Yb₈Ge₃Sb₅, a Metallic Mixed-Valent Zintl Phase Containing the Polymeric
¹-[Ge₄²⁺] Anions

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The structural diversity of main group cluster and oligomeric anions found in Zintl phases is astonishing.¹ Homeatomic anions of group 14 metalloids such as Ge are particularly diverse in the geometries they adopt to satisfy their octet. These include clusters such as the trigonal bipyramidal Ge₂⁺, the distorted tricapped trigonal prismatic Ge₃⁺,² the distorted bicapped square antiprismatic Ge₁₀⁻,³ the octahedral Ge₆⁻,⁴ the tetrahedral Ge₄⁺,⁵ and the Ge₄⁻ butterfly ion,⁶ to name a few. Many of these species were originally discovered as isolated fragments, but in several cases polymerization into extended structures has been observed.⁶⁻⁹

Recently, we have begun investigating the effects of including rare-earth ions in Zintl phases that have the ability to be mixed valent such as Eu(Eu²⁺/Eu³⁺) and Yb(Yb²⁺/Yb³⁺). The rationale behind this is that perhaps new and interesting phases may be stabilized by the presence of a mixed- or intermediate-valent “spectator” cation. This concept was illustrated in Yb₉Zn₄Bi₉, where the charge of the system can be balanced by (Yb²⁺/Yb³⁺) with tetrahedrally coordinated(Zn²⁻)₄, linearly coordinated and bridging (Bi⁻)₇, and singly coordinated (Bi²⁻).¹⁰ Mixed- or intermediate-valent rare-earth containing compounds can give rise to anomalous physical behavior such as Kondo insulating phenomena and heavy fermion occurrence as well as technologically relevant properties such as large thermoelectric power and anomalous thermal expansion.¹¹

We present here the new mixed-valent Zintl phase Yb₈Ge₃Sb₅, Ge and Sb containing Zintl phases are a small class of compounds,¹²⁻¹⁴ however, what makes Yb₈Ge₃Sb₅ an intriguing discovery is the presence of the new Zintl anion (4b-Ge⁰)/(2b-Ge²⁻), which adopts a one-dimensional infinite chain of edge-sharing tetrahedra isoelectronic with the SiS₂ structure,¹⁵ and the fact that it is stabilized by the presence of mixed- or intermediate-valent “spectator” cations. Third, this compound has only homeatomic bonding among its main group elements. It is highly unusual for Sb and Ge to coexist in a structure and not form bonds to each other. Band structure calculations and magnetic susceptibility data support the notion that Yb₈Ge₃Sb₅ is a mixed-valent Zintl phase.

The structure of Yb₈Ge₃Sb₅, see Figure 1A, is highly symmetric, crystallizing in the tetragonal I4/mmm space group, and can be decomposed into three main components. The first is the infinite chain ¹-[Ge₄²⁺] anions propagating along the c axis, Figure 1B. Using the Zintl/Klemm concept, we have assigned an oxidation state of 2⁻ to the Ge(1) atoms which form the bridge between the two tetrahedrally coordinated Ge(2) atoms (with a Ge(1)--Ge(2) distance of 2.531(1) Å), which has a formal charge assignment of zero. The second moiety is an Sb dimer formed by the bonding of symmetry equivalent Sb(3)--Sb(3) with a distance of 3.393(1) Å, which is similar to those reported for RE₆Ge⁵₋ₓSbₓ₁₋ₓ and ZrGeSb.¹²,¹³

The remaining species are isolated ions of Yb and Sb. The resulting structure can be charge-balanced as follows: (Yb²⁺)₈(Yb³⁺)₈(Ge₄⁻)₁₂-(Sb₅⁻)₁₂(Sb⁵⁻)₁₂. Inspection of the bond distances reveals that the Yb ions (Yb(3))¹⁵ is clearly more tightly coordinated and could be regarded as smaller and more highly oxidized. The Yb bond distances are Yb(1)--Ge(1) 3.151(1), Yb(1)--Sb(1) 3.156(1), Yb(1)--Sb(3) 3.371, and Yb(1)--Sb(2) 3.685(6) Å; Yb(2)--Sb(2) 3.065(1), Yb(2)--Sb(3) 3.360(1), and Yb(2)--Sb(1) 3.7569(7) Å; and Yb(3)--Ge(1) 2.9143(5), Yb(3)--Sb(1) 3.1215(6), Yb(3)--Sb(2) 3.1597(5), and Yb(3)--Ge(2) 3.2812(6) Å.

