

Defects in CrAs and related compounds as a route to half-metallic ferrimagnetism

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Half-metallic ferrimagnetism is crucial for spintronic applications with respect to ferromagnets due to the lower stray fields created by these materials. Studying the effect of defects in CrAs and related transition-metal chalcogenides and pnictides crystallizing in the zinc-blende structure, we reveal that excess of the transition-metal atoms leads to half-metallic ferrimagnetism. The surplus of these atoms are antiferromagnetically coupled to the transition-metal atoms at the perfect lattice sites. The needed condition to achieve half-metallic ferrimagnetism is to prevent the migration of the *sp* atoms to other sites and atomic swaps.

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The scientific research on spintronic materials has exploded during recent years.¹ Half-metallic ferromagnets like Heusler alloys^{2,3} (NiMnSb) or some oxides⁴ (CrO₂, Fe₃O₄, LSMO) play a central role since they can be used to maximize the efficiency of such devices due the almost perfect spin polarization at the Fermi level. The ideal case for applications would be a half-metallic antiferromagnet (also known as a fully compensated ferrimagnet) like the hypothetical Heusler compound CrMnSb. Such a compound would be a perfectly stable spin-polarized electrode in a junction device. Moreover, if used as a tip in a spin-polarized scanning tunneling microscope, it would not give rise to stray flux, and hence would not distort the domain structure of the soft-magnetic systems to be studied. In the absence of half-metallic antiferromagnets, the study of ferrimagnets becomes important. Van Leuken and de Groot have shown that doping of the semiconductor FeVSb results in a half-metallic ferrimagnet.⁵ Also some other Heusler compounds like FeMnSb (Ref. 3) and Mn₂VAl (Refs. 6 and 7) are predicted to be half-metallic ferrimagnets but no concrete experimental results exist. Recently Akai and Ogura have proposed another route to half-metallic antiferromagnetism based on the doping of diluted magnetic semiconductors.⁸

Since the discovery of half-metallic ferromagnetism in thin films of CrAs in the zinc-blende structure by Akinaga and co-workers in 2000,⁹ the transition-metal chalcogenides and pnictides have attracted considerable attention. Experimentally several such compounds have been grown in thin films, multilayers, or dot structures.¹⁰ A large number of *ab initio* calculations have also contributed to the understanding of the basic physics of these alloys.^{11–14} The gap in the minority-spin band arises from the hybridization between the *p* states of the *sp* atom and the triple-degenerate *t*_{2g} states of the transition metal.¹¹ As a result the total spin moment *M*_{*t*} follows the Slater-Pauling (SP) behavior, being equal in μ_B to *Z*_{*t*}–8 where *Z*_{*t*} is the total number of valence electrons in the unit cell.¹¹ Some of the most recent results include the study of the exchange bias in ferro-/antiferromagnetic interfaces,¹⁵ the study of the stability of the zinc-blende structure,¹⁶ and the study of dynamical correlations.¹⁷

States at the interfaces of these compounds with semicon-

ductors seem not to affect the half metallicity.¹⁸ On the other hand temperature effects (nonquasiparticle excitations and spin wave excitations) play a more crucial role.¹⁹ Also the appearance of defects and disorder can affect the half metallicity. Our initial aim in this paper is to study their consequences on the electronic and magnetic properties of CrAs and related compounds in the zinc-blende (ZB) structure. To have a global view of the behavior of defects, we have included six different compounds in our study: CrAs and its isovalent CrSb, CrSe and CrTe with one valence electron more than CrAs, and finally VAs and MnAs. The electronic structure calculations are performed using the full-potential nonorthogonal local-orbital minimum-basis band structure scheme, and disorder has been simulated using the coherent potential approximation.²⁰ We have used the theoretical equilibrium lattice constants for which the perfect compounds are half-metallic ferromagnets.²¹ Investigating the properties of antisites in these alloys where there is an excess of either the transition metal or the *sp* atom, e.g., Cr_{1+x}As_{1-x}, we show that in most cases the half-metallic ferromagnetism is destroyed, but the excess of Cr leads to the even more interesting half-metallic ferrimagnets. A study of atomic swaps as well as Cr antisites at the vacant sites reveals that they destroy completely the half metallicity.

