Electronic structure of \( M^+\)Sb-type filled tetrahedral semiconductors

Su-Huai Wei and Alex Zunger

Solar Energy Research Institute, Golden, Colorado 80401

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First-principles band-structure and total-energy calculations have been performed for \( \text{Li}_3\text{Sb} \), \( \text{K}_3\text{Sb} \), and \( \text{Cs}_3\text{Sb} \) in the cubic \( D_0\) structure. The structure of these \( M^+\)Sb octet semiconductors consists of a face-centered-cubic lattice \( A^+ \) in which three metal \( M^+ \) atoms occupy the interstitial sites, thereby completing the octet shell. The equilibrium lattice parameters and bulk moduli calculated from the total energy agree well with available experimental data. The semiconducting character of \( \text{K}_3\text{Sb} \) and \( \text{Cs}_3\text{Sb} \) is attributed to \( p-d \) repulsion between the anion \( p \) states and the unoccupied metal \( d \) states. The calculated charge density shows weak covalent bonding between like atoms and ionic bonding between unlike atoms. The covalency decreases and the ionicity increases with increasing metal atomic number, as the \( M^+ \) cores dilate the lattice. We find that the electronic structure of these compounds can be understood qualitatively by considering a skeleton of \( \text{Sb}^{5-} \) anions whose separation is determined by the otherwise nearly inert alkali ions \( M^+ \). The trends in the electronic properties in the series \( M = \text{Li}, \text{K}, \) and \( \text{Cs} \) then reflect the perturbations exerted by different \( M^+ \) ions through (i) charge transfer, (ii) \( p-d \) hybridization, and (iii) relativistic effects.

I. INTRODUCTION

Combination of the alkali metals \( (M) \) with antimony yields a group of interesting semiconductors which attracted considerable attention in past years.\(^1\) These materials possess relatively small electron affinities and high photoelectric quantum efficiencies in the visible region.\(^1,2\) As high-sensitivity photocathode materials, these compounds have been widely utilized in photometry, optical image, and other device applications.\(^1\)

Studies\(^1\) of the chemical composition, and x-ray and electron diffraction reveal that alkali-antimony compounds have the stoichiometric composition \( M_3\text{Sb} \) (where \( M \) can be one or more types of alkali-metal elements), crystallize either in (i) the hexagonal \( \text{Na}_3\text{As} \) structure (space group \( D_{6h}^\text{4} \)), (ii) the cubic (or, \( \beta \)) modification of the \( \text{BiF}_3 \) structure (space group \( O_\text{h}^\text{4} \), or the \( D_0\) structure, see inset to Fig. 1), or (iii) the partially disordered \( \text{NaTl} \) structure (space group \( O_\text{h}^\text{2} \)). The high photosensitivity\(^3\) of these systems is found in the cubic structure and has been attributed to band bending caused by a dipole layer at the surface of these highly electropositive systems.

Despite the large variations in atom size and properties of the different alkali elements in \( M_3\text{Sb} \) and the resulting dramatic changes in lattice constants of the compounds\(^4\)–\(^6\) \((a = 6.572 \, \text{Å} \) for \( \beta-\text{Li}_3\text{Sb} \), \( a = 8.493 \, \text{Å} \) for \( \text{K}_3\text{Sb} \), and \( a = 9.128 \, \text{Å} \) for \( \text{Cs}_3\text{Sb} \)), all the alkali-antimony compounds are semiconductors\(^1\) with surprisingly small variations of the band gap (all within \( 1.0-1.6 \, \text{eV} \)).\(^1,3\) This is rather unexpected since conventional volume \( (V) \) deformation potentials of band gaps \( -dE_g/d \ln V \) (ranging\(^7\) between 7 and 30 eV) would suggest that the larger-volume \( M_3\text{Sb} \) compounds (e.g., \( \text{K}_3\text{Sb} \), \( \text{Cs}_3\text{Sb} \)) might be metallic. Theoretical\(^8\) and experimental\(^9\) studies also indicate that the top of the valence bands for \( M_3\text{Sb} \) (except for \( \text{Li}_3\text{Sb} \)) is nearly dispersionless, a characteristic of ionic insulators, not semiconductors. The nature of the chemical bonding in \( M_3\text{Sb} \), i.e., whether they are ionic, covalent, or "charge-transfer semiconductors,"\(^10\) has similarly been a subject of ongoing theoretical\(^10,11\) and experimental investigation.\(^10,12\) (This subject is also of current interest because of its relation to the metal-nonmetal transition observed in several liquid alkali-pnictogen alloys.\(^13\))

