

Zinc-deficiency in intermetallics with the NaZn_{13} type Re-determination of the crystal structure and physical properties of EuZn_{13-x} ($x = 0.25(1)$)

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Abstract

Reported are the synthesis from zinc flux, crystal structure re-determination from single-crystal X-ray diffraction, and magnetic properties of EuZn_{13-x} ($x = 0.25(1)$). It crystallizes in the cubic NaZn_{13} type (Pearson's symbol $cF112$, space group $Fm\bar{3}c$, No. 226) with unit cell parameter $a = 12.1651(17)$ Å, determined at 120 K. The structure has two crystallographically unique zinc sites, one of which is partially occupied. This finding is consistent with previous experimental and theoretical work on related Zn-rich networks that suggests an optimal electron count of 27 electrons per formula unit. Temperature-dependent magnetization measurements confirm that the Eu ions in $\text{EuZn}_{12.75(1)}$ are divalent as evidenced from the effective magnetic moment of $7.98\mu_B$.

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1. Introduction

In recent years, intermetallic compounds crystallizing with the cubic NaZn_{13} structure type (or its tetragonally distorted variant, known as the $\text{Ce}_2\text{Ni}_{17}\text{Si}_9$ type) have received a lot of attention mainly due to their magnetic and thermoelectric properties [1–10]. Many new members of this family have been synthesized and their structures and properties studied, including BaLi_7Al_6 [1], $\text{EuCu}_{6.5}\text{Al}_{6.5}$ [2], CeBe_{13} [4], $\text{LaFe}_{13-x}\text{Si}_x$ [5], CeNi_9Si_4 [10], among others. The nature of the metal–metal interactions and the factors that govern the stability ranges for most of the studied systems are well-understood. However, the 2006 report by Wendorff and Röhr [3] on the structures and bonding in several long-known alkali- and alkaline-earth Zn- and Cd-rich binary phases suggested that there still are unanswered questions pertaining to some ostensibly simple systems.

Intrigued by the ideas from this recent study [3], we turned our attention to the Zn-rich part of the Eu–Zn phase diagram, where EuZn_{13} with the NaZn_{13} type is listed as a line compound

[11]. We also noticed that while the structure of EuZn_{13} has already been reported from powder X-ray diffraction [12,13] and its magnetic properties studied [14], refinement of the atomic coordinates and the anisotropic displacement parameters from single-crystal work have never been carried out. The lack of such important structural information hinted at possible omissions in the current literature. This attracted our attention because of the well-known fact that the crystal chemistry of many Eu-containing intermetallics is often analogous to that of the alkaline-earth metal Sr. Such parallel is explained by the tendency of Eu to be present as Eu^{2+} with a half-filled f-shell, rather than Eu^{3+} ($4f^6$), which is typical for all the other lanthanides trivalent state [15].

Herein, we report the crystal growth and the refinement of the structure of EuZn_{13} from single-crystal X-ray diffraction. Our investigation revealed a previously overlooked partial occupancy of one of the zinc sites, which confirmed that EuZn_{13-x} ($x \approx 0.25$) is indeed a non-stoichiometric compound, just like SrZn_{13-x} ($x \approx 0.23$) [3]. The deviation from the ideal composition is driven by the electronic requirements of the cubic NaZn_{13} structure type, which needs fewer electrons for optimal bonding [1–3]. Evidently, greater framework stability in this case and in all other isomorphous alkaline-earth coun-

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terparts is achieved through the removal of a specific type of Zn atoms, which leads to lower valence electron concentration. These ideas are discussed in a broader context as well.

2. Experimental part

2.1. Synthesis

All the manipulations were done in an argon-atmosphere glove box. The elements were purchased from Alfa and were used as received: rare-earth metals (ingots, 99.9%), zinc (shot, 99.999%). Reactions were carried out either in welded Nb-ampoules or in alumina crucibles, using the flux method [16,17]. In both cases, heating of the reaction mixtures was done in evacuated fused silica tubes.

At first, crystals of EuZn_{13-x} were serendipitously obtained from a reaction of europium, bismuth and zinc intended to produce the Zn analog of the recently reported $\text{Eu}_9\text{Cd}_{4,21(1)}\text{Bi}_9$ [18]. After the structure was established by X-ray crystallography, large $\text{EuZn}_{12.75(1)}$ crystals were grown from a Zn-flux reaction loaded with the ratio $\text{Eu}:\text{Zn} = 1:18$. The mixture was heated to 850°C at a rate of $200^\circ/\text{h}$; homogenized at this temperature for 20 h, and then cooled to 550°C at a rate of $3^\circ/\text{h}$. At this temperature, an additional annealing step of 48 h was found to produce the best single-crystals. After that, the excess of molten zinc was removed by centrifugation and the crystals were isolated. They were large, irregularly shaped, and had silver-metallic luster.

Synthesis of the isostructural LaZn_{13-x} and YbZn_{13-x} , which according to the Pearson's handbook [19] are the only other lanthanide–zinc binaries with this structure, was attempted using the same technique and similar heat treatment, but proved unsuccessful. The products of these flux reactions were LaZn_{11} and YbZn_{11} instead (BaCd_{11} structure type [19]). Stoichiometric LaZn_{13} and YbZn_{13} mixtures, sealed in Nb-tubes were also tried but failed to produce the targeted compounds with the NaZn_{13} structure. These sealed-tubes reactions were heated to 950°C , quenched in water and annealed at 600°C for 168 h. The main product of these reactions were the tetragonal $\text{La}_2\text{Zn}_{17}$ and $\text{Yb}_2\text{Zn}_{17}$ phases ($\text{Th}_2\text{Zn}_{17}$ structure type [19]).

