

**I-II-V half-Heusler compounds for optoelectronics: *Ab initio* calculations**

David Kieven and Reiner Klenk

*Helmholtz Zentrum Berlin für Materialien und Energie, Glienicker Str. 100, 14109 Berlin, Germany*

Shahab Naghavi, Claudia Felser, and Thomas Gruhn\*

*Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg Universität, Staudinger Weg 9, 55099 Mainz, Germany*

(Received 22 October 2009; revised manuscript received 12 January 2010; published 11 February 2010)

Half-Heusler compounds  $XYZ$  crystallize in the space group  $F\bar{4}3m$  and can be viewed as a zinc-blende-like  $(YZ)^-$  lattice partially filled with He-like  $X^+$  interstitials. In this work, we investigated I-II-V (eight-electrons) half-Heusler compounds by first-principles calculations in order to find suitable semiconductors for optoelectronics such as Cd-free buffer layer materials for chalcopyrite-based thin-film solar-cell devices. We report a systematic examination of band gaps and lattice parameters, depending on the electronegativities and the ion radii of the involved elements. Half-Heusler buffer materials should have a band gap of more than 2 eV to avoid absorption losses and a lattice constant of about 5.9 Å to match the crystal structure of the absorber material. With these criteria we selected seven half-Heusler compounds as candidates for a buffer layer material.

DOI: [10.1103/PhysRevB.81.075208](https://doi.org/10.1103/PhysRevB.81.075208)

PACS number(s): 71.20.Mq, 84.60.Jt, 71.15.Mb

**I. INTRODUCTION**

Ternary Cu-based chalcopyrite semiconductors such as  $p$ -type  $\text{CuInSe}_2$  (CISe) or  $\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$  (CIGSe) are excellent light-absorber materials for low-cost thin-film solar-cell applications. In conventional chalcopyrite solar cells, a CdS-buffer layer of around 50 nm thickness between the light-absorber and the  $n$ -type ZnO window layer is used to increase the performance of the device. Record efficiencies of 19.9% have been reported for the  $\text{ZnO}/\text{CdS}/\text{Cu}(\text{In}, \text{Ga})\text{Se}_2$  heterojunction.<sup>1</sup> To achieve a good solar-cell performance, an accurate design of the heterojunction between absorber and buffer layer is crucial. The buffer layer material should avoid unnecessary absorption losses and its crystal structure should ensure a good contact between absorber and buffer layer. It is desirable to have an inverted interface (conduction band of the absorber close to the Fermi level at the interface) and to avoid a barrier reduction at the interface in order to minimize recombination.<sup>2</sup> CdS seems to meet these conditions. However, much research activity is undertaken as to replace CdS by a less toxic buffer layer material.

An interesting class of materials are half-Heusler compounds  $XYZ$ , in which two elements  $Y$  and  $Z$  form a zinc-blende structure while  $X$  occupies one of the interstitial sites in between. The rather loosely packed crystalline structure is similar to that of chalcopyrite, so that a good surface contact between the two materials is expected if the lattice constants are in the same range. Of special interest are I-II-V compounds, in which the components  $X$ ,  $Y$ , and  $Z$  have 1, 2, and 5 valence electrons, respectively. One example is  $\text{LiZnP}$ , for which the crystalline structure and the electronic properties have been predicted with the help of local-density approximation (LDA) calculations<sup>3</sup> before they were analyzed experimentally.<sup>4-6</sup> Raman scattering indicated a strongly ionic bond between Li and P and a covalent bond between Zn and P in accordance with the theory.<sup>6</sup> The system may be viewed as a  $(\text{ZnP})^-$  zinc-blende lattice partially filled with  $\text{Li}^+$  ions. With the extra electron, the  $(\text{ZnP})^-$  sublattice is similar to the III-V semiconductor GaP, and, indeed,  $\text{LiZnP}$

is semiconducting.<sup>5</sup> Finite band gaps have also been measured for the  $\text{LiZnN}$ ,  $\text{LiMgP}$ , and  $\text{LiMgN}$ .<sup>7-9</sup> For other I-II-V compounds, finite band gaps have been found in LDA calculations.<sup>10-14</sup>

In this work, we use *ab initio* calculations to calculate electronic and geometrical properties of all I-II-V half-Heusler compounds that meet the ecological, technological, and economical minimal requirements to serve as a buffer layer material. The aim is to make a shortlist of compounds that are reasonable candidates for substituting CdS in the buffer layer. A good buffer layer material must meet several demands with respect to its electronic structure, the interaction with the adjacent materials, the electron affinity and other aspects. We have selected two primary criteria which should be fulfilled by a good substitute for CdS. For a reasonably small absorption loss, the band gap of the buffer material should not be smaller than 2 eV and the lattice constant should be around 5.9 Å for a good lattice matching with the absorber material.

