Electronic Supplementary Information for Dalton Transactions

Novel ternary alkaline-earth and rare-earth metal antimonides from gallium or indium flux. Synthesis, structural characterization and ^{121}Sb and ^{151}Eu Mössbauer spectroscopy of the series $A_7Ga_8Sb_8$ (A = Sr, Ba, Eu) and $Ba_7In_8Sb_8$ †

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SUPPORTING INFORMATION

Crystal chemistry of $Sr_7Ga_2Sb_6$

Detailed structure description of $Sr_7Ga_2Sb_6$ can be found elsewhere [S.-Q. Xia, J. Hullmann and S. Bobev, *J. Solid State Chem.*, 2008, **181**, 1909]; herein, we succinctly recap the most important features of this structure, which at least formally, is a substitution derivative of the body-centered cubic Th_3P_4 type ["*Pearson's Handbook of Crystallographic Data for Intermetallic Phases*", ed. P. Villars and L. D. Calvert, ASM International, Materials Park, OH, 2nd edn., 1991]. Notice that in the "parent" structure, all cations are located at the centers of distorted octahedra of antimony anions (Figure S1), and there is no Sb–Sb bonding. Therefore, one can expect the formula Sr_4Sb_3 to represent an electron-deficient compound, and indeed, such binary phase is not known.

The $Sr_7Ga_2Sb_6$ structure (or rather $Sr_{8-x}Ga_{2x}Sb_6$, x = 1/8) is the closest to Sr_4Sb_3, whereupon every eighth Sr^{2+} cation is missing and the vacant space is filled with a pair of Ga atoms (Figure S1). This disorder is akin to the disorder detailed for $A_7Ga_8Sb_8$ (A = Sr, Ba, Eu), and is apparently also completely random, as there is no evidence for a crystallographic long-range order. Here, unlike the previous case, the Ga_2-dimers are formed by two crystallographically independent Ga atoms, which are both about 12% occupied. The actual Ga–Ga separation is ca. 2.5 Å. As a consequence, the inclusion of the two Ga atoms in this octahedral atomic arrangement results in the formation of isolated $[Ga_2Sb_6]^{14-}$ fragments, isoelectronic and isostructural with the $[Sn_2P_6]^{12-}$ anions in the $Ba_6[Sn_2P_6]$ structure [B. Eisenmann, H. Jordan and H. Schäfer, *Z. Naturforsch.*, 1983, **38b**, 404]. Similar ethane-like units, parts of extended networks or arranged into double $[In_2Pn_6]^{12-}$ layers, zipped via Ga–Ga or In–In bonds are known in the structures of $Ba_2In_5Pn_5$ (Pn = P or As) [J. Mathieu, R. Achey, J.-H. Park, K. M. Purcell, S. W. Tozer and S. E. Latturner, *Chem. Mater.*, 2008, **20**, 5675], $EuIn_2Pn_2$ (Pn = P or As) [A. M. Goforth, P. Klavins, J. C. Fettinger and S. M. Kauzlarich, *Inorg. Chem.*, 2008, **47**, 11048; J. Jiang and S. M. Kauzlarich, *Chem. Mater.*, 2006, **18**, 435], and $BaGa_2Sb_2$ [G. Cordier, H. Schäfer and M. Stelter, *Z. Naturforsch.*, 1985, **40b**, 1100]. Analogous, albeit disordered motifs are present in the above-discussed $A_7Ga_8Sb_8$ (A = Sr, Ba, Eu) and $Ba_7In_8Sb_8$ as well.

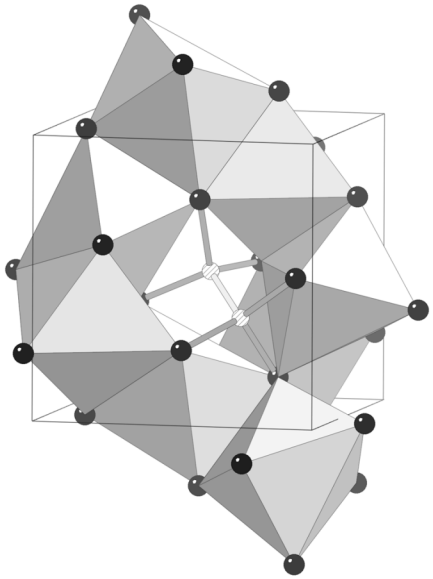

Fig. S1 Crystal structure of $Sr_7Ga_2Sb_6$. The polyhedral representation emphasizes the acentric way of packing of the antimony octahedra, each centered by the Sr^{2+} cations (not shown for clarity). 1/8 of the octahedra are empty, and the vacant space is filled with Ga dumbbells. The inclusion of two Ga atoms in such coordination environment results in the formation of ethane-like $[Ga_2Sb_6]$ fragments (shown in ball-and-stick representation): Sb – black circles, Ga – crossed circles.

^{121}Sb spectroscopy

^{121}Sb Mössbauer spectroscopic study of $Sr_7Ga_2Sb_6$ was done at 78 K. The collected spectrum is presented in Figure S2, alongside the spectra for $Eu_7Ga_8Sb_8$ (both at 4.2 K and 78 K) and $Ba_7In_8Sb_8$. $Sr_7Ga_2Sb_6$ contains a single crystallographic antimony site and a Zintl conform electron precise description leads to $(7Sr^{2+})[Ga_2Sb_6]^{14-}$ with isolated Sb^{3-} species. Consequently, the ^{121}Sb Mössbauer spectrum shows a single signal. Although the antimony atoms have site symmetry $\bar{4}$, there was no need to introduce a quadrupole splitting parameter within the fitting procedure. The ^{121}Sb spectrum shows a single signal. The isomer shifts (!) is –8.06 mm/sec; experimental line width is 4.4(1) mm/sec.

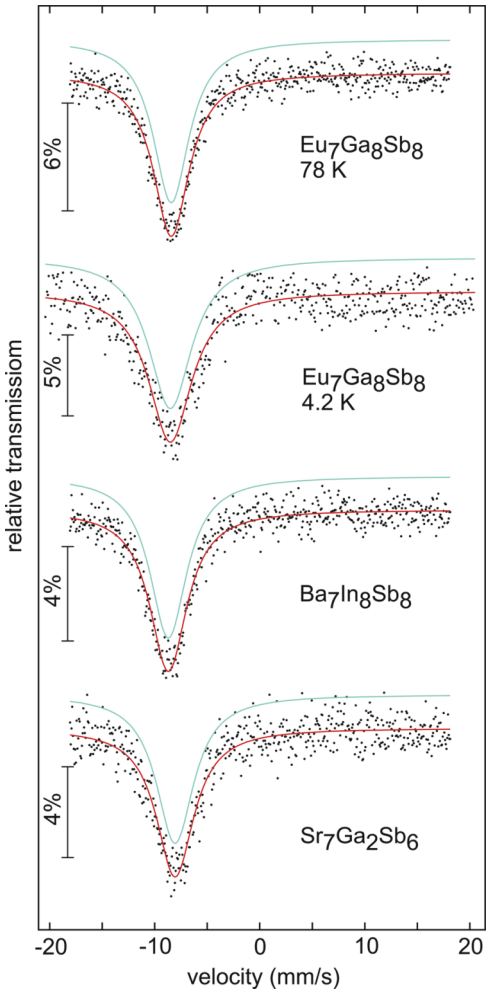

Fig.S2 Experimental and simulated ^{121}Sb Mössbauer spectra of $Eu_7Ga_8Sb_8$, $Ba_7In_8Sb_8$, and $Sr_7Ga_2Sb_6$.