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Structure of $Cd_{12.7(1)}Sb_{10}$

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The cadmium analogue of the thermoelectric material "β-Zn_4Sb_3" has been prepared by reaction of a mixture of the elements with nominal stoichiometry "$Cd_{57}Sb_{43}$" at 430 °C. The composition of this phase, previously assumed to be "Cd_4Sb_3" in analogy to "β-Zn_4Sb_3", has been determined to be approximately $Cd_{12.7(1)}Sb_{10}$, in agreement with recently revised formulations for the zinc analogue, which is now better described as $Zn_{13}Sb_{10}$. Single-crystal X-ray diffraction studies at 295 K showed that the structure of $Cd_{12.7}Sb_{10}$ (space group $R\bar{3}c$, $Z = 6$, $a = 13.0395(14)$ Å, $c = 13.0346(14)$ Å) is similar to that of $Zn_{13}Sb_{10}$, but with a more complex set of interstitial metal sites. The structure remains unchanged at 193 K. The electrical resistivity of $Cd_{12.7}Sb_{10}$ decreases linearly with decreasing temperature and shows a modest upturn near 35 K.

Introduction

Early investigations in the binary Cd−Sb system were motivated by the search for materials for use in semiconductor technology, but progress was hampered by the complexity of phase relationships and the ambiguity of structural data.[1−15] Recently, a renewed flurry of activity in the corresponding Zn−Sb system was unleashed by the discovery that "β-Zn_4Sb_3" may be a good thermoelectric material.[16−21] The promising properties of "β-Zn_4Sb_3" can be traced to the significant disorder introduced by the presence of multiple partially occupied Zn sites within an ordered framework structure.[22−26] This type of structure fulfills the characteristics required in the ideal model of a "phonon glass−electron crystal", the mantra now deeply ingrained in the thermoelectrics community.[27] Whereas the room-temperature polymorph, "β-Zn_4Sb_3" ($R\bar{3}c$), has a disordered structure,[22,23] the low-temperature polymorph, "α-Zn_4Sb_3" ($P\bar{1}$), shows no Zn deficiencies and was established to have a completely ordered structure with the composition $Zn_{13}Sb_{10}$.[24−26] This result suggests that the true composition of "β-Zn_4Sb_3" is also $Zn_{13}Sb_{10}$.

The analogous "Cd_4Sb_3" phase exists in the Cd−Sb system and is assumed to be isostructural to "β-Zn_4Sb_3",[10] but without the occurrence of polymorphism. Early electrical resistivity and thermopower measurements were conducted on $Zn_{4-x}Cd_xSb_3$ solid solutions, assumed to be complete in the entire range $0 < x < 4$.[5,6,8] More recent measurements were made on $Zn_{4-x}Cd_xSb_3$ samples restricted to $0.2 < x <$

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Table 1. Comparison of Structural Models

model	composition	data/parameters	$R(F)/R_w(F_o^2)^a$	$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	ρ_{calcd} (g cm^{-3})
full Cd occupancy	$Cd_{12}Sb_{10}$	809/18	0.0825/0.2387	8.28/−3.34	6.661
deficient Cd	$Cd_{10.6(1)}Sb_{10}$	809/19	0.0760/0.2221	8.11/−1.92	6.241
+ three interstitial Cd	$Cd_{12.4(1)}Sb_{10}$	809/34	0.0431/0.1029	2.51/−1.49	6.778
+ four interstitial Cd	$Cd_{12.8(1)}Sb_{10}$	809/39	0.0406/0.0966	2.23/−1.44	6.889
+ five interstitial Cd	$Cd_{12.9(1)}Sb_{10}$	809/44	0.0369/0.0849	1.13/−1.10	6.909
+ equal interstitial Cd U_{eq}	$Cd_{12.7(1)}Sb_{10}$	809/40	0.0371/0.0854	1.20/−1.28	6.875

[a] $R(F)$ for $F_o^2 > 2\sigma(F_o^2)$; $R_w(F_o^2)$ for all data.

