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Article

Valence Compounds versus Metals. Synthesis, Characterization, and Electronic Structures of Cubic Ae$_4$Pn$_3$ Phases in the Systems Ae = Ca, Sr, Ba, Eu; Pn = As, Sb, Bi

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The isostructural compounds Sr$_4$Bi$_3$, Ba$_4$Bi$_3$, and Ba$_4$As$_{\sim 2.60}$ were prepared by direct reactions of the corresponding elements and their structures determined from single-crystal X-ray diffraction data as anti-Th$_3$P$_4$ type in the cubic space group $I\bar{4}3d$, $Z = 4$ ($a = 10.101(1)$ Å, $10.550(1)$ Å, $9.973 (1)$ Å, respectively). The two bismuth compounds are stoichiometric, and the arsenide refines as Ba$_4$As$_{2.60(2)}$. Only unrelated phases are obtained for all binary combinations among the title components for either Ca or Sb. The magnetic susceptibility and resistivities of Ba$_4$Bi$_3$ and Eu$_4$Bi$_3$ show that they are good metallic conductors ($\sim$40 $\mu\Omega\cdot$cm at 298 K), whereas Ba$_4$As$_{2.60}$ exhibits ρ_{150} > 1000 $\mu\Omega\cdot$cm. The electronic structures of Sr$_4$Bi$_3$, Ba$_4$Bi$_3$, and Ba$_4$As$_3$ were calculated by TB-LMTO-ASA methods. Mixing of cation d states into somewhat disperse valence p bands on Bi results in empty bands at E_F and metallic behavior, whereas the narrower valence band in the electron-deficient Ba$_4$As$_3$ leads to vacancies in about 11% of the anion sites and a valence compound.

Introduction

R$_4$Pn$_3$ phases for R = rare-earth element, Pn (pnictogen) = As, Sb, Bi, are known to crystallize in the anti-Th$_3$P$_4$ type structure, especially for the larger metals La−Tb and Yb.[2] These compounds and their solid solutions have been extensively investigated because of their interesting magnetic and electronic properties. For example, the Gd compounds are ferromagnets,[3] the Ce compounds show interesting Kondo-type behaviors,[4] and the Yb compounds show valence fluctuation.[5] The bonding or, more precisely, the valence electron count for this stoichiometry and structure in most of these phases can be successfully rationalized in terms of

simple octet bonding schemes. Thus, for these pnictide compounds to be valence precise at least one of the four (crystallographically equivalent) rare-earth metal atoms must have an oxidation state of +3. (A higher fraction presumably yields a metallic phase.) For example, Sm$_4$Bi$_3$, Yb$_4$As$_3$, and Yb$_4$Bi$_3$ are mixed-valent materials with a 1:3 ratio of trivalent and divalent rare-earth ions.[6] An interesting pressure-induced valence instability was established for Sm$_4$Bi$_3$,[7] wherein the Sm^{+2} atoms shift toward the Sm^{+3} state, and the material goes from semimetallic to a metallic state in the transition.

Up to now, only a few pnictides with anti-Th$_3$P$_4$ type structures have been reported with nominally divalent cations: Eu$_4$Bi$_3$,[8] Ba$_3$P$_2$[9] ($\hat{=}$Ba$_4$P$_{2.67}$), and Ba$_8$As$_5$Au.[10] In Ba$_8$As$_5$Au, five As^{-3} and one Au$^-$ are disordered over the single anion site. For Eu$_4$Bi$_3$, the presence of the stoichiometric composition with only divalent cations was established by the effective magnetic moment, which suggested that the compound was deficient by one electron per formula unit.

