

Effects of biaxial strain on stability and half-metallicity of Cr and Mn pnictides and chalcogenides in the zinc-blende structure

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The effects of biaxial strain, imposed by epitaxial growth conditions, on the half-metallicity properties of Cr and Mn pnictides and chalcogenides were investigated using local spin-density-functional calculations. The minority band gaps were found to decrease significantly under the biaxial strain, whereas the spin-flip gaps changed only slightly. The calculations show that under epitaxial conditions for any choice of substrate, CrSe, MnAs, MnSe, and MnTe cannot be half metallic; CrAs and CrTe are barely half metallic as their SF gap is close to zero; and only CrSb and MnSb remain distinct half metals with spin-flip gaps of 0.9 and 0.3 eV, respectively.

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The Cr and Mn pnictides and chalcogenides in the metastable zinc-blende (ZB) structure.¹⁻³ have been intensively studied for spintronic applications because of their possible half-metallic nature.⁴⁻⁷ Many theoretical studies⁸⁻¹⁹ showed that most of the early TM pnictides and chalcogenides are half-metallic if they are grown on a semiconductor substrate with large enough lattice constants. This result is based on the fact that the spin-splitting and, therefore, the spin-flip (SF) gap of these compounds changes drastically with volume expansion and compression. Under large enough volume expansion, most of them will become half metallic.

It is well known that, in nature, these materials are stable in structures other than ZB. The previous theoretical calculations showed that the energy difference between ZB and the equilibrium structures, such as NiAs and MnP, for these compounds are rather small, about 0.2–1 eV. Thus, the ZB structure can become metastable under a reasonably small volume expansion. However, although these compounds are grown on a substrate with large lattice mismatch, relaxation along the perpendicular direction is expected and the strain should be biaxial. Recently, Zhao and Zunger²⁰ investigated the relative stability of NiAs and ZB structures under pseudomorphic epitaxial conditions. They argued that under epitaxial growth condition, for most of the Cr and Mn pnictides and chalcogenides, the NiAs structure is either always lower in energy than ZB or only becomes higher in energy under a lattice expansion that is larger than the ones that can be achieved by epitaxy on available semiconductor substrates.

Although persuasive, the above work cannot exclude the possibility of growing ZB, Cr, and Mn pnictides and chalcogenides as very thin films because, in such a case, the interface energy differences may be dominating the strain energy. Because of the better match in bonding topology across the interface, one may expect the ZB on ZB to have an advantage over NiAs on ZB. It has already been shown possible experimentally to grow superlattice structures with thin regions of the above compounds in ZB structure separated by regions of semiconductors. Such structures are often called digital doping superlattices. An example is CrAs in GaAs.^{21,22} In both cases, there are large tetragonal distortions

imposed on the sample. Therefore it is important to understand how the biaxial strain affects the electronic structure and the half metallicity. In this paper, we first study how large the relaxation is, or, in other words, how biaxial the strain is for different potential substrates. Based on that we will then discuss how this distortion affects the minority spin gap and the spin-flip gap, i.e., the position of the minority spin-conduction band minimum relative to the Fermi level of the majority spin.

The computational method used in this work is local-density-functional theory^{23,24} combined with a full-potential linearized muffin-tin orbital method.²⁵ Well-optimized basis sets and converged Brillouin-zone integrations using typically an $8 \times 8 \times 8$ mesh are used. Additionally, to compare small energy differences between different crystal structures, equivalent k -point sets are used.

