ac magnetic field. This behaviour is not a unique feature of the 5:4 phases, and has been found in other rare-earth intermetallic compounds such as Gd$_4$(Bi$_x$Sb$_{1-x}$)$_3$ [20] and RAl$_2$ (R = Gd, Dy, Er) [21]. All the measurements in [19–21] have been performed at a frequency of 125 Hz although in the particular case of GdAl$_2$ [21] χ''_{ac} was reported to be independent of frequency values between 55 and 1000 Hz. In contrast, we have discovered in Gd$_5$Ge$_4$ a strong effect of the excitation frequency on χ''_{ac} (no effects were seen on χ'_{ac}). Contrary to the results represented in the inset of figure 1 measured at 500 Hz, χ''_{ac} was found to be positive at all temperatures at a smaller frequency of 10 Hz. We carried out detailed studies of the frequency dependence of the ac susceptibility between 0.1 and 1000 Hz in a previously studied sample, Gd$_5$(Si$_{1.8}$Ge$_{2.2}$) [4], and found a crossover between positive and negative values of χ''_{ac} at a frequency of about 100 Hz [22]. Further systematic investigations are required before this effect is fully understood.

In order to support the proposed idea of the existence of structural effects associated with the observed magnetic behaviour, the LTE was measured following the same protocol as in
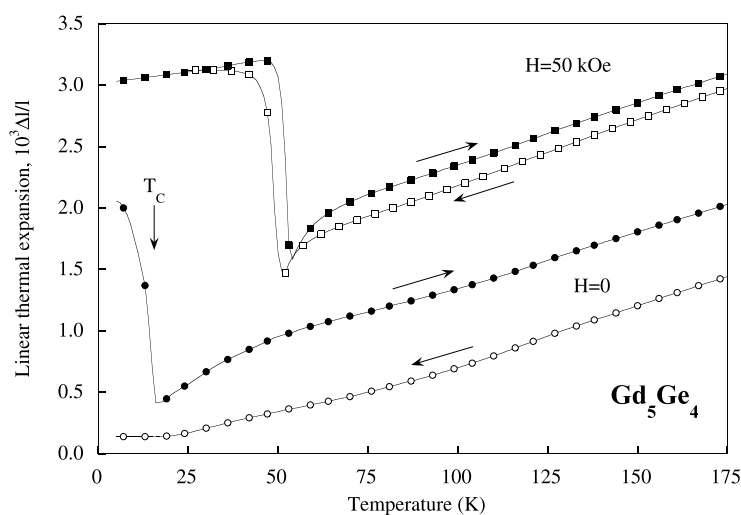
Figure 2. LTE ($\Delta l / l$) as a function of temperature of Gd$_5$Ge$_4$: zero-field run upon cooling ($\bigcirc$), zero-field run heating the sample after an isothermal application and removal of a magnetic field of 120 kOe at 5 K ($\bullet$), cooling ($\square$) and heating ($\blacksquare$) cycle in a field of 50 kOe.

the ac susceptibility described previously. The results are shown in figure 2. The sample was cooled down to 5 K in zero field, and, as can be observed (open circles), no anomaly is detected in the LTE (no difference was found between cooling and heating cycles). In a subsequent cycle, the sample was isothermally magnetized in a field of 120 kOe at 5 K, the field was removed, and the LTE recorded on heating (solid circles). A large and abrupt jump, $\Delta l / l \cong 0.16\%$, is observed in the LTE at T_C. This confirms the existence of strong structural effects associated with the FM → AFM first-order magnetic transition. No significant change was found at T_N. We note that the observed behaviour is remarkably similar to that reported previously in the Ge-rich composition Gd$_5$(Si$_{0.1}$Ge$_{0.9}$)$_4$ [5], where a stable FM [O(I)] phase exists at low temperatures. Therefore, it is quite plausible that the observed transition in the LTE corresponds to an O(I)(FM) → O(II) (AFM) first-order crystallographic transformation. Nevertheless, powder x-ray diffraction in an applied magnetic field should be actively pursued to confirm directly the proposed structural changes. We also performed heating and cooling cycles at constant applied fields of $H = 20$, 50, and 120 kOe; as an example, the results obtained in a field of 50 kOe have been included in figure 2. In all cases, a reversible first-order transition is observed at temperatures which increase with the magnetic field at a rate of $\sim$0.5 K kOe^{-1}. A thermal hysteresis of $\sim$5 K is also seen.

