Ba_8Ge_{43} revisited: a $2a' \times 2a' \times 2a'$ Superstructure of the Clathrate-I Type with Full Vacancy Ordering

Wilder Carrillo-Cabrera*, Serhij Budnyk, Yurii Prots, and Yuri Grin

Dresden, Max-Planck-Institut für Chemische Physik fester Stoffe

Received June 12th, 2004.

Professor Martin Jansen zum 60. Geburtstag gewidmet

Abstract. The reinvestigation of the crystal structure of Ba₈Ge₄₃ \Box_3 (space group $Ia\bar{3}d$, no. 230; a = 21.3123(5) Å; Z = 8; Pearson symbol cI408) shows a full ordering of the vacancies (\Box) in the germanium framework. This ordered crystal structure can be considered as a derivative of an ideal "Ba₈Ge₄₆" clathrate-I type structure ($Pm\bar{3}n$, a' = a/2) in which three Ge vacancies (per formula unit) are allowed to order in a cubic superstructure with a doubled unit cell parameter (\Box at the 24c site, space group $Ia\bar{3}d$). In the resulting Ge framework, each vacancy \Box is surrounded by four three-bonded (3b)Ge⁻ species. The ordering in crystals of as-cast samples (cooled in argon atmosphere, non-annealed) is partially disrupted. For the "as-cast" crystals, a short-range model is proposed based on the partial distribution of Ge on the 24c and 24d sites. From the electron balance, Ba_8Ge_{43} can be considered as a metallic Zintl phase with four excess electrons per formula unit. The Ba_8Ge_{43} phase is stable in the temperature range 770 - 810 °C and exists in equilibrium with Ba_6Ge_{25} and Ge. By decomposition of undercooled (metastable) Ba_8Ge_{43} , a new metastable binary $BaGe_{-5}$ phase is formed.

Keywords: Ba₈Ge₄₃; Clathrate-I; Superstructure; Lone pairs ordering; Ba–Ge Phase diagram

Ba_8Ge_{43} erneut untersucht: eine $2a' \times 2a' \times 2a'$ Clathrat-I Überstruktur mit vollständig geordneten Leerstellen

Inhaltsübersicht. Die erneute Untersuchung der Kristallstruktur von Ba₈Ge₄₃ \Box_3 (Raumgruppe *Ia* $\overline{3}d$, Nr. 230; a = 21.3123(5) Å; Z = 8; Pearson-Symbol *cI*408) zeigt eine komplette Ordnung der Defekte (\Box) innerhalb des Germaniumgerüstes. Diese geordnete Struktur kann als ein Abkömmling des idealen "Ba₈Ge₄₆" Clathrat-I-Typs (*Pm* $\overline{3}n$, a' = a/2) beschrieben werden, in der drei Defekte pro Formeleinheit in einer kubischen Überstrukturzelle mit verdoppeltem Gitterparameter (\Box auf der Lage 24*c* in der Raumgruppe *Ia* $\overline{3}d$) geordnet vorliegen mit vier dreibindigen (3b)Ge⁻-Spezies um jeden Defekt herum. Die Ordnung in Kristallen aus nicht-getemperter Proben wird gestört. Für die nicht-getemperten Kristalle wurde ein Ordnungsmodell mit partieller Verteilung von Ge auf den Lagen 24*c* und 24*d* vorgeschlagen. Die Elektronenbilanz zeigt, dass Ba₈Ge₄₃ als metallische Zintl-Phase mit vier Überschusselektronen pro Formeleinheit beschrieben werden kann. Die Phase Ba₈Ge₄₃ ist im Temperaturbereich von 770 °C bis 810 °C stabil und steht im Gleichgewicht mit Ba₆Ge₂₅ und Ge. Durch Zersetzung von unterkühltem, metastabilen Ba₈Ge₄₃ bildet sich eine neue metastabile binäre Phase BaGe₋₅.

Introduction

In our previous investigation [1], Ba_8Ge_{43} was characterized as a defect clathrate-I type structure with three missing Ge atoms in the covalent germanium framework (a' =10.6565(2) Å, space group $Pm\bar{3}n$, Z = 1). The single crystal was extracted from an as-cast " $Ba_3Ge_4C_2$ " sample after heat treatment at 850 °C (1h) under 40 Kbar pressure (cooled to room temperature under pressure in 5 min). Superstructure reflections were not detected in this investigation.

Nöthnitzer Str. 40

D-01187 Dresden/Germany E-mail: carrillo@cpfs.mpg.de

Tel: 0049-351-4646-3325

Fax: 0049-351-4646-3002

The structure refinement indicated that the Ge1 (6c) position was occupied by 50.5(4) % Ge, and a split model was applied to the surrounding Ge3 atoms (Ge3 \rightarrow 0.5 Ge31 + 0.5 Ge32). A short-range model with one Ge vacancy per hexagonal Ge₆ ring (two faces of the Ge₂₄ tetrakaidecahedron of Ba2 are hexagons) was anticipated. Based on the Zintl concept [2, 3], the following charge balanced formula was proposed for the title compound: (Ba²⁺)₈((3b)-Ge¹⁻)₁₂((4b)Ge⁰)₃₁(4e⁻), where (3b)Ge¹⁻ are three-bonded and (4b)Ge⁰ are four-bonded Ge species. It is assumed that lone electron pairs are attached to the (3b)Ge species in the covalently bonded germanium framework. Nevertheless, the question about the existence of an ordered superstructure in Ba₈Ge₄₃ remained open.

