Synthesis and Structural Characterization of $RE_6Cd_{23}T$ ($RE = \text{La–Gd}$; $T = \text{Sn, Sb, Pb, and Bi}$)

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Abstract

Synthetic methods and structural characterization are reported for 11 novel ternary compounds with the general formula $RE_6Cd_{23}T$ ($RE = \text{La–Gd}$; $T = \text{Sn, Sb, Pb, and Bi}$). Their crystal structures, as revealed by single-crystal and powder X-ray diffraction, are of the cubic $Zr_6Zn_{23}Si$ structure type ($cF120$, $Fm\bar{3}m$, $Z = 4$), a filled version of the Th_6Mn_{23} system. No Cd-containing rare-earth metal binaries are known to form with this structure, but the inclusion of small amounts of a third element allows the formation of the interstitially stabilized ternary structures. Temperature dependent dc magnetization measurements confirm local-moment magnetism due to RE^{3+} ground states for Ce, Pr, and Nd.

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1. Introduction

First synthesized in 1953, the compound Th_6Mn_{23} ($cF116$, space group $Fm\bar{3}m$) [1] is now the principle compound of its own structure type. Th_6Mn_{23} boasts a large, complex cubic unit cell featuring one site for Th (Wyckoff position $24e$) and four separate sites for Mn ($2 \times 32f$, $24d$, and $4a$). Also of note is the large octahedral void present at site $4b$, which has the potential to accept guest atoms as interstitials. One could consider such compounds part of a $Th_6Mn_{23}T$ structure type ($cF120$, $Fm\bar{3}m$), where T is a guest atom occupying the $4b$ hole; here, atom T can belong either to a species already present elsewhere in the structure [2,3] or a different species entirely [4,5]. For the purposes of this paper, the term “interstitial” will be used to refer to any compound falling within this subtype.

Transition metals (Mn and Fe in particular) have been shown to form Th_6Mn_{23} -type binary phases with a wide range of rare-earth elements [6–8]. Such is not the case with Cadmium, however, as Th_6Cd_{23} (originally reported from powder X-ray diffraction data) is the only binary Cd-rich phase adopting the Th_6Mn_{23} structure known to date [9]. Yet, there have been reports of Cd-containing ternary phases— $Na_6Cd_{16}Au_7$ (Th_6Mn_{23} -type) [10] and

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$\text{Ca}_6\text{Pt}_8\text{Cd}_{16}$ ($\text{Zr}_6\text{Zn}_{23}\text{Si}$ -type) [11]. In both cases, Cd fully occupies both 32*f* positions, with the 24*d* and 4*a* positions taken by the other transition metal (Au and Pt, respectively). Aside from the above-mentioned compounds, no other Cd-containing phases with the same structure have been reported to date. For further overview on Cd-intermetallics, the reader is referred to a recent review article on this subject [12].

During our previous work with the $\text{RE}_7\text{Zn}_{21}\text{T}_2$ family of compounds ($T = \text{Si, Ge, Sn, Pb}$) [13], a number of attempts were made to substitute Zn with Cd. These attempts at substitution were unsuccessful; however, they did yield a handful of ternary phases that, upon structural determination, were found to be $\text{RE}_6\text{Cd}_{23}\text{T}$ ($\text{RE} = \text{La–Gd}$; $T = \text{Sn, Sb, Pb, and Bi}$), filled variants of the $\text{Th}_6\text{Mn}_{23}$ structure with RE and Cd taking the places of Th and Mn, respectively. The recent study of the $\text{RE}_6\text{Mg}_{23}\text{T}$ family of compounds by Wrubl et al. [14] prompted further investigation into this new Cd-containing family.

2. Experimental Methods

2.1. Synthesis

All starting materials [rare-earth metals (ingot), Cd (shot), Pb (shot), Sn (shot), Bi (rod), Sb (shot) and Ge (powder)] were stored and loaded in a glove box under argon atmosphere to protect them from atmospheric water and oxygen. The Sb shot and Bi rods were crushed and ground into powder before use. The elements were sourced from either Alfa or Acros with stated purity greater than 99.9 %w (metal basis) and were used as received.

Due to the relatively volatile nature of Cd (b.p. 1040 K), the reaction mixtures were loaded into Nb containers, which were sealed at both ends with an arc welder under argon. The sealed samples were then encased in evacuated fused silica tubes to prevent oxidation of the Nb metal containers. As previously stated, these compounds were first discovered from reactions aimed at synthesizing $\text{RE}_7\text{Cd}_{21}\text{Sn}_2$ —the still undiscovered analogs of the $\text{RE}_7\text{Zn}_{21}\text{T}_2$ family—and the initial reaction conditions reflect this. These first reactions consisted of a reaction step at 1173 K (heating rate 133 K/h) for 12 h, followed by a secondary step at 1073 K (cooling rate 5 K/h), at which point they were removed from the tube furnace and allowed to cool to room temperature.