As reported in other compositions [4, 5], important magnetoelastic effects are expected whether the O(II) (AFM) → O(I) (FM) transformation can be triggered by an isothermal application of an external magnetic field. Magnetostriction isotherms, λ, at selected temperatures along the applied magnetic field are displayed in figure 3. As in [4, 5] the magnetostriction reflects a change in volume of the sample $\approx 3\lambda$, since we have also confirmed in this case that there are no significant changes, within the experimental error, by applying the magnetic field either parallel or perpendicular to the measuring direction. A hysteresis of $\sim$7 kOe is seen consistent with the first-order character of the field-induced transition (the field was swept at a speed of 15 kOe min^{-1}). In the 60 K isotherm, a complex behaviour is seen upon increasing the magnetic field. We have confirmed that this behaviour is observed only in a narrow temperature range between 55 and 65 K (note also that our maximum
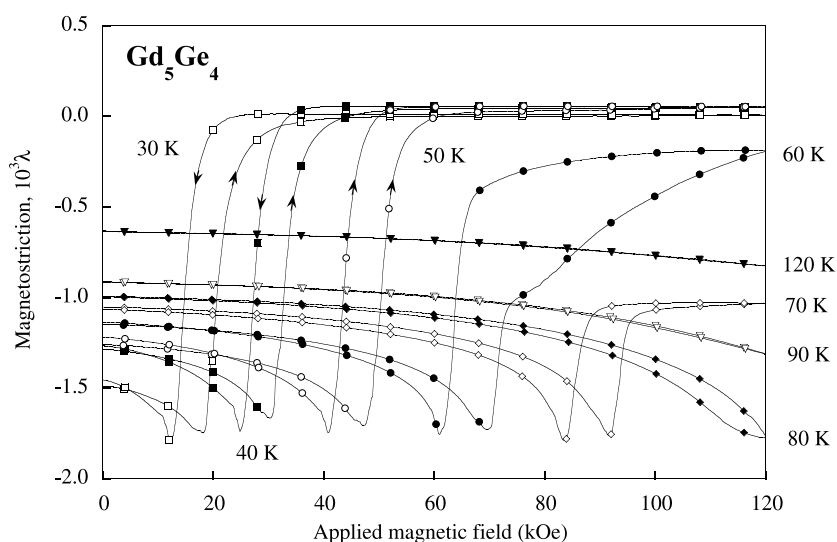
Figure 3. Magnetostriction isotherms (λ) of Gd$_5$Ge$_4$ along the applied field at selected temperatures displaying a reversible O(II)(AFM) $\leftrightarrow$ O(I)(FM) transition.

applied field is 120 kOe). The results are fully reproducible and do not depend on whether the magnetic field is applied parallel or perpendicular to the measuring direction. At this point we can only speculate that this behaviour might correspond to a complex magnetization behaviour, probably associated with a first-order magnetization process along some specific crystallographic direction. Magnetostriction measurements in a single crystal are required to confirm this point.

