

Effects of pressure on the magnetic and crystallographic structure of Er_5Si_4

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Extraordinary effects of the hydrostatic pressure on the crystallographic and magnetic properties of the Er_5Si_4 alloy have been examined by means of macroscopic (magnetization and linear thermal expansion) and microscopic (neutron powder diffraction) techniques. The high-temperature $O(I) \leftrightarrow M$ crystallographic transformation (observed at $T_1 \cong 215$ K at atmospheric pressure) shifts to low temperatures at the unexpectedly high rate of $dT_1/dP \cong -30$ K/kbar. In addition, the application of pressure induces an $O(I)$ reentrance in the low-temperature ferromagnetic state of Er_5Si_4 . The latter transformation (T_{r2}) is a reversible first-order-type structural phase transition shifting towards high temperature with pressure at a much lower rate of $dT_{r2}/dP \cong +6$ K/kbar. This low-temperature $O(I)$ crystal structure has a Curie temperature higher than that of the monoclinic polymorph, pointing out the importance of the interlayer covalentlike bonding to enhance the ferromagnetic interactions in these alloys. Above ~ 6 kbar, both structural transformations collapse, yielding a stable $O(I)$ phase throughout the whole temperature range. In light of these experimental findings, a complete P - T magnetic-crystallographic phase diagram of Er_5Si_4 has been constructed.

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INTRODUCTION

Hydrostatic pressure is a versatile tool that has an outstanding potential in bringing about a better understanding of the interplay between crystal structure and magnetism in members of an extended family of rare-earth-based intermetallic compounds $R_5(\text{Si}_x\text{Ge}_{1-x})_4$.¹⁻⁷ Many of these alloys exhibit an unusually strong magnetostructural coupling that gives rise to interesting magnetoelastic behaviors manifested as the existence of simultaneous magnetic and structural transformations that can be reversibly induced by changing

temperature, magnetic field, or hydrostatic pressure.^{1,7-13} External control of the unit cell volume without altering the chemical composition of $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ materials by applying hydrostatic pressure underlines the critical importance of the crystallographic structure not only in supporting a variety of magnetic structures in some of its members,^{14,15} but also in obtaining a good magnetocaloric performance.¹⁶

The discovery of the giant magnetocaloric effect (GMCE) in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys in 1997 (Refs. 17 and 18) facilitated a rapid growth of interest and new developments of near-

room-temperature magnetic refrigeration by opening numerous opportunities in the quest for novel materials with improved magnetocaloric properties^{19–22} and by triggering the design and fabrication of new prototype devices for magnetic refrigeration.^{23–26} The origin of the GMCE observed in this system is intrinsically associated with the coexistence of the magnetic and crystallographic transformations^{3,10} and, therefore, with the first-order character of the ferromagnetic ordering process which gives rise to the subsequent isothermal magnetic-field-induced entropy changes related to both the magnetic ordering and the difference in the entropies of the two crystallographic polymorphs involved.²⁷ An intriguing interplay between magnetism and structure in the $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ system has been evidenced by the application of hydrostatic pressure in polycrystalline⁴ and single-crystalline⁶ specimens of $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$. Here, the increasing pressure changes simultaneously the magnetic state and the crystallographic structure of the materials, displacing concomitantly the magnetic and structural transitions towards higher temperatures. However, in these cases the effect of pressure has been proven to be detrimental to the GMCE due to strengthening of the magnetoelastic coupling in the vicinity of the transformation.^{6,7} In contrast, the hydrostatic pressure has been shown to enhance the GMCE in polycrystalline $\text{Tb}_5\text{Si}_2\text{Ge}_2$. In this compound, at ambient pressure, the structural and magnetic anomalies are not coupled, and the structural change occurs approximately 10 K below $T_C=110$ K.¹⁵ Hydrostatic pressure significantly improves the MCE by recoupling both anomalies because the structural transition temperature and T_C exhibit different pressure dependences—the rate of change of the former is nearly one order of magnitude greater than that of the latter—subsequently merging the associated magnetic and structural entropy changes.¹⁶

The compound Er_5Si_4 reveals an even more spectacular decoupling of structure and magnetism. This system has been traditionally considered a simple ferromagnet (FM) with $T_C=30$ K displaying no structural anomalies below room temperature.^{8,28} However, recent research^{29–32} has demonstrated that this alloy undergoes a novel, purely structural transition in the paramagnetic state at $T_f \approx 200–230$ K. Er_5Si_4 transforms from a high-temperature orthorhombic (space group symmetry $Pnma$) Gd_5Si_4 -type phase [$O(I)$] to a low-temperature monoclinic (space group symmetry $P112_1/a$) $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure (M) completely independent of the magnetic ordering. These two intrinsically layered structures are most easily differentiated by the number of covalentlike Si-Si bonds connecting the consecutive layers; all the possible Si-Si pairs are bonded in the $O(I)$ polymorph, whereas only one-half of them are found in M - Er_5Si_4 .¹⁰