In a more recent work on Ba_8Ge_{43} [4], where the superstructure was not observed either (arc-melted sample), the refined crystal structure (space group $Pm\bar{3}n$) was the same as in the first structure determination [1], but a split model

^{*} Wilder Carrillo-Cabrera

Max-Planck-Institut für Chemische Physik fester Stoffe

was not applied. In an earlier report (high-frequency melted material) [5], even when superstructure reflections were observed by electron diffraction ([211] beam direction), a model for an *ordered* crystal structure was not suggested.

In the present investigation, accurate single-crystal X-ray diffraction intensity data were collected and the crystal structure is re-determined and discussed in detail (two representative crystals were studied, namely one from an annealed sample and one from an as-cast sample).

Experimental

Preparation and thermal analysis

To study the phase relationships of Ba_8Ge_{43} and Ba_6Ge_{25} [6] in the Ba-Ge system, samples (2-3 g) with compositions in the range Ba_{0.33}Ge_{0.67} to Ba_{0.10}Ge_{0.90} were prepared from the elements in open glassy carbon crucibles by high-frequency induction melting (argon atmosphere). In particular, several samples with nominal composition $Ba_{0.157}Ge_{0.843} \equiv Ba_8Ge_{43}$ were synthesized. The starting materials were handled in an argon-filled glove box (content of $O_2 < 1$ ppm, $H_2O < 1$ ppm). The homogenization annealing was performed in argon filled quartz ampoules with subsequent quenching in water. The main heat treatments were done at 650 °C and 795 °C (7 - 42 d). For investigation of the metastable behaviour of Ba₈Ge₄₃, some heat treatments were also carried out at lower temperatures (450 - 600 °C) for hours or several days. In all experiments, to avoid reaction with the quartz ampoule, each sample was wrapped in molybdenum foil (for heat treatments at $T \le 650$ °C) or inserted in a glassy carbon crucible (for heat treatments at 795 °C). The differential thermal analysis (DTA) was done on annealed samples (60-120 mg) in an argon protective atmosphere with the heating rate of 2 °C/min (Netzsch STA 409 EP). The DTA experiments used for the phase diagram determination were performed only on the series of Ba_xGe_{1-x} alloys (x = 0.10 - 0.33) annealed at 650 °C. The samples annealed at 795 °C (quenched in water) were used to establish the phase relationships of the high-temperature phase Ba₈Ge₄₃.

Differential scanning calorimetry (DSC; Netzsch STA 409C/CD) was performed to establish the decomposition temperature of Ba_8Ge_{43} (~ 60 mg; argon atmosphere, heating rate 10 °C/min).

Metallographical examination

Because Ba_8Ge_{43} and Ba_6Ge_{25} are chemically stable enough outside the argon box, the specimens for the metallographic investigations were polished using standard methods without final etching. The optical micrographs were obtained using differential interference contrast and partially polarized light (ZEISS Axioplan2 optical microscope). The chemical analyses were performed by the EDXS method (Philips XL30 SEM).

X-ray diffractometry

The X-ray powder diffraction intensities were collected on a Huber Guinier image plate camera G670 (Cu $K_{\alpha 1}$ radiation, $\lambda =$ 1.540598 Å) at room temperature. The lattice parameters were refined from the powder data applying the program package STOE WinXPOW [7]. LaB₆ was used as internal standard (a = 4.15695 Å). To verify the ordered structure for Ba_8Ge_{43} in the annealed bulk material, the atomic parameters were refined from X-ray powder diffraction data using the Rietveld method (STOE-STADI P diffractometer, linear PSD detector; $CuK_{\alpha 1}$ radiation; $10^\circ \le 2\theta \le 120^\circ$; 10990 points, step width = 0.01°).

Several single crystals were extracted mechanically from an as-cast batch and an annealed batch and tested by Laue photographs. The best from each batch was chosen for single-crystal X-ray diffraction experiments carried out on a Rigaku AFC7 four-circle diffractometer equipped with a Mercury CCD area detector. For each crystal, two measurements with short and long exposure times were performed to obtain accurate intensities for strong and weak reflections. Both data sets were scaled and combined by using the program XPREP [8].

The single-crystal structure refinements were carried out with the SHELXL-97 program [9]. Details of the single-crystal data collection and the structure refinement for the ordered (*annealed*) and the partially ordered (*as-cast*) Ba_8Ge_{43} crystals are summarized in Table 1.