**II. COMPOUND STRUCTURE AND METHODS**

So called half-Heusler materials (sometimes also Nowotny-Juza compounds) are ternary  $XYZ$  compounds with the space group  $F\bar{4}3m$ . The structure arises from three interpenetrating fcc lattices of  $X$ ,  $Y$ , and  $Z$  atoms. The primitive cell contains atoms  $X$ ,  $Y$ , and  $Z$  which are arranged at the positions  $\mathbf{r}_1=(0.5, 0.5, 0.5)$ ,  $\mathbf{r}_2=(0, 0, 0)$ , and  $\mathbf{r}_3=(0.25, 0.25, 0.25)$  with components in units of the cubic lattice constant  $a$ .  $XYZ$  half-Heusler compounds with a total number of eight valence electrons are likely to be semiconductors. The eight valence electrons are strongly bound as in a closed atomic  $K$  shell so that in many cases the conduction and the valence band are separated by a gap.<sup>10</sup> A similar effect is found for compounds with 18 valence electrons.<sup>15</sup> In this work, we focus on I-II-V half-Heusler compounds with elements from the first, second, and fifth main group, as well as the second subgroup of the periodic system of elements.

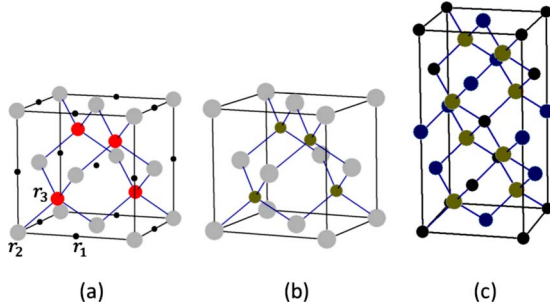


FIG. 1. (Color online) (a)  $XYZ$  half-Heusler crystal structure (space group  $F\bar{4}3m$ ) with  $X$  at  $\mathbf{r}_1=(0.5,0.5,0.5)$  (black),  $Y$  at  $\mathbf{r}_2=(0,0,0)$  (gray), and  $Z$  at  $\mathbf{r}_3=(0.25,0.25,0.25)$  (red/dark gray). Note the zinc-blende-like  $(YZ)^-$  lattice partially filled with He-like  $X^+$  interstitials. (b) CdS in the zinc-blende structure (space group  $F\bar{4}3m$ ) with Cd (gray) at  $(0,0,0)$  and S (green/dark gray) at  $(0.25,0.25,0.25)$ . (c) Chalcopyrite crystal structure of  $\text{CuInSe}_2$  (space group  $I42d$ ). Cu (black) is located at  $(0,0,0)$ , In (dark blue/dark gray) at  $(0,0,0.5)$  and Se (green/gray) at  $(z,0.25,0.125)$ . (The figure is in color only in the electronic version.)

With regard to an application in thin-film solar cells, we did not consider rare, toxic, radioactive, or technologically unfavorable elements so that we ended up with half-Heusler compounds  $XYZ$  with  $X=\text{Li, Na, and K}$ ,  $Y=\text{Mg, Ca, and Zn}$ , and  $Z=\text{N and P}$ , respectively. For all these compounds  $XYZ$ , element  $X$  has the lowest and element  $Z$  has the highest value of the Pauling electronegativity.

The conventional buffer layer material CdS can exist in the  $P63mc$  wurtzite as well as in the  $F\bar{4}3m$  zinc-blende structure. The two phases of CdS share many similarities. Both are in a 4:4 coordination and have similar optical properties.<sup>16,17</sup> The band gap of the two structures differs by less than 0.1 eV (Refs. 17 and 18) and the total-energy difference is only of the order of a few millielectron volt per atom.<sup>19</sup> The wurtzite modification is slightly more stable for bulk materials. Films grown by chemical-bath deposition can either have a hexagonal or a zinc-blende structure.<sup>18,20</sup> The cubic modification of CdS [Fig. 1(c)] is closely related to the half-Heusler structure [Fig. 1(a)] in which the  $Y$  and the  $Z$  components form a zinc-blende structure, which is stuffed by the  $X$  component.