1.2, showing improved thermoelectric properties compared to "β-Zn_4Sb_3".[17] It is not clear if the range of solid solubility between "β-Zn_4Sb_3" and "Cd_4Sb_3" was limited because of experimental difficulties or because of more intrinsic reasons, such as the possibility that the end-members may perhaps not really be perfectly isostructural. Given the presence of disorder already found in "β-Zn_4Sb_3", it would seem important to establish the detailed crystal structure of "Cd_4Sb_3" pending further investigations into its properties. We report here a structural investigation of "Cd_4Sb_3", similar to "β-Zn_4Sb_3" but with even more interstitial sites identified than previously reported for "β-Zn_4Sb_3".

Experimental Section

Synthesis. Starting materials were powders of Cd (99.999%, Cerac) and Sb (99.999%, Alfa-Aesar). A mixture corresponding to the nominal composition "$Cd_{57}Sb_{43}$" was placed within an evacuated fused-silica tube. The tube was heated at 650 °C for 24 h, slowly cooled to 430 °C over 4 d, kept at 430 °C for a further 4 d, and then quenched in cold water. Powder X-ray diffraction patterns collected on an Inel powder diffractometer (Cu Kα_1 radiation) equipped with a CPS 120 detector indicated single-phase product. Crystals selected for the single-crystal X-ray structure determination were prescreened by EDX analysis on an Hitachi S-2700 scanning electron microscope.

To ascertain the homogeneity range in this "Cd_4Sb_3" phase, a series of reactions was conducted as above but with nominal compositions varying between "$Cd_{55}Sb_{45}$" and "$Cd_{65}Sb_{35}$" in ∼1−2 at. % increments. On the basis of previous phase diagrams,[1,4,7,9,11,15] the neighboring phase identified as "Cd_3Sb_2" may be expected to form at compositions below ∼42% Sb. For these reactions, the second temperature dwell was set to 400 °C, below the lowest reported value for the peritectic decomposition temperature (∼410 °C) of "Cd_3Sb_2".[4] The products were analyzed by powder X-ray diffraction.

Structure Determination. Single-crystal X-ray diffraction data on a crystal selected from the "$Cd_{57}Sb_{43}$" reaction were collected at 295 K on a Bruker Platform/SMART 1000 CCD diffractometer using ω scans. Structure solution and refinement were carried out with use of the SHELXTL (version 6.12) program package.[28] Face-indexed numerical absorption corrections were applied. Inspection of the intensity pattern clearly revealed threefold rotational symmetry consistent with a trigonal lattice and systematic absences consistent with the presence of a c glide plane. On this basis, the centrosymmetric space group $R\bar{3}c$ was chosen.

Table 1 summarizes the progression of structural models considered in the course of the refinement. Direct methods established the initial positions of the main Cd (36f), Sb1 (18e), and Sb2 (12c) sites. Partial occupancy of the Cd site was signalled by its elevated displacement parameter (U_{iso} = 0.0419(5) Å^2) compared to those for the Sb sites (0.0244(4)−0.0257(4) Å^2). When refined, the occupancy of the Cd site converged to 0.88(1). At this stage, significant residual electron density was still present, as indicated in the difference electron density map. Additional interstitial Cd sites were introduced one at a time, with each successive model deemed acceptable by applying the Hamilton test for each site separately at a 0.5% significance level.[29] After five interstitial Cd sites were located, the difference electron density map became featureless and the calculated density approached its experimental value of 6.87(2) g/cm^3.[30] Because of the proximity of these interstitial Cd sites, there is high correlation of the occupancies with their displacement parameters. Therefore, the displacement parameters were refined isotropically and were constrained to be equal for all five interstitial Cd sites. The results of this refinement were no worse than previously, but with a reduction in the number of refined parameters. In the final refinement, the composition converged to $Cd_{12.7(1)}Sb_{10}$, corresponding to a calculated density of 6.875 g/cm^3, in excellent agreement with the experimental value.

Low-temperature X-ray diffraction data for the same crystal used above were measured at 193 K. The unit cell contracts as expected (a = 13.022(2) Å, c = 13.016(2) Å, V = 1911.3(8) Å^3) but the structure remains unchanged ($R(F)$ (for $F_o^2 > 2\sigma(F_o^2)$) = 0.041, $R_w(F_o^2)$ = 0.096) with all interstitial Cd sites still present.