A few propositions have been advanced: the cubic crystal structure of \( \beta-M_3\text{Sb} \) and the valences of \( M \) and \( \text{Sb} \) (one and five, respectively) have suggested to Suchet\(^14\) an "interstitial compensatory lattice model" in which the antimony atom and its nearest-neighbor alkali atoms (denoted \( M_\beta \)) form a covalently bonded lattice through \( s-p \) hybridization; the role of the other alkali atom (denoted \( M_\alpha \)) is then to provide one extra electron to compensate the covalent bond. This suggests that these compounds have the pseudo-face-centered ionic form \( [M_\beta\text{Sb}M_\beta]^+M_\alpha^- \). However, x-ray photoemission studies\(^15\) indicated for \( \text{Cs}_3\text{Sb} \) only a single type of Cs atom (predominantly in the Cs\(^+ \) form), in conflict with this model. Recently, Robertson,\(^10\) using the tight-binding method, has performed calculations for \( \text{Li}_3\text{Sb} \) and \( \text{Cs}_3\text{Sb} \) in an attempt to determine whether the chemical bonding is predominantly covalent or ionic. Based on his calculation of the ionicities (defined loosely as the atomic charge on the cation) he found that \( M_3\text{Sb} \) could be viewed as a "charge-transfer semiconductor" whose ionicity could be quite small due to the delocalization of the \( \text{Sb} \) orbitals. A study by Christensen\(^11\) indicates that, because of the large differences in size of the alkali atoms, remarkable differences in bonding exist between \( \text{Li}_3\text{Sb} \) and \( \text{Cs}_3\text{Sb} \). He suggests that \( \text{Li}_3\text{Sb} \) resembles a molecular crystal but that \( \text{Cs}_3\text{Sb} \) appears to be dominated by ionic bonding, similar to that in CsI. The band structure for \( \text{Cs}_3\text{Sb} \) has also been calculated by Nishikawa et al.\(^16\) using the augmented-plane-wave method.

In this paper we have performed systematic first-principles total-energy and band-structure calculations for...
\( \beta \)-M\(_3\)Sb \((M=\text{Li,K,Cs})\) in the ordered cubic \(\text{D}_0_3\) structure. In this crystal structure (inset to Fig. 1), four simple face-centered sublattices are mutually displaced along the body diagonal such that all nearest-neighbor distances equal \(\frac{1}{4}\) of this diagonal. There are two different types of crystallographically inequivalent cations in this structure: \(M_1\) with eight \(M_{\text{II}}\) cation as nearest neighbors, and \(M_{\text{II}}\) with four cations and four anions as nearest neighbors. The primitive lattice vectors are

\[
\begin{align*}
a_1 &= (0, \frac{1}{2}, \frac{1}{2})a, \\
a_2 &= (\frac{1}{2}, 0, \frac{1}{2})a, \\
a_3 &= (\frac{1}{2}, \frac{1}{2}, 0) a, \\
\end{align*}
\]
and the atomic site coordinates are as follows: Sb at

\[
\begin{align*}
\tau_1 &= (0,0,0)a, \\
\tau_2 &= (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a, \\
\tau_3 &= (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a, \\
\tau_4 &= (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a, \\
\end{align*}
\]
where \(a\) is the cubic lattice constant.

From total-energy calculations we have obtained the ground-state properties of these systems. The band structures of Li\(_3\)Sb, K\(_3\)Sb, Cs\(_3\)Sb, and that for a hypothetical crystal (Sb\(^{3-}\)\(^2\))\(^{2+}\) (with three additional positive charges uniformly distributed in the unit cell for charge neutrality) have isolated three physical contributions to the electronic structure: (i) lattice relaxation, (ii) \(p-d\) repulsion, and (iii) the relativistic effects. The chemical bonding in these compounds has been studied through charge-density plots.

II. METHOD OF CALCULATION

The total-energy and electronic band structures are calculated with use of the first-principles self-consistent general-potential linearized augmented-plane-wave (LAPW) method\(^{17}\) within the local-density-functional formalism.\(^{18}\) Several exchange-correlation functional forms\(^{19-21}\) have been used to test the dependence of ground-state properties (lattice constant, bulk modulus) on these potentials. Scalar relativistic effects (i.e., including directly all relativistic effects but the spin-orbit coupling) are incorporated for all valence states; spin-orbit coupling is included only in the calculation of the splitting \(\Delta_{\text{v}}\) of the \(\Gamma_5\) states at the valence-band maximum. Core states have been calculated fully relativistically in a spherical approximation. All core and valence states are calculated self-consistently without invoking the frozen-core approximation. Shape unrestricted potentials and charge densities are used throughout. The two special \(k\) points of Chadi and Cohen\(^{22}\) are used for the Brillouin-zone integration. The basis set consists of about 200 functions (a basis set of about 300 functions was, however, needed for the calculations which treat Cs \(5p\) states as valence states, see below). Eigenvalues of the valence states are converged to better than 0.03 eV (0.2 mRy). Finally, the density of states (DOS) is calculated using the tetrahedral integration method\(^{23}\) with a square broadening scheme (with a width of 0.16 eV, or 12 mRy) and eight primary \(k\) points.

