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$EuGa_{2\pm x}Ge_{4\mp x}$: preparation, crystal chemistry and properties

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Abstract

The title compound was prepared from a mixture of the elements by melting in a glassy carbon crucible (HF furnace, argon atmosphere). EuGa_{2±x}Ge_{4±x} crystallizes in a new structure type (orthorhombic symmetry, space group *Cmcm* (no. 63), *a*=4.1571(3) Å, *b*=11.268(1) Å, *c*=13.155(1) Å, *V*=616.2(2) Å³, *Z*=4, Pearson symbol *oC*28) and is characterized by a 3D framework of 4-fold bonded (4b) *E* atoms (*E*=Ga,Ge) with channels parallel to the short *a*-axis. The europium atoms lie in the *E*₁₈ holes of those channels. The structure can also be described as an intergrowth of segments from BaAl₂Si₂ and from a reconstructed diamond type of structure. The (Ga,Ge)₂₄ framework of the title compound is equivalent to that of the Si(Al) atoms in the zeolite structure of CsAlSi₅O₁₂. Magnetic susceptibility measurements show that EuGa_{2±x}Ge_{4±x} undergoes a transition from a paramagnetic to an antiferromagnetic ordered state at about 9 K. In the paramagnetic region, an oxidation state of 2+ for europium ($\mu_{eff} \approx 8 \mu_B/Eu$) was obtained. The crystal chemical formula of EuGa₂Ge₄ is Eu²⁺[(4b)Ga¹⁻]₂[(4b)Ge⁰]₄ according to a charge balanced Zintl phase. This was confirmed by quantum chemical calculations (TB-LMTO, ELF). However, like several other similar compounds, e.g. alkaline earth metal clathrates, EuGa_{2±x}Ge_{4±x} has a metal-like temperature dependence of the electrical resistivity with a low charge-carrier concentration in agreement with the low value of the calculated density of states. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rare earth compounds; X-ray diffraction; Crystal structure; Electrical conductivity; Magnetic measurements

1. Introduction

In the course of our investigations dealing with the formation and stability region of the two modifications of the clathrate Eu₈Ga₁₆Ge₃₀ (ratio (Ga,Ge)/Eu=5.75) in the Eu–Ga–Ge system [1], we discovered two new ternary phases, namely the (Ga,Ge)-rich compound EuGa₂Ge₄ (with the ratio (Ga,Ge)/Eu=6) and the (Ga,Ge)-poor compound Eu₃Ga₄Ge₆ (ratio (Ga,Ge)/Eu=3.33). Both occur as minority phases in equilibrium with the clathrate. The latter is monoclinic (space group *C2/m*, Pearson symbol *mC*52, *Z*=4, *a*=24.118(3) Å, *b*=4.3250(4) Å, *c*=11.001(1), β =91.77(1)°) and belongs to the family of compounds M₃Ga_{4+x}Ge_{6-x} (M=Ca, Eu, Yb) [2]. Because the composition EuGa_{2±x}Ge_{4+x} is very near to that of the clathrate Eu₈Ga₁₆Ge₃₀ we investigated in detail the crystal structure and properties of the title compound.

2. Experimental

The samples with atomic ratios Eu:Ga:Ge = (1-1.07):(2-2.14):(3.88-4.0) were prepared from the elements by melting in a high frequency furnace (argon atmosphere; Eu, 99.9%, Lamprecht, additionally distilled in vacuum; Ga, 99.99999%, Chempur; Ge, 99.9999%, ABCR). The element mixtures were placed in a open glassy carbon crucible, which was positioned in a quartz tube inside the coil of the high frequency furnace.

The lattice parameters were determined from X-ray powder data (Huber Guinier image plate camera G670, λ (Cu K_{$\alpha 1$})=1.540562 Å) by a least-squares refinement of the 2 θ values for 50 reflections in the range 23°<2 θ < 100°. LaB₆ was used as an internal standard (a= 4.15695(6) Å). Experimental details of the single-crystal investigation for EuGa₂Ge₄ are presented in Table 1.