At first, two separate reactions with compositions $\text{RE}_7\text{Cd}_{21}\text{Sn}_2$ and $\text{RE}_6\text{Cd}_{23}\text{Sn}$ were carried out in parallel. Powder X-ray diffraction revealed that the two reactions gave similar results; while the title compounds appeared to be the major products, there remained several peaks left unaccounted for. Subsequently, only the composition $\text{RE}_6\text{Cd}_{23}\text{T}$ was used and the heat-treatment procedure was augmented in order to improve the yields. The modified temperature profile went as follows: a reaction step at 1173 K (heating rate 133–160 K/h) for 12 h, a secondary step at 1073 K (cooling rate 5 K/h) for 36 h, and an annealing step at 673 K (cooling rate 20 K/h) for 48 h, at which point they were brought back down to the 373 K holding temperature. During the 1173 K reaction step the fused silica tubes were gently rotated a number of times to ensure homogenization. This was done by manually rotating the ampoule by grasping the portion of the neck that sticks out of the side of the tube furnace (using thermally insulating glove). The overall yields were much improved from this refined profile, though small amounts of impurity phase(s)— $\text{RE}_{13}\text{Cd}_{58}$ [15] and occasionally RECd_3 [16]—were still apparent from the powder X-ray diffraction patterns.

The products of the above-described reactions are all quite brittle and are easily ground with a mortar and pestle. Right out of the Nb tubes, they exhibit a light gray color and a metallic luster, which give way to a dull, uniform dark gray when ground into powder.

2.2. Powder X-Ray Diffraction

Powder X-ray diffraction data were obtained at room temperature from a Rigaku MiniFlex powder diffractometer equipped with filtered Cu K α radiation. Analysis of the resulting patterns was performed using JADE 6.5 software. The diffraction patterns of the title compounds were indexed easily, and matched the

simulations (generated from single crystal work) very well. In addition, the diffraction patterns revealed the title compounds to be relatively air stable—peak intensities remain unchanged over a period of one week.

2.3. Single Crystal X-Ray Diffraction

Single-crystal X-ray diffraction data were obtained from a Bruker APEX II CCD-based diffractometer equipped with a monochromated Mo K α radiation source ($\lambda = 0.71073$ Å). Data acquisition was managed by the Bruker-supplied software. All crystals were selected from freshly made samples and cut under an optical microscope to desired dimensions (typically less than 0.1 mm). Multiple crystals were screened before the best ones were chosen for intensity data collection. The data sets were obtained as batch runs from ω - ϕ scans, with step widths of 0.4–0.6°, and exposure times of 8–10 seconds per frame. Absorption correction based on equivalents was performed with the SADABS software [17]. The crystal structures solutions and refinements were accomplished using the SHELX family of programs [18]. Important numerical parameters from the crystallographic work are summarized in Table 1.

The structural solutions consistently yielded all 6 atomic positions known for the $Zr_6Zn_{23}Si$ structure type [4]. The refinements converged easily, and the difference Fourier maps were generally featureless. In the final step of the refinement process, the atomic coordinates and labels for all atoms were standardized with STRUCTURE TIDY [19]. The refined atomic coordinates/equivalent isotropic displacement parameters are given in Table 2.

Table 1

Crystal data and refinement parameters for the compounds of the $RE_6Cd_{23}T$ ($RE = La-Gd$; $T = Sn, Sb, Pb$, and Bi) series. All are isotypic, crystallizing in the cubic crystal system with the space group $Fm\bar{3}m$ (No. 225) with four formula units per unit cell ($Z = 4$). Data collection temperature is 200(2) K.

Compound	$La_6Cd_{23}Pb$	$Ce_6Cd_{23}Sn$	$Ce_6Cd_{23}Sb$	$Ce_6Cd_{23}Pb$	$Ce_6Cd_{23}Bi$
FW (g/mol)	3625.85	3544.93	3547.98	3633.42	3635.20
a (Å)	14.2845(3)	14.2117(5)	14.1755(7)	14.2133(5)	14.1946(6)
V (Å ³)	2914.7(1)	2870.4(2)	2848.5(2)	2871.3(2)	2860.0(2)
ρ_{calc} (g/cm ³)	8.26	8.20	8.27	8.40	8.44
μ [Mo K α] (cm ⁻¹)	306.6	267.4	270.1	317.1	321.0
T_{min}/T_{max}	0.083/0.167	0.215/0.280	0.213/0.277	0.127/0.236	0.076/0.209
Range in h, k, l	$-9 < h < 16$ $-20 < k < 16$ $-19 < l < 13$	$-19 < h < 19$ $-19 < k < 19$ $-19 < l < 19$	$-11 < h < 18$ $-20 < k < 18$ $-17 < l < 20$	$-15 < h < 11$ $-20 < k < 20$ $-16 < l < 12$	$-16 < h < 19$ $-14 < k < 20$ $-18 < l < 20$
Collected/unique data	2076/265	10842/248	3382/271	2171/265	2298/260
R_{int}/R_{σ}	0.0299/0.0188	0.0327/0.0075	0.0607/0.0280	0.0513/0.0294	0.0357/0.0181
Extinction coefficient	0.000038(5)	0.000166(6)	0.000026(4)	0.00015(1)	0.000010(3)
GOF	1.103	1.552	1.089	1.129	1.263
R_1 [$F_0 > 4\sigma(F_0)$] ^a	0.0186	0.0123	0.0220	0.0271	0.0211
R_1 [all data] ^a	0.0196	0.0130	0.0260	0.0307	0.0245
wR_2 [all data] ^a	0.0448	0.0287	0.0472	0.0626	0.0490
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ (e Å ⁻³)	0.97, -1.45	0.79, -0.46	1.18, -1.88	1.44, -2.21	1.34, -1.42