The existing body of knowledge about the 5:4 compounds is quite extensive, suggesting that the M -FM state may not be the equilibrium low-temperature state in Er_5Si_4 because the ground state throughout the series is usually $O(I)$ -FM.¹² Recent studies of the properties of Er_5Si_4 as a function of magnetic field have already shown that the magnetic field reversibly induces a structural transformation, shifting the equilibrium towards the orthorhombic phase and giving rise

to the $O(I)$ -FM state at low temperatures.³³ We believe that hydrostatic pressure may be a strong factor in modifying of the crystallographic structure of this alloy since pressure directly affects the volume of the unit cell and may induce an $O(I)$ reentrance at low temperatures. This is especially plausible taking into account that the M - Er_5Si_4 phase has a larger volume than the $O(I)$ state. Therefore, a thorough investigation of the magnetic and structural properties of Er_5Si_4 under hydrostatic pressure described in the present work presents an opportunity to clarify these points.

EXPERIMENT

A polycrystalline specimen of Er_5Si_4 was synthesized by arc melting of the constituent elements in a high-purity argon gas atmosphere. Further details on sample preparation and basic structural characterization at room temperature can be found elsewhere.^{29–31}

Linear thermal expansion (LTE) measurements under hydrostatic pressure up to 9 kbar (room-temperature value) have been carried out using the strain-gauge technique in a standard CuBe piston-cylinder cell. A mixture of mineral oils has been used as the pressure-transmitting medium, and the pressure at different temperatures has been determined using a Manganin pressure sensor.

A miniature CuBe pressure cell has been used for magnetization measurements in a commercial (Quantum Design, Inc.) superconducting quantum interference device (SQUID) magnetometer. In this case, the pressure is 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 5.6 kbar (value at 5 K) in the temperature range 5–300 K and in magnetic fields up to 50 kOe.

Neutron diffraction experiments have been performed on the high-intensity two-axis diffractometer D20 ($\lambda=2.40$ Å) at the Institute Laue-Langevin (ILL), in Grenoble (France). Neutron diffraction patterns have been dynamically acquired in heating runs within the temperature range 2–240 K, at atmospheric pressure, and under a hydrostatic pressure of 4 kbar and 10 kbar (values at room temperature) by means of a standard stainless-steel clamped cell.

RESULTS

Low-temperature magnetization isotherms have been measured at selected hydrostatic pressures ranging from 0 to 5.6 kbar (values at low temperature). Figure 1 illustrates the measurements carried out at 5 K (a), 20 K (b), and 40 K (c). At $T=5$ K, a change in the magnetic state of Er_5Si_4 with pressure is easily perceived when comparing the atmospheric-pressure isotherm with the applied-pressure measurements. At ambient pressure, a metamagneticlike anomaly is seen at about 10 kOe (also see Ref. 31), which is then followed by a hysteretic behavior. Magnetostriction experiments³³ point to a strong magnetoelastic anomaly associated with this behavior, which in other $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys usually indicates the occurrence of a structural change