Prior to the presentation of our results we have to briefly describe the zinc-blende structure. The unit cell is that of a fcc lattice with four atoms per unit cell (for a representation of the structure see Fig. 1 in Ref. 12). The *A* site located at (0 0 0) in Wyckoff coordinates is occupied by the Cr atoms in the case of CrAs and the *B* site (0.25 0.25 0.25) by As atoms. The *C* site at (0.5 0.5 0.5) and *D* site at (0.75 0.75 0.75) are vacant and have the same symmetry as the *A* and *B* sites, respectively, rotated by 90°. The need to introduce the vacant sites in the description of the ZB structure arises from possible migration of Cr atoms toward these sites.

The first case of possible defects under study is when either Cr or As atoms migrate to antisite positions occupied by the other chemical element without disturbing the vacant sites. In Fig. 1 we have gathered the total spin moment in the unit cell as a function of the concentration for all six studied compounds. In the case of Cr_{1+x}As_{1-x} positive values of the

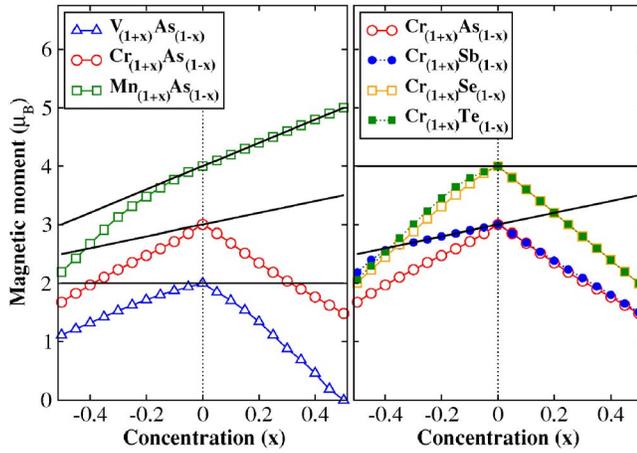


FIG. 1. (Color online) Total spin magnetic moment as a function of the concentration x for the studied $T_{1+x}Z_{1-x}$ compounds. Note that positive values of x correspond to excess of the transition-metal atom (T) and negative values of x to excess of the sp atom (Z). The solid black lines represent the Slater-Pauling behavior for the ideal compounds, which they cross at $x=0$.

concentration x correspond to Cr excess and thus the creation of Cr antisites, and negative values of x to the creation of As antisites. We have used a step of 0.05 and scanned all the region from $x=-0.5$ up to $x=0.5$. Comparing our results with the ideal SP behavior of the ideal half-metallic ferromagnets represented by the solid lines, we find that, except for the case of Mn antisites in MnAs and Sb antisites in CrSb, the total spin moment is far away from the ideal values, a clear sign that half-metallic ferromagnetism is lost.