The electrical resistivity and the Hall coefficient were measured using a standard four-point ac technique in the temperature ranges 2–400 K and 10–300 K, respectively. The Hall coefficient was measured in magnetic fields up to

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Table 1 Selected crystallographic data for EuGa₂Ge₄

Composition	EuGa ₂ Ge ₄
Structure type	EuGa ₂ Ge ₄
Crystal	grey metallic prism fragment,
	size 0.08×0.07×0.07 mm
Molar mass	581.76 amu
Space group; formula	<i>Cmcm</i> (No. 63); Z=4
units per unit cell	
Pearson code	oC28
Unit cell dimensions	a = 4.1571(3) Å, $b = 11.268(1)$ Å,
(powder data, see text)	c = 13.155(1) Å, $V = 616.2(2)$ Å ³
Data collection	Stoe IPDS, 250 exposures, $\Delta \phi = 0.8$,
	Ag K _{α} ($\lambda = 0.56086$ Å);
	$5^{\circ} < 2\theta < 48^{\circ}$
Data correction	numerical absorption correction,
	$\mu = 19.86 \text{ cm}^{-1},$
	min. and max. transmission: 0.229, 0.359
Structure refinement	SHELXL-97 [3] (24 variable parameters)
N(hkl) measured/unique	3891, 562
N(<i>hkl</i>) with $I > 2\sigma(I)$	434
GOOF	1.144
$R(F); wR(F^2)$	0.030; 0.063 $(I > 2\sigma(I))$
$R_{\rm all}(F); wR_{\rm all}(F^2)$	0.043; 0.066

13 T. The magnetic susceptibility was measured with a commercial SQUID magnetometer in magnetic field of 0.05 T in the temperature range 2–400 K.

3. Results and discussion

The preparation of single phase samples of $EuGa_{2\pm x}Ge_{4\mp x}$ was not possible, since the composition and the formation temperature of the $EuGa_{2\pm x}Ge_{4\mp x}$ phase and of the clathrate $Eu_8Ga_{16}Ge_{30}$ (= $EuGa_2Ge_{3.75}$) are very similar. $EuGa_{2\pm x}Ge_{4\mp x}$ as majority phase was obtained in a sample with the nominal composition $Eu_{1.07}Ga_{2.14}Ge_{4.0}$ immediately after the high frequency (HF) melting at temperatures $T > 900^{\circ}C$ (followed by cooling in argon atmosphere). Annealing of this sample at $T = 700^{\circ}C$ lead to the formation of the clathrate $Eu_8Ga_{16}Ge_{30}$ as majority phase. A heat treatment at $T = 510^{\circ}C$ for 43 days disclosed a non-equilibrium sample with about 85% of $EuGa_{2\pm x}Ge_{4\mp x}$ together with $Eu_8Ga_{16}Ge_{30}$, $Eu_3Ga_4Ge_6$ and Ge as minority phases.

For the determination of the homogeneity range, two samples with the compositions $EuGa_{1.88}Ge_{4.12}$ and $EuGa_{2.12}Ge_{3.88}$ were synthesized and annealed at 510°C for 43 days. Both are multi-phase samples. The crystallographic data indicate the occurrence of a homogeneity range $EuGa_{2\pm x}Ge_{4\mp x}$ for the title compound. The unit cell parameters vary from a=4.1578(4) Å, b=11.2678(6) Å, c=13.156(1) Å, V=616.4(1) Å³ (Ga-poor sample) to a=4.1497(4) Å, b=11.2702(7) Å, c=13.182(1) Å, V=616.5(2) Å³ (Ga-rich sample). Especially the clear difference in the *c* axis length should be noted together with practically constant unit cell volume. By EDX analysis, the

following compositions of the $EuGa_{2\pm x}Ge_{4\mp x}$ phase were obtained: $Eu_{1.01(1)}Ga_{1.99(1)}Ge_{4.01(1)}$ in the gallium-rich sample $EuGa_{2.12}Ge_{3.88}$ (in equilibrium with the clathrate $Eu_8Ga_{16.0(16)}Ge_{29.8(3)}$, see Fig. 1a) and $Eu_{1.01(1)}Ga_{2.00(4)}Ge_{3.99(5)}$ (with a large dispersion of the



Fig. 1. Microphotographs of the samples (a) $EuGa_{2.12}Ge_{3.88}$ (annealed at 510°C for 43 days, BSE image), (b) $EuGa_{1.88}Ge_{4.12}$ (annealed at 510°C for 43 days, optical image, insert BSE image) and (c) $Eu_{1.07}Ga_{2.14}Ge_{4.0}$ (as-cast, BSE image).



