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Half-metallic zinc-blende pnictides in real environments

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Abstract

The structural stability of half-metallic zinc-blende pnictides and the robustness of their half-metallic ferromagnetism in the presence of tetragonal and orthorhombic crystalline deformations are studied using a full-potential linear augmented plane wave method within the density-functional theory. The total energies of zinc-blende MnAs, CrAs, and CrSb are proved to increase with deformation increase, in contrast to those of other zinc-blende half-metallic pnictides, and therefore these three are stable against the deformations but the others are not. This is consistent with the experimental fact that only these three have been fabricated. On the other hand, the half-metallic ferromagnetism of the latter two is proved to be robust enough to survive large crystal deformations. This implies that half-metallic ferromagnetism may be achieved experimentally even in substantially deformed zinc-blende ultrathin films or layers of CrAs and CrSb in real environments.

In order to achieve high-performance electronic devices or basic computer units, it is desirable to use the spin freedom of electrons in addition to their charge freedom [1]. Half-metallic (HM) ferromagnets have attracted much attention because of their high spin polarization [2–6]. It is believed that HM ferromagnetic materials compatible with semiconductors can be used to achieve not only high spin polarization at quite high temperature but also good spin transport crossing interfaces in the nanoscale devices concerned. Replacing the group-III atoms of zinc-blende III–V semiconductors with some transition-metal (TM) atoms, one can obtain binary TM pnictides with zinc-blende (zb) structure. Some of them were proved theoretically to be nearly or true HM ferromagnets at their equilibrium lattice constants [7–10]. In some cases ferromagnetic Curie temperatures up to 700–1000 K, well above room temperature, were shown to be possible [11]. It is believed that with some of these HM ferromagnets one could achieve not only high spin polarization at quite high temperatures but also a long spin coherence length and compatibility with existing semiconductors.

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However, on the experimental side, only three zb TM pnictides, MnAs [12], CrAs [8], and CrSb [13], have been fabricated epitaxially, on some specific substrates, and other zb TM pnictides have not been realized, although much effort has been made in this direction. Furthermore, it was very difficult to fabricate the exact zb phases of those pnictides and what one usually obtained was, instead, some deformed structure [14]. Because the zb phases have been fabricated only in the form of ultrathin films or layers, epitaxially on or between some semiconductors [8, 12, 13], the effects of interfaces and surfaces are certainly very important to the structural properties [15]. Anyway, two fundamental questions need to be answered to allow further exploration in this active field: (1) Why have these three zb pnictides been fabricated experimentally while the others cannot be realized? (2) What happens to their HM ferromagnetism when they are subjected to some crystal deformations and thus become different from the standard zb structure?

In this paper, we shall answer these two questions by systematically investigating the structural stability of zb TM pnictides and their HM ferromagnetism in the presence of crystal deformations. We shall prove that the total energies of zb MnAs, CrAs, and CrSb increase with increasing crystal deformation and thus they are stable, while other zb TM pnictides can become lower in total energy with some deformation and thus are structurally unstable. This explains why the three zb pnictides have been fabricated on some specific substrates while the others cannot be realized. Furthermore, it will be shown that the zb CrAs and CrSb persist as HM ferromagnets even when they are substantially deformed into tetragonal or orthorhombic phases. This is of much interest, because such crystal deformations always exist in ultrathin film or layer samples of them grown epitaxially on or between semiconductors, respectively.

