Phase relationships and structural, magnetic, and thermodynamic properties of alloys in the pseudobinary Er$_5$Si$_4$-Er$_5$Ge$_4$ system

A. O. Pecharsky  
*Iowa State University*

Karl A. Gschneidner Jr.  
*Iowa State University*, cagey@ameslab.gov

Vitalij K. Pecharsky  
*Iowa State University*, vitkp@ameslab.gov

Deborah L. Schlagel  
*Iowa State University*, schlagel@iastate.edu

Thomas A. Lograsso  
*Iowa State University*, lograsso@ameslab.gov

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Phase relationships and structural, magnetic, and thermodynamic properties of alloys in the pseudobinary Er5Si4-Er5Ge4 system

**Abstract**
The room temperature crystal structures of Er$_5$Si$_x$Ge$_{4-x}$ alloys change systematically with the concentration of Ge from the orthorhombic Gd$_5$Si$_4$-type when x=4, to the monoclinic Gd$_5$Si$_2$Ge$_2$ type when 3.5 $\leq$ x $\leq$ 3.9 and to the orthorhombic Sm$_5$Ge$_4$ type for x $\leq$ 3. The Curie-Weiss behavior of Er$_5$Si$_x$Ge$_{4-x}$ materials is consistent with the Er$^{3+}$ state. The compounds order magnetically below 30 K, apparently adopting complex noncollinear magnetic structures with magnetization not reaching saturation in 50 kOe magnetic fields. In Er$_5$Si$_4$, the structural-only transformation from the monoclinic Gd$_5$Si$_2$Ge$_2$-type to the orthorhombic Gd$_5$Si$_4$-type phase occurs around 218 K on heating. Intriguingly, the temperature of this polymorphic transformation is weakly dependent on magnetic fields as low as 40 kOe ($dT/dH = -0.058 \text{ K/kOe}$) when the material is in the paramagnetic state nearly 200 K above its spontaneous magnetic ordering temperature. It appears that a magnetostructural transition may be induced in the 5:4 erbium silicide at $\sim 18 \text{ K}$ and above by 75 kOe and higher magnetic fields. Only Er$_5$Si$_4$ but none of the other studied Er$_5$Si$_x$Ge$_{4-x}$ alloys exhibit magnetic field induced transformations, which are quite common in the closely related Gd$_5$Si$_x$Ge$_{4-x}$ system. The magnetocaloric effects of the Er$_5$Si$_x$Ge$_{4-x}$ alloys are moderate.

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Phase relationships and structural, magnetic, and thermodynamic properties of alloys in the pseudobinary Er$_5$Si$_4$-Er$_5$Ge$_4$ system

A. O. Pecharsky, K. A. Gschneidner, Jr., V. K. Pecharsky, D. L. Schlager, and T. A. Lograsso

Materials and Engineering Physics Program, Ames Laboratory of the United States Department of Energy, Iowa State University, Ames, Iowa 50011-3020, USA

Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA

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The room temperature crystal structures of Er$_5$Si$_4$-Ge$_x$ alloys change systematically with the concentration of Ge from the orthorhombic Gd$_5$Si$_4$-type when $x = 4$ to the monoclinic Gd$_5$Si$_2$Ge$_2$ when $3.5 \leq x \leq 3.9$ and to the orthorhombic Sm$_5$Ge$_4$-type for $x \leq 3$. The Curie-Weiss behavior of Er$_5$Si$_4$-Ge$_x$ materials is consistent with the Er$^{3+}$ state. The compounds order magnetically below 30 K, apparently adopting complex noncollinear magnetic structures with magnetization not reaching saturation in 50 kOe magnetic fields. In Er$_5$Si$_4$, the structural-only transformation from the monoclinic Gd$_5$Si$_2$Ge$_2$-type to the orthorhombic Gd$_5$Si$_4$-type phase occurs around 218 K on heating. Intriguingly, the temperature of this polymorphic transformation is weakly dependent on magnetic fields as low as 40 kOe ($dT/dH = -0.058$ K/kOe) when the material is in the paramagnetic state nearly 200 K above its spontaneous magnetic ordering temperature. It appears that a magnetostructural transition may be induced in the 5:4 erbium silicide at $\sim$18 K and above by 75 kOe and higher magnetic fields. Only Er$_5$Si$_4$, but none of the other studied Er$_5$Si$_4$-Ge$_x$ alloys exhibit magnetic field induced transformations, which are quite common in the closely related Gd$_5$Si$_4$-Ge$_x$ system. The magnetocaloric effects of the Er$_5$Si$_4$-Ge$_x$ alloys are moderate.

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INTRODUCTION

Both the existence and crystallographic data of binary rare earth-germanium and rare earth-silicon compounds with the R$_5$T$_4$ stoichiometries (R=rare earth element, T=Si or Ge) were originally reported by Smith et al. Soon after, Holtzberg et al. described phase relationships in the pseudobinary Gd$_5$Si$_4$-Gd$_5$Ge$_4$ system. They also confirmed the crystallography and provided magnetic property data for the binary R$_5$T$_4$ silicides and germanides of heavy lanthanides, i.e., for R=Gd, Tb, Dy, Ho, and Er. All silicides were classified as ferromagnets. Within the series, Gd$_5$Si$_4$ has the highest Curie temperature, $T_C \approx 340$ K, and ferromagnetic ordering temperatures gradually decrease from $T_C = 225$ K for Tb$_5$Si$_4$ to $T_C = 140$ K, 76 K, and 25 K for Dy$_5$Si$_4$, Ho$_5$Si$_4$, and Er$_5$Si$_4$, respectively. Conversely, the germanides were reported to order antiferromagnetically at 15 and 47 K for Gd$_5$Ge$_4$ (recent data, however, indicate that Néel temperature of Gd$_5$Ge$_4$ is $\sim 128$ K), 30 K for Tb$_5$Ge$_4$, 40 K for Dy$_5$Ge$_4$, 21 K for Ho$_5$Ge$_4$, and 7 K for Er$_5$Ge$_4$. In the Gd$_5$Si$_2$Ge$_2$ system, Holtzberg et al. also found two extended solid solutions based on both Gd$_5$Si$_4$ and Gd$_5$Ge$_4$, and a new ternary phase with an unknown crystal structure.