Fig. 2. Observed (dotted line) and calculated (solid line) X-ray powder profile plots, Bragg peak positions (thick marks), and difference profile plot (lower part) from the full profile refinement of $EuGa_2Ge_4$ (as-cast sample $Eu_{1.07}Ga_{2.14}Ge_{4.0}$). The reflections marked (*) are from the minority phase $Eu_3Ga_4Ge_6$.

composition of the majority phase) in the gallium-poor sample $EuGa_{1.88}Ge_{4.12}$, which after a long heat treatment was still not in equilibrium (see eutectoidal microstructure in Fig. 1b). The presumable reaction is as follows: β - $Eu_8Ga_{16}Ge_{30} \rightleftharpoons EuGa_2Ge_4 + Eu(Ga,Ge)_y$, see also Ref. [1]. Apparently, the resolution of the EDX method does not allow to determine the homogeneity range more exactly.

Starting with the composition $Eu_{1.07}Ga_{2.14}Ge_{4.0}$, we succeeded in obtaining an as-cast sample with about 92% of $EuGa_{2\pm x}Ge_{4\mp x}$, which was used for our study. The EDX analysis of the $EuGa_{2\pm x}Ge_{4\mp x}$ phase in the polished sample results in the composition $Eu_{1.00(1)}Ga_{2.00(1)}Ge_{3.99(2)}$. Analysis of the X-ray diffraction pattern (Fig. 2) and microstructure (Fig. 1c) revealed, that the minority phase $Eu_3Ga_4Ge_6$ is also present (about 8%, as isolated inclusions). The single crystal used for structure determination was obtained from this sample.

The phase $EuGa_{2\pm x}Ge_{4\mp x}$ is grey metallic, brittle, relatively stable in air and moisture. A DTA experiment on the sample with nominal composition $EuGa_2Ge_4$ (85% of majority phase, annealed at 510°C for 43 days) shows peritectical reaction at 678°C and liquidus at 697°C. These temperatures are very close to 696°C ($\alpha \leftrightarrow \beta$ phase transition) and 699°C (liquidus, congruent formation) found for $Eu_8Ga_{16}Ge_{30}$ [1].

At the beginning of this study, when no suitable single

Table 3 Interatomic distances in EuGa₂Ge

Atoms	d (Å)	d_{average} (Å)	Atoms	d (Å)
E1-2E1	2.475(1)		Eu-2E2	3.366(1)
E3	2.510(1)	2.493	4E1	3.368(1)
<i>E</i> 2	2.513(1)		4E2	3.485(1)
			4E3	3.581(1)
E2 - 2E3	2.486(1)		2E1	3.993(1)
<i>E</i> 2	2.488(2)	2.493	2E2	4.143(1)
E1	2.513(1)			
E3-2E2	2.486(1)		2Eu	4.157(0)
E3	2.502(2)	2.496		
E1	2.510(1)			

crystals were available, the structure was determined by trial and error using the powder data (Rietveld method, program GSAS [4]). The X-ray powder pattern (Fig. 2) was indexed using the program WinXPOW [5]. The extinction conditions for the reflections corresponded with the space groups Cmcm or $Cmc2_1$. The centro-symmetric possibility was chosen. The unit cell parameters, the phase composition, the strong $(2\ 0\ 0)$ reflections, and the possible structural relationship to the structures $BaAl_2Si_2$ [7] (α - $BaCu_2S_2$ type [8]) and $BaCu_4S_3$ (space group *Cmcm*) allowed to choose an Eu position at (0,y,1/4) with y=0.25–0.30. The best diffraction intensity agreement was obtained for y = 0.29. The positions of the (Ga,Ge) atoms were localized from difference Fourier maps. The model was later confirmed and refined by using the single-crystal data. Positional and displacement parameters are presented in Table 2 and interatomic distances are listed in Table 3.

