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Barrelane-like germanium clusters in Eu_3Ge_5: Crystal structure, chemical bonding and physical properties

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Dedicated to the occasion of the 75th birthday of Prof. Hans Georg von Schnering

Abstract

Formation and crystal structure of the binary germanide Eu_3Ge_5 were investigated in detail. The compound forms peritectically at 1008 °C and does not undergo any phase transition down to room temperature. The crystal structure was determined first from X-ray powder diffraction data and was later confirmed by single-crystal X-ray diffraction: structure type Pu_3Pd_5, space group *Cmcm* (no. 63), $a = 9.7675(4)$ Å, $b = 7.9681(3)$ Å, $c = 9.8562(3)$ Å. The main building blocks are Ge_5^{6-} cluster anions surrounded by Eu^{2+} cations. The nearly tetragonal-pyramidal shape is suggested by the interatomic distances. Contrary to that, the bonding analysis with the electron localization function (ELF) reveals only two- and three-bonded germanium atoms forming a strongly distorted [1.1.1]-barrelane-like cluster. Despite the formal electron deficiency, compared to the barrelane C_5H_8, the electron counting in the cluster anion and its conformation cannot be interpreted applying the Wade's rules. In accordance with the calculated electronic density of states, Eu_3Ge_5 shows a metal-like temperature dependence of the electrical resistivity with a sharp change of $\rho(T)$ slope at the Néel point. Above the Néel point the inverse magnetic susceptibility reveals Curie–Weiss behavior with an effective moment of 8.11 μ_B (Eu^{2+}, $4f^7$ configuration) in agreement with the analysis of the chemical bonding. The $4f^7$ electronic configuration of europium is confirmed by Eu-L_{III} X-ray absorption spectroscopy.

Keywords: Europium germanide; Crystal structure; Magnetic behavior; Electrical resistivity; Bonding analysis; Electron localization function

1. Introduction

According to the literature data, the binary system europium–germanium seems to be rather simple compared to other rare-earth metals. The investigation of the phase diagram [1] shows the existence of five intermetallic compounds: Eu_3Ge, EuGe, Eu_2Ge_3, Eu_3Ge_5 and $EuGe_2$. The monogermanide EuGe adopts the crystal structure of the α-TlI (CrB) type, space group *Cmcm*, Pearson symbol *oC*8 [2–4]. The digermanide $EuGe_2$ was suggested to undergo a phase transition at 810 °C [1]. Its crystal structure belongs to an own structure type (space group $P\bar{3}m1$, Pearson symbol *hP*3) which has some similarity to CdI_2 [5]. This was confirmed in Ref. [6], but no phase transition was found. Eu_3Ge_5 was suggested to form peritectically and to exist in the temperature range between 755 and 1011 °C with a phase transformation at 810 °C [1]. The crystal structure of Eu_5Ge_3 was described as belonging to the Cr_5B_3 structure type (space group $I4/mcm$, Pearson symbol *tP*32 [7,8]). An additional binary germanide Eu_2Ge with the crystal structure of the $PbCl_2$ type (space group

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Pnma, Pearson symbol *oP*12) was reported recently [9]. We suppose, that one of the two latter compounds corresponds to the previously found and structurally non-characterized phase Eu_3Ge [1]. The aim of this work is to shed more light on formation, crystal structure, transport and magnetic properties of Eu_3Ge_5, with a special emphasis on the chemical bonding.

2. Experimental

2.1. Preparation

The binary germanide Eu_3Ge_5 was observed primarily as by-product together with EuGe in a sample with the nominal composition Eu_3Ge_4. This sample was prepared by heating the elements in a sealed niobium container for 4 h up to 840 °C, was then kept for 1 h at this temperature and finally cooled down to room temperature within 17 h. After re-grinding and compacting, the powder was additionally annealed at 880 °C for 24 h. A single crystal (called hereafter II) was obtained by mechanical fragmentation of the sample after annealing.

For a systematic investigation of the formation conditions, several samples with the nominal compositions Eu_xGe_{100-x} ($x = 33.3$, 35.0, 36.5, 37.5, 38.0, 38.5, 42.0 and 50.0) were prepared in sealed Ta tubes applying high frequency (HF) furnace using Eu (99.9 mass%, Lamprecht, distilled in vacuum prior to use) and Ge (99.9999 mass%, ChemPur) as starting components. All handlings were performed in a glove-box system in highly purified argon with monitored oxygen and H_2O levels lower than 0.1 ppm. After the HF heating the Ta crucibles were sealed in evacuated quartz tubes and annealed at several temperatures between 780 and 1000 °C for 3–4 weeks, respectively, to check possible phase transitions as reported in the literature. Finally, all samples were quenched by submerging the quartz tubes in cold water.

