

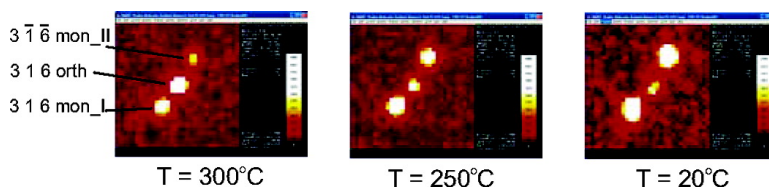
Article

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On the High-Temperature Phase Transition of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ Yurij Mozharivskiy,[†] Alexandra O. Pecharsky,[†] Vitalij K. Pecharsky,^{†,‡} and Gordon J. Miller^{*,§}

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Abstract: The first-order monoclinic-to-orthorhombic ($\beta \rightarrow \gamma$) phase transition of the giant magnetocaloric material $\text{Gd}_5\text{Si}_2\text{Ge}_2$ was studied using in situ high-temperature single-crystal X-ray diffraction. A special crystal mounting procedure was developed to avoid crystal contamination by oxygen or nitrogen at high temperatures. The elastic $\beta \rightarrow \gamma$ transformation occurs at 300–320 °C during heating, and it is reversible during fast and slow heating and slow cooling but irreversible during rapid cooling. Contrary to theoretical predictions, the macroscopic distribution of the Si and Ge atoms remains the same in both the orthorhombic γ -polymorph and the monoclinic β -phase. It appears that interstitial impurities may affect stability of both the monoclinic and orthorhombic phases. In the presence of small amounts of air, the $\beta \rightarrow \gamma$ transformation is complete only at 600 °C. The interslab voids, which can accommodate impurity atoms, have been located in the structure, and an effect of partially filling these voids with oxygen or nitrogen atoms on the $\beta \rightarrow \gamma$ transition is discussed.

Introduction

Discovery of the giant magnetocaloric effect in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ ^{1,2} drew strong interest to the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ phases, which is due both to their potential applications in magnetic refrigeration^{3,4} and the intimate relationship between their structure and physical properties.^{5–11} The giant magnetocaloric effect,² colossal magnetostriction,^{5,7} and giant magnetoresistance^{6,8,9} in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ alloys result from coupling magnetic orderings with reversible first-order structural transformations.^{10,12} Like other phases in the $\text{Gd}_5(\text{Si}_x\text{Ge}_{1-x})_4$ system, $\text{Gd}_5\text{Si}_2\text{Ge}_2$ possesses a remarkable ability to cleave or reform covalent-like T – T bonds between distinct two-dimensional $\infty^2[\text{Gd}_5T_4]$ slabs (T is a mixture of Ge and Si atoms) upon change in temperature or magnetic

field.¹⁰ In $\text{Gd}_5\text{Si}_2\text{Ge}_2$, the low-temperature ferromagnetic form (α -polymorph, stable in a zero magnetic field below -1 °C) adopts an orthorhombic Gd_5Si_4 -type structure ($Pnma$) with T – T dimers between the $\infty^2[\text{Gd}_5T_4]$ slabs, and the room-temperature paramagnetic form (β -polymorph, stable in a zero magnetic field above -1 °C) has a monoclinic $\text{Gd}_5\text{Si}_2\text{Ge}_2$ -type structure ($P112_1/a$), in which half of the T – T interslab dimers are broken.

According to single-crystal X-ray diffraction (XRD), there is no macroscopic Si/Ge redistribution during the orthorhombic–monoclinic (OR–MO) α – β transformation.¹⁰ This allows the phase transition to remain reversible, which is one of the requirements for magnetic refrigeration. Another interesting feature of this α – β transformation in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ is the fact that the low-temperature structure has a higher symmetry ($Pnma$) than the high-temperature structure ($P112_1/a$), although entropy contribution to the Gibbs free energy usually implies the reverse structural sequence with temperature.¹³ Analysis of the electronic structure of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ by Choe et al.¹⁰ and later by Pecharsky et al.¹⁴ has shown that this unusual phase sequence arises from the strong magnetic exchange coupling in the orthorhombic phase. The magnetic exchange energy is large enough to overcome the unfavorable entropy contribution even near room temperature.

Monoclinic β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$ transforms into an orthorhombic paramagnetic γ -phase (Gd_5Si_4 -type) at high temperatures. In situ powder XRD studies showed that this high-temperature monoclinic-to-orthorhombic transition occurs over an extended tem-

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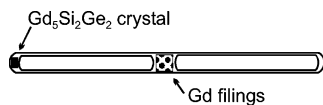


Figure 1. Mounting of a $\text{Gd}_5\text{Si}_2\text{Ge}_2$ single crystal and Gd filings inside a capillary.

perature range (between ~ 200 and ~ 460 °C) with the largest change in the phase ratio at ~ 320 °C and is irreversible: once the orthorhombic γ -phase is formed, it does not transform back into the monoclinic β -phase upon cooling.¹⁵ From the Gibbs free energy/entropy relationship, this MO–OR transformation is indeed an expected structural transition. Theoretical predictions indicated that the high-temperature $\beta \rightarrow \gamma$ transition may be triggered by macroscopic changes in the Si/Ge site occupancies, which render the transition irreversible.¹⁴ In view of present-day knowledge, a better insight into the $\beta \rightarrow \gamma$ transition—physical property relationships for this class of compounds as well as for their future practical applications.

Experimental Section

X-ray Studies. Multiple crystals were extracted from the stoichiometric $\text{Gd}_5\text{Si}_2\text{Ge}_2$ alloy (prepared from Ames Laboratory Gd with purity of 99.8 at. %, Aldrich Si and Ge with purity of 99.999 wt %; preparation method can be found in ref 10) and checked for quality using the Laue method ($\text{CuK}\alpha$ radiation). After initial screening, three crystals with dimensions ranging from $20 \times 40 \times 45 \mu\text{m}^3$ to $35 \times 45 \times 65 \mu\text{m}^3$ were selected for further X-ray diffraction analysis. To prevent crystal contamination at high temperatures, neither glue nor cement was used to mount crystals; instead, a special crystal mounting procedure was developed. Two specimens were prepared by placing a crystal at the bottom of a 0.2-mm capillary and by fixing it in place by a 0.1-mm capillary (all capillaries had wall thicknesses of 0.01 mm, glass #50, Hampton Research). Freshly prepared Gd filings (getter) were put on the top of the inner 0.1-mm capillary and fixed by another 0.1-mm capillary (Figure 1). The outer 0.2-mm capillaries were sealed using a microtorch and then mounted in 0.9-mm stainless steel tubes using temperature-resistant cement. The third crystal was mounted the same way but without Gd getter. At that point, room-temperature X-ray diffraction data were collected. Prior to high-temperature data collection, the center sections of the two specimens (position of Gd filings) were heated to ~ 500 °C for 1 s to absorb nitrogen and oxygen, since crystal mounting was performed in air. As was later apparent from the X-ray diffraction data, the temperature at the end of the capillaries, where the single crystals were located, must have risen above the transition temperature and then dropped suddenly, since an orthorhombic component, previously undetected at room temperature, was present in the single crystals together with the two monoclinic components.