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This was considered to be consistent with the measured metallic behavior, although the room temperature resistivity, about 1.29(1) $\Omega \cdot$cm, seems much too high for this type of compound. (Anomalous magnetic and electronic behavior had been reported before for this compound.[11]) For Ba_3P_2, the positional parameter of phosphorus in a defect anti-Th_3P_4 type structure was refined only from powder pattern data, with an assumed occupancy for P of $^{2.67}/_3 = 0.89$ in analogy with the known inverse (C-type) Ce_2S_3 in this structure type.[9] A black color but a high resistivity were also reported. Thus, phases with divalent cations in pnictides with this type structure should, if stoichiometric, be one electron deficient and metallic, whereas if they are substoichiometric as Ae_4-$Pn_{2.67}$, they might reasonably be assumed to be closed shell and semiconductors.

There have been no published results regarding such compounds between Ca, Sr, or Ba and Sb or Bi. However, we were encouraged to make the present study by the unpublished accidental discoveries of nominal Ba_4As_3, Sr_4-Bi_3, and Ba_4Bi_3 in this structure type during an exploration for compounds analogous to $Ca_{16}Sb_{11}$.[12] A diffraction study of the last example in the subgroup $R3c$ also suggested that it was fully stoichiometric.[13] (The present compounds are not to be confused with the orthorhombic (*Pbam*) Sr_4As_3 and Ba_4P_3 phases.[14]) In order to understand the stoichiometries and electronic properties of these anti-Th_3P_4 type pnictides, we have examined the syntheses and physical properties of A_4Pn_3 compounds for A = Ca, Sr, Ba, Eu with, in part, Pn = As, Sb, and Bi. We also report a density-functional-theory study of the electronic structure of several members of this series.

Experimental Section

Syntheses. All operations were carried out in a N_2-filled glovebox with the moisture level below 1 ppm. The compositions Ba_4Bi_3, Sr_4Bi_3, $Ba_4As_{2.67}$, and Eu_4Bi_3 were synthesized from stoichiometric mixtures of the following elements: Ba (99.9%), Sr (99.9%), As (99.99%), Bi (99.999%) (all from Alfa-Aesar), and Eu (99.9% total, Ames Laboratory). Mixtures were loaded in niobium containers that were sealed by arc welding under argon and then enclosed in fused silica ampules that were in turn evacuated and flame-sealed. All compounds except Eu_4Bi_3 could be prepared by the following process: About 300 mg of the appropriate mixture was first heated to 700 °C and held for 6 h; then, the temperature was increased to 1050 °C, held for 6 h, and quenched to room temperature. The sample was reheated at 800 °C for 140 h and finally cooled to room temperature at 3 °C/h. Pure Eu_4Bi_3 can be easily obtained by simply quenching after reaction at 1100 °C for 36 h. All compounds are dark and brittle and very air sensitive. X-ray powder patterns (Enraf-Nonius 552 Guinier camera, Cu $K\alpha_1$ radiation, $\lambda = 1.540562$ Å, and NIST silicon as an internal standard) were used for phase analyses of the products. Pure phases (to X-rays) were obtained for the Ba_4Bi_3, Eu_4Bi_3, and $Ba_4As_{2.67}$ compositions, whereas a Ba_4-

Table 1. Crystallographic Data for Ae_4Pn_3

	Ba_4Bi_3	Sr_4Bi_3	$Ba_4As_{2.60}$
fw	1176.3	977.42	743.4
space group, Z		$I\bar{4}3d$ (No.220), 4	
a (Å)	10.550(1)	10.101(1)	9.973(1)
V (Å^3)	1174.3(2)	1030.6(2)	992.0(2)
ρ (Mg/m^3)	6.653	6.299	4.978
μ (mm^{-1})	57.906	71.492	24.15
R1/wR2 [$I > 2\sigma(I)$]	0.034/0.078	0.038/0.065	0.021/0.047

As_3 stoichiometry also produced about 15% of an unknown. The highest yield of Sr_4Bi_3 was about 85% plus the very stable Sr_{11}-Bi_{10}. Attempts to produce the isostructural antimonides for Ca, Sr, and Ba as well as Ca_4Bi_3 failed, giving the corresponding known $Ae_{11}Pn_{10}$ phases with the $Ho_{11}Ge_{10}$ type structure[15] in ~95% yields. The other minor products, e.g., ~5% Ca, were not seen.