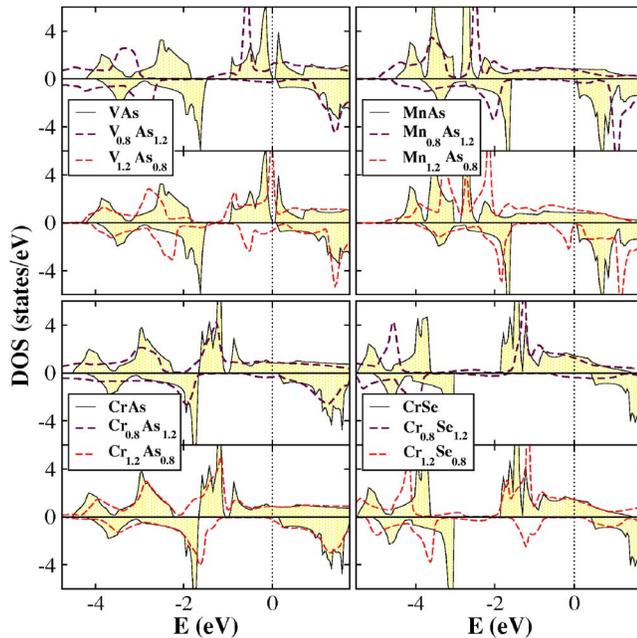


FIG. 2. (Color online) Density of states (DOS) for the studied compounds. Positive DOS values correspond to the majority-spin electrons and negative to the minority ones. The Fermi level is scaled to the zero of the energy axis. CrSb and CrTe compounds present DOSs similar to those of CrAs and CrSe, respectively, with the Fermi level near the middle of the gap.

To understand this behavior we have drawn in Fig. 2 the total density of states DOS for some selected cases and in Table I we have gathered the spin magnetic moments for two different values of the concentration x . When there is an excess of the sp atom (negative values of x) the effect on the electronic structure is milder. Some of the p states that were located at the nonoccupied minority-spin antibonding states move lower in energy due to the change in the Coulomb repulsion and are now crossing the Fermi level. These states are present in all cases. For CrSb where the Fermi level is deep in the gap, the compound keeps its half metallicity up to about $x=-0.4$. The impurity sp atoms at the antisite positions have very small spin moments parallel to the ones of the transition-metal atoms.

The case of transition-metal antisites at the B site occupied by the sp atoms is more interesting. In CrAs each Cr atom in the A sublattice has four As atoms as first neighbors. When we create an excess of Cr atoms, these impurities take the place of As atoms occupying the B sublattice of the ZB structure. Cr (Mn) atoms are well known to demonstrate ferromagnetic or antiferromagnetic coupling depending on the distance between neighboring Cr (Mn) atoms. The distance for the transition from antiferromagnetic to ferromagnetic coupling is smaller for Mn than for Cr. A similar effect but less intense is also present for the V atoms although V has a less pronounced magnetic behavior than Cr and Mn.

When we create an excess of Mn in MnAs, the Mn impurities at the B site have ferromagnetic coupling between them since the intrasublattice interactions are positive as was discussed in the paper by Sařiođlu *et al.* on the exchange interactions in these compounds.²² The two sublattices are ferromagnetically coupled and as shown in Table I all Mn atoms have positive spin moments. Mn impurity atoms at B sites have a tetrahedral symmetry with four Mn atoms at the A sites as first neighbors. Thus the $d-d$ hybridization for Mn impurities is larger and the minority double-degenerate e_g states are occupied (there is a new minority peak just below the Fermi level in Fig. 2) while all five majority d states are occupied, showing a spin moment of around $3\mu_B$. On the other hand Mn at the perfect sites have now both As and Mn atoms as first neighbors, the hybridization effects are larger, and their spin moment is smaller with respect to the perfect compound. Thus the exchange interactions in MnAs are such that, as shown in Fig. 1, the half-metallic ferromagnetism is conserved for the case of Mn antisites at the sublattice occupied by As.

The Cr impurity atoms at the B sites, in contrast to the Mn atoms, are antiferromagnetically coupled to the Cr atoms at the A sites due to the small distance between the sites at the A and B sublattices. This phenomenon destroys the ferromagnetism but not the half metallicity. Shirai and collaborators have also shown antiferromagnetic coupling in the case of atomic swaps in CrAs.¹⁴ The d states of the Cr impurities are well localized and the minority-spin (now minority is defined by Cr atoms at the A site) gap still exists. This is illustrated in Fig. 3 where we present the Cr-resolved DOS. In the upper left panel is the perfect CrSe case and in the upper right panel the case of Cr antisites at the B sublattice ($\text{Cr}_{1.1}\text{Se}_{0.9}$ alloy). The Cr impurity atoms in $\text{Cr}_{1.1}\text{Se}_{0.9}$ have all five bonding minority states occupied as well as the ma-

TABLE I. Total and atom-resolved spin magnetic moments for the compounds under study. As impurity we denote the atoms that are located at antisite positions. Note that the atomic moments have been scaled to one atom.