Table 1 continued

Compound	$Pr_6Cd_{23}Sn$	$Pr_6Cd_{23}Pb$	$Nd_6Cd_{23}Sn$	$Nd_6Cd_{23}Pb$	$Sm_6Cd_{23}Pb$	$Gd_6Cd_{23}Pb$
FW (g/mol)	3549.68	3638.17	3569.33	3658.18	3694.49	3735.89
a (Å)	14.148(2)	14.1574(3)	14.131(2)	14.1162(9)	14.0431(4)	13.9936(7)

$V (\text{\AA}^3)$	2832.2(7)	2837.6(1)	2821.8(8)	2812.9(3)	2769.42(14)	2740.2(2)
$\rho_{\text{calc}} (\text{g/cm}^3)$	8.32	8.52	8.40	8.64	8.86	9.06
$\mu [\text{Mo K}\alpha] (\text{cm}^{-1})$	277.7	327.7	285.6	337.4	357.4	377.8
$T_{\text{min}}/T_{\text{max}}$	0.247/0.337	0.085/0.182	0.395/0.481	0.184/0.208	0.268/0.404	0.169/0.397
Range in h, k, l	$-19 < h < 19$	$-19 < h < 8$	$-19 < h < 19$	$-14 < h < 18$	$-13 < h < 19$	$-18 < h < 18$
	$-19 < k < 19$	$-17 < k < 19$	$-19 < k < 19$	$-20 < k < 20$	$-19 < k < 19$	$-12 < k < 11$
	$-19 < l < 19$	$-18 < l < 15$	$-19 < l < 19$	$-14 < l < 20$	$-13 < l < 18$	$-18 < l < 8$
Collected/unique data	10618/242	2298/258	9793/242	3336/271	4101/258	2891/238
$R_{\text{int}}/R_{\sigma}$	0.0556/0.0114	0.0347/0.0195	0.0532/0.0130	0.0532/0.0226	0.0604/0.0233	0.0536/0.0259
Extinction coefficient	0.000160(4)	0.00018(1)	0.000241(8)	0.000105(9)	0.000126(8)	0.000015(4)
GOF	1.302	1.189	1.231	1.053	1.157	1.107
$R_1 [F_0 > 4\sigma(F_0)]^a$	0.0105	0.0185	0.0124	0.0219	0.0227	0.0209
$R_1 [\text{all data}]^a$	0.0129	0.0192	0.0141	0.0236	0.0259	0.0239
$wR_2 [\text{all data}]^a$	0.0212	0.0392	0.0277	0.0532	0.0504	0.0452
$(\Delta\rho)_{\text{max}}, (\Delta\rho)_{\text{min}} (\text{e \AA}^{-3})$	0.62, -0.78	1.06, -1.90	0.70, -0.60	1.38, -1.53	1.69, -2.42	1.65, -2.00

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2 F_o^2 + (A \cdot P)^2 + (B \cdot P)]$, and $P = (F_o^2 + 2F_c^2)/3$. A and B are weight coefficients, respectively. CIFs have been deposited with the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; Email: crysdata@fiz-karlsruhe.de), with depository numbers: CSD-431964 for $\text{La}_6\text{Cd}_{23}\text{Pb}$, CSD-431965 for $\text{Ce}_6\text{Cd}_{23}\text{Sn}$, CSD-431966 for $\text{Ce}_6\text{Cd}_{23}\text{Sb}$, CSD-431967 for $\text{Ce}_6\text{Cd}_{23}\text{Pb}$, CSD-431968 for $\text{Ce}_6\text{Cd}_{23}\text{Bi}$, CSD-431969 for $\text{Pr}_6\text{Cd}_{23}\text{Sn}$, CSD-431970 for $\text{Pr}_6\text{Cd}_{23}\text{Pb}$, CSD-431971 for $\text{Nd}_6\text{Cd}_{23}\text{Sn}$, and CSD-431972 for $\text{Nd}_6\text{Cd}_{23}\text{Pb}$, CSD-432214 for $\text{Sm}_6\text{Cd}_{23}\text{Pb}$, and CSD-432215 for $\text{Gd}_6\text{Cd}_{23}\text{Pb}$.