Room- and high-temperature X-ray diffraction data were collected on a Bruker SMART Apex CCD diffractometer with $\text{MoK}\alpha$ radiation, equipped with a Nonius crystal heater.¹⁶ During the high-temperature experiments, the temperature was stable to within ± 1 K with respect to the value set for an experiment. Three sets of 30 frames with 0.3° scans in ω and with an exposure time of 10 s per frame were collected to obtain lattice parameters at various temperatures (Table 1). The fraction of the orthorhombic component was evaluated from the intensities of the Bragg reflections and is plotted in Figure 2. Crystallographic data for the two crystals sealed with Gd getter showed no statistically significant differences and, thus, only experimental results for one of the crystals are given here. Diffraction data at 20 °C and 400 °C were collected in a reciprocal hemisphere with 0.3° scans

in ω and with an exposure time of 10 s per frame. The range of 2θ extended from 4° to 57° . Integrated intensities were extracted and then corrected for Lorentz and polarization effects through the SAINT program.¹⁷ For the twinned monoclinic crystal at 20 °C, orientation matrices of the two twin components were used during integration with the SAINT program. The unit cell dimensions were originally obtained by indexing from 200 to 999 reflections and then were refined using all observed Bragg reflections after integration. The lattice parameters during cooling are likely to deviate from the absolute values, which is due to the irreversible crystal displacement upon heating.

The empirical absorption correction for the untwinned orthorhombic crystal at 400 °C was based on modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 3\sigma(I)$ (program SADABS);¹⁷ for the twinned crystal at 20 °C, it was done by modeling a transmission surface of each twinned component by spherical harmonics using overlapping and nonoverlapping equivalent reflections with $I > 3\sigma(I)$ (program TWINABS).¹⁷ The structure solution was obtained by direct methods and refined on F^2 by the full-matrix, least-squares method. The structural data for the monoclinic polymorph at 20 °C and for the orthorhombic one at 400 °C are listed in Tables 2–4. The refined compositions of the monoclinic and orthorhombic phases are $\text{Gd}_5\text{Si}_{2.02(2)}\text{Ge}_{1.98(2)}$ and $\text{Gd}_5\text{Si}_{2.05(4)}\text{Ge}_{1.95(4)}$, and the differences between the two compositions and the as-prepared $\text{Gd}_5\text{Si}_2\text{Ge}_2$ stoichiometry are statistically insignificant. Thus, the chemical formulas of the two polymorphs can be written as $\text{Gd}_5\text{Si}_2\text{Ge}_2$. No interstitial oxygen or nitrogen atoms were found in any of the crystals from the differential electron density maps computed after completion of the refinements. However, their presence in the crystals after heating has to be assumed (see below), but because of their low X-ray scattering power and small amounts in the structures they could not be detected.

Electronic Structure Calculations. To gain insights into the role of impurities in the structures of β - and γ - $\text{Gd}_5\text{Si}_2\text{Ge}_2$, tight-binding linear muffin–tin–orbital calculations using the atomic sphere approximation (TB–LMTO–ASA)¹⁸ were carried out using the crystallographic data of room-temperature β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$. To satisfy the overlap criteria of the atomic spheres in the TB–LMTO–ASA method, empty spheres were included in the unit cell. The 4f electrons of Gd were treated as core electrons, which is a good approximation because β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$ is paramagnetic. Previous crystallographic and theoretical studies on β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$ indicated preference of Ge atoms for T1 positions and Si atoms for T2 and T3 sites,^{19,20} which is consistent with our experimental results (see occupancies of the T sites in Table 3). Since mixed positions cannot be dealt with in the LMTO method, full separation of Ge (on T1 sites) and Si (on T2 and T3 sites) atoms was assumed. Two oxygen-containing models (see Figure 9 below) were considered for β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$: in the first model, only voids A were occupied by oxygen atoms (O is at $x = 0.375$, $y = 0.006$, and $z = 0.471$, site 4e); in the second model, only voids C were occupied by oxygen atoms (O is at $x = 0$, $y = 1/2$, $z = 1/2$, site 2d). In both models, only one oxygen atom was assumed in the unit cell of β - $\text{Gd}_5\text{Si}_2\text{Ge}_2$ (the resulting composition was $\text{Gd}_5\text{Si}_2\text{Ge}_2\text{O}_{0.25}$), which agrees with the low impurity concentration as inferred from the single-crystal X-ray diffraction results.

Experimental Results and Discussion

Monoclinic Twin Law. Mutual Orientation of Monoclinic and Orthorhombic Lattices. All tested monoclinic crystals were twinned from room temperature up to the transition temperature. The monoclinic components are rotation twins

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Table 1. Crystallographic Data for the $Gd_5Si_2Ge_2$ Single Crystal upon Heating from 20 to 400 °C and Cooling from 400 to 20 °C