Physical Properties. The resistivities of Ba_4Bi_3 and Eu_4Bi_3 were examined by the electrodeless "Q" method with the aid of a Hewlett-Packard 4342A Q meter.[16] This method is particularly suitable for measurements on highly air-sensitive samples. For this purpose, 86.1 and 104.2 mg samples of powdered Ba_4Bi_3 and Eu_4-Bi_3 with grain diameters between 150 and 250 μm, respectively, were dispersed with chromatographic alumina and sealed in Pyrex tubes under He. Measurements were made at 34 MHz over the range 120−291 K. The magnetization of Ba_4Bi_3 and Eu_4Bi_3 was measured on a Quantum Design MPMS SQUID magnetometer at a field of 3 T over the temperature range 6−300 K. Typically, 30−60 mg of the sample was sealed within a fused silica tubing in which it was held between two tightly fitting rods of the same material.[17] Corrections were applied for the holder and the ion core diamagnetism.

Structure Determination. Single crystals of nominal Ba_4Bi_3 (0.2 × 0.25 × 0.4 mm^3), Sr_4Bi_3 (0.15 × 0.15 × 0.25 mm^3), and Ba_4-$As_{2.67}$ (0.11 × 0.18 × 0.07 mm^3) were mounted in glass capillaries inside the glovebox. The crystals were first checked by Laue photography for their singularities and then transferred to a Rigaku AFC6R automatic diffractometer for data collection, which took place at room temperature with the aid of monochromated Mo $K\alpha$ radiation. Cell constants and an orientation matrix for data collection were determined from least-squares refinements of the setting angles of 25 centered reflections. The diffraction data were corrected for Lorentz and polarization effects and for absorption with the aid of three ψ-scans of reflections at different 2θ values. To be sure of the refined substoichiometry $Ba_4As_{2.58(6)}$, a second crystal (0.15 × 0.18 × 0.27 mm^3) was selected from another synthesis, and data were collected on a SMART APEX CCD diffractometer at room temperature. All the structures were solved and refined in cubic acentric $I\bar{4}3d$ with the aid of the SHELXTL V5.1 software package. The barium bismuthide was solved as a merohedral twin. Some details of the crystallographic and refinement parameters are given in Table 1. Table 2 contains the atomic positional and the isotropic equivalent displacement parameters, and Table 3 gives the important bond distances therein. The results reported for $Ba_4As_{2.60(2)}$ came from the CCD data.

Computational Details. TB-LMTO-ASA electronic band structure calculations were carried out for Sr_4Bi_3 and Ba_4Bi_3 as well as for hypothetical Ba_4As_3 with the aid of the Stuttgart LMTO47

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters for Ae$_4$Pn$_3$

compd	atom	x	y	z	U_{eq}
Ba$_4$Bi$_3$	Ba	0.0730(1)	x	x	10(1)
	Bi	$^3/_8$	0	$^1/_4$	9(1)
Sr$_4$Bi$_3$	Sr	0.0728(1)	x	x	14(1)
	Bi	$^3/_8$	0	$^1/_4$	13(1)
Ba$_4$As$_{2.60(2)}$	Ba	0.0780(1)	x	x	30(1)
	As[a]	$^3/_8$	0	$^1/_4$	24(1)

[a] Occupancy = 0.866(7).

