Structural, bonding, and electronic properties of IIA-IV antifluorite compounds

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We have studied the electronic and structural properties of the antifluorite compounds Mg_2X ($X=$ Si, Ge, Sn), Be_2C, and hypothetical compounds Mg_2C and Be_2Si using the first-principles pseudopotential total energy method. Five of the compounds are small-gap semiconductors, while Be_2Si is a metal. Calculated lattice constants agree well with experiment for the four known compounds, but are consistently a few percent smaller than the reported values. The bulk moduli of this group of materials follow a semiempirical formula for B_0 to within $\sim 5\%$. Bulk moduli calculated from first principles, corrected for the underestimation of the lattice constant, agree well with the available experimental values.

I. INTRODUCTION

The $A_2^{IIA}B^{IV}$ antifluorite semiconductors, which are isovalent to the group-IV elemental semiconductors, exist in a structure which is similar to the diamond structure. The B^{IV} atoms occupy fcc sites and the two A^{IIA} atoms are at $\pm \tau$, where $\tau = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a$. The resulting structure has space group O_h^5 ($Fm3m$), which is slightly different than the space group of the diamond structure, O_h^7 ($Fd3m$), but is closely related. Because of the presence of nonidentical atoms, the antifluorite IIA-IV's can be expected to display effects arising from increases in ionicity and changes in unit cell volume relative to the reference group-IV system. However, many properties are similar to their group-IV counterparts and therefore these compounds have potential technological applicability as well as scientific importance.

Although there have been numerous studies of the electronic structure of these materials,[1-7] to our knowledge there are no published reports of *ab initio* theoretical studies of their structural properties using first-principles techniques. In addition, few *ab initio* studies of the electronic properties of these materials exist to date. Differences in the band structures and valence charge densities of Si in the diamond structure and a generic antifluorite silicide were discussed in Ref. 1 and results of an *ab initio* calculation for Mg_2Si in particular were presented. Here we examine the electronic and structural properties of six antifluorite structure IIA-IV materials. Two of these compounds Be_2Si and Mg_2C are hypothetical materials not known at present to exist.

The electronic structure calculations yield bands which are similar to the early empirical pseudopotential results. Valence electron charge density studies yield information about bonding properties. In particular, the two carbides are fairly ionic compared to Mg_2Si. The three compounds Mg_2X ($X =$ Si, Ge, and Sn) have similar charge densities and Be_2Si is a covalently bonded metal. The distributions of charge in these systms can be understood in terms of differences in Pauling electronegativities[8] for the constituent atoms.

We also find that, although the IIA-IV antifluorites, especially Be_2C and Mg_2C, are quite ionic compared to group-IV and even group III-V semiconductors, their bulk moduli follow a semiempirical formula[9,10] based on these covalently bonded and partially covalent materials quite well. We have not studied other structures for the two hypothetical materials and are therefore unable to quantitatively estimate the stability of the antifluorite structure for these cases. However, the calculated structural and electronic properties for the these materials appear physically reasonable and interesting.

II. CALCULATIONAL METHOD

We use the standard *ab initio* pseudopotential method[11] to calculate the single-particle energy levels within the local density approximation (LDA).[12] The exchange and correlation potential derived[13] from the Monte Carlo calculations of Ceperley and Alder[14] is used. Hamann-Schlüter-Chiang[15] potentials are used for Mg, Si, Ge, and Sn. Troullier-Martins[16] soft pseudopotentials are used for the strong Be and C cores in order to achieve good convergence for the structural and electronic properties with a reasonably sized basis set.

The self-consistent calculation uses a plane wave basis set with a cutoff in the kinetic energy $(\mathbf{k} + \mathbf{G})^2$ of 40 Ry. A larger basis set containing plane waves up to a cutoff energy of 75 Ry was used to repeat the calculations for Be_2C and Mg_2C as a test for the convergence of the calculations at the lower cutoff. Structural properties for the higher cutoff differed by less than 1% for the lattice constants and by at most 2.5% for B_0 (for Mg_2C). These errors should be an upper limit on the error for the less ionic materials. Since Be_2Si has a nonzero density of states at the Fermi level, 60 $\mathbf{k}$ points in the irreducible zone were used to obtain a good sampling of the Brillouin zone. For the five semiconducting compounds, only 10 $\mathbf{k}$ points were needed.