$\text{CuInSe}_2$  itself is a chalcopyrite (space group  $I42d$ ), which can be viewed as a derivative compound of the zinc-blende structure. Figure 1(b) shows the  $\text{CuInSe}_2$  structure with Cu at  $(0,0,0)$ , In at  $(0,0,0.5)$ , and Se at  $(z,0.25,0.125)$ .

Calculations are done with the full-potential linear augmented plane-wave (LAPW) WIEN2K code.<sup>21</sup> It is well known that the density-functional theory (DFT) based calculations underestimate the band gap for semiconductors. Therefore, most promising compounds are also studied with CRYSTAL06,<sup>22</sup> which implements the Hartree-Fock and Kohn-Sham self-consistent field method in combination with the DFT. For the exchange-correlations potential we used the hybrid functional B3LYP and compare these results with the DFT results calculated with generalized gradient approximation (GGA) using the WIEN2K program package.

### III. RESULTS AND DISCUSSION

We examined 18  $XYZ$  compounds in the half-Heusler structure using LAPW calculations with  $X=\text{Li, Na, and K}$ ,  $Y=\text{Mg, Ca, and Zn}$ , and  $Z=\text{N and P}$ , respectively. For comparison we studied CdS in the zinc-blende structure. Due to the close relation between the zinc-blende and the half-Heusler structure, electronic properties are directly comparable. For every compound we optimized the cell volume before calculating the band structure.

In the DFT calculations with GGA, CdS shows a direct gap of 1.00 eV and a lattice constant of 5.948 Å. A comparison with the experimentally measured band gap of 2.48 eV (Ref. 23) shows that the calculated band gap is indeed too low. Therefore, it was not surprising to obtain almost touching valence and conduction band for the chalcopyrite  $\text{CuInSe}_2$  which has a band gap of 1.01 eV.<sup>24</sup>

In principle, the components  $X, Y, Z$  of a half-Heusler material can be distributed in various ways on the sites  $\mathbf{r}_1=(0.5,0.5,0.5)$ ,  $\mathbf{r}_2=(0,0,0)$ , and  $\mathbf{r}_3=(0.25,0.25,0.25)$  of the cubic unit cell. The most stable configuration is characterized by the lowest total energy of the system. For symmetry reasons the total energy remains unchanged if the elements on  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are swapped. For each compound we have determined the total energy of the three discriminable states in which  $(X,Y,Z)$  are arranged on  $(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ ,  $(\mathbf{r}_3,\mathbf{r}_1,\mathbf{r}_2)$ , and  $(\mathbf{r}_2,\mathbf{r}_3,\mathbf{r}_1)$ , respectively. The band structure and the character of the bonds between the atoms may depend sensitively on the arrangement of the elements on the lattice sites, as shown for the case of  $\text{LiZnAs}$  by DFT calculations.<sup>14</sup> For the compounds studied we found configurations with  $X$  at  $\mathbf{r}_1$ ,  $Y$  at  $\mathbf{r}_2$ , and  $Z$  at  $\mathbf{r}_3$  to be most stable. All results, presented in the following, refer to the stable configurations.

Band gaps obtained from WIEN2K calculations are shown in Table 1. The highest direct band gap of 2.28 eV was obtained for  $\text{LiMgN}$  [experimental value 3.2 eV (Ref. 9)], whereas almost touching valence and conduction band were found for  $\text{NaZnN}$ ,  $\text{KZnN}$ , and  $\text{KZnP}$ .

The compounds  $\text{NaZnP}$ ,  $\text{LiZnN}$ ,  $\text{NaMgN}$ ,  $\text{KMgP}$ , and  $\text{NaMgP}$  show direct energy gaps between 0.44 and 1.47 eV. An *ab initio* study of  $\text{NaZnP}$  predicts<sup>12</sup> that the tetragonal  $\text{Cu}_2\text{Sb}$ -type structure with a calculated band gap of  $E_{\text{gap}}^{\text{calc}} \approx 0.6$  eV is slightly more stable than the half-Heusler structure with  $E_{\text{gap}}^{\text{calc}} \approx 0.4$  eV. This result is in agreement with experimental findings.<sup>25</sup> An indirect transition was found for  $\text{LiMgP}$ ,  $\text{LiZnP}$ ,  $\text{KMgN}$ , and all tested compound  $XYZ$  with  $Y=\text{Ca}$ . The indirect band gaps vary between 0.13 eV for  $\text{KMgN}$  and 2.21 eV for  $\text{LiCaN}$ .  $\text{LiZnP}$  reveals a direct band gap of 14.1 eV, not much higher than the indirect band gap of 1.35 eV. A direct band gap has been found experimentally for  $\text{LiZnP}$  and also for  $\text{LiMgP}$  in contradiction to our findings.<sup>5,8</sup> This discrepancy between DFT calculations and experiments has already been mentioned by Kalarasse and Benecer<sup>11</sup> for  $\text{LiZnP}$  and by Yu *et al.*<sup>26</sup> for  $\text{LiMgP}$ .

