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The modulated structure of intermediate-valent CeCoGa

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Abstract: CeCoGa was synthesized by melting of the elements in an arc-melting furnace as well as in a sealed niobium tube in an induction furnace. A further annealing step improves the purity and crystallinity of the samples significantly. Its structure was refined on the basis of single-crystal X-ray diffractometer data at different temperatures. Already at room temperature CeCoGa crystallizes in a superstructure of the HT-CeCoAl type. This superstructure can be described in the (3+1)D superspace group $C2/m(\alpha 0 \gamma)00$; $\alpha = 2/3$, $\gamma = 1/3$ with a temperature independent q -vector ($Z = 4$). For the 300 K data (also for 90 K) the commensurate modulated structure could be refined with 1336 F^2 values, 56 variables and residuals of $wR = 0.0348$ for the main and $wR = 0.0605$ for the satellites of 1st order [$a = 1101.7(1)$, $b = 436.0(1)$ and $c = 482.4(1)$ pm, $\beta = 103.2(1)^\circ$]. Furthermore a description in a transformed 3D supercell with the space group $C2/m$ and $Z = 12$ is possible. For the 90 K data this 3D supercell was refined with 1289 F^2 values, 56 variables and a residual of $wR = 0.0409$ [$a = 1618.8(1)$, $b = 435.3(1)$ and $c = 1094.1(1)$ pm, $\beta = 119.3(1)^\circ$]. The relation of the HT-CeCoAl type structure, the (3+1)D modulated and the 3D supercell structure are discussed on the basis of a group-subgroup relation. By thermal analysis and magnetic measurements the phase transition temperature to the HT-CeCoAl type structure is stated slightly above 475 K. Furthermore intermediate cerium valence was identified by the magnetic susceptibility.

Keywords: cerium; group-subgroup scheme; intermediate valence compound; modulated structure.

Introduction

The physical properties of ternary intermetallic cerium compounds $Ce_xT_yX_z$ (T = transition metal; X = elements of the 3rd, 4th, or 5th main group, Mg, Zn, or Cd) strongly depend on the cerium valence and the Ce ($4f$)– nd hybridization [1]. The trivalent cerium compounds with [Xe] $4f^1$ configuration show magnetic ordering at low temperatures. Typical examples are the 10 K ferromagnet CeAuGe [2], the 4 K ferri- or ferromagnet CeRhSn₂ [3], or the 46 K antiferromagnet CeScGe [4]. The other extreme is an almost empty $4f$ shell which means a cerium valence close to tetravalent and Pauli paramagnetic behavior (essentially magnetism deriving from the conduction electrons). Such a population of the Ce $4f$ -shell has been observed for e.g. CeRhIn [5], Ce₂Ni₂Mg [6], and CeRhZn [7].

A more complicated situation exists for the cerium intermetallics with partially filled $4f$ shell. This leads to mixed valence behavior [8]. Depending on the number of crystallographic cerium sites one can classify these materials into two groups (Batlogg scheme [9, 10]): (i) homogeneous and inhomogeneous mixed valence and (ii) static mixed valence. Examples for the first group are CeRu₂Mg₅ [11], Ce₂Ru₄Mg₁₇ [12], CeRhSn (ZrNiAl type) [13], CeIrGe (TiNiSi type) [14] and Ce₂Ni₃Si₅ (U₂Co₃Si₅ type) [15] with single cerium sites.

The group (ii) shows a more complicated structural behavior. The simplest example is Ce₂RuZn₄ [16, 17] which contains only seven atoms within its unit cell, but two crystallographically independent cerium sites, trivalent Ce1 and intermediate-valent Ce2. The Ce1 atoms show antiferromagnetic ordering below $T_N = 2$ K. Besides, several complex structures with up to nine crystallographically independent cerium sites (and cerium valences) have been reported, e.g. Ce₁₆Ru₈In₃₇ [18], Ce₂₃Ru₇T₄ (T = Mg, Zn and Cd) [19], Ce₉Ru₄Ga₅ [20, 21], Ce₂Ru₂Ga₃ [22], or Ce₁₃Ru₂Sn₅ [23]. All these compounds show drastically shortened Ce–Ru distances as a consequence of the intermediate cerium valence. It is remarkable, that this phenomenon is pronounced for ruthenium-based cerium intermetallics [24, 25].