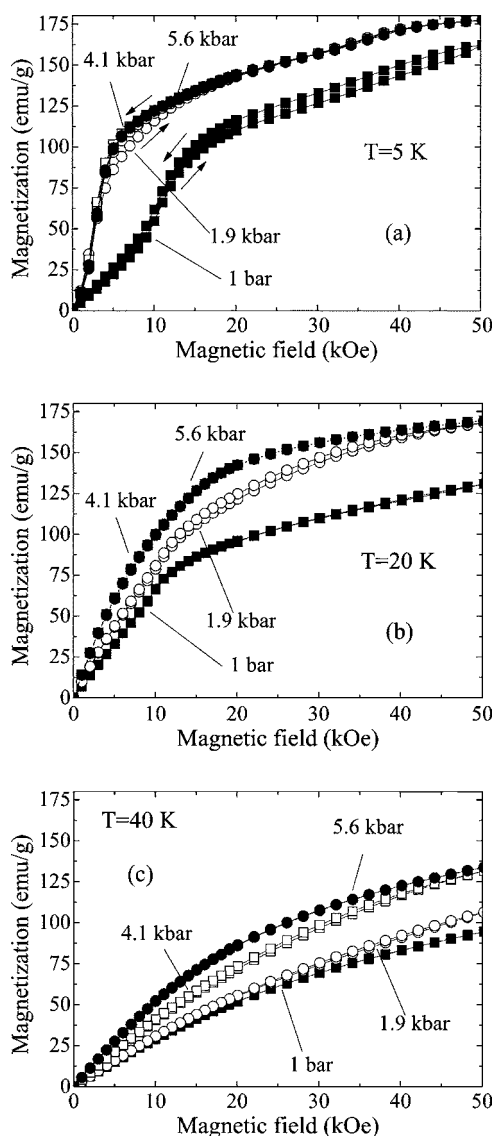


FIG. 1. The magnetization isotherms of Er_5Si_4 measured at selected pressures and temperatures in the vicinity of the magnetic ordering: (a) 5 K, (b) 20 K, and (c) 40 K.

simultaneously modifying the magnetic ordering of the system. The magnetization at 50 kOe reaches $5.5\mu_B/\text{Er}$ atom. On the other hand, at pressures of 1.9 kbar and higher a rapid increase of the magnetization associated with domain walls movement is observed at low fields. After that, the magnetization smoothly increases with the magnetic field reaching about $6.0\mu_B/\text{Er}$ atom at 50 kOe, some 10% higher than the ambient pressure value. It is worth noting that this behavior remains essentially unchanged at higher pressures, so the changes induced by pressure at 5 K are already accomplished at 1.9 kbar. In all the cases, the magnetization remains far from the expected value for the saturation magnetization of $gJ=9\mu_B/\text{Er}$. From these results, we deduce that certain modifications of the magnetic and/or crystallographic properties of Er_5Si_4 are induced by pressure, which is similar to other $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds that adopt the $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type crystal structure at atmospheric pressure. The same behavior is reproduced at $T=10$ K (these data are

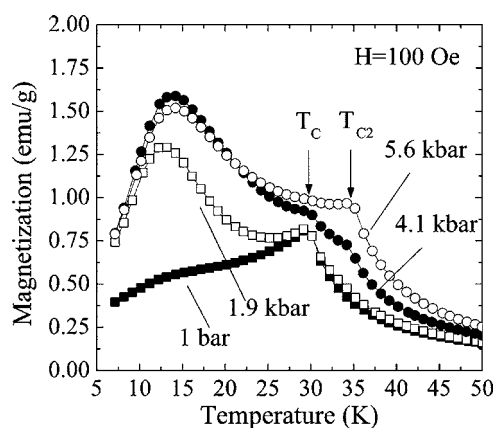


FIG. 2. Low-field magnetization of Er_5Si_4 as a function of temperature and hydrostatic pressure measured in a 100 Oe magnetic field during heating. The ordering temperatures of the two hypothetical phases are marked with arrows.

not shown here), but with a greater (15%) increase of the magnetization at 50 kOe with pressure. At 20 K, the magnetization of the ambient-pressure isotherm has decreased due to the proximity of T_C (~ 30 K) and the 1.9 kbar isotherm represents a crossover between the low-pressure low-magnetization state and the high-pressure high-magnetization regime; the high-pressure magnetization value is 30% higher than that at normal pressure [Fig. 1(b)]. Here, the pressure-induced changes are completed at $P \geq 4.1$ kbar, as evidenced by the identical isotherms measured at 5.6 kbar and 4.1 kbar. Finally, at $T=40$ K [10 K higher than $T_C = 30$ K (Ref. 31)] the magnetic signal has significantly decreased, but the same general pressure-induced features are still observed. Once again, a low-magnetization behavior is found at low pressures ($P \geq 1.9$ kbar) and the 5.6 kbar measurement displays a much greater magnetization value, almost 45% larger than the ambient-pressure signal [Fig. 1(c)]. It is remarkable that the decrease of the magnetization with increasing temperature at 50 kOe is much more rapid in the low-pressure state than in the high-pressure phase, suggesting the existence of stronger FM correlations at high hydrostatic pressures.

Low-field dc magnetization measurements ($H=100$ Oe) have been performed on heating in the proximity of the magnetic phase transition at different hydrostatic pressures, and these are depicted in Fig. 2. The ambient-pressure experiment shows a marked peak at $T_C=30$ K, which corresponds to the FM ordering of the M crystallographic phase of Er_5Si_4 . The application of pressure induces two apparently independent processes. First is the growth of a low-temperature anomaly ($T \sim 10$ – 20 K) that slowly shifts towards higher temperatures and gradually broadens upon increasing pressure. The second is the appearance of a new peak a few kelvin above the zero-pressure anomaly, at $T_{C2} \approx 35$ K. It is noteworthy that the contribution from the peak at T_{C2} is gradually increasing with rising pressure while the anomaly at T_C progressively diminishes. At 5.6 kbar, this new anomaly at T_{C2} becomes dominant but the peak at T_C has nearly disappeared. In addition, neither of these two transition temperatures are affected by the increasing pressure