Room-temperature X-ray diffraction data for a separate crystal from the same synthesis batch were also analyzed, leading to a refined composition of $Cd_{12.8(1)}Sb_{10}$ ($R(F)$ (for $F_o^2 > 2\sigma(F_o^2)$) = 0.033, $R_w(F_o^2)$ = 0.072). The recurrence of the same five interstitial Cd sites lends support to their authenticity. The positional parameters and occupancies converged to values that were identical to those in the first refinement, within standard uncertainties.

Crystal data and further details of the first data collection are given in Table 2. Atomic positions were standardized with the program STRUCTURE TIDY.[31] Final values of the positional and displacement parameters are given in Table 3. Interatomic distances are listed in Table 4. Further data, in the form of a Crystallographic Information File (CIF), are available as Supporting Information or may be obtained from Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany (No. CSD-417610).

Electrical Resistivity. The electrical resistivity was measured on fragments extracted from the "$Cd_{57}Sb_{43}$" reaction. Standard four-probe measurements were conducted between 2 and 300 K on a Quantum Design PPMS system equipped with an ac transport controller (Model 7100), with a current of 100 μA and a frequency of 16 Hz.

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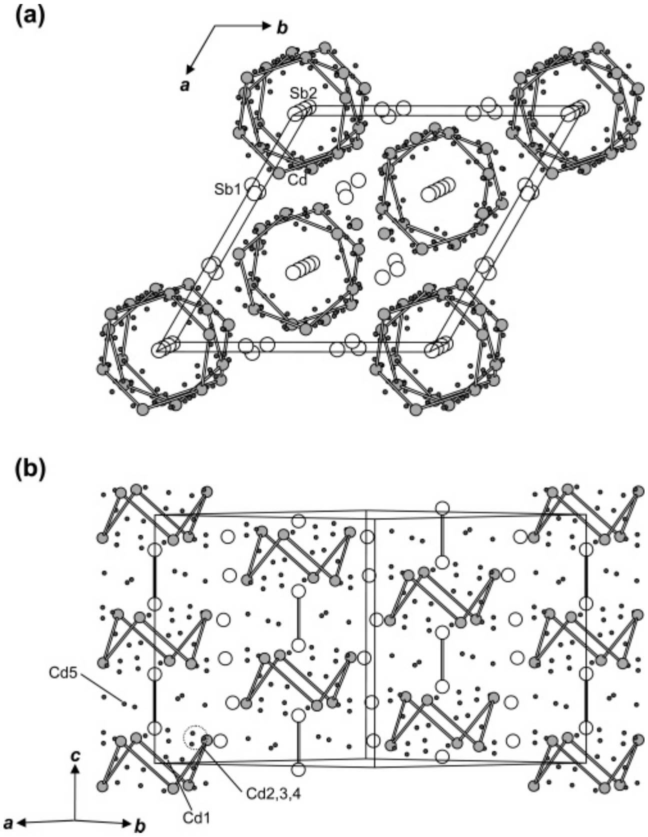

Figure 1. Structure of $Cd_{12.7}Sb_{10}$ viewed down the (a) [001] direction and (b) approximately [110] direction. The shaded circles are the main Cd sites, the small solid dots are interstitial Cd sites, and the open circles are Sb atoms.