The most remarkable compound in this family of materials is CeRuSn [26–32] which shows temperature-induced

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modulations and its nuclear structure was described within the superspace formalism in (3+1) dimensions. The nuclear modulation vector showed a strong initial temperature dependence and then tends towards a value close to $q = (0\ 0\ 0.35)$. These structural changes are paralleled by subtle changes in the magnetic and transport behaviors (R.-D. Hoffmann et al., unpublished results).

CeCoAl and CeCoGa [33] show the same Bi_2Pd type [34–36], subcell structure, space group $C2/m$, as CeRuSn along with anomalies for the anisotropic displacement parameters. So far, no temperature-dependent diffraction experiments and only preliminary physical property studies have been reported [37–41]. In extension of our detailed studies on CeRuSn we have recently investigated the CeCoAl structure [42]. The aluminide shows a second-order phase transition at 271 K and the low-temperature structure can be described in the (3+1)D space group $C2/m(\alpha 0\gamma)00$ with $q = (2/3, 0, 2/5)$. Again, the striking crystal chemical features are short Ce–Co distances. The modulated structure of the higher congener CeCoGa is reported herein.

Experimental

Synthesis

CeCoGa was synthesized by reaction of the elements in an arc-melting furnace as well as in arc-welded niobium tubes. Latter one was performed to ensure a good crystallinity for single crystal data collection. Therefore, ingots of cerium (Sigma-Aldrich), cobalt powder (Koch Chemicals, >99.5%) and gallium lumps (Johnson Matthey) were used, except of Co all with stated purities of 99.9% or higher. The air- and moisture-sensitive cerium ingots were cut into suitable pieces and kept in Schlenk tubes under argon prior to the reaction. The elements were weighed in the ideal atomic ratio of 1:1:1 and arc-welded [43] in a niobium tube under 800 mbar argon, which was placed in a water-cooled brass crucible. Argon was purified with titanium sponge (900 K), silica gel and molecular sieves. The niobium ampoule was subsequently placed in the water-cooled sample chamber of an induction furnace (Hüttinger Elektronik, Freiburg, Germany, Typ TIG 1.5/300) [44] and heated under a steady flow of argon to ~1500 K and kept for about 10 min. High quality single crystals were achieved by lowering the temperature slowly (5–10 K/min) to 900 K and keeping this temperature for about 6 h; afterwards the sample was quenched by switching off the power supply. As temperature control unit a Metis MS09 (Sensortherm) pyrometer (accuracy ± 50 K) was used. The obtained polycrystalline sample showed metallic luster and no reaction with the niobium tube was observed.

Especially for the reaction via arc-melting it was important to purify the cobalt powder by heating in dilute muriatic acid (10%) for a short time. This procedure leads to a reduced amount of CeGa_2 as by-product. After the reaction in the arc-melting furnace a cold-pressed pellet ($\varnothing$ 6 mm) was annealed for further 4 weeks in an evacuated

silica ampoule at 770 K to enhance the purity of the sample. The powder keeps its dark gray color also after months at air.

X-ray diffraction

The polycrystalline CeCoGa sample was characterized by powder X-ray diffraction using a Guinier camera equipped with an image plate system (Fujifilm, BAS-1800). $\text{Cu K}\alpha_1$ radiation and α -quartz ($a = 491.30$ and $c = 540.46$ pm) as an internal standard have been used. The monoclinic lattice parameters (Table 1) have been derived from a least-square refinement. Proper indexing of the diffraction lines was ensured by an intensity calculation [45] using the positional parameters of the superstructure obtained from the single crystal investigation. The subcell parameters are in good agreement to results from literature [37].

Irregularly shaped crystal fragments were obtained by mechanical fragmentation of the annealed CeCoGa sample. The crystals were glued to thin quartz fibers using bees wax and their quality was tested by Laue photographs on a Buerger camera (white molybdenum radiation, image plate technique, Fujifilm, BAS-1800). The data set was measured on a Stoe StadiVari diffractometer equipped with a Mo micro focus source and a Pilatus detection system. Due to a Gaussian-shaped profile of the X-ray source scaling was applied along with the numerical absorption corrections for all data sets. The relevant crystallographic data and details of the data collections and evaluations are listed in Table 1.

EDX analysis

Semiquantitative EDX analyses of the single crystal fragment, which was used for data collection, was studied by using a Zeiss EVO® MA10 scanning electron microscope in variable pressure mode with CeO_2 , Co, and GaP as standards. The equiatomic stoichiometry was confirmed by analysis at several points of the single crystal. Furthermore no impurity elements heavier than sodium (especially from the container material) were detected.