Further details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldhafen, Germany, fax: (+49)7247-808-666, e-mail: crysdata@fiz.karlsruhe.de, on quoting the depositary numbers CSD-no. 414162 (ordered) and CSD-no. 414163 (partially ordered).

Results and discussion

Phase relationships

To optimize the preparation conditions and to determine the stability range of Ba_8Ge_{43} and its phase relationships, the germanium-rich part of the Ba-Ge phase diagram [10] was reinvestigated. A revised variant of the Ge-rich region is proposed in Fig. 1 (T > 430 °C; 75–100 at.% Ge). The temperature values taken for the phase diagram are the onset points of the heat-flow peaks registered in the DTA curves.

The phase Ba_8Ge_{43} is stable in the range 770 - 810 °C, forming peritectically and decomposing eutectoidally into Ba₆Ge₂₅ and Ge. According to metallographic and X-ray powder diffraction data, the samples with compositions in the range $Ba_{0.19}Ge_{0.81}$ - $Ba_{0.10}Ge_{0.90}$ and annealed at 650 °C contain Ba₆Ge₂₅ and Ge. By studying samples containing Ba₈Ge₄₃ and Ba₆Ge₂₅, pre-annealed at temperatures between 770 °C and 810 °C, it was found that, if the cooling was not enough rapid, apart of the decomposition of Ba₈Ge₄₃ into Ba₆Ge₂₅ and primary germanium at the grain boundaries, a metastable phase BaGe_{~5} together with secondary germanium (very thin inclusions; difficult to be observed even with SEM) were found to precipitate within the Ba₈Ge₄₃ grains. The EDXS analysis of the metastable phase gave the composition $Ba_{0.99(1)}Ge_{5.01(1)}$. The $BaGe_{\sim 5}$ phase is the only optically active one (suggesting a non-cubic structure) of all four phases present in the samples, therefore, it can be easily identified using polarized light. E.g. see the microstructure of the Ba_{0.17}Ge_{0.83} sample annealed at 795 °C for 20 days and fast cooled in water (Fig. 2). A piece of the $Ba_{0.17}Ge_{0.83}$ sample (containing mostly Ba_8Ge_{43}) and Ba_6Ge_{25}) was used for a DSC experiment and the result is shown in Fig. 3. There is an 'anomalous' exothermic peak with an onset at 458 °C, originating from the decomposi-

	ordered (annealed)	partially ordered (as-cast)
Crystal	grey metallic clump	grey metallic clump
Crystal size	$0.130 \times 0.070 \times 0.040$ mm	$0.080 \times 0.060 \times 0.040 \text{ mm}$
Space group: formula units	HF mened, 795 C 7 42 d, fast cooled in water $Ia\bar{3}d$ (no. 230), $Z = 8$	HF mened, cooled in argon atmosphere
Pearson code	<i>cI</i> 408	
Unit cell dimensions	a = 21.3123(5) Å, $V = 9680.3(4)$ Å ³	a = 21.3123(6) Å, $V = 9680.3(5)$ Å ³
(powder data)	(107 reflections)	(71 reflections)
Density (calculated)	$5.791 \text{ g} \cdot \text{cm}^{-3}$	
Absorption coefficient	32.61 mm^{-1}	
<i>F</i> (000)	14592	
Data collection	Rigaku AFC7, Mercury CCD; λ (Mo <i>k</i> $4.6^{\circ} < 2\theta < 67.7^{\circ}$	$f_{\alpha} = 0.71073 \text{ Å}$
Absorption correction	Multi-scan method	
Min. and max. transmission	0.101, 0.356	0.180, 0.355
Refined parameters	40	
Goodness-of-fit on F^2	1.605	1.621
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min}$	$+1.4, -2.4 \text{ e} \cdot \text{Å}^{-3}$	$+1.9, -1.9 \text{ e} \cdot \text{Å}^{-3}$
N(hkl) measured	42604	47159
N(hkl) unique	1585 [R(int) = 0.053]	1590 [R(int) = 0.061]
$N'(hkl)$ with $I > 2\sigma(I)$	1452	1412
$R_{\rm gt}(F)$	0.050	0.057
$w R_{\rm all}(F^2)$	0.090	0.089

Table 1 S	elected	crystallograp	iic data	for or	dered	(annealed) and	partially	y ordered	(as-cast)) Ba ₈ Ge ₄₃ .
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Fig. 1 Revised phase diagram of the Ba-Ge system in the germanium-rich region. Dashed lines at temperatures below 650 °C show the metastable behavior of Ba₈Ge₄₃.