In order to calculate the equilibrium lattice constant and bulk modulus of each material, the total energy was calculated for at least five volumes from about $0.8V_0$ to $1.2V_0$ where V_0 is the equilibrium volume. Equilibrium volumes (lattice constants) and bulk moduli B_0 were found by fitting the energy versus volume curves to the Birch equation of state.[17]

III. RESULTS AND DISCUSSION

A. Valence charge densities

Valence charge densities for Be_2C, Be_2Si, and Mg_2X ($X = C$, Si, Ge, and Sn) are given in Figs. 1 and 2. While the distribution in charge shows some covalent character for Be_2Si, Mg_2Si, Mg_2Ge, and Mg_2Sn, the two carbides are extremely ionic. Even though the group-IV site is eight-fold coordinated compared to only fourfold coordination for the group-IIA site, the group-IV atom is found to attract most of the valence charge. This is especially true in the carbides, due to the strength of the poten-
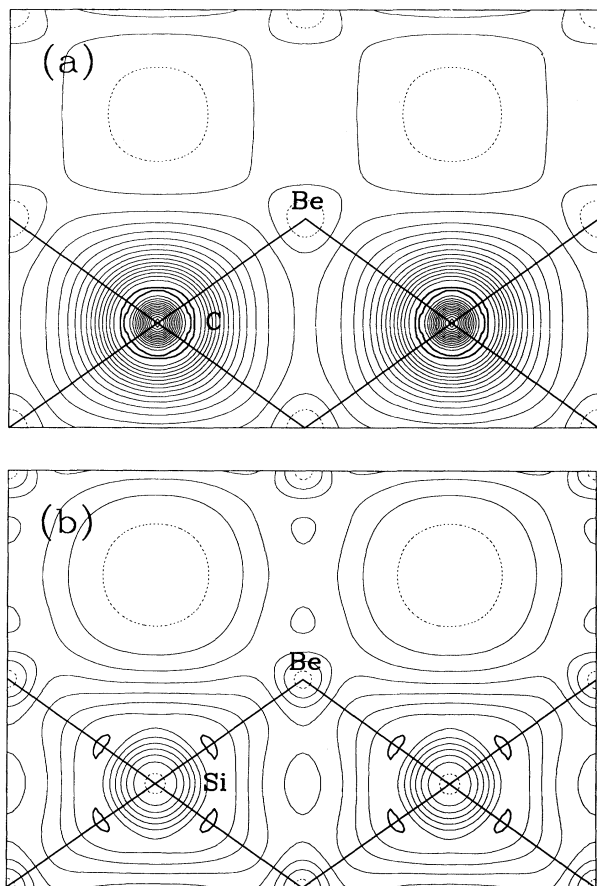

FIG. 1. The valence charge densities for (a) Be_2C and (b) hypothetical Be_2Si at their equilibrium volumes are shown. Contours are drawn for (a) 2,4,...,34 and (b) 2,4,...,16 electrons per unit cell. The lowest contour is drawn as a dotted line and the highest contour is drawn as a bold line.

tial of this first-row element. Bonding maxima similar to group-IV elemental semiconductors are present for Mg_2X ($X = Si$, Ge, and Sn) and Be_2Si, but are missing in both of the carbides.

The maximum in $\rho(r)$ is highest in Mg_2C (54.4 electrons/Ω_c) due to the strong carbon core compared to the much weaker magnesium potential. For Be_2C, the maximum in the charge density is still very high (ρ_{max} is 34.4 electrons/Ω_c), but lower than for Mg_2C because the beryllium core is more electronegative than magnesium. As expected, the charge distributions for Mg_2Si, Mg_2Ge, and Mg_2Sn are similar both in shape and absolute value. The maximum in $\rho(r)$ for these compounds is 24.5, 24.3, and 21.2 electrons/Ω_c, respectively. Finally, Be_2Si is the least ionic of the six compounds—ρ_{max} is only 16.2 electrons/Ω_c—and its charge distribution strongly resembles a weaker version of the three Mg_2X ($X = Si$, Ge, and Sn).

These trends in the charge distributions scale with the differences in atomic electronegativities[8,18] ΔX. For Be_2C and Mg_2C, the Pauling ΔX_P are 1.3 and 1.0, respectively. For MgX ($X = Si$, Ge, and Sn), $\Delta X_P = 0.60$, while for Be_2Si, ΔX_P is 0.30. Thus, we expect that the the three Mg_2X ($X = Si$, Ge, and Sn) will have similar band structures and bulk moduli. Band splitting and gaps in Mg_2C and Be_2C should be larger than, but qualitatively similar to, Mg_2Si. But, since Be_2Si is the least ionic and the charge is delocalized, the electronic properties can be significantly different than the other five. We find, in fact, that this is the case.