Table 3. Selected Interatomic Distances (Å) in Ae$_4$Pn$_3$ Phases

	Ba$_4$Bi$_3$	Sr$_4$Bi$_3$	Ba$_4$As$_{2.60}$
Pn−Ae × 4	3.537(1)	3.384(1)	3.2923(6)
Pn−Ae × 4	3.772(1)	3.614(1)	3.6236(6)
Ae−Pn × 3	3.537 (1)	3.384(1)	3.2923(6)
Ae−Pn × 3	3.772(1)	3.614(1)	3.6236(6)
Ae−Ae × 3	4.040(1)	3.870(1)	3.8756(7)
Ae−Ae × 2	4.5684(5)	4.3739(5)	4.3185(5)

program.[18] Exchange and correlation effects were treated in a local spin density approximation (LDA).[19] All relativistic effects except spin−orbit coupling were taken into account using a scalar relativistic approximation.[20]

Within the atomic sphere approximation (ASA), space is filled with small overlapping Wigner−Seitz (WS) atomic spheres. The symmetry of the potential is considered to be spherical inside each WS sphere, and a combined correction is used to take into account the overlapping part.[21] The radii of the WS spheres were obtained under the requirement that the overlapping potential is the best achievable approximation to the full potential, and they were so determined by an automatic procedure. The maximal overlap should not be too large because the error in the kinetic energy introduced by the combined correction is proportional to the fourth power of the relative sphere overlap. Since the structures under examination are not dense-packed, interstitial "empty spheres" (ESs) were also introduced to achieve space filling with minimal overlap. The optimal positions and the radii for the empty spheres were also determined automatically according to the described method.[22]

The basis set of short-ranged atom-centered TB-LMTOs comprises the ns, np, $(n-1)$d, and $(n-2)$f orbitals for the two alkaline-earth metals (Sr, $n = 5$; Ba, $n = 6$) and the 4s, 4p, and 4d orbitals for the arsenic. For Sr, the p and f orbitals were downfolded, for Ba, just the p orbitals. In the case of the pnictogens, the 4s, 4p, and downfolded 4d orbitals were used for As, and the 6s, 6p, and downfolded 6d and 5f orbitals for Bi. The Löwdin downfolding technique[18] allows the derivation of few-orbital effective Hamiltonians by keeping only the relevant degrees of freedom and integrating out the irrelevant ones. The **k**-space integrations were performed by the tetrahedron method.[22]

To illustrate the contribution of different atoms to the overall densities-of-states (DOSs), energy-resolved and atom-projected densities-of-states (PDOSs) were used. The PDOS shows only the

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density of states associated with the respective atom. The Fermi level was chosen as an internal reference level in all cases.

Results and Discussion

Stoichiometry. The problem we have faced lies with the supposed (Ae)$_4$Pn$_3$ phases with the inverse Th$_3$P$_4$-type structure that may form for Ae = Ca−Ba (and Eu) and Pn = As−Bi. It is important to establish the correct stoichiometries, the related properties, and the theoretical reasons for these findings. The structure type contains only well separated Pn atoms and does not offer any suggestion of Pn−Pn bonding. Thus, if these compounds are Zintl (valence) phases, then electron conservation would require a stoichiometry and oxidation states of (Ae^{+2})$_4$(Pn^{-3})$_{2.67}$, and semiconducting (or insulating) and diamagnetic properties should follow. (This circumstance is common in the normal-valent sequisulfides and selenides of the rare-earth elements, e.g., ref 23.) On the other hand, an Ae$_4$Pn$_3$ stoichiometry would appear to require the presence of a hole in the pnictide valence band or equivalent, and this would presumably lead to metallic properties. Possible participation of the cations in this event would appear important. A third possibility is that one or more in this family of compounds with a 4:3 proportion and this structure type do not exist. We find that all three situations in fact occur with binary combinations of As, Sb, or Bi with the alkaline-earth metals. The actual situation with the reported black Ba$_3$P$_2$[9] (Ba$_4$P$_{2.67}$ vs Ba$_4$P$_3$) does not seem to have been clarified, although the former valence type compound seems probable.