We use the full-potential linear augmented plane wave (FLAPW) method within the density-functional theory [16], as implemented in the Vienna WIEN2k package [17]. The generalized gradient approximation (GGA) [18] is used for the exchange–correlation potential. The full relativistic effect is taken into account for core states but the scalar approximation is used for the others, with the spin–orbit coupling neglected. We use the parameters $R_{\mathrm{mt}}\ K_{\max} = 8.5$ and $l_{\max} = 10$. 3000 k points in the first Brillouin zones are used for deformation-free calculations but 8000–12 000 k points are used when calculating deformed structures. The radii of the muffin tins are adjusted so as to achieve the best accuracy of the self-consistent calculations. A strict convergence standard is used for all our self-consistent calculations.

zb MnAs, CrAs, and CrSb were fabricated experimentally, but their experimental lattice constants are not available [8, 12, 13]. For the MnAs the lattice constant was obtained by extrapolating those of the dilute magnetic semiconductors $Ga_{1-x}Mn_xAs$ with $0.01 < x < 0.07$ [12], and thus is not reliable because the x used is too small. For the zb phase, its theoretical equilibrium lattice constant is obtained by optimizing its total energy against different volumes. The equilibrium lattice constants of the three zb pnictides are 5.717, 5.659, and 6.138 Å, respectively, larger than the 5.6533 Å for GaAs. Their energy bands and density of states (DOS) can be calculated with the equilibrium lattice constants. The HM gap E_{g}, the key parameter, for a HM ferromagnet is defined as the smaller of E_{v} and E_{c}, where $-E_{\mathrm{v}}$ is the top of the valence band from the Fermi level and E_{c} the bottom of the conduction band from the Fermi level. If $E_{\mathrm{g}} < 0$, we need to set $E_{\mathrm{g}} = 0$ because a negative E_{g} essentially means a zero HM gap. A positive E_{g} is necessary for a true HM ferromagnet. The MnAs has $E_{\mathrm{g}} = 0$; therefore it is not truly HM. The CrAs and CrSb have quite large HM gaps: 0.46 and 0.77 eV at their equilibrium lattice constants [9, 10]. For the NiAs phase the two equilibrium lattice constants can be obtained by first optimizing the volume in terms of total energy and then optimizing their ratio. The metastable energy E_{t} of the zb phase is defined as the difference of its minimal total energy per formula unit and that of the ground-state NiAs phase. The

Table 1. The theoretical equilibrium lattice constants a_{eq}, moments m_{eq}, HM gaps E_{geq}, metastable energies E_t, and shear moduli C' and the relative volume changes $\Delta v_r = (V - V_{eq})/V_{eq}$, at which the HM gap E_{geq} is still positive, for the four zb TM pnictides.

Name	a_{eq} (Å)	m_{eq} (μ_B)	E_{geq} (eV)	E_t (eV)	C' (GPa)	Δv_r (%)
MnAs	5.717	3.91	—	0.9	∼3	+5∼
MnSb	6.166	4	0.15	0.9	—	−6 to +12
CrAs	5.659	3	0.46	0.9	5	−12 to +27
CrSb	6.138	3	0.77	1.1	∼1	−20 to +60

equilibrium lattice constants a_{eq}, moments m_{eq}, HM gaps E_{geq}, and metastable energies E_t of all the HM zb pnictides (including the nearly HM MnAs) are presented in table 1. The bismuth pnictides are not included because their HM property is destroyed by their strong spin–orbit effect [19]. The metastable energies of all the zb pnictides are higher than 0.9 eV.

We now address the first question. Since the volumes of the zb pnictides have been optimized, there are only two freedoms for deformations: tetragonal and rhombohedral deformations with the volume fixed. Total energies of the deformed zb pnictides as functions of deformation parameters need to be calculated to answer the question. A zb pnictide is thought to be stable only if its total energy always increases with deformation increase. The zb CrAs has been proved to be stable against crystal deformations in this way [20] but the zb MnBi and MnSb were proved to be unstable [21]. In the upper panel of figure 1 we present the total energies of the zb CrAs, CrSb, and MnAs as functions of the lattice constant ratio c/a, where c is the lattice constant along the z direction and a that along the x or y direction. For this kind of deformation, the volume $V = a^2c$ is kept the same as that of the exact equilibrium zb structure [22]. The zb CrAs is best as regards stability, but the zb MnAs and CrSb both are still stable. The shear moduli C' of all the three stable zb pnictides are presented in table 1. It is obvious that the zb CrAs, MnAs, and CrSb are very soft, but still stable against the deformations. They are, as expected, the three zb pnictide phases that have already been fabricated experimentally [8, 12, 13]. In contrast, the other HM zb pnictides cannot be realized experimentally because they cannot exist with any deformation and always transform to NiAs phases, the corresponding ground-state phases, although great efforts have been made to realize them [23]. This therefore explains why the three HM zb pnictides have been fabricated, but the others have not.