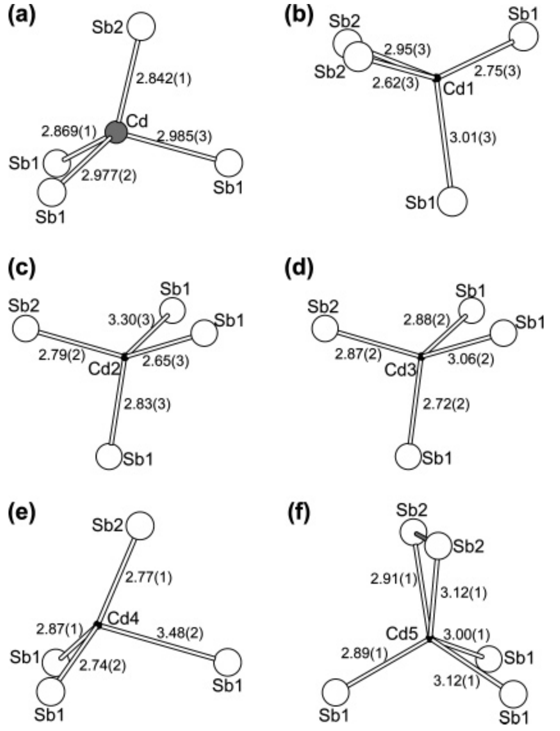

Figure 2. Coordination of Sb atoms around the Cd sites in $Cd_{12.7}Sb_{10}$.

Results and Discussion

Three binary phases have been previously identified in the Cd−Sb phase diagram: "Cd_3Sb_2", "Cd_4Sb_3", and CdSb, the first two being metastable.[1,4,9,11,15] The crystallization behavior of these phases is rather complex and has not yet been completely resolved.[30,32] Our synthesis of "Cd_4Sb_3" closely satisfied the conditions required to yield homogeneous product, viz. use of a stoichiometric initial composition and annealing temperatures in the range 430−450 °C.[32] In a series of reactions with loading compositions varying from 35 to 45 at. % Sb, we observed the best phase purity of "Cd_4Sb_3" only within the range of 43−44% Sb. Below 43% Sb, significant amounts of another phase, presumably "Cd_3Sb_2", were formed. Above 44% Sb, the major phase was CdSb,[33] with no traces of "Cd_4Sb_3" present. The cell parameters refined for the "Cd_4Sb_3" phase present in all reactions where it was observed showed little variation and no clear dependence with loading composition (Figure 1 in Supporting

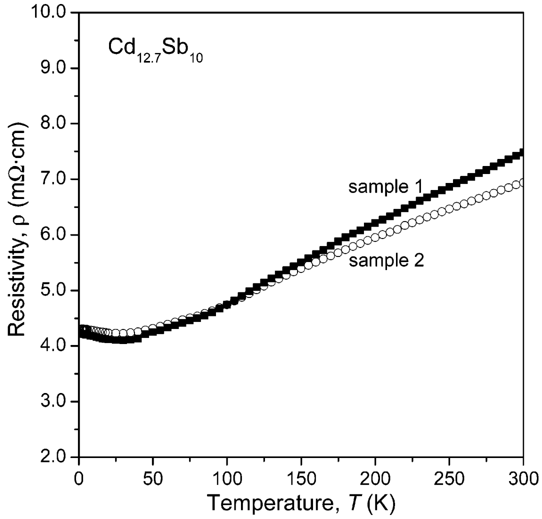

Figure 3. Electrical resistivity of $Cd_{12.7}Sb_{10}$.

Table 2. Crystallographic Data for $Cd_{12.7(1)}Sb_{10}$

formula	$Cd_{12.7(1)}Sb_{10}$
formula mass (amu)	2648.73
space group	$R\bar{3}c$ (No. 167)
a (Å)	13.0395(14)
c (Å)	13.0346(14)
V (Å^3)	1919.3(4)
Z	3
ρ_{calcd} (g cm^{-3})	6.875
crystal dimensions (mm)	0.198 × 0.169 × 0.079
radiation	graphite monochromated Mo Kα, $\lambda = 0.71073$ Å
μ(Mo Kα) (cm^{-1})	206.57
transmission factors	0.057−0.238
2θ limits	6.24° ≤ 2θ(Mo Kα) ≤ 66.28°
data collected	$-19 \le h \le 19$, $-19 \le k \le 19$, $-19 \le l \le 19$
no. of data collected	8162
no. of unique data, including $F_o^2 < 0$	809
no. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	727
no. of variables	40
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.037
$R_w(F_o^2)^b$	0.085
goodness of fit	1.317
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	1.20, −1.28

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$ where $p = [\max(F_o^2,0) + 2F_c^2]/3$.