III. RESULTS AND DISCUSSION

A. Total-energy and ground-state properties

The total and cohesive energies as a function of lattice parameter were calculated for Li\(_3\)Sb, K\(_3\)Sb, and Cs\(_3\)Sb in the cubic (\(\beta\)) \(\text{D}_0_3\) structure and are depicted in Fig. 1. The calculated total energies using the Wigner\(^{19}\) interpolation formula at three values of the lattice parameter were fitted to a quadratic form and interpolated to obtain the zero-temperature equilibrium lattice constant \(a_{0\text{eq}}\) and bulk modulus \(B\). The cohesive energies, using the Von Barth–Hedin spin-polarized exchange correlation potential (in the Hedin-Lundqvist paramagnetic limit), are obtained by subtracting the spin-unrestricted atomic total energy.
energies (including spin-polarization corrections which are 0.37, 0.25, 0.21, and 1.35 eV for Li, K, Cs, and Sb, respectively) from the crystal total energies. The calculated cohesive energies are assumed to be independent of specific correlation form. These results are summarized in Table I where they are compared with the experimental data\(^5\)\(^,\)\(^12\) and with the linear—muffin-tin-orbital (LMTO) results of Christensen\(^4\)\(^,\)\(^11\)\(^,\)\(^26\) for Li\(_3\)Sb and Cs\(_3\)Sb. In our calculation for Cs\(_3\)Sb we treat the partially delocalized Cs 5p states as variational valence-band states, i.e., on the same footing as all the other valence electrons. We find that treating the 5p states as dispersionless core states (but self-consistently) gives a lattice constant which is about 3.5% too small.\(^26\) We find that our calculated lattice constants are systematically smaller than the observed ones. (This can partially be attributed to thermal expansion; our results correspond to 0 K.) Our results indicate that bulk K\(_3\)Sb and Cs\(_3\)Sb are very soft compared to conventional semiconductors (\(B \approx 400-1000\) kbar),\(^24\) whereas Li\(_3\)Sb is more than twice as hard. The calculated cohesive energies \(E_c\) are about 1–2 eV larger than the experimental values,\(^25\) a common situation for local-density calculations which neglect dynamical correlation (e.g., multiplet effects).\(^3\) The larger cohesive energy of Cs\(_3\)Sb relative to K\(_3\)Sb is probably due to the additional bonding through the low-lying delocalized Cs 5p orbitals, which could increase the binding energy of Cs\(_3\)Sb by about 0.9 eV.\(^11\) The larger \(p-d\) repulsion in Cs\(_3\)Sb (see below) also contributes to the increased cohesion of Cs\(_3\)Sb.

The dependence of the calculated ground-state properties on the exchange-correlation energy has been examined. Wigner’s\(^9\) interpolation formula (W), the Hedin-Lundqvist\(^20\) correlation (HL) and the Ceperley-Alder correlation (CA) formula as parametrized by Perdew and Zunger\(^21\) have been used to calculate ground-state properties for Li\(_3\)Sb. We find \(a_0 = 6.497, 6.403,\) and 6.407 Å using the W, HL, and CA correlation energies, respectively. The changes in the bulk moduli are within 6% for all types of correlation energies. This general trend (i.e., a 1% larger lattice constant with the Wigner correlation relative to HL and CA) has been found previously for III-V compound semiconductors and other materials.\(^27\)

### B. Band structure and density of states

Calculated band structures of Li\(_3\)Sb, K\(_3\)Sb, and Cs\(_3\)Sb (using the Wigner exchange correlation) at their observed lattice parameters are depicted in Figs. 2(a)–2(c) along some high-symmetry lines. The total density of states and angular momentum and site projected local density of states are given in Figs. 3(a)–3(c). Eigenvalues and \(l\)-decomposed local charge characters at high symmetry points are listed in Table II.

All three compounds are semiconductors with band structures that show an overall similarity to those of III-V or II-VI systems. The lowest \((L_{1e}+\Gamma_{1p}-X_{1p})\) valence band, in all cases, is an Sb 5s band, separated by a heteropolar gap from the upper valence band (an Sb 5p band for Li\(_3\)Sb, an Sb 5p—metal d band for K\(_3\)Sb and Cs\(_3\)Sb). The conduction bands are a mixture of Sb 4d and metal s,p orbitals (see Table II).

For Li\(_3\)Sb we find the lower valence band (VB) to be located at \(E_v - 9.3\) eV (where \(E_v\) is the \(\Gamma_{1s}\) valence-band maximum) with a bandwidth of 0.9 eV. The upper valence bands have a width of 3.7 eV. The spin-orbit splitting at the valence-band maximum (VBM) is 0.62 eV. The conduction bands (CB) are a mixture of the Li 2s, 2p and the Sb 4d states. The indirect \((I)\) band gap is \(E_v^I = 0.74\) eV, whereas the direct \((D)\) band gap at \(\Gamma\) is \(E_g^D = 2.20\) eV. The experimental situation concerning the band gap of Li\(_3\)Sb is not clear. The estimated band gap is about 2.9 eV, which we think might be the direct transition. (The small calculated band gap is a general feature of the local density formalism.\(^23\)) The calculated LMTO gap \(E_v^L\) of Ref. 11 is 0.74 eV (0.14 eV was cited erroneously).\(^29\) There is an overall topological resemblance of the band structure calculated by Christensen\(^11\) and the present results.

