

## Decoupling of the Magnetic and Structural Transformations in $\text{Er}_5\text{Si}_4$

V. K. Pecharsky,<sup>1,2,\*</sup> A. O. Pecharsky,<sup>1</sup> Y. Mozharivskyj,<sup>1</sup> K. A. Gschneidner, Jr.,<sup>1,2</sup> and G. J. Miller<sup>3</sup>

<sup>1</sup>*Ames Laboratory, Materials and Engineering Physics Program, Iowa State University, Ames, Iowa 50011-3020, USA*

<sup>2</sup>*Department of Materials Science and Engineering, Iowa State University, Ames, Iowa 50011-2300, USA*

<sup>3</sup>*Department of Chemistry, Iowa State University, Ames, Iowa 50011-3111, USA*

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$\text{Er}_5\text{Si}_4$  is a member of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  family of alloys, where  $R$  = rare earth metal. Many of these compounds display a strong coupling between the magnetic and crystal lattices. In the naturally layered  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  materials, inter- and intralayer interactions can be controlled by chemical and physical means; thus their physical properties can be tailored within wide limits. The  $\text{Er}_5\text{Si}_4$  is unique in that the temperature dependent structural sequence is opposite that of other representatives of this family. The magnetism of  $\text{Er}_5\text{Si}_4$  is reflective of its exceptional place within the series.

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The work by Holtzberg *et al.* [1] on  $R_5\text{Si}_4$  and  $R_5\text{Ge}_4$  compounds was all but ignored for 30 years despite reporting a counterintuitive and rare [2] result: the ferromagnetic (FM) ordering temperature of  $\text{Gd}_5\text{Si}_4$  (335 K) is greater than that of pure Gd metal (294 K) by  $\sim 40$  K despite a 44 mol % dilution by the nonmagnetic silicon. The rediscovery of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  compounds ( $R$  = rare earth element) [3], followed by over 100 reports to date, linked a wealth of remarkable physics to the distinctly layered structures of these alloys [4,5]. Considering 15 different  $R$  elements, excluding Sc and Pm, and  $x$  varying from 0 to 4, these materials form a vast arena for both basic and applied physics by providing numerous opportunities to clarify elusive structure-property relationships, and to exploit the unique sensitivity of these compounds toward a variety of chemical and physical triggers. Bonding between the well-defined  $\sim 0.7$  nm thick layers of atoms (slabs) and the resultant magnetic, transport, and thermodynamic properties of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  alloys can be controlled by varying either or both  $R$  [6,7] and  $x$  [8]. In addition to chemical means, the interlayer interactions over a broad range of  $x$  can be manipulated by temperature [9,10], pressure [11], and magnetic field [12]. Presently, a substantial, yet far from complete, body of knowledge exists about the Gd compounds but little is known about the physics and chemistry of  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  alloys with  $R$  = Pr [13,14], Nd [6,15], Tb [7,16–18], and Dy [9,19], while compounds with the other rare earths remain virtually unexplored.

Every  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  material studied to date adopts the  $\text{Gd}_5\text{Si}_4$ -type structure in the FM ordered state. Both magnetically disordered and antiferromagnetically (AFM) ordered compounds are known to have the  $\text{Sm}_5\text{Ge}_4$ -,  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -, or  $\text{Gd}_5\text{Si}_4$ -type structures, depending on either or both the value of  $x$  and the nature of the lanthanide atom. The binary silicides of Gd, Tb, and Dy, which exist with the  $\text{Gd}_5\text{Si}_4$ -type structure in the paramagnetic (PM) state, order magnetically at low temperatures via second order transformations without changing their crystal structure. Conversely, every known  $R_5(\text{Si}_{4-x}\text{Ge}_x)$

