Magnetic-field-induced structural phase transition in $Gd_5(Si_{1.8}Ge_{2.2})$

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We present direct evidence that the giant magnetocaloric effect recently discovered in the $Gd_5(Si_{1.8}Ge_{2.2})$ alloy is associated with a field-induced first-order structural transition from a $P112_1/a$ monoclinic (paramagnetic) to a *Pnma* orthorhombic (ferromagnetic) structure. A large volume contraction of $\Delta V/V \cong 0.4\%$ takes place spontaneously at the transition temperature, $T_C \cong 240$ K. The reported structural transition can be induced reversibly by application of an external magnetic field, producing strong magnetoelastic effects. [S0163-1829(98)51246-5]

A vast number of compounds are known to exhibit structural transformations when subject to changes in temperature, pressure, and/or composition. Nevertheless, the occurrence of a structural phase transition stimulated by the application of an external magnetic field is rather exceptional and just a few cases have been reported in the literature. An extensively studied example is MnAs where a first-order structural phase transition from an orthorhombic (MnP-type) to a hexagonal structure (NiAs-type) takes place on cooling through ≈306 K, this compound ordering ferromagnetically at this transition.[1] The detailed *H-T* phase diagram has been reported by Zieba, Shapira, and Foner[1] and, for instance at 327 K, the applied field required to induce the structural transition is ≅5.1 T (3.1 T) for increasing (decreasing) fields. More recently, Asamitsu *et al.*[2] have reported on the existence of a structural phase transition induced by an external magnetic field in the family of magnetoresistive perovskites $La_{1-x}Sr_xMnO_3$. Currently, such systems with a strong coupling between crystallographic structure and magnetism are of both great scientific and technological importance since other physical properties of relevance, e.g., magnetocaloric effect, magnetostriction, and/or magnetoresistance, may be maximized in the vicinity of these magnetostructural phase transitions. Recent studies[3–6] on the giant magnetocaloric effect observed in the $Gd_5(Si_xGe_{1-x})_4$ alloys ($x \leqslant 0.5$) have renewed the interest in this series of intermetallic compounds. The structural and magnetic properties of the binary compounds Gd_5Si_4 and Gd_5Ge_4 were already reported 30 years ago.[7,8] Although both systems crystallize in the same Sm_5Ge_4-type orthorhombic structure (space group *Pnma*),[7] the Si-based compound orders ferromagnetically at $T_C \cong 335$ K,[8] while the Ge-based one orders antiferromagnetically (or ferrimagnetically) at $T_N \cong 125$ K and ferromagnetically at $T_C \cong 20$ K.[4,8] The complete magnetic phase diagram and a comprehensive room-temperature structural characterization in the whole composition range for the pseudobinary $Gd_5(Si_xGe_{1-x})_4$ alloys has been published recently by Pecharsky and Gschneidner.[4,6] Of particular interest is the composition range $0.24 \leqslant x \leqslant 0.5$, where the crystal structure is no longer orthorhombic but monoclinic (space group $P112_1/a$) (Ref. 6) bringing about a drastic change in the magnetic behavior. These alloys undergo a first-order magnetic transition to a low-temperature ferromagnetic state and associated with it, a giant magnetocaloric effect (highest reported to date) has been discovered.[3] Therefore, an accurate explanation of the physical origin of this magnetic phase transition would be of great significance. In this contribution we report a thorough experimental study of the low-temperature first-order phase transition in $Gd_5(Si_{1.8}Ge_{2.2})$, demonstrating that it is indeed a first-order structural transition to an orthorhombic phase. This magnetostructural transition can be induced reversibly by applying an external magnetic field, producing strong

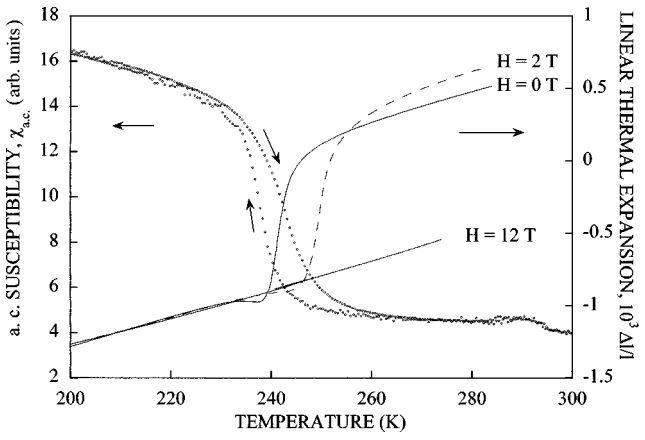

FIG. 1. ac magnetic susceptibility (χ_{ac}) as a function of temperature of $Gd_5(Si_{1.8}Ge_{2.2})$ and linear thermal expansion ($\Delta l/l$) as a function of (decreasing) temperature at several applied magnetic fields ($H = 0$, 2, and 12 T).

magnetoelastic effects and consequently making these alloys also attractive in view of their potential technological applications for magnetostrictive transducers.

