Magnetic Ordering in CeZnGe

Wilfried Hermes and Rainer Pöttgen

Institut für Anorganische und Analytische Chemie and
NRW Graduate School of Chemistry, Universität Münster,
Corrensstraße 30, D-48149 Münster, Germany

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

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CeZnGe crystallizes with the hexagonal YPtAs-type structure, space group P63/mmc, \(a = 430.0(2)\) pm, \(c = 1678.8(10)\) pm. A phase-pure sample was synthesized from the elements in a sealed tantalum crucible in a high-frequency furnace. Magnetic susceptibility measurements have revealed a trivalent cerium with an experimental magnetic moment of \(2.67(1) \mu_B/\text{Ce atom}\). Ferromagnetic ordering sets in at \(T_C = 4.6(2)\) K.

Key words: Intermetallics, Cerium, Magnetic Properties

Introduction

Intermetallic cerium compounds with two crystallographically independent sites are fascinating materials with respect to their magnetic properties. Several scenarios are possible: (i) both cerium sites are trivalent like in CeRhSn2 [1 – 3], (ii) one site is trivalent and the second one is close to tetravalent like in the unique compounds CeRuSn [4, 5] or Ce2RuZn4 [6, 7], or (iii) both cerium sites are almost tetravalent as in CeRhZn [8]. The YPtAs structure type [9] is of particular interest in a search for related cerium compounds with two inequivalent sites. This structure type is derived from the well known AlB2 type [10] by differently puckered \(\text{Pt}_3\text{As}_3\) hexagons. With cerium as the rare earth component, so far, the YPtAs-type compounds CeNiP [11], CeNiAs [12, 13], CeZnGe [14], and CeZnSn [15, 16] have been reported. Among these compounds only the magnetic properties of CeZnSn (ferromagnetic ordering at \(T_C = 5.2(1)\) K [16]) have been investigated. We have now extended our systematic studies of equiatomic cerium intermetallics to include CeZnGe. While we completed our manuscript an independent report on the CeZnGe structure has been published [14].

Experimental Section

Synthesis

Starting materials for the preparation of CeZnGe were a cerium ingot (Johnson-Matthey), zinc granules (Merck), and germanium lumps (Wacker), all with stated purities better than 99.9 %. Pieces of the cerium ingot were first arc-melted [17] to a small button under an argon atmosphere. The argon was purified before with molecular sieves, silica gel, and titanium sponge (900 K). Subsequently the elements were weighed in the ideal 1:1:1 atomic ratio and arc-welded in a tantalum ampoule under an argon pressure of 700 mbar. The ampoule was then placed in a water-cooled sample chamber [18] of an induction furnace (Hüttinger Elektronik, Freiburg, Typ TIG 5/300) and heated three times for 5 min at 1370 K. After the third step the sample was kept at 1370 K for 10 min, then rapidly cooled to 920 K, and subsequently annealed at this temperature for another 6 h. Finally the tube was quenched to r.t. by switching off the power of the generator. The brittle CeZnGe sample could readily be separated from the tantalum tube by mechanical fragmentation. No reaction with the crucible material was evident. CeZnGe is stable in air over several weeks.

EDX data

Semi-quantitative EDX analyses of the crystal investigated on the diffractometer and of the bulk sample were carried out with a Leica 420i scanning electron microscope with CeO2, Zn, and Ge as standards. The experimentally observed composition was close to the equiatomic one. No impurity elements heavier than sodium (detection limit of the instrument) were observed.

X-Ray powder and single crystal data

Polycrystalline CeZnGe was characterized through a Guinier powder pattern (imaging plate detector, Fujifilm BAS-1800 read-out system) with CuK\(\alpha\) radiation and \(\alpha\)-quartz \((a = 491.30, c = 540.46\) pm) as an internal standard. Least-squares refinement of the powder data yielded the hexagonal lattice parameters \(a = 430.0(2)\) and \(c = 1678.8(10)\) pm, in good agreement with the data given recently by Pani et al. \((a = 429.8(1), c = 1675.5(3)\) pm) [14]. Proper indexing was ensured by an intensity calculation [19].

Small single crystals of CeZnGe were selected from the crushed sample, and their quality was tested by Laue photographs on a Buerger camera using white Mo radiation. Intensity data were collected on a Stoe IPDS II diffractometer (graphite-monochromatized MoK\(\alpha\) radiation; oscillation mode, numerical absorption correction). Our structure refinement \((P6_3/mmc, \text{Ce1}: \text{Wyckoff position } 2a; \alpha, 0, 0; \text{Ce2}: 2b; \alpha, \text{0, 0, 0})\)
Fig. 1. Temperature dependence of the magnetic susceptibility ($\chi$ and $\chi^{-1}$ data) of CeZnGe measured at 10 kOe.