T, °C	space group	str. type	a, Å	b, Å	c, Å	γ , °	V, Å ³
20	$P112_1/a^a + Pnma$	$Gd_5Si_2Ge_2^a + Gd_5Si_4$	7.585(1)	14.783(2)	7.768(2)	93.36(1)	869.6(3)
100	$P112_1/a^a + Pnma$	$Gd_5Si_2Ge_2^a + Gd_5Si_4$	7.592(2)	14.806(2)	7.778(2)	93.16(1)	872.9(4)
200	$P112_1/a^a + Pnma$	$Gd_5Si_2Ge_2^a + Gd_5Si_4$	7.597(1)	14.853(3)	7.797(2)	93.09(1)	878.6(4)
300	$P112_1/a$	$Gd_5Si_2Ge_2$	7.613(2)	14.868(3)	7.819(2)	92.83(2)	883.9(4)
310	$Pnma^a + P112_1/a$	$Gd_5Si_4^a + Gd_5Si_2Ge_2$	7.5420(8)	14.845(2)	7.825(2)	90	876.1(3)
320	$Pnma^a + P112_1/a$	$Gd_5Si_4^a + Gd_5Si_2Ge_2$	7.5427(9)	14.852(2)	7.830(2)	90	877.2(3)
330	$Pnma$	Gd_5Si_4	7.5444(8)	14.851(2)	7.830(2)	90	877.3(2)
340	$Pnma$	Gd_5Si_4	7.5456(8)	14.851(2)	7.830(2)	90	877.4(2)
400	$Pnma$	Gd_5Si_4	7.5569(9)	14.838(4)	7.837(1)	90	878.8(4)
340	$Pnma$	Gd_5Si_4	7.556(1)	14.858(4)	7.832(1)	90	879.2(4)
300	$Pnma^a + P112_1/a$	$Gd_5Si_4^a + Gd_5Si_2Ge_2$	7.541(1)	14.847(2)	7.832(2)	90	876.8(3)
250	$P112_1/a^a + Pnma$	$Gd_5Si_2Ge_2^a + Gd_5Si_4$	7.594(3)	14.82(1)	7.811(7)	92.98(5)	878(1)
200	$P112_1/a$	$Gd_5Si_2Ge_2$	7.599(1)	14.848(3)	7.800(2)	93.12(2)	878.8(4)
100	$P112_1/a$	$Gd_5Si_2Ge_2$	7.5987(9)	14.823(3)	7.800(2)	93.24(1)	877.1(3)
20	$P112_1/a$	$Gd_5Si_2Ge_2$	7.5888(9)	14.829(3)	7.787(2)	93.28(1)	874.8(3)

^a Lattice parameters of the dominant phase are given.

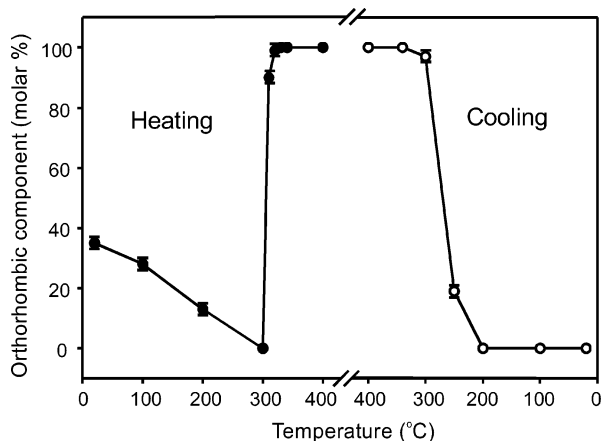


Figure 2. Fraction of the orthorhombic component for the first crystal during heating and cooling (first cycle). The 400 °C point during heating and cooling is the same experimental point.

around the a axis and have common a and c axes (see Figure 3a). There were always dominant and minor components called I and II, respectively. This monoclinic twin law is identical to that reported earlier for β - $Gd_5Si_2Ge_2$.^{10,21}

During the structural transformation at high temperatures, all observed reflections can be indexed to two original monoclinic lattices I and II and to the newly formed orthorhombic lattice (Figure 3b). From the mutual orientation of the reciprocal lattices, positions of the lattices in direct space were obtained (Figure 3a). Like the two monoclinic lattices, the orthorhombic and monoclinic lattices share the a and c axes. While the monoclinic components I and II are rotation twins around the a axis, there is no symmetry operation that can transform the monoclinic and orthorhombic lattices into each other, which is due to discontinuous changes in the lattice parameters (a feature intrinsic to any first-order transition). Although a similar monoclinic-to-orthorhombic (MO-OR) transition occurs in $Gd_5Si_2Ge_2$ below room temperature, it is the first time that the coexistence of the monoclinic and orthorhombic phases was detected in a single crystal of $Gd_5Si_2Ge_2$.

The spatially resolved transformation of the monoclinic and orthorhombic lattices (Figure 3a) provides a model of the transition on the atomic level. Formation of the orthorhombic structure from the monoclinic structures occurs through a shear

movement of the two-dimensional $\infty^2[Gd_5T_4]$ slabs: two adjacent slabs slide along the a axis to form the interslab $T1-T1$ dimers (Figure 3c). Since, in both structures, the ac plane is parallel to the slabs, the shear movement of the slabs creates the orthorhombic lattice that share the a and c axes with the monoclinic lattice, but they have a different spatial position of the b axis.

Phase Transitions. X-ray data for the two $Gd_5Si_2Ge_2$ crystals sealed in capillaries with Gd getter were consistent and indicated a phase transition between ~ 300 °C (appearance of the orthorhombic phase) and ~ 320 °C (disappearance of the monoclinic phase) on heating. The onset temperatures for the formation of the monoclinic phase upon cooling were slightly different: the monoclinic phase appeared at 300 °C in the first crystal and at 280 °C in the second crystal. This difference in the transition temperatures upon cooling is most likely to result from the contamination levels: while the first crystal was larger and concentration of impurities was likely to be smaller, the second crystal was smaller and level of impurities was expected to be larger (the same absorption rate of impurities is assumed for the two crystals at elevated temperatures). In both cases, the transitions are hysteretic, which is indicative of a first-order nature of the β - γ transformation.

The number of known and fully characterized phases of $Gd_5Si_2Ge_2$ is extended to three: the ferromagnetic low-temperature polymorph of $Gd_5Si_2Ge_2$ (below -1 °C, $Pnma$ space group),¹⁰ which is referred to as the α -form; the paramagnetic room-temperature modification ($P112_1/a$ space group) named the β -form;^{1,10} and the paramagnetic high-temperature phase (above 320 °C, $Pnma$ space group) called the γ -form (Figure 4). The X-ray single-crystal results, reported here and in ref 10, indicate that distribution of the Ge and Si atoms between the slabs ($T1$ or $T1A$ and $T1B$ sites) and inside the slabs ($T2$ and $T3$ sites) remains identical within three ($\beta \rightarrow \alpha$) and two ($\beta \rightarrow \gamma$) standard deviations upon the transitions. Although presence of a microscopic order-disorder transition upon heating cannot be excluded, it appears that the $\beta \rightarrow \gamma$ crystallographic transformation is not coupled with a macroscopic redistribution of Si and Ge atoms over the corresponding sites (single-crystal diffraction provides experimental data integrated over the volume of the entire specimen). Thus, these results do not support theoretical prediction¹⁴ of the role of macroscopic, completely statistical distribution of Si and Ge atoms in the stabilization of γ - $Gd_5Si_2Ge_2$. Therefore, the $\beta \rightarrow \gamma$ transformation is likely to be driven by increase in the lattice entropy (higher degeneracy of the

