

## Pressure-Induced Three-Dimensional Ferromagnetic Correlations in the Giant Magnetocaloric Compound $Gd_5Ge_4$

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The giant magnetocaloric compound  $Gd_5Ge_4$  is the only member of the  $Gd_5(Si_xGe_{1-x})_4$  family where three-dimensional exchange interactions between two-dimensional correlated layers of the crystallographic structure are so weak that spontaneous ferromagnetism does not set in at any temperature. In this Letter we explore the possibility to reach the ferromagnetic state by application of hydrostatic pressure. Linear thermal expansion and magnetic measurements under pressure reveal that the reduction of the unit cell volume induces a spatially phase-segregated ground state below 10 kbar.

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$Gd_5(Si_xGe_{1-x})_4$  is a unique class of materials where many interesting properties and intriguing behavior have been recently discovered [1]. The unprecedented giant magnetocaloric effect [2], strong magnetoelastic effects [3,4], and giant magnetoresistance [5,6] can be highlighted as the most relevant. This phenomenology has been associated with the intrinsically layered crystallographic structure combined with a magnetic-martensitic first-order phase transformation [7]. The coupled magnetic-crystallographic transition can be induced reversibly by the change of external parameters such as temperature or external magnetic field [1,4]. Therefore, these alloys are attractive for their potential applications in magnetic refrigeration and/or as magnetostrictive/magnetoresistive transducers.

Three extended solid solution regions exist in the temperature-composition ( $T$ - $x$ ) phase diagram [8,9]: the Si-rich solid solution,  $0.575 \leq x \leq 1$ , has the orthorhombic  $Gd_5Si_4$ -type structure [O(I)]; the intermediate phase,  $0.4 < x \leq 0.503$ , has a room-temperature monoclinic ( $M$ ) structure; and the Ge-rich region,  $0 < x \leq 0.3$ , crystallizes in the  $Gd_5Ge_4$ -type structure [O(II)]. All three structures are composed of identical two-dimensional (2D) sub-nanometer-thick layers (slabs) interconnected via partially covalent interslab  $X$ - $X$  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/reforming specific covalent  $X$ - $X$  bonds [7] and the low-temperature ground state for all compositions  $0 < x \leq 1$  is always ferromagnetic (FM) with all the slabs being interconnected, i.e., with the O(I) structure. The  $M$  structure is always paramagnetic (PM), whereas the O(II) can support either PM or antiferromagnetism (AFM) [4,9]. The magnetic behavior of the  $R_5(Si_xGe_{1-x})_4$  compounds can be understood qualitatively in terms of competition between intralayer (within the 2D slabs, conventional indi-

rect  $4f$ - $4f$  RKKY) and interlayer exchange interactions (between slabs, direct Gd-Si/Ge-Gd superexchange propagated via the  $X$ - $X$  bonds) [1,10]. Furthermore, the occurrence of two distinct types of crystal structures in the PM phase [ $M$  and O(I) polymorphs] in the same alloy with  $x \cong 0.5$  [11] has clearly demonstrated the paramount role of the interslab coupling on the magnetism of  $Gd_5(Si_xGe_{1-x})_4$ . First principle electronic structure calculations have helped reach a better understanding of these compounds [12].

In sharp contrast with the magnetic behavior of the Ge-rich compounds with  $0 < x \leq 0.3$ , no FM phase is observed in  $Gd_5Ge_4$  in zero magnetic field and down to the lowest measured temperature [13,14].  $Gd_5Ge_4$  orders antiferromagnetically at  $\sim 130$  K, this system presenting a very complex magnetic field-temperature ( $H$ - $T$ ) phase diagram and an interesting magnetoelastic behavior [15]. A fully irreversible field-induced O(II) (AFM)  $\rightarrow$  O(I) (FM) transformation takes place below  $\approx 10$  K, this becoming fully reversible above  $\approx 20$  K. Between  $\approx 10$  K and  $\approx 20$  K the field-induced transition is partially reversible and a spatially phase-segregated O(II) + O(I) state is found at low temperatures. Recent high-resolution x-ray diffraction in applied magnetic fields up to 35 kOe has uncovered the nature of the field-induced magnetostructural transformation at the atomic level [16].