Thermal analysis

Thermal analysis of CeCoGa was performed by differential scanning calorimetry using a NETZSCH DSC 204 F1 apparatus. A polycrystalline sample (28.930 mg) was put in a small aluminum pan, and the subsequent measurement was conducted under an argon atmosphere. The cooling and heating rates were 10 K/min and an empty aluminium pan was used as a reference. The NETZSCH Proteus software was employed for data treatment.

Magnetic measurements

Magnetic susceptibility measurements of CeCoGa were carried out on a Quantum design physical-property-measurement-system (PPMS) using the VSM-oven option (vibrating sample magnetometer). For the measurement one piece of the polycrystalline sample with a

Tab. 1: Crystallographic data and structure refinement of the ambient and low temperature data sets for CeCoGa; superspace group $C2/m(\alpha 0\gamma)00$ with $q = 2/3, 0, 1/3$; $Z = 4$ and supercell space group $C2/m$; $Z = 12$.

Empirical formula	CeCoGa		
Formula weight/g mol ⁻¹	268.8		
Unit cell dimensions/pm	$a = 1626.2(2)$		
(Guinier powder data at room temperature)	$b = 437.1(1)$		
	$c = 1098.4(2)$		
	$\beta = 119.2(1)^\circ$		
Cell volume/nm ³	0.6815		
Crystal size/ μm^3	$90 \times 30 \times 30$		
Diffractometer type	StadiVarl		
Wave length/pm	71.073 (MoK α)		
Temperature/K	300	90	90
Calculated density/g cm ⁻³	7.91	7.97	7.97
Unit cell dimensions/pm	$a = 1101.7(1)$	$a = 1099.3(1)$	$a = 1618.8(1)$
	$b = 436.0(1)$	$b = 435.3(1)$	$b = 435.3(1)$
	$c = 482.4(1)$	$c = 481.1(1)$	$c = 1094.1(1)$
	$\beta = 103.2(1)^\circ$	$\beta = 103.3(1)^\circ$	$\beta = 119.3(1)^\circ$
Volume/nm ³	0.2256	0.2240	0.6723
Detector distance/mm	40	40	40
Exposure time/s	10	26	26
Integr. param. (A, B, EMS)	9.0, -8.0, 0.030	9.0, -8.0, 0.030	9.0, -8.0, 0.030
Satellite profile factor	0.8	0.8	0.8
Absorption coefficient/mm ⁻¹	38.5	38.8	38.8
Transm. Ratio, max/min	0.77/0.10	0.76/0.11	0.76/0.11
F (000)/e	464	464	1392
θ range for data collection/ $^\circ$	2.6–32.8	2.6–32.4	2.6–32.4
Range in hkl	$\pm 16, \pm 6, \pm 7$	$\pm 16, \pm 6, \pm 7$	$\pm 23, \pm 6, \pm 16$
Total no. reflections	8440	8299	8299
Independent reflections/ R_{int}	1336/0.0433	1289/0.0402	1289/0.0402
Reflections with $I \geq 3\sigma(I)$	838/0.0278	1000/0.0128	1000/0.0128
Main + Satellite (1 st order)	442 + 894	430 + 859	
Data/parameters	1336/56	1289/56	1289/56
Goodness-of-fit on F^2	0.82	1.15	1.15
$R1/wR2$ for $I \geq 3\sigma(I)$	0.0192/0.0400	0.0176/0.0409	0.0176/0.0409
Main	0.0155/0.0348	0.0138/0.0331	
Satellites 1 st order	0.0289/0.0605	0.0258/0.0546	
$R1/wR2$ (all data)	0.0345/0.0418	0.0269/0.0427	0.0269/0.0427
Main	0.0194/0.0352	0.0166/0.0340	
Satellites 1 st order	0.0663/0.0661	0.0478/0.0577	
Extinction coefficient	205(6)	252(9)	252(9)
Largest diff. peak/hole, /e Å ⁻³	0.71/-0.91	0.81/-0.89	1.08/-1.37

weight of 37.341 mg was fixed to a heater stick using alumina based cement. The sample was investigated in the temperature range of 300–650 K with a magnetic flux density of 10 kOe. No heating of the sample was performed after centering at 1000 Oe to ensure a virgin sample due to the fact that a structural instead of a magnetic phase transition is investigated.