Very intriguing magnetic phenomena take place below $\sim$20 K [14]. In this temperature range, application of the magnetic field for the first time induces the FM state in the entire volume of the AFM Gd$_5$Ge$_4$. Below $\sim$10 K this FM phase is stable after removal of the magnetic field, i.e., the AFM $\rightarrow$ FM metamagnetic transition is irreversible. Between $\sim$10 and 20 K a fraction of the sample volume is converted back to the AFM state, i.e., the low-temperature zero-field state is phase segregated into AFM and FM regions. We have studied the magnetoelastic effects associated with this behaviour, and the results are summarized in figure 4. In all cases the sample was cooled in zero field down to the measuring temperature, i.e. the initial state was in all cases the AFM [O(II)]. At 5 K (figure 4(a)) the first application of the magnetic field (open symbols) induces the transition into the FM state and a sharp jump of $\lambda \approx 0.16\%$ takes place at a critical field $H_C \approx 22$ kOe. We associate this effect with a field-induced O(II) (AFM) $\rightarrow$ O(I) (FM) irreversible structural transition, since no anomaly is detected upon removing the field, i.e. the sample remains in the final deformation state. Subsequent measurements (solid symbols) yield no magnetoelastic effects, consistent with the fact that the final O(I) (FM) state is stable. This is not the case at higher temperatures. For instance, at 8 K, the final field-induced O(I) (FM) state is metastable upon removal of the magnetic field, see figure 4(b). This can be seen in the time relaxation of the magnetostriction upon removal of the magnetic field, see inset of figure 4(b). The relaxation is approximately logarithmic and extremely sluggish, i.e. in 10^4 s just 10% of the sample has been transformed back into the AFM state. A similar behaviour was observed previously [14] by placing the sample at 4.3 K in an undercritical field. At 14 K the field-induced transition is partially reversible, as shown in figure 4(c). Upon removal of the magnetic field $\approx$54% of the sample
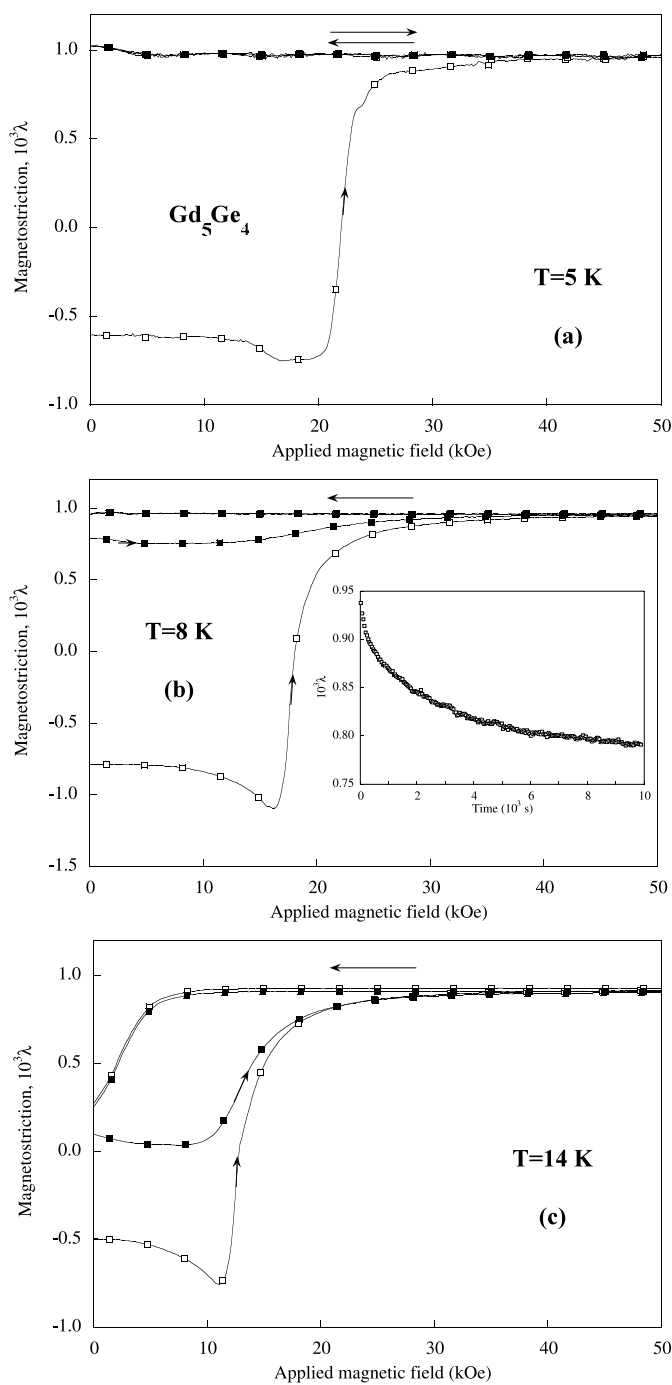
Figure 4. Magnetostriction isotherms (λ) of Gd_5Ge_4 along the applied field at selected temperatures: (a) $T = 5$ K showing an irreversible O(II) (AFM) $\rightarrow$ O(I) (FM) transition, (b) $T = 8$ K showing an irreversible transition and strong relaxation effects in zero field (inset), (c) $T = 14$ K displays a partially reversible transformation. In all cases the maximum applied field was 120 kOe, but only values up to 50 kOe have been plotted for clarity. In all cases, ($\square$) is the first run and ($\blacksquare$) is a second field increase and reduction.
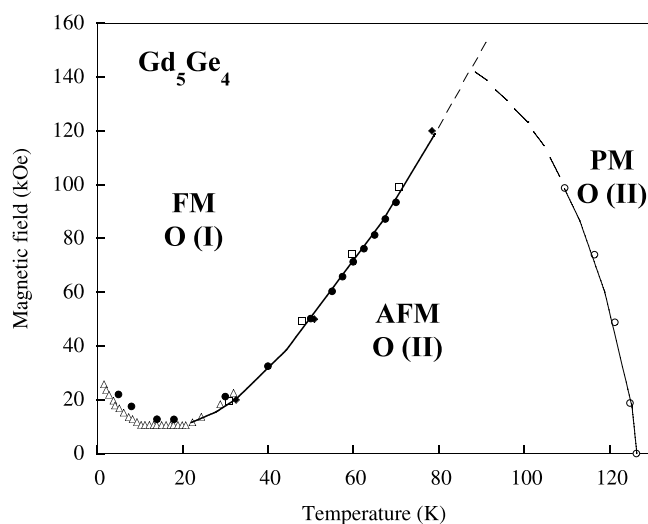
Figure 5. Magnetic and crystallographic H–T phase diagram of Gd$_5$Ge$_4$. PM, FM and AFM label different magnetic phases and O(I) and O(II) denote different crystallographic structures, as defined in the text. The open symbols ($\triangle$, $\square$, $\bigcirc$) are magnetization and heat capacity data taken from [15]; the solid symbols are from the present work, either from magnetostriction isotherms upon increasing the field ($\bullet$) or LTE in constant fields ($\blacklozenge$).