B. Electronic properties

Table I lists the calculated fundamental band gaps and available experimental values for the six antifluorite compounds. All gaps are found to be indirect from Γ to X. For Be_2Si, the difference between fifth band at X (X_3) and the Γ_{15} level is given. The systematic underestimation of the band gaps is due to our use of the LDA. We find that the relative magnitudes of the LDA gaps for Mg_2Si, Mg_2Ge, and Mg_2Sn, however, agree better with the experimental ranges than values from a previous empirical pseudopotential method (EPM) calculation[5] do. From the trend in the series, then, Be_2C and Mg_2C are expected to have gaps of several eV.

Calculated band structures for Mg_2Si and Mg_2C are given in Fig. 3. Comparison of the band structure from our *ab initio* calculation for Mg_2Si with a previous EPM calculation[5] shows good agreement, although the fundamental band gap is underestimated in our study. This is to be expected, as the LDA systematically underestimates band gaps. The ordering of the valence and conduction band levels is the same, but the present calculation predicts that the Γ_1-Γ'_{25} splitting is 0.13 eV compared to 0.74 eV (EPM). At X, the first two levels in the conduction band are 0.46 eV apart compared to 0.12 eV calculated from EPM.

The band structures for Mg_2Ge and Mg_2Sn also agree very well with EPM.[5] In contrast to Mg_2Si, the splitting and ordering of the X_3 and X_1 conduction band levels in
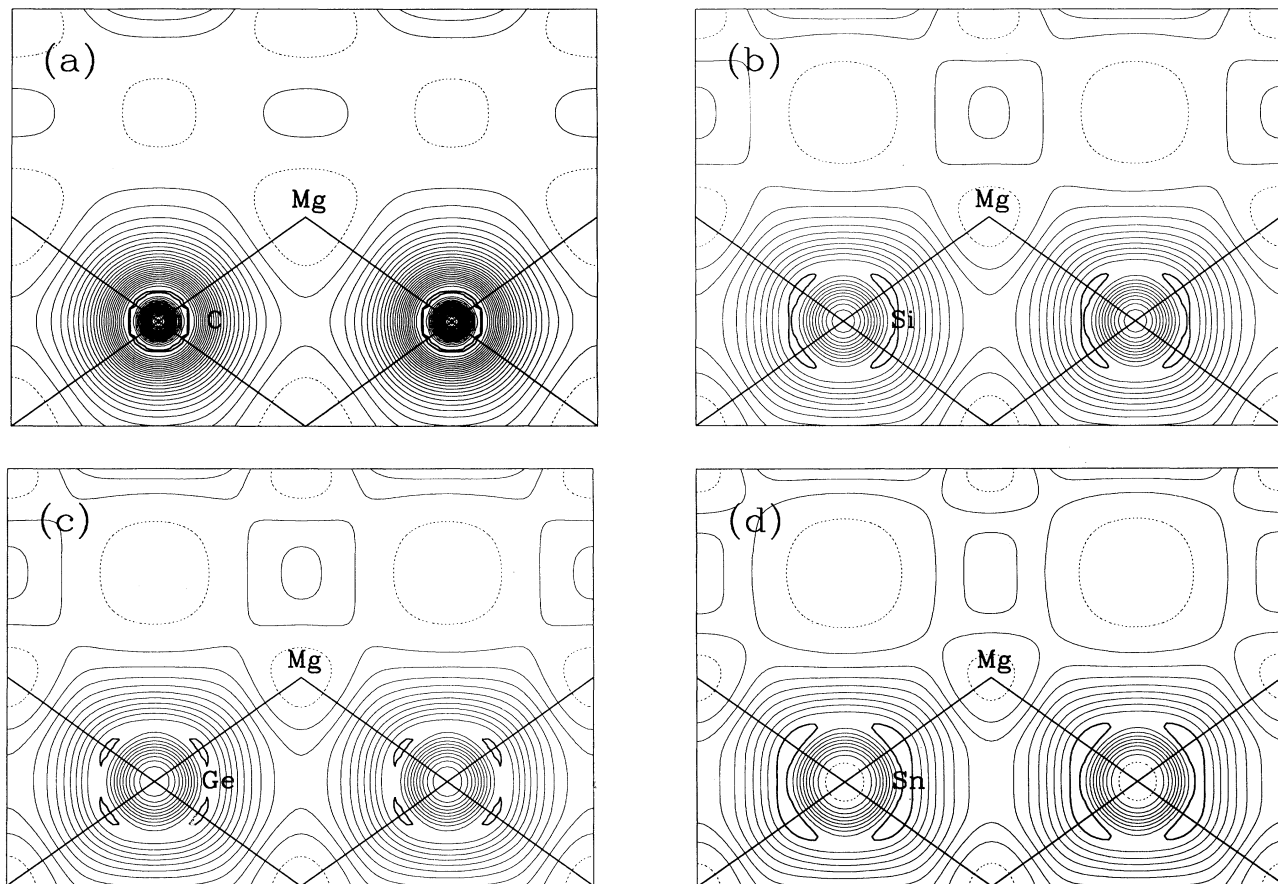
FIG. 2. The valence charge densities for (a) Mg_2C, (b) Mg_2Si, (c) Mg_2Ge, and (d) Mg_2Sn at the equilibrium volumes are shown. Contours are drawn for (a) 2,4,...,54, (b) 2,4,...,24, (c) 2,4,...,24, and (d) 2,4,...,20 electrons per unit cell. The lowest contour is drawn as a dotted line and the highest contour is drawn as a bold line.