Compound	x	Total	T (Cr, V, Mn)	Z (As, Sb, Se, Te)	T impurity
$\text{Cr}_{1+x}\text{As}_{1-x}$	0	3.0	3.4	-0.4	
	0.1	2.7	3.3	-0.4	-2.8
	0.2	2.4	3.2	-0.4	-2.9
$\text{Cr}_{1+x}\text{Sb}_{1-x}$	0	3.0	3.5	-0.5	
	0.1	2.7	3.5	-0.5	-3.3
	0.2	2.4	3.5	-0.5	-3.4
$\text{Cr}_{1+x}\text{Se}_{1-x}$	0	4.0	4.2	-0.2	
	0.1	3.6	4.1	-0.2	-3.1
	0.2	3.2	4.0	-0.2	-3.1
$\text{Cr}_{1+x}\text{Te}_{1-x}$	0	4.0	4.2	-0.2	
	0.1	3.6	4.1	-0.2	-3.3
	0.2	3.2	4.0	-0.2	-3.3
$\text{V}_{1+x}\text{As}_{1-x}$	0	2.0	2.3	-0.3	
	0.1	1.7	2.0	-0.2	-1.1
	0.2	1.3	1.7	-0.2	-1.1
$\text{Mn}_{1+x}\text{As}_{1-x}$	0	4.0	4.3	-0.3	
	0.1	4.2	4.2	-0.3	3.3
	0.2	4.4	4.0	-0.4	3.3

urity e_g states and thus spin magnetic moments of around $-3\mu_B$. The minority bonding and antibonding states are separated by a gap, keeping the half-metallic character of the compound. As we increase the concentration of Cr impurities

at the B sites the unoccupied minority states of the Cr impurities start forming a broader band and they approach the Fermi level. No general statement can be drawn from the total spin magnetic moments since half-metallic ferrimagnets do not follow the SP behavior and we have to look at the total DOS for several high values of the concentration x to

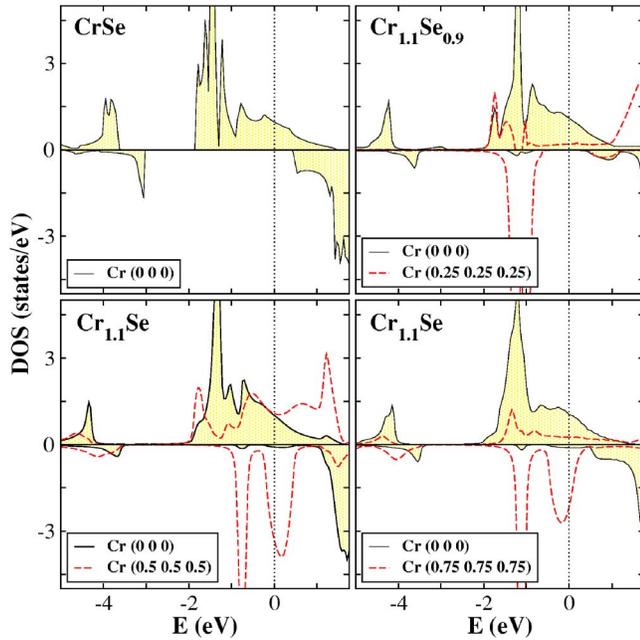


FIG. 3. (Color online) Cr-resolved DOS for the ideal CrSe compound (upper left panel), for Cr at the ideal A site and Cr impurity at a B site occupied by Se in the perfect compound in the case of $\text{Cr}_{1.1}\text{Se}_{0.9}$ (upper right panel). In the lower panels the case of Cr antisites at vacant C (left) and D (right) sites.

