Ab initio study of the crystal and electronic structure of mono- and bi-alkali antimonides: Stability, Goldschmidt-like tolerance factors, and optical properties

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Mono- and bi-alkali antimonides, X$_2$YSb (X and Y from Group I), are promising for next-generation electron emitters due to their capability of producing high-quality electron beams. However, these materials are not yet well understood, in part due to the technical challenges in growing pure, ordered alkali antimonides. For example, in the current literature there is a lack of complete understanding of the mechanically stable crystal structures of these materials. As a first step towards understanding this issue, this paper presents an ab initio study of stability of single-crystal mono- and bi-alkali antimonides in the $D_0_3$ structure, the structure generally assumed in the literature for these materials. Finding that many of these materials actually are unstable in the $D_0_3$ structure, we formulate a new set of Goldschmidt-like tolerance factors that accurately predict $D_0_3$ stability using a procedure analogous to machine-learning perceptron-based analysis. Next, we consider possible stable structures for materials that we predict to be unstable in the $D_0_3$ structure. Taking as examples the mono- and bi-alkali antimonides Cs$_8$Sb and Cs$_3$KSb, which also are technologically interesting for photoemission and photoabsorption applications, respectively, we note that the most unstable phonon displacements are consistent with the cubic structure, and we therefore perform extensive ab initio searches to identify potential ground-state structures in a cubic lattice. Our X-ray diffraction experiments confirm that indeed these two materials are not stable in the $D_0_3$ structure and show scattering that is consistent with our new, proposed stable structures. Finally, we explore ab initio the implications of the breaking of the $D_0_3$ symmetry on the electronic structure, showing significant impact on the location of the optical absorption edge.

I. INTRODUCTION

Alkali antimonides have been, and continue to be of great interest as potential high-quality electron emitters for various applications, including electron accelerators and ultrafast electron diffraction and microscopy.\cite{1,2,3,4,5} Despite their promise, these materials are not very well understood, in part because growth of single-crystal alkali antimonides remains very challenging: the resulting materials are often polycrystalline or disordered,\cite{2,5} thereby limiting the understanding of the equilibrium crystal structures and thus of the ultimate promise of these materials as electron emitters. Moreover, even once successfully grown, single-crystal versions of these materials are extremely sensitive to vacuum conditions and can survive only in ultra-high-vacuum in their thin film forms, making experimental studies of their structural and optoelectronic properties extremely challenging.\cite{5}

Previous work has generally assumed the $D_0_3$ structure (Fig. 1a) as the crystal structure for mono- and bi-alkali antimonides, X$_2$YSb (X and Y are Group I alkali metals).\cite{1,7,8,9,10,11,12,13,14,15,16,17} However, a very recent publication on the first ever successful epitaxial growth of Cs$_8$Sb finds that, although the thin-film structure is cubic and single crystal, it is not clear whether the structure is $D_0_3$ or some other cubic phase with lower symmetry.\cite{5} To complicate the matter, the Materials Project database\cite{18} reports imaginary phonon frequencies and thus mechanical instability for Cs$_8$Sb in the $D_0_3$ structure.

To clarify the crystal structures of all possible mono- and bi-alkali antimonides (X$_2$YSb), we report below the results of a detailed ab initio study of the mechanical stability of twenty-five X$_2$YSb materials in the $D_0_3$ structure. For X and Y, we explore Li, Na, K, Rb, and Cs, the five alkali metals most likely to be used as electron emitters.\cite{19,20} We exclude Fr because it is impractical, as its most stable isotope has a very short half-life of merely 21 minutes.\cite{21} Our predictions of the stability of these materials in the $D_0_3$ structure show a clear pattern corresponding to multiple machine-learning perceptron criteria\cite{22} that lead us to propose a set of physically motivated Goldschmidt-like tolerance factors\cite{23} for the stability of the X$_2$YSb materials.

Next, to better understand potentially stable crystal structures, we choose to further study two of our predicted $D_0_3$-unstable materials, Cs$_8$Sb and Cs$_3$KSb, which are technologically interesting for photoemission\cite{24} and photoabsorption\cite{10,11} applications, respectively. For these materials, we present the results of an extensive search for stable cubic structures, finding full consistency with our X-ray diffraction measurements. Finally, we present ab initio results on the impact of the resulting breaking of $D_0_3$ symmetry in these materials on their electronic structure and optical absorption properties.