Mg_2Ge and Mg_2Sn agree quantitatively with the EPM calculation. The splitting between the first two conduction band levels at Γ, however, is still smaller here than in EPM. For Mg_2Ge (Mg_2Sn), the Γ'_{25}-Γ_1 splitting is calculated to be 1.00 eV (0.25) compared to 1.88 eV (1.71) from EPM.

In the more ionic compound Mg_2C, the shape of the valence bands is essentially the same as in the other four Mg_2X compounds. The conduction bands, however, are much different. The splitting between the first two conduction band states at Γ is much more dramatic and as a result, the crossing along Δ found in the other three Mg compounds does not occur in Mg_2C. Whereas the fifth and sixth bands in Mg_2Si are very close in energy for a wide variety of symmetry k points, they overlap only a few tenths of an eV in Mg_2C.

Calculated band structures for Be_2C and Be_2Si are shown in Fig. 4. To our knowledge, there are no published band structures for Be_2C, although the compound is known to exist. Compared to the Mg compounds, the order of the first two conduction band levels at Γ in Be_2C is reversed. The Γ'_{25} comes down below the Γ_1 level to be the lowest first conduction band state at Γ.

We can understand this based on the character of the

charge distribution for these levels. Charge densities for the Γ_{15}, Γ'_{25}, and Γ_1 levels in Be_2C are shown in Fig. 5. The Γ_{15} level is similar to the total valence charge density and is concentrated on the group-IV atom site. The Γ'_{25} state, however, is significant only around the group-IIA sites and negligible on the group-IV sites. The Γ_1 is concentrated around the group-IV atom and in the interstitial regions and is negligible on the group-IIA sites. Since the Be potential is much stronger than the Mg potential, the change in level orderings between Mg_2C and

TABLE I. Calculated (LDA and EPM) and experimental values for the fundamental gap of six antifluorite IIA-IV compounds. Calculated values using EPM (Ref. 5) are given in parentheses. All gaps are from Γ to X and are given in eV.