2.4. Magnetic Susceptibility Measurements

A physical property measurement system by Quantum Design (PPMS) was employed for the field cooled (FC) direct current (dc) magnetic susceptibility measurements. Applied magnetic field (H) was set at 3 kOe and the temperature range for the measurements was from 5 K to 300 K. Polycrystalline samples (ca. 100–150 mg) were loaded into gel capsules, the remaining volume of which were packed with cotton to keep the samples in place. The raw magnetization (M) data was corrected for capsule material contribution and converted to molar susceptibility ($\chi_m = M/H$), which was later normalized per mole of rare-earth element. The paramagnetic Weiss temperatures and effective magnetic moments were calculated from the linear fitting of the inverse magnetic susceptibility vs temperature, according to the Curie-Weiss law [20].

3. Results

3.1. Synthesis

Peak positions and intensities corresponding to the title phases were easily identified for nearly every reaction composition tested. Out of all the attempted reactions, those aimed at synthesizing the compounds $(\text{Ce/Pr/Nd})_6\text{Cd}_{23}\text{Pb}$ yielded the purest products, with all three shown to be either phase-pure or very nearly so by powder diffraction. The remaining compositions yielded varying amounts of binary impurity phases in addition to the title phases. Attempts to synthesize the yet undiscovered $\text{Ce}_6\text{Cd}_{23}$ binary phase failed, producing instead a mixture of other binary phases, providing evidence for the necessary presence of either group 14 or 15 element for the realization of this structure.

Table 2

Atomic Coordinates and Equivalent Isotropic Displacement Parameters (U_{eq}^a) for $\text{Ce}_6\text{Cd}_{23}T$ ($T = \text{Sn, Sb, Pb, and Bi}$)

Atom	Site	x	y	z	$U_{\text{eq}} [\text{\AA}^2]$
$\text{Ce}_6\text{Cd}_{23}\text{Sn}$					

Ce	24e	0.27880(4)	0	0	0.0129(2)
Cd1	32f	0.33754(3)	x	x	0.0183(2)
Cd2	32f	0.12477(3)	x	x	0.0164(2)
Cd3	24d	0	1/4	1/4	0.0131(2)
Sn	4b	1/2	1/2	1/2	0.0166(3)
Cd4	4a	0	0	0	0.0251(1)
<hr/> Ce ₆ Cd ₂₃ Sb					
Ce	24e	0.28120(5)	0	0	0.0126(2)
Cd1	32f	0.33380(4)	x	x	0.0150(2)
Cd2	32f	0.12375(3)	x	x	0.0153(2)
Cd3	24d	0	1/4	1/4	0.0134(2)
Sb	4b	1/2	1/2	1/2	0.0141(4)
Cd4	4a	0	0	0	0.0199(5)
<hr/> Ce ₆ Cd ₂₃ Pb					
Ce	24e	0.27652(7)	0	0	0.0144(3)
Cd1	32f	0.33845(5)	x	x	0.0188(3)
Cd2	32f	0.12557(4)	x	x	0.0173(3)
Cd3	24d	0	1/4	1/4	0.0140(3)
Pb	4b	1/2	1/2	1/2	0.0175(4)
Cd4	4a	0	0	0	0.0234(7)
<hr/> Ce ₆ Cd ₂₃ Bi					
Ce	24e	0.27793(7)	0	0	0.0147(2)
Cd1	32f	0.33483(4)	x	x	0.0177(3)
Cd2	32f	0.12452(4)	x	x	0.0167(2)
Cd3	24d	0	1/4	1/4	0.0151(3)
Bi	4b	1/2	1/2	1/2	0.0157(3)
Cd4	4a	0	0	0	0.0223(6)

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

The most commonly encountered impurity phase appears to have been the hexagonal $RE_{13}Cd_{58}$ with the incidental occurrence of the cubic $RECd_3$. Many powder diffraction patterns (particularly those of the Sn compounds) included a trio of prominent impurity peaks in the range of $2\theta = 33\text{--}37^\circ$ —the positions and intensities of which corresponded with the three most intense Bragg reflections for each respective 13:58 phase. This speculation was confirmed for crystals obtained from a $La_6Cd_{23}Sn$ sample—a standard unit cell scan on a crystal from this batch returned a hexagonal cell with parameters $a = 15.8 \text{ \AA}$ and $c = 15.6 \text{ \AA}$ —a near perfect match for $La_{13}Cd_{58}$ [15]. This finding differs from the Wrubl study [14], which found $REMg_3$ as the primary impurity phase for $RE_6Mg_{23}T$ reactions. This is understandable, seeing that $La_{13}Mg_{58}$ has not yet been discovered, and that the 13:58 phase is closer in composition to the $RE_6Cd_{23}T$ than is a 1:3 phase. Wrubl et al. offered a topological analysis of the $RE_6Mg_{23}T$ and $REMg_3$ phases [14], and the structural relationship described therein applies to their Cd-counterparts just as well. No deeper structural relationship, however, has been identified for $RE_{13}Cd_{58}$ beyond mere stoichiometric similarity.