EuGa₂Ge₄ represents a new structure type (Pearson symbol oC28). In the structure (Fig. 3), there are three *E* sites (*E*1, *E*2 and *E*3, *E*=Ga,Ge) and one Eu site. The Eu substructure looks like a distorted body-centred pseudo-tetragonal lattice with (100) as basal plane. The shortest Eu–Eu distance is 4.1571(3) Å (along [100]) and the next shortest are 6.009(1) and 6.969(1) Å. Considering Eu–*E* distances shorter than 4.2 Å, the coordination sphere of the europium atom is an E_{18} polyhedron shown in detail in Fig. 4b (face symbol $6^26^26^18^2$ according to [6]). The E_{18} polyhedron is a derivative of the regular hexa-edge-stellated hexagonal prism (6^66^2), and in a more distorted form is also present in the related BaAl₂Si₂ structure (α -BaCu₂S₂ type) for Ba atoms (Fig. 4a; $4^46^26^{182}$). With two 8-rings, the E_{18} cage in EuGa₂Ge₄ (and BaAl₂Si₂) is

Atomic coordinates and displacement parameters (in Å ²) fo	or EuGa ₂ Ge ₄
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Atom	Position	x	у	Z	U_{11}	U_{22}	U ₃₃	U_{12}	U_{13}	U_{23}
Eu(1)	4c	0	0.29127(6)	1/4	0.0109(4)	0.0189(3)	0.0257(4)	0	0	0
$E(1)^{a}$	8 <i>f</i>	0	0.24449(8)	0.55086(7)	0.0101(5)	0.0101(4)	0.0168(5)	0	0	-0.0027(3)
$E(2)^{a}$	8 <i>f</i>	0	0.56887(7)	0.34457(7)	0.0091(5)	0.0092(4)	0.0117(4)	0	0	-0.0006(3)
$E(3)^{\mathrm{a}}$	8 <i>f</i>	0	0.02700(8)	0.59225(7)	0.0084(5)	0.0110(4)	0.0161(5)	0	0	0.0027(3)

The anisotropic displacement factor was taken as $2\pi^2 [h^2 a^{*2} U_{11} + \cdots + 2klb^* c^* U_{23}]$.

^a E = 1/3Ga + 2/3Ge.

Table 2



Fig. 3. Crystal structure of $EuGa_2Ge_4$ showing the connectivity of the *E* atoms and the packing of the $Eu@E_{18}$ polyhedra. The -E1-E1- zigzag chains (along the short *a*-axis) and the *E*2–*E*2 and *E*3–*E*3 bonds (parallel and nearly parallel to the *c*-axis) form a 3D network E_{24} , E=(Ga,Ge). This is built of the -E-E- zigzag chains parallel to [100] and of the puckered 2D nets of 6-rings in *boat* and *chair* conformation parallel to (010). The **A** and **B** layers in the network are discussed in text (see also Fig. 5).



Fig. 4. Environment of the cations in $BaAl_2Si_2$, face symbol of the polyhedron $4^46^38^2$ (a), in $EuGa_2Ge_4$, 6^58^2 (b), and in $Ba_8Ga_{16}Ge_{30}$, $5^{12}6^2$ for Ba2 (c). All the polyhedron's edges in (c) represent covalent E-E bonds. In (a) and (b), there are some 'broken' bonds (represented by thin lines) and puckered hexagonal faces.

relatively open as compared to the E_{24} cage $(5^{12}6^2)$ in the clathrate-I structures, e.g. in Ba₈Ga₁₆Ge₃₀ [10] (Fig. 4c).

The E-E bond lengths in EuGa₂Ge₄ (2.475–2.513 Å) are similar to those observed for the clathrate-I compounds



Fig. 5. Relationship between the crystal structures of BaAl₂Si₂ (a), EuGa₂Ge₄ (b) and CsAlSi₅O₁₂ (c). The **A** and **B** layers (cf. Fig. 3) are labelled. The BaAl₂Si₂ structure can be obtained from EuGa₂Ge₄ by shifting the **B**'' blocks (by 1/2, -1/4, 1/10) and joining them. The E_{24} -network in EuGa₂Ge₄ is equivalent to the $(EO_{4/2})_{24}$ -framework in the CsAlSi₅O₁₂ zeolite.