compound which has a  $\text{Sm}_5\text{Ge}_4$ - or  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure in the PM state, becomes ferromagnetic with a simultaneous martensiticlike structural change to the  $\text{Gd}_5\text{Si}_4$ -type structure via a first order transformation. In this Letter, we report on the heat capacity, magnetism, a sluggish but reversible crystallographic transformation just below room temperature, and an unexpected decoupling of the crystal and magnetic lattices at low temperature in  $\text{Er}_5\text{Si}_4$ . The observed sequence of transformations is unusual in that the erbium silicide is the only known member of this extended family of materials where the reversible orthorhombic  $\text{Gd}_5\text{Si}_4$ -type to monoclinic  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type distortion occurs on cooling. Moreover, the monoclinic PM  $\text{Er}_5\text{Si}_4$  orders magnetically at low temperature without the martensiticlike crystal structure change. Both features are just opposite to all of the other cases in the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  systems reported to date.

The  $\text{Er}_5\text{Si}_4$  alloy was prepared by arc-melting high purity components in an argon atmosphere. The Er was 99.89 at. % pure with major impurities (in ppm atomic) as follows: O(399), C(278), H(166), F(123), N(72), Fe(30), Cl(16), and the Si was 99.9995 wt % pure. The phase purity of the alloy button was verified by x-ray powder diffraction and metallography, which indicated the presence of up to 5 vol % of  $\text{ErSi}$  [3 to 8 vol % of an impurity phase is often observed in other members of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  series [7]]. Examination of several off-stoichiometric  $\text{Er}_{5+y}\text{Si}_4$  alloys shows that the amount of the  $\text{ErSi}$  impurity is reduced when  $y \cong 0.05$ , likely pointing to non-negligible losses of Er during the preparation of  $\text{Er}_5\text{Si}_4$ . The heat capacity was measured using an adiabatic heat-pulse calorimeter [20] and dc magnetization using a Lake Shore magnetometer. The temperature dependent single crystal diffraction data were collected using Bruker SMART Apex CCD diffractometer.

The heat capacity of  $\text{Er}_5\text{Si}_4$ , measured in 0, 5, 10, and 50 kOe magnetic fields, is shown in Fig. 1. The  $\lambda$ -type anomaly, observed at  $T = 30$  K in zero magnetic field, is indicative of a second order magnetic order-disorder transformation. A low magnetic field (5 kOe) suppresses

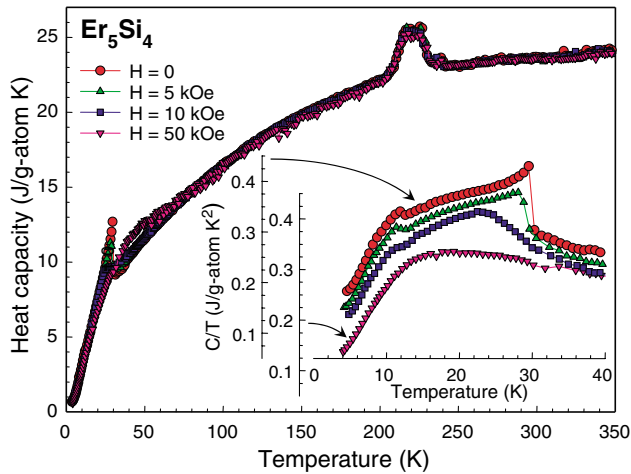


FIG. 1 (color online). The heat capacity of  $\text{Er}_5\text{Si}_4$  measured from  $\sim 4$  to 350 K in 0, 5, 10, and 50 kOe magnetic fields. The inset, in which each curve except zero field data has been displaced downwards by 25 mJ/g-atom  $\text{K}^2$ , clarifies the low temperature anomaly.

the temperature of this anomaly by a few degrees, perhaps indicating the presence of an AFM component or incomplete collinearity of the spin structure of  $\text{Er}_5\text{Si}_4$ . The magnetic entropy is shifted towards high temperature by stronger than 5 kOe magnetic fields, which points to a FM state when the magnetic field reaches and exceeds  $\sim 10$  kOe (see the inset in Fig. 1). A cusp, observed in the low magnetic fields at  $T \cong 12$  K, is consistent with the presence of a small amount of ErSi impurity, which orders antiferromagnetically at 11.5 K [21], although it may be intrinsic to  $\text{Er}_5\text{Si}_4$ . A second distinct anomaly, observed between  $\sim 205$  and  $\sim 235$  K on heating, remains unaffected by a magnetic field, thus clearly indicating the nonmagnetic nature of the high temperature phase transformation. Considering that immediately below 205 and above 235 K the heat capacity exhibits conventional behavior, we conclude that despite the  $\sim 30$  K range over which the phase transition occurs, thermodynamically this is a first order phase transformation. Its magnetic field independence is indicative of a structural transition in the PM state.