For K\(_3\)Sb, the width of the valence states is consider-
ably smaller. The lower valence band is located at $E_v - 7.31$ eV, with a band width of only 0.2 eV. The upper valence band is similarly narrow (1.26 eV wide). The highest valence band ($L_{3g} - \Gamma_{150} - X_{5v}$) is almost dispersionless. The calculated spin-orbit splitting $\Delta_0$ is 0.43 eV at the valence-band maximum (VBM). Our results, therefore, do not agree with an estimation of $\Delta_0$ as about 0.7 eV of Ref. 30. We find this material to be a direct- ($\Gamma_{1c} - \Gamma_{150}$) band-gap semiconductor. The calculated direct band gap $E_g^D = 0.56$ eV is smaller than the experimental value of $1.4$ eV. Compared with the conduction bands of Li$_3$Sb, those of K$_3$Sb are more complicated due

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**FIG. 2.** Band structures of cubic (a) Li$_3$Sb, (b) K$_3$Sb, and (c) Cs$_3$Sb calculated with the Wigner (Ref. 19) exchange-correlation at the experimental lattice constants. The origin of the coordinate system is at the Sb site. The band-gap regions are shaded. Dashed lines indicate doubly degenerate states. The Cs $5p$ (semicore) bands are not shown in this plot.

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**FIG. 3.** Total density of states (DOS), and angular-momentum and site projected local DOS of (a) Li$_3$Sb, (b) K$_3$Sb, and (c) Cs$_3$Sb. For the local DOS, the dashed lines are the $s$ component, the dotted lines are the $p$ component, and the solid lines are the $d$ component. The zero of energy is at the VBM.
TABLE II. Calculated [using Wigner's exchange correlation (Ref. 19)] one-electron eigenvalues (in eV) and \( l \)-decomposed local charge character (in percentages) inside atomic muffin-tin (MT) spheres of cubic Li\(_3\)Sb \((a=6.572 \text{ Å}, R_{\text{MT}}=1.370 \text{ Å})\), K\(_3\)Sb \((a=8.493 \text{ Å}, R_{\text{MT}}=1.767 \text{ Å})\), and Cs\(_3\)Sb \((a=9.128 \text{ Å}, R_{\text{MT}}=1.900 \text{ Å})\) at high-symmetry points. For each state the \( l \) characters are given for Sb (first row), M\& (second row), and M\&\& (third row). The energy zero is at the \( \Gamma_{15} \) valence-band maximum.

<table>
<thead>
<tr>
<th>State</th>
<th>Li(_3)Sb</th>
<th>K(_3)Sb</th>
<th>Cs(_3)Sb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{1v} )</td>
<td>( -9.31 )</td>
<td>( 63 )</td>
<td>( 85 )</td>
</tr>
<tr>
<td>( \Gamma_{15e} )</td>
<td>( 0 )</td>
<td>( 0 )</td>
<td>( 57 )</td>
</tr>
<tr>
<td>( \Gamma_{1c} )</td>
<td>( 22 )</td>
<td>( 0 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( \Gamma_{12c} )</td>
<td>( 7.28 )</td>
<td>( 0 )</td>
<td>( 19 )</td>
</tr>
<tr>
<td>( \Gamma_{25c} )</td>
<td>( 2.98 )</td>
<td>( 0 )</td>
<td>( 11 )</td>
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<td>( \Gamma_{15e} )</td>
<td>( 4.92 )</td>
<td>( 0 )</td>
<td>( 4 )</td>
</tr>
<tr>
<td>( X_{1v} )</td>
<td>( -8.42 )</td>
<td>( 74 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( X_{xy} )</td>
<td>( -3.27 )</td>
<td>( 32 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( X_{yz} )</td>
<td>( -2.12 )</td>
<td>( 37 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( X_{1c} )</td>
<td>( 0.74 )</td>
<td>( 6 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( X_{3e} )</td>
<td>( 3.07 )</td>
<td>( 0 )</td>
<td>( 11 )</td>
</tr>
<tr>
<td>( L_{1v} )</td>
<td>( -8.67 )</td>
<td>( 70 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( L_{2v} )</td>
<td>( -3.74 )</td>
<td>( 0 )</td>
<td>( 29 )</td>
</tr>
<tr>
<td>( L_{3v} )</td>
<td>( -0.63 )</td>
<td>( 0 )</td>
<td>( 51 )</td>
</tr>
<tr>
<td>( L_{1c} )</td>
<td>( 2.29 )</td>
<td>( 15 )</td>
<td>( 0 )</td>
</tr>
<tr>
<td>( L_{3e} )</td>
<td>( 2.22 )</td>
<td>( 0 )</td>
<td>( 8 )</td>
</tr>
<tr>
<td>( 0 )</td>
<td>( 13 )</td>
<td>( 2 )</td>
<td>( 0 )</td>
</tr>
</tbody>
</table>
to the presence of the unoccupied K 3d orbitals. These d orbitals have an important role in determining the structure of the upper valence band, the band gap, and the spin-orbit splitting at the VBM. This will be discussed in more detail in the following section. We also find a noticeable separation between the lowest CB (L_1c^-\Gamma_1c^-X_1c^-) and the upper CB at about 1.5 eV above the conduction-band minimum.