The discovery of the giant magnetocaloric effect in Gd$_5$Si$_2$Ge$_2$ (Ref. 10) triggered a widespread research of the pseudobinary Gd$_5$Si$_4$-Ge$_4$ system. In 1997, Pecharsky and Gschneidner reported, and later Morellon et al. and Pecharsky et al. refined the pseudobinary phase diagram. At present, it is well established that the Si-rich alloys adopt the orthorhombic Gd$_5$Si$_4$-type structure at room temperature when $x \geq 2.1$ and that they order ferromagnetically on cooling via a second-order phase transition. The intermediate solid solutions with $1.5 < x < 2.1$ crystallize in the monoclinic Gd$_5$Si$_2$Ge$_2$-type structure at room temperature. When cooled, they undergo a transformation to the Gd$_5$Si$_4$-type structure, which is coupled with ferromagnetic ordering. Thermodynamically, these are first-order phase transitions. The Ge-rich solid solution alloys have the orthorhombic Sm$_5$Ge$_4$-type crystal structure at room temperature when $x \leq 1.2$ and the majority of them exhibit two successive transformations below room temperature. A second-order paramagnetic to antiferromagnetic transition occurs at nearly constant temperature ($\sim 130$ K) regardless of the alloy composition. A first-order transformation, during which a crystallographic transition from the Sm$_5$Ge$_4$-type structure coupled with an antiferromagnetic to ferromagnetic transition, is observed at lower temperatures with $T_C$ strongly dependent on the value of $x$. It is worth noting that in a zero magnetic field, only the high temperature paramagnetic-antiferromagnetic transition occurs in pure Gd$_5$Ge$_4$. Both the monoclinic Gd$_5$Si$_2$Ge$_2$ and the orthorhombic Sm$_5$Ge$_4$-type alloys exhibit the giant magnetocaloric effect around their respective first-order magnetostructural phase transition temperatures.

Of the eight possible R$_5$Si$_4$Ge$_{4-x}$ systems, where R is heavy lanthanide, the Gd$_5$Si$_4$Ge$_{4-x}$ alloys are the most studied to date. Over the last few years, several reports describing both the interaction of components and physical properties of compounds have been published for Tb$_5$Si$_4$Ge$_{4-x}$ by Morellon et al., Huang et al., Ritter et al., Tegus et al., Thuy et al., Yoa et al., and Lee et al. and for Dy$_5$Si$_4$Ge$_{4-x}$ by Gschneidner et al. and Ivtchenko et al. Preliminary results have been also reported about some individual intermetallics, including Ho$_5$Si$_2$Ge$_2$ by Thuy et al., Yb$_5$Si$_4$ by Cerny and Alamdi-Yardi, and Yb$_5$Ge$_4$ by Pani and Palenzona. Despite limited amount of available data, it
is quite evident that systems with heavy lanthanides demonstrate both similarities and differences when compared to the Gd$_5$Si$_2$Ge$_4$-type alloys, thus pointing to a complexity of interactions between heavy lanthanides, germanium, and silicon at the R$_5$T$_4$ stoichiometries.

Only a little research has been carried out on the Er$_5$Si$_4$Ge$_{4-x}$ system. Besides original reports by Smith et al. and Holtzberg et al., phase equilibria, electrical resistivity, and thermal expansion of binary silicides of Er were reported by Luzan et al. but only above room temperature. According to Ref. 29, Er$_5$Si$_4$ forms peritectically at 2150 K and it belongs to the Sm$_5$Ge$_4$-type structure with lattice parameters \( a = 7.28 \), \( b = 14.37 \), and \( c = 7.595 \) Å at room temperature. On the contrary, Kotur and Parasyuk claim that they did not observe the formation of Er$_5$Si$_4$ at 870 K. Recently, Pecharsky et al. and Mozharivskyj et al. established that Er$_5$Si$_4$ adopts the Gd$_5$Si$_2$-type structure at room temperature. On cooling, it transforms into the monoclinic Gd$_5$Si$_2$Ge$_2$-type phase between 210 and 200 K while remaining paramagnetic, and the monoclinic polymorph of Er$_5$Si$_4$ orders magnetically at \( \sim 30 \) K. Its magnetic ground state is complex showing a distinct ferromagnetic component. According to our preliminary temperature dependent x-ray powder diffraction studies, the magnetically ordered Er$_5$Si$_4$ retains the monoclinic Gd$_5$Si$_2$-type structure down to \( -5 \) K in a zero magnetic field. In this respect, the silicide of erbium is quite different from all other members of the extended R$_5$T$_4$ system as well as the extended Th$_5$Si$_4$ family studied to date, where the ferromagnetic order has been always associated with the Gd$_5$Si$_2$-type structure.

Here we report on the relationships between chemical composition, crystal structure, magnetic, thermal, and magnetocaloric properties of several pseudobinary alloys in the Er$_5$Si$_4$Ge$_{4-x}$ system. As we will describe below, this system exhibits much greater deviations from the related Gd$_5$Si$_2$Ge$_{4-x}$ alloys when compared to Tb$_5$Si$_2$Ge$_{4-x}$ and Dy$_5$Si$_2$Ge$_{4-x}$, thus demonstrating that physical properties of these intriguing R$_5$T$_4$ family of materials can be adjusted over a broad range of values.