 $Eu_8Ga_{16}Ge_{30}$ [1,9] and $Ba_8Ga_{16}Ge_{30}$ [10]. The notation of the clathrate structure types I-VII is taken from [11]. There are only slight differences among the average distances d(E-E) in the environment of E1, E2 and E3 (2.493–2.497 Å, Table 3). The pairs of E2 and E3 atoms form E2-E2 and E3-E3 dumbbells, which are further connected together with -E1-E1- zigzag chains (parallel to [100]) to a three-dimensionally infinite (3D) network. This characteristic 3D network E_{24} of 4-fold bonded (4b)E atoms (Figs. 3 and 5b) exhibits 5-, 6-, and 8-rings (there are chair and boat 6-rings in the network). Part of this framework are puckered 2D nets of boat and chair 6-rings parallel to the (010) plane. The puckered 8-rings form channels along the short [100] axis which are further stacked to form thick 2D layers (**B** type in Fig. 3) parallel to the (001) plane. The Eu atoms are located within these channels. The thick **B** layers are separated by thin **A** layers made of parallel stacked 5-ring tubes. The A layers are made only of (Ga,Ge) atoms. The stacking sequence of the 2D layers in the structure of $EuGa_2Ge_4$ is ... ABAB'..., where the \mathbf{B}' layer is displaced with respect to \mathbf{B} (along the *a*-axis by 1/2,0,0) and the A layer is derived from the A layer by reflection.

The networks of four-bonded E atoms characterize the structure of $EuGa_2Ge_4$ (ratio Eu:E=1:6) as well as that of clathrates and germanium. The structural relationship is demonstrated in Fig. 6 which shows a fragment of the germanium structure in a projection nearly along [110] (Fig. 6a) and one A layer of $EuGa_2Ge_4$ viewed nearly along [100] (Fig. 6b). The A layer of (Ga,Ge) atoms is merely a reconstructed fragment of the germanium structure (compare dashed regions in Fig. 6a,b). The reconstruction is realized using the same connectivity of the (4b)Enodes and maintaining the lattice periodicity along $[110]_{\text{Ge}}/[100]_{\text{EuGa}_2\text{Ge}_4}$: $a(\text{EuGa}_2\text{Ge}_4) \approx a(\text{Ge})/\sqrt{2}$. The polyhedral pore E_8 (5⁴) in the clathrate structure of Ba₈Ga₁₆Sn₃₀ (clathrate-VIII) [10] can be derived from the E_{10} pore in germanium (6⁴), using the E_9 pore in $EuGa_2Ge_4$ (5²6²) as an intermediate stage, by breaking some bonds and creating new ones in such a way that some chair 6-rings transform into puckered 5-rings and boat 6-rings (Fig. 6c-e).

The literature search revealed that the characteristic E_{24} network of $EuGa_2Ge_4$ with circuit symbol $(5^{4}68)_{1}(5^{3}6^{3})_{1}(5^{2}6^{3}8)_{1}$ (Wells notation) has an analogue among the zeolites. By bridging each E-E bond of the E_{24} framework of $EuGa_2Ge_4$ by oxygen atoms (E–O–E, Fig. 5c) the (ideal) structure of the compound $CsAlSi_5O_{12}$ [12] can be obtained: Eu[Ga₂Ge₄ \square_{12}]=Cs[AlSi₆O₁₂]. Another structure, namely BaAl₂Si₂ (BaCu₂S₂ type; Fig. 5a) can be derived from that of $EuGa_2Ge_4$ by shifting the **B**" layers (by 1/2, -1/4, 1/10) and stacking to an distorted E_{16} framework of 4-fold (4b)E atoms with stacking sequence \dots **BB**["] \dots In this way, EuGa₂Ge₄ can be described as an intergrowth structure of alternatively stacked layers of



Fig. 6. Comparison between the diamond-type structure of germanium (a) and the characteristic puckered double layer in the EuGa₂Ge₄ structure (b). In (a) and (b), equivalent building units are dashed. Derivation of the $[5^4]$ polyhedral E_8 pore (e) in the Ba₈Ga₁₆Sn₃₀ structure, starting from a $[6^4]$ polyhedral E_{10} pore in the germanium structure (c) and passing through the intermediate $[5^26^2]$ polyhedral E_9 pore in EuGa₂Ge₄ (d). All the structures contain four-connected nets with *E* atoms at the nodes, E =Ge, (Ga,Sn), (Ga, Ge).

