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CHAPTER 9. ALLOYS AND COMPOUNDS

Magnetic, Magnetothermal, and Magnetoelastic Properties of $Gd_5(Si_{1.95}Ge_{2.05})$ near the Magnetostructural Phase Transition

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Abstract—The $Gd_5(Si_xGe_{4-x})$ system with $0 \le x \le 2.1$ undergoes a magnetostructural phase transition, which can be triggered by a magnetic field above Curie temperature. During the transition, colossal magnetostrictive, giant magnetocaloric, and giant magnetoresistance effects are observed. Experimental studies of the $Gd_5(Si_{1.95}Ge_{2.05})$ composition using magnetic susceptibility, magnetization, magnetostriction, linear thermal expansion, heat capacity, and direct magnetocaloric effect measurements confirm that both the structural and magnetic phase changes occur simultaneously at 262 K in a zero magnetic field. The magnetocaloric effect values in a low magnetic field (14 kOe) calculated from the heat capacity and measured directly are in reasonable agreement in the high temperature region (above 262 K). Below Curie temperature, the direct measurements show a negative magnetocaloric effect, which is unexpected for a ferromagnetic system and likely originates from a complex metastable process of magnetization, leading to an increase in the entropy of the sample in a low magnetic field.

INTRODUCTION

The ability of the magnetic field to induce a magnetostructural phase transition in the intermetallic $Gd_5(Si_xGe_{4-x})$ is of considerable importance from both experimental and theoretical perspectives. A detailed crystallographic study [1] demonstrated that the high temperature paramagnetic (PM) phases crystallize in the orthorhombic (space group Pnma) Gd_5Si_4-type crystal structure when $x > 2$. The crystal structures in the PM state are of monoclinic (space group $P112_1/a$) $Gd_5(Si_2Ge_2)$-type when $0.96 < x < 2$ and of orthorhombic (space group Pnma) Gd_5Ge_4-type when $x < 0.8$. The low temperature ferromagnetic (FM) phases have the orthorhombic (space group Pnma) Gd_5Si_4-type crystal structure over the entire range of concentrations, i.e., when $0 \le x \le 4$ [2–4]. Each intermetallic $Gd_5(Si_xGe_{4-x})$ phase is formed by a periodic arrangement of well-defined building blocks (slabs), layers with strongly interacting 4*f*-, 3*p*- and 4*p*-elements, while the properties of $Gd_5(Si_xGe_{1-x})_4$ materials are determined by both interactions within and between the slabs [5].

The silicon-rich compositions ($x > 2$) are ordered magnetically (from the PM to FM state) through a second order magnetic phase transition [1, 5]. The crystallographic first-order phase transition from a monoclinic to an orthorhombic symmetry occurs simultaneously with the PM to FM magnetic transformation in the intermediate range of concentrations when $0.96 \le x \le 2$ [1, 3–5]. The germanium-rich compounds ($x < 0.8$) initially undergo a second-order PM to antiferromagnetic (AFM) magnetic phase transition without a crystallographic phase change followed by the first-order crystallographic isostructural (orthorhombic Gd_5Ge_4-type to orthorhombic Gd_5Si_4-type) phase transition accompanied by an AFM to FM magnetic transformation with lowering temperatures [1, 2, 5]. Recent results [6] indicate that the intermediate monoclinic (in the PM state) phase can be stabilized by appropriate heat treatment in the $2 < x \le 2.1$ range of concentrations.

The application and the removal of a dc magnetic field above the respective Curie temperatures triggers reversible magnetostructural phase transitions in the $Gd_5(Si_xGe_{4-x})$ system [1–5]. In order to explain the origin of the correlation between the crystallographic and magnetic phases, a number of models have been proposed. For example, variation of the exchange interaction originating from the breaking of interslab covalent Si(Ge)-Si(Ge) bonds and a simultaneous decrease in the unit-cell volume calculated from the RKKY model were considered in [4]. The contributions different from the indirect exchange one due to bonding changes was considered in [7, 8]. The role of density of states at the Fermi level, which is quite sensitive to the unit-cell volume changes and thus can control the transition, was considered in [9]. Regardless of the mechanism of the combined magnetic-crystallographic phase change, colossal magnetostriction, a giant magnetocaloric effect (MCE), and giant magnetoresistance observed in the title system [1–4, 7, 10–12] open up a broad range of technological applications for $Gd_5(Si_xGe_{1-x})_4$ materials.