**ALLOY PREPARATION AND CHARACTERIZATION**

A total of 13 alloys in the Er$_5$Si$_4$Ge$_{4-x}$ system with \( x \) varying from \( -4 \) to \( 0 \) were prepared by arc melting of stoichiometric mixtures of pure components in an argon atmosphere on a water-cooled copper hearth using high purity components. The Er metal was prepared by the Materials Preparation Center of the Ames Laboratory and it was 99.86 at. % (99.99 wt. %) pure. The major impurities in ppm atomic (and in ppm by weight) were as follows: O, 400 (40); C, 280 (20); N, 70 (6); F, 120 (14); H, 170 (1), and Fe, 30 (10). The Si and Ge were purchased from Meldform Metals (United Kingdom) and were 99.999 wt. % pure. Every alloy was remelted six times; alloy buttons were turned over after each melting to improve their homogeneity. The weight of each alloy did not exceed 20 g to ensure fast cooling. Weight losses after the melting were in the range from 0.3 to 0.5 wt. %, therefore alloy stoichiometries were assumed to remain unchanged after the preparation. All the alloys were examined in the as-prepared condition, without heat treatment.

In addition to arc-melted buttons, in this study we examined nonoriented large-grain leftovers extracted from a sample of Er$_5$Si$_4$ which has been used to prepare single crystals by Bridgman technique. This alloy was first arc melted (both the Er and Si were of the same purity as mentioned above) and then electron beam welded in a tungsten Bridgman crucible. The crucible was placed inside a tungsten mesh resistance furnace under a pressure of \( 6.7 \times 10^4 \) Pa and slowly heated to 1970 K. Then the chamber was back-filled with high purity argon to \( 2.8 \times 10^3 \) Pa to equalize the pressures inside and outside the crucible. The crucible was then heated to 2320 K, after which it was withdrawn from the heat zone at the rate of 8 mm/h. While some reaction of the melt with the crucible walls was noted, x-ray powder diffraction indicated phase purity of the as-grown ingot.

The samples described in this work were extracted from the middle of the as-solidified ingot as scraps that remained after cutting out specimens for other property measurements.

The crystal structures and phase compositions of the alloys were characterized by x-ray powder diffraction. The x-ray powder diffraction data were collected on a Rigaku TTRAX rotating anode diffractometer equipped with a wide angle goniometer using Mo Ka radiation between \( 8^\circ -11^\circ \) and \( 50^\circ \) of 2θ with a 0.01° step. The crystal structures were refined in an isotropic approximation by using Rietveld technique. The resulting profile residuals \( (R_p) \) were lower than 10% and the derived Bragg residuals \( (R_B) \) did not exceed 6%.

Magnetic susceptibility and magnetization measurements were performed on a Lake Shore dc/ac magnetometer-susceptometer, model 7225. Temperature dependent ac magnetic susceptibilities were measured between 5 and 320 K in an ac magnetic field with a 5 Oe amplitude and a 125 Hz frequency in a zero bias dc field. Magnetization was measured as a function of temperature between 5 and 320 K in various dc magnetic fields between 1 and 50 kOe. Isothermal magnetization data were collected in the vicinities of magnetic phase transition temperatures in dc magnetic fields varying from 0 to 50 kOe with a 2 kOe step.

The heat capacities were measured using a semiadiabatic heat pulse calorimeter from \( -3.5 \) to \( 350 \) K in various constant dc magnetic fields ranging from 0 to 100 kOe. The phase transition temperatures were determined from both the magnetic and calorimetric measurements. The magnetocaloric effect in terms of the isothermal magnetic entropy change \( (\Delta S_M) \) and the adiabatic temperature change \( (\Delta T_{ad}) \) was calculated from either or both magnetic and calorimetric data as described by Pecharsky and Gschneider.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Erbium silicide: Er$_5$Si$_4$**

The room-temperature crystal structure of Er$_5$Si$_4$ was confirmed using x-ray powder diffraction data collected from several different samples at ambient temperature and employing the crystallographic parameters obtained from the single crystal structural investigation in Ref. 31. The refined
TABLE I. Room temperature crystallographic data of selected compounds in the Er$_5$Si$_4$-Er$_5$Ge$_4$ pseudobinary system.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Structure type</th>
<th>Space group</th>
<th>a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>γ, °</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_5$Si$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.27</td>
<td>14.32</td>
<td>7.58</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.289</td>
<td>14.37</td>
<td>7.591</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.28</td>
<td>14.37</td>
<td>7.595</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (I)$^a$</td>
<td>Gd$_5$Si$_4$</td>
<td>Pnma</td>
<td>7.2838(6)</td>
<td>14.363(1)</td>
<td>7.5943(6)</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (I)$^a$</td>
<td>Gd$_5$Si$_4$</td>
<td>Pnma</td>
<td>7.2931(3)</td>
<td>14.374(1)</td>
<td>7.5980(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (II)$^a$</td>
<td>Gd$_5$Si$_4$</td>
<td>Pnma</td>
<td>7.2927(3)</td>
<td>14.374(1)</td>
<td>7.5973(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (III)$^a$</td>
<td>Gd$_5$Si$_4$</td>
<td>Pnma</td>
<td>7.2940(6)</td>
<td>14.374(1)</td>
<td>7.5973(5)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$<em>4$Ge$</em>{0.2}$</td>
<td>Gd$_5$Si$_4$Ge$_2$</td>
<td>P11$_2_1$/a</td>
<td>7.3681(3)</td>
<td>14.412(1)</td>
<td>7.5728(4)</td>
<td>92.958(3)</td>
<td>d</td>
</tr>
<tr>
<td>Er$_5$Si$<em>4$Ge$</em>{0.4}$</td>
<td>Gd$_5$Si$_4$Ge$_2$</td>
<td>P11$_2_1$/a</td>
<td>7.3745(4)</td>
<td>14.412(1)</td>
<td>7.5746(4)</td>
<td>92.960(3)</td>
<td>d</td>
</tr>
<tr>
<td>Er$_5$Si$<em>4$Ge$</em>{0.5}$</td>
<td>Gd$_5$Si$_4$Ge$_2$</td>
<td>P11$_2_1$/a</td>
<td>7.3777(3)</td>
<td>14.420(1)</td>
<td>7.5786(3)</td>
<td>92.948(2)</td>
<td>d</td>
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<tr>
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<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.4528(3)</td>
<td>14.443(1)</td>
<td>7.5456(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Si$<em>4$Ge$</em>{1.5}$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.4548(3)</td>
<td>14.442(1)</td>
<td>7.5456(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
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<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.4671(3)</td>
<td>14.451(1)</td>
<td>7.5517(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.4862(3)</td>
<td>14.466(1)</td>
<td>7.5609(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.5448(3)</td>
<td>14.515(1)</td>
<td>7.6081(3)</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.51</td>
<td>14.41</td>
<td>7.59</td>
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<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_5$Ge$_4$</td>
<td>Pnma</td>
<td>7.536</td>
<td>14.506</td>
<td>7.600</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Sample I is the stoichiometric arc-melted alloy containing $\sim$5 vol. % of Er$_{5-x}$Si$_x$ impurity; sample II is off-stoichiometric arc-melted alloy, which is a single phase material within the sensitivity of x-ray powder diffraction analysis; sample III is the stoichiometric Bridgman-grown single phase material.