Figure 1 shows how the elastic energy varies with c/a ratio for different imposed strains ($\delta a/a_0$) for CrAs and CrSe, where a_0 is the equilibrium lattice constant of the undistorted, i.e., cubic ZB structure. Note that $\delta a/a_0$ determines the strain in the ab plane and c/a the relaxation in the perpendicular direction. Isotropic strain corresponds to $c/a = 1$, and different δa values correspond to different possible substrates. The corresponding volume change is $\delta V/V_0 \approx 3(\delta a/a_0)(c/a)_{\text{opt}}$, where $(c/a)_{\text{opt}}$ is the optimum c/a corresponding to each δa . Figure 1 shows that the relaxation in the [001] direction greatly reduces the elastic energy. For example, for isotropic expansion ($c/a=1$) by $\delta a/a_0=4\%$ without relaxation for CrAs (corresponding to the cross section of the $c/a=1$ line with the appropriate parabola), the energy increases by ~ 0.15 eV compared to the equilibrium energy of ZB, whereas with relaxation (biaxial strain, corresponding to the minimum of the appropriate parabola), the energy only increases by ~ 0.01 eV. Similar results (even stronger) hold under compression. This is, of course, not surprising since the volumes for isotropically and biaxially strained cells are quite different.

Figure 1 also shows that CrAs is, strictly speaking, not metastable in cubic ZB structure. If it were possible to grow in a ZB-like structure as bulk, i.e., with the same bond topology, it would have a tetragonal distortion $c/a \neq 1$. The

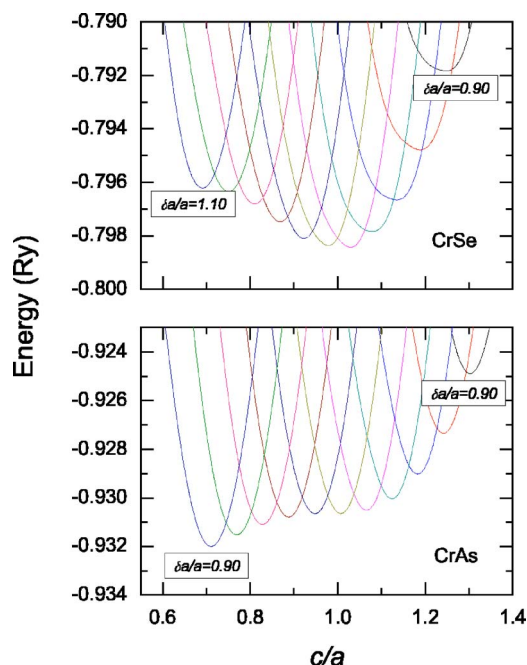


FIG. 1. (Color online) The energy vs [001] strain c/a for different biaxial strains $\delta a/a_0$ in the (001) plane for CrAs and CrSe. The values of $\delta a/a_0$ are varying from left to right from 1.10 to 0.90 in steps of 0.02.

optimum a and c/a for a ZB-like structure CrAs fall outside the range of values studied in this work. However, although CrAs is grown on the surface of a semiconductor substrate, the imposed biaxial strain is defined by the lattice constant of the substrate. The lattice along the perpendicular direction will relax accordingly. If the lattice constant of the substrate is close to a_0 for CrAs, the relaxation along the perpendicular direction will be small and the structure will be close to cubic ZB. A similar energy dependence on the strains is found for the other pnictides, including CrSb, MnAs, and MnSb. The chalcogenides behave differently from the pnictides. The cubic structure is, indeed, “metastable” in the sense that the energy for ZB-like structures occurs for $c/a = 1$. Again, although they are grown on the surface of a substrate, the biaxial strain imposed on it will be defined by the lattice constants of the substrate and the problem of an optimum free-standing ZB-like structure does not occur.

Figure 1 indicates that the relaxation along the perpendicular direction might be large. To view it clearly, we present the optimized c/a value in Fig. 2 together with the c/a values for biaxial strains that keep the volume or the bond length. The line $c/a=1$ shows the isotropic strain. Figure 2 clearly shows that the relaxation along the perpendicular direction is very large and much closer to assuming volume conservation than to assuming isotropic strain. Actually the relaxed volume under the strain is always slightly smaller than the equilibrium cubic ZB volume, no matter whether the biaxial strain is positive or negative. The relaxed c/a , however, are very close to those obtained by assuming bond-length conservation under biaxial strain. In other words, the optimum c/a is determined by bond length rather than volume conservation and far from isotropic.