Structure refinement

In the top part of Figure 1 a cutout of the reciprocal $h1l$ -layer of CeCoGa at 300 K is presented. Already at this

temperature additional reflections are observed that are not consistent with the subcell (HT-CeCoAl type structure, drawn in black [42]) reported in literature [37]. Detailed analysis of the diffractometer data set leads to two different approaches. The first one is the description of the structure by a modulation analogous to CeCoAl [42]. For the second one no additional dimension has to be used and only a transformation to the blue superstructure (cp. Figure 1; bottom part) is necessary. In this case a C -centered monoclinic lattice is present and the systematic extinctions are compatible with the space group $C2/m$. Despite of the possibility of a 3D structure solution, we decided

Fig. 1: Projection of a cutout of the reciprocal $h1l$ -layer of CeCoGa at 300 and 90 K. The subcell with HT-CeCoAl type structure at room temperature is drawn in black and designated reflections are labeled; the positions of the extinct reflections due to the C centering are symbolized by green, open squares. Black dashed arrows represent the q -vector ($q = 2/3, 0, 1/3$) for the $(3+1)$ D modulated structure of CeCoGa and the orange lines symbolize the supercell approximant (extinct reflections for $1/3a^*$ are omitted). The main and the satellite reflections of the 1st order (positive and negative direction) are drawn as yellow squares, red circles and black triangles, respectively. The alternative cell of the transformed 3D structure is presented in blue. The intensity scale is based on $(3\ 1\ 1)$ as the strongest reflection of the cutout. Yellow pixels are drawn with $I > 1\%$ and black $> 0.7\%$.

also to use the $(3+1)$ D modulated structure for better comparison with CeCoAl. For this modulation a X - as well as a C -centered monoclinic lattice can be used (*vide infra*). One particularity that should be mentioned for the integration is the profile factor of 0.8 for the satellite reflection to take the low intensity of these reflections into account. Nevertheless, significantly stronger satellites are observed for CeCoGa than for CeCoAl.

To illustrate the deficits of the structure solution in the subcell known from literature we also performed a structure solution with the corresponding parameters for the 300 K data set. The starting atomic parameters were deduced using the charge-flipping algorithm of Superflip [46] and the CeCoGa structure was refined with anisotropic displacement parameters for all atoms based on F^2 with Jana2006 [47]. As already known for CeRuSn [26] and CeCoAl [42] an enhanced U_{33} (approx. $5 \times U_{11}$) parameter of 1060 pm^2 for the Co site is observed. This is illustrated in Figure 2 and points again towards attractive interactions between Ce and Co as reason for the formation of a superstructure. Nevertheless, a check for the correct composition has been executed. Therefore, the occupancy parameters were refined in a separate series of least-squares cycles and all sites are fully occupied within three standard deviations.

Due to our experiences with CeRuSn (*vide supra*) we performed X-ray single crystal investigations also at 90 K to check for further structural changes, but no additional reflections are observed at this temperature (cp. Figure 1). Nevertheless, in comparison to the subcell a lot of strong, additional reflections can be observed along a^* and c^* . An orange lattice is introduced in Figure 1 in order to underline the positions of these reflections. Therefore, two times of a^* as well as c^* have to be divided by three to capture all reflections, but only two of the possible eight satellites for a C -centered $3a \times 3c$ approximant structure can be regularly observed. Consequently, a simple multiplication of the a - and c -axis by a factor of three is not reasonable and a description of RT-CeCoGa as $(3+1)$ D commensurate

Fig. 2: Refinement of the CeCoGa data set at 300 K with the subcell (HT-CeCoAl type structure). Cerium, cobalt and gallium atoms are drawn as gray, black filled and open circles, respectively (displacement ellipsoids at 99% probability).

modulated superstructure has to be favored. Following CeCoAl, the space group $C2/m(\alpha 0 \gamma)00$ but with $q = (2/3, 0, 1/3)$ is used. The transformation matrix displayed below has to be applied to obtain the 3D structure in $C2/m$. Referring to the q -vector drawn in Figure 1 by black arrows, only satellites with 1st order can be identified undoubtedly. Second order satellites would be superimposed on the same position of a 1st order one of another main reflection.

$$\text{Transformation matrix: } \begin{bmatrix} -1 & 0 & 2 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix}$$