Then we turn to the second question. Epitaxy is a powerful method for fabricating these materials. With this method, the HM zb pnictides, as thin films or layers, are often grown epitaxially on or between some specific semiconductors [8, 12–14, 24, 25]. The zb crystalline structures should be realized in their inner parts when their thicknesses are large enough, but nowhere when their thicknesses are very small. It is unavoidable that the samples are subject to some crystalline deformations due to the surface or interfacial effects. Therefore, it is of real interest to determine whether the HM ferromagnetism is robust enough to survive such crystal deformations. As shown in the lower panel of figure 1, the moment of the zb MnAs is enhanced a little when it is subject to volume-conserving tetragonal deformations, but the moments of the zb CrAs and CrSb persist as 3 μ_B with the lattice constant ratio c/a changes by up to −30% and +25%. The spin-dependent DOS of the zb CrAs, CrSb, and MnAs with c/a being 0.85 and 1.15 are presented in figure 2. It is very clear that their spin-dependent DOS around their Fermi levels and thus the HM gaps of the CrAs and CrSb change very little with such large deformations. The corresponding spin-dependent band structures are shown in figure 3. There are some changes in the band structures, but the change is not substantial. The projected DOS of the

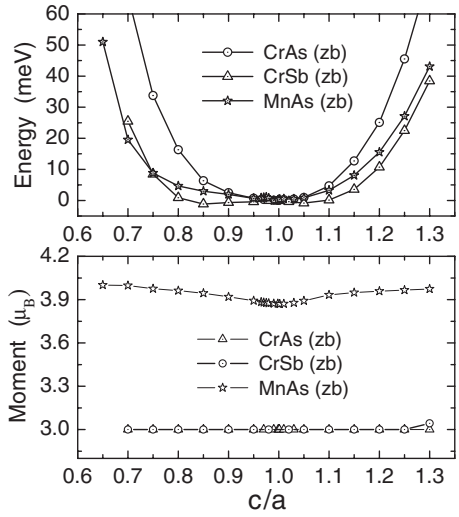

Figure 1. Total energies (upper panel) and magnetic moments (lower panel) of the three tetragonally deformed zb pnictides as functions of the ratio c/a of the lattice constants, where c is the lattice constant along the z direction and a that along the x or y direction. The three zb phases are stable against the crystal deformation within the calculation accuracy. The moments of the CrAs and CrSb remain 3 μ_B with the c/a ratio being in between -30% and +25%.

