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

I. Galanakis1, K. Özdoğan2, E. Şaşoglu3,4,‡ and B. Aktaş2
1 Department of Materials Science, School of Natural Sciences, University of Patras, GR-26504 Patra, Greece
2 Department of Physics, Gebze Institute of Technology, Gebze, 41400, Kocaeli, Turkey
3 Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
4 Fatih University, Physics Department, 34500, Büyükçekmece, İstanbul, Turkey
(Dated: November 4, 2018)

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 the excess of the transition-metal atoms leads to half-metallic ferrimagnetism. The surplus of these atoms are antiferromagnetically coupled to the transition-metal atoms sitting 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 the atomic swaps.

PACS numbers: 75.47.Np, 75.50.Cc, 75.30.Et

The scientific research on the spintronic materials has exploded during the last years [1]. Half-metallic ferromagnets like Heusler alloys (NiMnSb [2, 3]) or some oxides (CrO2, Fe3O4, LSMO [4]) 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 fully-compensated ferrimagnet) like CrMnSb, where the majority spin and minority spin densities of states are not identical, as for common antiferromagnets. Such a compound would be a perfectly stable spin-polarized electrode in a junction device. And moreover if used as a tip in a spin-polarized STM, it would not give rise to stray flux, and hence would not distort the domain structure of the soft-magnetic systems to be studied. Unfortunately, CrMnSb does not crystallize in the structure which is theoretically predicted to present half-metallicity. 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 [6] and Mn2VAl [6, 7] are predicted to be half-metallic ferrimagnets but no concrete experimental results exist.

Since the discovery of half-metallic ferromagnetism in thin films of CrAs in the zinc-blende structure by the group of Akinaga in 2000 [8], the transition-metal chalcogenides and pnictides have attracted considerable attention. Experimentally several such compounds have been grown in thin-films, multilayers or dots structures [9]. A large number of ab-initio calculations have also contributed to the understanding of the basic physics of these alloys [10, 11, 12]. The gap in the minority-spin band arises from the hybridization between the p-states of the sp atom and the triple-degenerated t2g states of the transition-metal [10]. As a result the total spin-moment, \( M_s \), follows the Slater-Pauling (SP) behavior being equal in \( \mu_B \) to \( Z_e - 8 \) where \( Z_e \) the total number of valence electrons in the unit cell [12]. Some of the most recent results include the study of the exchange bias in ferro/antiferromagnetic interfaces [12], the study of the stability of the zinc-blende structure [13], and the study of dynamical correlations [14].

States at the interfaces of these compounds with semiconductors seem not to affect the half-metallicity [13]. On the other hand temperature effects play a more crucial role [10]. At low temperatures the interaction of the electrons with magnons leads to non-quasiparticle excitations in the minority gap above the Fermi level [17], while at higher temperatures spin wave excitations lead to new states in the gap above and below the Fermi level [18]. Except interface states and temperature, the third main effect which can destroy half-metallicity is the appearance of defects and disorder. Our initial aim in this manuscript 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 isovalence 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 (FPLO) and disorder has been simulated using the coherent potential approximation [15]. We have used the theoretical equilibrium lattice constants for which the perfect compounds are half-metallic ferromagnets [20]. Investigating the properties of antisites in these alloys where there is an excess of either the transition metal or the sp atom, e.g. \( \text{Cr}_{1+\delta}\text{As}_{1-\delta} \), we show that in most cases the half-metallic ferrimagnetism 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-

‡ E. Şaşoglu and B. Aktaş contributed equally to this work.
metallicity.

Prior to the presentation of our results we have to shortly describe the zinc-blende structure (zb). The unit cell is that of a f.c.c. lattice with four atoms per unit cell. The A site located at (000) 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 towards these sites.

The first case of possible defects under study is when either Cr or As atoms migrate at 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 CrAs each positive values of the concentration x correspond to Cr-excess and thus the creation of Cr antisites while 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.

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 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.