2.2. Crystallographic studies

Powder X-ray diffraction: X-ray powder diffraction patterns were taken on a Rigaku MiniFlex powder diffractometer, using nickel-filtered $\text{Cu K}\alpha$ radiation. Data were collected at room temperature in θ – θ mode ($2\theta_{\text{max}} = 85^\circ$) with a step size of 0.05° . Silicon was used as an internal standard. The data analysis was carried out with the aid of JADE [20] and GSAS [21] programs. According to the powder diffraction patterns, $\text{EuZn}_{12.75(1)}$ was obtained as a pure phase from the Zn-flux reaction and was used in the magnetic susceptibility measurements (below). Powder X-ray diffraction also confirmed that polycrystalline $\text{EuZn}_{12.75(1)}$ is stable in air for longer than 1 month.

Single-crystal X-ray diffraction: A crystal for intensity data collection was selected from the flux reaction, cut in Paratone N oil to dimensions $0.07\text{ mm} \times 0.04\text{ mm} \times 0.04\text{ mm}$ and mounted on a glass fiber. Data collection was carried out using a Bruker SMART CCD-based diffractometer at -153°C (cooling with cold nitrogen stream). A full sphere of reciprocal space data were acquired in four batch runs with scans in different ω and ϕ angles. $2\theta_{\text{max}}$ was 54.78° . The SAINT software package was used for the integration and the cell refinement [22]. Semi-empirical absorption correction based on equivalents was applied with SADABS [23]. The structure was refined by full matrix least squares methods on F^2 using SHELXL [24] and using the NaZn_{13} structure as a starting model [25]. All positions were refined with anisotropic displacement parameters. Additionally, the occupancy of each of the three sites was checked by freeing the site occupancy factor (SOF) of an individual atom while the remaining SOF's were kept fixed. This method showed that the Zn2 site (Wyckoff 8b) is underoccupied, while Zn1 and the Eu sites are fully occupied within 3σ . The occupancy for Zn2 was refined to be 75(1)%.

In the final refinement cycles, 11 parameters, including the atomic positions, thermal parameters, SOF for Zn2, and an extinction coefficient were refined against 104 structure factors. The final difference Fourier map is flat with the highest peak/deepest hole of $\pm 0.6\text{ e}^-/\text{\AA}^3$ less than 1 \AA away from Zn1. Additional details of the data collection and structure refinement are given in

Table 1

Selected single-crystal data collection and refinement parameters for $\text{EuZn}_{12.75(1)}$

Formula	$\text{EuZn}_{12.75(1)}$
Formula weight	985.43
Radiation	$\text{Mo K}\alpha$, 0.71073 \AA
Crystal system	Cubic
Space group, Z	$Fm\bar{3}c$, 8
Temperature	120 K
Unit cell parameter ^a	$12.1651(17)\text{ \AA}$
Volume	$1800.3(4)\text{ \AA}^3$
Density (ρ_{calc})	7.27 g/cm^3
θ range	3.35 – 27.39°
Absorption coefficient (μ)	40.04 mm^{-1}
Reflections collected	3001
Independent reflections, R_{int}	104, 0.057 (all data)
Final R_1 ($I > 2\sigma(I)$) ^b	0.0129
Final wR_2 ($I > 2\sigma(I)$) ^b	0.0262
Extinction coefficient	0.00035(3)
Largest peak/hole in the diff. map	0.59 – $-0.64\text{ e}^-/\text{\AA}^3$

^a The unit cell parameter obtained from room temperature powder X-ray diffraction is $a = 12.214(1)\text{ \AA}$.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, and $w = 1/[\sigma^2 F_o^2 + (0.0095P)^2]$, $P = (F_o^2 - 2F_c^2)/3$.

Table 2

Atomic coordinates and equivalent isotropic displacement parameters (U_{eq})^a for $\text{EuZn}_{12.75(1)}$

Atom	Wyckoff position	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
Eu	8a	1/4	1/4	1/4	0.0087(3)
Zn1	96i	0	0.11957(4)	0.17894(4)	0.0092(2)
Zn2 ^b	8b	0	0	0	0.0081(7)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

^b The refined site occupation factor is 0.748(7).

Table 1. Positional and equivalent isotropic displacement parameters, and relevant interatomic distances are listed in Tables 2 and 3. Further details on the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD 418399.

2.3. Magnetization measurements

Magnetization measurements (M) were carried out in a Quantum Design MPMS2 SQUID magnetometer from 5 to 290 K using an applied magnetic field (H) of 500 Oe. The polycrystalline specimen was prepared from 17 mg of single

Table 3

Selected bond distances (\AA) in $\text{EuZn}_{12.75(1)}$

Atomic pair	Distance (\AA)
Eu–Zn1 $\times 24$	3.5376(6)
Eu–Eu $\times 6$	6.0826(9)
Zn1–Zn1 $\times 2$	2.5554(8)
Zn2	2.6181(6)
Zn1 $\times 2$	2.6871(9)
Zn1 $\times 4$	2.7159(7)
Zn1	2.909(1)
Zn2–Zn1 $\times 12$	2.6181(6)

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