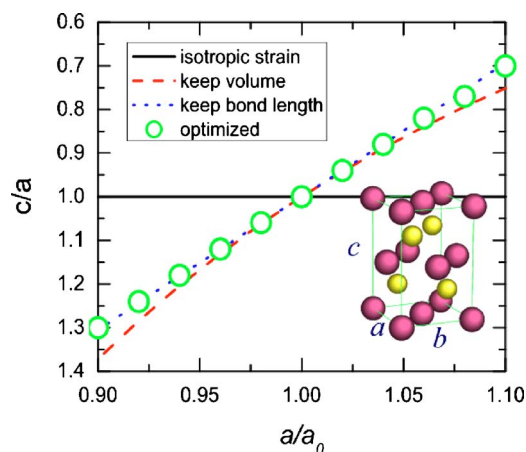


FIG. 2. (Color online) The optimized-induced strain along [001] (circles), compared to the strain that maintains the ZB equilibrium volume (dashed line), the strain that keeps the bond length (dotted line), and the isotropic strain (solid horizontal line) vs imposed biaxial strain for CrAs. The inset shows the conventional cell for ZB structure with distortions along the c direction.

The large relaxation in the perpendicular direction should also strongly effect the electronic structure and the half metallicity of the TM pnictides and chalcogenides. Although the strain is isotropic, the systems have a tendency to become “more half-metallic” by increasing their spin-flip gaps and the minority spin band gaps. This is caused by the stronger spin splitting of the d bands, which originates from the volume expansion and, hence, weakening the interactions between the TM atoms and the surrounding anions. However, the relaxation of the system in the perpendicular direction tends to keep the bond length. Therefore it should reduce the effects of lattice expansion in the ab plane. Figure 3 shows how the SF gap, VBM, and minority gaps change with the c/a values. The SF gap increases monotonically for all compounds and linearly for pnictides and Cr chalcogenides with increasing c/a ratio. Interestingly, the VBM has a minimum for a c/a ratio around 1.0, which corresponds to a cubic structure. In contrast, the minority band gap has a maximum around $c/a=1$. This feature reflects that the cubic structure has the largest splitting between its d states with different symmetry. Although c/a deviates from 1, the cubic symmetry is broken and the d states with different symmetries e and t_2 mix with each other and, therefore, lower the gap between their bands.

To see the total effect of the biaxial strain on the electronic structure and the magnetic properties of the system, we plot the partial density of states (PDOS) of Cr d states for CrSb in Fig. 4. One can see that the SF gap changes drastically while 6% of the isotropic strain is imposed. On the other hand, the minority spin gap changes only slightly. Under isotropic strain of 0.06, the spin-flip gap is $E_{sf}=1.3$ eV, whereas the minority spin band gap is $E_g=2.3$ eV in comparison to $E_{sf}=0.9$ eV and $E_g=2.0$ eV, respectively, at the equilibrium ZB lattice constant. The PDOS for d_{xy} , d_{xz} , and d_{yz} are the same because of the cubic symmetry and are referred to as the t_2 orbitals. Similarly, the PDOS for $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ are the same and referred to as e

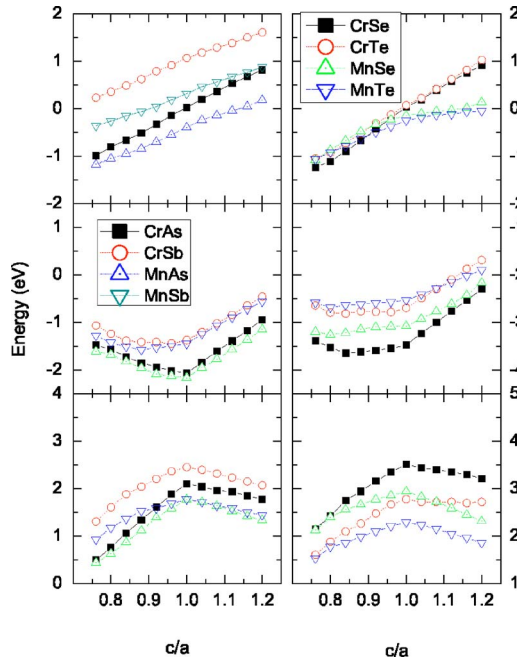


FIG. 3. (Color online) The SF gap (first row), VBM relative to Fermi level (second row), and minority spin gap (third row) for both pnictides (left panel) and chalcogenides (right panel) vs c/a ratio. The lattice constants in the ab plane are kept at the equilibrium value a_0 .