The nonmagnetic nature of the high temperature phase transformation in  $\text{Er}_5\text{Si}_4$  is also confirmed by measurements of the magnetization as a function of temperature, which are shown in Fig. 2. A steplike anomaly is observed in the inverse magnetic susceptibility between  $\sim 210$  and  $\sim 228$  K on heating and a similar anomaly occurs between  $\sim 215$  and  $\sim 200$  K on cooling. The presence of hysteresis confirms the first order nature of this transition. Both below  $\sim 200$  K (down to  $\sim 40$  K) and above  $\sim 230$  K, the inverse magnetic susceptibility follows the Curie-Weiss law with  $p_{\text{eff}} = 9.61(1)\mu_B$  and  $\theta_p = 20.9(5)$  K for the phase stable below  $\sim 200$  K, and  $p_{\text{eff}} = 9.73(1)\mu_B$  and  $\theta_p = 30.1(8)$  K for the phase stable above  $\sim 230$  K. The effective magnetic moments in both phases are close to the theoretically expected value for a

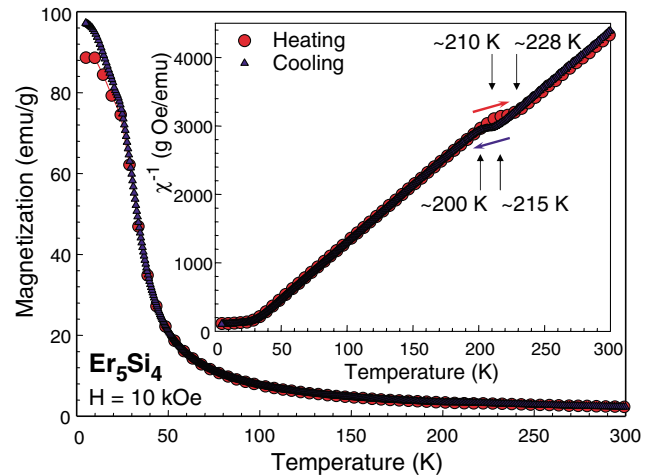


FIG. 2 (color online). The behavior of the magnetization of  $\text{Er}_5\text{Si}_4$  measured on heating and cooling in a 10 kOe magnetic field. The inset shows the inverse magnetic susceptibility measured in the same magnetic field. The vertical arrows indicate the beginning and the end of the steplike anomalies.

free  $\text{Er}^{3+}$  ion, which is  $9.58\mu_B$ . The behavior of the magnetization as a function of temperature in a 10 kOe magnetic field indicates ferro- or ferrimagnetic ordering below  $\sim 30$  K, which is further evidenced by the differences in the magnetization measured on heating and cooling below the same temperature.

The nature of the magnetic order below  $T \cong 30$  K was further clarified by measuring the isothermal magnetization of the  $\text{Er}_5\text{Si}_4$  compound, which is shown in Fig. 3. The behavior of the initial magnetization below 30 K points to a complex magnetic ground state with a distinct FM component but the material remains far from saturation in the 50 kOe magnetic field. At  $T = 5$  K, the  $M(H)$  exhibits a field-induced metamagneticlike transition at  $H_{\text{cr}} \cong 10$  kOe. This anomaly appears to be intrinsic to  $\text{Er}_5\text{Si}_4$  (also see the isotherm at 15 K, where the