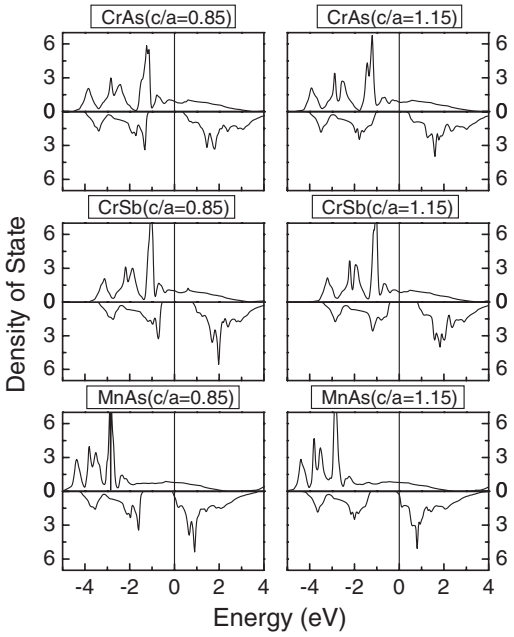

Figure 2. The spin-dependent DOS of the three zb pnictides subject to the volume-conserving tetragonal deformations. The first row of panels is for CrAs, the second row for CrSb, and the last row for MnAs. The DOS for the two c/a ratios, 0.85 (left column of panels) and 1.15 (right column), are presented. The upper part of every panel shows the majority-spin DOS and the lower part the minority-spin DOS.

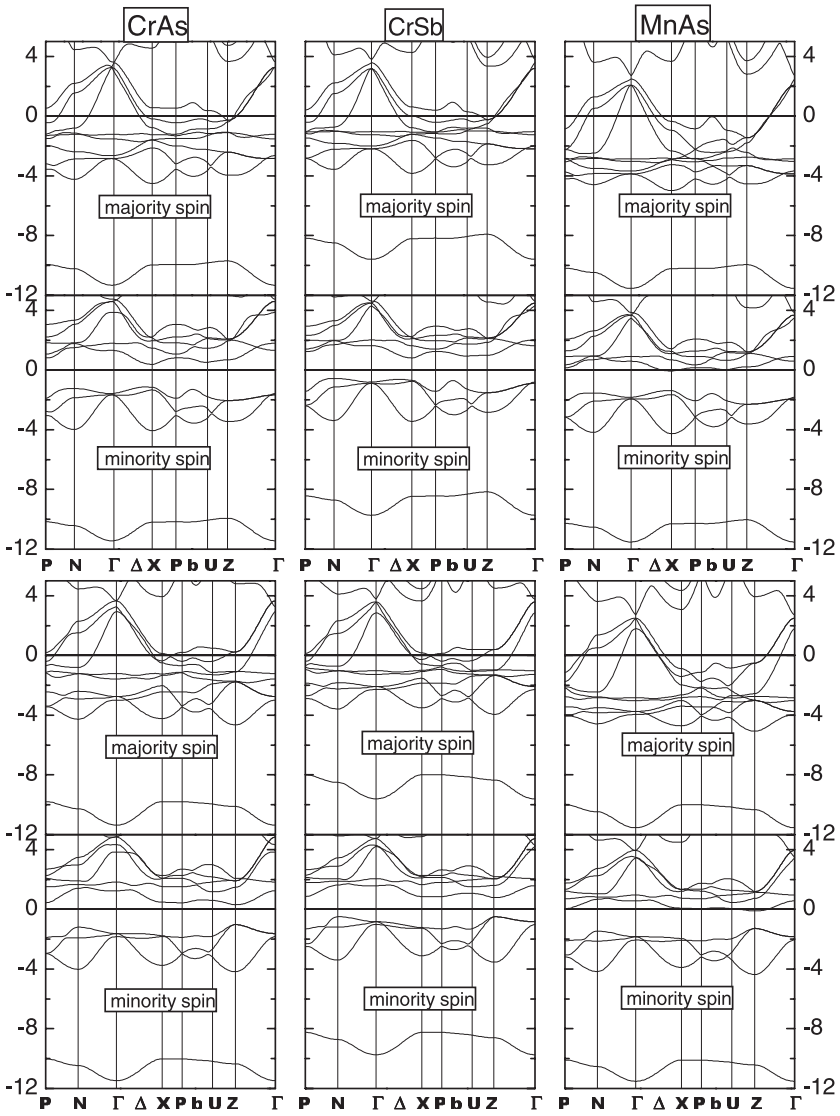

Figure 3. The spin-dependent bands of the three zb pnictides subject to the volume-conserving tetragonal deformations. The first row of panels is for CrAs, the second row for CrSb, and the last row for MnAs. The DOS for the two c/a ratios, 0.85 (left column of panels) and 1.15 (right column), are presented. The upper part of every panel shows the majority-spin DOS and the lower part the minority-spin DOS.