From a different approach, the effect of hydrostatic pressure is that of reducing the volume of the cell, and thus we may expect an enhancement of the interlayer interactions, favoring the ferromagnetic O(I) state, in a fashion similar to Si doping (increasing  $x$ ). From the experimental compressibility values [17], a hydrostatic pressure of  $\sim 1$  kbar would reduce the unit cell volume of  $Gd_5Ge_4$  to that of  $x = 0.025$ , and therefore, a FM state should set in at  $T_C = 40$  K [9]. Nevertheless, the effect of chemical pressure may be quite different from that of a pure cell contraction caused by the applied hydrostatic pressure. The aim of this work is to investigate the

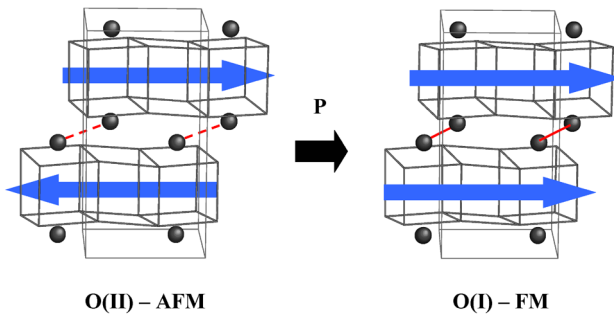


FIG. 1 (color online). Schematic representation of the crystallographic and magnetic structures of  $\text{Gd}_5\text{Ge}_4$  in the  $(a, b)$  plane at low temperature [16]. Only the  $X = \text{Ge}$  atoms participating in the  $X$ - $X$  covalentlike bonds are depicted as solid spheres. A solid line linking the  $X$  atoms represents a formed bond [O(I)], whereas a dashed line is used for a broken one [O(II)]. Gray arrows are used to illustrate the change in the magnetic coupling as a function of hydrostatic pressure.

possibility to induce three-dimensional (3D) ferromagnetic correlations in  $\text{Gd}_5\text{Ge}_4$  upon application of an external hydrostatic pressure as illustrated in Fig. 1.

The alloy with nominal composition  $\text{Gd}_5\text{Ge}_4$  was synthesized by arc melting of 99.9 wt% pure Gd and 99.9999 wt% pure Ge under a high-purity argon atmosphere. The sample is essentially single phase with a minor amount ( $\sim 6\%$ ) of a secondary  $\text{Gd}_5\text{Ge}_3$  phase. More details on this sample characterization can be found in an earlier work [15].

Linear thermal expansion (LTE) and compressibility measurements under pressure up to 13 kbar were performed using the strain-gauge technique in a standard CuBe piston-cylinder cell. A mixture of mineral oils was used as the pressure transmitting medium and the pressure values at different temperatures were determined using a Manganin pressure sensor. A miniature hydrostatic pressure cell was used for magnetization and ac susceptibility measurements in a commercial (Quantum Design Ltd.) superconducting quantum interference device magnetometer. The pressure value was determined at low temperatures using the known pressure dependence of the critical temperature of the superconducting state of a Pb sensor placed inside the cell. The magnetization has been measured under pressures up to 8 kbar at temperatures from 5 to 300 K.

In Fig. 2 we display the LTE of  $\text{Gd}_5\text{Ge}_4$  at different values of the applied hydrostatic pressure. Upon application of pressure, a distinct anomaly develops in the LTE curve and a clear jump is detected at higher pressure values. According to our investigation of the magnetoelastic behavior of this compound—see, e.g., Fig. 2 in [15]—this anomaly signals the existence of a pressure-induced low-temperature O(I)-FM phase, the amount of this phase being reflected in the magnitude of the jump. From the results shown in Fig. 2, the slope of the pressure-