With respect to phase-purity, two general trends were observed in the powder diffraction data. Phase purity of $RE_6Cd_{23}T$ reached a maximum for $RE = Ce$ and steadily decreased through the rest of the explored part of the lanthanide series. Specifically, we note that no compounds beyond Gd were found, suggesting that the phase is

avored for the early to mid-late rare-earth metals (larger atomic sizes; lower melting points). In addition, the identity of atom T also seem to have played a role in the product purity as well, with yields of the targeted $RE_6Cd_{23}T$ phase steadily increasing in the order of $Sb < Bi < Sn < Pb$. In other words, heavier (larger) interstitials resulted in better yields compared to their lighter (smaller) counterparts. Although not fully quantified yet, it appears that pnictogen interstitials are less effective “fillers” compared to the tetrrels. We are currently experimenting with the heavy triels (group 13 elements) and the heavy chalcogens (group 16 elements) to check if $RE_6Cd_{23}T$ phases can be made.

3.2. Crystal Structure

Within the space group $Fm\bar{3}m$, the $4a$ and $4b$ Wyckoff sites have identical site symmetry [21]. Thus, the structure of Th_6Mn_{23} can be equivalently described as both $cF116-f^2eda$ and $cF116-f^2edb$, the latter having an origin shift of $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ relative to the former. For the filled Th_6Mn_{23} -type structure $Zr_6Zn_{23}Si$, the standard presentation is $cF120-f^2edba$, with position $4b$ occupied by the Si atom. In order to be consistent with standardized settings, our discussion on Th_6Mn_{23} and $Zr_6Zn_{23}Si$ -type structures will follow the notations $cF116-f^2eda$ and $cF120-f^2edba$, respectively. Note that in this presentation, position $4b$ is taken to be the interstitial, while the $4a$ position is taken by Cd4 (Table 2). We also note that the $Zr_6Zn_{23}Si$ prototype exhibits small Zn deficiency on the Zn4 site, which is apparently not the case with any of the 11 refined $RE_6Cd_{23}T$ structures—in spite of the slightly enlarged U_{eq} for this atom (Table 2), refining Cd4 with freed site occupation factor (SOF) showed that its SOF does not vary from full (within 3σ). To support this conclusion, the $Ce_6Cd_{23}Pb$ structure, the one with the largest equivalent displacement parameter (U_{eq}) for Cd4, was drawn with anisotropic displacement parameters, and the illustration is provided as Supporting Information. It shows that even though the thermal ellipsoid (90% probability level) for Cd4 is larger than the rest, the difference is not as significant as it is for Zn4 and the rest of the atoms in $Zr_6Zn_{23}Si$ [4].

One immediate observation was the miniscule contribution of atom T to the overall size of the unit cell. Looking through the $Ce_6Cd_{23}T$ series in Table 1, one can see that the three respective values of the lattice parameters are all within 0.02 Å of each other. The nearest-neighbor interatomic distances in Table 3 lend support to this observation, as the $Ce-T$ distances (d_{Ce-T}) differ only by just over 0.03 Å despite the noticeably greater difference in the covalent radii of Sn, Pb, and Bi (1.39, 1.46, and 1.48 Å, respectively [22]). By contrast, the $Ce_6Mg_{23}T$ series was reported to have an increase in d_{Ce-T} by about 0.1–0.2 Å from one period to the next [14], behaving more conventionally in this regard.

The positions of Cd1 and Cd2 do seem to shift within the cell in response to the size of the T atom. Cd2, for example is noticeably closer to Cd3 and farther away from Cd4 when $T = Pb$ as compared with $T = Sn$. This may indicate some form of structural shift to accommodate larger guest atoms. The low magnitude of these shifts may be due to bond-length constraints within the Cd sub-lattice.

When analyzing the Cd–Cd distances given in Table 3, it should first be noted that Cd has a covalent radius of 1.44 Å [22] and an elemental distance $d_{Cd-Cd} = 2.98$ Å [23]. With these in mind, it can be inferred that the shorter Cd1–Cd3 contacts ($d_{Cd1-Cd3} \approx 2.90$ Å) are bonds of covalent character, while the longer Cd1–Cd2 and Cd2–Cd3 contacts ($d_{Cd1-Cd2} \approx 3.11$ Å, $d_{Cd2-Cd3} \approx 3.07$ Å) are of a more delocalized metallic-like character.