zb CrAs and CrSb subject to volume-conserving orthorhombic deformations $a/b = 1.16$ and 1.30 are presented in figure 4, with c being fixed at the equilibrium lattice constant a_{eq}, where a, b, and c are the lattice constants along the x, y, and z directions, respectively. The only clear change is that the top of the minority-spin valence bands moves upward with the parameter a/b increasing. As a result, the HM gaps will be reduced on increasing the orthorhombic deformations. However, they persist as HM ferromagnetic even with $a/b = 1.32$. The band structures for the same structural parameters are shown in figure 5. For $a/b = 1.16$, there

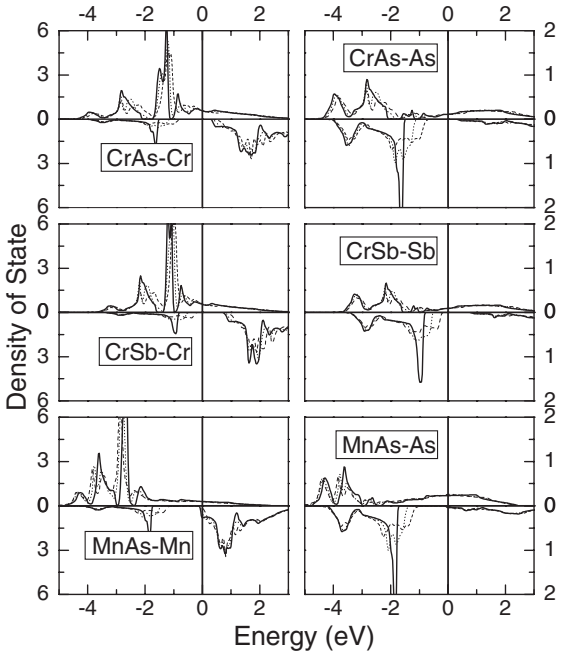

Figure 4. The projected spin-dependent DOS of the zb CrAs (upper panels) and CrSb (lower panels) subject to the volume-conserving orthorhombic deformations $a/b = 1.16$ (dotted curve) and 1.30 (dashed curve). The upper part of every panel shows the majority-spin DOS and the lower part the minority-spin DOS.

are no clear changes. For $a/b = 1.30$, there are no clear changes in the case of the CrAs and MnAs, but the filled minority-spin bands just below the Fermi level move upward, almost touching the Fermi level, in the case of the CrSb. Therefore, at least in the cases of the zb CrAs, CrSb, and MnAs, the HM or nearly HM ferromagnetism is indeed robust enough to survive even large volume-conserving deformations.

What do these theoretical results imply for experiment? Various effects of surfaces and interfaces can drive the lattice constants from the equilibrium ones or make the crystal structures deform from the standard zb structure. It has been shown, in table 1, that the HM zb CrAs and CrSb are robust enough to survive real volume deviations, and the nearly HM zb MnAs even becomes a true HM ferromagnet when its volume is expanded by approximately 5%. Because the bulk moduli B of these zb pnictides are much larger than their shear moduli C', the tetragonal crystal deformations are much more favourable in energy than the isotropic volume deviations. The zb pnictides may transform into tetragonal or orthorhombic phases because of the effects of surfaces and interfaces. However, their HM ferromagnetism will still be retained, even in the presence of large crystal deformations. With these points in mind, the experimental results [8, 12, 13], especially the latest result on deformed CrAs films [14], can be understood.

In summary, we have investigated the structural stability of HM zb pnictides and the robustness of their HM ferromagnetism in the presence of crystal deformations by using an accurate first-principles density-functional method. zb MnAs, CrAs, and CrSb are proved to become higher in total energy with increasing volume-conserving deformation, but the other zb HM pnictides can become lower in total energy with tetragonal crystal deformations.