tion of the undercooled Ba₈Ge₄₃ phase into the intermediate BaGe_{~5} phase (\cong Ba₈Ge₄₀) and germanium: Ba₈Ge₄₃ \rightarrow Ba₈Ge₄₀ + 3 Ge. The endothermic peak with an onset at 616 °C represents the transformation of the metastable phase $BaGe_{\sim 5}$ ($\cong Ba_8Ge_{40}$) into the equilibrium phases Ba_6Ge_{25} and Ge: $3/_4$ $Ba_8Ge_{40} \rightarrow Ba_6Ge_{25} + 5$ Ge. The second endothermic peak (onset at 780 °C) revels the reaction back to Ba_8Ge_{43} ($Ba_6Ge_{25} + Ge \rightarrow Ba_8Ge_{43}$) and the third, broader and highest endothermic peak (onset at 820 °C) represents the peritectic decomposition of both, Ba₈Ge₄₃ and the remaining Ba₆Ge₂₅ (cf. decomposition temperatures 810 °C and 815 °C, respectively, in Fig. 1). In the DSC curve, the onset temperature values of the last two reactions are shifted by about 10 °C as compared to those obtained from the DTA curves (2 °C/min; samples pre-annealed at 650 °C) used for the determination of the Ba-Ge phase diagram in Fig. 1. The difference might be caused by the different heating rate which was 5 times faster for DSC in comparison with DTA. Thus, we estimated that for low heating rates the two first reaction temperatures should be shifted down by about 8 °C (to \sim 450 °C and \sim 608 °C, respectively, in Fig. 1).

The DTA/DSC experiments and further low temperature heat-treatments on samples pre-annealed at 795 °C suggest that the $BaGe_{\sim 5}$ phase is a metastable phase that forms readily at temperatures in the range 460 - 600 °C from its high-temperature precursor Ba8Ge43 which is undercooled well below its equilibrium eutectoid decomposition temperature. BaGe_{~5} is kinetically a very "sluggish" phase (even after 3 months at 460 °C it is still present). Thus, the transformation to the equilibrium phases $(Ba_6Ge_{25} + Ge)$ needs overheating. In Fig. 1, dashed lines indicate the metastable behaviour for the undercooled Ba₈Ge₄₃.

The EDXS analysis for Ba₈Ge₄₃ resulted in the composition $Ba_{8,0(1)}Ge_{42,9(1)}$. The Ba_8Ge_{43} lattice parameter was found to be the same for annealed (21.3123(5) Å) and ascast (21.3123(6) A) samples, suggesting a phase with constant composition. The symmetry and the lattice parame-



Fig. 2 Microstructure of a $Ba_{0.17}Ge_{0.83}$ sample annealed at 795 °C and fast cooled in water. (a) Precipitation of $BaGe_{-5}$ and Ge in the predominantly two-phase material (optical image, polarized light). (b) Back-scattered electron image pointing up the different kinds of germanium precipitation at the grain boundaries and inside the grains.

ters of $BaGe_{5}$ could not be determined. The X-ray diffraction pattern is complex and rich in reflection peaks.

Crystal structure determination

Ideal atomic coordinates for Ba₈Ge₄₃ in the space group $Ia\bar{3}d$ can be derived from those for the $Pm\bar{3}n$ parent structure, taking into account that $a(Ia\bar{3}d) = 2 \times a'(Pm\bar{3}n)$ and the relationship between the crystallographic sites of both space groups.

For a description of the Ba₈Ge₄₃ structure in the space group $Pm\bar{3}n$ (defect clathrate-I type structure, a' = 10.6565(2) Å, Z = 1), five crystallographically independent atom positions were needed: two Ba positions (Ba1 at the 2a site, Ba2 at the 6d site) and three Ge positions (3 Ge1 at 6c, 16 Ge2 at 16i, 24 Ge3 at 24k) [1]. Because the Ge1 site was only occupied by 50 %, a split model for the neighboring Ge3 sites (Ge3 \rightarrow 0.50 Ge31 + 0.50 Ge32) was refined, and a short-range ordered model for the Ge environment around Ba2 (with two well-distant Ge vacancies \Box) was suggested [1].



Fig. 3 Thermal behavior of a $Ba_{0.17}Ge_{0.83}$ sample pre-annealed at 795 °C (DSC, heating rate 10 °C/min).

In an ordered crystal structure with a superstructure, seven crystallographically independent atom sites are needed: two Ba positions (Ba1 at the 16*a* site, Ba2 at the 48*g* site) and five Ge positions (Ge1 at 24*d*, Ge2 at 32*e*, Ge2' at 96*h*, Ge3 at 96*h* and Ge3' at 96*h*), as listed in Table 2. In contrast to the number of Ba sites, which are equal (2) in both space groups, each Ge site in the space group $Pm\bar{3}n$ (parent structure) splits into two sites in the space group $Ia\bar{3}d$ (superstructure). In particular, the Ge1 site (6*c*, $Pm\bar{3}n$) would split into Ge1 (24*d*, $Ia\bar{3}d$) and Ge1' (24*c*, $Ia\bar{3}d$) sites, but the refinement of the fully ordered structure for the *annealed* crystal reveals that the Ge1' site is empty.