$^b$Diffraction data were collected at $T=300$ K.

$^c$During Rietveld refinement, a small yet measurable amount of the monoclinic polymorph of Er$_5$Si$_4$ was also detected (Ref. 33), but these results are not included in the table, nor are they shown in Fig. 1.

$^d$This study.

The x-ray powder diffraction pattern [Fig. 1(a)] of the arc-melted stoichiometric Er$_5$Si$_4$, hereafter called sample I, clearly indicates the presence of a small amount of an impurity phase. The latter was identified as Er$_3$Si$_2$, hereafter called sample II, in an attempt to obtain a single-phase material. As seen in Fig. 1(b), no impurity phase(s) can be detected in this alloy within the sensitivity of the x-ray powder diffraction technique. The unit cell dimensions of Er$_{5.05}$Si$_4$ (Table I) show no statistically significant differences when compared to those of Er$_5$Si$_4$. Considering the full occupancy of all sites, we conclude that Er$_5$Si$_4$ is a stoichiometric compound, and despite small weight losses observed during the arc melting, the evaporation of the Er metal was substantial enough to shift the as-prepared Er$_5$Si$_4$ alloy into the Er$_{5-x}$Si$_x$+Er$_5$Si$_4$ two-phase region of the Er-Si phase diagram. Consistent with this conclusion, is the x-ray powder diffraction pattern (not shown) of the stoichiometric Er$_5$Si$_4$ prepared using the Bridgman technique, from now on called sample III, indicating a single phase alloy because evaporative losses from a sealed crucible were indeed negligible. Its unit cell dimensions (Table I) deviate from those of both arc-melted materials by no more than two standard deviations, i.e., the differences in the unit cell dimensions of the three different Er$_5$Si$_4$ samples, are statistically insignificant. A non-negligible discrepancy seen between the three sets of powder diffraction data (samples I, II, and III) and the unit cell dimensions determined in the course of single crystal (sample I) investigation is likely related to a lower absolute precision attainable in a single crystal diffraction experiment when compared with the high resolution powder diffraction data.

For the arc-melted alloy, the dc magnetization data (Figs. 2 and 3) indicate two phase transformations that occur in Er$_5$Si$_4$ below room temperature. On cooling, a structural transition is observed in the paramagnetic state between 210 K to 200 K (Fig. 3, inset) and a ferromagnetic-like or ferrimagnetic-like ordering occurs in low magnetic fields at $\sim$30 K (Figs. 2 and 3). The structural transition is hysteretic:
it takes place between 215 K and 225 K on heating, as illustrated in Fig. 3, inset. The behavior of the ac magnetic susceptibility of polycrystalline Er$_5$Si$_4$, which according to Ref. 40 is $T_N = 11.5$ K.

FIG. 1. (Color online) Fragments of the x-ray powder diffraction patterns of (a) the arc-melted Er$_5$Si$_4$ alloy (sample I) and (b) the arc-melted Er$_{5.05}$Si$_4$ alloy (sample II). The points represent observed data and the lines drawn through the data points correspond to the calculated patterns. The differences, $Y_{\text{obs}} - Y_{\text{calc}}$, are shown at the bottom of each plot. The upper set of vertical bars in (a) and the only set in (b) represent calculated positions of Bragg peaks ($K\alpha_1$ components only) of the orthorhombic Er$_5$Si$_4$. The lower set of vertical bars in (a) indicates the same for ErSi, which belongs to the orthorhombic CrB-type structure. The most obvious difference between the two patterns is the absence in (b) of Bragg peaks at $2\theta = 10.44^\circ$ and $13.29^\circ$ corresponding to ErSi impurity.

FIG. 2. (Color online) The dc magnetization of the arc-melted polycrystalline Er$_5$Si$_4$ alloy (sample I) measured as a function of temperature in 2, 10, 20, and 30 kOe magnetic fields on heating the zero magnetic field cooled sample. The inset shows the behavior of the ac magnetic susceptibility of polycrystalline Er$_5$Si$_4$. The short vertical arrow in the inset indicates Néel temperature of ErSi, which is metamagnetic above 16 kOe at $T = 2.16$ K (Ref. 41), and it is indicative of a magnetic field induced metamagnetic transition intrinsic to Er$_5$Si$_4$. Although the low temperature magnetic structure of Er$_5$Si$_4$ remains unknown, available magnetic property data point to a complex noncollinear arrangement of the magnetic moments of Er below 30 K in low magnetic fields.