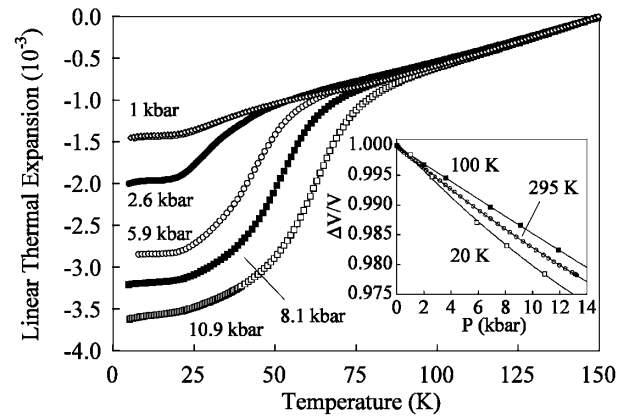


FIG. 2. Linear thermal expansion as a function of temperature under selected values of the applied hydrostatic pressure (the values shown are the actual pressure values at the transition temperature). The ambient pressure curve almost coincides with the 1 kbar one and has not been included for the sake of clarity; see, e.g., [15]. In the inset the relative change in volume of the sample at selected temperatures is displayed.

induced transformation can be estimated as  $dT_C/dP \approx 4.8(4)$  K/kbar.

We have carried out compressibility measurements at room temperature, the relative change in volume being nonlinear in the 0–13 kbar pressure range; see inset of Fig. 2. The value of the compressibility at low pressures is  $\kappa = -(1/V)dV/dP = 1.85(1)$  Mbar $^{-1}$ , very similar to that measured in other  $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$  alloys [17]. With this value and the difference in volume between the spontaneous O(II) and field-induced O(I) phases [16] we can expect that over  $\approx 6.2$  kbar the O(I)-FM ground state should be stabilized within the entire sample volume, although this value is underestimated by the usual decrease of the compressibility when lowering the temperature.

In order to correlate the structural behavior with the magnetic properties we have carried out a systematic study of the magnetism of  $\text{Gd}_5\text{Ge}_4$  as a function of temperature, applied magnetic field, and applied hydrostatic pressure. In Fig. 3 we display the temperature dependence of the magnetization in an applied field of 500 Oe [this field is much smaller than the lowest critical field ( $\approx 11$  kOe) needed to induce the FM state at any temperature] at selected values of the applied hydrostatic pressure: 0, 1.3, and 8 kbar (maximum pressure). As expected [13–15], at ambient pressure no FM state is detected down to 5 K (open circles) but application and removal of 50 kOe at 5 K induces a FM state that remains up to  $\approx 14$  K (open squares). As is clearly seen in Fig. 3, an applied hydrostatic pressure of 1.3 kbar is sufficient to induce a FM signal at  $\approx 35$  K (heating), the value of which at 5 K is much lower than that obtained when applying and removing 5 T at ambient pressure. Therefore, from this and the results in Fig. 2, we can

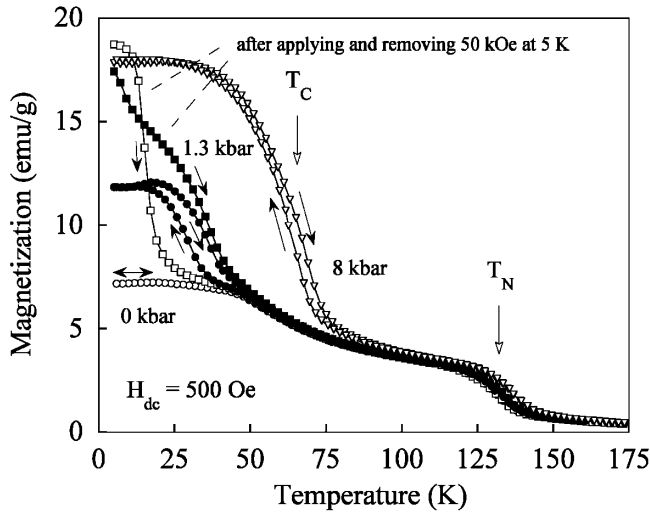


FIG. 3. Magnetization in an applied field of 500 Oe as a function of temperature under selected values of the applied hydrostatic pressure (the values shown are the actual pressure values at 5 K). Solid arrows indicate the direction of temperature change.

interpret these data supposing that the sample volume at 1.3 kbar is spatially phase segregated into O(II)-AFM and O(I)-FM regions; i.e., 1.3 kbar is sufficient to enhance the interlayer interactions favoring 3D FM correlations. As far as we know, this is the first time phase-separation phenomena have been observed in a pure 4f localized-moment system upon application of hydrostatic pressure. If we apply and remove isothermally a magnetic field of 50 kOe at 5 K and 1.3 kbar, a full FM signal is recovered (solid squares). Should this physical picture be correct, a higher pressure should increase the relative volume of the O(I)-FM regions. This is indeed the case since the FM signal at 8 kbar is almost maximum. We therefore propose that a hydrostatic pressure of 8 kbar is able to induce a O(I)-FM ground state in the majority of the sample with a  $T_C \approx 65$  K (heating).