Two approaches and ways have been utilized to differentiate A$_4$Pn$_{2.67}$ from A$_4$Pn$_3$ formulations, semiquantative syntheses and structural refinements. Reactions of samples loaded as Ba$_4$Bi$_3$, Eu$_4$Bi$_3$, and Sr$_4$Bi$_3$ gave the pure targets for the first two according to their Guinier powder patterns (i.e., >95% yields) and the third, 85% Sr$_4$Bi$_3$, 15% Sr$_{11}$Bi$_{10.}$ Conversely, reactions loaded with the compositions Ba$_3$Bi$_2$ ($\equiv$Ba$_4$Bi$_{2.67}$) and Eu$_3$Bi$_2$ gave $\sim$90% of the cubic M$_4$Bi$_3$ structure plus the known M$_{16}$B$_{11}$ for both. Likewise, the products from loaded Ba$_4$As$_{2.67}$ and Ba$_4$As$_3$ samples produced powder patterns for pure Ba$_4$As$_{2.6}$ and the same plus $\sim$15% of an unknown (presumably arsenic-richer) phase, respectively. Note that these semiquantitative synthesis features are powerful evidence for the assigned stoichiometries. In parallel, structural refinements of Ba$_4$Bi$_3$ and Sr$_4$Bi$_3$ showed that once all atoms were input, successive variations of occupation factors led to no significant changes from unity. Similarly, separate sets of diffraction data collected for different crystals with Rigaku and Bruker CCD diffractometers led to refined compositions Ba$_4$As$_{2.58(6)}$ and Ba$_4$As$_{2.60(2)}$, respectively. On the other hand, attempted syntheses of the (Ba,Sr)$_4$Sb$_3$ and Ca$_4$(Pn)$_3$ phases produced only other known phases (see Experimental Section).

Structure. The three stoichiometric A$_4$Bi$_3$ compounds A = Sr, Ba, Eu are antitypes of the Th$_3$P$_4$ structure, and the same is true for Ba$_4$As$_{2.6}$ save for the $^1/_9$ random vacancies

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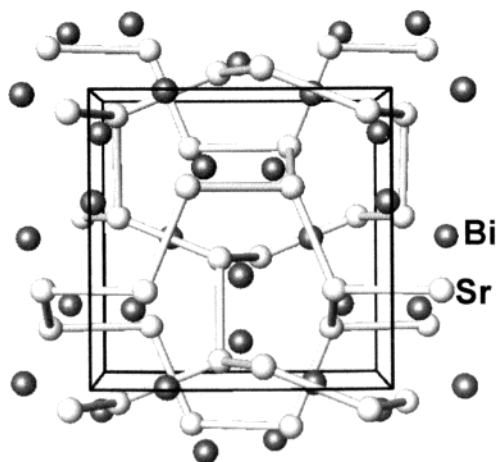
Figure 1. (100) view of the linked Sr atoms that form two three-dimensional enantiomeric networks in Sr_4Bi_3. The Bi atoms are well separated from one another.

on the anion lattice. The structure is quite simple in local environments but complex as a whole. The divalent cations occupy the position $16c$ (x, x, x) in which they form two enantiomeric networks (Figure 1). The Bi (As) atoms in positions $12a$ $(^3/_8, 0, ^1/_4)$ generate three condensed diamond-like networks each composed of 3-connected 6-membered rings. Note that the anionic network has no variable parameters, and thus, the interatomic distances are inter-related by the lattice constants. Furthermore, there are no direct interactions between the anions, the Pn−Pn distances being greater than 4.7 Å for the bismuthides and 4.6 Å in the arsenide. The Bi(As) atoms are coordinated by eight cations, and the cations have six Pn atoms and five cation nearest neighbors, three of the five cations having shorter distances to each other, 4.040(1) and 3.840(1) Å in Ba_4Bi_3 and $Ba_4As_{2.6}$, respectively.