FIG. 3. (Color online) The dc magnetizations of the arc-melted polycrystalline Er$_5$Si$_4$ (sample I), Er$_5$Si$_3.5$Ge$_{0.5}$ and Er$_5$Ge$_4$ alloys as functions of magnetic field measured at $T = 5$ K. The vertical arrows point to the onsets of the corresponding metamagnetic transitions. The inverse magnetic susceptibility of polycrystalline Er$_5$Si$_4$ measured in a 20 kOe magnetic field during both cooling and heating is shown in the inset with the arrows indicating the direction of temperature change.
The anomaly is, therefore, it becomes much more pronounced when compared to the magnetic field vector is unknown, the data presented in Fig. 4 shed some light on the orientation of crystallographic axes of this specimen with respect to the magnetic field. For the single phase Er$_5$Si$_4$ (sample III), the magnetization versus temperature is shown in Fig. 4. It was measured using a randomly oriented apparently single-grain specimen extracted from the material prepared using Bridgman technique in order to clarify whether or not the lowest temperature anomaly is intrinsic to Er$_5$Si$_4$. By comparing both Fig. 2 and its inset with Fig. 4, it is easy to see that the lowest temperature anomaly around $T=12$ K is still present in the low field dc magnetization of pure Er$_5$Si$_4$. In fact, it becomes much more pronounced when compared to the sample shown in Fig. 2. The anomaly is, therefore, intrinsic to Er$_5$Si$_4$ and its correspondence with the Neél temperature of ErSi is coincidental.

Even though the orientation of crystallographic axes of this specimen with respect to the magnetic field vector is unknown, the data presented in Fig. 4 shed some light on the nature of the magnetic ordering at $T=30$ K and point to a considerable magnetocrystalline anisotropy of the compound (e.g., the values of magnetization in Fig. 4 are substantially lower than the corresponding values in Fig. 2). The temperature of the cusp, which is observed around 30 K in the 1 kOe $M(T)$ data, is suppressed to $T=27$ K and $T=19$ K by 10 and 20 kOe magnetic fields, respectively. This behavior is consistent with a strong antiferromagnetic component in the magnetic structure of the material. It is interesting to note that the temperature of the broad anomaly observed at $\sim 12$ K remains unaffected by magnetic fields of 20 kOe and below. In magnetic fields higher than 30 kOe, the $M(T)$ of Er$_5$Si$_4$ becomes consistent with the predominantly ferromagnetic or ferrimagnetic arrangement of spins in the material.

The magnetic ordering temperatures and the Curie-Weiss parameters of Er$_5$Si$_4$ are listed in Table II. Predictably, the structural change around 220 K has a significant effect on the paramagnetic Curie temperature of the material. The monoclinic polymorph of the 5:4 erbium silicide has lower paramagnetic Curie temperature ($\Theta_p=19.6$ K) when compared to the orthorhombic polymorph ($\Theta_p=30.3$ K). The lowering of $\Theta_p$ indicates a weakening of exchange interactions and is consistent with the notion that the presence of covalentlike Si$_2$ dimers results in strengthening of magnetic interactions between the two-dimensional slabs. The dimers are found between every slab in the Gd$_5$Si$_4$ type (the orthorhombic polymorph) and only between every other slab in the Gd$_5$Si$_2$Ge$_2$ type (the monoclinic phase). For both crystallographic modifications of the compound, positive paramagnetic Curie temperatures are indicative of the ferromagnetic or ferrimagnetic ground state of the material.

Consistent with the behavior of the magnetization, the heat capacity of the arc-melted Er$_5$Si$_4$ [sample I, Fig. 5(a)] also displays two distinct irregularities. The low-temperature $\lambda$-type anomaly, which occurs at $\sim 30$ K in zero magnetic field, is transformed into a rounded peak by increasing magnetic field as expected for a second-order paramagnetic-ferromagnetic (or ferrimagnetic) phase transformation. The high temperature peak observed between $\sim 210$ K and $\sim 300$ K is still observable in a magnetic field of 20 kOe.

### Table II. Magnetic properties of selected compounds from the Er$_5$Si$_4$-Er$_5$Ge$_4$ pseudobinary system.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure type</th>
<th>From $M(T)$</th>
<th>From $C_p(T)$</th>
<th>$\Theta_p$ (K)</th>
<th>$\rho_{eff}$ ($\mu_B$)$^a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er$_5$Si$_4$</td>
<td>“Sm$_3$Ge$_4$”</td>
<td>25</td>
<td>20</td>
<td>9.86</td>
<td>This study</td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (I)</td>
<td>Gd$_5$Si$_4$</td>
<td>30.3$^b$</td>
<td>9.71$^b$</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$_4$ (I)</td>
<td>Gd$_5$Si$_2$Ge$_2$</td>
<td>19.6$^d$</td>
<td>9.63$^d$</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$_3$Ge$_0$.5</td>
<td>Gd$_5$Si$_2$Ge$_2$</td>
<td>15.9</td>
<td>9.55</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$_3$Ge</td>
<td>Sm$_3$Ge$_4$</td>
<td>17</td>
<td>9.57</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$_2$Ge$_1.5$</td>
<td>Sm$_3$Ge$_4$</td>
<td>12.3</td>
<td>9.39</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Si$<em>1.95$Ge$</em>{2.05}$</td>
<td>Sm$_3$Ge$_4$</td>
<td>13.9</td>
<td>9.56</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_3$Ge$_4$</td>
<td>14</td>
<td>9.56</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Er$_5$Ge$_4$</td>
<td>Sm$_3$Ge$_4$</td>
<td>10</td>
<td>9.73</td>
<td>This study</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

$^a$The theoretical value of the effective magnetic moment for a free Er$^{3+}$ ion is 9.58$\mu_B$.

$^b$Determined from the Curie-Weiss fit of the data measured on heating between 250 K and 310 K.

$^c$The compound adopts this monoclinic crystal structure upon cooling below $\sim 200$ K.