Also from the data in Fig. 3 we can estimate a value of  $dT_N/dP \approx 0.73$  K/kbar and  $dT_C/dP \approx 4.9$  K/kbar, the latter in good agreement with the LTE data. For a more precise determination, we carried out ac magnetic susceptibility measurements at 0, 1.3, 2.2, 4.7, and 7.7 kbar (not shown here) yielding values of  $dT_N/dP = 0.76(5)$  K/kbar and  $dT_C/dP = 5.3(3)$  K/kbar. The transition temperature of the secondary 5:3 phase at  $\approx 49$  K does not shift significantly under pressure. The value  $dT_N/dP$  is comparable, within the experimental error, to that found in the  $x = 0.1$  alloy, but, in contrast, the value of  $dT_C/dP$  is higher [17]. According to the Clausius-Clapeyron relation at a first-order transition in the form  $dT/dP = \Delta V/\Delta S$ , relating the slope in the  $P$ - $T$  phase diagram to the change in volume  $\Delta V$  and entropy  $\Delta S$  involved in the transition, in the case of  $\text{Gd}_5\text{Ge}_4$ , either  $\Delta V$  is higher and/or  $\Delta S$  is smaller as compared

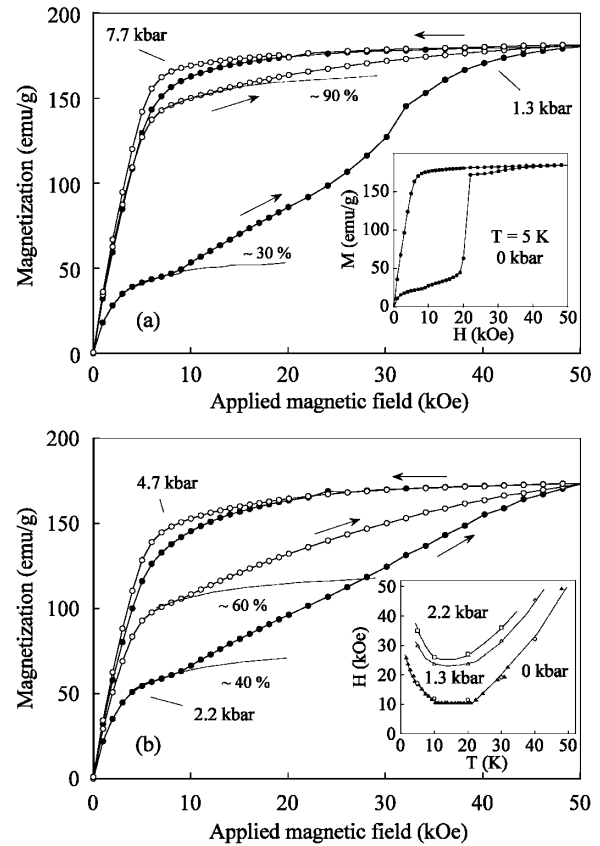


FIG. 4. Magnetization isotherms at 5 K under selected values of the applied hydrostatic pressure of 1.3 and 7.7 kbar (a) and 2.2 and 4.7 kbar (b). For comparison the magnetization isotherm at 5 K and ambient pressure is displayed in the inset of (a). In the inset of (b) the thermal dependence of the upper critical fields at 0, 1.3, and 2.2 kbar (open symbols) are displayed together with zero-pressure results taken from [15] (solid symbols).

with the  $x = 0.1$  alloy. By using  $\Delta V = 9.8 \text{ \AA}^3$  [16] and  $\Delta S \approx 25 \text{ J/Kg-K}$  [2], a value of  $dT/dP \approx 5.5$  K/kbar is obtained, in excellent agreement with our experimental value of  $5.3(3)$  K/kbar.

