The Zintl Phase Eu₂Si

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Received November 22nd, 2001.

Abstract. The Zintl phase Eu₂Si was synthesized from elemental europium and silicon in a sealed tantalum tube in a high-frequency furnace at 1270 K and subsequent annealing at 970 K. Investigation of the sample by X-ray powder and single crystal techniques revealed: Co₂Si (*anti*-PbCl₂) type, space group *Pnma*, a = 783.0(1), b = 504.71(9), c = 937.8(1) pm, wR2 = 0.1193, 459 F² values and 20 variables. The structure contains two europium and one silicon site. ¹⁵¹Eu Mössbauer spectroscopic data show a single signal at an

isomer shift of -9.63(3) mm/s, compatible with divalent europium. Within the Zintl concept electron counting can be written as $(2Eu^{2+})^{4+}Si^{4-}$, in agreement with the absence of Si-Si bonding. Each silicon atom has nine europium neighbors in the form of a tri-capped trigonal prism. The silicon coordinations of the Zintl phases Eu_2Si , Eu_5Si_3 , EuSi, and $EuSi_2$ are compared.

Keywords: Zintl Phases; Crystal structure; Europium

Die Zintl-Phase Eu₂Si

Inhaltsübersicht. Die Zintl-Phase Eu₂Si wurde aus elementarem Europium und Silicium in einer verschweißten Tantalampulle im Hochfrequenzofen bei 1270 K synthetisiert und anschließend bei 970 K getempert. Untersuchungen der Probe mit Röntgen-Pulverund Einkristalldaten ergab: Co₂Si (*anti*-PbCl₂)-Typ, Raumgruppe *Pnma, a* = 783,0(1); *b* = 504,71(9); *c* = 937,8(1) pm; wR2 = 0,1193; 459 F²-Werte und 20 variable Parameter. Die Struktur enthält zwei kristallographisch unterschiedliche Europiumplätze.

Introduction

The binary system europium-silicon is so far characterized by the silicides Eu₅Si₃ (Cr₅B₃ type, space group *I4/mcm*) [1, 2], EuSi (CrB type, space group *Cmcm*) [3–8], and EuSi₂ (α -ThSi₂ type, space group *I4₁/amd*) [5–14]. These silicides contain purely divalent europium and chemical bonding can be rationalized by the Zintl-Klemm concept: (5Eu²⁺)¹⁰⁺[Si₂⁶⁻][Si⁴⁻], Eu²⁺Si²⁻ and Eu²⁺[2Si⁻]. According to the electron count the Si⁴⁻ anions are isolated, Si²⁻ forms zig-zag chains, Si⁻ a three-dimensional network with three-connected silicon and the Si₂⁶⁻ dumb-bells are isoelectronic with chlorine. During a systematic study of the EuX (X = Si, Ge, Sn) tetrelides *Loewenhaupt* [5] reported on a new binary silicide with the approximate composition ~Eu₄Si₅ with a yet unknown structure. This phase, however, has not been reported in other studies.

Institut für Anorganische und Analytische Chemie Westfälische Wilhelms-Universität Münster Wilhelm-Klemm-Straße 8 D-48149 Münster Fax: (+49)-(0)251-83-36002 E-mail: pottgen@uni-muenster.de ¹⁵¹Eu Mössbauer-spektroskopische Daten zeigen nur ein Signal bei einer Isomerieverschiebung von -9.63(3) mm/s, was mit zweiwertigem Europium kompatibel ist. Im Rahmen des Zintl-Konzepts kann die Formel als $(2Eu^{2+})^{4+}Si^{4-}$ geschrieben werden, in Übereinstimmung mit der Abwesenheit von Si-Si-Bindungen. Jedes Siliciumatom hat neun Europiumnachbarn in Form eines dreifach überkappten trigonalen Prismas. Die Siliciumkoordination in den Zintl-Phasen Eu₂Si, Eu₅Si₃, EuSi, und EuSi₂ wird verglichen.

