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The new Zintl phases $Eu_{21}Cd_4Sb_{18}$ and $Eu_{21}Mn_4Sb_{18}$

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ABSTRACT

Crystals of two new Zintl compounds, $Eu_{21}Mn_4Sb_{18}$ and $Eu_{21}Cd_4Sb_{18}$ have been synthesized using the molten metal flux method, and their structures have been established by single-crystal X-ray diffraction. Both compounds are isotypic and crystallize in the monoclinic space group $C2/m$ (No. 12, $Z=4$). The structures are based on edge- and corner-shared $MnSb_4$ or $CdSb_4$ tetrahedra, which make octameric $[Mn_8Sb_{22}]$ or $[Cd_8Sb_{22}]$ polyanions. Homoatomic Sb–Sb bonds are present in both structures. The Eu atoms take the role of Eu^{2+} cations with seven unpaired 4*f* electrons, as suggested by the temperature-dependent magnetization measurements. The magnetic susceptibilities of $Eu_{21}Mn_4Sb_{18}$ and $Eu_{21}Cd_4Sb_{18}$ indicate that both phases order anti-ferromagnetically with Néel temperatures of ca. 7 K and ca. 10 K, respectively. The unpaired 3*d* electrons of the Mn atoms in $Eu_{21}Mn_4Sb_{18}$ do contribute to the magnetic response, however, the bulk magnetization measurements do not provide evidence for long-range ordering of the Mn spins down to 5 K. Electrical resistivity measurements suggest that both compounds are narrow band gap semiconductors.

1. Introduction

The compounds formed between the alkali- and alkaline-earth metals and the post-transition elements from groups 13–15 are known as Zintl phases [1,2]. The boundaries of the Zintl family have been extended many times, and today's definition of Zintl phases includes some of the lanthanides, as well as some of the transition metals. The Zintl–Klemm concept explains their structures and bonding by assuming that electrons transfer from the less electronegative metals to the more electronegative ones, therefore each element achieves a closed shell state [3–5]. As a result, Zintl phases are nominally semiconductors (poor metals), and have been recognized for their excellent thermoelectric properties [6–11].

Our research group, in recent years, has studied and identified a large number of novel and peculiar structures among the ternary pnictides. Some relevant examples can be found in the "9–4–9" family alone [12–14], where a wealth of new compounds have been successfully synthesized and structurally characterized. Based on the above, it might be argued that the corresponding *AE*–*T*–*Pn* systems (*AE*= Ca, Sr, Ba, Eu, Yb; *T*=Mn, Zn, Cd; *Pn*= As, Sb, Bi), which have been the subject of research interest for the past 2–3 decades, still present unexplored "phase space".

Another testament to this conjecture is the series, which we can call the "21–4–18" family [15–17]. Since the discovery of the archetype $Sr_{21}Mn_4Sb_{18}$ in 2000 [18], the series has been extended by almost a dozen new compounds. We will draw the attention to the fact that $AE_{21}T_4Pn_{18}$ phases form with three different structures and the crystal chemistry was reviewed by us recently in a paper dealing with $Ca_{21}Zn_4As_{18}$, $Ca_{21}Zn_4Sb_{18}$, $Eu_{21}Zn_4As_{18}$ and $Eu_{21}Zn_4Sb_{18}$. What is peculiar about the "21–4–18" family is the fact that except for α- and β-$Ca_{21}Mn_4Sb_{18}$ [17], there is no evidence for polymorphism in any other $AE_{21}T_4Pn_{18}$ systems. For a given elemental mixture, one of the three structures is always realized, and the origins for the apparent structural preference are not yet understood. In the previous paper, we also noted the surprising observation that $Ca_{21}Mn_4Sb_{18}$, $Ca_{21}Zn_4As_{18}$ and $Ca_{21}Zn_4Sb_{18}$ are known, yet, their Yb-analogs are elusive–if one were to evoke a spatial argument for that, it can be easily countered by the fact that the ionic radii of Ca^{2+} and Yb^{2+} are almost identical, 1.00 Å and 1.02 Å, respectively [19].