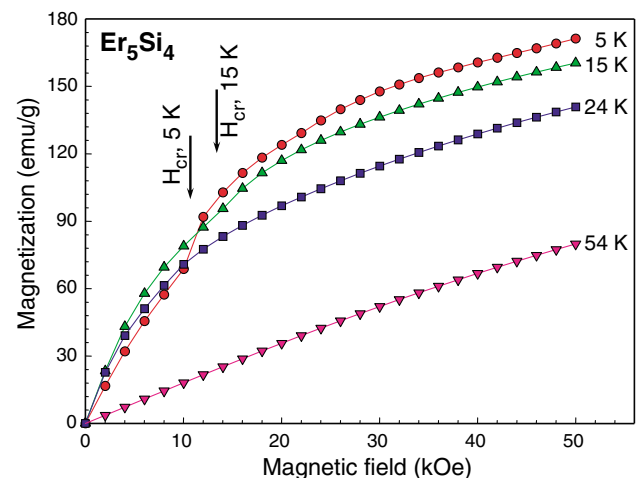


FIG. 3 (color online). The isothermal magnetization of  $\text{Er}_5\text{Si}_4$  measured at 5, 15, 24, and 54 K. The vertical arrows point to metamagneticlike anomalies observed at 5 and 15 K.

TABLE I. Crystallographic data of  $\text{Er}_5\text{Si}_4$  at 293 and 203 K.

Atom	$x/a$	$y/b$	$z/c$	$U(10^{-4} \text{ \AA}^2)$
$T = 293 \text{ K}$ ; Sp. gr. $Pnma$ ; $a = 7.2838(6)$ , $b = 14.363(1)$ , $c = 7.5943(6) \text{ \AA}$				
Er1	0.01987(5)	0.59614(3)	0.18016(4)	84(1)
Er2	0.32293(5)	0.12320(3)	0.17864(4)	72(1)
Er3	0.15473(6)	1/4	0.51179(6)	72(2)
Si1	0.1540(3)	0.0391(2)	0.4703(3)	93(6)
Si2	0.0262(4)	1/4	0.1048(4)	93(6)
Si3	0.2737(4)	1/4	0.8704(4)	85(6)
$T = 203 \text{ K}$ ; Sp. gr. $P112_1/a$ ; $a = 7.3460(9)$ , $b = 14.375(2)$ , $c = 7.5571(9) \text{ \AA}$ , $\gamma = 92.992(2)^\circ$				
Er1A	-0.00355(7)	0.59762(4)	0.18031(8)	43(1)
Er1B	0.01782(7)	0.90166(4)	0.18089(8)	42(1)
Er2A	0.32896(7)	0.12239(4)	0.17835(8)	33(1)
Er2B	0.35346(7)	0.37920(4)	0.16654(8)	39(1)
Er3	0.17404(9)	0.25341(4)	0.50624(7)	35(1)
Si1A	0.1515(5)	0.0399(3)	0.4713(5)	39(8)
Si1B	0.2002(5)	0.4584(3)	0.4635(5)	53(9)
Si2	0.0457(4)	0.2489(3)	0.1087(4)	38(8)
Si3	0.2910(5)	0.2481(3)	0.8684(4)	48(8)

anomalous kink is observed at a higher critical field), yet the presence of the  $\text{ErSi}$  impurity, which is AFM below 11.5 K [21], may result in a similar behavior. At  $T = 54 \text{ K}$ , erbium silicide displays typical PM behavior.

Considering the presence of a nonmagnetic transition (200 to 230 K), the crystal structure of  $\text{Er}_5\text{Si}_4$  was comprehensively studied as a function of temperature (Table I). At  $T = 293 \text{ K}$ , the compound crystallizes in the orthorhombic  $\text{Gd}_5\text{Si}_4$ -type structure (see Fig. 4, right), where short Si-Si distances are found between every slab. When cooled to 203 K,  $\text{Er}_5\text{Si}_4$  adopts the monoclinic  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type crystal structure, (Fig. 4, left), where short Si-Si distances are preserved between pairs of neighboring slabs, while between the next neighbor pairs the corresponding distances expand by more than 30%, from 2.48 to 3.28 Å. As seen in Fig. 4, the displacement anisotropy of Si atoms is notably stronger in the monoclinic phase when compared to the same in the orthorhombic phase. Although potentially affected by the lower accuracy of the diffraction data due to intrinsic twinning observed in the monoclinic state, the difference in the atomic displacement anisotropy reflects considerable changes in the interslab interactions, which affect the PM behavior of the two  $\text{Er}_5\text{Si}_4$  phases (see Fig. 2).