Half-Heusler materials  $XYZ$  can be viewed as a zinc-blende structure of  $(YZ)^-$  with  $X^+$  interstitials, where  $Y$  and  $Z$  are covalently bound. The band structure of  $\text{LiZnP}$  was successfully explained as the electronic structure of a hypothetical  $(\text{ZnP})^-$  semiconductor, for which the conduction bands are modified by the presence of the  $\text{Li}^+$  cation.<sup>3</sup> With the

TABLE I. Equilibrium lattice constants  $a_{calc}$  and values of the band gap  $E_{gap}^{calc}$  calculated with GGA (WIEN2K) and B3LYP (CRYSTAL06). Experimental values for band gaps are shown in the last column for comparison.

XYZ	$a_{calc}/\text{\AA}$		$a_{exp}/\text{\AA}$	$E_{gap}^{calc}/\text{eV}$		$E_{gap}^{exp}/\text{eV}$
	(WIEN2K)	(CRYSTAL06)		(WIEN2K)	CRYSTAL06	
LiMgN	5.010	4.916	4.955 <sup>a</sup>	2.28 (direct)	4.37	3.2 <sup>a</sup>
LiMgP	6.022	5.976	6.005 <sup>b</sup>	1.55 (indirect)	2.90	2.43 <sup>b</sup>
LiCaN	5.553	5.531		2.21 (indirect)	3.78	
LiCaP	6.501			1.95 (indirect)		
LiZnN	4.924	4.911	4.910 <sup>c</sup>	0.52 (direct)	2.34	1.91 <sup>c</sup>
LiZnP	5.766	5.786	5.765 <sup>d</sup>	1.35 (indirect)	2.66	2.04 <sup>d</sup>
NaMgN	5.443	5.424		0.77 (direct)	2.08	
NaMgP	6.375	6.334		1.47 (direct)	2.76	
NaCaN	5.858	5.748		1.15 (indirect)	3.03	
NaCaP	6.785			1.95 (indirect)		
NaZnN	5.358			0		
NaZnP	6.149	6.162		0.44 (direct)	1.65	
KMgN	6.005			0.13 (indirect)		
KMgP	6.847			0.96 (direct)		
KCaN	6.286	6.297		0.68 (indirect)	2.14	
KCaP	7.201			1.54 (indirect)		
KZnN	5.959			0		
KZnP	6.673			0		
CdS (reference)	5.948	6.061	5.830 <sup>e</sup>	1.00	2.59	2.48 <sup>g</sup>
CuInSe <sub>2</sub> (absorber)		$c=5.783$	5.851 <sup>f</sup>	0	1.06	1.01 <sup>h</sup>

<sup>a</sup>Reference 9.

<sup>b</sup>Reference 8.

<sup>c</sup>Reference 7.

<sup>d</sup>Reference 5.

<sup>e</sup>Reference 28.

<sup>f</sup>Reference 29.

<sup>g</sup>Reference 23.

<sup>h</sup>Reference 24.

extra electron, the (ZnP)<sup>-</sup> zinc-blende structure should behave like a III-V semiconductor and, indeed, DFT calculations have shown that the band structure of (ZnP)<sup>-</sup> is very similar to that of GaP.<sup>3</sup> Pauli repulsion between conducting electrons and the Li<sup>+</sup> on the  $\mathbf{r}_1$  modifies the shape of the lowest conduction band. At the  $\Gamma$  point the lowest conduction-band electrons are localized around  $\mathbf{r}_2$  and  $\mathbf{r}_3$  while states at the X point have their maximum close to  $\mathbf{r}_1$ . Therefore, adding the Li<sup>+</sup> anion raises mostly the X point energy of the conduction band.