EXPERIMENT

A polycrystalline $Gd_5(Si_{1.95}Ge_{2.05})$ sample was prepared by arc melting in an argon atmosphere from sto-

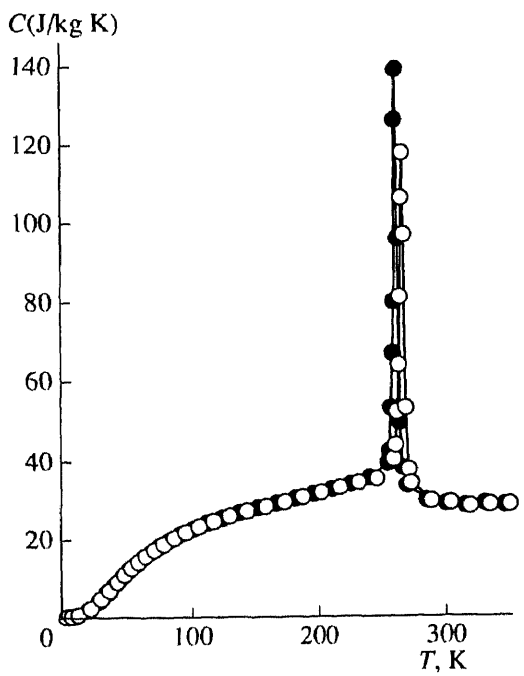

Fig. 1. The heat capacity of $Gd_5(Si_{1.95}Ge_{2.05})$ as a function of temperature in (closed symbols) zero and (open symbols) 14 kOe magnetic fields.

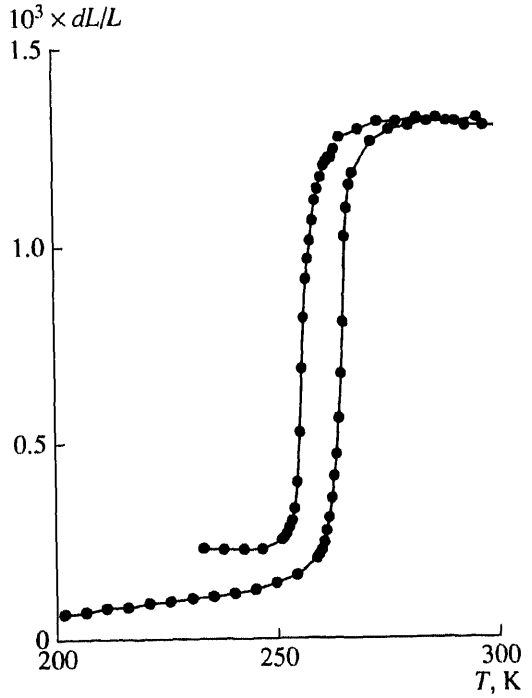

Fig. 2. Linear thermoexpansion of $Gd_5(Si_{1.95}Ge_{2.05})$ as a function of temperature measured on heating and cooling in a zero magnetic field.