The structure solution of the $[3+1]D$ approach again was performed with Superflip [46] and the refinement on F^2 with Jana2006 [47]. In contrast to CeCoAl not for all elements harmonic position modulations could be used to describe the atom domains correctly, which are shown in Figure 3. Only for Ce and Ga one harmonic position modulation is sufficient, while for Co saw tooth modulation has to be performed. Therefore, a crenel type function was selected. Furthermore it was possible to refine the modulated anisotropic displacement parameters (ADP) with first order for all atoms. Using the commensurate option with the transformed supercell, $t_0 = 0$ and $C2/m$ for the approximant, a second order was not possible for the positions as well as the ADPs due to constraints. A $t_0 = 1/2N = 1/(2 \times 3) = 1/6$ is not reasonable – it leads to a disordered approximant; the commensurate section intersects the discontinuity of the positional modulation function. The atom domains of the 90 K data set are depicted together with the corresponding modulation functions in Figure 3 and the values are listed in Table 2. Ce and Ga exhibit slight position modulations along the a -axis and the c -axis. However, the Co atom domain shows a discontinuity. At some point a critical Ce–Co distance is reached and the atom cannot stay anymore on the same side of the modulation interval. Consequently, it reappears on the opposite one. This finds especially expression along the c -axis and is in accordance with the enhanced U_{33} value of Co in the subcell refinement. A final difference electron-density synthesis, which exhibits no significant peaks or holes, underlines a suitable refinement of the modulation functions. Details of the refinements are listed in Table 1, while Table 3 contains the average, minimum and maximum distances for the 90 K data set.

As mentioned above the structure can also be refined in 3D. Also in this case the correct composition and site assignment was checked by refinement of the occupancy parameters in separate series of least-squares cycles. All sites were fully occupied within three standard deviations.

Fig. 3: Graphic representation of the atom domains of the commensurately modulated structure in x_1 (top) and x_3 (bottom) of CeCoGa at 90 K. For Ce and Ga a harmonic position modulation has been realized, while for Co a crenel type modulation has to be chosen. In all cases a summation of the projection directions has been applied (100 pm). Contour levels are >0 with $\Delta = 8, 4$ and 4 for Ce, Co and Ga, respectively.

The final difference electron-density synthesis was flat. Details of the refinement and the positional parameters are listed in Tables 1 and 4. Further information on the structure refinements is available.¹

The relation of the space groups of the subcell (HT-CeCoAl type structure), the $(3+1)D$ modulated structure and the 3D superstructure is also described by the Bärnighausen formalism [48–51], which is displayed in Figure 4. The $(3+1)D$ structure projects via an a_3 onto 3D

¹ Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD-429882 (300 K data, $[3+1]D$), CSD-429884 (90 K data, $[3+1]D$) and CSD-429883 (90 K data, 3D superstructure).

Tab. 2: Atom positions, anisotropic displacement parameters (pm^2) and Fourier coefficients of the modulation functions ($\sin, \cos, \times 10^3$) of CeCoGa at 90 K. All Wyckoff sites are $4i$. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. $U_{12} = U_{23} = 0$.

Atom	Wave	x	y	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Ce		0.12742(2)	0	0.32219(4)	111(1)	104(1)	102(1)	25(1)	106(1)
	sin	−29(1)	0	68(1)	1(1)	0(1)	−3(1)	0(1)	
	cos	−81(1)	0	−80(1)	3(1)	2(1)	−2(1)	−1(1)	
Co $x4_0 = 5/12$		0.19416(4)	0	0.86324(10)	120(2)	107(2)	148(2)	37(1)	124(1)
	ort(1)	−80(1)	0	−824(1)	2(2)	1(2)	−1(2)	0(2)	
	ort(2)	−27(1)	0	−96(1)	3(2)	−3(2)	15(3)	6(2)	
Ga		0.41448(3)	0	0.18918(8)	116(1)	101(1)	122(1)	30(1)	113(1)
	sin(1)	58(1)	0	179(1)	−1(2)	0(2)	−2(2)	−2(1)	
	cos(1)	−85(1)	0	−100(1)	−2(2)	2(2)	1(2)	1(2)	

Tab. 3: Interatomic distances (pm) for CeCoGa at 90 K (average, minimum, maximum) for the $3a \times 3c$ approximant. Standard deviations are equal or smaller than 1.0 pm.