$^d$Determined from the Curie-Weiss fit of the data measured on heating between 50 and 190 K.
240 K is magnetic field independent in this range of magnetic fields, and is indicative of a first-order transformation despite the 40 K peak width. Both the behavior and location of this anomaly are commensurate with the structural transition observed in Er$_5$Si$_4$ in this temperature range. A minor broad abnormality observed around 11 K in the zero field heat capacity is in line with the ac magnetic susceptibility data and it may be slightly enhanced by the presence of ErSi impurity.

For the single phase large-grain Er$_5$Si$_4$ (sample III), the heat capacity [Fig. 5(b)] is in excellent agreement with all the results that have been already described above, except that the anomaly at ~218 K corresponding to the structural transformation narrows and clearly becomes a single peak instead of a double peak structure seen in Fig. 5(a). After subtracting the baseline heat capacity between 190 K and 240 K determined by a third order polynomial approximation of the data from 150 K to 190 K and from 240 K to 250 K and corresponding integration, the entropy of the polymorphic transformation of Er$_5$Si$_4$ is $\Delta S_{tr} = 0.24$ J/g at K.

Another unexpected feature is that the position of the 218 K heat capacity peak corresponding to the structural transition in the paramagnetic state is evidently influenced by magnetic field, as seen in the insets of Fig. 5(b) and Fig. 6. Both the peak and the underlying crystallographic-only transformation are suppressed nearly linearly between 40 and 100 kOe at the rate $dT/dH = -0.058$ K/kOe. To the best of our knowledge, to date there have been no reports that the relatively weak (40 to 100 kOe) magnetic field is able to measurably affect the temperature of a crystallographic transition in the paramagnetic state approximately 200 K above the spontaneous magnetic ordering temperature. Although we do not have sufficient data to speculate on the mechanism of this phenomenon, we believe that it is related to both the large localized magnetic moment of Er and presumably unusually strong spin-orbit coupling in the material. We also believe that the effect of the magnetic field on this polymorphic transformation that does not involve magnetic order should be highly anisotropic because we did not observe a measurable change in the position of the heat capacity peak in the polycrystalline Er$_5$Si$_4$ (samples I and II) in magnetic fields as high as 100 kOe (see Ref. 31 and Fig. 5).

The behavior of the heat capacity in the vicinities of both the low temperature and the high temperature anomalous regions is clarified in Fig. 6. Consistently with the magnetization data, a broad bump around 11 K remains field independent as long as the magnetic field is 50 kOe or lower. When the field reaches 75 kOe and greater, however, it induces an additional heat capacity peak suggestive of a metamagnetic transition, which rapidly and nearly linearly $(dT/dH = 0.32$ K/kOe) moves towards high temperature as the magnetic field increases. Thus, this new peak occurs at ~18, ~23, and ~26 K in the 75, 90, and 100 kOe magnetic fields, respectively. Both the appearance and the behavior of this peak resemble closely that observed in polycrystalline Gd$_5$Ge$_4$ (Ref. 8) except for the difference in the critical mag-
netic fields: the field-induced heat capacity anomaly appears at 20 kOe in Gd$_5$Ge$_4$, while it only becomes apparent at 75 kOe in Er$_5$Si$_4$. It is quite feasible, therefore, that this behavior is reflective of a previously unknown magnetostructural transition that occurs in Er$_5$Si$_4$ in this range of temperatures and magnetic fields.

The magnetocaloric effect of Er$_5$Si$_4$, calculated in terms of both the extensive (the isothermal magnetic entropy change, $\Delta S_M$) and intensive (the adiabatic temperature change, $\Delta T_{ad}$) variables from the heat capacity data, is shown in Fig. 7. At and above $\sim$30 K, the MCE remains positive even for the lowest magnetic field change of 0 to 10 kOe, thus supporting a notion about the presence of a ferromagnetic signature in the ground state of Er$_5$Si$_4$. The small negative MCE observed below $\sim$30 K in a 10 kOe field is indicative of a complex magnetic structure. As the upper magnetic field increases from 10 to 100 kOe, the main MCE peak remains at $T = 30.4$ K, which is consistent with a second order ferromagnetic ordering in a zero magnetic field. When the magnetic field reaches and exceeds 75 kOe, the new $\Delta S_M$ peaks are induced at 16.7, 22.1, and 25.7 K, and the new $\Delta T_{ad}$ peaks occur at 11.8, 15.0, and 100 kOe magnetic fields, respectively. The magnitudes of these additional peaks increase with the increasing field faster than the magnitudes of the main MCE peaks, which is similar to the behavior of the magnetocaloric effect in Gd$_5$Ge$_4$.\cite{footnote1} Without additional crystallographic data, we can only speculate that since below $\sim$200 K Er$_5$Si$_4$ adopts the monoclinic Gd$_5$Si$_4$Ge$_2$-type crystal structure in both the paramagnetic and magnetically ordered states, the high magnetic fields (greater or equal to 75 kOe) induce a transition to the Gd$_5$Si$_4$-type structure, which is coupled to the ferromagnetism of the material, just as it happens in Ge-rich Gd$_5$Si$_{4-x}$Ge$_x$ alloys.\cite{footnote1,footnote2}

**Intermediate phase: Er$_5$Si$_{3.5}$Ge$_{0.5}$ to Er$_5$Si$_{3}$Ge$_{1}$**

Upon substituting as little as 2.5 at. % of Ge for Si, the room temperature crystal structures of the Er$_5$Si$_{4-x}$Ge$_x$ alloys change from the orthorhombic Gd$_5$Si$_4$ type to the monoclinic Gd$_5$Si$_4$Ge$_2$ type. The monoclinic structure is preserved at room temperature from the Er$_5$Si$_{1.5}$Ge$_{0.5}$ to Er$_5$Si$_{1.1}$Ge$_{0.9}$ stoichiometry, and an x-ray powder diffraction pattern of the latter composition is depicted in Fig. 8. The lattice parameters of several alloys from this region are listed in Table I. According to x-ray powder diffraction data little, if any (see Fig. 8), to a few vol. % of the orthorhombic Er$_5$Si$_{1-x}$Ge$_x$ impurity phase can be found in the as-prepared alloys from this phase region.