The structure refinement for the as-cast crystal indicated that the Ge1 position is not fully occupied and that the Ge1' site has a low occupancy parameter. The occupancies of the Ge1 and Ge1' sites are complementary (Ge1 is the major site and Ge1' is the minor site). The stronger elongation of the displacement ellipsoid of the Ge3 and Ge3' positions (average sites are not shown in Table 3) in the as-cast crystal as compared to those in the annealed crystal (Table 2), confirms a *partial order* for these Ge neighbors of Ge1 and Ge1', and split positions were introduced in the final model for the as-cast crystal (Table 3). Also, the feature that Ba2 effectively shifts towards the center point between two vacancies at Ge1' (as compared to the average special position for Ba2 in the $Pm\bar{3}n$ subcell) was also taken into account in the split model and a split position Ba2' (Table 3) was introduced at a position shifted in a direction towards the center between two vacancies at Ge1 which is opposite to the shift of Ba2.

Fully ordered crystal structure

As mentioned before, in the annealed (795 °C) and fast-cooled specimen the crystal structure is fully ordered (Table 2). Thus, the Ge1 (24*d*) site is fully occupied and the complementary Ge1' (24*c*) site is totally empty. Fig. 4a shows a

Atom	Site	X	У	Ζ	U_{11}	U_{22}	U ₃₃	U_{12}	U_{13}	U_{23}
Bal	16 <i>a</i>	0	0	0	92(2)	U_{11}	U_{11}	2(2)	U_{12}	U_{12}
Ba2	48g	1/8	0.24720(2)	-v + 1/4	159(3)	286(2)	U_{22}^{11}	-22(2)	U_{12}^{12}	-17(2)
Gel	24d	3/8	0	1/4	113(5)	100(3)	U_{22}^{22}	0	0	0
Ge2	32 <i>e</i>	0.09144(3)	х	х	104(2)	U_{11}	U_{11}^{22}	-15(2)	U_{12}	U_{12}
Ge2'	96h	0.08999(3)	0.40513(3)	0.09097(3)	103(3)	103(3)	92(3)	21(2)	-13(2)	10(2)
Ge3	96h	0.49942(3)	0.15332(3)	0.05629(3)	112(3)	110(3)	116(3)	-1(2)	1(2)	-2(2)
Ge3′	96h	0.00111(3)	0.16667(3)	0.06549(3)	128(3)	153(3)	164(3)	-4(2)	8(2)	33(2)

Table 2 Atomic coordinates and displacement parameters (in pm²) for fully ordered Ba₈Ge₄₃. Standard deviations are given in parentheses.

Table 3 Atomic coordinates and displacement parameters (in pm^2) for partially ordered Ba₈Ge₄₃, *split model*. Standard deviations are given in parentheses.

Atom	Site	x	У	Ζ	$U_{11}(U_{\rm iso})$	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Bal	16 <i>a</i>	0	0	0	104(2)	U_{11}	U_{11}	3(2)	U_{12}	U12
Ba2 ^a	48g	1/8	0.2470(1)	-v + 1/4	187(5)	318(6)	U_{22}^{11}	-19(2)	U_{12}^{12}	0(8)
Ba2' b	48g	1/8	0.2540(8)	-v + 1/4	235(35)					
Gel ^a	24d	3/8	0	1/4	117(6)	106(4)	U_{22}	0	0	0
Ge1' b	24c	1/8	0	1/4	176(28)					
Ge2	32e	0.09147(3)	X	X	120(2)	U_{11}	U_{11}	-18(2)	U_{12}	U_{12}
Ge2'	96h	0.09028(3)	0.40565(3)	0.09110(3)	119(3)	119(3)	109(3)	23(2)	-16(2)	15(2)
Ge3A a	96h	0.49957(5)	0.15315(5)	0.05621(5)	126(2)					
Ge3B ^b	96h	0.4990(4)	0.1644(4)	0.0642(4)	126					
Ge3'A a	96h	0.00090(5)	0.16690(6)	0.06554(5)	152(2)					
Ge3'B ^b	96h	0.0009(4)	0.1540(4)	0.0554(4)	152					

^{a)} Occ(Ba2) = Occ(Ge1) = Occ(Ge3A) = Occ(Ge3'A) = 0.880(4)

^{b)} Occ(Ba2') = Occ(Ge1') = Occ(Ge3B) = Occ(Ge3'B) = 0.120

fragment of the superstructure equivalent to the unit cell of the subcell in $Pm\bar{3}n$. The Ba1 and Ba2 atoms are coordinated by 20 and 22 Ge atoms, respectively (Figs. 4b, 4c). The cage of Ba1 is a distorted Ge₂₀ pentagondodecahedron formed by 14 four-bonded (4b)Ge atoms and 6 threebonded (3b)Ge atoms. The Ge environment around Ba2 is a 2-openings "nido" tetrakaidekahedron (Ge_{24-2}) which due to the missing Ge atoms is truncated at two corners, resulting in a hexakaidecahedron with 10 pentagonal, 4 quadrangular, and 2 triangular faces. Thus, each Ba2 atom is surrounded by 16 four-bonded (4b)Ge atoms and 6 threebonded (3b)Ge atoms. Particularly, the holes (\Box) at Ge1' (24c) are arranged around a 4_1 four-fold screw axes to form chiral helices along the {100} directions (Fig. 5). The Ba1 and Ba2 germanium environments are shown in Fig. 6 as two condensed polyhedra with Ge labels and Ge-Ge bond lengths (see also Table 4).