In Figs. 2(a) and 2(b), the band structures of LiMgP and NaMgP are shown. One can see that they are quite similar to each other. Close to the band gap, the band structures of the two compounds are also similar to that of GaP, suggesting that (MgP)<sup>-</sup> may be viewed as a III-V semiconductor. While LiMgP is an indirect semiconductor with the conduction band minimum at X, exchanging Li<sup>+</sup> with Na<sup>+</sup> leads to a direct semiconductor with the conduction-band minimum at  $\Gamma$ . Considering, that Na has more core electrons than Li, this change is in agreement with the considerations in the last paragraph.

It is remarkable that the band structures of the half-Heusler compounds shown are also very similar to the band structure of cubic CdS [Fig. 2(d)], which is a II-VI semiconductor. The similarity of the band structures of half-Heusler materials and CdS is quite encouraging for the idea of substituting CdS by a half-Heusler compound in the buffer layer.

The bonds between Y and Z in the (YZ)<sup>-</sup> zinc-blende structure are predominantly covalent, they are more or less polar, depending on the Pauling electronegativities  $\chi_Y$  and  $\chi_Z$  of the components Y and Z.<sup>10</sup> The difference  $\chi_Z - \chi_Y$  between the Pauling electronegativities is also correlated with the bandwidth of the compound.<sup>10</sup> In Fig. 3, the band gap for half-Heuslers XYZ with Z=P and X=Li, Na, and K is shown as a function of  $\chi_Z - \chi_Y$  for elements Y=Mg, Ca, and Zn, respectively. For a given X, the band gap increases monotonically with the difference of the Pauling electronegativity. For Z=N we found the same trend (not shown here). The same effect was observed for similar half-Heusler compounds with X=Li by Kandpal *et al.*<sup>10</sup>

Furthermore, we found that the band gap increases with the electropositive character of the element X. This result

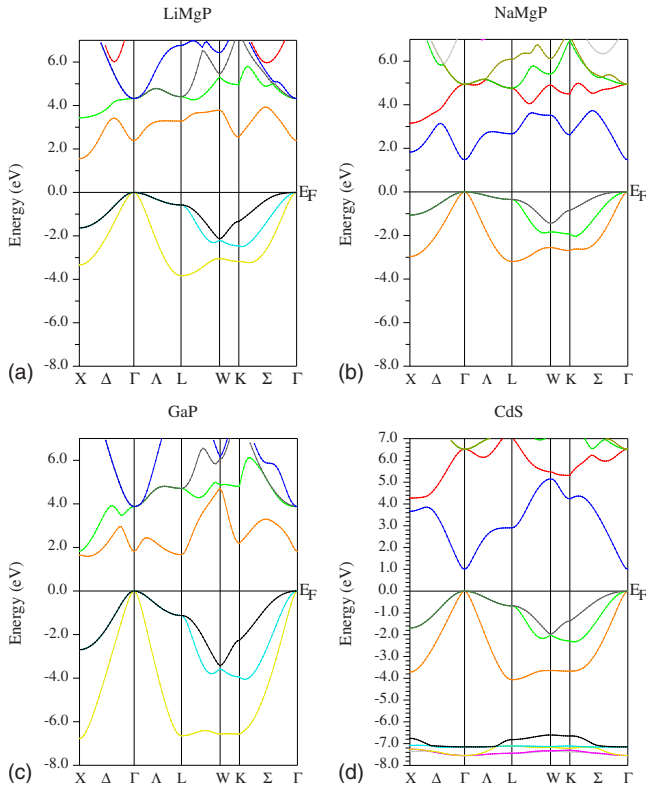


FIG. 2. (Color online) Band diagram of the half-Heusler compounds (a) LiMgP, (b) NaMgP, (c) of the III-V semiconductor GaP, and (d) of CdS in the zinc-blende structure. Calculations were done with the WIEN2K code. (The figure is in color only in the electronic version.)

agrees with the picture of a zinc-blende-like structure of  $(YZ)^-$ , where the negative charge from the element X stabilize the covalent bond between the element Y and Z.<sup>10</sup> A similar effect has been discussed for 18-electron compounds.<sup>15</sup> The influence of the presence of  $X^+$  on the conduction bands of the  $(YZ)^-$  zinc-blende structure has been discussed for I-II-V half-Heuslers by Carlsson *et al.*<sup>27</sup>