Properties. Figure 2a shows resistivity data for a single-phase sample of Ba_4Bi_3 measured by the "Q" method. The results are characteristic of a moderately poor metal, with $\rho_{298} = 43.6$ $\mu\Omega$·cm and a mean temperature dependence of 0.09(1)% K^{-1}, the sign of the latter being taken as the defining characteristic of a metal. The magnetic susceptibility results for Ba_4Bi_3 are shown in Figure 2b. Above 12 K, the data are almost temperature-independent, $\sim 6.9 \times 10^{-4}$ emu/mol after container and ion core corrections, and the magnitudes are quite typical for Pauli-paramagnetism in such phases. The magnetic susceptibilities and electronic resistivities of Eu_4Bi_3 powder were also remeasured. The magnetic results are almost the same as reported before[8] with an effective magnetic moment of 7.5(1) μ_B, closely corresponding to the expected result for Eu^{+2}. On the other hand, the electrodeless "Q" method gave $\rho_{298} = 38.1$ $\mu\Omega$·cm and a mean temperature dependence of 0.30(1)% K^{-1} for Eu_4Bi_3. This is much more in line with the behavior of Ba_4Bi_3 than the evidently erroneous result reported earlier for Eu_4Bi_3, $\rho_{298} = 1.29(1)$ Ω·cm.[8] Resistivity measurements on $Ba_4As_{2.60}$ by the "Q" method were also attempted, but the resistivity was too large to give an answer by this method. A lower limit of 1000 $\mu\Omega$·cm was estimated at 150 K, which is reasonable in view of the probable band gap (below).
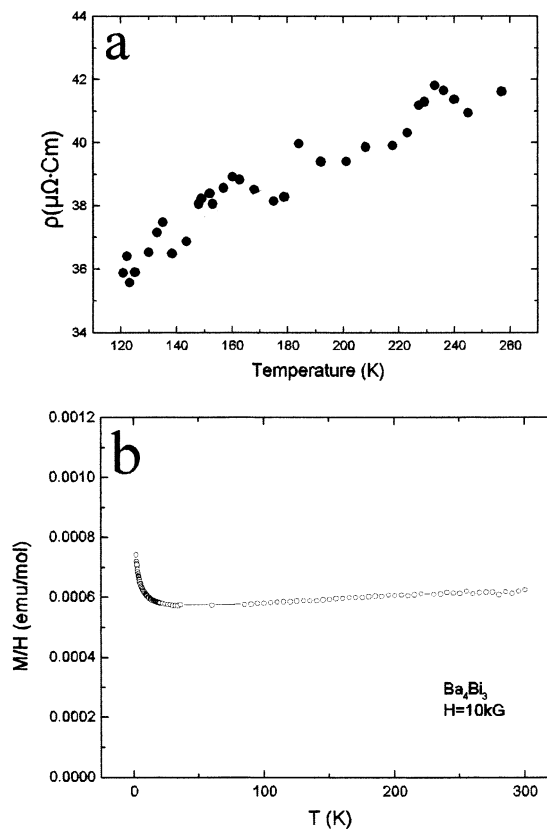

Figure 2. (a) Resistivity data vs temperature for a single phase sample of Ba_4Bi_3 ($\mu\Omega$·cm) as obtained by the "Q" method. (b) Molar magnetic susceptibilities of Ba_4Bi_3 (emu·mol^{-1}) as a function of temperature (K).

Band Structures. While the structure of the Ae_4Pn_3 compounds is fairly simple, the electronic structures are somewhat more difficult to rationalize. According to the Zintl−Klemm concept, it is assumed that the alkaline-earth metals are cations and donate their electrons. Accordingly, it has often become a simple matter to apply octet rules to judge generally well-delineated electron counts according to octet rules. Since there are no Pn−Pn bonds in these compounds, a formal electron counting suggests a one-electron deficiency per formal unit for Ba_4Bi_3 and Sr_4Bi_3, whereas $Ba_4As_{\sim2.67}$ is assumed to be a Zintl phase with the appropriate substoichiometry.