orbitals, using the notations for irreducible representations of the point group T_d . However, while the relaxation along the perpendicular direction is added, the effect the changes of the c/a ratios compensates the compression and expansion. The two PDOS in the lower row in Fig. 4 reveal that the SF gap changes back to ~ 0.9 eV. As shown in the lower right panel in Fig. 4, the SF gap reduces back to a value near 0.9 eV and the minority band gap to a value of 2 eV. Another important

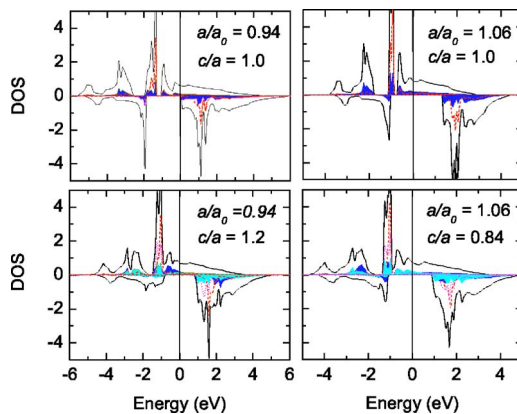


FIG. 4. (Color online) DOS for CrSb under tensile isotropic strain (top) and under biaxial strain with relaxation (bottom). The imposed strain in (001) plane are all 0.06. Solid lines are for spin-up and spin-down total DOS. The filled areas are for d_{xy} , d_{yz} , and $d_{xz}(t_2)$ states and the red dashed lines are for $d_{3z^2-r^2}$, and $d_{x^2-y^2}(e)$ states, respectively. In the bottom figure, light blue refers to d_{xz} and d_{yz} and dark blue to d_{xy} like PDOS, the pink dotted line to $d_{x^2-y^2}$, and dashed orange line to $d_{3z^2-r^2}$.

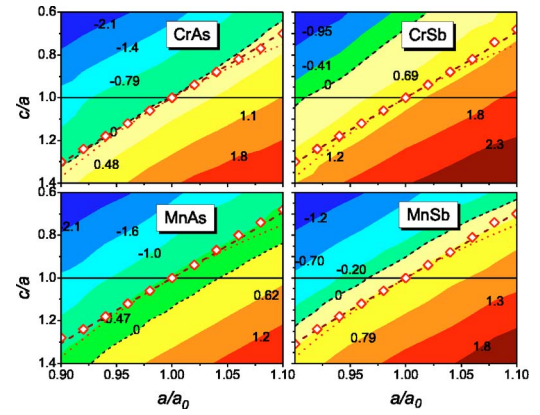


FIG. 5. (Color online) Contour plot for spin-flip gaps for CrAs, CrSb, MnAs, and MnSb. The solid, dotted, and dashed lines show the ideal c/a values for isotropic strain and the strains that keep the volume or the bond length, respectively. The unfilled diamond points show the optimized c/a for different a/a_0 . The dashed line along the border between the green and yellow regions shows the zero spin-flip gap.

feature in the PDOS is that now $d_{xy} \neq d_{xz} = d_{yz}$ and $d_{x^2-y^2} \neq d_{3z^2-r^2}$. The symmetry is reduced from cubic to tetragonal, and we may label these, respectively, b_2 , e , b_1 , and a_1 orbitals using the irreducible representations of the group D_{2d} . The splitting between the two types of b_2 and e PDOS, indicated by light- and dark-blue shading is $\sim 0.1 \pm 0.1$ eV and contributes to the broadening of the d bands. However, the change of the overall spin splitting caused by the volume change is much larger and is the dominant effect.