 $BaAl_2Si_2$ (type **B**) and layers of a reconstructed diamond-type structure (e.g. germanium, layer type **A**).

Despite the topological similarity of the E_{24} framework in EuGa₂Ge₄ and of the zeolites, the 8-ring channels in EuGa₂Ge₄ are relatively narrow (the *E*-*E* bonds are shorter than the *E*-O-*E* bridges), and the Eu atoms are 'well protected'. Indeed, the phase is stable in humid air at room temperature, and the samples can even be polished without protective atmosphere. This means that the Eu atoms are really trapped in the E_{18} cages. On the other hand, the cages are more 'open' in comparison with type-I and -II clathrates among the silicides, germanides or stannides [10,13,14]. Therefore, it is more appropriate to call these types of stable inorganic compounds with open covalent cages the clathrate-like compounds as opposed to the clathrates, which contain closed cages (with 5- and 6-rings) without small pores in between. The chiral clath-



Fig. 7. Temperature dependence of the electrical resistivity, $\rho(T)$, of EuGa₂Ge₄. The inset shows a close-up of the low-temperature range.

rate-IX Ba₆Ge₂₅ structure (disclosing a chiral 3D framework of condensed pentagondodecahedra with a zeolitelike 3D channel labyrinth [15]) and the clathrate-VIII Ba₈Ga₁₆Sn₃₀ structure (containing small pores in the network (Fig. 6e) and disclosing polyhedral cages with 'broken' bonds as edges [10]) can also be thought of as an intermediate between clathrates and zeolites. They are obviously located on the clathrate side because of a larger amount of closed cages in the network.

The temperature dependence of the electrical resistivity, $\rho(T)$, for EuGa₂Ge₄ is displayed in Fig. 7. Upon cooling, ρ decreases approximately linearly between 400 and 100 K, and then more steeply between 100 and 15 K. At 9 K, ρ passes over a shallow maximum and then continues to decrease linearly. With absolute values of ρ of several hundred $\mu\Omega$ cm and a residual resistance ratio (R(300) K)/R(2 K)) of only 2.4, EuGa₂Ge₄ may be classified as a poor metal. The temperature dependence of the charge carrier concentration, n(T), was extracted from the Hall effect data using a one band model (Fig. 8). The fact that the field dependence of the Hall resistivity $\rho_{\rm H}(B)$ is linear in the entire temperature range (curves at 10 and 300 K are shown in the inset of Fig. 8) indicates that a one band model provides a good description of the data. The negative sign of $\rho_{\rm H}(B)$ is in agreement with the charge carriers being electron-like. The absolute value of the carrier concentration is quite low and the temperature dependence is very weak. Thus, the temperature dependence of the resistivity is mainly due to a temperature dependence of the mobility, which increases from approximately 50 cm^2/Vs at room temperature to 120 cm^2/Vs at 10 K. The maximum of ρ at 9 K marks the onset of magnetic ordering, as is confirmed by the magnetic susceptibility measurements (Fig. 9). Between 100 and 400 K, the data are well described by a simple Curie fit with an effective magnetic moment of approximately 8 μ_B per Eu



Fig. 8. Temperature dependence of the charge-carrier concentration, n(T), of EuGa₂Ge₄. The inset shows the magnetic field dependence of the Hall resistivity, $\rho_{\rm H}(B)$.



Fig. 9. Inverse of the magnetic susceptibility χ versus temperature *T* in the field of 500 Oe (\bullet , experimental data; —, calculated values according to the Curie–Weiss law with $\mu = 8 \mu_{\rm B}/{\rm Eu}$). The inset shows $\chi(T)$ at low temperatures.

atom, in good agreement with the moment of a free Eu⁺² ion (7.94 $\mu_{\rm B}$ /Eu). The maximum at 9 K and the weak decrease of χ at lower temperatures (inset of Fig. 9) indicate that EuGa₂Ge₄ orders antiferromagnetically ($T_{\rm N} =$ 9 K) and therefore may be classified as a local moment antiferromagnet.