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Table 2. Crystal Data and Structure Refinement of Gd₅Si₂Ge₂

temperature, °C	20(1)	400(1)
space group	<i>P</i> 112 ₁ / <i>a</i> ^a	<i>Pnma</i>
composition	Gd ₅ Si _{2.02(2)} Ge _{1.98(2)}	Gd ₅ Si _{2.05(4)} Ge _{1.95(4)}
lattice parameters ^b	<i>a</i> = 7.5869(9) Å <i>b</i> = 14.810(2) Å <i>c</i> = 7.7855(9) Å γ = 93.223(2)° <i>V</i> = 873.3(2) Å ³	<i>a</i> = 7.5569(9) Å <i>b</i> = 14.838(4) Å <i>c</i> = 7.837(1) Å γ = 90° <i>V</i> = 878.8(4) Å ³
Z	4	4
independent reflections ^c	3685	1057
completeness to 2 θ = 57°	94.8%	94.0%
data/parameters	3685/88	1057/50
goodness-of-fit on <i>F</i> ²	0.967	1.011
final <i>R</i> indices [<i>I</i> / σ (<i>I</i>) > 2]	<i>R</i> ₁ = 0.0311, <i>wR</i> ₂ = 0.0545	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0766
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0493, <i>wR</i> ₂ = 0.0578	<i>R</i> ₁ = 0.0506, <i>wR</i> ₂ = 0.0809
largest diff. peak/hole, e/Å ³	2.44/−2.38	2.13/−1.90

^a Standard setting for the monoclinic structure is *P*12₁/*c*1 with *a* = 14.810(2), *b* = 7.7855(9), *c* = 7.5869(9) Å, and β = 93.223(2)° and can be achieved through the following cyclic permutation of the unit cell vectors: **a, b, c** → **b, c, a**. The above setting (*P*112₁/*a*) is used so that a direct comparison can be made with the orthorhombic structure. ^b Lattice parameters of the monoclinic phase were obtained before the orthorhombic phase was formed during heating the Gd getter (lattice parameters of the monoclinic phase at 20 °C in Table 1 were derived after the orthorhombic phase was formed). ^c Symmetry equivalent reflections were treated as independent during twin refinement.

Table 3. Atomic and Equivalent Isotropic Displacement Parameters (*U*_{eq}, Å²) for Monoclinic β -Gd₅Si_{2.02(2)}Ge_{1.98(2)} (20 °C) and Orthorhombic γ -Gd₅Si_{2.05(4)}Ge_{1.95(4)} (400 °C)^a

atom	occupancy Si/Ge, %	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}
20 °C					
Gd1A		−0.00503(6)	0.59848(3)	0.18078(5)	0.0093(1)
Gd1B		0.01746(5)	0.90105(3)	0.18227(5)	0.0096(1)
Gd2A		0.32989(5)	0.12200(3)	0.17757(5)	0.0078(1)
Gd2B		0.35647(5)	0.38125(3)	0.16325(5)	0.0084(1)
Gd3		0.17517(6)	0.25350(3)	0.50564(5)	0.0082(1)
T1A	42.8/57.2(5)	0.15434(16)	0.04086(9)	0.47061(15)	0.0100(4)
T1B	43.2/56.8(5)	0.20650(16)	0.45770(9)	0.46407(15)	0.0095(4)
T2	59.9/40.1(5)	0.04703(18)	0.24841(10)	0.10812(18)	0.0098(5)
T3	55.8/44.2(5)	0.29085(17)	0.24808(9)	0.86890(16)	0.0077(4)
400 °C					
Gd1		0.01862(7)	0.59663(5)	0.18127(7)	0.0185(2)
Gd2		0.32428(7)	0.12233(4)	0.17652(6)	0.0161(2)
Gd3		0.15622(9)	1/4	0.51072(9)	0.0161(2)
T1	42.8/57.2(8)	0.1597(2)	0.0401(1)	0.4690(2)	0.0204(6)
T2	62/38(1)	0.0281(3)	1/4	0.1067(3)	0.018(1)
T3	57/43(1)	0.2745(3)	1/4	0.8706(3)	0.0157(9)

^a Anisotropic temperature factors and other crystallographic details can be obtained from the authors upon request.

Table 4. Interslab and Intraslab *T*–*T* Bond Distances in Gd₅Ga₂Ge₂ at 20 °C (*P*112₁/*a*) and 400 °C (*Pnma*)^a

20 °C		400 °C	
atoms	distance, Å	atoms	distance, Å
T1A–T1A(2)	2.615(2)	T1–T1(4)	2.729(3)
T1B–T1B(2)	3.484(2)		
T2–T3(4)	2.625(2)	T2–T3(4)	2.620(4)

^a Number of bonds per unit cell is given in parentheses.

electronic and vibrational states because of the higher symmetry), rather than by increasing configurational entropy (fully statistical distribution of the Si and Ge atoms).

The high-temperature β – γ transition in Gd₅Si₂Ge₂ appears to be fully reversible during both slow and fast heating, reversible during slow cooling, and irreversible during rapid cooling (temperature change during slow heating and cooling was 20 °C/min, during fast heating and cooling ~10 and ~14 °C/s, respectively). The first indication of the stability of the orthorhombic γ -phase at room temperature was observed after heating the Gd getter in the capillary, which resulted in an uncontrolled temperature increase of the Gd₅Si₂Ge₂ crystals over 320 °C, followed by rapid cooling. The fact that the orthor-

hombic γ -phase is only kinetically but not thermodynamically stable at room temperature was proven by the subsequent heating of one of the crystals (Figure 2). As the temperature rose from 20 to 200 °C, the fraction of the γ -phase decreased and at 300 °C only the monoclinic β -phase was present. Further heating produced only the orthorhombic γ -polymorph. Feasibility of supercooling the γ -form was tested by switching off the heater current on the high-temperature unit, which led to a temperature drop from 350 to 80 °C in less than 20 s. The rapidly cooled crystal contained ~70% of the orthorhombic γ -phase.