The general features of the band structures of Sr_4Bi_3, Ba_4Bi_3, and the hypothetical Ba_4As_3 are quite similar. Each consists of four distinctively different areas of bands. First are low lying "semicore" pnictogen s bands with a low degree of dispersion and bandwidth, followed by the "valence" bands composed mainly of pnictogen p orbitals around the Fermi level. The top levels of these broad band area cross E_F, the Fermi level, with special steepness around Γ. These bands also contain substantial contributions from alkaline-earth-metal p and, most important, d states, particularly for the two bismuth compounds. The alkaline-earth metal d states themselves occur in wide bands at higher energies above a gap, starting ~ 1.3 eV above the Fermi level; Sr/Ba p bands mix substantially with Pn p, and thus, they are important. The substantial density of states at the Fermi level for Sr_4Bi_3 and Ba_4Bi_3 indicates an open band character of the bismuth anion and explains the metallic properties of those
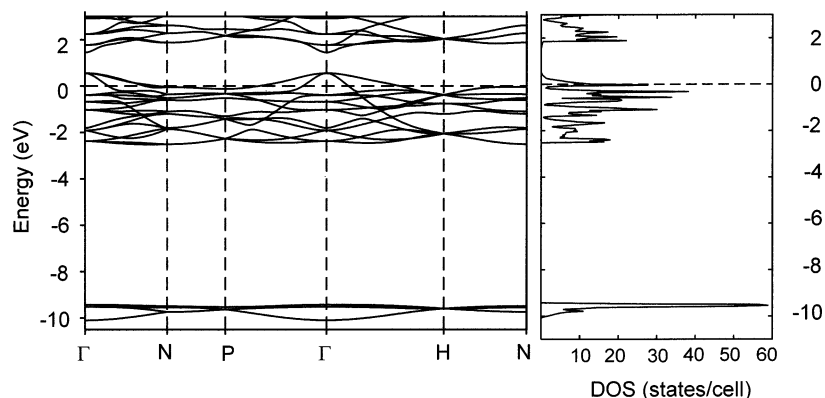
Figure 3. Band structure and densities-of-states for Sr_4Bi_3 ($E_F = 0$).
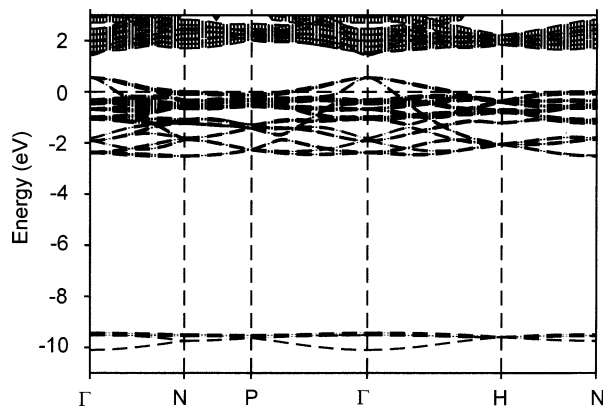

Figure 4. Band structure in the fatband representation for Sr d in Sr_4Bi_3 in the valence band region. Note the strong d-contribution to the levels right below the Fermi level.
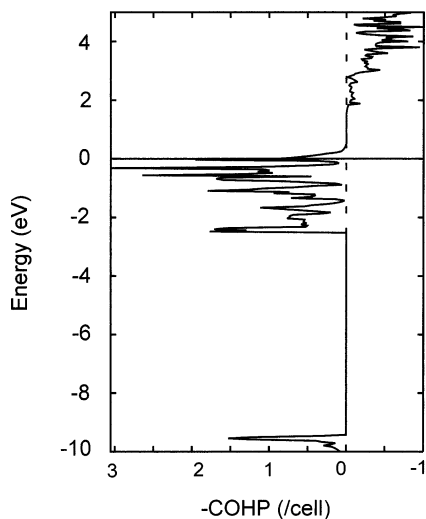

Figure 5. COHP data for Sr−Bi interactions in Sr_4Bi_3 as a function of energy. Positive COHP values are bonding.

compounds. The band and DOS data for the strontium member are shown in Figure 3, and Figure 4 illustrates in a fatband representation the participation of Sr 4d orbitals in the valence band. Likewise, the cation−anion covalency in Sr_4Bi_3 is emphasized by the COHP curve in Figure 5, and that for Ba_4Bi_3 is similar.

