

Yb₈Ge₃Sb₅, a Metallic Mixed-Valent Zintl Phase Containing the Polymeric ¹_∞[Ge₃⁴⁻] Anions

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The structural diversity of main group cluster and oligomeric anions found in Zintl phases is astonishing.¹ Homoatomic 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 Ge₅²⁻,² the distorted tricapped trigonal prismatic Ge₉²⁻,³ the distorted bicapped square antiprismatic Ge₁₀²⁻,⁴ the octahedral Ge₆⁴⁻,⁵ the tetrahedral Ge₄⁴⁻,⁶ and the Ge₄⁴⁻ butterfly ion,⁷ 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⁺)₈(Yb³⁺) with tetrahedrally coordinated (Zn²⁻)₄, linearly coordinated and bridging (Bi¹⁻)₇, and singly coordinated (Bi²⁻)₂.¹⁰ 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 homoatomic 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,¹⁶ 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_∞[Ge₃⁴⁻] 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 3.339(1) Å,

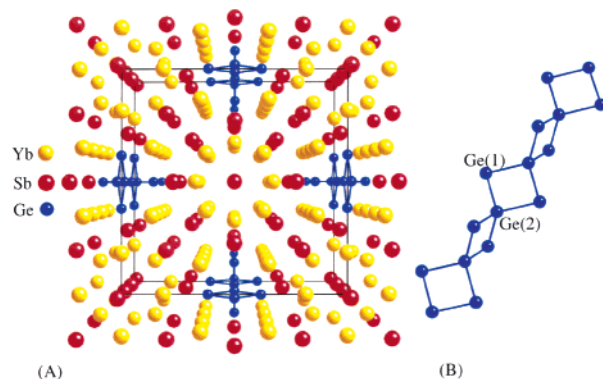


Figure 1. (A) The overall structure of Yb₈Ge₃Sb₅ as viewed along the *c* axis. (B) A segment of the infinite chain of edge sharing tetrahedra composed of the Zintl ion ¹_∞[Ge₃⁴⁻]. Formally, this chain is isoelectronic to SiS₂.

which is similar to those reported for RE₆Ge_{5-x}Sb_{11+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⁺)₆(Yb³⁺)₂(Ge₃)⁴⁻(Sb³⁻)₄(Sb²⁻). Inspection of the bond distances reveals that one of the Yb ions (Yb(3))¹⁷ 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) 3.6865(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⁺)₅(Yb³⁺)₃(Ge⁴⁻)₃(Sb³⁻)₅. 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 $\mu_{\text{eff}} = 5.7 \mu_B$ per formula unit and $\theta = -168$ K, Figure 2.¹⁸ The calculated effective magnetic moment for the first charge-balancing scheme is 6.3 μ_B ,¹⁹ whereas for the second ((Yb²⁺)₅(Yb³⁺)₃(Ge₃)⁴⁻(Sb³⁻)₅) it would be 7.9 μ_B . 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 μ_B . The changing moment could be due to a temperature-induced valence fluctuation similar to that observed in YbGaGe.¹¹

Because the ¹_∞[Ge₃⁴⁻] chain possesses formally both Ge⁰ and Ge²⁻ atoms (an example of bonded atoms of mixed oxidation

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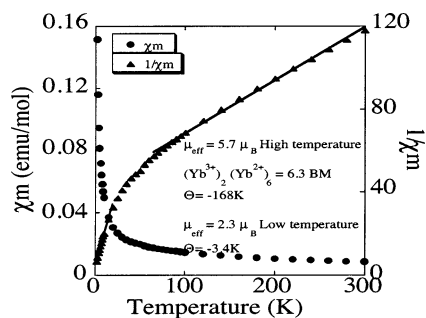


Figure 2. Temperature-dependent susceptibility data for $\text{Yb}_8\text{Ge}_3\text{Sb}_5$.