For CsSb, the band structure is very similar to that of K$_2$Sb, except that the valence band is even narrower. The Cs 5p core states are found at 3.1 and 2.0 eV below the bottom (\Gamma_1p) of the valence band for Cs$_3$ and Cs$_2$I ions, respectively (i.e., at \epsilon_p = 10.0 eV and \epsilon_p = 8.9 eV, respectively). The different 5p levels are due to the different local environments of the two types of Cs ions in the crystal. The lowest valence band is located at \epsilon_p = -6.94 eV and its bandwidth is only 0.13 eV. The upper valence bands have a width of 0.86 eV. Our calculated \Delta_0 for Cs$_3$Sb is 0.42 eV. This material has a calculated indirect band gap of \Eg = 0.62 eV. The VBM is located at \X_5p and the CBM is at \Gamma_1c. The direct band gaps at \Gamma and \X are 1.02 and 1.03 eV, respectively. Experimentally, a band gap of 1.6 eV was measured for a partially disordered phase of Cs$_3$Sb (with O$_2$ symmetry) at 300 K. The LMTO results\cite{1,2} for the indirect band gap is 0.52 eV (1.04 eV was reported erroneously\cite{2} in Ref. 11).

C. The physics of chemical trends in M$_3$Sb band structures

1. Volume dilation effects

To understand the physical factors deciding the chemical trends in the band structures of M$_3$Sb (Fig. 2) we have calculated the band structure of a hypothetical (Sb$^3^-$)$^3^+$ crystal in the face-centered-cubic structure, at the observed lattice parameters of the actual M$_3$Sb compounds (Fig. 4). To preserve electrical neutrality, we have added a uniform background of three positive charges. Table III compares the results to those obtained for actual M$_3$Sb compounds. As the lattice parameter increases in the M = Li \rightarrow M = K \rightarrow M = Cs sequence, the band structure of (Sb$^3^-$)$^3^+$ shows the following. (i) A reduced width of the lower, (L_1c^-\Gamma_1c^-\X_1c^-) Sb 4s band as well as of the upper valence band. This effect is simply due to a reduced Sb-Sb overlap with increasing lattice constant. (ii) Since the volume deformation potentials \(-d\Eg(\Gamma_1c^-\rightarrow\Gamma_1c^-)/d\lnV\) and \(-d\Eg(\Gamma_1c^-\rightarrow\X_1c^-)/d\lnV\) of tetrahedral semiconductors are positive,\cite{12} but that of \(-d\Eg(\Gamma_1c^-\rightarrow\X_1c^-)/d\lnV\) is negative,\cite{12} a volume increase along the Li$_3$Sb \rightarrow K$_3$Sb \rightarrow Cs$_3$Sb sequence reduces the \Gamma_1c^- \rightarrow \Gamma_1c^- and \Gamma_1c^- \rightarrow \X_1c^- band gaps, but raises the \Gamma_1c^- \rightarrow \X_1c^- band gap. Hence, the “directness” of the band gap increases in the Li \rightarrow K \rightarrow Cs sequence simply due to volume dilation effects. Table III and the comparison of Fig. 4 to Fig. 2 indicate that the electronic structure of M$_3$Sb compounds, to zero order, is that of an (Sb$^3^-$)$^3^+$ structure with Sb-Sb separations determined by the type of cation.

2. p-d repulsion effects

We next consider effects omitted by the (Sb$^3^-$)$^3^+$ model. In a real M$_3$Sb compound, included there are unoccupied metal atom p and d orbitals (above the Sb p orbital) accessible to bonding in the compound. Since in D$_0$$_6$ symmetry the metal p and M$_2$d orbitals have an identical representation (\Gamma_{13}) to that of the Sb p orbitals, the two can interact. In this interaction, the (lower) bonding combination (i.e., the VBM) is pushed to lower energy; hence, the VBM is depressed relative to its value in the hypothetical (Sb$^3^-$)$^3^+$ compound. This p-d repulsion has the following consequences.