The $Gd_5(Si_{1.8}Ge_{2.2})$ sample has been synthesized by arc melting the constituent elements (with purities better than 99.9%) under a high-purity argon atmosphere. The quality of the sample was checked by means of x-ray diffraction and scanning electron microscopy. The room-temperature x-ray patterns confirm the existence of a monoclinic main phase ($P112_1/a$) with unit-cell parameters $a=7.586(1)$ Å, $b=14.799(1)$ Å, $c=7.779(1)$ Å, and $\gamma=93.18(1)°$ in good agreement with those reported in Ref. 6, and minor amounts of a secondary orthorhombic phase (*Pnma*), identified as $Gd_{5.0}(Si_{2.1}Ge_{1.9})$ by electron-beam microprobe analysis. The ac magnetic susceptibility was determined using the permeability method. In this technique, the sample formed the core of a microtransformer with ten turns in both primary and secondary coils. An ac current of 10 mA with a frequency $\approx$1 kHz was kept constant in the primary coil. The ac signal of the secondary coil was proportional to the magnetic susceptibility of the sample. Step-scanned powder diffraction patterns were collected at some selected temperatures ranging from 200 to 300 K using a D-max Rigaku system with rotating anode coupled to a helium flow cryostat from Oxford Instruments. The temperature control was better than 0.1 K and the diffractometer was operated at 45 kV and 160 mA. The Cu K$\alpha_{1,2}$ radiation was selected by means of a graphite monochromator and the data were collected from 20° to 60° (2θ) with a step size of 0.02° and a counting time of 2 s/step. Thermal-expansion and magnetostriction measurements were performed using the strain-gauge technique in a superconducting coil that produces steady magnetic fields up to 12 T. Measurements under hydrostatic pressure were carried out in a CuBe cell, both pressure and temperature being measured *in situ* using a manganin pressure sensor and a Thermocoax thermocouple, respectively.

The ac magnetic susceptibility of the sample in the temperature range 200–300 K can be seen in Fig. 1. An abrupt transition is clearly evidenced at $T_C=238\pm0.5$ K for decreasing temperatures with a thermal hysteresis of around 5 ± 0.5 K. The value of the transition temperature is in good agreement with the one observed for $Gd_5(Si_{1.72}Ge_{2.28})$ (235 K), the slight increase being consistent with the smaller Ge content as expected from the magnetic phase diagram.[4] A small anomaly is also perceptible at $T=295\pm1$ K that we have associated with the second-order paramagnetic-ferromagnetic transition of the secondary phase $Gd_{5.0}(Si_{2.1}Ge_{1.9})$ detected in our electron microscopy studies and also in agreement with the magnetic phase diagram of the $Gd_5(Si_{1-x}Ge_x)_4$ series.[4] We have also observed that upon annealing the sample at 1400 °C in an Ar atmosphere for 4 h, this anomaly vanishes, the first-order one at $\cong$240 K remaining unchanged. These results, together with the magnetization and heat-capacity experiments given in Refs. 3 and 4, support the conclusion that only one first-order magnetic phase transition from a high-temperature paramagnetic to a low-temperature ferromagnetic state takes place. In order to get a deeper insight into the nature of this uncommon magnetic behavior (first-order character of the paramagnetic-ferromagnetic transition), linear thermal-expansion measurements at decreasing temperatures ranging from 200–300 K and at different applied magnetic fields from 0 to 12 T have been performed. The results are displayed in Fig. 1. As can be observed, the first-order magnetic transition is accompanied with a large jump in the spontaneous ($H=0$ T) linear thermal expansion ($\Delta l/l$), corresponding to a volume change of $\omega=3(\Delta l/l)\cong0.4\%$. This volume anomaly is of the same order of magnitude as those associated with first-order antiferro-ferromagnetic transitions present in other magnetic alloys, e.g., FeRh (Ref. 9) and $Hf_{1-x}Ta_xFe_{2-y}$.[10] On increasing the external magnetic field, this volume change is gradually shifted to higher temperatures at a rate of 4.5 K/T in good agreement with previous values obtained from magnetization and specific heat versus magnetic field in $Gd_5(Si_2Ge_2)$ (5.5 K/T) (Ref. 3) and $Gd_5(Si_{1.72}Ge_{2.28})$ (4.3 K/T).[4] This magnetic-field dependence of the transition temperature as determined from linear thermal-expansion measurements points to the possibility of inducing the low-temperature ferromagnetic phase by applying a moderate magnetic field, obtaining a large magnetostriction value. Furthermore, it is worth pointing out that the volume decreases when cooling through the transition, i.e., the cell volume in the low-temperature ferromagnetic phase is smaller ($\omega\cong0.4\%$) than in the high-temperature paramagnetic one. This fact is in contradiction with the generalized physical picture of the magnetovolume effects being transitions from