The dependence of the results on the alkaline-earth metal cation is quite clear from the calculations. The Bi valence bands in Sr_4Bi_3 have a higher dispersion and width than in the Ba compound in which the electrons are somewhat more localized. In other words, the strontium cations have the larger charge potential (charge/radius ratio) and tend to polarize the "soft" bismuth anion and destabilize its anionic charge even though mixing of cation (mainly d) states into the valence band is slightly greater for barium.

On the other side, the influence of the anions in this class of compounds can be studied by a comparison with Ba_4-$As_{2.67}$ or, better, the idealized Ba_4As_3 (with fully occupied anion positions) with Ba_4Bi_3. Most important is the change of bandwidth and dispersion upon replacement of Bi by As. The dispersion of the valence bands (which are mainly pnictogen p in character) around the Fermi level is distinctly (~16%) less in the comparable (hypothetic) arsenic analogue. This shows the general periodic tendency of lighter anions to stabilize electrons in their valence shells, whereas heavier elements tend to have more disperse, less localized valence bands, and a greater tendency to metallicity. Therefore, an open shell anion is less favorable for arsenic. The hypothetical Ba_4As_3 lacks one electron for a closed valence shell, and the system responds by removing $1/9$ of the 12 As and four bands per cell to give just the closed shell result with disordered monoanions and vacancies.

The regularities with antimony are worth noting again; no Ae_4Sb_3 compounds could be isolated for Ae = Ca, Sr, Bi. Rather, principally the alternative $Ae_{11}Sb_{10}$ phases are formed instead. Antimony is clearly a better anion former than is bismuth, and it does so in other products rather than generate vacancies in this lattice or an open valence band. The regular trends we note for the series As−Sb−Bi also parallel the increase in metallic characteristics as s−p mixing diminishes and the former orbitals become more corelike.[24]

Finally, the valence problems associated with Ae_4Pn_3 compositions in the anti-Th_3P_4 structure type can presumably also be expressed in ternary systems through partial substitution of lower-valent anions on that lattice or interstitially. Three examples are suggestive, but no properties are known and the compositions themselves are not entirely certain. Earlier attempts to make ternary derivatives of Mn_5Si_3 structures of Ca_5Sb_3 and Ba_5Sb_3 stuffed with interstitial S or I gave mixed anion varieties of $(Th_3P_4)^{-1}$ structures instead as $Ca_4Sb_{2.4}S_{0.4}$ and $Ba_4Sb_{2.5}I_{0.5}$.[25] The former, which has the

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same composition as the valence compound sought, Ca_5-$Sb_3S_{0.5}$, was obtained in quantitative yield according to the Guinier powder pattern, presumably with 6.7% vacancies on the mixed anion lattice. The iodide was obtained as a mixture from a Ba_5Sb_3I composition but was later obtained in ~80% yield and refined from single crystal data for the composition $Ba_4Sb_{2.5}I_{0.5}$. (Distinguishing the latter two elements would be problematic). Finally, the present structure type was also found in about 80% yield, presumably as $Ba_4Bi_{2.5}F_{0.5}$ (along with $Ba_{16}Sb_{11}$ and a trace of BaF_2) from an attempt to prepare Ba_5Sb_3F in the orthorhombic Ca_5Sb_3F structure.[9,26] In this case, the fluoride would presumably lie in the tetrahedral interstitial cavities in this structure type. Further studies in these areas could be profitable.

Supporting Information Available: Tables of additional crystallographic and refinement parameters for Ba_4Bi_3, Sr_4Bi_3, and $Ba_4As_{2.60}$. Figures of magnetic susceptibility and resistivity data for Eu_4Bi_3. These materials are available free of charge via the Internet at http://pubs.acs.org.

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