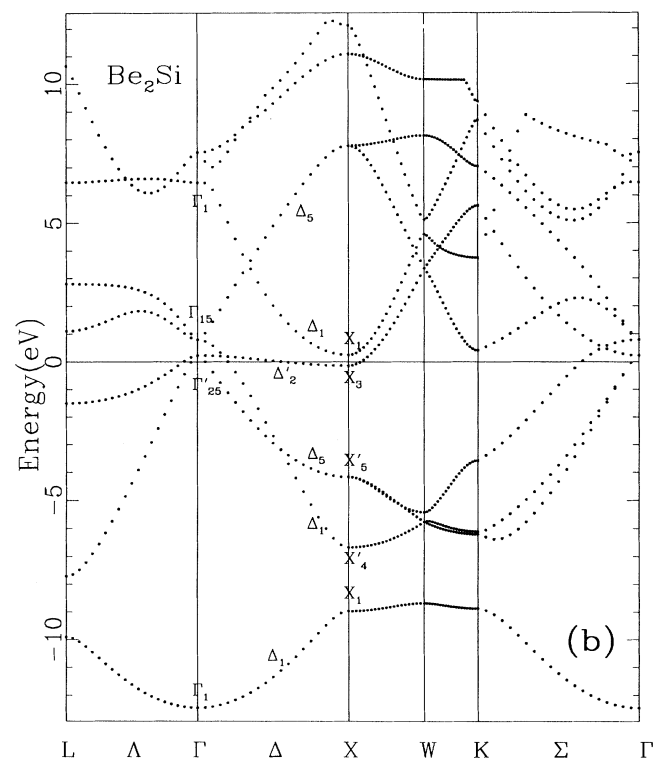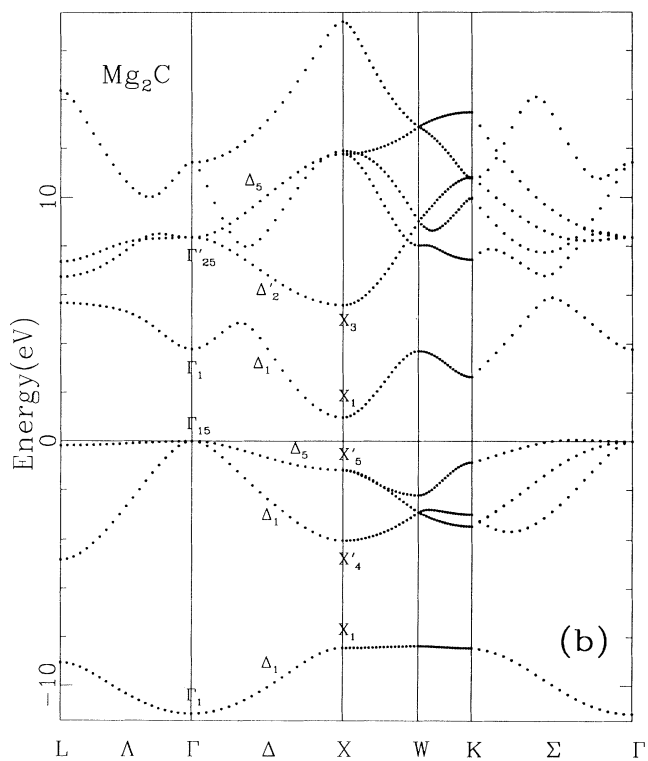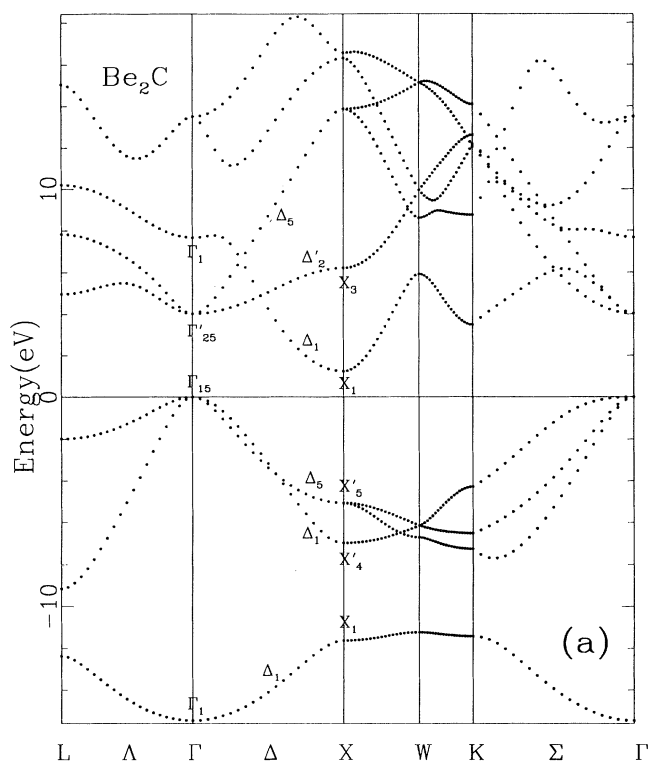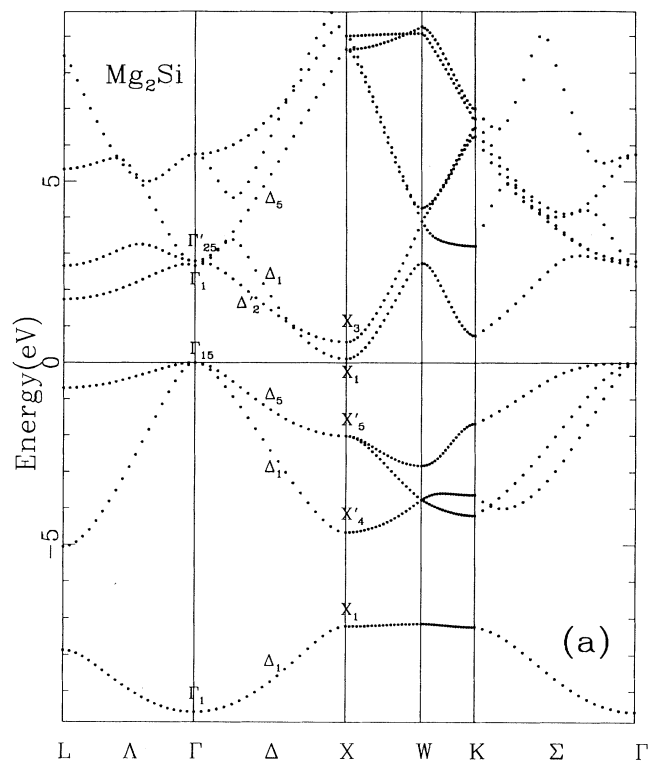|	E_{gap}^{theor} (eV)	E_{gap}^{expt} (eV)
Be_2C	1.239	
Be_2Si	-0.354 (X_3 to Γ'_{25})	
Mg_2C	0.973	
Mg_2Si	0.118 (0.53)	0.65–0.78
Mg_2Ge	0.166 (0.92)	0.67–0.76
Mg_2Sn	0.026 (0.64)	0.23–0.36

FIG. 3. Calculated one-electron energy levels along symmetry lines for (a) Mg$_2$Si and (b) Mg$_2$C.