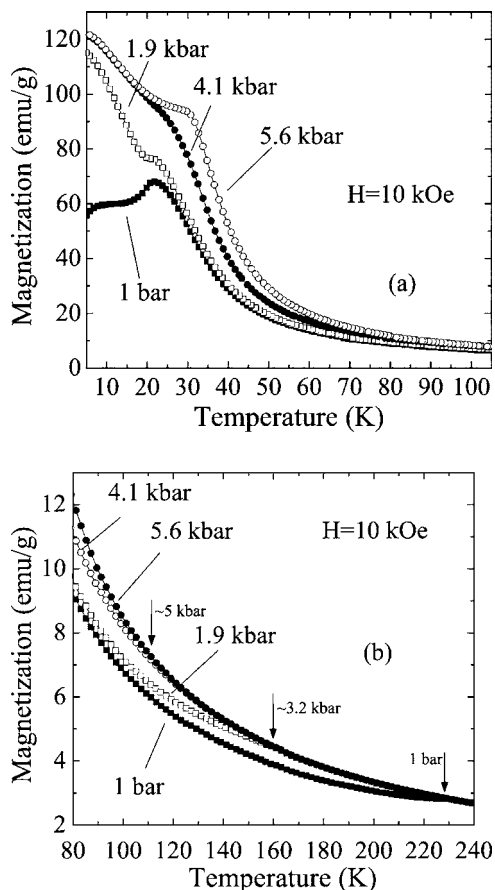


FIG. 3. Temperature dependences of the high-field magnetization of Er_5Si_4 measured at selected pressures in a 10 kOe magnetic field during heating. (a) Details of the pressure dependence in the vicinity of the low-temperature magnetic ordering. (b) Effect of pressure on the high-temperature $O(\text{I}) \leftrightarrow M$ crystallographic transition. The vertical arrows in (b) indicate the approximate transition temperature at each pressure.

within the experimental accuracy—i.e., both $dT_C/dP \cong 0 \pm 0.1$ K/kbar and $dT_{C2}/dP \cong 0 \pm 0.1$ K/kbar. This behavior is consistent with weak pressure dependence of purely magnetic transitions observed in $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ compounds⁴ and in $\text{Tb}_5\text{Si}_2\text{Ge}_2$.⁵ A changeover from T_C to T_{C2} is consistent with the physical picture of a certain equilibrium state between two phases with different ordering temperatures that exist at intermediate pressures. Here, the increasing pressure reduces the concentration of the main phase with $T_C=30$ K, which is stable at ambient pressure, by transforming it into a new phase with $T_{C2}=35$ K, which becomes dominant at pressures over 5 kbar. A similar microscopic model has been found in Gd_5Ge_4 .²

The interesting behavior of Er_5Si_4 is further clarified by the high-field dc magnetization measurements ($H=10$ kOe). The low-temperature range is displayed in Fig. 3(a), and the regime of the high-temperature structural-only transformation is shown in Fig. 3(b). At low temperatures, the ambient-pressure measurement resembles the low-field curve shown in Fig. 2 with an obviously higher magnetic signal. A pressure of 1.9 kbar induces a spectacular increase of the low-temperature magnetization, which nearly doubles the

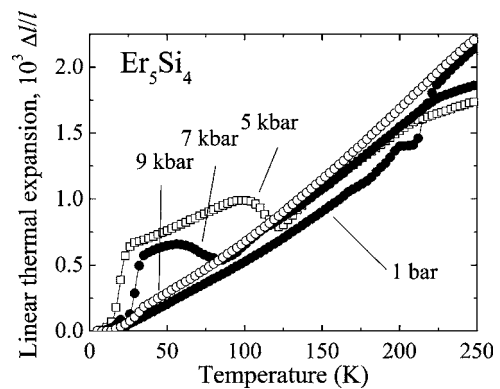


FIG. 4. The linear thermal expansion as a function of temperature measured on heating at selected values of hydrostatic pressure (the pressure values given are recorded at room temperature).