We have recently started a more systematic study on ternary rare earth metal iridium silicides [15, 16]. Studies in the europium based system revealed a presumably new compound. Investigation by X-ray powder and single crystal data indeed revealed that it is a binary silicide. Herein we report on the synthesis and structure refinement of the Zintl phase Eu_2Si , the so far most metal-rich phase in the binary system europium-silicon.

Experimental

Starting materials for the preparation of Eu₂Si were sublimed pieces of europium (Johnson-Matthey) and silicon lumps (Wacker) both with stated purities better than 99.9 %. The moisture sensitive europium pieces were kept in Schlenk tubes under argon prior to the reactions. The argon (Messer-Griesheim 4.8) was purified by titanium sponge (870 K), molecular sieves, and silica gel. Small europium pieces were mixed with silicon powder in the ideal 2:1 atomic ratio (total weight ca. 800 mg) and sealed in a small tantalum tube (volume ca. 1 cm³) under an argon pressure of about 800 mbar. Details concerning the arc-welding equipment are given elsewhere [17].

The tube was subsequently placed in a water-cooled sample chamber [18] of a high-frequency furnace (Hüttinger TIG 1.5/300) and first heated under flowing argon at about 1270 K for one minute. The reaction between europium and silicon was indirectly visible

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Eu ₂ Si
332.01 g/mol
a = 783.0(1) pm
b = 504.71(9) pm
c = 937.8(1) pm
$V = 0.3706 \text{ nm}^3$
Pnma (No. 62)
Z = 4
5.95 g/cm ³
$10 \times 10 \times 40 \ \mu m^3$
1.49
33.6 mm^{-1}
560
50 mm
20 min
0-160.5° / 1.5°
11-13
3° to 28°
$\pm 10, \pm 5, \pm 12$
2623
$459 (R_{int} = 0.1383)$
273 ($R_{sigma} = 0.1288$)
459 / 20
0.872
R1 = 0.0487, wR2 = 0.1099
R1 = 0.0822, wR2 = 0.1193
0.009(1)
2.27 and $-2.24 \text{ e/}\text{Å}^3$

Table 1 Crystal data and structure refinement for Eu_2Si .

through a heat flash within the sample chamber. The tube was subsequently annealed at 970 K for another hour. After the annealing procedure the silvery sample could easily be separated from the tube. Eu_2Si is moisture sensitive. The sample was kept in Schlenk tubes under dry argon.

Eu₂Si was characterized through its powder diffractogram (Stoe Stadi P) using CuK α_1 radiation and silicon (a = 543.07 pm) as an external standard. The lattice parameters (Table 1) were obtained from a least-squares fit of the powder data. The correct indexing was ensured by an intensity calculation [19] taking the atomic positions from the structure refinement. The lattice parameters determined from the powder and the single crystal agreed well. In all powder patterns a small amount of Eu₂Si₃ was observed. The ratio Eu₂Si/Eu₅Si₃ was estimated to about 90/10. Most likely, a small amount of europium distilled to the colder part of the tantalum tube, leading to the europium poorer phase. This behavior was also observed for samples with the starting composition 2.5Eu/1Si.

A freshly crushed surface of the sample and the composition were studied in a scanning electron microscope (*LEICA* 420 I) using SiO_2 and EuF_3 as standards. A typical cleaved surface (Figure 1) shows lamellar crystal growth. Energy dispersive analyses of the larger platelets revealed compositions very close to the ideal one (Eu₂Si).

An irregularly shaped single crystal of Eu_2Si was isolated from the annealed sample by mechanical fragmentation and examined by Laue photographs on a Buerger camera in order to establish suitability for intensity data collection. Single crystal intensity data were collected at room temperature by use of a Stoe image plate system (IPDS) with graphite monochromatized MoK α radiation (71.073 pm) in oscillation mode. A numerical absorption correction was applied to the data.

Isotypism of Eu₂Si with the orthorhombic PbCl₂ type [20] was already evident from the powder data. Space group *Pnma* was found to be correct during the structure refinement. All relevant crystallo-



Fig. 1 Scanning electron micrograph of a freshly crushed surface of a Eu₂Si fragment.