FIG. 4. Calculated one-electron energy levels along symmetry lines for (a) Be$_2$C and (b) Be$_2$Si.

Be$_2$C arises because the energy of the Γ'_{25} level is lowered relative to the Γ_1 level in the beryllium compound.

Aside from the ordering at Γ, the Be$_2$C band structure differs from the five other compounds in the ordering of the top three valence levels at W and K. In this structure, the levels at W and K are all concentrated on the

FIG. 5. Charge density for (a) valence band maximum Γ_{15} and conduction band levels (b) Γ'_{25} and (c) Γ_1 for Be$_2$C are shown. Contours are drawn for (a) 0.5,1.0,...,17.0, (b) 0.5,1.0,...,4.5, and (c) 0.5,1.0,...,13.5 electrons per unit cell. The lowest contour is drawn as a dotted line and the highest contour is drawn as a bold line.

group-IV element and thus are very localized in Be$_2$C. At W and K, the ordering of the valence band levels is from lowest to highest in localization according to the maxima in $\rho(r)$. The third and fourth states at K have $\rho_{max}(r)$ of 5.4 and 7.4 electrons per unit cell, respectively, while at K the second, third, and fourth states have $\rho_{max}(r)$ of 5.6, 7.2, and 9.0 electrons per unit cell, respectively. This is not a kinetic energy effect, however, which would be strongest in the most ionic compound Mg$_2$C, where we find the ordering preserved. The reordering in Be$_2$C is due to the strong Be potential and the fact that the states with the lowest $\rho_{max}(r)$ have a larger contribution of charge near the Be atom and thus have lower energy in the Be$_2$C than in the less ionic materials.

An extreme case of the lowering of the Γ'_{25} level is found in Be$_2$Si [see Fig. 4(b)]. Here, the Γ'_{25} is lower in energy than the Γ_{15}, which causes the system to be metallic. However, it is not metallic because of band overlap—it is a true metal. Both the Γ_{15} and the Γ'_{25} levels are triply degenerate. Along Δ, both split into a doubly degenerate Δ_5 level and a singly degenerate level. When the Γ_{15} and Γ'_{25} levels cross, the Δ_5 bands do not cross and thus produce bands similar to those in Mg$_2$Si. The Δ_5 level from the lower Γ level evolves into the third and fourth levels at X (the doubly degenerate X'_5 level) and the Δ_5 level from the higher-energy Γ state disperses upwards along Γ to X. The singly degenerate states produced by the Γ_{15} and Γ'_{25} levels, however, have different symmetry. The Γ_{15} produces a Δ_1 which must becomes an X'_4 state at X, whereas the Γ'_{25} level produces a Δ'_2 level which becomes an X_3 state at X. Since the second state at X in Be$_2$Si is an X'_4 (as in Mg$_2$Si), by symmetry requirements the Δ_1 line must cross the Fermi level. Therefore, from the band structure point of view, Be$_2$Si is a metal for two different reasons: the strong Be potential causes a reordering of the Γ_{15} and Γ'_{25} levels and then group symmetry requirements produce a band along Δ which crosses the Fermi level.

Although the ordering in the Γ levels is much different in Be$_2$Si than in Mg$_2$Si, the valence band levels away from Γ are more like Mg$_2$Si than like Be$_2$C. This is not surprising since the overall charge density of Be$_2$Si is more similar to Mg$_2$X (X = Si, Ge, and Sn) than to Be$_2$C.

C. Structural properties

Calculated equilibrium lattice constants and available experimental values are shown in Table II. For Be$_2$C and Mg$_2$C, the calculations done with a 75 Ry cutoff differ by only 0.1% with the calculations done at the lower cutoff energy. Since these two compounds have the strongest atomic potentials and therefore require a larger basis set to represent the resulting wave functions of the solid, we expect this error to give a good upper limit on the error for the other lattice constants.