Wrubl et al. [14], in their analysis of the electronic structure of $La_6Mg_{23}C$, reported similar findings—an overall metallic character (given by the position of the Fermi level), with stronger, more covalent-character interactions for the Mg1–Mg3 and Mg2–Mg4 contacts [14]. Polar La–C interactions are indicated to be the strongest by far, while La–Mg interactions are significantly weaker and likely metallic in character. Lastly, Mg–C interactions were found to be antibonding near the Fermi level.

Table 3

Interatomic distances for the compound of the $Ce_6Cd_{23}T$ series. Distances for the remaining five structures can be found tabulated in the Supporting Information.

Neighbor	Distances (Å)
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Contact	Ce ₆ Cd ₂₃ Sn	Ce ₆ Cd ₂₃ Sb	Ce ₆ Cd ₂₃ Pb	Ce ₆ Cd ₂₃ Bi
Ce – <i>T</i>	3.143(1)	3.102(1)	3.176(1)	3.152(1)
Ce – Cd1	3.370(1) × 4	3.414(1) × 4	3.364(1) × 4	3.412(1) × 4
Ce – Cd2	3.328(1) × 4	3.337(1) × 4	3.312(1) × 4	3.315(1) × 4
Cd1 – Cd2	3.117(1) × 3	3.097(1) × 3	3.111(1) × 3	3.095(1) × 3
Cd1 – Cd3	2.902(1) × 3	2.894(1) × 3	2.904(1) × 3	2.897(1) × 3
Cd2 – Cd1	3.117(1) × 3	3.097(1) × 3	3.111(1) × 3	3.095(1) × 3
Cd2 – Cd3	3.117(1) × 3	3.079(1) × 3	3.072(1) × 3	3.077(1) × 3
Cd2 – Cd4	3.071(1)	3.039(1)	3.091(1)	3.061(1)
Cd3 – Cd1	2.902(1) × 4	2.894(1) × 4	2.904(1) × 4	2.897(1) × 4
Cd3 – Cd2	3.117(1) × 4	3.079(1) × 4	3.072(1) × 4	3.077(1) × 4
Cd4 – Cd2	3.071(1) × 8	3.039(1) × 8	3.091(1) × 8	3.061(1) × 8
<i>T</i> – Ce	3.143(1) × 6	3.102(1) × 6	3.176(1) × 6	3.152(1) × 6

Based on these findings, the authors asserted that atom *T* plays a central role in the stabilization of $RE_6Mg_{23}T$ [15], as their attempts to synthesize RE_6Mg_{23} binaries failed, whereas Ba_6Mg_{23} is already established in the literature [24]. Ba and La both contribute their s and d orbitals in these structures, and so Ba contributes only two valence electrons whereas La contributes three [14]. Wrubl et al. also postulated that the electronegative interstitial withdraws the third valence electron of *RE* and, in doing so, stabilizes the electron surplus that a RE_6Mg_{23} -type binary system would not otherwise have tolerated [14].

We can infer that this stabilization effect holds true for $RE_6Cd_{23}T$ (as mentioned earlier, RE_6Cd_{23} could not be synthesized). However, a direct analogy between the two 6:23:1 electronic structures may not be possible. The difference between χ_{Cd} and χ_{RE} (0.49–0.59) is significantly larger than the difference between χ_{Mg} and χ_{RE} (0.11–0.21). The *RE*–Cd interactions are likely more polar than those between Mg and *RE*, and so we would expect the *RE*–Cd interatomic distances to contract relative to what would be expected based purely on covalent radii.

Undoubtedly, a comparison of the $Ce_6Mg_{23}Sn$ and $Ce_6Cd_{23}Sn$ crystal structures revealed that $d_{Mg-Ce} > d_{Cd-Ce}$ by about 0.1 Å for all complementary Mg/Cd positions [14]. In addition, the values of both d_{Ce-Sn} and cell parameter *a* were lower for $Ce_6Cd_{23}Sn$ (by magnitudes of ~0.06 Å and ~0.4 Å, respectively) than those for $Ce_6Mg_{23}Sn$.

It is worth noting, however, that the Mg–Mg distance in elemental Mg ($d_{Mg-Mg} = 3.197$ Å) is greater than the Cd–Cd distance for elemental Cd [23], which may partially account for the greater volume of the $Ce_6Mg_{23}Sn$ unit cell. Also of note is the difference in the number of contacts for each Cd position, which may contribute to distortion of Cd–Cd bond distances from the ideal—a possibility previously put forth by Samal and Corbett [11]. A more formal and in-depth exploration into the electronic structure of $RE_6Cd_{23}T$ is arguably warranted.