The ability to quench the high-temperature orthorhombic γ -polymorph can be related to structural changes during the phase transition (see Figure 4). As the crystal is slowly cooled, the vibrational energy of the atoms, which is proportional to *kT*, is sufficiently large to overcome the entropy contribution and strain created by a 0.7% change of the phase volume [the lattice parameters of the supercooled orthorhombic γ -phase at 20 °C are *a* _{γ} = 7.534(1), *b* _{γ} = 14.765(4), *c* _{γ} = 7.760(3) Å, and *V* _{γ} = 863.2(5) Å³ as compared to those of the monoclinic β -phase: *a* _{β} = 7.585(1), *b* _{β} = 14.783(2), *c* _{β} = 7.768(2) Å, γ _{β} = 93.36(1)°, and *V* _{β} = 869.6(3) Å³]. As the crystal is rapidly quenched, the vibrational energy suddenly decreases, but strain

b axis.

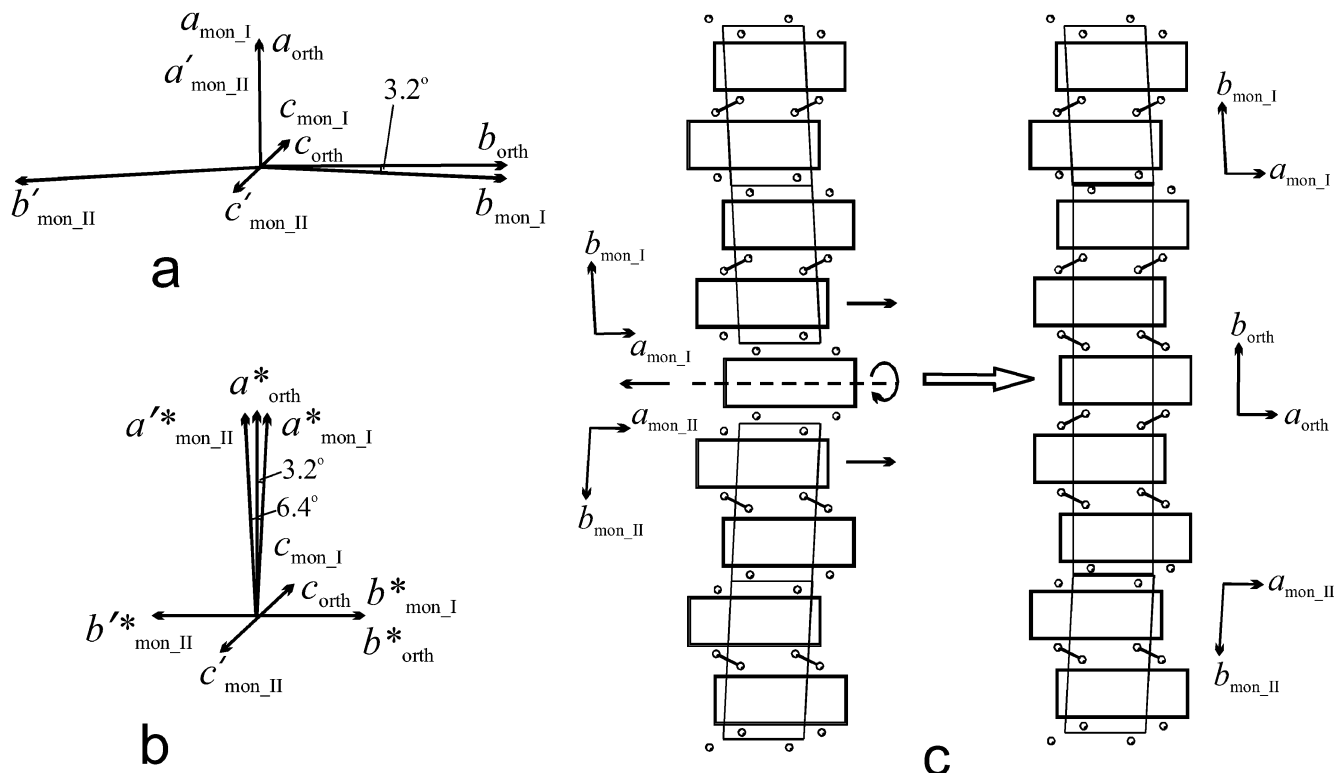


Figure 3. Mutual orientation of the real (a) and reciprocal (b) lattices of the dominant monoclinic twin component (component I), the minor monoclinic twin component (component II), and the orthorhombic component of the $Gd_5Si_2Ge_2$ crystal during the monoclinic-to-orthorhombic transition. (c) Formation of the orthorhombic structure (on the right) from the monoclinic twin structures (on the left) through the shear movement of the slabs. The dashed line in the left part of the figure indicates the twin axis.

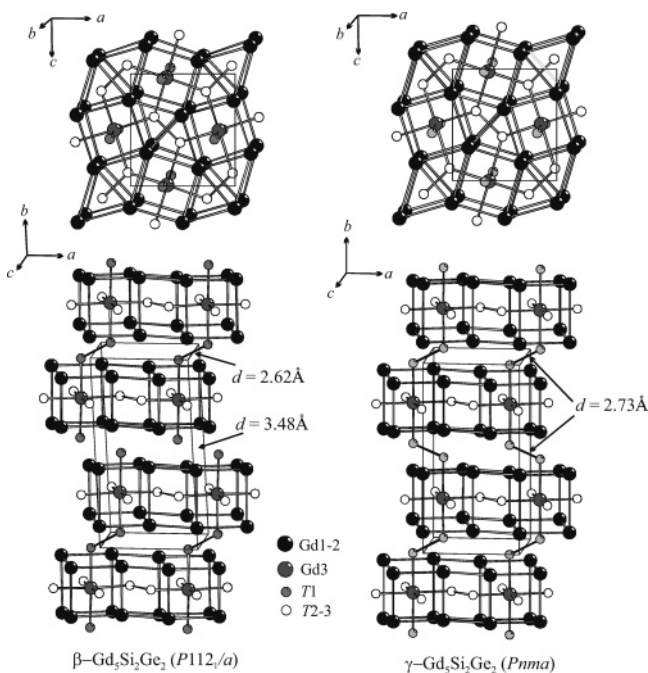


Figure 4. In both monoclinic and orthorhombic structures, the Gd (32-434) nets form 2D slabs with the Gd3 in pseudo-cubic and T2-3 in trigonal prismatic voids (top projections). While in orthorhombic γ - $Gd_5Si_2Ge_2$, the slabs are linked through the covalent-like T1-T1 bonds, in monoclinic β - $Gd_5Si_2Ge_2$ half of the T1-T1 dimers between the slabs are broken.

remains considerable and no atomic rearrangement occurs. The elastic character of the β - γ transition was proven by monitoring

the fractions of the orthorhombic γ - and monoclinic β -phases during their coexistence at different temperatures: the amount of the orthorhombic γ -polymorph increased only when the temperature, but not the holding time, was increased, which is indicative of the elastic nature of the transformation.