For each Ba_8Ge_{43} formula unit, 31 Ge atoms are fourbonded (4b) and 12 Ge atoms (at Ge3' sites for the full ordered structure) are three-bonded (3b). Assuming 2e⁻ Ge-Ge bonds, the formal charge balance for the title compound can be written as $(Ba^{2+})_8((3b)Ge^{1-})_{12}$ $((4b)Ge^0)_{31}(4e^-)$. According to this, Ba_8Ge_{43} is a metallic Zintl phase [11] with few conduction electrons. Metallic or semimetallic properties are expected for this compound. We assume in the following that in the germanium framework each three-bonded (3b)Ge3' atom in Ba_8Ge_{43} has attached a lone pair of electrons. In contrast to the so-called dangling bonds observed on the surface of semiconductors like silicon [12], the lone pairs in Ba_6Ge_{25} and Ba_8Ge_{43} can be considered as inner dangling bonds.

Partially ordered crystal structure

As stated before for the as-cast specimen, its crystal structure is not fully ordered and it was refined using a split model (Table 3). Thus, the as-cast crystal (cooled in the glove box, argon atmosphere) contains structural defects, involving primarily the Ge1/Ge1' sites and their next neighbors. Short-range ordered models for the germanium environment around Ba2 (majority site) and Ba2' (minority site) are proposed in Fig. 7. The environment of the majority Ba2 site (associated with Ge vacancies at the 24*c* site; Fig. 7a) is matching quit well with that of the fully ordered structure (Fig. 6). The *d*(Ge–Ge) bond lengths in the environment of the minority Ba2' component (associated with Ge vacancies at the 24*d* site) are somewhat different, but within a similar range (2.443 – 2.600 Å).

Superstructure in the X-ray powder data

Superstructure reflections in the X-ray powder diffraction patterns of Ba₈Ge₄₃ were observed for the as-cast and the annealed samples. Despite of cooling in water, the quenching of Ba₈Ge₄₃ was not perfect, because the Ba₈Ge₄₃ samples contained minor amounts of its decomposition products (the sealed quartz ampoule enclosing the sample and crucible seems to be a relatively bad thermal conductor). The best annealed sample has about 97 wt-% Ba₈Ge₄₃ and the refinement of its X-ray powder diffraction data using the Rietveld method (GSAS program [13]) confirms the superstructure model for the bulk material (46 variables; wR(P) = 0.077, R(P) = 0.059; $R(F)_{Ge} = 0.048$,



Fig. 4 Fragments of the crystal structure of Ba_8Ge_{43} . (a) Distorted pentagondodecahedra (black) and hexakaidecahedra ($\hat{=}$ defect tetrakaidecahedra, grey) in the germanium framework. (b) Ge_{20} pentagondodecahedron centered by Ba1 with three-bonded (3b)Ge and four-bonded (4b)Ge germanium atoms. (c) Germanium environment around Ba2. Two Ge atoms are missing in the Ge_{24-2} defect tetrakaidecahedron, producing three-bonded (3b)Ge species around the defects.

 $R(F)_{Ba8Ge43} = 0.058$; ~3 wt-% Ge). The strongest superstructure reflections of Ba_8Ge_{43} are outlined in Fig. 8, where a relevant part of the X-ray diffraction pattern is shown.



Fig. 5 Three condensed Ge_{24-2} defect tetrakaidecahedra with their missing atoms (small grey cubes) showing the spiral substructure of the Ge vacancies along the {100} directions.

Table 4 Interatomic distances for fully ordered Ba₈Ge₄₃ (cf. Fig. 6).

Atoms		Distance, Å	Atoms	Distance, Å
Ba1	-Ge2	3.375(1) 2×	Gel –Ge3	2.528(1) 4×
	-Ge2'	$3.395(1) 6 \times$	Ge2 –Ge2	2.477(2)
	-Ge3	$3.481(1) 6 \times$	-Ge3'	$2.566(1) 3 \times$
	-Ge3'	3.817(1) 6×	Ge2' -Ge2'	2.441(1)
Ba2	-Ge3'	$3.421(1) 2 \times$	-Ge3	2.511(1)
	-Ge3'	3.518(1) 2×	-Ge3	2.514(1)
	-Ge3	$3.552(1) 2 \times$	-Ge3'	2.531(1)
	-Ge3	3.639(1) 2×	Ge3 –Ge2'	2.511(1)
	$-\Box$	3.726 2×	-Ge2'	2.514(1)
	-Gel	3.810(1) 2×	-Gel	2.528(1)
	-Ge2	3.886(1) 2×	-Ge3'	2.611(1)
	-Ge2'	3.925(1) 2×	Ge3' -Ge2'	2.531(1)
	-Ge2'	3.926(1) 2×	-Ge2	2.566(1)
	-Ge3'	3.973(1) 2×	-Ge3	2.611(1)
	-Ge2'	4.111(1) 2×	- 🗆	$2.182.4 \times$
	-Ge3	4.323(1) 2×		

Further crystallographic remarks

Even if the unit cell of the $2a' \times 2a' \times 2a'$ superstructure of Ba₈Ge₄₃ is relative large, the arrangement of the structural building units and their connectivity nets can be described with few characteristic graphs or diagrams. The point configuration for Ba1 (16*a*) and for the ideal position of Ba2



Fig. 6 Coordination polyhedra of Ba1 and Ba2 sharing a pentagonal face with the lengths of the Ge–Ge bonds for the fully ordered structure.



