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Remarkably Diverse Interstitial Chemistry of the Polar Intermetallic Phase Zr_5Sb_3

Sir:

We have found that the hexagonal phase Zr_5Sb_3 exhibits a rich interstitial chemistry in which any one of at least 18 different elements (Z) with a wide variety of normal valence requirements can be bonded in the center of octahedral Zr_6Sb_6 units therein. An essential feature of this structure (Mn_5Si_3 type) is the presence of chains of confacial trigonal antiprismatic ("octahedral") Zr_6 units sheathed by antimony (Figure 1).

In the past, a number of compounds with the Mn_5Si_3 structure have been surmised or shown to bond heteroatoms in the octahedral sites within the chain or, in some cases, even to *require* the third atom for stability,[1,2] oxygen or carbon in the Zr_5Sb_3 case, for example.[3] Similar Zr_5Sb_3Z phases with Z = Ni, Cu, or Zn have also been reported,[4] although this seems chemically counterintuitive alongside the oxygen example. However, these phases were all prepared by sintering elemental mixtures in evacuated fused-silica containers at 800 °C for up to 8 weeks, a procedure that raises questions about both possible contamination by the container and inadequate equilibration at this relatively low temperature. Furthermore, products were identified only by comparison of lattice constants plus intensities of calculated vs observed X-ray powder diffractometer data, and we have found similar changes in both can be mimicked by other products, those of the binary Zr_5Sb_{3+x}, for example.[5]

Suitable synthetic techniques have now been refined so that distinctive samples that are *single phase* by Guinier powder diffraction can be regularly produced. Arc melting of the samples under argon followed by annealing, sintering of the powdered mixtures at ~1100 °C, or vapor phase transport utilizing ZrI_4 near 1300 °C have all been utilized, generally in Ta containers. These techniques were first applied to the identification of the ten intermediate phases in the Zr–Sb binary system and, in particular, to establish that the binary Zr_5Sb_3 does exist in the Mn_5Si_3 structure.[6] In fact, a nonstoichiometric Zr_5Sb_{3+x} with self-interstitials over the range $0 \leq x \leq 0.4$ is present according to a single-crystal structural study coupled with variations in the Guinier-based lattice constants as a function of composition. A second, nonrelevant structure of the Y_5Bi_3 type is obtained at high temperatures.[5]

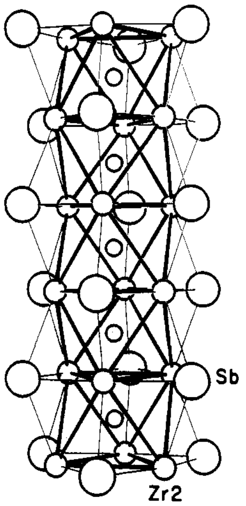

Figure 1. Portion of a confacial Zr_6Sb_6 octahedral chain in Zr_5Sb_3: large circles, Sb; midsized circles, Zr; small circles, interstitial site.

The variety of interstitials Z that may be individually incorporated in the Zr_5Sb_3 host is chemically astounding. Those established to date sort out in a periodic array as follows:

						C		O
					Al	Si	P	S
Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
Ru			Ag				Sb	

Especially noteworthy is the occurrence of all the elements in the fourth period from iron through selenium. On the other hand, the lighter alkali and alkaline-earth metals have yielded only negative results while Cr and Mn are problematical. A majority of the ternary phases have been identified on the basis of shifts in Guinier-based lattice parameters observed for sintered or vapor-phase-transported samples. The lattice constant variations, which have earlier been used as the diagnosis for compound formation, are neither particularly large (≤4% over the whole range) nor informative about the relative dimensional changes within the Zr_6Z units. A few of the phases appear to be non- or substoichiometric (Fe, Co, Ni, S, Sb).

Most importantly, the location and occupancy of the interstitial in the Zr_5Sb_3Z phases have been established by seven single-crystal X-ray studies for Z = Fe, Zn, Si, $S_{0.7}$, Al (where some site interchange with Sb apparently occurs), a mixed $Fe_{2/3}In_{1/3}$ system, and the self-interstitial $Sb_{0.16}$. (Data for the iron and sulfur examples are given in the supplementary material.) These appear to be the first single-crystal studies reported on any phases in this general structure class beyond those involving self-interstitials that are in the fully occupied limit known as the Ti_5Ga_4-type structure.[3] A recent Rietveld refinement of high-temperature X-ray powder data has also delineated the $Zr_5Al_3O_{0.3}$ analogue.[7]

This series of structures provides some useful generalizations. The dimensional changes seen in the structures on incorporation of the seven Z examples are largely limited to a 0.22-Å range in the shared edges of the trigonal antiprisms that lie normal to the chain (Figure 1). In contrast, Zr–Sb distances remain quite uniform throughout, while the limited (0.09 Å) expansion along the chain may be viewed as a restriction imposed by the presence of a second, linear, parallel and tightly bound zirconium chain in the structure with a $c/2$ repeat (not shown).