ichiometric amounts of high-purity components (Gd 99.95 wt % pure, and Si and Ge, both 99.99 wt % pure) and then annealed in a helium atmosphere at 1270 K for three days. The X-ray powder diffraction data collected on a Scintag diffractometer using CuK_α radiation revealed that the sample has a monoclinic crystal structure at room temperature (space group $P112_1/a$) and the following lattice parameters: $a = 7.586(1)$, $b = 14.808(2)$, $c = 7.780(1)$ Å, and $\gamma = 93.16(2)°$. No impurity phases were detected from X-ray powder diffraction data. The magnetostriction and thermal expansion were measured using the strain–gauge technique. The heat capacity data in constant magnetic fields were collected using a semiadiabatic heat pulse calorimeter [13]. Both the magnetization and magnetostriction were measured in pulse magnetic fields up to 150 kOe. Direct measurements of the magnetocaloric effect were carried out adiabatically in magnetic fields up to 15 kOe. The typical time of switching the field on and off was ~1 sec. The magnetocaloric effect was also calculated from the heat capacity data. The details of the direct MCE measurements and calculations and the corresponding accuracy are described in [14–17].

RESULTS AND DISCUSSION

The heat capacity of $Gd_5(Si_{1.95}Ge_{2.05})$ measured on heating from 4.2 K in a zero and 14-kOe magnetic field is shown in Fig. 1. The phase transition occurs at ~262 K in $H = 0$ kOe and the transition temperature increases with increasing magnetic field. The spontaneous thermal expansion rapidly changes in the same temperature region as shown in Fig. 2. Both the heat capacity behavior (Fig. 1) and the presence of temperature hysteresis in the thermal expansion data (Fig. 2) clearly indicate the first-order nature of the phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$. Similar features of the phase transition were noted earlier in $Gd_5(Si_2Ge_2)$ [10] and $Gd_5(Si_{1.8}Ge_{2.2})$ [3] samples, which have the same monoclinic $Gd_5(Si_2Ge_2)$-type crystal structure at room temperature. Subsequent X-ray diffraction studies [3, 4] demonstrated that the low temperature FM phases have an orthorhombic Gd_5Si_4-type crystal structure. The *ac* magnetic susceptibility data, shown in Fig. 3, confirm that the crystallographic transition between the high-temperature monoclinic phase and the low-temperature orthorhombic phase is accompanied by a change in the magnetic state of $Gd_5(Si_{1.95}Ge_{2.05})$.

In order to examine the magnetostructural phase transition in more detail, the magnetization and magnetostriction measurements were carried out in pulse magnetic fields up to 150 kOe. The magnetization and magnetostriction isotherms for the high-temperature ($T > 262$ K) phase are shown in Figs. 4 and 5, respectively. The values of the magnetostriction measured both parallel and perpendicular to the magnetic field vector were the same within the experimental error.

Broad (~20 kOe) hysteresis measured in both magnetization and magnetostriction provides additional evidence of the first-order nature of the phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$. The critical magnetic fields for the

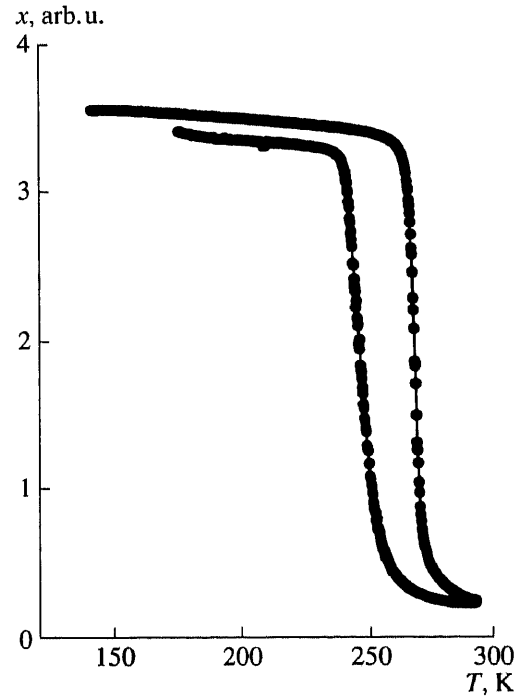

Fig. 3. The *ac* magnetic susceptibility of $Gd_5(Si_{1.95}Ge_{2.05})$ as a function of temperature.