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Table 3. Positional and Equivalent Isotropic Displacement Parameters for $Cd_{12.7(1)}Sb_{10}$

atom	Wyckoff position	occupancy	x	y	z	U_{eq} or U_{iso} (Å^2)[a]
Cd	36f	0.820(11)	0.24070(12)	0.0775(3)	0.09416(10)	0.0359(4)
Cd1	36f	0.020(3)	0.058(3)	0.181(3)	0.020(3)	0.039(2)
Cd2	36f	0.030(3)	0.069(2)	0.239(2)	0.126(3)	0.039(2)
Cd3	36f	0.051(3)	0.0730(13)	0.2390(13)	0.0826(15)	0.039(2)
Cd4	36f	0.068(10)	0.2248(16)	0.035(3)	0.1036(11)	0.039(2)
Cd5	36f	0.071(2)	0.2340(9)	0.1341(9)	0.2335(7)	0.039(2)
Sb1	18e	1	0.35469(6)	0	$^1/_4$	0.0286(2)
Sb2	12c	1	0	0	0.14108(6)	0.0272(2)

[a] $\mathbf{U}_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor. Interstitial Cd sites (Cd1 to Cd5) were refined isotropically.

Table 4. Selected Interatomic Distances (Å) for $Cd_{12.7(1)}Sb_{10}$

Cd−Sb2	2.842(1)	Cd3−Sb1	2.72(2)
Cd−Sb1	2.869(1)	Cd3−Sb2	2.87(2)
Cd−Sb1	2.977(2)	Cd3−Sb1	2.88(2)
Cd−Sb1	2.985(3)	Cd3−Sb1	3.06(2)
Cd−Cd	3.033(3)	Cd4−Sb1	2.74(2)
Sb2−Sb2	2.839(2)	Cd4−Sb2	2.77(1)
Cd1−Sb2	2.62(3)	Cd4−Sb1	2.87(1)
Cd1−Sb1	2.75(3)	Cd4−Sb1	3.48(2)
Cd1−Sb2	2.95(3)	Cd5−Sb1	2.89(1)
Cd1−Sb1	3.01(3)	Cd5−Sb2	2.91(1)
Cd2−Sb1	2.65(3)	Cd5−Sb1	3.00(1)
Cd2−Sb2	2.79(2)	Cd4−Sb1	3.12(1)
Cd2−Sb1	2.83(3)	Cd5−Sb1	3.12(1)
Cd2−Sb1	3.30(3)		

Information). The true composition was established from the crystal structure to be restricted between $Cd_{12.7}Sb_{10}$ and $Cd_{13}Sb_{10}$ (Table 1), corresponding to 43.5−44.1% Sb, which is consistent with the limited homogeneity range inferred from the synthetic experiments above and from metallographic, thermal, and other analyses elsewhere.[1,4,7,9,11,15]

The core part of the structure of $Cd_{12.7}Sb_{10}$ is built up from the main Cd and two types of Sb atoms, corresponding to the idealized formulation $Cd_{12}Sb_{10}$ if the Cd site is fully occupied (Figure 1). This part of the structure is the same as that in "β-Zn_4Sb_3" and can be described in terms of a close-packed arrangement of Sb atoms forming tetrahedral voids that are filled by M atoms (M = Zn, Cd).[21] In analogy to another description that was devised to help draw out the differences between the structural polymorphs of "Zn_4Sb_3",[24,26] the Cd atoms are arranged in six-membered rings (Cd−Cd, 3.705 Å) in chair conformation (or as flattened octahedral Cd_6 clusters) alternately stacked with singly bonded Sb_2 pairs (Sb2−Sb2, 2.839(2) Å) along the c direction. Between these stacks lie isolated Sb1 atoms.