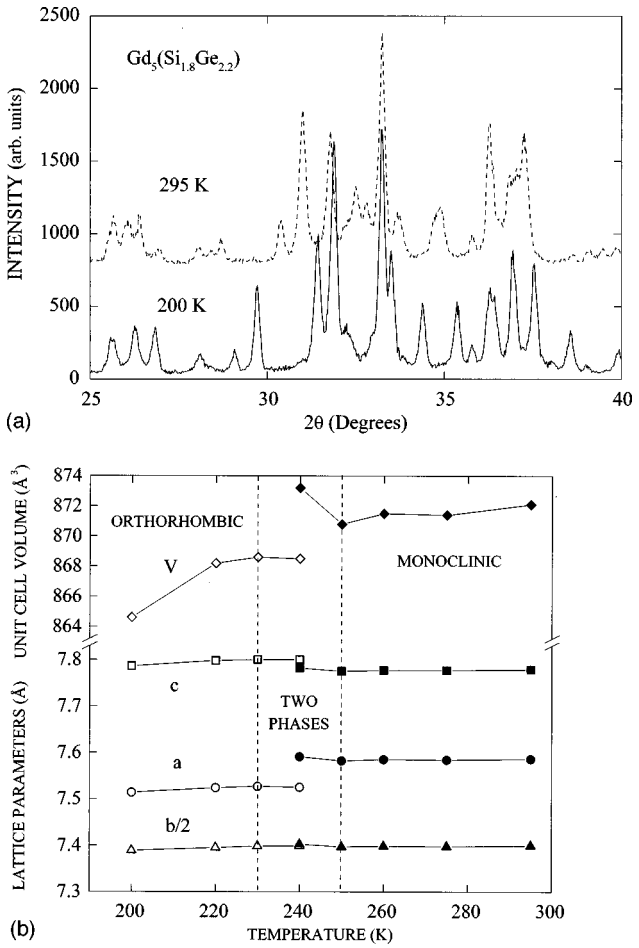

FIG. 2. (a) X-ray diffractograms of $Gd_5(Si_{1.8}Ge_{2.2})$ above ($T=295$ K) and below ($T=200$ K) the first-order transition in the selected angular range $2\theta=25°-40°$. (b) Thermal dependence of the cell parameters and unit-cell volume.