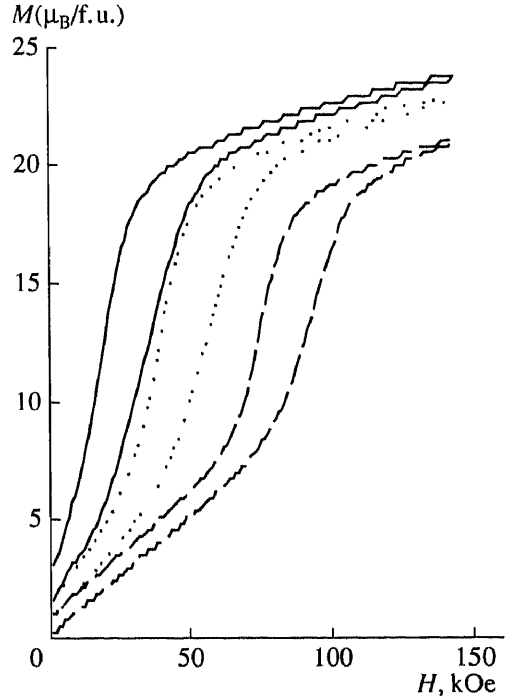

Fig. 4. The isothermal magnetization of $Gd_5(Si_{1.95}Ge_{2.05})$ in a pulsed magnetic field.

start and completion of the transformation increase with the increasing temperature. It is seen that both the magnetic state and crystal structure are considerably changed under the influence of the magnetic field thus confirming the behavior observed earlier for different compositions of $Gd_5(Si_xGe_{4-x})$ [1–8, 10–12, 18] and its interpretation as a reversible magnetostructural phase transition induced by an external magnetic field. In particular, in the compound $Gd_5(Si_{1.8}Ge_{2.2})$ [3] of monoclinic structure at room temperature, the magnetic field induces transition (from the PM to FM state) and simultaneously the change of crystal structure from monoclinic to orthorhombic of Gd_5Si_4 type. Consequently, the simultaneous transformation of both the magnetic and crystal structures in $Gd_5(Si_{1.95}Ge_{2.05})$ is accompanied by a colossal magnetostriction (Fig. 5), a giant magnetoresistance [18], and a giant magnetocaloric effect (see below).

Investigation of the magnetocaloric effect in the vicinity of this phase transition is complicated by the strong dependence of the results on the measurement technique, as well as on the measurement procedure. We measured the MCE directly in the magnetic field of 14 kOe using two different methods and calculated it using the heat capacity data. In the first series of direct measurements, the sample was initially heated to 320 K (i.e., was transformed into the paramagnetic state) and then cooled step by step with the stabilization of the temperature at every 2 K to collect the next MCE point, which was done by increasing the magnetic field to 14 kOe. In the second series, the sample was heated up to 320 K after each measured point, and then it was cooled to the desired temperature before making the next ΔT measurement. The obtained results are shown in Fig. 6. The MCE behavior has a distinct maximum

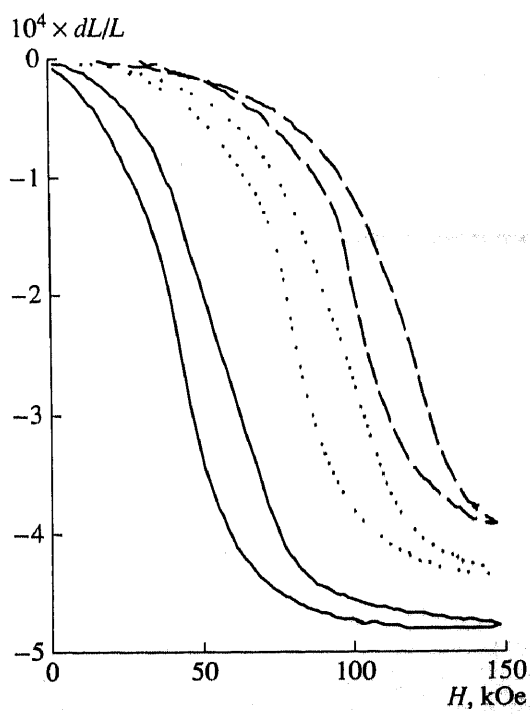

Fig. 5. The isothermal magnetostriction, *dL/L*, of $Gd_5(Si_{1.95}Ge_{2.05})$.