The lattice constants calculated vary between 4.924 Å (LiZnN) and 7.201 Å (KCaP). In Fig. 4 the lattice constants

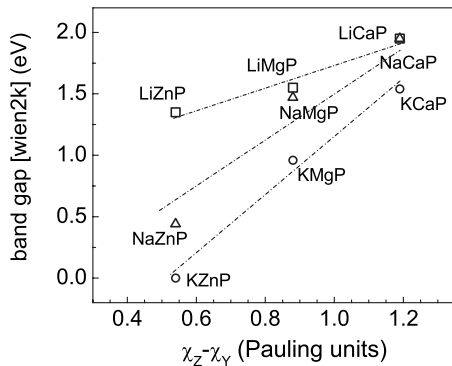


FIG. 3. Dependence of the band gaps (WIEN2K) of XYZ compounds ( $X=Li, Na, K$ ) on the Pauling electronegativity difference between the element  $Z=P$  and  $Y=Mg, Ca, Zn$ , respectively.

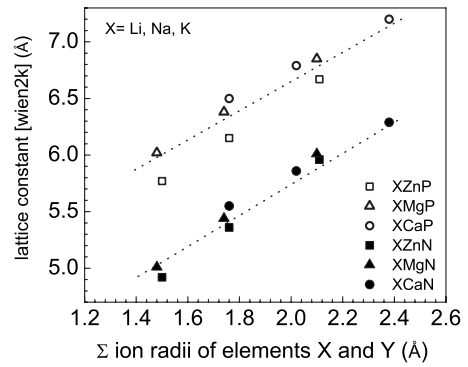


FIG. 4. Lattice constants of XYZ compounds plotted against the sum of the ion radii of element X and Y (ion radii for ions with removed valence electrons).

of XYZ compounds are plotted against the sum of the ion radii of X and Y for  $Z=N$  and  $Z=P$ , respectively. For  $Z=N$  the data points show an approximately linear behavior. They can be fitted by a straight line with a slope of 1.5. Looking closer, one finds small but systematic deviations from the linear behavior. The linear dependence on the ion radius of the X compound varies slightly with the chosen Y element. For the resulting best-fit lines, the slope increases and the offset decreases with increasing electronegativity of the Y component. This effect is more pronounced for the compounds with  $Z=P$ . Here, the compounds with  $Y=Zn$  have distinctly lower lattice constants. On average, the slope for compounds with  $Z=P$  is about 1.4, similar to that found for  $Z=N$ . Changing from  $Z=N$  to  $Z=P$  the lattice constant increases by approximately 0.9 Å. This strong increase cannot be ascribed to the larger ion radius of phosphor alone. The increase in the lattice constant must also be related to the lower electronegativity of phosphor, which reduces the strength of the covalent bond between the Z and Y elements as well as the polarization of the charge distribution in the unit cell.

The observed trends help to choose promising materials from the great number of possible combinations. Considering our reference buffer layer material CdS we can make a preselection of seven interesting compounds (LiMgP, LiCaN, LiZnP, NaMgN, NaMgP, NaCaN, and KCaP) with lattice constants and band gaps close to calculated values for CdS. Some of these compounds were calculated also with CRYSTAL06 (full optimization mode) in order to get more realistic values with regard to the band gaps. Results from the calculations are summarized in Table I.

Lattice constants calculated with WIEN2K and CRYSTAL06 show only a slight difference and are close to experimental data (see Table I). The band gaps from CRYSTAL06 are without exception higher than the values of WIEN2K. For CdS we found 2.59 eV which is 0.11 eV to high in comparison to the experimental value [2.48 eV (Ref. 23)]. For LiMgP, LiMgN, LiCaN, LiZnP, LiZnN, NaMgN, NaMgP, NaCaN, and KCaP we found band gaps of 2.90, 4.37, 3.78, 2.66, 2.34, 2.08, 2.76, 3.03, and 2.14 eV, respectively. For the chalcopyrite absorber CuInSe<sub>2</sub> we obtain 1.06 eV which is comparable to experimental results (1.01 eV for a single crystal<sup>24</sup>).