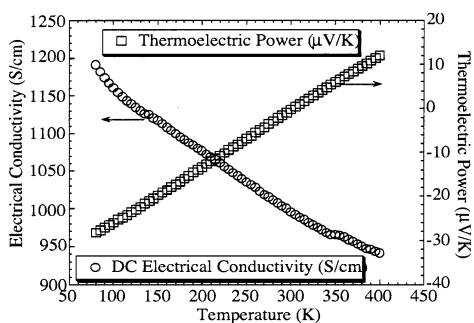


Figure 3. Temperature-dependent electrical conductivity (four probe) and thermopower performed on a polycrystalline ingot.

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 and all Ge and Sb site occupancies are refined to the full value (>96%); second, the Ge(1)–Ge(2) distance of 2.531(1) Å is substantially shorter than Sb–Ge bonds found in other compounds which range between 2.653 and 2.834 Å.^{12,13} The Ge(1)–Ge(2) distance is comparable to other reported Ge–Ge distances that range from 2.43 to 2.59 Å.^{2–4} In addition, the title compound can be made in quantitative yield by a direct stoichiometric combination of the elements.²⁰ These facts are consistent with the absence of Sb atoms in $(\text{Ge}_3)^{4-}$. Despite the rarity of having bonded atoms of mixed oxidation states, similar cases exist as for example in Cs_2Te , where formally Te^{4+} and Te^{2-} atoms coexist in the same anion species.²¹

Band structure calculations performed on the title compound show²² that the Yb(3) orbital contributions near the Fermi level (E_F) are much more hybridized as compared to Yb(1) and Yb(2) ions.²³ The calculations indicate strongly hybridized Yb 5d bands, with Ge and Sb p-bands allowing electrons from a putative Yb^{2+} to transfer into the conduction band to become Yb^{3+} or an intermediate-valent state. The calculations also indicate $\text{Yb}_8\text{Ge}_3\text{Sb}_5$ to be metallic, and this is confirmed by the charge-transport measurements shown in Figure 3. The conductivity, which is ~ 980 S/cm at 300 K, increases monotonically with falling temperature, characteristic of a metal.²⁴ The thermopower shows anomalous behavior, being small and negative at low temperature and becoming positive above room temperature. The change in sign suggests a change in carrier type that could be linked to the temperature-induced valence fluctuation mentioned above. The likely cause of the metallic behavior is the incomplete electron transfer from the Yb ions to the anionic network due to the hybridization of the Yb(3) d states.

The compound $\text{Yb}_8\text{Ge}_3\text{Sb}_5$ is stabilized because the “spectator” Yb atoms are in a mixed-valent state. It contains the new Zintl ion

$^{1-}(\text{Ge}_3)^{4-}$, which is also mixed valent featuring Ge atoms in two different oxidation states. Its metallic nature notwithstanding, $\text{Yb}_8\text{Ge}_3\text{Sb}_5$ is an unusual, nonclassical phase whose structure and magnetic susceptibility are properly rationalized by the Zintl/Klemm concept. Exploiting the potential of mixed- or intermediate-valent “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 $\text{Yb}_8\text{Ge}_3\text{Sb}_5$ (PDF and CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (16) Crystal data for $\text{Yb}_8\text{Ge}_3\text{Sb}_5$: Mw = 2210.84; tetragonal, space group $I4/mmm$, $a = 15.8965(8)$ Å $c = 6.8206(5)$ Å, $V = 1723.56(18)$ Å³, $Z = 4$, $d_{\text{calc}} = 8.52$ g/cm³, $\mu = 55.708$ mm⁻¹, $R1/wR = 3.08\%/6.61\%$ for all the 613 unique reflections, 5791 total reflections ($R_{\text{int}} = 4.51\%$), and 32 parameters. X-ray diffraction data were collected at 173 K on a Bruker SMART CCD diffractometer, graphite-monochromatized Mo K α radiation (0.71073 Å). An empirical absorption correction was applied using SADABS. The structure was solved by direct methods and refined with the SHELXL suite of programs.
- (17) The Wyckoff multiplicity of Yb(3) is twice that of Yb(1) and Yb(2); as such, Yb(3) is not formally 3+ but is actually an intermediate-valent ion.
- (18) 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.
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- (20) If Sb atoms were present in $^{1-}(\text{Ge}_3)^{4-}$ 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.
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- (23) Band structure calculation plots are available in the Supporting Information
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