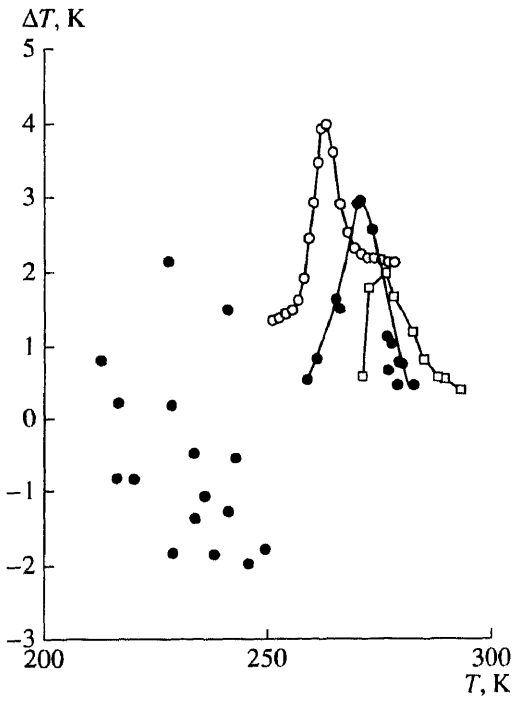

Fig. 6. The magnetocaloric effect, ΔT, of $Gd_5(Si_{1.95}Ge_{2.05})$. The solid lines are polynomial approximations.

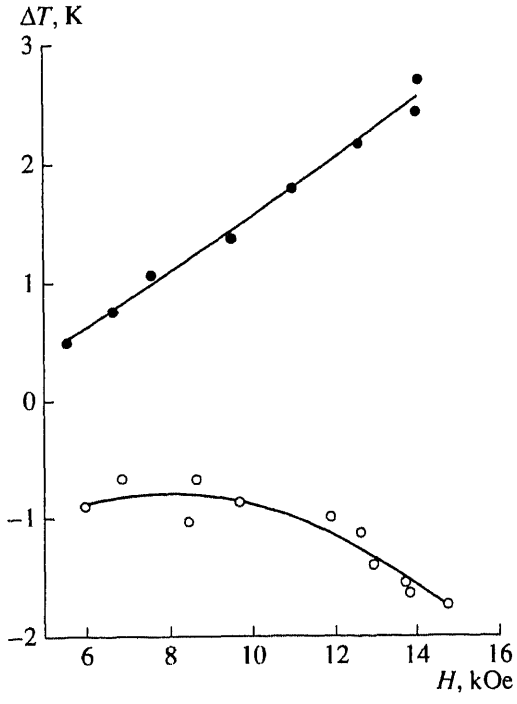

Fig. 7. The magnetocaloric effect, ΔT, of $Gd_5(Si_{1.95}Ge_{2.05})$ as a function of magnetic field. The measurements were carried out as in series 2.

above 262 K, when the sample is paramagnetic in a zero magnetic field and then is switched from the PM state into the FM state by the increasing magnetic field. The largest value of the MCE observed in the first series of measurements ($\Delta T_{max} = -2.0$ K) is somewhat lower than that observed in the second series of measurements, i.e., $\Delta T_{max} = 3.0$ K. The observed behavior suggests that the enthalpy of the first-order phase transformation plays a role in the large value of the MCE. Consequently, the magnetic field hysteresis contributes to the lower value of the MCE peak observed in the first series. Typical isothermal MCE curves measured above and below the Curie temperature following the procedures of the second series are shown in Fig. 7. The values measured at 266 K increase almost linearly and display no sudden changes. The observed behavior is understood if one assumes that the system remains in the two-phase state upon each application of the magnetic field because the largest available magnetic field (H_{max} = 15 kOe) was not strong enough to complete the phase transition. This assumption agrees well with the *T–H* phase diagram of $Gd_5(Si_{1.95}Ge_{2.05})$ [17].