During the transition, the unit cell dimensions change considerably, as illustrated in Fig. 5: the  $a$  axis undergoes the largest change and the  $b$  axis varies the least, which is consistent with the similar phase transformation observed in  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  [10]. When compared to  $\text{Gd}_5\text{Si}_2\text{Ge}_2$  and to all other representatives of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  family studied to date, the phase sequence in the  $\text{Er}_5\text{Si}_4$  compound is reversed; i.e., the room temperature modification adopts the orthorhombic  $\text{Gd}_5\text{Si}_4$ -type structure and the low temperature polymorph has the monoclinic  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure. Furthermore, in the Gd-based

system, the crystallographic phase change is coupled with the  $\text{FM} \leftrightarrow \text{PM}$  transformation, while in  $\text{Er}_5\text{Si}_4$ , the crystal lattice is no longer coupled with the magnetic sublattice. All unit cell dimensions exhibit quite an unusual behavior in the vicinity of the phase transition, as indicated by highly nonlinear increases before relaxing at the respective final values (Fig. 5). Although the nature of this anomaly is at present unknown, it is consistent with the complex structure of the corresponding heat capacity peak (see Fig. 1), which is a convolution of several separate peaks, potentially signaling the presence of one or more intermediate states.

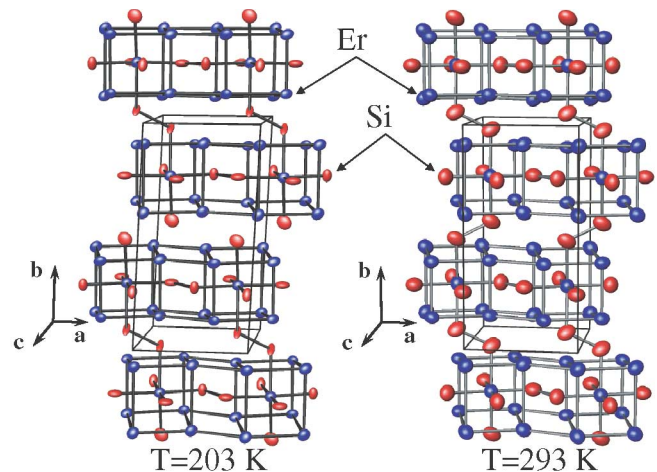


FIG. 4 (color online). The models of the crystal structure of the monoclinic  $\text{Er}_5\text{Si}_4$  at 203 K (left) and orthorhombic  $\text{Er}_5\text{Si}_4$  at 293 K (right) shown with anisotropic displacement ellipsoids of all atoms at 99.99% probability. The considerable change of the displacement anisotropy is likely to be due to the considerable change of the interactions between the layers, which are shown as bonded Er-Er and Er-Si atoms.

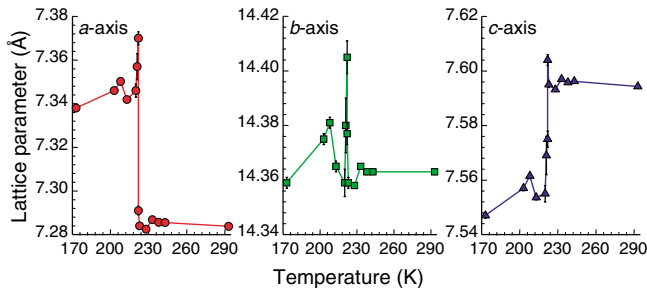


FIG. 5 (color online). The lattice parameters of  $\text{Er}_5\text{Si}_4$  determined from single crystal diffraction data during heating from 173 to 293 K. The vertical bars represent least squares standard deviations of lattice parameters.