Fig. 7 Short-range ordered models with corresponding Ge–Ge bond lengths for the partially ordered (*as-cast*) crystal. (a) Germanium environment around the majority Ba2 site. (b) Ge_{24-2} polyhedron of the minority Ba2' site.

(48g with y = 1/4) are I_2 and W_2 , respectively. By connecting all the positions of these point configurations (using



Fig. 8 The observed X-ray powder diffraction pattern of an annealed Ba_8Ge_{43} sample in the range $26^\circ < 2\theta < 41^\circ$. The Bragg peak positions (vertical bars) and the difference profile plot (solid line, bottom part) are shown. The strongest superstructure reflections of Ba_8Ge_{43} are indexed. A peak of the minority phase (Ge) is highlighted.

the shortest distance), the I_2 and W_2 graphs (called "frame-works" in [14]) are obtained.

One feature of great interest for us is the graph related to the holes at Ge1'(24c) in the fully ordered structure. For the as-cast specimens, the minority vacancies at Ge1 (24d) site may also be ordered, and the corresponding graph is also considered here. The inspection of the point configurations reveals that the related Ge1 (24d) and Ge1' (24c) sites are far from being "equivalent". The point configuration for the Ge1' (24c) site is V^* (three-connected nodes) and for the Ge1 (24d) site it is S^* (four-connected nodes). While, the V* graph consists of two interpenetrating enantiomorphic graphs, namely the V^- and the V^+ graphs (Fig 9a, orange and blue nets, respectively) [14–17], the S^* graph is only one net (yellow, Fig. 9b) [14, 17]. Each vacancy (\Box) is represented by its surrounding Ge4 tetrahedron (orange or blue) of Ge3' atoms for V* graph in Fig. 9a (or yellow tetrahedra of Ge3B atoms for the S* graph in Fig. 9b). The periodic nodal surfaces (PNS) [18] $I_2 - Y^{**}$ (also called $Ia\bar{3}d$ $< (211)_0^1 (220)_0^1 > Ia\bar{3}d$, with the notation used in [19]) and the complementary one $C(I_2 - Y^{**})$, also called $Ia\bar{3}d <$ $(211)^1_{\pi}(220)^1_0 > Ia\bar{3}d$, envelope the V* and S* graphs, respectively [15, 17] (Figs. 9a and 9b).

Additional inspection reveals that periodic surfaces derived from the PNS $Ia\bar{3}d < (211)^{1}_{\pi} > Ia\bar{3}d [17, 20]$ with isovalue f(x,y,z) = 0.63 (further denoted as $|Ia\bar{3}d < (211)^{1}_{\pi} > Ia\bar{3}d|_{f=0.63}$) envelopes very closely the (\Box)Ge₄ tetrahedra. Thus, for the description of the V* tetrahedral arrangement the isosurface $|Ia\bar{3}d < (211)^{1}_{\pi} > Ia\bar{3}d|_{f=0.63}$ is the adequate one, and for the S* tetrahedral array the isosurface $|Ia\bar{3}d < (211)^{1}_{\pi} > Ia\bar{3}d|_{f=0.63}$ is sufficient. Fig. 9c illustrates the ordered





Fig. 9 Topology of the Ba₈Ge₄₃ structure. (a) $I_2 - Y^{**}$ periodical nodal surface with the V^* graph of the Ge1' sites. (b) Complementary $C(I_2 - Y^{**})$ periodical nodal surface with the S^* graph of the Ge1 sites. The V^* graph is composed of the interpenetrating V^- (orange net) and V^+ (blue net) partial graphs. (c) Ordered Ba₈Ge₄₃ structure (blue Ge₂₀ pentagondodecahedra, beige Ge₂₄₋₂ defect tetrakaidecahedra) with the isosurface $|Ia\bar{3}d| < (211)_{\pi}^{-1} > Ia\bar{3}d|_{f=0.63}$ as a space partitioner. The white 3(b)Ge3' atoms lie at the isosurface. The dark green labyrinths contain the lone pairs of the 3(b)Ge3' species, as well as the Ge2–Ge2 dumbbells.

Ba₈Ge₄₃ structure together with the $|Ia\bar{3}d < (211)_{\pi}^{1} > Ia\bar{3}d|_{f=0.63}$ _{0.63} isosurface, revealing the labyrinth organization. The (3b)Ge3' atoms are located on the isosurface and the lone pairs are directed into the green labyrinths. The neighboring Ge2–Ge2 dumbbells are also located in the green labyrinths.