Atom 1	#	Atom 2	d_{av}	d_{min}	d_{max}
Ce:	1	Co	248.7	225.1	271.1
	1	Co	253.7	221.0	292.3
	2	Ga	315.3	313.9	317.6
	2	Co	319.9	314.3	329.1
	2	Ga	323.9	322.1	327.2
	2	Ga	331.6	328.1	334.8
	1	Ga	336.2	329.4	349.1
	1	Co	345.2	338.1	349.3
	2	Ce	357.9	354.4	365.1
	1	Ce	360.4	354.3	372.7
Co:	1	Ce	367.1	362.6	369.4
	2	Ga	247.7	245.1	250.0
	1	Ce	248.7	225.1	271.1
	1	Ce	253.7	221.0	292.3
	1	Ga	257.3	249.3	265.1
	2	Co	269.1	266.3	274.7
	2	Ce	319.9	314.3	329.1
	1	Ce	345.2	338.1	349.3
Ga:	2	Co	247.7	245.1	250.0
	1	Co	257.3	249.3	265.1
	1	Ga	290.5	286.6	298.2
	1	Ga	314.6	290.8	326.6
	2	Ce	315.3	313.9	317.6
	2	Ce	323.9	322.1	327.2
	2	Ce	331.6	328.1	334.8
	1	Ce	336.2	329.4	349.1

space. This transformation of the approximant is equivalent to an $i3$ symmetry reduction in 3D. As a consequence of the $i3$ transformation three independent crystallographic sites are realized for each atom type. For comparison the ideal and observed positions are listed in Figure 4 leading to significant deviations especially for two Co-sites, which will be discussed later in the crystal structure part.

Crystal chemistry

Already at 300 K CeCoGa crystallizes in a superstructure of the HT-CeCoAl type. A refinement of the 300 K data set in the subcell exhibits a significantly enlarged U_{33} anisotropic displacement parameter of the Co-atom (cp. Figure 2). As result of the isomorphic transition of index $i3$ a symmetry reduction takes place and some atoms can move from the ideal positions. In Figure 5 a $3a \times 3c$ approximant for CeCoGa at 90 K is drawn in comparison to the average Co-positions. Latter ones are marked by closed blue circles. It is obvious that one third of the Co-atoms is still very close to the average position, while two thirds have been moved up or down along the c -axis. The average Ce and Ga positions are omitted because only slight movement is observable, which is just a response to the Co displacements. For comparison the calculated and refined positions are listed in Figure 4. The significant movement of the Co-atoms is most likely caused by attractive interactions with Ce, which are expressed in a distinct reduction of the corresponding distances. Thus the two shortest Ce–Co distances are drawn in Figure 5 and some of these are marked with two different colors and numbered to understand the context between the structure and the t -plots depicted in Figures 6 and 7.

In Figure 6 the displacement of the different atoms is shown as a function of t . The dashed lines symbolize the commensurate t sections, which mark the realized atom positions and distances in the approximant structure with $t_0 = 0$ on a grid of $1/N = 1/3$. According to this plot the most significant displacement is observed for Co along dz , which is totally in line with the refined modulation functions (*vide supra*). Due to the crenel function that has to be used for description of the Co-atom domains, a large step of the displacement at $t = 0.5$ is observed. In the case of a commensurate modulated structure this feature is

Table 4: Atom positions and anisotropic displacement parameters (pm²) of the supercell structure of CeCoGa at 90 K ($t_0 = 0$; $C2/m$). U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor. Coefficients U_{ij} of the anisotropic displacement factor tensor of the atoms are defined by: $-2\pi^2[(ha)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. All Wyckoff sites are $4i$ and $U_{12} = U_{23} = 0$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Ce1	0.0680(1)	0	0.1899(1)	99(1)	105(1)	106(1)	45(1)	105(1)
Ce2	0.7291(1)	0	0.8536(1)	105(1)	105(1)	107(1)	49(1)	107(1)
Ce3	0.3977(1)	0	0.5335(1)	103(1)	102(1)	107(1)	51(1)	105(1)
Co1	0.2207(1)	0	0.4122(1)	150(3)	105(3)	154(3)	92(3)	129(2)
Co2	0.9111(1)	0	0.1131(1)	142(3)	108(3)	137(3)	80(3)	124(2)
Co3	0.5372(1)	0	0.7262(1)	127(3)	109(3)	131(3)	69(3)	120(2)
Ga1	0.9286(1)	0	0.3525(1)	119(2)	100(2)	119(2)	60(2)	112(2)
Ga2	0.5912(1)	0	0.9974(1)	119(3)	103(2)	122(2)	63(2)	113(2)
Ga3	0.2549(1)	0	0.6682(1)	121(3)	100(2)	123(2)	63(2)	114(2)

Fig. 4: Left: Relation of the (3+1)D commensurate modulated structure and the 3D space groups of CeCoGa. Right: Group-subgroup scheme in the Bärnighausen formalism [48–51] for the average structure of CeCoGa (HT-CeCoAl type structure) and RT-CeCoGa. The Index for the isomorphic (i) symmetry reduction, the unit cell transformations, and the evolution of the atomic parameters are given. The Index a is introduced for the formation of the approximant of the modulated structure.