Theoretical values calculated from the first-principles method used here slightly underestimate the lattice constant. A similar underestimation is found for lattice constants predicted from simple sums of Pauling tetrahedral covalent radii.[8] The excellent agreement between
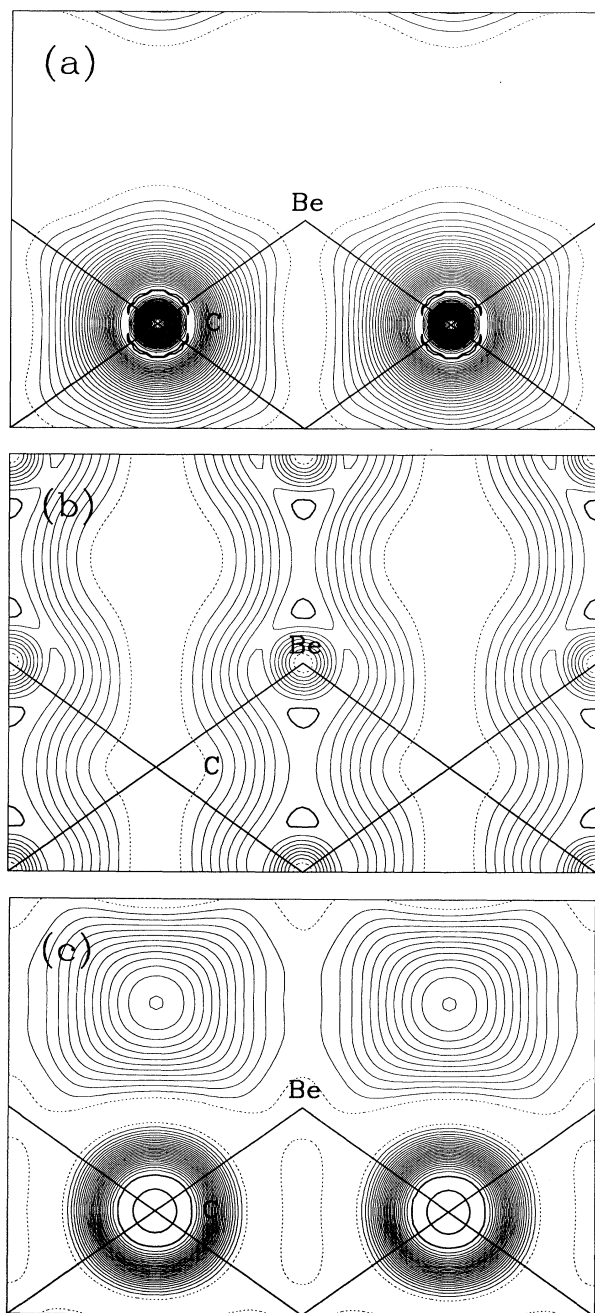
TABLE II. Calculated and experimental values of the equilibrium lattice constant for six antifluorite semiconductors. For Be_2C and Mg_2C, the lattice constant calculated with a 75 Ry basis is given in parentheses. The value of the lattice constant assuming a bond length equal to the sum of Pauling's tetrahedral covalent radii (Ref. 8) is shown. Experimental values are from Ref. 19.

	a_0^{theor} (Å)	$a_0^{Pauling}$ (Å)	a_0^{expt} (Å)
Be_2C	4.23 (4.23)	4.23	4.33
Be_2Si	5.18	5.15	
Mg_2C	5.00 (5.00)	5.01	
Mg_2Si	6.09	5.94	6.39
Mg_2Ge	6.12	6.05	6.378
Mg_2Sn	6.52	6.47	6.765

the theoretical lattice constant and $a_0^{Pauling}$ is reasonable for the less ionic compounds, but is surprising for Be_2C and Mg_2C.

Bulk moduli calculated from fitting the Birch equation of state[17] to the first-principles energy versus volume curves are given in Table III. Available experimental values are also shown for comparison. Although the range of experimental values is fairly wide for Mg_2Si and Mg_2Ge, the *ab initio* calculated values overestimate even the highest reported measured value. We can better understand this difference by examining a semiempirical (SE) formula for the bulk modulus and the variation of B_0^{SE} with bond length.

D. Semiempirical formula for B_0

Because of their similarity to the group-IV elemental semiconductors, this class of materials might be expected to obey the same semiempirical model[9,10] for the bulk moduli of group-IV, III-V, and II-VI semiconductors. This model was first formulated for tetrahedrally bonded group-IV elements with scaling arguments based on the Phillips–Van Vechten scheme[21] for characterizing the covalent and ionic nature of those materials based on their spectral properties. The bulk modulus for purely covalent solids was found to vary as the average homopolar energy gap in the reflectivity spectrum divided by the volume of the bond charge. It has been extended to in-

clude ionic solids and structures of lower coordination number. The resulting formula is

$$B_0(\text{GPa}) = \frac{\langle N_c \rangle}{4} \frac{(1971 - 220\lambda)}{d^{3.5}}, \quad (1)$$

where λ is a measure of the ionicity of the compound, $\langle N_c \rangle$ is the average coordination number, and d is the average nearest-neighbor bond length in angstroms.