If the interaction between the two Sb(3) atoms is considered nonbonding, a different charge-balancing scheme would result: (Yb²⁺)₉(Yb³⁺)₉(Ge⁴⁻)₉(Sb⁵⁻)₉. The two charge-balancing schemes would produce different physical properties. Specifically, the magnetic susceptibility would be quite different and therefore diagnostic for which scheme is most appropriate. Variable-temperature magnetic susceptibility data showed that above 120 K the data followed a Curie/Weiss law with μeff = 5.7 μB per formula unit and θ = −168 K, Figure 2.¹⁸ The calculated effective magnetic moment for the first charge-balancing scheme is 6.3 μB,¹⁹ whereas for the second ((Yb²⁺)₉(Yb³⁺)₉(Ge⁴⁻)₉(Sb⁵⁻)₉) it would be 7.9 μB. Based on the susceptibility measurements, the first scheme seems most consistent. Below 120 K, the inverse susceptibility deviates from the Curie/Weiss law until approximately 40 K. The Curie/Weiss law is followed in the low-temperature region from 2 to 40 K with a resulting magnetic moment of 2.3 μB. The changing moment could be due to a temperature-induced valence fluctuation similar to that observed in YbGaGe.¹¹

Because the ¹-[Ge₄²⁺] chain possesses formally both Ge⁰ and Ge²⁻ ions (an example of bonded atoms of mixed oxidation...
states), we made an extensive effort to show that the chain is composed exclusively of Ge atoms and not a disordered Sb/Ge set. First, Sb and Ge are readily distinguishable by X-ray scattering.

The compound \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \) is stabilized because the "spectator" cations to stabilize new phases and to control their physical properties can now augment this concept.

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**Supporting Information Available:** Tables of crystallographic details, atomic coordinates, isotropic and anisotropic displacement parameters for all atoms and interatomic distances, and angles for Yb-Ge-Sb (PDF and CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

**Figure 2.** Temperature-dependent susceptibility data for \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \).

**Figure 3.** Temperature-dependent electrical conductivity (four probe) and thermoelectric performance on a polycrystalline ingot.

**References**

16. Crystal data for \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \): \( M_w = 3944.00 \pm 0.00 \) mol, \( a = 5.8965(1) \) Å, \( b = 6.8206(1) \) Å, \( c = 17.2356(18) \) Å, \( \beta = 90.0000 \), \( V = 6.8206(1) \) Å
17. Magnetic measurements were performed on a Quantum Design superconducting quantum interference device (SQUID) with MPMS software. Susceptibility measurements were made in both field cooled and zero field cooled modes. An applied field of 500 Oe was used. The magnetization was linear with field up to 3000 Oe.
19. If Sb atoms were present in \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \) it would change the stoichiometry substantially away from \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \). Cold pressing 1 mmol of Yb, 0.38 mmol of Ge, and 0.63 mmol of Sb into a pellet (this is the observed 8:3:5 ratio) and arc melting them gives a single phase of \( \text{Yb}_8\text{Ge}_3\text{Sb}_5 \). The phase purity was improved by annealing the cast pellet at 750 °C for 1 week. Yields were quantitative. Microprobe elemental analysis found the atomic ratios to be 8:3:2:9:4:8 for Yb, Ge, and Sb, respectively, in very good agreement with the refinement.
20. Band structure calculations were performed using the self-consistent full-potential linearized augmented plane wave method (LAPW) within density functional theory (DFT) using the generalized gradient approximation (GGA) for the exchange and correlation potential. Scalar relativistic corrections were added, and the spin-orbit interaction (SOI) was incorporated using a second variational procedure. The calculations were performed with the WIEN2k program.
21. Band structure calculation plots are available in the Supporting Information.
22. There are, however, several examples of closed-shell, valence-precise materials which are metallic: (a) Li, B.; Corbett, J. D. Inorg. Chem. 2002, 41, 3944. (b) Krames, M. T.; Laughrey, J. T.; Corbett, J. D. Inorg. Chem. 2001, 40, 7020.