remains in the FM state. The isotherms at $T \geqslant 18$ K were fully reversible as already shown in figure 3.

Based on the present study of the magnetoelastic properties of Gd$_5$Ge$_4$, and on previous works carried out in different composition alloys of the Gd$_5$(SiGe)$_4$ series [4, 5], we can conclude that the first-order AFM–FM transition is accompanied by a simultaneous structural transformation from the orthorhombic O(II) to the O(I) structure. In figure 5 we reproduce the phase diagram from [15] together with the critical fields and transition temperatures obtained in our study of LTE isofields and magnetostriction isotherms. The solid thick curve corresponds to a reversible first-order crystallographic–magnetic transition from the O(II) AFM phase to the O(I) FM state. Below $\approx$20 K this transition is partially reversible, and becomes completely irreversible below $\approx$10 K.

Similar phenomenology has been found recently in other rare-earth intermetallic compounds such as TbFe$_{4.4}$Al$_{7.6}$ [23], La(FeCoAl)$_{13}$ [24], and Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$ [25]. In the case of TbFe$_{4.4}$Al$_{7.6}$ a field-induced irreversible transition has been identified at 5 K, this transformation being accompanied by a giant orthorhombic distortion [23]. The magnetic phase diagram of the La(Fe$_{0.876}$Co$_{0.007}$Al$_{0.12}$)$_{13}$ cluster intermetallic compound closely resembles that of Gd$_5$Ge$_4$. This system undergoes an irreversible transition from an AFM to a FM state below 17 K, the FM state being retained after switching off the field [24]. This metamagnetic transition, as studied in (undoped with Co) La(FeAl)$_{13}$ compounds, is accompanied by a huge volume magnetostriction [26]. A comprehensive study has been carried out in Ce(Fe$_{0.96}$Al$_{0.04}$)$_2$ by means of dc magnetization and magnetotransport measurements focused on the first-order transition from ferromagnetism to antiferromagnetism. Manekar *et al* [25] interpreted their findings in terms of kinetic arrest of a first-order transition. In all these cases, as in Gd$_5$Ge$_4$, strong structural effects are associated with the field-induced first-order transition. Therefore, independent of the microscopic details of the phase transition, we believe that the situation in Gd$_5$Ge$_4$ could be the same as proposed in [25]: the freezing of the FM state

after removing the magnetic field takes place because the kinetics of the reversed FM $\rightarrow$ AFM transition is hindered, and at sufficiently low temperatures and high magnetic fields arrested, since the structural relaxation becomes larger than the experimental timescales. The strong relaxation effects, metastability, and AFM + FM phase segregation at low temperatures can also be interpreted in the same scenario. Other interesting examples in condensed matter physics with analogous behaviour are the $R_{0.5}Sr_{0.5}MnO_3$ colossal magnetoresistance perovskites [27].

4. Conclusions

In summary, we have found important magnetoelastic effects at the first-order AFM–FM transition in the Gd_5Ge_4 alloy. Our results support the existence in this system of a coupled crystallographic–magnetic transition from a Gd_5Ge_4-type *Pnma* (AFM) to a Gd_5Si_4-type *Pnma* (FM) state. Depending on the temperature range, a distinct behaviour is seen: the field-induced O(II)(AFM) $\rightarrow$ O(I) (FM) transformation is fully irreversible below $\approx$10 K. In addition, at 8 K, the final field-induced O(I) (FM) state is metastable upon removal of the field and a time relaxation effect is seen on the magnetostriction. Between $\approx$10 and $\approx$20 K the field-induced transition is partially reversible and a phase segregated AFM+FM state is found at low temperatures. Above $\approx$20 K the O(II) (AFM) $\leftrightarrow$ O(I) (FM) is fully reversible. These effects are characteristic of first-order transitions where, at sufficiently low temperatures and high magnetic fields, structural relaxation times become larger than the experimental timescales. A revised magnetic and crystallographic H–T phase diagram is proposed.

Acknowledgment

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