The negative values of the MCE observed below the Curie temperature are quite unexpected. The MCE data measured below ~260 K (see Fig. 6) show no reasonable dependence on temperature and are scattered, showing both negative and positive values, but the isothermal MCE (ΔH = 14 kOe) data at T = 241 K (see Fig. 7) systematically show larger negative values as the magnetic field increases, thus eliminating the unlikely possibility of unexplained experimental errors. In order to verify the magnetic state of the sample, we measured the isothermal magnetization (Fig. 8). Below the Curie temperature, its behavior is that of a typical ferromag-

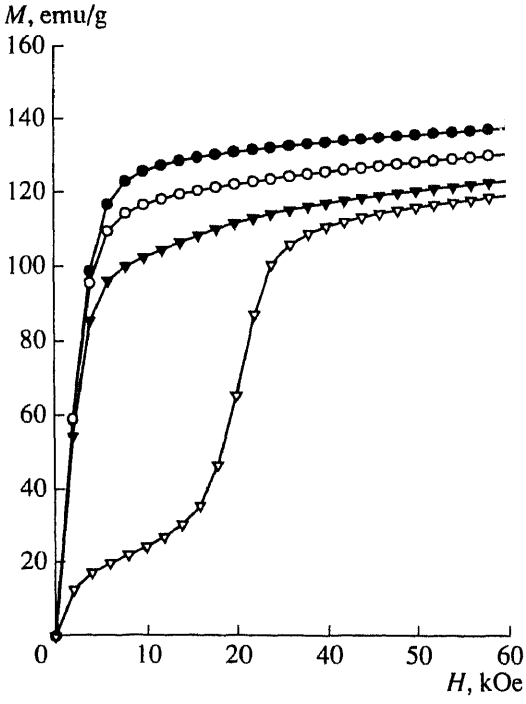

Fig. 8. The isothermal magnetization of $Gd_5(Si_{1.95}Ge_{2.05})$.

net and sudden steplike increases with a field in the high temperature region agree well with the magnetostructural phase transition. Since it is known that the magnetocaloric effect originating from a ferromagnetic paraprocess should be positive, the negative MCE, i.e., the increase of the magnetic entropy caused by the external magnetic field may correspond to the unusual transformation of the domain structure or may suggest some kind of inhomogeneous magnetic and/or structural state below the Curie temperature. We note that the phase transition in $Gd_5(Si_{1.95}Ge_{2.05})$ has a rather complicated character: the observed broad thermal (~10 K) and magnetic field (~10 to 20 kOe) hystereses are both intrinsic to the first-order phase transition, and, hence, this transition is extended over a wide range of magnetic fields and temperatures. This observation is also supported by the X-ray diffraction data of $Gd_5(Si_{1.8}Ge_{2.2})$ [3], which display the existence of the two phases over an ~10-K range above and below the Curie temperature. Thus, the negative MCE below the Curie temperature may be associated with the nucleation kinetics and/or with the existence of the intermediate metastable phases in the process of rapid (a few seconds) direct measurements.

Based on the available experimental data, we conclude that a simultaneous magnetic (from the high-temperature paramagnetic to the low-temperature ferromagnetic state) and crystallographic (from the high temperature monoclinic to the low-temperature orthorhombic crystal structure) phase transformation occurs in the $Gd_5(Si_{1.95}Ge_{2.05})$ compound at ~262 K in a zero magnetic field. Above 262 K, the sample undergoes a magnetostructural phase transition induced by a magnetic field. The magnetocaloric effects calculated from the heat capacity and measured directly are in fair agreement above the Curie temperature. In the low temperature region (below 260 K), the unexpected negative MCE is observed most likely associated with the nonequilibrium processes which occur during the unusual phase transformation in this complex intermetallic system.

ACKNOWLEDGMENTS

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