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II. PROCEDURE

Here, we describe our overall ab initio procedures, leaving additional details in the Supplemental Material. The ab initio study of mechanical stability performed in this work requires electronic structure calculations and phonon dispersion calculations of the X2YSb materials. All electronic structure calculations employ the plane-wave density-functional theory framework as implemented in the JDFTx software package. All phonon calculations employ a modified version of the frozen phonon method, which allows calculations of phonons at arbitrary wave vectors using a real-space method, as implemented within JDFTx.

To determine the mechanical stability of X2YSb materials in the D03 structure, we employ the following procedure. First, we relax the atoms and the lattice from the D03 structure as a starting point, using face-centered cubic (fcc) primitive cell. We find 5 materials to be unstable with respect to these relaxations. Next, to identify instability at wavelengths incommensurate with our primitive cell, for the remaining materials we calculate the phonon dispersion relations to identify any imaginary frequencies, finding an additional 10 unstable materials. After tabulating the results, we find that stability of the X2YSb materials follows criteria describable through machine-learning perceptron-based analysis. Due to the small data set of 25 materials, we do not require the perceptron algorithm itself and determine the criteria manually.

Next, to identify stable structures for the materials that are unstable in the D03 structure, we focus on Cs2Sb and Cs2KSb, searching for stable cubic structures through multiple sets of perturbation-relaxations as follows. For each set, we begin with the atoms in the D03 structure in the conventional cubic unit cell, then we uniformly displace the atomic locations by 0.05 Å, and subsequently relax the atoms until all forces are \( \leq 0.01 \text{ eV/Å} \). We repeat this procedure until we identify a mechanically stable structure as confirmed by calculation of the resulting phonon dispersion relations.

For comparison with our X-ray measurements, we then calculate the powder X-ray diffraction patterns of the above resulting stable structures using VESTA. The details of the experimental setup and the growth and X-ray measurement conditions of our samples are given elsewhere.

Finally, to study optical absorption properties, we compute linear optical absorption coefficients by first calculating the contributions of direct photoexcitation processes to the imaginary part of the dielectric constant, \( \varepsilon_2 \), by employing the Wannier interpolation method and Monte Carlo integration as described in Ref. 35. We then use the resulting \( \varepsilon_2 \) as a function of photon frequency \( \omega \) to calculate the linear absorption coefficient \( \alpha(\omega) \) as described in Ref. 36.

III. RESULTS AND DISCUSSION

A. Stability of the D03 structure

Relaxing within a primitive face-centered cubic (fcc) cell immediately reveals the following five materials (out of the twenty-five under consideration) to be unstable in the D03 structure: K2LiSb, Rb2LiSb, Rb2NaSb, Cs2LiSb, and Cs2NaSb. The phonon dispersion relations of the remaining materials (plots in Supplemental Material) reveal ten of those materials to have imaginary phonon frequencies and thus also be mechanically unstable. We further note that all of these materials with imaginary phonon frequencies show instability at the X-point in the fcc Brillouin zone. This then leaves ten materials in our study which are mechanically stable in the D03 structure.

Regarding the unstable phonon displacements, we find that the imaginary branches at the X-point in the fcc Brillouin zone always exhibit a double degeneracy. The complex phonon polarization vectors of these two modes correspond to either the polarization vector shown in Fig. 1b or to a second vector generated via a 90-degree rotation with respect to the axis along the phonon wave-vector direction. The real (gray arrows, Fig. 1b) and imaginary (red arrows, Fig. 1b) parts of these complex