obsolete because this situation is never realized as it can be seen from the positions of the commensurate t sections. In the top part of Figure 7 the distance modulations of Co–Co and Co–Al are displayed, while in the bottom part the Co–Ce ones are shown. In the latter one again the realized distances are marked with the same colors known from Figure 5. It is obvious that the average Co–Ce (247.8 and 253.7 pm) distances are placed close to the remaining inversion centers, while the very short distances are at positions of removed ones due to the symmetry reduction. In this structure the shortest Co–Ce distances are observed with 221.0 and 225.1 pm, which is only slightly above the shortest distances reported so far for CeCoAl with 218.8 pm. However, this is also far below the sum of the covalent radii of Ce and Co with 281 pm [52], which

can only be explained by a significant amount of tetravalent cerium. This will be discussed in more detail in the magnetic properties part (*vide infra*). Further distances are listed in Table 3. Enlarged anisotropic displacement parameters give hint for insufficient structural refinements. The opposite way around small, round atoms underline the reasonability of the refinement. In Tables 2 and 4 the ADPs for the modulated structure and the superstructure are listed. Furthermore the ADPs of Co as a function of t are plotted in Figure 8. In all cases small and similar values are observed, pointing towards a very good structure refinement. So far, we only discussed superficially how the introduced modulation, respectively the symmetry reduction

Fig. 5: Top part: $3a \times 3c$ approximant structure of CeCoGa at 90 K. Cerium, cobalt and gallium atoms are drawn as black, blue, and red circles, respectively. The crescents mark the atoms with $y = 1/2$. To emphasize the position modulation of Co, the ideal Co positions are symbolized by blue circles. The shortest Ce–Co distances are highlighted in green and purple, these distances are additionally marked in the t -plot (cp. Figure 7). In the bottom part a cutout with a slightly tilted b -axis is presented. Emphasized Ce–Co distances are 247.8, 221.0, 292.3 for green 1–3 and 250.0, 271.3, 225.1 for purple 1–3, respectively.

Fig. 6: Displacement modulations as a function of t . Black, blue and red lines represent Ce, Co and Ga, respectively. Solid lines symbolize modulations along dz , while modulations along dx are drawn with dashed lines. The gray dashed lines indicate the commensurate t sections with $t_0 = 0$. Green and purple crosses mark the shortest Ce–Co distances corresponding to Figure 7.

Fig. 7: Distance modulations as a function of t for Co–Co, Ga–Co (top) and Ce–Co (bottom). Black, blue and red lines represent Ce, Co and Ga, respectively. The gray dashed lines indicate the commensurate t sections with $t_0 = 0$. Green and purple crosses mark the shortest Ce–Co distances corresponding to Figure 5.

Fig. 8: Anisotropic displacement parameter (ADP) modulations of Co as a function of t . The dashed lines indicate the commensurate t sections with $t_0 = 0$.

according to the transformation influences the structure. It has already been mentioned that at the positions of removed symmetry elements the strongest Co displacements and as a consequence thereof the shortest Co–Ce distances are observed. In Figure 9 the symmetry thinning by a factor of 3 from the subcell to the transformed structure is symbolized according to the space group diagrams. The top panel shows the projection of the $3a \times 3c$

Fig. 9: Symmetry element thinning from the average cell (HT-CeCoAl type) (bottom) to the $3a \times 3c$ approximant structure for RT-CeCoGa (middle and top). The black dashed lines symbolize the lattice of the subcell and the crescents mark the atoms with $y = 1/2$. In the top part the two shortest Ce–Co distances are drawn and the coloration symbolizes the arrangement of these. Areas with different pattern (filled and striped) are related by an inversion center. The unit cell and the corresponding symmetry elements of the transformed 3D supercell are drawn in red.

approximant along the monoclinic axis. For the approximant structure no symmetry symbols are drawn because this cell exhibits the space group $X2/m$. In the X-centered cell of the $3a \times 3c$ approximant only a ninth of the symmetry elements would still be present. This is in line with the group-subgroup scheme (Figure 4) showing the standard $C2/m$ settings with a symmetry thinning of $1/3$. Again the two shortest Co–Ce distances are drawn and areas with different colors exhibit different distances, while same colors, but different pattern (filled and striped) are related by an inversion center. White areas exhibit an inversion center in the middle. Due to the coloring the remaining symmetry elements and the relation to the transformed cell can be identified. For the last point it has to be taken into account that one half of the drawn atoms are at

$y = 1/2$, which are marked by crescents. Summing up, it is stated that the symmetry thinning is a consequence of attractive interactions between cerium and cobalt as it is already known for cerium and ruthenium.