(i) The band gaps of Cs$_3$Sb and K$_3$Sb are finite, whereas that of (Sb$^3^-$)$^3^+$ at the respective lattice constants of

![FIG. 4. Band structure of cubic Sb$^3^-$(with three compensating positive charges) at the lattice constants of the respective M$_3$Sb compounds (a) \(a = 6.572\, \text{Å}\), (b) \(a = 8.493\, \text{Å}\), and (c) \(a = 9.128\, \text{Å}\). The band-gap regions are shaded. Dashed lines indicate doubly degenerate states. The origin of the coordinate systems is at the Sb site.](https://example.com/.band_structure.png)
TABLE III. Comparison of the bandwidths and band gaps of Li$_3$Sb, K$_3$Sb, Cs$_3$Sb with those obtained in a calculation for a fictitious Sb$^{3-}$ lattice with three compensating (uniform background) positive charges at their respective lattice constants. All energies are in eV. $W_{	ext{VBM}}$ and $W_{	ext{VB2}}$ are the widths of the lower and upper valence bands; $W_{\text{tot}}$ is the total valence-band width.

<table>
<thead>
<tr>
<th>Properties</th>
<th>$a=6.572$ Å</th>
<th>$a=8.493$ Å</th>
<th>$a=9.128$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li$_3$Sb</td>
<td>Sb$^{3-}$</td>
<td>K$_3$Sb</td>
</tr>
<tr>
<td>$W_{\text{VBM}}$ (X$<em>{\text{g}}$-$\Gamma</em>{\text{g}}$)</td>
<td>0.89</td>
<td>1.15</td>
<td>0.20</td>
</tr>
<tr>
<td>$W_{\text{VB2}}$ ((\Gamma_{\text{15s}})-L$_{\text{2p}}$)</td>
<td>3.74</td>
<td>4.03</td>
<td>1.26</td>
</tr>
<tr>
<td>$W_{\text{tot}}$ ((\Gamma_{\text{15s}})-(\Gamma_{\text{15s}}))</td>
<td>9.31</td>
<td>9.69</td>
<td>7.31</td>
</tr>
<tr>
<td>$E_{\text{g}}^\text{(d)}$ ((\Gamma_{\text{15s}})-(\Gamma_{\text{15s}}))</td>
<td>2.20</td>
<td>1.23</td>
<td>0.56</td>
</tr>
<tr>
<td>$E_{\text{g}}^\text{(s)}$ (X$<em>{\text{g}}$-$\Gamma</em>{\text{15s}}$)</td>
<td>0.74</td>
<td>0.63</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Cs$_3$Sb and K$_3$Sb nearly vanishes [Figs. 4(b) and 4(c)].

(ii) The (Sb $p$)-(Sb $s$) separation in K$_3$Sb and Cs$_3$Sb (\(\Gamma_{\text{15s}}\)-\(\Gamma_{\text{15s}}\)), or $W_{\text{tot}}$ in Table III) is smaller than the value in the free Sb ion (8.08 eV) or in the hypothetical (Sb$^{3-}$)$^{3+}$ system, due to this depression of \(\Gamma_{\text{15s}}\) by $p$-$d$ and $p$-$p$ repulsions.

(iii) The upper valence band (\(\Gamma_{\text{15s}}\)-L$_{\text{2p}}$ or $W_{\text{VB2}}$ in Table III) is narrower in the actual M$_3$Sb material since its low-lying empty $d$ and $p$ orbitals repel it.

(iv) The X$_{\text{g}}$ band in Cs$_3$Sb is higher than \(\Gamma_{\text{15s}}\) [the opposite situation prevails in (Sb$^{3-}$)$^{3+}$ at the Cs$_3$Sb lattice constant], leading to an "inverted valence band," since the low-lying Cs $d$ orbitals effectively depress the \(\Gamma_{\text{15s}}\) state.

(v) The spin-orbit splittings of the valence-band maximum (\(\Delta_0\) in Table I) are smaller for $M=K$ and $M=Cs$ than for $M=Li$ because of hybridization with metal $d$ orbitals in $M=K$, Cs ($d$ orbitals contribute to \(\Delta_0\) with opposite signs than $p$ orbitals).

We tested our model of $p$-$d$ repulsion by artificially removing the K 3d orbitals inside the muffin-tin spheres from the basis functions. We found that K$_3$Sb became metallic with an "inverted" band gap of $-1.07$ eV (i.e., \(\Gamma_{\text{15s}}\) was lower than \(\Gamma_{\text{15s}}\)), $W_{\text{tot}}$ increased to 8.94 eV, and the calculated spin-orbit splitting \(\Delta_0\) became 0.62 eV, close to the Sb atomic value of 0.63 eV. This confirms the expected perturbative effects of cation $p$ and $d$ orbitals on the band structure of (Sb$^{3-}$)$^{3+}$.

3. Cation $s$ orbital effects

Within a pseudopotential picture, the effective $s$ potential for valence electrons becomes shallower and more delocalized in the Li$_3$Na$\rightarrow$K$_3$Rb$\rightarrow$Cs series (see Fig. 5 in Ref. 33) due to pseudopotential cancellation effects. This is reflected in our all-electron results in an upwards shift in the $s$ orbital energies (Table IV) and in a decrease in electronegativity (1.0, 0.8, and 0.7 for Li, K, and Cs, respectively, on Pauling’s scale$^{34}$). This trend has the following consequences:

(i) Cs transfers its $s$ charge to Sb more effectively than do Li or K, resulting in an increased ionicity. Cs$_3$Sb tends to have a larger band gap based on the atomic orbital energies.