On the other hand, one may expect that isotropic compression of the lattice constant, while maintaining the ZB structure, will strengthen the interactions between the TM and the neighboring anions and delocalize the d electrons. As a result it will reduce the spin splitting and therefore reduce the spin-flip gap. The half-metallicity could be totally destroyed under sufficient compression. As shown by previous calculations, many TM pnictides and chalcogenides are not half-metallic in the ZB state until a minimum critical lattice constant is reached. However, the relaxation in a biaxially compressed lattice, relative to the ZB equilibrium lattice constant, is in the other direction (see Fig. 2) and, thus, should also have an opposite effect on the electronic structure and half-metallicity. As Fig. 4 shows, the isotropic compression by -6% decreases the spin-flip gap to almost zero. However, with the relaxation along the z direction, this spin-flip gap is found to be 0.9 eV, which is almost the same as for the equilibrium geometry. This indicates that the half-metallicity can be kept even when CrSb is grown on a semiconductor substrate with lattice constant 6% smaller than that of ZB CrSb.

The above results are similar for other TM pnictides and chalcogenides. Figures 5 and 6 show the SF gaps for all the compounds calculated in this work with different a/a_0 and c/a values. The contour lines for SF gaps are generally parallel to each other. For all the compounds, the optimized c/a values are close to the ideal values that keep the bond length. These c/a values go almost parallel with the contour lines of equal SF gaps, indicating that the epitaxially grown Cr or Mn

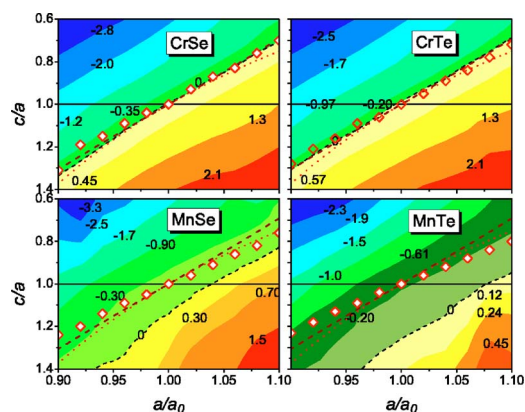


FIG. 6. (Color online) Contour plot for spin-flip gaps for CrSe, CrTe, MnSe, and MnTe. See the caption for Fig. 5 for notations.

pnictides or chalcogenides have intrinsic SF gaps that change only slightly on different semiconductor substrate. This is a result of the fact that the system maintains its bond length under biaxial strain, so that the compounds can be categorized by their intrinsic SF gap. Some compounds are not half metals no matter how large the lattice constant is for the substrate. This includes CrSe, MnAs, MnSe, and MnTe. Some other compounds, such as CrAs and CrTe, are barely half metals, as their SF gaps are very small, although not zero. There are only two clearly half metals, CrSb and MnSb. Their SF gaps are about 0.9 and 0.3 eV.

It is also important to note that the two compounds that show the most robust half-metallic properties are both antimonides. The heavy anions can be expected to exhibit sig-

nificant spin-orbit interaction. It will cause a splitting of the states near the valence band maximum at the Γ point. However, since the Fermi level is ~ 1 eV above the VBM and the minority gap is ~ 2 eV, the splitting of the states near the VBM can hardly change the half metallicity of both systems.

Of course, the above discussions are only for the systems grown on the surface of semiconductors. If the ZB TM pnictides or chalcogenides are formed in the bulk area of semiconductors by clustering or precipitates during the growth of dilute magnetic semiconductors, the strain imposed by the lattice mismatch will be closer to isotropic. As the calculations show, this kind of strain will cost large elastic energies. Therefore the system will likely accommodate strain-relieving defects and dislocations and prevent the high-quality TM pnictide or chalcogenide ZB precipitate to grow.

In this paper we discussed the strain effects on the half-metallicity and the optimum c/a ratios for a given in-plane lattice constant fixed by a substrate assuming that a ZB-like structure is indeed the favored structure. Complementary to our work, a recent study²⁰ also investigated the relative stability of different crystallographic phases under pseudomorphic epitaxial conditions. This places further restrictions on the feasibility of the growth of ZB half-metallic compounds and, in particular, may limit the achievable film thickness.

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