It is interesting that the lone pairs in the full ordered Ba_8Ge_{43} structure occupy a part of the double channels of the $I_2 - Y^{**}$ PNS (blue in Fig. 9a). The same PNS envelopes

the ${}^{3}_{\infty}$ [RhBi_{8/2}] polyhedral framework in RhBi₄ structure with a hyperbolic lone-pair structure in the double channels of the *Y*^{**} gyroide (the $I_2 - Y^{**}$ nodal surface is complementary to the *Y*^{**} gyroide) [15].

The symmetry of the *defect-free* structure of the clathrate-I type belongs to the space group $Pm\bar{3}n$. Our determination of the fully disordered variant of the Ba₈Ge₄₃ structure [1], resulted in exactly a half-occupied position Ge1. Consulting the *International Tables for Crystallogra*-

	2 Bal 2 <i>a</i>	6 Ba2 6d	30	Gel 16 C		G e2 6i	24 Ge3 24k	
Pm3n $(P4_2/m\overline{3}2/n)$	0	1/4	1.	1/4		0.1836		0
	0 0	1/2 0	(1.	$\begin{array}{c c} x \\ 2 \\ x \end{array}$		r r	0.3196 0.1213	
$\begin{matrix} k4\\2a_1, 2a_2, 2a_3 \end{matrix}$								
$\bigvee_{L=\overline{2}} d$	16 Ba1 16 <i>a</i>	48 Ba2 48g	24 Ge1 24 <i>d</i>	24 □ 24 <i>c</i>	32 Ge2 32 <i>e</i>	96 Ge2' 96h	96 Ge3 96h	96 Ge3' 96h
$(I4_1/a\overline{3}\ 2/d)$	0	1/8	3/8	1/8	0.0914	0.0900	0.4994	0.0011
· · ·	0 0	0.2472 - <i>y</i> +1/4	0 1/4	0 1/4	x x	0.4051 0.0910	0.1533 0.0563	0.1667 0.0655

Fig. 10 Group-subgroup relationship between the fully disordered and fully ordered Ba₈Ge₄₃ structures, using the formalism [22]. The table shows the corresponding atomic positions (rounded numbers) with Wyckoff symbols. By ordering of the vacancies (\Box) at the 24*c* sites, only the initial positions Ge2 and Ge3 subdivide into two independent positions each.

phy [21], one can easily deduce that the real structure of Ba₈Ge₄₃ described here represents a maximal non-isomorphic subgroup of the space group $Pm\bar{3}n$ namely the variant IIb: $Ia\bar{3}d$ (a' = 2a, b' = 2b, c' = 2c). This group-subgroup relationship leads to a 'klassengleich' [22] (class-equivalent) symmetry reduction of index 4 with enlarged cell, i.e. $Pm\bar{3}n$ ($P 4_2/m \bar{3} 2/n$) – $k4 (2a_1, 2a_2, 2a_3) \rightarrow Ia\bar{3}d$ ($I 4_1/a$ $\bar{3} 2/d$). The group-subgroup and atomic positions relationships are summarized in Fig. 10.

The adoption of the 24c site for the \Box vacancies (24 per unit cell) in fully ordered Ba_8Ge_{43} crystals means that the four lone electron pairs associated with each Ge vacancy prefer, for spatial reasons, to surround a site of lower symmetry, i.e. 24c (site symmetry 222) instead of the alternative site 24d (site symmetry $\bar{4}$).

4 Conclusions

The Ba₈Ge₄₃ phase is stable between 770 °C and 810 °C, and contains defects in its Ge network which are fully ordered in a superstructure ($Ia\bar{3}d$) of the clathrate-I type ($Pm\bar{3}n$) with $a(Ia\bar{3}d) = 21.3123$ Å $= 2 \times a'(Pm\bar{3}n)$. The vacancy ordering can be disrupted if the samples are not annealed or after annealing they are cooled slowly.

The space group of the defect-free clathrate-I structure is $Pm\bar{3}n$. The real structure of Ba₈Ge₄₃ ($Ia\bar{3}d$) represents a maximal non-isomorphic subgroup for the space group $Pm\bar{3}n$ in the case of ordering. This group-subgroup relationship produces a 'klassengleich' symmetry reduction of index 4. Note added in proof: A similar $2 \times 2 \times 2$ superstructure was found independently for the rubidium-tin clathrate Rb₈Sn₄₄ \square_2 [23]. In this crystal structure, the superstructure is caused by a *partial* ordering of the vacancies.

Acknowledgments. Prof. Dr. H. G. von Schnering and Dr. M. Baitinger are gratefully acknowledged for valuable comments. The authors thank Dr. R. Ramlau and Mrs. P. Scheppan for the SEM/ EDXS study, Dr. R. Niewa and Mrs. S. Müller for the DTA/DSC measurements, and Dr. R. Cardoso Gil and Mr. S. Hückmann for recording the X-ray diffraction patterns.

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