normal-pressure value, whereas the anomaly near T_C begins to diminish. Higher pressure does not significantly increase the maximum magnetization value, mimicking the saturation of the pressure effects observed in the magnetization isotherms. Again, this behavior appears equivalent to that found in Gd_5Ge_4 .² At high pressure—i.e., in the 4.1- and 5.6-kbar curve—the anomaly at T_C is shifted towards higher temperatures. In fact, during the pressure application process the maximum of the derivative $|dM/dT|$ has shifted from its initial temperature of $T_C=30$ K to its maximum pressure temperature of 35 K, which corresponds to the new anomaly at T_{C2} found in the low-field experiments. These results indicate that the hydrostatic pressure induces remarkable changes in the magnetic state of Er_5Si_4 . The increase of the magnetization signal at low temperature could be interpreted as the favoring of a more collinear FM structure, whereas a higher T_C should be related to stronger FM interactions. All of this can be explained by assuming the onset of the $O(\text{I})$ crystallographic structure, similar to what happens in Er_5Si_4 at low temperature with the application of a magnetic field.³³

The high-temperature magnetization shown in Fig. 3(b) reveals an even more drastic effect of pressure. The structural $O(\text{I}) \leftrightarrow M$ transformation, which is detected by an observable change of slope in the magnetization²⁹ as indicated by vertical arrows in the plot, is shifted to low temperatures at an unprecedented rate of $dT_1/dP \cong -23(1)$ K/kbar. While it was expected that pressure should have a strong effect on this structural transition due to the higher unit cell volume of the M phase with respect to the $O(\text{I})$ state, such an extreme change of the transition temperature has not been observed to date among any of the 5:4 compounds [in $\text{Gd}_5\text{Si}_2\text{Ge}_2$, for example, dT_1/dP is $\sim 3-5$ K/kbar for polycrystalline³⁴ and single-crystalline⁶ specimens, respectively, and it is ~ 2.6 K/kbar in polycrystalline $\text{Tb}_5\text{Si}_2\text{Ge}_2$ (Ref. 5)]. This is indeed an extraordinary result, indicating how easy an external parameter can modify the physical properties of some of the $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys. The influence of the paramagnetic state must be the key to understanding this phenomenon, and we believe that in the absence of magnetic ordering, the sensitivity of a system to volume changes induced by pressure is maximized. This implies that the magnetic ordering that either overlaps with the structural phase change (as in

$\text{Gd}_5\text{Si}_2\text{Ge}_2$) or occurs in the immediate vicinity of the same (as in $\text{Tb}_5\text{Si}_2\text{Ge}_2$) moderates the volume changes that pressure can induce when the magnetism is not part of the physical mechanism of the transformation.

In order to complement the pressure-induced magnetic phenomena and uncover associated structural effects, we measured the LTE of Er_5Si_4 as a function of temperature and pressure. In the experiments performed on heating, as can be seen in Fig. 4, the $O(I) \leftrightarrow M$ structural transformation is signaled by a complex LTE anomaly between 200 and 230 K at ambient pressure. The anomalous and damped shape of the jump in the 1-bar curve is surely associated to the effect induced by the freezing of the transmitting medium in the vicinity of the structural transition, which might give rise to spurious signal in the strain gages. The 5-kbar (pressure value at room temperature) experiment shows a tremendous decrease of the transition temperature from ~ 215 K (a midpoint of the anomaly observed between 200 K and 230 K) down to approximately $T_t \cong 115$ K which is equivalent to the rate $dT_t/dP \cong 30(1)$ K/kbar assuming a linear dependence of T_t on pressure between 1 bar and 5 kbar. This is similar to the 23(1) K/kbar value obtained from the magnetization measurements and the difference is expected considering the uncertainty in the determination of the transition temperature in a gradual and extended first-order transformation, especially in the case of this broad high-temperature crystallographic transition that at 1 bar spans a temperature range of more than 30 K.^{29,32} What was not expected is a second jump in the opposite direction at a lower temperature ($T_{t2} \cong 20$ K at 5 kbar). It is important to note that this step recovers the LTE obtained from the extrapolation of the Grüneisen-type behavior for the high-temperature $O(I)$ phase, so it is reasonable to assume that a reentrance of the same $O(I)$ crystallographic structure is occurring under pressure at low temperature. The 7-kbar measurement presents both transformations even closer to each other; the temperatures are $T_t \cong 75$ K for the high-temperature change and $T_{t2} \cong 30$ K for the low-temperature reentrant behavior. Finally, the 9-kbar measurement results in the collapse of both transitions and the $O(I)$ structure becomes the only stable polymorph in the whole temperature range. A nearly indistinguishable (at this scale) kink remains seen at $T=35$ K coinciding with the pressure-induced peak observed in the magnetization data, and it likely manifests a spontaneous volume magnetostriction effect due to the magnetic ordering of $O(I)$ phase of Er_5Si_4 . All structural transformations of Er_5Si_4 are first order like, as follows from thermal hysteresis values of $\Delta T \cong 3-4$ K that have been observed in all the measurements (the cooling curves are not shown in Fig. 4 for clarity). The possibility of the nucleation of a new crystallographic structure at low temperature by applying pressure has been previously reported in Gd_5Ge_4 ,² but the cancellation of two structural transformations which collapse together under the influence of hydrostatic pressure is an extraordinary and heretofore unreported phenomenon in the family of 5:4 intermetallic rare-earth compounds.