The behavior of the monoclinic  $\text{Er}_5\text{Si}_4$  below  $\sim 200$  K is quite different from that observed in the monoclinic phases in  $\text{Gd}_5(\text{Si}_{4-x}\text{Ge}_x)$  and  $\text{Tb}_5(\text{Si}_{4-x}\text{Ge}_x)$  systems. The latter two systems always undergo a coupled magnetic-crystallographic transition from a PM monoclinic  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type phase to an FM orthorhombic  $\text{Gd}_5\text{Si}_4$ -type phase via a first order phase transformation on cooling [3–10]. Clearly, this is not the case in  $\text{Er}_5\text{Si}_4$ , where the magnetic ordering at  $\sim 30$  K is a second order phase transformation process (see Fig. 1). X-ray powder diffraction data confirm that the crystal structure of  $\text{Er}_5\text{Si}_4$  remains unchanged across 30 K in magnetic fields up to 35 kOe [22]. Therefore, the major difference between all previously known monoclinic  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  compounds and the  $\text{Er}_5\text{Si}_4$  phase is that magnetic and crystallographic lattices remain decoupled in the latter.

Similarly to the  $\text{Gd}_5(\text{Si}_{4-x}\text{Ge}_x)$  system with  $x \cong 2$  [4,23], the orthorhombic  $\text{Er}_5\text{Si}_4$  phase has a higher paramagnetic Curie temperature ( $\theta_p = 30.1$  K) than the monoclinic  $\text{Er}_5\text{Si}_4$  phase ( $\theta_p = 20.9$  K), thus indicating the enhancement of the effective magnetic exchange parameter when all Si-Si bonds between the layers are in place. This observation confirms the role of interslab exchange in defining the magnetic properties of this system [4,5]. Unlike the  $\text{Gd}_5\text{Si}_{-2}\text{Ge}_{-2}$  compounds, where a monoclinic-to-orthorhombic structural transition in the range  $\sim 600$  to  $\sim 800$  K is thermoelastic and irreversible [4,23], the crystallographic transition observed in  $\text{Er}_5\text{Si}_4$  is reversible. The crystallographic transformation after heating from  $\sim 170$  to  $T = 222$  K occurs slowly and is completed over  $\sim 10$  h period at  $T = 222$  K, in line with the broad heat capacity anomaly (see Fig. 1). Furthermore, cycling  $\text{Er}_5\text{Si}_4$  through the crystallographic transition has no effect on either the structural or the magnetic transformation temperatures, which is in contrast to what has been observed in  $\text{Gd}_5\text{Si}_{1.95}\text{Ge}_{2.05}$  [24], where the cycling-induced shift of the transition temperature was associated with redistribution of the Si and Ge atoms. It appears, therefore, that the absence of the third component (Ge) and the loss of the corresponding degree of freedom related to the distribution of Si and Ge atoms

within and between the slabs has considerable influence on both the structural and magnetic properties of  $\text{Er}_5\text{Si}_4$ .

In conclusion, the binary  $\text{Er}_5\text{Si}_4$  compound, previously classified as a simple ferromagnet with  $T_c = 25$  K [1], exhibits an unexpected crystallographic phase transition between 200 and 230 K. The crystallographic phase sequence is opposite to all other known members of the  $R_5(\text{Si}_{4-x}\text{Ge}_x)$  series, and the low temperature monoclinic  $\text{Er}_5\text{Si}_4$  phase shows a surprising decoupling of the crystal and magnetic sublattices. The magnetic properties of two crystallographic modifications of  $\text{Er}_5\text{Si}_4$  are different, as follows from the differences in their paramagnetic behavior. Exchange interactions appear to be enhanced in the orthorhombic phase, where short Si-Si bonds exist between all slabs.

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\*Electronic address: vitkp@ameslab.gov

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