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FIG. 1. (Color online) (a) D03 structure of mono- and bi-alkali antimonides (X2YSb), (b) complex phonon polarization vector of an imaginary branch at the X-point in the face-centered-cubic Brillouin zone (corresponding to phonon wavevector directed upwards) found in all materials under study that exhibit imaginary phonon frequencies, (c) atomic displacements from the D03 structure to the stable structure of Cs2Sb (X = Y = Cs), and (d) atomic displacements from the D03 structure to the stable structure of Cs2KSb (X = Cs, Y = K); Group I elements (X, green spheres, and Y, purple spheres), antimony (Sb, brown spheres), real part of phonon polarization vector (gray arrows), imaginary part of phonon polarization vector (red arrows), atomic displacements (blue arrows).
polarization vectors correspond to two distinct unstable phonon displacements of the atoms in real space. To understand the significance of these displacements, we note that, as shown in Fig. 1a, the $D_{03}$ crystal structure for $X_2YSb$ consists of a simple cubic lattice of $X$ atoms, with all cube body centers occupied by alternating $Y$ and $Sb$ atoms. The unstable displacements at the $X$-point in the fcc Brillouin zone thus consist of either shearing of the $X$ atoms relative to the $Y$ and $Sb$ atoms, or shearing of the $Y$ and $Sb$ atoms relative to the $X$ atoms. These displacements suggest that the relative size of the $X$ atoms to the $Y$ and $Sb$ atoms plays an important role in determining the stability of the material in the $D_{03}$ structure, with the simple-cubic “cage” formed by the $X$ atoms being destabilized by the $Y$ and $Sb$ atoms at the cage centers if the $Y$ or $Sb$ atoms are either too large or too small compared to the natural size of the cage. With this in mind, we summarize our stability results in Table I, arranging the $X$ and $Y$ atoms in order of their corresponding atomic radii. Confirming our simple hypothesis, indeed the table demonstrates that combinations with either very small or very large $Y$ atoms and with either very small or very large $X$ atoms can be unstable. The next section below provides a more quantitative analysis of these observations.

TABLE I. Mechanical stability of $X_2YSb$ in the $D_{03}$ structure: stable ($\circ$), unstable (x).

| $Y_1$ | Li$_2$ | Na$_2$ | $X_2$ | K$_2$ | Rb$_2$ | Cs$_2$ |
|-------|--------|--------|-------|-------|--------|--------|
| Cs$_1$ | x | o | o | x | x |
| Rb$_1$ | x | o | o | x | x |
| K$_1$ | o | o | o | x | x |
| Na$_1$ | o | o | x | x | x |
| Li$_1$ | o | x | x | x | x |

B. Tolerance factors

To begin the quantitative analysis, Fig. 2 displays the results of Table I in the phase space of the atomic radii$^{37}$ of $X$ ($r_X$) and $Y$ ($r_Y$). As discussed above, we expect there to be upper and lower bounds of stability in terms of the relative size of the $X$ atom to the $Y$ and $Sb$ atoms, corresponding to the ratios $r_Y/r_X$ and $r_{Sb}/r_X$, respectively. Therefore, in Fig. 2 we consider four perceptron lines, two corresponding to upper and lower bounds for the ratio $r_Y/r_X$ (1.00 < $r_Y/r_X$ < 1.55) and two corresponding to upper and lower bounds for the ratio $r_{Sb}/r_X$ (0.66 < $r_{Sb}/r_X$ < 1.01). We see that these four lines indeed separate the stable region from the unstable regions of the phase space, confirming that the relative size of the $X$ atom to the $Y$ and $Sb$ atoms plays a key role in determining the stability of $X_2YSb$ in the $D_{03}$ structure.

Next, to simplify our results yet further and make them more analogous to the Goldschmidt tolerance factor for perovskites,$^{23}$ we consider the possibility of constructing one-dimensional tolerance factors. As discussed above, both ratios, $r_Y/r_X$ and $r_{Sb}/r_X$, of the stable materials are bounded. We therefore propose the following two simple tolerance factors for determination of stability: the arithmetic mean of the ratios, $t_1 \equiv (r_Y + r_{Sb})/(2r_X)$, and the geometric mean of the ratios, $t_2 \equiv \sqrt{r_Y r_{Sb}/r_X}$. Fig. 3 shows that indeed, both of these Goldschmidt-like tolerance factors work well for all twenty-five materials in our study with the bounds 0.83 < $t_1$ < 1.28 and 0.81 < $t_2$ < 1.25, respectively.

Finally, we note that, from the above considerations, we expect the above size-based ratios to be useful as well for the more general class of $X_2YM$ materials, where $M$ can be any Group V metal or semimetal. Moreover, it is at least plausible that approximately the same numerical bounds for stability will hold when $r_{Sb}$ is replaced with $r_M$.