Effects of Impurities. It has been noticed that after the third heating of one of the two specimens containing Gd getter, a small amount ($\sim 2\%$ as judged from the relative intensities of the Bragg reflections) of the monoclinic β -polymorph remains well above the transition temperature of 320°C established during the first heating. The β -phase disappeared only after the temperature was raised to 450°C . When the same crystal was slowly cooled for the third time, the orthorhombic γ -polymorph ($\sim 5\%$) was still observed at room temperature (Figures 5 and 6). Further cycling of the crystal through the transition region significantly increased the fractions of β - and γ -domains above and below the transition region found in a virgin crystal and shifted the onset of the phase transformation to higher and lower temperatures, respectively, in effect broadening the hysteresis. Inclusion of impurities in the crystal structure was a likely cause of the observed changes, since small amounts of nitrogen and oxygen are always present in the capillary (even if nearly all oxygen and nitrogen had been initially absorbed by the Gd getter, some quantities would have been later released by the Gd getter and then reabsorbed by the $Gd_5Si_2Ge_2$ crystal to establish a new thermodynamic equilibrium).

Effect of impurities on the stability of the monoclinic β -polymorph of $Gd_5Si_2Ge_2$ and the transition temperature was

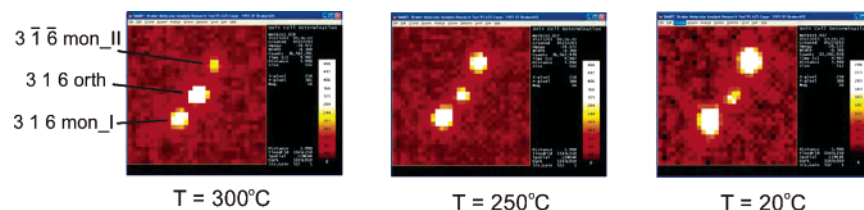


Figure 5. Impurities stabilize the orthorhombic structure below the transition temperature (slow cooling, third cycle). The orthorhombic phase remains at room temperature. Reflections of orthorhombic and monoclinic components are 16 times magnified.

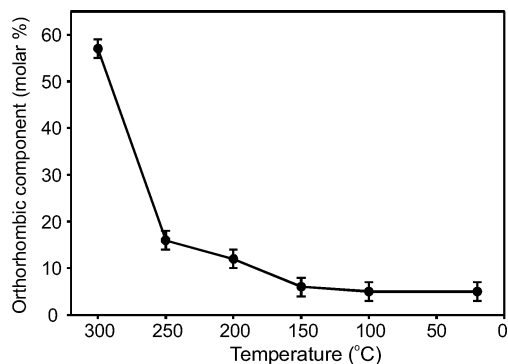


Figure 6. Fraction of the orthorhombic component for the first crystal during cooling in the third cycle.

tested on the third crystal that was sealed without the Gd getter. During slow heating, the orthorhombic γ -phase appeared only at 350 °C, and the monoclinic β -phase disappeared only after the crystal was heated to 600 °C (Figures 7 and 8). These observations differ drastically from those obtained for the crystals sealed with Gd filings in capillaries, for which the $\beta \rightarrow \gamma$ transformation was initially confined to the 300–320 °C range upon heating. Single-crystal refinements of the monoclinic structure at 20 and 350 °C and orthorhombic structure at 600 °C for the third crystal indicated neither change in the composition nor in the Si/Ge distribution within two standard deviations. Although no interstitial oxygen or nitrogen atoms were detected at 350 and 600 °C, which results from their low X-ray scattering power and small amounts in the structure, their presence has to be assumed.

Structural analysis of monoclinic β - and orthorhombic γ -Gd₅-Si₂Ge₂ provides some clues to where these interstitial atoms can be located. Both structures have skewed prismatic voids A (and B, C for β -Gd₅Si₂Ge₂) between the ∞^2 [Gd₅T₄] slabs (Figure 9), which can be also viewed as twinned skewed trigonal prisms fused along one side. Interestingly, their volume is close to the volume of similar in shape intraslab voids filled with T₂ and T₃ atoms (Figure 9). Since the intraslab voids are occupied by silicon and germanium atoms, the interslab voids can be assumed to be rather easily occupied by smaller in size oxygen and nitrogen atoms, as well as by other impurities such as hydrogen, boron, carbon, and fluorine atoms.

From analysis of the interatomic distances, the interstitial O and N atoms are likely to form bonds with the neighboring Gd1–2 and T₁ atoms of two adjacent ∞^2 [Gd₅T₄] slabs (Figure 9). The O/N environment with respect to Gd is unfavorable only in voids B since the Gd–O/N bonds are too short as compared to $d_{\text{Gd–O}} = 2.23\text{--}2.74$ Å in monoclinic Gd₂O₃,²² $d_{\text{Gd–O}} = 2.30\text{--}2.34$ Å in cubic Gd₂O₃,²³ and $d_{\text{Gd–N}} = 2.49$ Å in cubic GdN.²⁴

On the other hand, the Ge–O/N distances for all three voids are reasonable and close to those found in corresponding binary phases ($d_{\text{Ge–O}} = 1.74$ Å in trigonal GeO₂²⁵ and $d_{\text{Ge–N}} = 1.76\text{--}1.96$ Å in trigonal Ge₃N₄).²⁶ Thus, geometric considerations indicate possible presence of O/N impurities in β -Gd₅Si₂Ge₂ (voids A and C) and γ -Gd₅Si₂Ge₂ (voids A). Electronic aspects of an inclusion of O atoms into the β -Gd₅Si₂Ge₂ structure were analyzed using TB–LMTO–ASA calculations. Two oxygen-containing models with either void A or void C filled produced similar densities of states (DOS), but filling of void A is energetically preferred by 5.6 eV/void, and thus only the DOS for the first β -Gd₅Si₂Ge₂O_{0.25} model is presented in Figure 10. This preference is expected since the Gd–O bonds are shorter and thus stronger in void A than in void C. Electronic predictions correlate well with structural analysis of the $\beta \rightarrow \gamma$ transformation: while filling of voids A would only hinder the $\beta \rightarrow \gamma$ transition, filling of the voids C would completely impede the transformation though isolating T₁ atoms and, thus, preventing formation of interslab T₁–T₁ dimers. Completeness of the $\beta \rightarrow \gamma$ transformation in the contaminated crystals, although at higher temperatures, points at filling of voids A. Obviously, filling of voids A but not voids B in monoclinic β -Gd₅Si₂Ge₂ will result in the symmetry reduction of the orthorhombic γ -Gd₅Si₂Ge₂ unit cell upon the $\beta \rightarrow \gamma$ transition (the *m* plane is lost). This symmetry reduction is expected to be noticeable only at high impurity concentrations and when the oxidation progresses fast, or otherwise, the orthorhombic symmetry will be restored when extra impurity atoms enter voids B (which are now equivalent to voids A) of pseudo-orthorhombic γ -Gd₅Si₂Ge₂. Filling of the voids B will render the $\beta \rightarrow \gamma$ transition irreversible, since now shear movement of the ∞^2 [Gd₅T₄] slabs and cleavage of the interslab T₁–T₁ dimers is impossible.