Thermal analysis and magnetic properties

For CeCoAl a phase transition temperature of 271 K could be determined for the transition from the subcell (HT-CeCoAl type structure) to the commensurate modulated structure (LT-CeCoAl), which was classified as phase transition of second order according to a λ – anomaly in the heat capacity [42]. Due to the almost identical behavior of CeCoGa, the same phase transition can also be expected for this compound at higher temperatures. In general, higher transition temperatures are observed for heavier homologs, which was nicely shown for the three carbides Sc_3TC_4 with $T = Co, Ru$ and Os . At room temperature all three structures can be described in the Sc_3CoC_4 type structure with the space group $Immm$. Below 70, 233 and 255 K the Co, Ru and respectively the Os compound exhibit monoclinic distortions (Sc_3IrC_4 type structure, space group $C2/m$) [53, 54]. In order to investigate the probable structural phase transition from the RT-CeCoGa to the HT-CeCoAl type structure, thermal analysis as well as high temperature magnetic susceptibility measurements were performed.

In Figure 10 the second cycle of a DSC measurement in the temperature range from 293 to 525 K is depicted. According to this picture a reversible phase transition around 480 K is clearly revealed for this displacive phase transition. The onsets of the phase transitions for the

Fig. 10: Differential scanning calorimetry measurement of CeCoGa in heating and cooling mode.

heating and cooling curve are determined to 478(2) and 475(2) K, respectively.

Figure 11 presents the magnetic susceptibility and its reciprocal in the temperature range from 300 to 650 K measured with an applied magnetic field of 10 kOe. A phase transition in the same temperature range is also clearly revealed by the magnetic properties. Analogous to the DSC measurement the onset is defined at 479(2) K, which is in good accordance to the values obtained by thermal analysis. Due to the very short Ce–Co distances also intermediate cerium valence can be expected for CeCoGa. Unfortunately, we were not able to synthesize a sample that contains <10% of CeGa₂ as impurity phase. CeGa₂ is known to order antiferromagnetically at $T_N = 4.1$ K [55]. As a consequence thereof the low-temperature behavior of the magnetic susceptibility data has not been investigated and no data fitting was performed. Despite of the presence of CeGa₂, which exhibits exclusively Ce³⁺, the absolute values of the inverse magnetic susceptibility prove undoubtedly an intermediate cerium valence. Furthermore a less increase of the reciprocal magnetic susceptibility after the phase transition points towards a higher amount of trivalent cerium at higher temperatures. By reference to the similarity with CeCoAl, the very short Ce–Co distance of 221 pm and the susceptibility measurement intermediate cerium valence can clearly be stated for CeCoGa. Deviations from Curie-Weiss behavior and a reduced magnetic moment were already reported for the binary Ce₂₄Co₁₁ [56].

Conclusion

The structure of CeCoGa at room temperature can be described in the (3+1)D space group $C2/m(\alpha 0 \gamma)00$ with

Fig. 11: Temperature dependence of the magnetic susceptibility (χ and χ^{-1} data) of CeCoGa measured at 10 kOe.

$q = (2/3, 0, 1/3)$ as well as by a superstructure with the 3D monoclinic space group $C2/m$. In comparison to the subcell (HT-CeCoAl type), which also crystallizes in the monoclinic space group $C2/m$, the lattice parameters of the 3D structure are transformed to $a = 1618.8$, $b = 435.3$ and $c = 1094.1$ pm, and $\beta = 119.3^\circ$. Single crystal data collection down to 90 K revealed no further structural transitions. However, thermal analysis and magnetic measurements clearly prove that the phase transition from the subcell (HT-CeCoAl type structure) to the RT-CeCoGa type structure takes place slightly above 475 K. Due to the similarity with CeCoAl also for CeCoGa a phase transition of second order can be predicted. This phase transition is forced by interactions between Co and Ce and leads to very short Ce–Co distances (221.0 and 225.1 pm) in the superstructure. These are far below the sum of the covalent radii and can only be explained by partially tetravalent cerium. An intermediate cerium valence was confirmed by susceptibility measurements, though no fitting with the Curie-Weiss law was reasonable. Beside the well-investigated Ce–Ru intermetallic compounds, CeCoAl and CeCoGa establish a second class of compounds showing an extraordinary bonding situation combined with intermediate cerium valence.

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