Another observation deserving of a specific mention is that $Ce_6Cd_{23}Bi$ has a smaller unit cell than $Ce_6Cd_{23}Sn$, despite having a greater covalent radius of *T* ($r_{Bi} = 1.48$ Å vs. $r_{Sn} = 1.39$ Å) [22], and a greater Ce–*T* interatomic distance ($d_{Ce-Bi} = 3.152$ Å vs. $d_{Ce-Sn} = 3.143$ Å). It can also be noted that, while $d_{Ce-Bi} > d_{Ce-Sn}$, the various Cd–Cd contacts are somewhat shorter in $Ce_6Cd_{23}Bi$ as compared with those in $Ce_6Cd_{23}Sn$.

Given that $\chi_{Bi} > \chi_{Sn}$, it follows that Bi can more strongly sequester Ce's third valence electron. It then follows, from the stabilization effect discussed earlier, that the greater localization of these electrons lends greater stability to the rest of the structure. It is by this mechanism that the various Cd–Cd bonds, as well as the unit cell itself, relax and contract in spite of Bi's greater size. This could also explain the short d_{Ce-Bi} , as compared to the sum of their covalent radii.

Analogous findings were reported for $Ce_6Mg_{23}As$, which possessed a shorter d_{Ce-T} , lattice parameter *a*, and several shorter d_{Cd-Cd} when compared to $Ce_6Cd_{23}Si$ [14]. By analogy, these results were likely due to the electronegativity of As overcoming the effect of its size in determining the unit cell volume of the resulting structure.

Fig. 1. Local coordination geometry for the RE, Cd3, Cd4, and interstitial atoms *T*. Only next nearest-neighbors have been included in these representations.

The electronegativity of *T* also seems to influence the size of the various coordination polyhedra. Looking at Table 3, *T* = Sb yields noticeably shorter $d_{\text{Ce}-T}$ and $d_{\text{Cd2}-\text{Cd4}}$ as well as longer $d_{\text{Cd2}-\text{Cd3}}$ and $d_{\text{Ce}-\text{Cd2}}$ compared with *T* = Sn. This occurs in spite of the similarity of Sn and Sb covalent radii [22], and one could infer that it is the result of the increased electronegativity from Sn to Sb. This comparison holds true for Pb and Bi as well. We can interpret this as a contraction of the *T* and Cd4 coordination polyhedra, while the Cd3 polyhedra appear to become slightly larger.

As has been noted before in the literature [3], $\text{Th}_6\text{Mn}_{23}$ and $\text{Zr}_6\text{Zn}_{23}\text{Si}$ -type compounds adopt rather complex structures and are difficult to visualize directly. It becomes rather easy, however, once the coordination spheres of the individual atoms are considered separately. For the sake of graphical clarity, we have decided to include only covalently bonded neighbor atoms in the presented coordination polyhedra (Figures 1 and 2). The octahedral coordination about atom *T* has already been established and discussed. As for Cd3, the Cd1 and Cd2 neighbors coordinate as a pair of truncated trigonal prisms. Cd4 has 8 equidistant Cd2 neighbors that form a centered cubic arrangement. Lastly, the one *T*, four Cd1, and four Cd2 neighbors of RE form a more irregular polyhedron whose shape resembles that of a monocapped tetragonal prism. Cd1 nor Cd2, as discussed have very few neighbors that are distances indicative of covalent bonds, and have therefore been excluded from our simplified descriptive model. However, if one considers the weak interactions (over 3.0–3.1 Å long) between Cd1 and Cd2, the latter can be seen as forming distorted cubane-like clusters in the interstices between the rare-earth polyhedra (Supporting information). Other, more in-depth structural descriptions have been put forth elsewhere [2,14,25].

In this simplified structural representation, with the Cd3 polyhedra removed from view, the Cd4 coordination cubes appear to be arranged in a face-centered cubic sub-lattice, as seen in Figure 2. The Ce–*T* octahedra are also observed to adapt this arrangement, as would be inferred by the symmetric equivalence of positions 4*a* and 4*b* [21]. What is more, the Cd3 polyhedra form their own mesh-like sub-lattice arrangement, which fills in the gaps between the two previously mentioned *fcc* arrangements. Thus, the overall structure of $\text{RE}_6\text{Cd}_{23}\text{T}$ can be roughly described as two interpenetrating *fcc* sub-lattices, one shifted ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) relative to the other (i.e., rock-salt like), suspended within a Cd3 polyhedral mesh.

Fig. 2. Representations of the entire polyhedral structural description (left) and the interpenetrating *fcc*-like sublattices made up of *RE*-octahedra centered by *T*-atoms and Cd4-cubes centered by Cd4 atoms (right). Online color: *T*-atom centered octahedra of rare-earth metal atoms are drawn in red-orange, Cd4-centered cubes made up of Cd2 atoms are drawn in blue. The Cd3-centered polyhedra of four Cd1 and four Cd2 atoms are shown in grey. Unit cells are outlined.