Extended Hückel band calculations on Zr_5Sb_3 and its sulfur and iron derivatives provide some enlightenment about the bonding and electronic distributions. As might be anticipated for such a polar host, the empty cluster exhibits a broad valence band that lies well below the Fermi level E_F. This contains all antimony 5p states plus appreciable contributions from 4d orbitals on both types of zirconium required for covalency in the bonding. A broad conduction band above about −1.5 eV contains only zirconium

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(1) Rossteutscher, W.; Schubert, K. *Z. Metallkd.* **1965**, *56*, 813.
(2) Nowotny, H.; Benesovsky, F. In *Phase Stability in Metals and Alloys*; Rudman, P. S., Stringer, J., Jaffee, R. I., Eds.; McGraw-Hill: New York, 1966; p 319.
(3) Pearson, W. B. *The Crystal Chemistry and Physics of Metals and Alloys*; Wiley-Interscience: New York, 1972; pp 718, 720.
(4) Rieger, W.; Parthé, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 456.
(5) Garcia, E.; Corbett, J. D. *Inorg. Chem.* **1988**, *27*, 2353.
(6) Garcia, E.; Corbett, J. D. *J. Solid State Chem.* **1988**, *74*, 440, 452.
(7) Kim, S.-J.; Kematick, R. J.; Yi, S. S.; Franzen, H. F. *J. Less-Common Met.* **1988**, *137*, 55.

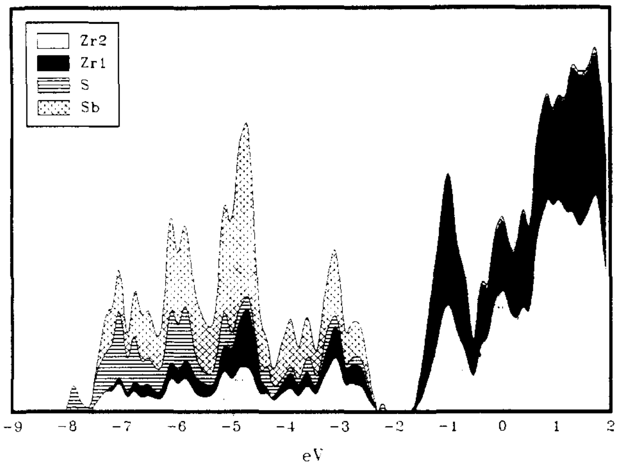

Figure 2. Densities-of-states results for Zr_5Sb_3S by atom type according to extended Hückel band calculation (24 k points). Zr2 is in the confacial chains. Only zirconium 4d and antimony and sulfur valence p orbitals are important in this region.

contributions and the 11 (=5 × 4 − 3 × 3) electrons that remain after antimony bonding and nonbonding states are filled. Some of these electrons may then be utilized in the formation of strong Zr–Z bonding and with little perturbation of the Zr_5Sb_3 matrix beyond a suitable expansion or contraction of the octahedral interstice.

As shown by the densities of states in Figure 2, formation of Zr_5Sb_3S is accompanied by the appearance of Zr–S bonding states in the lower half of the valence band with a corresponding loss from the conduction band of two electrons per sulfur together with some zirconium 4d states on the atoms in the trigonal antiprismatic chain. On the other hand, the valence band of the host is largely unchanged on formation of Zr_5Sb_3Fe from Zr_5Sb_3, the iron 4s and 3d states appearing instead in the gap and in the lower regions of the conduction band. Changes in overlap populations emphasize the gain in Zr–Z bonding and the loss of what was only weak Zr–Zr bonding within the confacial chains.

The following generalities seem to apply to this unusual class of chemicals:

(1) Zr_5Sb_3 is a strongly bonded host (mp ~1400 °C) dominated by Zr–Sb bonding and with 11 electrons in the conduction band.

(2) The addition of interstitial Z to the chain produces strong Zr–Z bonding, with the loss of only moderate Zr–Zr bonding in the empty chain and with little perturbation of the Zr–Sb host.

(3) Electrons and zirconium 4d orbitals necessary to bind Z are readily available in the conduction band states.

(4) All of the Z elements so far incorporated also form very stable binary compounds with zirconium. Although this indicates something of the strength of the bonding gained in the formation of the ternary phases, it does not of course address the relative stability of alternate phases.

Interestingly, analogous but isolated zirconium clusters are known for octahedral $Zr_6X_{12}Z$ (X = Cl, I) phases, and comparable structural and some calculational data are available for Z = B–N, Al, Si, Mn, Fe, etc.[8-10] We note that what can be viewed as an oxidation of the Zr_6 cluster surrounding Z in the series Zr_xZ_y–Zr_5Sb_3Z–$Zr_6X_{12}Z$ results in a distinctive decrease in both Zr–Zr bonding and Zr–Z separations. The particular cases with Z = Fe have been recently described.[10]

Details on the synthesis, structures, and properties of this interesting collection of Zr_5Sb_3Z compounds as well as for other analogous hosts (e.g., Zr_5Sn_3, La_5Ge_3 and Ca_5Sb_3) will be forthcoming.

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Supplementary Material Available: A listing of the positional parameters and distances for $Zr_5Sb_3S_{0.7}$ and Zr_5Sb_3Fe (2 pages). Ordering information is given on any current masthead page.

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(8) Ziebarth, R. P.; Corbett, J. D. *J. Am. Chem. Soc.* **1985**, *107*, 4571.

(9) Smith, J. D.; Corbett, J. D. *J. Am. Chem. Soc.* **1986**, *108*, 1927.

(10) Hughbanks, T.; Rosenthal, G.; Corbett, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1511.

(11) Ames Laboratory—DOE is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82.

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