Table 2 Atomic coordinates and anisotropic displacement parameters (pm²) for Eu₂Si. All atoms are situated on the Wyckoff position 4*c* (x 1/4 *z*) of space group *Pnma*. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. U₂₃ = U₁₂ = 0.

Atom	X	Ζ	U11	U ₂₂	U ₃₃	U ₁₃	U _{eq}	
Eu1	0.9810(2)	0.6806(2)	225(10)	258(12)	247(8)	-4(7)	243(6)	
Eu2	0.3439(2)	0.4216(2)	284(10)	176(11)	205(8)	3(7)	222(6)	
Si	0.247(1)	0.1000(9)	253(44)	147(53)	222(42)	-14(34)	207(18)	

Table 3 Interatomic distances (pm), calculated with the lattice parameters taken from X-ray powder data of Eu_2Si . All distances shorter than 504 pm (Eu-Eu), 445 pm (Eu-Si), and 482 pm (Si–Si) are listed. Standard deviations are given in parentheses.

Eu1:	1 2 2 2 1 1 2 2 2 1 2 2	Si Eu2 Eu2 Si Eu2 Eu2 Eu2 Eu1 Eu1	320.5(9) 338.6(6) 365.4(2) 370.9(2) 371.5(7) 373.8(2) 388.3(2) 412.6(1) 423.4(3)	Eu2:	1 2 1 2 1 2 1 2 1	Si Si Eu1 Eu1 Eu2 Eu1	310.9(9) 311.1(5) 316.5(9) 365.4(2) 370.9(2) 373.8(2) 380.9(3) 388.3(2)	Si:	1 2 1 2 2	Eu2 Eu2 Eu1 Eu1 Eu1	310.9(9) 311.1(5) 316.5(9) 320.5(9) 338.6(6) 371.5(7)
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graphic data and experimental details for the data collection are listed in Table 1.

The starting atomic parameters were deduced from an automatic interpretation of direct methods with SHELXS-97 [21] and the structure was successfully refined using SHELXL-97 (full-matrix least-squares on F^2) [22] with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in a separate series of least-squares cycles. All sites were fully occupied within two standard deviations and in the final cycles the ideal occupancies were assumed again. A final difference Fourier syntheses revealed no significant residual peaks (see Table 1). The positional parameters and



Fig. 2 Projection of the Eu₂Si structure onto the xz plane. All atoms lie on mirror planes at y = 1/4 (thin lines) and y = 3/4 (thick lines), respectively. The europium and silicon atoms are drawn as open and filled circles. The trigonal prisms around the silicon atoms are emphasized.

interatomic distances are listed in Tables 2 and 3. Listings of the observed and calculated structure factors are available¹⁾.

The 21.53 keV transition of ¹⁵¹Eu with an activity of 130 MBq (2 % of the total activity of a ¹⁵¹Sm:EuF₃ source) was used for the Mössbauer spectroscopic experiments. The measurements were performed with a commercial helium bath cryostat. The temperature of the absorber was kept at 78 K. The source was kept at room temperature. The sample was placed within a thin-walled PVC container at a thickness corresponding to about 10 mg Eu/cm².

Results and Discussion

The Zintl phase Eu₂Si is the so far most metal-rich compound in the binary system Eu/Si. Eu₂Si adopts the orthorhombic *anti*-PbCl₂ [20] (Co₂Si [23]) type structure. This structure also occurs for the isotypic europium and ytterbium based Zintl phases Eu₂Sn [24] and Yb₂Sn [25], and the alkaline earth (*AE*) metal based compounds AE_2X (*AE* = Ca, Sr, Ba; *X* = Si, Ge, Sn, Pb) [26–35].

A projection of the Eu₂Si structure onto the xz plane is presented in Figure 2. The silicon atoms have a slightly distorted trigonal prismatic europium coordination (Figure 3). The coordination sphere is augmented by three further europium atoms which are situated on the rectangular faces of these prisms (tri-capped trigonal prism). Within the x direction the prisms are condensed via common edges while they share common triangular faces along the y direction.