The DOS curves of β -Gd₅Si₂Ge₂ and β -Gd₅Si₂Ge₂O_{0.25} have similar behavior over the whole energy range of valence electrons except for regions below –15 eV (not shown) and around –5 eV. The states in these two energy windows are bonding and come predominantly from the O 2s and 2p orbitals with some contribution from Ge1 and Gd1–2 orbitals. Behavior of the DOS in β -Gd₅Si₂Ge₂O_{0.25} from –10 to –6 eV and above –4 eV, with the latter region being dominated by the Gd states, is similar to the DOS in β -Gd₅Si₂Ge₂, which is due to the low oxygen level as well as to a large difference in the orbital energies of oxygen and neighboring atoms. Thus, a presence of only one O atom per unit cell does not substantially alter Gd–Gd interactions between and within the ∞^2 [Gd₅T₄] slabs. Since the Gd orbitals build most of the states in the conduction band and the physical properties are dependent on the DOS at and around the Fermi level, we can anticipate similar physical properties for slightly contaminated β -Gd₅Si₂Ge₂.

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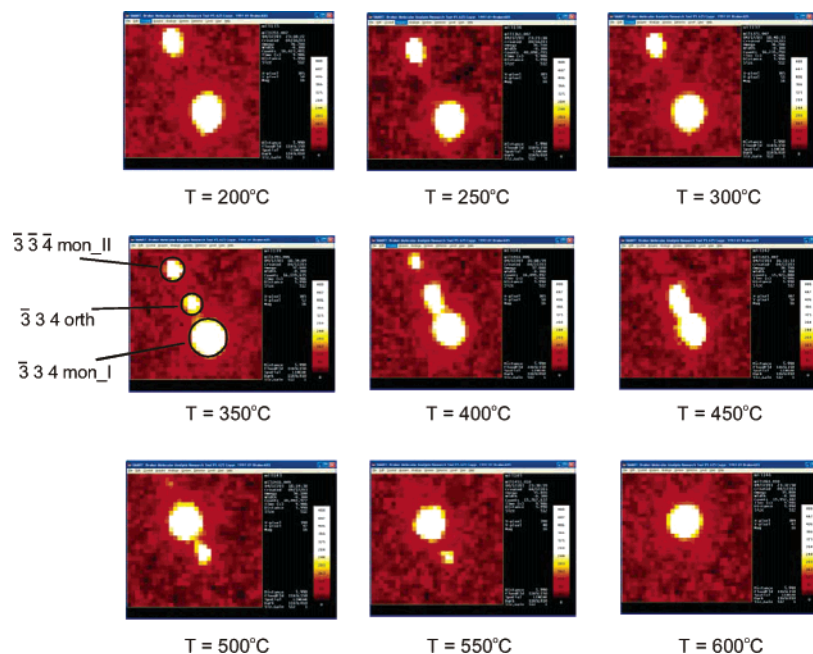


Figure 7. The monoclinic-to-orthorhombic transition in $Gd_5Si_2Ge_2$ starts at 350 °C and ends at 600 °C, when oxygen and nitrogen are present in the capillary (no Gd getter).

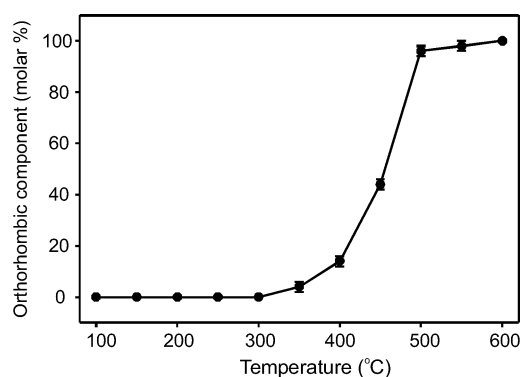


Figure 8. Fraction of the orthorhombic component during heating when oxygen and nitrogen are present in the capillary (no Gd getter).

On the basis of the LMTO results for β - $Gd_5Si_2Ge_2O_{0.25}$, we can expect that inclusion of one N atom into the unit cell of β - $Gd_5Si_2Ge_2$ will have a relatively small effect on the electronic structure and that the N atom will also tend to go into void A. There is only one type of void, namely A, in the structure of γ - $Gd_5Si_2Ge_2$, and it is likely to accommodate O or N atoms at high temperatures. In analogy with β - $Gd_5Si_2Ge_2$, a low level of O/N contamination of γ - $Gd_5Si_2Ge_2$ is believed to bring only small changes to the overall bonding between and within the $\infty^2[Gd_5T_4]$ slabs. In contaminated crystals, the shear movement of the $\infty^2[Gd_5T_4]$ slabs, accompanied by formation and cleavage of the $T1$ – $T1$ dimers, will now have to overcome changes in the O/N-neighboring atom interactions. This additional energetic contribution, which can be viewed as internal friction during the structural transformation, is likely to raise the transition temperature during heating and to lower it during cooling. Some parts of a crystal, especially surface layers, are going to have a larger impurity concentration and, in addition, some voids B will be filled. Those regions of the crystal are likely to remain orthorhombic even after cooling to room temperature. In addition, cycling through the β – γ transition temperature will inevitably increase the impurity level and will result in a larger