(ii) Relativistic effects, stronger for $s$ than for $p$ or $d$ orbitals and increasing rapidly with atomic number, change the band structures of M$_3$Sb in proportion to the position of the metal $s$ orbitals. For example, relativistic effects reduce the direct band gap (\(\Gamma_{\text{15s}}\)-\(\Gamma_{\text{15s}}\)), because the $\Gamma_{\text{15s}}$ state originates from the metal $s$ states, and has therefore a larger relativistic lowering than the \(\Gamma_{\text{15s}}\) states, which have $p$ character (even though the \(\Gamma_{\text{15s}}\) states are more localized). However, the reduction of band gap due to relativistic effects decreases with increasing lattice constant because the \(\Gamma_{\text{15s}}\) states become more delocalized.

The band gaps of the M$_3$Sb series are hence determined by a combination of (a) volume deformation effects [leading to $E_g$(Li$_3$Sb) $> E_g$(K$_3$Sb) $> E_g$(Cs$_3$Sb)], (b) $p$-$d$ repulsion effect (depressing the VBM of Cs$_3$Sb more than that of K$_3$Sb or of Li$_3$Sb, hence acting in the opposite direction to volume deformation effects), and (c) ionicity effects (increasing the band gaps in the order Cs $> K $ $> Li$). We find that effect (a) dominates Li$_3$Sb, which has the largest band gap in this series (despite its smaller ionicity relative to the other two), and that effects (b) and (c) (stronger in Cs than in K) are responsible for $E_g$(Cs$_3$Sb) $> E_g$(K$_3$Sb).

4. Electrostatic effects: The interstitial insertion rule

The conduction bands of M$_3$Sb differ in a number of ways from those of (Sb$^{3-}$)$^{3+}$.$^{35}$ Wood et al.,$^{36}$ Carlsson et al.,$^{36}$ and Wei and Zunger$^{37}$ have advanced the "interstitial insertion rule," which explains such modifications in terms of the nature and amplitude (small or large) of conduction-band states at sites where atoms are interstitially introduced. This rule, specialized here for alkali atoms, states that conduction bands with $s$ ($p,d$) character at interstitial site $\alpha$ are raised (lowered) when an alkali atom is introduced into site $\alpha$. A number of such changes are related to this rule.

(i) The L$_{\text{3c}}$ state of (Sb$^{3-}$)$^{3+}$ at the lattice constant of Li$_3$Sb (a non-$s$ state), is lowered by about 2 eV in Li$_3$Sb

TABLE IV. Calculated atomic orbital energies of Sb, Li, K, and Cs within the local-density formation. The energy zero is placed at Sb $5p$ states.

<table>
<thead>
<tr>
<th>Atom</th>
<th>States</th>
<th>$\varepsilon$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb</td>
<td>5$s$</td>
<td>-8.08</td>
</tr>
<tr>
<td></td>
<td>5$p$</td>
<td>0</td>
</tr>
<tr>
<td>Li</td>
<td>2$s$</td>
<td>2.12</td>
</tr>
<tr>
<td>K</td>
<td>4$s$</td>
<td>2.57</td>
</tr>
<tr>
<td>Cs</td>
<td>6$s$</td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>5$p$</td>
<td>-8.59</td>
</tr>
</tbody>
</table>
ELECTRONIC STRUCTURE OF $M\text{Sb}$-TYPE FILLED ...  

FIG. 5. Calculated valence charge-density contours (in units of $10^{-3}$ e/a.u.$^3$) for (a) Li$_3$Sb, (b) K$_3$Sb, and (c) Cs$_3$Sb (without Cs 5$p$ states) on the (110) plane. Successive contours are separated by $4\times10^{-3}$ e/a.u.$^3$. Plots are drawn with the correct proportion of the lattice parameters. Dashed regions in (a) show Li-Li bond.

(ii) The strongly dispersive $\Gamma_{25\varepsilon}$ (a non-$s$ state) $X_{3\varepsilon}$ (an $s$-like state) band in (Sb$^{3-}$)$^{3+}$ with lattice constant of Li$_3$Sb is lowered (for $\Gamma_{25\varepsilon}$) and raised (for $X_{3\varepsilon}$) in Li$_3$Sb, becoming dispersionless in real Li$_3$Sb [compare Figs. 4(a) and 2(a)].

(iii) In (Sb$^{3-}$)$^{3+}$ at the lattice constant of Cs$_3$Sb, the $X_{1\varepsilon}$ (s-like) and $X_{3\varepsilon}$ (non-$s$-like in K$_3$Sb and Cs$_3$Sb due to the proximity of the metal $d$ orbitals) are pushed upwards (for $X_{1\varepsilon}$) and downwards (for $X_{3\varepsilon}$) when Cs is introduced [compare Figs. 4(c) and 2(c)]. This explains the reversal of $X_{1\varepsilon}$ and $X_{3\varepsilon}$ states in Cs$_3$Sb relative to the corresponding (Sb$^{3-}$)$^{3+}$.