3.3. Magnetism

Phase-pure material could only be obtained for the $RE_6Cd_{23}Pb$ portion of the series, and so measurements could only be performed on polycrystalline $Ce_6Cd_{23}Pb$, $Pr_6Cd_{23}Pb$, and $Nd_6Cd_{23}Pb$. As seen in Figure 3, the magnetic responses for all three phases obey the Curie-Weiss law $\chi(T) = C/(T-\theta_p)$, where C is the Curie constant ($N_A\mu_{eff}^2/3k_B$) and θ_p is the paramagnetic Weiss temperature, in both high and low-temperature regions. The effective magnetic moments, calculated from the Curie constants ($\mu_{eff} = 2.44(3) \mu_B$ for $Ce_6Cd_{23}Pb$; $\mu_{eff} = 3.65(2) \mu_B$ for $Pr_6Cd_{23}Pb$; $\mu_{eff} = 3.66(2) \mu_B$ for $Nd_6Cd_{23}Pb$), are very close to the theoretical values for free RE^{3+} ions, calculated from the Hund's rules ($2.54 \mu_B$ for Ce^{3+} ; $3.58 \mu_B$ for Pr^{3+} ; $3.62 \mu_B$ for Nd^{3+}) [20]. This confirms the local-moment magnetic behavior due to the 4f electron(s) from the rare-earth metal. θ_p for all three samples is negative— $\theta_p = -10$ K for $Ce_6Cd_{23}Pb$; $\theta_p = -9$ K for $Pr_6Cd_{23}Pb$; and $\theta_p = -13$ K for $Nd_6Cd_{23}Pb$ —suggestive of weak antiferromagnetic correlations. However, there are no visible signs for ordering in neither $\chi(T)$ nor $d\chi(T)/dT$ plots.

The magnetic properties of both Th_6Mn_{23} and $Zr_6Zn_{23}Si$ -type structures appear to depend largely on interactions of the elements on site 24e with those occupying the 24d and 4a positions. For the Th_6Mn_{23} -type family RE_6Mn_{23} ($RE = Y, Nd, Sm, Gd-Tm, Lu$), the Mn sub-lattice was found to undergo collinear ferrimagnetic ordering at high temperatures, whereas the rare-earth metal sub-lattice was found to adopt non-collinear ordering at low temperatures [26].

On the other hand, the $Zr_6Zn_{23}Si$ -type phase $Mn_8Pd_{15}Si_7$ (for which sites 4a and 32f were of mixed Pd/Mn occupancy) was found to exhibit both ferromagnetic and antiferromagnetic effects in competition with each other [27]. In both of these cases, the elements occupying positions 24d and 4a were themselves paramagnetic, so it is understandable that they would undergo magnetic interactions both with each other and with paramagnetic elements present at 24e. All of the tested interstitial elements *T*, as well as elemental Cd, are diamagnetic, rendering such exchange interactions impossible in $RE_6Cd_{23}T$.

Fig. 3. χ_m vs. temperature for $RE_6Cd_{23}Pb$ ($RE = Ce, Pr, \text{ and } Nd$). The insets show the inverse susceptibility vs. temperature, and the red lines are representing the linear fits of the data to the Curie-Weiss law.

Conclusion

The discovery of $RE_6Cd_{23}T$, preceded by that of $RE_6Mg_{23}T$, warrants further exploratory work on the crystal chemistry of other compounds with the cubic $Zr_6Zn_{23}Si$ structure type, as these ternary families only add to the potential phase-space available for investigation. In addition, the use of more electronegative elements (such as Cd) in place of Mg could give rise to new, more polar interactions, giving rise to unusual electronic structures.

In that regard, our two next target systems to work on will be as follows. First, we will attempt to extend this chemistry to the element Zn beyond the principle compound $Zr_6Zn_{23}Si$. Alternate synthetic approaches may need to be taken, as it will be difficult to formulate a reaction scheme that favors a 6:23:1 phase over the already established 7:21:2 phases. Second, we will attempt to form other rare-earth metal and Cd-containing phases by including different elements T than the ones already explored, such that T will have higher electronegativity and enhanced ability to sequester the “surplus” electrons from the rare-earth metals. In the context of the 6:23:1 chemistry discussed here, and extrapolating from the phase $La_6Mg_{22}Al$ which has already been described [28], we think it will be worth trying out other substituents and expanding on the 6:22:1 chemistry as well.

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Appendix A.

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc..... The information consists of additional crystallographic data for $RE_6Cd_{23}T$ ($RE = La, Pr, Nd, Sm, Gd$; $T = Sn, Pb$), as well as a representation of the distorted cubane-like clusters made up of Cd1 and Cd2, found in the interstices between the rare-earth metal polyhedra, a layer-by-layer breakdown of the structure following the polyhedral description in the text, and an illustration of the unit cell of the $Ce_6Cd_{23}Pb$ structure, with all the atoms shown with their anisotropic displacement parameters.