In subsequent studies, we finally synthesized $Yb_{21}Mn_4Sb_{18}$, as well as its Eu-analog $Eu_{21}Mn_4Sb_{18}$. With this paper, we report on these experimental findings. In short, the magnetic response of these phases (vide infra) was difficult to interpret, which prompted us to seek the isostructural Eu- and Yb-based compounds with the magnetically-silent d^{10} metals Zn and Cd. $Eu_{21}Zn_4Sb_{18}$ was successfully synthesized, but found to crystallize with the $Ba_{21}Cd_4Sb_{18}$ structure type (orthorhombic space group *Cmce* (No. 64, $Z=8$)) [16]. $Eu_{21}Cd_4Sb_{18}$ and $Eu_{21}Mn_4Sb_{18}$, in the other hand,

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were found to be isotypic with β–$Ca_{21}Mn_4Sb_{18}$ [15] and $Sr_{21}Mn_4Sb_{18}$ [18] (monoclinic space group $C2/m$ (No. 12, $Z=4$)). Neither $Yb_{21}Zn_4Sb_{18}$ nor $Yb_{21}Cd_4Sb_{18}$ could be prepared during this study. Since the subject of the synthesis and thermoelectric properties of $Yb_{21}Mn_4Sb_{18}$ will be at the focus of a forthcoming paper, we will not discuss it in this article [20].

2. Experimental

2.1. Synthesis

Eu metal is fairly sensitive to air, therefore all handling of the materials was done inside an argon-filled glove box. The raw metals were purchased from Alfa or Aldrich and were used as received: Eu (ingots, 99.9%), Yb (ingots, 99.9%), Mn (pieces, 99.98%), Cd (shot, 99.999%), Sb (shot, 99.99%) and Pb (granules, 99.999%).

At the outset, we note that $Eu_{21}Mn_4Sb_{18}$ can be obtained in reasonable yields only if Mn is used in 2-or 3-fold excess. This issue probably comes about from the high melting point of Mn, and/or its low solubility in the flux. For example, the most successful reaction in making this phase was an experiment loaded with the elemental ratio of Eu: Mn: Sb: Pb =21: 10: 18:100. The very large quantity of Pb is to serve as a Pb flux. The mixture (contained in a 2 cm^3 alumina crucible covered on the top with quartz wool) was placed within a fused silica tube, which was then evacuated and flame-sealed. The reaction proceeded as follows: heating to 1273 K over 12 h; homogenization at this temperature for 24 h, and then cooling to 773 K at a rate of 10 K/h. Then, the excess of Pb flux was removed by decanting it. The fused silica ampoule was brought back into the glove box and opened. The reaction outcome consisted of many irregular grey crystals, later identified as $Eu_{10}Mn_6Sb_{13}$ [21], and few darker, almost black irregular crystals, which were identified as $Eu_{21}Mn_4Sb_{18}$. Interestingly, the yield of $Eu_{10}Mn_6Sb_{13}$ from the same elemental mixture, but using Sn as a flux, was almost quantitative, which may suggest that understanding the solubility of the reactants/products in the flux will be the key for optimizing the reaction conditions.

Variations of the stoichiometry and/or reaction temperature and cooling rates did not yield $Eu_{21}Mn_4Sb_{18}$ as a single product. In addition to $Eu_{10}Mn_6Sb_{13}$ [21], other side products such as $Eu_{11}Sb_{10}$ [22] and $EuMn_2Sb_2$ [23] we also observed. $Eu_{21}Cd_4Sb_{18}$ was also successfully synthesized through same method with typical by-products being $Eu_{11}Cd_6Sb_{12}$ [24] and $EuCd_2Sb_2$ [25].

2.2. Powder X-ray diffraction

X-ray powder diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer using filtered Cu Kα radiation (λ=1.54056 Å). The data were analyzed with the JADE 6.5 software package. It must be noted here that the complex structures/large unit cells/low symmetry were the reason the diffraction patterns looked very complicated and the phase identification was hindered. For all structural work, single-crystal X-ray diffraction data was the method of choice. The powder patterns of fresh samples and samples left on the laboratory bench for 2–3 weeks were identical. This suggests that the air-sensitivity of the title compounds is negligible over the specified period of time.