Fig. 2. Low-temperature susceptibility (zero-field-cooling and field-cooling mode) of CeZnGe at 100 Oe (kink-point measurement). The inset shows the derivative $d\chi/dT$ of the field-cooling curve with a peak at the Curie temperature of $T_C = 4$ K.

Fig. 3. Magnetization isotherm of CeZnGe measured at 2.5 K.

Fig. 4. Temperature dependence of the specific heat of CeZnGe in zero magnetic field.

Physical property measurements

15.046 mg of the CeZnGe sample was packed in kapton tape and attached to the sample holder rod of a VSM for measuring the magnetic properties in a Quantum Design Physical-Property-Measurement-System in the temperature range 2.1 – 305 K with magnetic flux densities up to 80 kOe. For heat capacity ($C_P$) measurements (2.1 – 50 K) 9.175 mg of CeZnGe was glued to the platform of a pre-calibrated heat capacity puck using Apiezon N grease.

Discussion

Crystal chemistry

The equiatomic compounds CeZnX with $X = \text{Ge, Sn, Pb}$ [20] crystallize with the YPtAs-type structure, with an $AB B' A'$ stacking sequence of ordered Zn$_3$X$_3$ hexagons. This Zn-X ordering leads to a quadrupled $c$ parameter with respect to the AlB$_2$-type subcell. For CeZnSi [21, 22] only a disordered AlB$_2$ subcell structure has been reported. Single crystal studies on the silicide and the plumbide (X-ray powder data for

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot.anforderung.html), on quoting the deposition number CSD-420186.
CeZnPb: $a = 463.7(2), c = 1669.6(6)$ pm [20]) are in progress. The Zn–Ge intralayer distances of 251 pm in CeZnGe are close to the sum of the covalent radii of 247 pm [23], indicating substantial Zn–Ge bonding. The puckering of the Zn$_3$Ge$_3$ hexagons (118° Ge–Zn–Ge) is less pronounced as compared to the Zn$_3$Sn$_3$ hexagons (Sn–Zn–Sn = 115°) in CeZnSn [16]. For more details of the crystal chemistry and chemical bonding of YPtAs-type intermetallic compounds we refer to previous work [10, 14–16, 24].

**Magnetic behavior**

In Fig. 1, we show the dc susceptibility of CeZnGe as a function of temperature measured under an external applied field of 10 kOe. $\chi$ increases with decreasing temperature and exhibits a sudden upturn below 7 K, as if undergoing ferromagnetic ordering. The inverse susceptibility deviates from Curie-Weiss law just below 50 K, due to splitting to the $J = 5/2$ ground state of Ce$^{3+}$ and/or the onset of short-range magnetic interactions. From the high-temperature fit of $\chi$ (see Fig. 2), we obtain the paramagnetic Curie temperature $\theta_p$ of $-14.7(5)$ K and an effective Bohr magneton number $\mu_B$ of 2.67(1) $\mu_B$/Ce atom, in close agreement with the expected value of 2.54 $\mu_B$ for a free Ce$^{3+}$ ion. The low-field ($H = 100$ Oe) susceptibility is plotted in Fig. 2 for the zero-field-cooled (ZFC) and field-cooled (FC) state. In the inset of Fig. 2 we have plotted the first derivative of $\chi$ (FC) to get the precise ordering temperature of $T_C = 4$ K. The anomaly around 7.5 K may be indicative of a trace amount of CeZn$_2$ ($T_N = 7.5$ K) [25], although the powder pattern and EDX analysis showed virtually pure CeZnGe.

The magnetization isotherm taken at 2.5 K is shown in Fig. 3. The magnetization increases steeply up to an external field strength of around 0.025 T, and above this field strength the curve becomes more pronounced, and $M$ varies with $H$ as in an antiferromagnet with a tendency to saturate at higher fields. The saturation magnetization (sm) at 80 kOe amounts to $M_{\text{exp}}(\text{sm}) = 1.00(5)$ $\mu_B$/Ce atom, significantly reduced from the theoretical one for Ce$^{3+}$ of 2.14 $\mu_B$/Ce atom. Saturation moments in the range of 1 $\mu_B$/Ce atom are frequently observed for similar cerium intermetallics, e.g. CeAuSn [26] or CeNiIn$_2$ [27]. These small values of the saturation moment are due to crystal field splitting effects on the $J = 5/2$ ground state of the Ce$^{3+}$ ion. The specific heat ($C_P$) data for CeZnGe are plotted in Fig. 4. The Curie-Temperature of 4.6(2) K is characterized by a broad $\lambda$-like anomaly.

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