With regard to experimental band gap data [CdS,<sup>23</sup> CuInSe<sub>2</sub>,<sup>24</sup> LiZnP,<sup>5</sup> LiMgP,<sup>8</sup> LiZnN,<sup>28</sup> and LiMgN (Ref. 29)],



the band gaps from CRYSTAL06 are overestimated but closer to the experimental values than the WIEN2K results. It has to be pointed out that we were handling quite ionic structures (especially the structures with Mg or Ca) and in CRYSTAL06 the application of specially diffuse basis sets for ionic compounds is restricted. Therefore, there could be an intrinsic error of the method which results in an overestimation of the calculated band gaps.

If the lattice parameter of the buffer material differs from that of the absorber, a deformation of the lattice geometry may occur close to the contact region. For the choice of a suitable buffer material one should also take into account the variation in the band structure if the lattice parameter is changed. Using WIEN2K, we have studied how the band gap changes if the lattice of a half-Heusler is adapted to the crystalline structure of the chalcopyrite absorber CuInSe<sub>2</sub> (Table II). We assumed a lattice deformation of the half-Heusler from a cubic ( $F\bar{4}3m$ ) to a tetragonal structure ( $I4m2$ ), where the lattice constants ( $a=b$ ) distorted to the lattice parameter of CuInSe<sub>2</sub> (5.783 Å) and the lattice constant  $c$  was changed to optimize the volume of the new structure. Lattice data for CuInSe<sub>2</sub> were taken from fully optimized calculation of CRYSTAL06. As can be seen from Table II, there is a variation in band gaps due to the distorted structure. The highest absolute change we found for NaMgN (about  $-0.6$  eV), and the lowest one for LiZnP ( $+0.03$  eV) and LiMgP ( $+0.04$  eV). In comparison, the band gap of CdS decreases by 0.02 eV. For KCaN we observed a change from an indirect gap of 0.68 eV to a direct gap of 0.85 eV.

#### IV. CONCLUSIONS

In this work we presented first-principles calculations in order to find potential half-Heusler materials for use in optoelectronic devices such as Cd-free buffer layer materials in chalcopyrite-based solar cells. We chose two criteria to iden-

TABLE II. Results obtained with GGA calculations for cubic CdS and a selection of half-Heusler materials. Shown are lattice constants  $a_{calc}$ , and calculated band gap  $E_{gap}^{calc}$  for the equilibrium cubic structure as well as  $E_{gap}^{calc}$  for a tetragonal structure with lattice constants  $a=b=5.783$  Å, corresponding to the corresponding lattice constants of CuInSe<sub>2</sub>.

	$a_{calc}/\text{Å}$	$E_{gap}^{calc}/\text{eV}$	$E_{gap}^{calc}/\text{eV}$
	WIEN2K cubic	WIEN2K cubic	WIEN2K tetragonal
CdS (reference)	5.948	1.00 (direct)	0.98 (direct)
NaMgN	5.443	0.77 (direct)	0.15 (direct)
LiCaN	5.553	2.21 (indirect)	1.80 (indirect)
LiZnP	5.766	1.35 (indirect)	1.38 (indirect)
NaCaN	5.858	1.15 (indirect)	1.25 (indirect)
LiMgP	6.022	1.55 (indirect)	1.59 (indirect)
KCaN	6.286	0.68 (indirect)	0.85 (direct)
NaMgP	6.358	1.47 (direct)	1.80 (direct)

tify interesting materials. Good candidates must have an adequate band gap ( $E_{gap} > 2$  eV) to avoid absorption losses and a lattice constants of about 5.9 Å to match the crystal structure of the absorber material. With our *ab initio* methods we found seven compounds (LiMgP, LiCaN, LiZnP, NaMgN, NaMgP, NaCaN, and KCaN) which fulfill these criteria. Only slight band-gap variations due to lattice matching with the chalcopyrite absorber CuInSe<sub>2</sub> occurred for LiZnP and LiMgP. Direct band gap compounds such as LiMgN should be also interesting candidates for light-emitting diodes.

#### ACKNOWLEDGMENT

The authors are grateful to the BMU for the financial support (Projects No. 0327665[A-E]).