The various Eu-Eu interactions range from 365 to 388 pm. In view of the Eu-Eu distances of 397 pm in elemental *bcc* europium [36] and the electron transfer from europium to silicon, these contacts may only be considered as weakly bonding. The longer Eu1-Eu1 contacts (413 and 423 pm) may not be considered as bonding, however, from a geometrical point of view, these additional Eu1 atoms still



Fig. 3 Coordination of the silicon atoms in the Zintl phases Eu_2Si , Eu_5Si_3 , EuSi, and $EuSi_2$. The europium and silicon atoms are drawn as open and filled circles, respectively. Atom designations and relevant distances (in units of pm) are indicated.

belong to the coordination sphere of Eu1. Both europium sites have three and four silicon neighbors, respectively, at Eu-Si distances ranging from 311 to 339 pm, comparable to the sum of the atomic radii of 321 pm [37]. Two further silicon neighbors occur at the much longer Eu1–Si distance of 372 pm for the Eu1 atoms. Also in this case these atoms belong to the Eu1 coordination sphere.

Although the sample consisted of a mixture of approximately 90 % Eu₂Si and 10 % Eu₅Si₃ we recorded a ¹⁵¹Eu Mössbauer spectrum at 78 K (Figure 4) in order to get information on the valence state of the europium atoms. We observed a single signal at an isomer shift δ = -9.63(3) mm/s with an experimental line width of $\Gamma =$ 2.7(1) mm/s and an electric field gradient ΔE_{O} = 9.0(6) mm/s. Also an asymmetry parameter $\eta = 0.7(1)$ was refined. Our recent susceptibility data of Eu₅Si₃ [1] revealed divalent europium. In view of the absence of a signal around 0 mm/s we can assume purely divalent europium in Eu₂Si. The experimentally observed line width of 2.7(1) mm/s is slightly larger than the usual line width of 2.3 mm/s for europium. This slight enlargement, and most likely also the asymmetry parameter, certainly account for the mixture Eu₂Si / Eu₅Si₃. Based on the ¹⁵¹Eu Mössbauer spectroscopic data we can assume that the europium atoms have transferred two valence electrons to the silicon atoms. Electron counting can then be written as $(2Eu^{2+})^{4+}Si^{4-}$ classifying Eu₂Si as a Zintl phase.

In Figure 3 we compare the silicon coordinations of the various binary Zintl phases in the europium-silicon sys-

¹⁾ Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-412248.



Fig. 4 Experimental and simulated ¹⁵¹Eu Mössbauer spectrum of a Eu₂Si/Eu₅Si₃ mixture at 78 K.

tem. For the Si1 atoms of Eu_5Si_3 and the silicon atoms in Eu_2Si , EuSi, and $EuSi_2$ we observe the same coordination type, i.e. tri-capped trigonal prims. In all cases the trigonal prisms are formed by the europium atoms. Depending on the composition of the silicide, the atoms on the rectangular faces are europium atoms for the most metal-rich silicide (Eu_2Si) and silicon atoms for the silicon-rich silicide ($EuSi_2$). In Eu_5Si_3 [1, 2] and EuSi [3–8] we observe europium and silicon atoms. The Si2 atoms in Eu_5Si_3 have the higher coordination number 10 in the form of a capped square antiprism. Due to the higher coordination number we observe larger Eu-Si distances, i.e. 333 and 383 pm.

Summing up, we have prepared the Zintl phase Eu₂Si with *anti*-PbCl₂ type structure. ¹⁵¹Eu Mössbauer spectroscopic data revealed divalent europium leading to an electron count $(2Eu^{2+})^{4+}Si^{4-}$. In the corresponding germanium system we already got powder samples of Eu₂Ge / Eu₅Ge₃ mixtures. These investigations are still in progress.

We are grateful to *Dr. P. Mayer* (Department Chemie, LMU München) for the single crystal data collection and to *Hans-Jürgen Göcke* for the work at the electron microscope. This work was financially supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft. R. M. is indebted to the Alexander von Humboldt Foundation for a research grant.

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