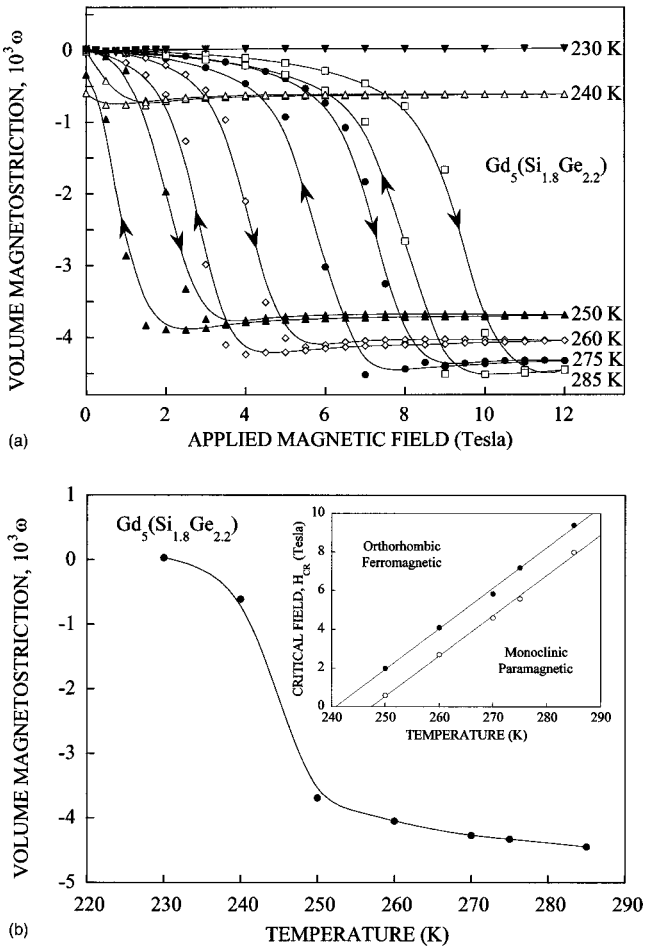

FIG. 3. (a) Volume magnetostriction (ω) isotherms at some selected temperatures. (b) Thermal dependence of the volume magnetostriction at the maximum applied magnetic field (12 T). The line is a visual guide. The inset shows the temperature dependence of the critical field, H_{CR}, for increasing (●) and decreasing (○) applied magnetic field.

a low-volume low-moment to a high-volume high-moment state, as reported in a broad class of magnetic solids, including intermetallic alloys, such as, for instance, the Invar compound Fe_3Ni and the anti-Invar FeRh,[11] and transition-metal oxides.[12] A plausible explanation of this unexpected and puzzling magnetic and magnetovolume effect might be the existence of an structural change at T_C. In order to examine this possibility in detail, an x-ray-diffraction study of the crystallographic structure in the temperature range 200–300 K has been carried out.

X-ray-diffraction patterns at 295 and 200 K are plotted in Fig. 2(a). As can be seen, the diffractograms show big differences between them, indicating the presence of a structural transition. The pattern collected at 295 K can be indexed in the $P112_1/a$ monoclinic cell in agreement with Ref. 6. On the contrary, the pattern at 200 K cannot be indexed in the same monoclinic cell but in the *Pnma* orthorhombic one similar to that reported for the $Gd_5(Si_xGe_{1-x})_4$, $x>0.5$, system at room temperature.[6] The pattern profiles were analyzed using the Rietveld refinement program FULLPROF (Ref. 13) and the atomic coordinates determined in Ref. 6 were used as starting point. Fig. 2(b) shows the thermal evolution of the lattice parameters and unit-cell volume obtained. The transition starts at $\cong 245\pm 5$ K and is completed at $\cong 235\pm 5$ K when the sample is cooled down from 295 K. Within this temperature range ($\cong 235\pm 5-245\pm 5$ K), the two phases coexist in agreement with the proposed first-order character of the transition. A sharp change in the *a* cell parameter is observed at the transition [see Fig. 2(b)], being smaller for the orthorhombic phase ($\Delta a/a\cong -0.9\%$). The *b* axis decreases and the *c* axis increases slightly at the transition ($\Delta b/b\cong -0.1\%$ and $\Delta c/c\cong +0.2\%$). Consequently, the unit-cell volume is around a $0.4\pm 0.1\%$ lower for the orthorhombic phase in agreement with our results from linear thermal expansion measurements (see Fig. 1). These abrupt changes in the lattice parameters and unit-cell volume follow the ones observed at room temperature in the $Gd_5(Si_xGe_{1-x})_4$ system at the concentration $x=0.5$.[6] Our results demonstrate that the observed magnetic transformation at $T_C\cong 240$ K is indeed a first-order structural transition from a monoclinic ($P112_1/a$) structure (high-temperature high-volume paramagnetic state) to an orthorhombic (*Pnma*) one (low-temperature low-volume ferromagnetic state).