Considering magnetic properties of Er$_5$Si$_{3.5}$Ge$_{0.5}$ as an example representative for this phase region, both the dc magnetization and ac magnetic susceptibility measurements (Fig. 9) indicate antiferromagnetic (or ferrimagnetic) ordering at $\sim$25 K. The paramagnetic Curie temperature of Er$_5$Si$_{3.5}$Ge$_{0.5}$ (Table II) is positive and the effective magnetic moment is nearly identical to that of the free Er$^{3+}$ ion.

**FIG. 7.** (Color online) The magnetocaloric effect of Er$_5$Si$_4$ (sample III) calculated from heat capacity data: the isothermal magnetic entropy change (a) and the adiabatic temperature change (b). The values shown near the curves indicate the final magnetic field. The initial magnetic field was 0 in all cases.

**FIG. 8.** (Color online) A fragment of the x-ray powder diffraction pattern of the Er$_5$Si$_{3.5}$Ge$_{0.5}$ alloy. The points represent observed data and the line drawn through the data points corresponds to the calculated pattern. The difference, $Y_{obs} - Y_{calc}$, is shown at the bottom of the plot. The set of vertical bars represents calculated positions of Bragg peaks (for both $K\alpha_1$ and $K\alpha_2$ components) of the monoclinic Er$_5$Si$_{3.5}$Ge$_{0.5}$. 144419-7
The low temperature heat capacity measured in a zero magnetic field, which is shown in Fig. 10, displays a \( \lambda \)-type anomaly with a maximum at 28 K indicating that the magnetic ordering in \( \text{Er}_5 \text{Si}_{3.5} \text{Ge}_{0.5} \) is a second-order phase transformation. Additional weak heat capacity anomaly observed around 10 K in a zero magnetic field is consistent with the anomalous behavior of the magnetization at \( T > 10 \) K in 2 kOe and 10 kOe magnetic fields, see Fig. 9. Neither the heat capacity nor magnetic measurements indicate any other transitions between \( 4 \) K and \( 350 \) K. The \( \lambda \)-type anomaly is transformed into a cusp at \( 22 \) K by a 10 kOe magnetic field, which also points to an antiferromagnetic ground state of the material. Magnetic fields exceeding 10 kOe, however, suppress the magnetic contribution to heat capacity below the zero magnetic field magnetic ordering temperature \( T_N \) but broaden and increase it immediately above the zero magnetic field \( T_N \), which is typical of ferromagnetic behavior.

These features are in agreement with the isostructural magnetization of \( \text{Er}_5 \text{Si}_{3.5} \text{Ge}_{0.5} \) measured at \( T = 5 \) K (Fig. 3), which shows a metamagneticlike transformation with a critical magnetic field around 11 kOe.

The magnetic moment remains near 60% of its expected saturation value of \( 9 \mu_B \) per Er atom in a 50 kOe magnetic field. Unlike in the pure \( \text{Er}_5 \text{Si}_4 \), a 75 kOe magnetic field does not induce an additional low temperature transformation(s) as can be concluded from the absence of any additional heat capacity peaks in \( \text{Er}_5 \text{Si}_{3.5} \text{Ge}_{0.5} \). It is feasible, however, that magnetostructural transitions may be induced in this phase region by magnetic fields greater than 75 kOe. The magneticcaloric effect of \( \text{Er}_5 \text{Si}_{3.5} \text{Ge}_{0.5} \) shown in Fig. 11 is moderate, and it is slightly smaller than that of \( \text{Er}_5 \text{Si}_4 \).

**Erbium germanide: \( \text{Er}_5 \text{Ge}_4 \) and the corresponding solid solution**

Beginning from the \( \text{Er}_5 \text{Si}_4 \) stoichiometry and ending with the 5:4 erbium germanide, the as-prepared alloys crystallize in the \( \text{Sm}_5 \text{Ge}_4 \)-type structure at room temperature, thus making it the most extensive solid solution region in the \( \text{Er}_5 \text{Si}_{x} \text{Ge}_{4-x} \) system. The alloy with the \( \text{Er}_5 \text{Si}_{3.5} \text{Ge}_{2.5} \) composition contains both the monoclinic \( \text{Gd}_5 \text{Si}_2 \text{Ge}_2 \)-type and the orthorhombic \( \text{Sm}_5 \text{Ge}_4 \)-type phases, thus indicating that a narrow two-phase region separates the intermediate monoclinic phase and the \( \text{Er}_5 \text{Ge}_4 \)-based solid solution in this system. Since the boiling temperature of Ge (2830 °C) is considerably lower than that of Si (3145 °C) and it is slightly lower than the boiling temperature of Er (2868 °C), losses of Ge due to evaporation begin to exceed losses of Er during the arc melting, and a small amount (~5 vol. % according to Rietveld refinement) of \( \text{Er}_5 \text{Ge}_4 \) phase forms in the as-prepared \( \text{Er}_5 \text{Ge}_4 \), see Fig. 12. The unit cell parameters of several alloys from this extended solid solution region are listed in Table I.
The dc magnetization measurements indicate that Er$_5$Si$_3$Ge$_4$ (Fig. 13), Er$_5$Si$_{2.5}$Ge$_{1.5}$, Er$_5$Si$_{1.95}$Ge$_{2.05}$, and Er$_5$Ge$_4$ (Fig. 13) order antiferromagnetically at 20, 18, 17, and 14 K, respectively. The Curie-Weiss parameters of these three alloys are found in Table II. For Er$_5$Ge$_4$, they are in fair agreement with those reported by Holtzberg et al. The low temperature heat capacity of Er$_5$Ge$_4$ is shown in Fig. 14. The $\lambda$-type anomaly, observed in a zero magnetic field around 14 K, corresponds to the cusp observed at the same temperature in the low magnetic field dc magnetization data and it indicates that the transition is second order. Zero magnetic field heat capacity of Er$_5$Ge$_4$ also displays additional cusp-like anomaly at $\sim$7.5 K, which is not seen in the magnetization data, likely due to the lack of available experimental data points. Considering that the magnetic ordering temperature of the Er$_5$Ge$_3$ impurity is 38 K, this heat capacity cusp seems to be intrinsic to Er$_5$Ge$_4$, however, more detailed investigations are needed before its nature is better understood. Behavior of the heat capacity in nonzero magnetic fields is consistent with the isothermal magnetization of Er$_5$Ge$_4$ measured at $T=5$ K (Fig. 3), which shows a metamagneticlike transformation with a critical magnetic field around 6 kOe.