C. Stable crystal structures

With the stability of the $X_2YSb$ materials in the $D_{03}$ structure understood, we next turn to the search for stable structures of the materials we find unstable. In this work, we consider one mono-alkali antimonide and one bi-alkali antimonide, specifically choosing Cs$_3Sb$ and Cs$_3KsB$, which are technologically interesting for photoemission$^{24}$ and photoabsorption,$^{10,11}$ respectively. To search for stable structures of these materials, we begin by noting that the most unstable phonon modes occur at the $X$-point of the face-centered-cubic Brillouin
Next, we compare the expected peak locations for the powder X-ray diffraction (XRD) pattern from our predicted stable structure with our experimental XRD measurements. (Setup and details described elsewhere.$^{32,33}$) We note that our experimental samples posses texture due to the specific growth method and conditions, which favor certain crystal growth orientations over others. Thus, the relative sizes of the resulting scattering orientations cannot be compared directly to our theoretical calculations, and, moreover, some peaks expected from the powder XRD may be missing from our experiments. Therefore, the most meaningful comparison to our theoretical results is to compare only the peak locations which we actually observe in the experiments. Accordingly, we interpret any measured peaks beyond the calculated $D0_3$ peaks to be experimental evidence of breaking of the $D0_3$ symmetry, but we do not necessarily expect to detect all peaks calculated from our predicted structures. Finally, to eliminate uncertainty due to subtle differences between density-functional theory and experimental lattice constants, we normalize both our theoretical and experimental peak locations so that the $hkl = 111$ Bragg peak appears exactly at a plane separation of $1/\sqrt{3}$ times the cubic lattice constant $a$.

The first two columns of Table II show our measured XRD peaks for Cs$_3$Sb along with the cubic Miller indices $hkl$ corresponding to those peaks. The last two columns show our theoretical powder XRD peaks for Cs$_3$Sb in the $D0_3$ structure and the predicted stable structure, respectively. As expected, the experimental data does not exhibit clearly all of the theoretical peaks. The experiment does show an excellent match to the 222 peak expected for both the $D0_3$ and our predicted structure, confirming that the structure in our sample forms a cubic lattice. Furthermore, we note that the 210 peak does not appear in the $D0_3$ structure but does appear in our measurements, which clearly indicates symmetry breaking and is consistent with our theoretical findings that this material is not stable in the $D0_3$ structure. Finally, the predicted stable structure does show the 210 peak, consistent with our experiments.

Having considered the mono-alkali antimonide Cs$_3$Sb, we now consider the bi-alkali antimonide Cs$_2$KSb. Following the same procedure as for Cs$_3$Sb, we again find a single stable structure with no imaginary phonon frequencies. The resulting structure for Cs$_2$KSb (Fig. 1d shows nearly the same displacement pattern from the $D0_3$ structure as we found for Cs$_3$Sb, with the Y-site atoms (K) assuming the largest displacements (each along one of four tetrahedral (111) directions, the pattern which can be anticipated from a displacement pattern [Fig. 1b, red arrows] from the most unstable phonon mode in the $D0_3$ structure), and both the Sb atoms and the X-site atoms (Cs) showing significantly smaller displacements. Moreover, as can be expected from the above, our theoretical and experimental X-ray diffraction results for this material are indeed very similar to those of Cs$_3$Sb (Table II), so that our predicted stable

\begin{align*}
\delta_1 &= \frac{(r_Y + r_{Sb})}{2r_X} \\
\delta_2 &= \frac{\sqrt{r_{Sb}}}{r_X}
\end{align*}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3}
\caption{Proposed Goldschmidt-like tolerance factors for the $X_2YSb$ materials in the $D0_3$ structure: materials stable (circles) and unstable (×) in the $D0_3$ structure, bounds of the stable-phase region (dashed lines).}
\end{figure}
structure is fully consistent with the structure observed in our experiments, which breaks the $D0_3$ symmetry and exhibits the 210 peak consistent with a cubic lattice.