With the aim of performing a conclusive experiment to unveil the nature of structural phase transitions induced by hydrostatic pressure, we have performed neutron diffractions

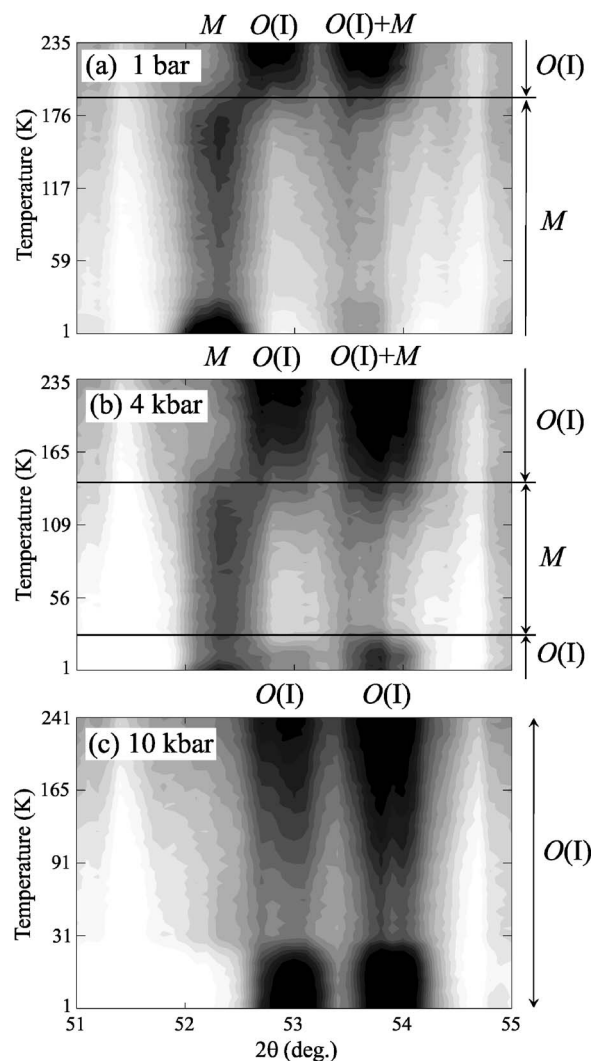


FIG. 5. Contour plots of the thermodiffractograms of Er_5Si_4 collected in D20 at various hydrostatic pressures (values are listed at room-temperature): (a) ambient pressure, (b) 4 kbar, and (c) 10 kbar (note the nonlinear scales of the temperature). Darker color represents stronger intensity areas, whereas lighter color depicts weaker intensity zones.

experiments under pressure. In Fig. 5 we present the contour plots of the D20 thermodiffractograms collected on heating at several pressures (values listed are at room temperature) of (a) 0 kbar, (b) 4 kbar, and (c) 10 kbar. The assignments of the different peaks are shown with labels indicating the phases that contribute significantly to each observed peak: M for a monoclinic line, $O(I)$ for an orthorhombic reflection, and $M+O(I)$ for a peak with a mixed contribution. Figure 5(a) reproduces the results of Refs. 29, 30, and 32 which reported that the room-temperature $O(I)$ structure is conserved on cooling down to ~ 200 K, where a structural transition to the low-temperature M phase occurs. Below 30 K, an increasing intensity of the M peaks is evident due to the onset of the FM ordering at $T_C \approx 30$ K, which adds the contribution of the magnetic scattering to the already existent nuclear intensity with M symmetry. It is worth remarking on the uniform increase of the overall background on heating,

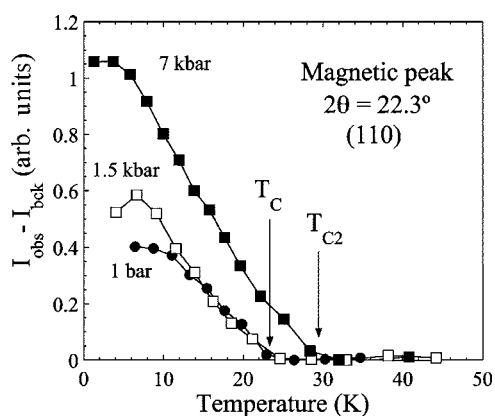


FIG. 6. Integrated intensity of a magnetic peak of Er_5Si_4 collected in D20 at selected pressure values. The background has been subtracted. The ordering temperatures of the M and $O(I)$ phases are indicated with arrows for two extreme pressures: i.e., 0 kbar where the system is in the M state and 7 kbar for the $O(I)$ phase.