To investigate and justify further the pressure-induced enhancement of 3D FM correlations and the emergence of the O(I)-FM phase within the O(II)-AFM ground state, we carried out magnetization isotherms at selected temperatures and applied pressures. The results at 5 K are displayed in Fig. 4. The sharp O(II) (AFM)  $\rightarrow$  O(I) (FM) metamagnetic transition observed at ambient pressure—see inset of Fig. 4(a)—gets smoother and a clear low field ferromagnetic signal that increases under pressure is clearly seen, demonstrating our previous hypothesis that the sample is spatially segregated into O(I)-FM and O(II)-AFM regions. Upon increasing the field the AFM regions transform irreversibly into FM ones, the critical field is, e.g., 30 kOe at 1.3 kbar, this being the origin of the large hysteresis observed. It is noteworthy that the upper critical field for the field-induced metamagnetic

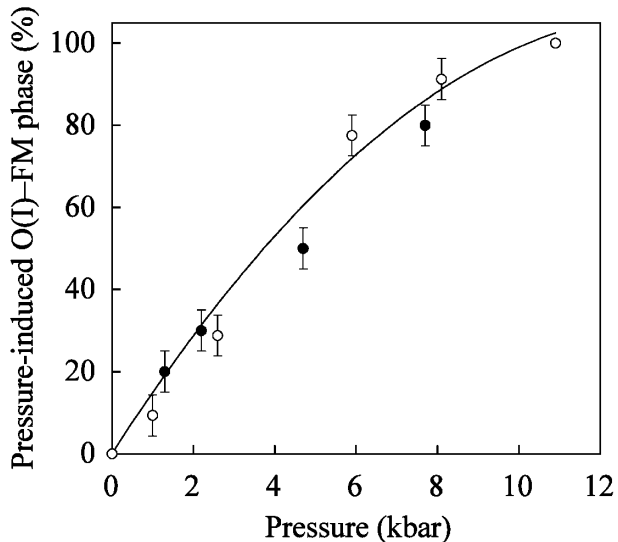


FIG. 5. Percentage of pressure-induced O(II)-FM phase as estimated from LTE results (open circles) and magnetization measurements (solid circles). The line is a guide for the eye.

transition increases with pressure as shown in the inset of Fig. 4(b). At this point we can just speculate this might be due to a change in the AFM structure with pressure. The relative percentage of the pressure-induced O(I)-FM phase can be estimated from the saturation of this component as has been indicated in Fig. 4 for the different pressure values. This percentage has been corrected by  $\approx 10\%$  to take into account the FM signal from the saturation of the 5:3 impurity—see inset of Fig. 4(a)—and the increase in the magnetization in the AFM phase.

The final values are displayed in Fig. 5 (solid circles) together with the results obtained from the LTE data—see Fig. 2—assuming that the jump in the LTE at 10.9 kbar corresponds to 100% of a O(I)-FM transformed phase at low temperatures. As can be seen the results are in very good agreement, this being strong evidence of the physical picture presented to interpret the LTE and magnetization results as a function of pressure. From the results in Fig. 5 we can be quite confident that at pressures above  $\approx 10$  Kbar the entire volume of the sample at low temperatures below  $T_C$  (10 Kbar)  $\cong 53$  K is FM crystallizing in the O(I) structure.

In conclusion, we have explored the possibility to induce 3D ferromagnetic correlations in the giant magnetocaloric alloy  $\text{Gd}_5\text{Ge}_4$  by means of LTE and magnetic measurements at different applied pressures. As a main result, application of hydrostatic pressure induces a spa-

tially phase-segregated ground state where O(I)-FM and O(II)-AFM regions coexist within the sample volume. It has been predicted that at pressures of over 10 kbar, the low-temperature O(I)-FM ground state is stabilized in the entire sample volume. We propose a physical picture where the effect of pressure is to reduce the interatomic distances, thus enhancing the interlayer interactions in this naturally nanolayered material. This should favor the formation of specific covalent bonds, inducing a first-order pressure-induced magnetostructural transformation from an O(II)-AFM to an O(I)-FM structure. A microscopic confirmation of this physical picture by x-ray diffraction studies under pressure would be of the utmost importance and significance.

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