Well-crystallized specimens of Eu_3Ge_5 were obtained by using K-Ge flux. A starting mixture of elemental K, Eu and Ge in an atomic ratio of 2:1:2 (with a total mass of about 1.5 g) was sealed into a tantalum container under purified argon atmosphere. The container was heated up to 960 °C within 10 h, kept at this temperature for the next 5 h and slowly cooled down (10 °C/h) to room temperature. After heat treatment the sample contained numerous prism-like crystals embedded into a potassium matrix. X-ray powder diffraction pattern revealed reflections of Eu_3Ge_5 and K_4Ge_4. Excess of potassium monogermanide was removed by washing with ethanol. A single crystal (called hereafter I) was selected from the residual after washing. The crystals of Eu_3Ge_5 appeared to be stable against air and moisture for several days.

2.2. Characterization

Phase identification was performed by room temperature X-ray powder diffraction by the Guinier technique (Huber Image Plate Camera G670, radiation, Co$K\alpha_1$, $\lambda = 1.78890$ Å or Cu$K\alpha_1$, $\lambda = 1.54056$ Å $5° \leqslant 2\theta \leqslant 100°$, step width 0.005°, 6 × 30 min scans) using LaB_6 ($a = 4.15962$ Å) or Ge ($a = 5.65735$ Å) as internal standard. For the X-ray examination the powders were sealed between two polyimide foils as a general prevention against oxidation.

Differential thermal analysis (DTA) was performed in alumina or niobium crucibles in a protective argon atmosphere (Netzsch STA 409, heating rate 20 K/min). Differential scanning calorimetry (DSC) investigations were done in a Netzsch DSC 404C apparatus in sealed niobium crucibles. The peak onset temperature values were used for further interpretation.

Details of the single-crystal X-ray diffraction experiments are summarized in Table 1. Two different crystals (I and II, cf. *Preparation*) were investigated. All crystallographic calculations were made with the program packages WinCSD [10] and SHELXL [11].

The dc magnetization was measured in the temperature range 1.8–400 K in applied magnetic fields up to 7 T using a SQUID magnetometer MPMS XL-7 (Quantum Design). A dc Faraday pendulum magnetometer SUS-10 (A. Paar, Graz, Austria) has been applied for measurements at elevated temperatures (300–1125 K) in external fields up to 1.3 T.

Table 1
Crystallographic information, data collection and handling for Eu_3Ge_5

Crystal	I (twin)	II (non-twin)
Crystal size, mm^3	0.040 × 0.050 × 0.055	0.080 × 0.120 × 0.120
Space group	*Cmcm* (no. 63)	
Formula units/cell, *Z*	4	
Unit cell parameters[a]		
a (Å)	9.7675(4)[a]	9.796(1)[b]
b (Å)	7.9681(3)[a]	7.971(1)[b]
c (Å)	9.8562(3)[a]	9.851(1)[b]
V (Å^3)	767.09(9)[a]	767.1(1)[b]
Calc. density (g/cm^3)	7.09	7.09
Diffractometer	Rigaku AFC7	Bruker Smart Platform
Detector	Mercury CCD	CCD
Radiation, λ	Mo$K\alpha$, 0.71073 Å	Mo$K\alpha$, 0.71073 Å
Absorpt. coeff, μ (mm^{-1})	43.3	43.3
Scans, step	φ, ω, 0.6°	Ω
2θ range up to	62.4°	68°
Ranges for *h, k, l*	$-13 \leqslant h \leqslant 13$	$-14 \leqslant h \leqslant 14$
	$-10 \leqslant k \leqslant 11$	$-12 \leqslant k \leqslant 12$
	$-14 \leqslant l \leqslant 14$	$-15 \leqslant l \leqslant 15$
$N(hkl)$ measured	3687	5844
$N(hkl)$ used for refinement[c]	3310	825
Refined parameters	28	27
$R(F)$, w$R(F^2)$[d]	0.028, 0.072	0.030, 0.076
Extinction parameter	0.0022(1)	0.00046(7)
Residual peaks (e/Å^3)	−2.03/3.42	−1.99/2.61

[a]Powder diffraction data.
[b]Single crystal data.
[c]For a refinement of a twin, the data set was not merged.
[d]The residuals are defined as follows: $R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; w$R(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]\}^{1/2}$.