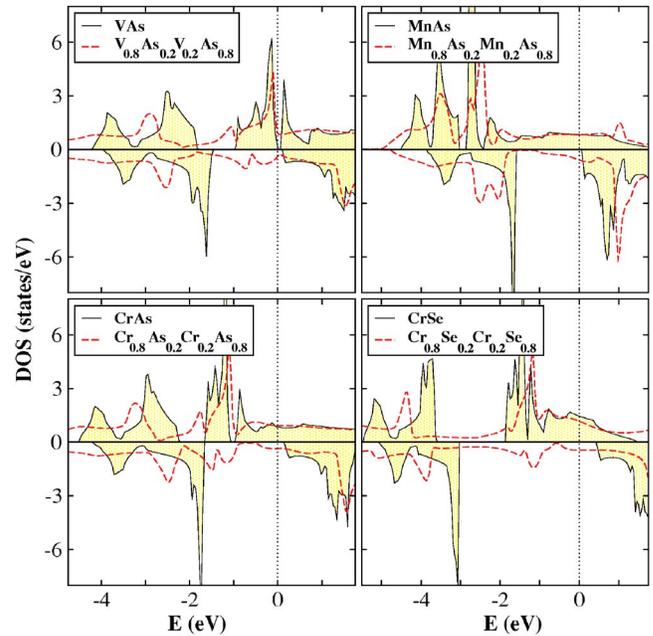


FIG. 4. (Color online) DOS for the case of atomic swaps where 20% ($x=0.2$) of the transition-metal and sp atoms have exchanged sites.

identify where the half metallicity is lost for these compounds; e.g., as shown in Fig. 2 for CrAs for $x=0.2$ the half metallicity is lost while for CrSe the case for $x=0.2$ is half metallic. Our investigation showed that the Cr compounds are half metallic up to concentrations $x=0.15$ for CrAs, 0.2 for CrSb, 0.5 for CrSe, and 0.5 for CrTe. We should also note that the width of the gap is now much smaller since impurity states occur in the low-energy part of the gap.

For the VAs compound, shown in Fig. 2, the V impurity atoms are antiferromagnetically coupled to the V atoms at the ideal sites and the physics of these systems is similar to that of the Cr-based compounds. But even for $x=0.05$ the impurity states cross the Fermi level and although a gap exists the half metallicity is lost.

We have also studied the case of the creation of Cr antisites at the vacant sites (lower panels in Fig. 3) and atomic swaps (Fig. 4). Cr antisites at the vacant sites completely destroy half metallicity since the Fermi level now crosses the minority triple-degenerate t_{2g} states. But these antisites are expected to have high formation energies since the Fermi level is now located at a peak of the minority DOS. Atomic swaps mean that also sp atoms move to the A sites and the effect is even more intense than in the case of simple sp antisites presented above. Even for small values correspond-

ing to the dilute limit the impurity states destroy completely the minority-spin gap. The intensity of these states increases rapidly with the percentage of swaps and the total spin moment decreases faster than in the case of simple sp antisites.

We have studied the effect of antisites and atomic swaps in the case of transition-metal pnictides and chalcogenides crystallizing in the ZB structure. sp antisites and atomic swaps destroy the half metallicity. Mn antisites in MnAs keep the half-metallic ferromagnetic character of the perfect compounds. Cr impurities in the case of antisites at the sublattice occupied by the sp atoms couple antiferromagnetically to the existing Cr atoms at the ideal sites and destroy ferromagnetism. But these compounds stay half metallic for a large concentration of antisites. Cr antisites at the vacant sites on the other hand completely destroy half metallicity. Thus we have presented an alternative way to create half-metallic ferrimagnets for realistic spintronic application by simply introducing Cr antisites in existing experimental structures based on CrAs or CrSb. It is an open experimental question if the zinc-blende structure for such a concentration of defects is feasible as either thin films or multilayers with semiconductors. We expect these results to stimulate further interest in both the theoretical and experimental research in the emerging field of magnetoelectronics.

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