which is clearly reflected in a gradual rise of the signal of the diffraction peaks. This effect is due to the temperature dependence of the signal coming from the massive pressure cell and pressure-transmitting medium, and it is observable in all the experiments performed. The application of a 4-kbar hydrostatic pressure induces drastic changes in the crystallographic structures involved in this study. First of all, the high-temperature first-order $O(I) \rightarrow M$ phase transition is shifted down to $T_f \sim 145$ K, which is in an excellent agreement with the macroscopic LTE results. In addition, the intensity of the pure M reflection is clearly diminished at the low-temperature regime with respect to the 0 kbar and the rise of a new peak in the position of the $O(I)$ line is observed at very low temperatures ($T < 20$ K). Finally, the thermodiffractogram collected at 10 kbar shows the complete disappearance of the intermediate M phase and the stability of the $O(I)$ state over the whole temperature range.

A strong background, produced both by the pressure cell and the pressure transmitting medium, makes it difficult to reliably assign different reflections to different magnetic phases and precludes adequate refinement of the crystallographic and magnetic structures as a function of pressure. The measurement of the background without a sample in the pressure cell has been discarded, as the absence of the sample volume would change the amount of transmitting medium inside the cell and, thus, the neutron absorption. On the other hand, the refinement of the 10-kbar spectrum at 2 K after subtracting the signal in the PM state (i.e., 40 K) has been performed. Although this correction is not fully satisfactory, as both crystal structures coincide but their nuclear contributions can be different, some qualitative information about the new high-pressure low-temperature Er_5Si_4 phase can be obtained. These fits indicate the onset of a FM ordering along the b axis with some canting in the ac plane, which is analogous to the ambient-pressure magnetic structure supported by the $O(I)$ crystallographic phase.^{28,32} In addition, the integration of the magnetic peaks at different pressures permits one to demonstrate the changing magnetic properties of the system—e.g., a change in the ordering tem-

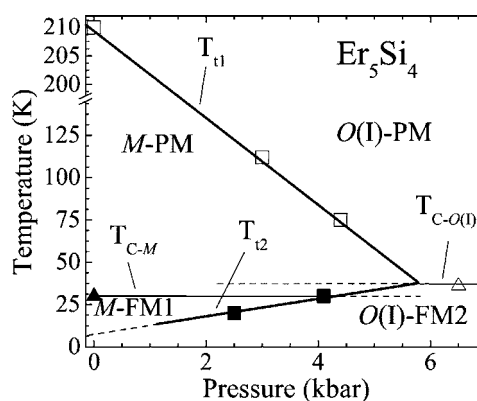


FIG. 7. The magnetic and crystallographic P - T phase diagram of Er_5Si_4 . Open squares represent the high-temperature $O(I) \leftrightarrow M$ transformation (T_t), whereas solid squares are used for the low-temperature pressure-induced $O(I)$ reentrance (T_{t2}). Both sets of values are extracted from LTE data. Triangles are used for the magnetic transition temperatures of the two pure structural phases—i.e., solid triangle for the pure M phase at ambient pressure and open triangle for the pure $O(I)$ phase at high pressure. In addition, these magnetic transition lines are labeled as defined in the text. Thick solid lines depict the magnetic and/or crystallographic phase boundaries, and dotted lines are used for the magnetic ordering of the minority phase involved in the first-order crystallographic transformation.

perature of the phases involved. In Fig. 6, we depict the integrated intensity of the magnetic reflection (110) after subtracting the background, which is common to both crystallographic structures, as a function of the temperature and hydrostatic pressure. The ordering temperature abruptly changes due to the onset of a different crystallographic structure. As can be seen in Fig. 6, the continuous change in concentrations of the low-pressure (orders at T_C) and the high-pressure (orders at T_{C2}) phases is hidden by the superposition of the contributions coming from the two magnetic structures, so the transformation can only be detected by observing the maximum pressure and the ambient pressure results, where only pure phases exist. At 1 bar, the M system orders at $T_C \sim 23$ K, whereas at ~ 7 kbar, the $O(I)$ phase becomes magnetic at $T_{C2} \sim 29$ K. Although the exact temperature values do not coincide with the macroscopic values (29 and 35 K, respectively), which can be explained in terms of completely different experimental setups and a different method of determination of T_C , the difference in the Curie temperatures is in a good agreement with that observed in the macroscopic magnetic measurements. In the light of these results, the use of more suitable neutron or synchrotron x-ray diffraction techniques to obtain low-background data at high pressure to obtain a precise refinement of the crystal and magnetic phases is an experimental challenge that will be considered in future works.