The excess of M in the formula "M_4Sb_3" relative to $M_{12}Sb_{10}$ could be rectified by invoking disorder of M into the Sb1 site.[12] This model has since been disproven by recent structure determinations on "β-Zn_4Sb_3".[21,22,26] For "Cd_4Sb_3", however, this cannot be so hastily dismissed because of the similar size of Cd and Sb (with Pauling metallic radii R_1 = 1.38 and 1.39 Å, respectively).[34] The alternative explanation was already foreseen by Ignat'ev et al., who speculated that additional Cd atoms must be introduced into the $Cd_{12}Sb_{10}$ framework, allowing the possibility for the formation of a solid solution.[10] Five such interstitial Cd sites have now been resolved (Figure 1). The occupancies of these sites range from 0.02 (Cd1) to 0.07 (Cd5), while the main Cd site itself is deficient with an occupancy of 0.82. Physically unrealistic Cd−Cd distances involving these interstitial sites are precluded by their low occupancies, with individual unit cells accommodating only the few interstitial Cd atoms which would be positioned near the vacancies of the main Cd site on a local level. The coordination environments of Sb atoms around each of the Cd sites are shown in Figure 2. The coordination around the main Cd and interstitial Cd1−Cd3 sites is more or less tetrahedral (CN4), whereas it is nearly trigonal planar (CN3) around Cd4 if the 3.48(2) Å distance is neglected. The coordination around Cd5 becomes distorted square pyramidal (CN5), as one of the tetrahedron vertices is replaced by an Sb_2 pair. Most of the Cd−Sb distances are in good agreement with typical literature values (2.8−3.0 Å)[33,35−37] and with the sum of the Pauling metallic radii (2.77 Å).[34] There are some short Cd−Sb distances (2.62(3), 2.65(3) Å) involving the least occupied interstitial sites, but when their large standard uncertainties are taken into account, they are comparable to the shortest value (to our knowledge) of 2.705(2) Å found in $Cd_4Sb_2I_3$.[35]

Because the sets of interstitial sites are not identical, "Cd_4Sb_3" and "β-Zn_4Sb_3" could be described as filled variants of each other. There also exists the possibility that perhaps additional interstitial sites may have been overlooked in the structure determinations of "β-Zn_4Sb_3", as signalled by large anisotropic displacement parameters that could indicate site splitting.[22] After standardization, the Cd3 and Cd5 sites are equivalent to the Zn1 and Zn3 sites, respectively, whereas the Cd4 site (0.225, 0.035, 0.104) is significantly displaced compared to the Zn2 site (0.202, 0.094, 0.025) in "β-Zn_4Sb_3".[26] The Cd1 and Cd2 sites are new. In general, the distances to Cd atoms are 0.2 Å longer than those to Zn atoms, a difference of about 13%. A rule of thumb is that solid solutions tend not to form when the difference in radii of the component elements exceeds ~15%.[38] Indeed, the mutual solubility of Cd and Zn metals themselves is less than 4 at. %.[39] These structure and size considerations suggest that solid solubility in "$Zn_{4-x}Cd_xSb_3$" may be limited as well, or if solid solutions do form, there may be preferential distribution of the interstitial Zn and Cd atoms.

Figure 3 shows the electrical resistivity of two samples of $Cd_{12.7}Sb_{10}$ extracted from the same reaction from which

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crystals were selected for structure determination. The resistivity shows metallic-like behavior, decreasing as the temperature is lowered but with a shallow upturn near 35 K, and the absolute values of the resistivity are high ($\rho_{300} =$ 7 mΩ•cm). These observations are consistent with a highly degenerate semiconductor. Previous resistivity measurements on "Cd_4Sb_3" have given erratic results.[1,6−8] Our measurements seem to be in good agreement with recent ones on "β-Zn_4Sb_3",[16,18,21,26] except that there do not appear to be any dramatic low-temperature transitions.

In this study, we have located the interstitial Cd sites present in "Cd_4Sb_3" and thereby ascertained the true composition of this phase to be close to $Cd_{12.7}Sb_{10}$. There is more disorder present here than in the zinc analogue, $Zn_{13}Sb_{10}$, which may imply a lower thermal conductivity. The disorder persists down to 193 K and probably lower temperatures. The results presented here should provide impetus for further investigation into the physical properties of $Cd_{12.7}Sb_{10}$ and a comparison of its electronic structure with that of the Zn analogue.

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Supporting Information Available: One X-ray crystallographic file in CIF format and a plot of cell parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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