Finally, as a control case, we have also performed XRD measurements on $K_2CsSb$, a promising electron emitter which we predict to be stable in the $D0_3$ structure. We find that, indeed, the experimental peaks exhibited by this material are different from those found for $Cs_3Sb$ and $Cs_2KSB$ (Table II) and that they are now fully consistent with expectations for the $D0_3$ structure. We thus find full consistency between our experimental measurements and our predictions for both $D0_3$-stable and $D0_3$-unstable materials.

### D. Electronic structure and optical absorption properties

Having confirmed experimentally that $Cs_3Sb$ and $Cs_2KSB$ indeed break $D0_3$ symmetry, we turn finally to consider the impact of the symmetry breaking on the optical properties of these materials, both of which are of interest for photo-applications.

#### TABLE II. Bragg-plane distances $d$ for X-ray scattering peak positions, normalized by lattice constant $a$, for cubic $Cs_3Sb$, $Cs_2KSB$, and $K_2CsSb$: cubic Miller indices $hkl$ (first column), measured $d/a$ for $Cs_3Sb$ (second column), $Cs_2KSB$ (third column), and $K_2CsSb$ (fourth column), calculated $d/a$ for the $D0_3$ structure of $Cs_3Sb$, $Cs_2KSB$, and $K_2CsSb$ (fifth column), and for the stable structures of $Cs_3Sb$ and $Cs_2KSB$ (sixth column).

| $hkl$ | $Cs_3Sb$ | $Cs_2KSB$ | $K_2CsSb$ | $D0_3$ Stable structure |
|-------|----------|-----------|-----------|-------------------------|
| 222   | 0.285    | 0.288     | 0.289     | 0.288675                |
| 311   |          |           | 0.301511  | 0.301511                |
| 310   |          |           | 0.301511  | 0.316228                |
| 221   |          |           |           | 0.333333                |
| 220   |          | 0.353     |           | 0.353553                |
| 211   |          |           |           | 0.408248                |
| 210   | 0.436    | 0.453     |           | 0.447214                |
| 200   |          |           |           | 0.500000                |
| 111   | $1/\sqrt{3}$ | $1/\sqrt{3}$ | $1/\sqrt{3}$ | $1/\sqrt{3}$ |

FIG. 4. Calculated linear absorption coefficient of (a) $Cs_3Sb$ and (b) $Cs_2KSB$ in the $D0_3$ structure (dashed curves) and the stable structures predicted in this work (solid curves).

IV. CONCLUSIONS

This work presents a detailed ab initio study of the stability of 25 mono- and bi-alkali antimonides $X_2YM$ (X and Y from Group I; M = Sb, a Group V semimetal) in the $D0_3$ structure, the structure commonly assumed in the literature for these materials. We find that a significant number of the antimonide materials under study are actually unstable in the $D0_3$ structure and that the instability evident in the imaginary phonon branches can be explained in terms of size mismatches among the atomic radii of the involved species. Accordingly, we provide three independent sets of atomic-size criteria that can be used to determine the stability of these compounds: a set of four machine-learning perceptron criteria (1.00 < $r_Y/r_X$ < 1.55 and 0.66 < $r_M/r_X$ < 1.01), and two different versions of Goldschmidt-like tolerance factors (0.83 < $(r_Y + r_M)/(2r_X) < 1.28$ or 0.81 < $(r_Y + r_M)/(r_X < 1.25)$).

Finally, for $Cs_3Sb$ and $Cs_2KSB$, which prove unstable in the $D0_3$ structure, we identify stable cubic structures, which we find to break $D0_3$ symmetry along directions indicated by the unstable phonon displacements at the $X$-point in the face-centered-cubic Brillouin zone. These stable structures are consistent with our experimental X-
ray scattering data, which indeed indicate broken $D_0^3$ symmetry and suggest cubic structure. Finally, in terms of electronic properties, we note that the nature of the band gap changes from indirect to direct upon breaking of the $D_0^3$ symmetry, lowering the optical gaps as reflected in the calculated linear absorption coefficients.

The above results will be useful in optimizing the growth and ascertaining the promise of alkali antimonides for next-generation electron emitters, for example by clarifying the nature of the primitive unit cell and by allowing more accurate predictions of photoabsorption and photoemission properties. Future work will include exploration beyond the antimonides ($M = \text{Sb}$) to include other Group V semimetals and metals (As, Bi).

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