2.3. Single-crystal X-ray diffraction

For the intensity data collection on the single-crystal diffractometer, flux-grown crystals were picked and cut with a scalpel to the desired dimensions (less than 100 μm). This was done under a microscope in a drop of Paratone-N oil. In order to evaluate the crystal quality preliminary rotation images were acquired. The work was carried out on a Bruker *SMART* and APEX 2 CCD-based diffractometer (monochromatized Mo Kα radiation, $\lambda=0.71073$ Å). By using cold nitrogen steam, the temperature was kept at 200 K during the data collection–the Paratone-N oil hardens at these conditions and immobilizes the crystal during the experiment. The programs *SMART* and *SAINT* [26] was used to acquire and process data. *SADABS* was used for the semi-empirical absorption correction [27]. The structures were easily solved by direct methods, and were refined with the full-matrix least squares on the F^2 method, as implemented in *SHELXTL* [28]. Refined parameters included the scale factor and atomic positions with the corresponding anisotropic displacement parameters. In the final step, the atomic positions were standardized by *STRUCTURE TIDY* [29].

Table 1
Selected single-crystal data collection and structure refinement parameters for $Eu_{21}Cd_4Sb_{18}$ and $Eu_{21}Mn_4Sb_{18}$. Both structures are with the monoclinic space group $C2/m$ (No. 12) with four formula units per cell.

Empirical formula	$Eu_{21}Cd_4Sb_{18}$	$Eu_{21}Mn_4Sb_{18}$
Formula weight, g mol^{-1}	5832.26	5602.42
Radiation	graphite-monochromated Mo Kα, λ=0.71073 Å	
Temperature, K	200(2)	200(2)
Crystal dimensions (μm)	90 × 60 × 60	70 × 60 × 50
a, Å	18.068(4)	18.0227(10)
b, Å	17.228(4)	17.1988(9)
c, Å	17.651(4)	17.5981(9)
β, °	91.942(4)	91.876(1)
V, $Å^3$	5491(2)	5451.9(5)
ρ_{calcd}, g cm^{-3}	7.06	6.83
μ (Mo Kα), cm^{-1}	337.5	333.6
2θ (Mo Kα) range	2.30–56.16°	2.32–59.14°
Unique data with $F_o^2 > 2\sigma(F_o^2)$	5749 (R_{int}=0.044)	7374 (R_{int}=0.023)
Variables	216	216
GOF on F^2	0.991	1.204
R_1 [$I > 2\sigma(I)$][a]	0.028	0.021
wR_2 [$I > 2\sigma(I)$][a]	0.050	0.045
R_1 [all data][a]	0.039	0.024
wR_2 [all data][a]	0.053	0.046
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$, e $Å^{-3}$	2.32/–1.63	1.56/–1.33

[a] $R1=\sum||F_o|-|F_c||/\sum|F_o|$; $wR2=[\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w=1/[\sigma^2F_o^2+(A\cdot P)^2+(B\cdot P)]$, and $P=(F_o^2+2F_c^2)/3$; A, B – weight coefficients. In the case of $Eu_{21}Cd_4Sb_{18}$: $A=0.0152$ and $B=0$; for $Eu_{21}Mn_4Sb_{18}$: $A=0.013$ and $B=54.516$. For additional information, the reader is referred to the CIFs in the Supporting Information.

Selected crystallographic information and refinement parameters for $Eu_{21}Cd_4Sb_{18}$ and $Eu_{21}Mn_4Sb_{18}$ are summarized in Table 1. Final positional and equivalent isotropic displacement parameters are shown in Tables 2 and 3. Relevant interatomic distances and angles are listed in Table 4. CIFs have also been deposited with Fachinformationszentrum Karlsruhe, 76,344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) with depository numbers: CSD-430851 for $Eu_{21}Mn_4Sb_{18}$ and CSD-430852 for $Eu_{21}Cd_4Sb_{18}$.

2.4. Property measurements

Field-cooled (FC) direct-current (DC) magnetization measurements on polycrystalline samples were performed in a Quantum Design PPMS from 5 to 300 K in an applied magnetic field of 5000 Oe. The measured specimens were single-crystals of $Eu_{21}Cd_4Sb_{18}$ or $Eu_{21}Mn_4Sb_{18}$ that were selected under a microscope from freshly prepared samples, and then were ground into powders. The materials were weighed and loaded in gel capsules and filled with cotton to prevent them moving under the magnetic field. The raw magnetization data were corrected for the holder