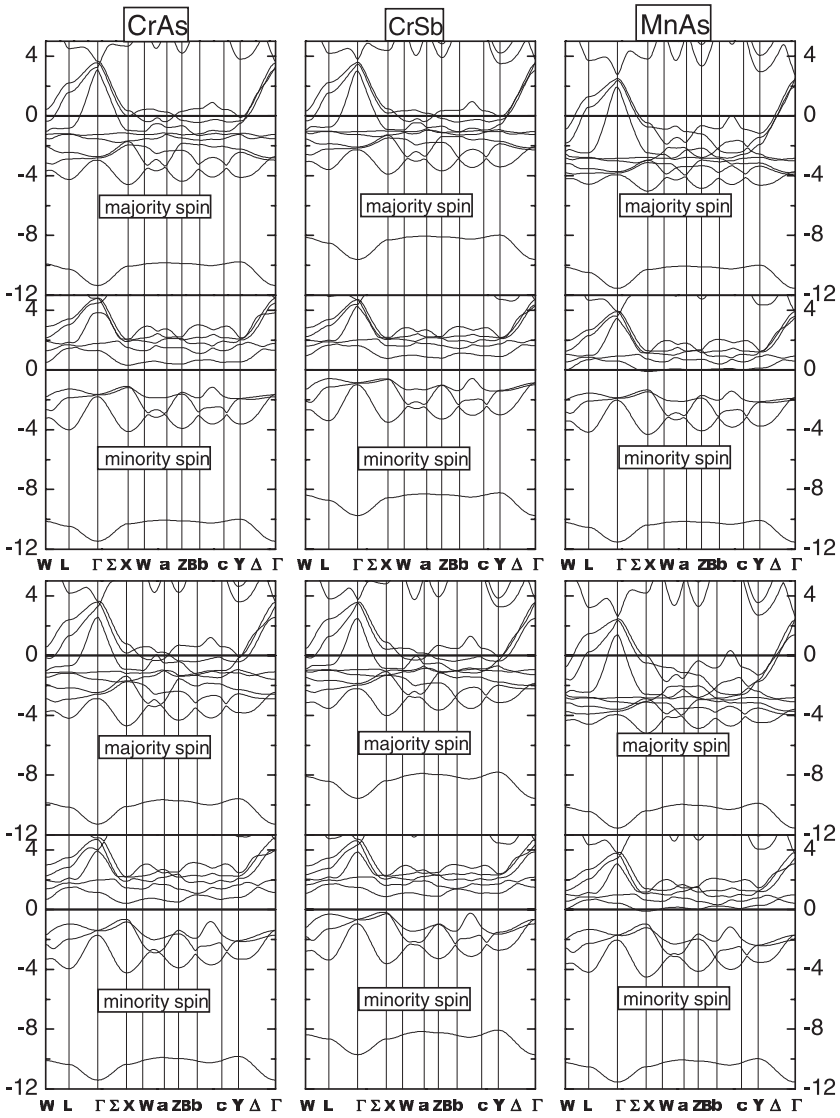

Figure 5. The projected spin-dependent bands of the zb CrAs (upper panels) and CrSb (lower panels) subject to the volume-conserving orthorhombic deformations $a/b = 1.16$ (dotted curve) and 1.30 (dashed curve). The upper part of every panel shows the majority-spin DOS and the lower part the minority-spin DOS.

Therefore, the three zb pnictides are stable against crystal deformations but the others are not. This is consistent with the experimental fact that only these three pnictides have been fabricated. On the other hand, the spin-dependent densities of states around the Fermi levels of the three zb pnictides are proved to remain almost unchanged even with large tetragonal deformations. HM gaps of zb CrAs and CrSb remain nonzero even in the presence of large crystal deformations. This implies that HM ferromagnetism can be achieved experimentally even in substantially deformed ultrathin zb films or layers of them in real environments.

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