Considering the magnetic susceptibility data and assuming all E-E bonds in the E_{24} framework to be single bonds, EuGa₂Ge₄ should be a charge balanced Zintl phase: Eu²⁺[(4b)Ga¹⁻]₂[(4b)Ge⁰]₄. However, the electrical transport measurements show that it has a metal-like behaviour with a very low concentration of the charge carriers. Similar results have been observed for the clathrate-I compounds Sr₈Ga₁₆Ge₃₀ and Ba₈Ga₁₆Ge₃₀ [16,17].

To analyze this situation, quantum chemical calculations were performed by means of the TB-LMTO method [18]. One of the possible ordering models in the space group $P2_12_12_1$ was used for calculation purposes (see Fig. 10) (compare Fig. 10a and Fig. 3). The chemical bonding was analysed with the Electron-Localization-Function (ELF [19]). The maxima of both, total ELF and ELF for valence electrons (ELFV), are located on the Ga-Ge or Ge-Ge bonds of the 3D network (Fig. 10b,c). Slight displacements of some maxima from the direct contacts are caused by a tension in the covalently bonded network. This agrees well with the bond angles from the crystallographic data, which are remarkably different $(\pm 10^{\circ})$ from the tetrahedral value. The integration of the electron density in the basins of each maximum gives values close to 2 (1.7-2.2 electrons, program BASIN [20], details of the procedures are described elsewhere [21]). This corresponds well with the conventional electron count according to the Zintl concept, whereby the small deviations from the ideal value of 2 could also find an explanation in the bond tension in the 3D network. The calculated density of states for the model (see Fig. 10) shows a relatively small DOS value at the



Fig. 10. Ordering model¹ for $EuGa_2Ge_4$ (b) and isosurfaces of ELF=0.6 (a) and ELFV=0.75 (c). The scale for ELF and ELFV (upper part) ranges from 0 (blue) to 1 (white).



Fig. 11. Calculated electronic density of states (DOS) for the ordering model shown in the legend to Fig. 10 of $EuGa_2Ge_4$.

Fermi level (1.75 states per unit cell, Fig. 11) which is in agreement with the high resistivity and low charge-carrier density derived from the Hall effect measurements. This value contains mainly contributions of the *s*-electrons of Eu as well as of the valence electrons of Ga and Ge. The *f*-electrons of europium are well localized (cf. value of the effective magnetic moment).

4. Concluding remarks

During the preparation of this work, a paper about the structure, conductivity and thermopower of $EuGa_2Ge_4$ [22] appeared. In contrast to our findings, the authors found primarily holes as charge carriers from the positive sign of the thermopower. This result agrees with the occurrence of the homogeneity range we determined: a hole conductivity can be expected on the gallium-rich side of the homogeneity range. The single crystals of $EuGa_2Ge_4$ investigated in [22] were grown from a gallium-rich flux (x > 0).

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¹Space group $P2_12_12_1$; a = 4.1571 Å, b = 11.268 Å, c = 13.155 Å; Eu in 4(*a*) x y z, x = 1/4, y = 0.79127, z = 1/4; Gel1 in 4(*a*), x = 1/4, y = 0.25551, z = 0.05086; Gel2 in 4(*a*), x = 1/4, y = 0.25551, z = 0.44914; Gel1 in 4(*a*), x = 1/4, y = 0.06887, z = 0.34457; Gal2 in 4(*a*), x = 1/4, y = 0.06887, z = 0.15543; Gel1 in 4(*a*), x = 1/4, y = 0.47300, z = 0.40775; Gal2 in 4(*a*), x = 1/4, y = 0.47300, z = 0.09225. The sites Gel1 and Gel2 correspond to the site *E*1 in the space group *Cmcm*, Gel1 and Gal1 correspond to *E*2, and Gel1 and Gal2 correspond to *E*3.

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