DISCUSSION

In light of all experimental evidence presented above, a following physical scenario explaining this complex and intriguing phenomenology can be formulated. This is summa-

alized in the P - T magnetic-crystallographic phase diagram we propose in Fig. 7, which has been constructed using data extracted from the magnetization and LTE measurements as a function of pressure and afterwards confirmed by neutron diffraction experiments. At ambient pressure, the already known $O(I) \leftrightarrow M$ structural transformation takes place at $T_i \approx 200$ – 230 K. The $PM \rightarrow FM1$ transition at ambient pressure occurs at $T_C = T_{C-M} = 29$ K. We use the subscript M to highlight that the FM1 ordering is supported by the M -type crystallographic phase. With the exception of spin reorientation observed by neutron powder diffraction at ~ 15 K, which is not represented in the diagram for clarity, no further changes below T_{C-M} are observed, although the possibility of a structural change at ambient pressure and very low temperature cannot be excluded entirely because all of our experiments were limited to 2 K. When pressure increases, T_i rapidly decreases at the exceptionally high rate of $dT_i/dP \approx -23$ – 30 K/kbar. This extraordinary strong pressure dependence may be a consequence of the absence of a magnetic ordering anomaly in the vicinity of the structural transition. In addition, the increasing pressure causes reentrance of the high-temperature $O(I)$ structure at low temperature. This phase boundary exhibits a much lower pressure dependence, which is on the order of $dT_{i2}/dP \approx 6$ K/kbar and is quite comparable with the already known pressure dependence values for magnetostructural transformations of several other 5:4 compounds. The second magnetic anomaly found in the magnetization and LTE data at $T_{C2} = T_{C-O(I)} \approx 35$ K is associated with the magnetic ordering forming a complex FM2 state of the new $O(I)$ structure nucleating at low temperature. As this pressure-induced crystallographic transformation is of first-order type, a phase coexistence of the M and $O(I)$ phases is observed over a considerable range of temperatures (~ 10 and 30 K) and pressures (~ 2 and 5.5 kbar). Therefore, anomalies associated with both structures—i.e. $T_{C-M} = 30$ K and $T_{C-O(I)} = 35$ K—should be observed along a wide range of intermediate pressures (for example, see the coexistence of both anomalies in Fig. 3). At higher pressures, both crystallographic transition temperatures T_i and T_{i2} get closer to each other in such a way that at ~ 6 kbar both transitions collapse into a tricritical point and the intermediate M state disappears and so does the magnetic anomaly associated with this phase. By extrapolating the pressure dependences of both anomalies, this occurs approxi-

mately at $P \approx 5.8$ kbar. At higher pressure, only the $O(I)$ state remains stable in the whole sample volume and an FM transition takes place at the magnetic ordering temperature of the $O(I)$ phase—i.e., $T_{C-O(I)} = 35$ K. The different ordering temperatures of the M and $O(I)$ phases highlight once again the influence of the crystal structure on the magnetic interactions of the $R_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys.

CONCLUSIONS

In summary, we have carried out a comprehensive investigation of the effects of the hydrostatic pressure on the magnetic and crystallographic structure of the compound Er_5Si_4 which has given rise to the elaboration of the P - T magnetic-crystallographic phase diagram. An extraordinary decrease of the high-temperature $O(I) \leftrightarrow M$ crystallographic transition ($T_i \approx 200$ – 230 K) has been evidenced at a rate of $dT_i/dP \approx -23$ – 30 K/kbar. In addition, a simultaneous nucleation of an $O(I)$ -FM state at low temperatures has been demonstrated at a pressure rate of ~ 6 K/kbar. At high pressures, both anomalies collapse, which stabilizes the $O(I)$ - Er_5Si_4 phase over the whole temperature range. The Curie temperature of the low-temperature FM phase— $T_{O(I)} = 35$ K—is measurably higher than that of the M state— $T_M = 30$ K. This physical picture agrees with the already established concept of the enhancement of the FM exchange interactions promoted by the onset of the $O(I)$ structure due to the increased number of covalentlike Si-Si (Si-Ge and/or Ge-Ge) bonds interconnecting the layered structure of the 5:4 alloys and the subsequent creation of new exchange paths for the FM-like superexchange interaction via partially covalent (i.e., directional) bonds.

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