The magnetostriction measurements have been performed along the parallel ($\lambda_\parallel$) and perpendicular ($\lambda_\perp$) directions to the applied magnetic field. Both magnetostriction values, within the experimental error and in the whole temperature range studied, were found to be independent of the field direction ($\lambda_\parallel=\lambda_\perp$) and consequently the volume magnetostriction was evaluated as $\omega=3\lambda_{\parallel(\perp)}$. In Fig. 3(a) we display the experimental volume magnetostriction isotherms at some selected temperatures. As may be observed, a large value of the volume magnetostriction $\omega\cong(4.5\pm 0.2)\times 10^{-3}$ is reached at temperatures $T>T_C$ and above a certain critical field. The saturation magnetostriction values are virtually constant above the first-order transition, vanishing rapidly as we approach the transition temperature. In Fig. 3(b) the thermal dependence of the volume magnetostriction at the maximum applied field (12 T) can be seen. The value of the field-induced volume magnetostriction is negative and compares very well with the results from the spontaneous linear thermal expansion (Fig. 1) and thermal dependence of the unit-cell volume from the low-temperature x-ray-diffraction data [Fig. 2(b)]. In addition, when the magnetic field is brought back to zero, the system recovers the initial state [see Fig. 3(a)]. This constitutes a clear evidence that the mechanism which produces the spontaneous effect, i.e., a first-order structural transition, can be triggered reversibly by the application of a magnetic field through a field-induced first-order transition at a certain critical field H_{CR}. This is also confirmed in Fig. 1 where it is seen that at 12 T the anomaly in the linear thermal expansion has been suppressed in the temperature range studied. The values of H_{CR}, obtained at the maximum slope of the volume magnetostriction isotherms, display a linear dependence with temperature in the range of our available magnetic fields [see inset of Fig. 3(b)]. Such behavior has already been observed at the antiferro-ferromagnetic field-induced transition in the FeRh (Ref. 9) and $Hf_{1-x}Ta_xFe_{2-y}$ (Ref. 10) alloys. A hysteresis of about 2 T is also observed, reinforcing the fact that the field-induced structural transition is of first order.

Because of the observed intimate relation between the crystallographic structure and the magnetic behavior in this

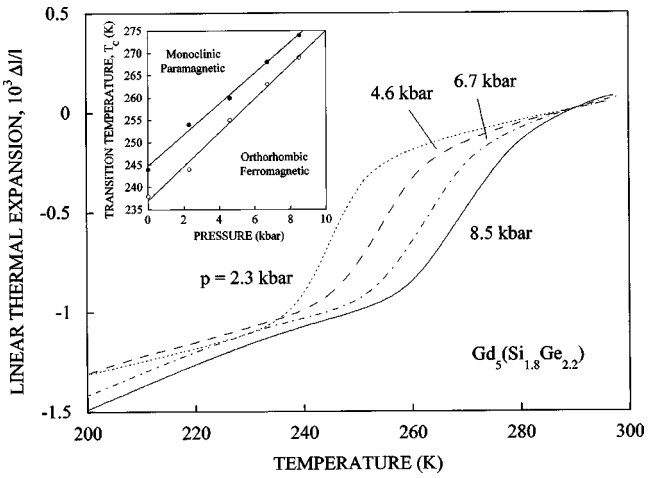

FIG. 4. Linear thermal-expansion measurements for decreasing temperatures under different hydrostatic pressures. The inset shows the pressure dependence of the transition temperature, T_C, for increasing (●) and decreasing (○) temperature.

compound, the application of an external hydrostatic pressure, thus changing the interatomic distances, should modify the transition temperature, stabilizing the low-volume ferromagnetic phase. In Fig. 4, the linear thermal expansion versus temperature at different hydrostatic pressures is shown. As is observed the transition temperature increases as a function of pressure at a rate of $dT_C/dp=+3.79$ K/kbar ($dT_C/dp=+3.46$ K/kbar) for decreasing (increasing) temperatures, confirming the proposed role of the interatomic distances in producing the first-order transition. In order to check our results for self-consistency we have made use of the Clausius-Clapeyron equation, $dP/dT=\Delta S/\Delta V$, relating the slope in a P-T phase diagram of a first-order transition to the change in volume ΔV and entropy ΔS involved in the transition. From our experimental results, an entropy change associated with the first-order transition of $\Delta S\cong 15$ J/mol K can be estimated, in good agreement from the heat-capacity results reported in.[3] An analogous equation can also be explored in terms of the slope in the H-T phase diagram and the change in magnetization ΔM, $dH/dT=-\Delta S/\Delta M$. From our results for dT_C/dH and a ΔM value estimated from Ref. 3, this expression yields $\Delta S\cong 22$ J/mol K and is therefore also consistent with the heat-capacity results.

In summary, we have found that the origin of the first-order phase transition observed in $Gd_5(Si_{1.8}Ge_{2.2})$, and responsible for the giant magnetocaloric effect observed in this family of compounds,[3] is a first-order structural transition from a monoclinic-paramagnetic to an orthorhombic-ferromagnetic structure. This structural transition can be induced reversibly by the application of an external magnetic field, producing large magnetoelastic effects and making these alloys attractive also from the point of view of their potential applications for magnetostrictive transducers. Since the magnetic behavior in these compounds arises from the Gd localized moments, a large two-ion magnetoelastic coupling in the paramagnetic phase may play a role in the field-induced structural transition. Theoretical models including both structural and magnetic parameters should be developed to confirm this point.

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