\*gruhn@uni-mainz.de

- <sup>1</sup>I. Repins, M. A. Contreras, B. Egaas, C. DeHart, J. Scharf, C. L. Perkins, B. To, and R. Noufi, *Prog. Photovoltaics* **16**, 235 (2008).
- <sup>2</sup>R. Klenk, *Thin Solid Films* **387**, 135 (2001).
- <sup>3</sup>D. M. Wood, A. Zunger, and R. de Groot, *Phys. Rev. B* **31**, 2570 (1985).
- <sup>4</sup>R. Basewicz and T. F. Ciszek, *Appl. Phys. Lett.* **52**, 1150 (1988).
- <sup>5</sup>K. Kuriyama and T. Katoh, *Phys. Rev. B* **37**, 7140 (1988).
- <sup>6</sup>K. Kuriyama, Y. Takahashi, and K. Tomizawa, *Phys. Rev. B* **47**, 13861 (1993).
- <sup>7</sup>K. Kuriyama, T. Kato, and T. Tanaka, *Phys. Rev. B* **49**, 4511 (1994).
- <sup>8</sup>K. Kuriyama, K. Kushida, and R. Taguchi, *Solid State Commun.* **108**, 429 (1998).
- <sup>9</sup>K. Kuriyama, K. Nagasawa, and K. Kushida, *J. Cryst. Growth* **237-239**, 2019 (2002).
- <sup>10</sup>C. Kandpal, C. Felser, and R. Seshadri, *J. Phys. D* **39**, 776

(2006).

- <sup>11</sup>F. Kalarasse and B. Bennecer, *J. Phys. Chem. Solids* **67**, 1850 (2006).
- <sup>12</sup>G. Jaiganesh, T. M. A. Britto, R. D. Eithiraj, and G. Kalpana, *J. Phys.: Condens. Matter* **20**, 085220 (2008).
- <sup>13</sup>L. H. Yu, K. L. Yao, Z. L. Liu, and Y. S. Zhang, *Phys. Lett. A* **367**, 389 (2007).
- <sup>14</sup>S.-H. Wei and A. Zunger, *Phys. Rev. Lett.* **56**, 528 (1986).
- <sup>15</sup>D. Jung, H.-J. Koo, and M.-H. Whangbo, *J. Mol. Struct.: THEOCHEM* **527**, 113 (2000).
- <sup>16</sup>P. Hofmann, K. Horn, A. M. Bradshaw, R. L. Johnson, D. Fuchs, and M. Cardona, *Phys. Rev. B* **47**, 1639 (1993).
- <sup>17</sup>M. Cardona, M. Weinstein, and G. A. Wolff, *Phys. Rev.* **140**, A633 (1965).
- <sup>18</sup>O. Zelaya-Angel and R. Lozada-Morales, *Phys. Rev. B* **62**, 13064 (2000).
- <sup>19</sup>S. Datta, T. Saha-Dasgupta, and D. D. Sarma, *J. Phys.: Condens. Matter* **20**, 445217 (2008).

- <sup>20</sup>O. Zelaya-Angel, L. Hernandez, O. de Melo, J. J. Alvarado-Gil, R. Lozada-Morales, C. Falcony, H. Vargas, and R. Ramirez-Bon, *Vacuum* **46**, 1083 (1995).
- <sup>21</sup>G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt, and L. Nördström, *Phys. Rev. B* **64**, 195134 (2001).
- <sup>22</sup>R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N. M. Harrison, I. J. Bush, *et al.*, *Crystal 2006 Users Manual* (University of Torino, Torino, Italy, 2006).
- <sup>23</sup>C. Junhao, T. Dietl, J. Gutowski, B. K. Meyer, W. Dobrowolski, T. Story, K. Sebald, and T. Voss, *New Data and Updates for II-VI Compounds*, Landolt-Börnstein, New Series, Group III, Vol. 44, Pt. B (Springer-Verlag, Berlin, 2009).
- <sup>24</sup>H. Dittrich, N. Karl, S. Kück, and H. Schock, *Ternary Compounds, Organic Semiconductors*, Landolt-Börnstein, New Series, Group III, Vol. 41, Pt. E (Springer-Verlag, Berlin, 2000).
- <sup>25</sup>H. Kabbour, L. Cario, and F. Boucher, *J. Mater. Chem.* **15**, 3525 (2005).
- <sup>26</sup>L. H. Yu, K. L. Yao, and Z. L. Liu, *Solid State Commun.* **135**, 124 (2005).
- <sup>27</sup>A. E. Carlsson, A. Zunger, and D. M. Wood, *Phys. Rev. B* **32**, 1386 (1985).
- <sup>28</sup>D. Rodic, V. Spasojevic, A. Bajorek, and P. Oennerud, *J. Magn. Magn. Mater.* **152**, 159 (1996).
- <sup>29</sup>S. Schorr and G. Geandier, *Cryst. Res. Technol.* **41**, 450 (2006).