To understand this behavior we have drawn in Fig. 2 the total 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 which were located at the non-occupied 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 sitting in the A-sublattice has four As atoms as first neighbors. When we create an excess of Mn atoms in MnAs, the Mn 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 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 sitting at the B-site are ferromagnetically coupled between them since the intra-sublattice interactions are positive as was discussed in the paper by Sasoçoğlu et al. on the exchange interactions in these compounds [21]. 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 tetra-

![FIG. 1: (Color online) Total spin magnetic moment as a function of the concentration x for the studied T_{1-x}Z_{x} compounds. Note that positive values of x correspond to excess of the transition metal atom (T) while 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.](image)

| Compound          | x | Total T (Cr,V,Mn) Z (As,Sb,Se,Te) T imp |
|-------------------|---|---------------------------------------|
| Cr_{1+x}As_{1-x}  | 0 | 3.0 3.4                                |
|                   | 0.1| 2.7 3.3                               |
|                   | 0.2| 2.4 3.2                               |
| Cr_{1+x}Sb_{1-x}  | 0 | 3.0 3.5                                |
|                   | 0.1| 2.7 3.5                               |
|                   | 0.2| 2.4 3.5                               |
| Cr_{1+x}Se_{1-x}  | 0 | 4.0 4.2                                |
|                   | 0.1| 3.6 4.1                               |
|                   | 0.2| 3.2 4.0                               |
| Cr_{1+x}Te_{1-x}  | 0 | 4.0 4.2                                |
|                   | 0.1| 3.6 4.1                               |
|                   | 0.2| 3.2 4.0                               |
| V_{1+x}As_{1-x}   | 0 | 2.0 2.3                                |
|                   | 0.1| 1.7 2.0                               |
|                   | 0.2| 1.3 1.7                               |
| Mn_{1+x}As_{1-x}  | 0 | 4.0 4.3                                |
|                   | 0.1| 4.2 4.2                               |
|                   | 0.2| 4.4 4.0                               |
hedral 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-degenerated $e_g$ states are occupied (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. 3 the half-metallic ferromagnetism is conserved for the case of Mn antisites at the A site and the physics of these systems is similar to CrAs and CrSe, respectively, with the Fermi level near the middle of the gap.

The Cr impurity atoms at the B sites, contrary 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. 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 (Cr$_{1.1}$Se$_{0.9}$ alloy). The Cr impurity atoms in Cr$_{1.1}$Se$_{0.9}$ have all five bonding minority states occupied as well as the majority $e_g$ 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 in 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 the total DOS for several dense values of the concentration $x$ to identify where the half-metallicity is lost for these compounds; e.g. as shown in Fig. 3 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 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 panel is Fig. 3) and the atomic swaps (Fig. 4). Cr antisites at the vacant sites...
Cr-impurities in the case of antisites at the sublattice off-metallicity. Mn antisites in MnAs keep the half-metallic sp-chalcogenides crystallizing in the zb structure. The swaps in the case of the transition-metal pnictides and completely destroy half-metallicity since the Fermi level have exchanged sites. 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. Most of these states are 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 corresponding to the dilute limit the impurity states destroy completely the minority-spin gap. We have studied the effect of antisites and atomic swaps destroy the half-metallicity. Mn antisites in MnAs keep the half-metallic sp-chalcogenides crystallizing in the zb structure. The swaps in the case of the transition-metal pnictides and completely destroy half-metallicity since the Fermi level have exchanged sites. But these antisites are expected to have high formation energies since 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 corresponding 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 the transition-metal pnictides and chalcogenides crystallizing in the zb structure. The sp antisites and the atomic swaps destroy the half-metallicity. Mn antisites in MnAs keep the half-metallic ferromagnetic character of the perfect compounds. The 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 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. We expect these results to stimulate further interest in both the theoretical and experimental research in the emerg-
CrSe (0.582 nm), CrSb (0.606 nm), and CrTe (0.610 nm). [21] E. Şaşoğlu, I. Galanakis, L. M. Sandratskii and P. Bruno, J. Phys.: Condens. Matter 17, 3915 (2005).