For homopolar semiconductors, $\lambda = 0$, while $\lambda = 1$ and 2 for group III-V and II-VI zinc-blende materials. If we follow this simple rule, each group-II element in the antifluorites would look locally like a $\lambda = 2$ compound resulting in the group-IV element having a net charge of -4. The resulting average λ is $(2 + 2 + 4)/3 = 8/3$. Each group-II atom is fourfold coordinated while each group-IV atom is eightfold coordinated, so $\langle N_c \rangle \sim 16/3$. Then, the semiempirical formula for the antifluorite IIA-IV materials is

$$B_0^{SE}(\text{GPa}) = \frac{4}{3} \frac{(1971 - 220\frac{8}{3})}{d^{3.5}}$$
$$= 1846 \ d(\text{Å})^{-3.5}. \quad (2)$$

Bulk moduli calculated with Eq. (2) using d_0 from our *ab initio* calculation as well as using d_0 from available experimental values are shown in Table III. We compare these values with the *ab initio* B_0 and experimental values given there. The first-principles bulk moduli agree within about $\sim 5\%$ with the semiempirical formula using d_0^{theor}. A least-squares fit to the calculated bulk moduli assuming $B_0 = \alpha d^{-\beta}$ gives $\alpha = 1910.95$ and $\beta = 3.57$, which is in very good agreement with the form of Eq. (1).

Both the first-principles and semiempirical $B_0(d_0^{theor})$ overestimate the reported measured values for these materials. Given that the theoretical lattice constants are all several percent smaller than the experimental a_0's, the first-principles bulk moduli may be high simply because of the small lattice constants. Using the scaling $B_0 \sim d^{-3.5}$ of Eq. (1) and using the experimental lattice constants, one can correct the first-principles bulk moduli for the underestimated lattice constants. The corrected values are given in Table III. These corrected values agree very well with experiment and the semiempirical formula used with the experimental bond length. Thus, the calculated bulk moduli are larger than the mea-

TABLE III. Shown are the theoretical values for the bulk moduli based on *ab initio* calculations for a 40 Ry (75 Ry) basis set and computed from a semiempirical formula (Refs. 9 and 10) using the theoretically determined and experimental bond lengths, "corrected" bulk moduli, and experimental bulk moduli in GPa for six antifluorite structure semiconductors. The corrected bulk moduli are first-principles B_0 adjusted for the theoretical underestimation of the lattice constant according to the scaling $B_0 \sim d^{-3.5}$ of the semiempirical formula. Experimental values are from Ref. 20.

	$B_0^{ab\ initio}$	$B_0^{SE}(d_0^{theor})$	$B_0^{SE}(d_0^{expt})$	$B_0^{corrected}$	B_0^{expt}
Be_2C	214.2 (215.9)	221.7	204.5	197.7	
Be_2Si	103.2	109.5			
Mg_2C	130.7 (134.1)	123.7			
Mg_2Si	59.2	61.9	52.4	50.1	46.3–55
Mg_2Ge	57.6	60.9	52.7	49.9	44.0–54.7
Mg_2Sn	47.4	48.9	42.9	41.6	41.2

sured values, but this can be explained in terms of the underestimation of the lattice constants.

IV. CONCLUSIONS

We have studied the bonding, electronic, and structural properties of Be_2C, Mg_2X (X = Si, Ge, and Sn), and hypothetical compounds Be_2Si and Mg_2C from first principles. The calculated lattice constants underestimate the reported values by up to 5%, which causes an overestimation of the calculated bulk moduli. Calculated values of B_0 agree well with a semiempirical formula based on scaling arguments. When the underestimation of a_0 is taken into account, corrected values of B_0 agree very well with experimental values.

All six compounds have lattice constants that agree with the lattice constants predicted by Pauling tetrahedral radii[8] and follow the semiempirical formula for the bulk modulus.[9,10] This is expected for the four less ionic compounds Be_2Si and Mg_2X (X = Si, Ge, and Sn), but is surprisingly good for the more ionic carbides.

Calculated band structures for Mg_2X (X = Si, Ge,

and Sn) agree very well with previously published EPM (Ref. 5) calculations. Differences between the "prototypical" band structure of Mg_2Si and those of Mg_2C, Be_2C, and Be_2Si can be explained in terms of ionicity and group symmetry effects. We predict that Mg_2C is an indirect-gap semiconductor with a modest gap, The very light compound Be_2Si is predicted to be a metal because of the very strong Be atomic potential and group symmetry requirements. Experimental production of Be_2Si and Mg_2C is encouraged to test our predictions.

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