Similar to the other Er$_5$Si$_{1-x}$Ge$_{4-x}$ alloys, the magnetic moment of Er$_5$Ge$_4$ is about 60% of its expected saturation value of $9\mu_B$ per Er atom in a 50 kOe magnetic field. The magnetocaloric effect in the germanide (Fig. 15) is moderate and its maximum value is nearly the same as that of the 5:4 erbium silicide.
CONCLUSIONS

Although at present we do not have enough experimental data to propose even a preliminary composition-temperature diagram in order to summarize phase relationships and magnetism of the Er$_5$Si$_4$Ge$_{4-x}$ system, it is clear that the magnetic behaviors are more different than similar when compared with the Gd$_3$Si$_2$Ge$_{4-x}$ system. Both systems are analogous in that there are two structurally different orthorhombic phases (Er$_3$Si$_4$ and the Er$_3$Ge$_4$-based solid solution vs the Gd$_3$Si$_2$-based and Gd$_3$Ge$_4$-based solid solutions) which are separated by the monoclinic phase region. Furthermore, substituting Si by Ge has similar effect on the room temperature crystallography in both systems: increasing the concentration of Ge results first, in the loss of one-half of the Si$_2$ dimers between the slabs (monoclinic phase) and second, all of the interslab Si$_2$ dimers in the Er$_5$Ge$_4$-based and in the Gd$_3$Ge$_4$-based solid solutions.

The most significant differences, in addition to the extent of the three phase regions in paramagnetic state, are as follows: first, the magnetic ordering temperatures of Er$_5$Si$_4$Ge$_{4-x}$ alloys are much lower than those of Gd$_3$Si$_2$Ge$_{4-x}$ alloys; second, the magnetic ordering temperatures show a weak dependence on the composition (i.e., on the value of $x$) in the Er-based system and the magnetic structures appear to be quite complex; third, in all the studied Er$_5$Si$_4$Ge$_{4-x}$ alloys, the magnetic ordering is decoupled from the crystal lattice in low magnetic fields; fourth, it appears that in magnetic fields the magnetic ordering is decoupled from the crystal lattice in the Er$_5$Si$_4$Ge$_{4-x}$ system is much lower than that in the Gd$_3$Si$_2$Ge$_{4-x}$ system, where both the crystal and magnetic lattices are not only coupled but they are easily affected by relatively low magnetic fields over a broad range of concentrations.

An intriguing observation that magnetic fields as low as 40 kOe may affect the temperature of the crystallographic-only transformation from the paramagnetic monoclinic Er$_5$Si$_4$ to the orthorhombic Gd$_3$Si$_2$-type polymorph, which is also paramagnetic, is likely related to large localized magnetic moments of Er and to unusually strong spin-orbit coupling. Its understanding requires further experimental and theoretical studies. It is also important to emphasize that many of the as arc-melted Er$_5$Si$_4$Ge$_{4-x}$ alloys can contain small amounts of impurity ErSi$_2$Ge$_{1-x}$ or Er$_2$Si$_3$Ge$_{4-x}$ phases, which may somewhat affect both the observed behavior and the interpretation of the data.

Note added in proof. As follows from recent quantitative x-ray powder diffraction analysis, only $\sim$40 mol.% of the monoclinic Er$_5$Si$_4$ is converted into the orthorhombic Er$_5$Si$_4$ phase during slow heating between 190 and 240 K. The entropy of the corresponding polymorphic transformation, therefore, should be increased from the mentioned above 0.24 J/g at K to $\sim$0.6 J/g at K.

ACKNOWLEDGMENTS

The authors thank D. C. Kesse and J. L. Anderson for their help in preparing some of the Er$_5$Si$_4$Ge$_{4-x}$ alloys. This work was supported by the Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. W-7405-ENG-82.
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42 When our work was completed and undergoing a review, Cadogan et al. (Ref. 42) reported a neutron scattering study of Er$_5$Si$_4$. Their Er$_5$Si$_4$ specimen does not exhibit a structural transition from the high temperature orthorhombic Gd$_5$Si$_4$-type structure to the low temperature monoclinic Gd$_5$Si$_2$Ge$_2$-type structure around 200 K found in our sample. The Er$_5$Si$_4$ alloy of Ref. 42 retains the Gd$_5$Si$_4$-type structure between 4 K and 300 K, which is likely a consequence of employing commercial “99.9%” purity Er in the sample preparation. Although the results of Ref. 42 are most certainly affected by the high concentration of interstitial impurities that are normally present in commercial-purity Er (see Ref. 43), the magnetic structure of impurities-stabilized orthorhombic Er$_5$Si$_4$(C$_x$O$_y$· · ·) is complex and temperature dependent, which is consistent with the magnetic properties of the monoclinic Er$_5$Si$_4$ samples employed in this study.
43 The sample used in the magnetization measurements shown in Fig. 4 was a piece collected after a large grain located in sample III was used to cut a single crystal from the Er$_5$Si$_4$ specimen. Neither the single crystalline nature, nor the orientation of this piece was analyzed using a backscatter Laue technique. It is, therefore, possible that the sample contained several small grains with similar orientations.