D. Charge densities and chemical bonding

Because it is somewhat arbitrary to define charges inside muffin-tin spheres (and from these ionicities) it is not sufficient to study the chemical bonding in this way alone. We have therefore plotted the charge densities of Li$_3$Sb [Fig. 5(a)], K$_3$Sb [Fig. 5(b)], and Cs$_3$Sb [Fig. 5(c)] in the (110) plane at their experiment lattice constants. For Li$_3$Sb we find that the chemical bonding between $M_{II}$ and the Sb atom is partially ionic and partially covalent with larger ionic character. (Because of the delocalized nature of the Sb 5$p$ states, this ionic character is often obscured by looking only at the total charge contained within atom-centered spheres.) We also find that there is considerable covalent bonding in the cation-cation bonds [dashed region in Fig. 5(a)] and anion-anion bonds due to the small lattice constant. This can be seen even more clearly in Fig. 6(a) (dashed region), which shows the charge density along the [111] direction. For K$_3$Sb and Cs$_3$Sb, with larger lattice constants and an increased repulsiveness of the $s$ potential, more charge is

FIG. 6. Charge-density (in units of $10^{-3}$ e/a.u.$^3$) plots along the $M_{II}$-Sb bond for (a) Li$_3$Sb, (b) K$_3$Sb, and (c) Cs$_3$Sb. Shaded (dashed) regions show $M$-Sb ($M-M$) bonds.
transferred to the Sb atom, hence the covalent bonding becomes weaker for both like atoms and unlike atoms (it almost disappears in Cs$_3$Sb). As more charge is transferred to the Sb atom, the Sb 5p states become even more extended. These trends can be seen clearly in Figs. 6(b) and 6(c). Our results, therefore, indicate that in M$_3$Sb, like atoms (M-M, Sb-Sb) tend to have covalent bonds and M-Sb interactions tend to be ionic. This is reasonable considering the large electronegativity differences between the alkali metals and Sb atom. The longer the bond length, the more the charge transfer. For Cs$_3$Sb, we find that Cs exists predominantly in the Cs$^{+1,-e\cdot}$ form (where e is a small positive number due to the attractive singularity of the Coulomb potential near the nuclei). Our results therefore support the conclusion drawn from the photoemission measurements of Bates et al.\(^{13}\) that Cs atoms in Cs$_3$Sb are predominantly in the Cs$^+$ form. The half covalent, half ionic model\(^{15}\) is not valid for Cs$_3$Sb, but is approximately true for Li$_3$Sb due to the smaller lattice constant. Our interpretation is also similar to that of Robertson\(^{16}\) except that his definition of ionicity is vitiated for smaller bond length because of the delocalized Sb 5p orbitals.

IV. CONCLUSION

We have calculated the ground state properties at $T=0$ K and the electronic band structures of the alkali-antimony compounds Li$_3$Sb, K$_3$Sb, and Cs$_3$Sb. The ground-state properties obtained by minimizing the total energy are in good agreement with experiment. For Cs$_3$Sb we find that correct treatment of the partially delocalized Cs 5p states is necessary to obtain the correct lattice constant. Electronic structure calculations for M$_3$Sb demonstrate that these systems can be considered to low order as an Sb$^{5-}$ lattice with its lattice constant determined by the alkali atom cores. Insertion of the alkali ions into the hypothetical Sb$^{5-}$ sublattice interstitial sites can be treated as a perturbation: the relative shift of the eigenvalues upon insertion can be understood in terms of (i) p-d repulsion, (ii) cation s orbital effects (including relativistic effects), and (iii) the “interstitial insertion rules.” We find the maxima of valence band for K$_3$Sb and Cs$_3$Sb are very flat and structureless, a property which may be responsible for the high photoelectric efficiency of this system (besides the surface induced effects), especially for Cs$_3$Sb. The interaction between the Sb 5p states and the unoccupied alkali d states is found to be responsible for the semiconducting properties and flatness of the upper valence band. Calculated charge-density maps indicate that like atoms in M$_3$Sb tend to have covalent bonding and unlike atoms tend to have ionic bonding. With increasing lattice constant the covalency decreases but the ionicity increases. We find Li$_3$Sb has both covalent bonding and ionic bonding but Cs$_3$Sb is almost purely ionic.

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Treatment (1) of Table IV of Ref. 17 was used here. The larger lattice constants obtained by Christensen (Ref. 11) (cf., Table I), especially for Cs$_3$Sb, are probably due to the use of the renormalized frozen-core approximation. Such an approximation has been known (see Ref. 17) to exaggerate the lattice parameter, particularly when one renormalizes and freezes the rather extended Cs 5p orbitals.

27N. E. Christensen (private communication).