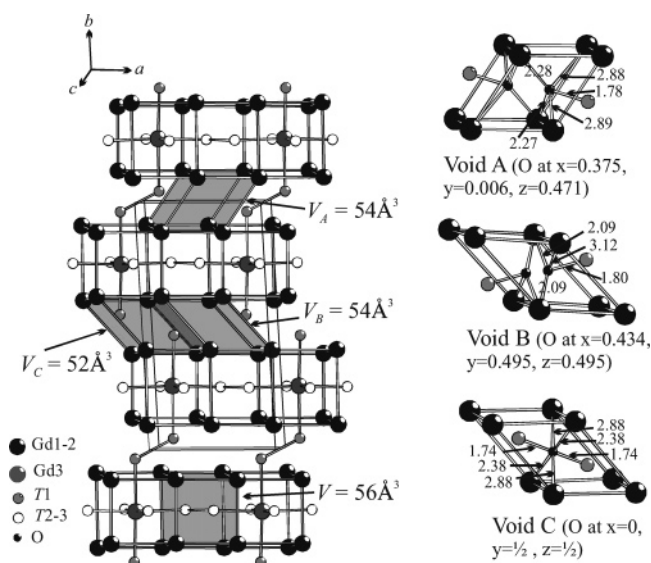


Figure 9. (Left) Interlayer prismatic voids (shown in gray) and their volumes in monoclinic β - $Gd_5Si_2Ge_2$. A similar intraslab void occupied by the $T2$ and $T3$ atoms is also shown. (Right) Positions of oxygen atoms in the interlayer voids and the nearest-neighbor bond distances.

fraction of the crystal remaining orthorhombic after cooling. That is exactly what was observed during our experiments. Also because of relatively fast filling of the interslab holes by oxygen or nitrogen at elevated temperature (as judged from the changes in the β – γ transition temperature of the third crystal), the smaller crystal is saturated faster with impurities than the larger one.

The same will hold true for heating: with each cycle, a larger fraction of a crystal will remain monoclinic above the initial transition temperature (T_i) of 320 °C and higher temperatures will be needed to fully transform the β -polymorph into the γ -polymorph. When the third crystal without Gd getter was heated, a significant amount of oxygen and nitrogen is believed to have entered the structure of $Gd_5Si_2Ge_2$ and, as a result, to

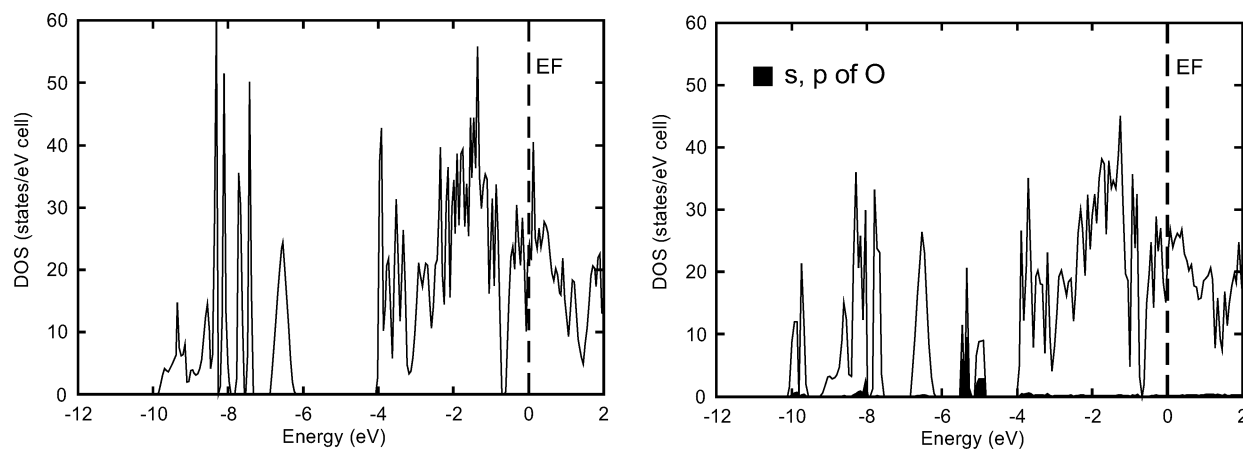


Figure 10. Total and some projected densities of states (DOS) of β -Gd₅Si₂Ge₂ (left) and β -Gd₅Si₂Ge₂O_{0.25} (right) with one O atom in void A. Ge atoms are in the T1 site, Si atoms are in the T2 and T3 sites.

have affected the $\beta \rightarrow \gamma$ transition temperature to a larger extent ($\Delta T_t \approx 300$ °C). These conclusions on the role of impurities in the single crystals of Gd₅Si₂Ge₂ agree well with high-temperature X-ray powder diffraction data obtained on the ground bulk Gd₅Si₂Ge₂ alloy in dynamic vacuum.¹⁵ According to the powder diffraction results, the $\beta \rightarrow \gamma$ transition occurs over extended temperature range with the largest change in the phase ratio at ~ 320 °C and is irreversible and also incomplete: around 30 vol % of β -Gd₅Si₂Ge₂ remains at ~ 460 °C, the highest tested temperature. We believe that heating of the sample chamber causes degassing of its walls and the sample holder and, thus, results in slow oxidation/contamination of the powder sample and renders the transition sluggish and irreversible.

Conclusions

A special crystal mounting procedure was used to perform high-temperature single-crystal X-ray diffraction studies. It was shown that the monoclinic-to-orthorhombic ($\beta \rightarrow \gamma$) phase transition in Gd₅Si₂Ge₂ is driven by increase in the lattice entropy (higher degeneracy of the electronic and vibrational states because of the higher symmetry) but not by configurational entropy (fully statistical, macroscopic distribution of the Si and Ge atoms). The macroscopic Si/Ge occupancies are identical within two standard deviations in the monoclinic β - and orthorhombic γ -polymorphs. The elastic $\beta \rightarrow \gamma$ transformation,

which occurs at 300–320 °C upon heating, is reversible during fast and slow heating and slow cooling but irreversible during rapid cooling. Oxygen and nitrogen impurities apparently stabilize the orthorhombic and monoclinic phases below and above the transition region, respectively, raise the temperature at which transition is complete to 600 °C, and make the $\beta \rightarrow \gamma$ transition irreversible. The spatially resolved transformation of the monoclinic and orthorhombic lattices provides a model of the transition on the atomic level. Interlab voids, which can accommodate oxygen and nitrogen atoms, have been located in both structures. Filling these interlab holes with impurity atoms is believed to impede shear movement of the slab and to make the transition more hysteretic.

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Supporting Information Available: X-ray crystallographic data, in CIF format, for β -Gd₅Si₂Ge₂ at 20 °C and γ -Gd₅Si₂Ge₂ at 400 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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