

## Surface half-metallicity of CrAs in the zinc-blende structure

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The development of new techniques such as the molecular beam epitaxy have enabled the growth of thin films of materials presenting novel properties. Recently it was made possible to grow a CrAs thin-film in the zinc blende structure. In this contribution, the full-potential screened KKR method is used to study the electronic and magnetic properties of bulk CrAs in this phase as well as the Cr and As terminated (001) surfaces. Bulk CrAs is found to be a half-metallic ferromagnet for all three GaAs, AlAs and InAs experimental lattice constants with a total spin magnetic moment of  $3\mu_B$ . The Cr-terminated surface retains the half-metallic character of the bulk, while in the case of the As-termination the surface states destroy the gap in the minority-spin band.

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The mainstream charged electronics has ignored the electron spin but recently a new field, the so called magnetoelectronics or spintronics, has emerged that combines magnetic elements with the existing conventional electronics to produce devices with new or enhanced properties.<sup>1</sup> The interest in this field has increased after the simultaneous discovery of giant magneto resistance (GMR) by the groups of Fert<sup>2</sup> and Grünberg.<sup>3</sup> Although the achieved progress, there are still central problems that have not been well solved. The injection of spin polarized current from a ferromagnet into a semiconductor remains still an open challenge.<sup>4</sup> The most successful attempts concern the injection of spin-current from a dilute magnetic semiconductor such as GaMnAs, where Mn atoms have substituted Ga atoms. Ohno *et al.*<sup>5</sup> and Fiederling *et al.*<sup>6</sup> have used such contacts to inject spin-polarized electrons and holes, respectively, into GaAs obtaining an efficiency of 90% spin-polarized current in GaAs. The advantage of dilute magnetic semiconductors is their coherent growth on semiconductors and their half-metallicity, i.e., the minority band presents a gap at the Fermi level, and thus electrons at the Fermi level are 100% spin polarized.<sup>7</sup> But existing magnetic semiconductors have very low Curie temperature  $T_c$  and thus are unattractive for industrial applications. Other known half-metallic materials are CrO<sub>2</sub> and La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3</sub>,<sup>8</sup> thin films of which have been found to present practically 100% spin polarization at the Fermi level at low temperatures<sup>8,9</sup> but they also have low  $T_c$ . Finally the half-metallic Heusler alloys such as NiMnSb (Refs. 10,11) present a  $T_c$  far above the room temperature, but their surfaces are not half-metallic<sup>12</sup> and experimentally it is difficult to control the stoichiometry of their surfaces.<sup>13</sup>

Akinaga and collaborators have managed to grow thin films of CrAs on GaAs(100) substrates by molecular-beam epitaxy.<sup>14</sup> They have found that CrAs is ferromagnetic at room temperature with a  $T_c$  larger than 400 K and they have deduced a total spin-magnetic moment of  $3\mu_B$ . Bulk CrAs adopts either the MnP-type structure showing a helimagnetic-paramagnetic transition at 256 K, or it crystallizes as Cr<sub>2</sub>As which is an antiferromagnet with a Néel temperature of 393 K. So the structure of the thin film cannot be one of the two stable bulk structures. Akinaga *et al.* have made the assumption that CrAs adopts the zinc blende (Zb) structure of GaAs, presented in Fig. 1, and using the full-

potential linearized augmented-plane-wave (FLAPW) method they have shown that in the ferromagnetic case Zb-CrAs would be a half-metal with a total spin magnetic moment of  $3\mu_B$  in agreement with the experiment. Afterwards, Shirai<sup>15</sup> continued the theoretical study of the 3*d*-transitional monoarsenides and showed that the ferromagnetic phase for Zb-CrAs should be more stable than the antiferromagnetic solution. He also calculated the theoretical equilibrium lattice constant and found a value of 0.58 nm, which lies in-between the experimental lattice constants of GaAs (0.565 nm), AlAs (0.566 nm), and InAs (0.606 nm). Due to the existence of two vacant sites per unit cell in the Zb structure, CrAs can adopt the lattice constant of all GaAs, AlAs, or InAs for the first few monolayers without deforming due to strain. So CrAs in the zinc blende structure combines the advantages of a very high  $T_c$  with the coherent growth on GaAs or InAs. In this contribution I will study the electronic and magnetic properties of bulk CrAs and its (001) surfaces taking into account both possible terminations, Cr or As, for different lattice constants using an *ab initio* technique. I will show that the surface terminated at Cr keeps the half-metallic character of the bulk CrAs, making it a serious candidate for an “ideal” spin-injection into GaAs, AlAs or InAs.

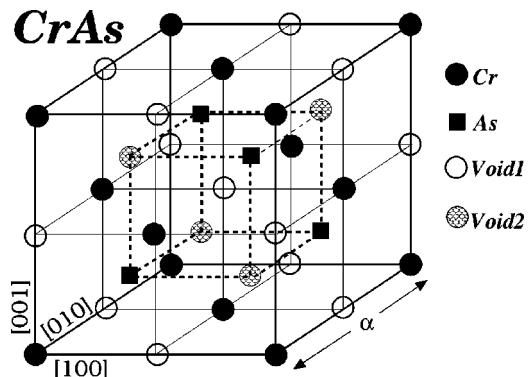


FIG. 1. Schematic representation of the zinc blende structure. To model the system in our calculations we assume the existence of two non-equivalent vacant sites. The lattice consists of four fcc sublattices. The unit cell is that of an fcc lattice with four atoms per unit cell: Cr at (0 0 0), As at  $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$  and the two vacant sites at  $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$  and  $(\frac{3}{4} \frac{3}{4} \frac{3}{4})$ .

To perform the calculations, I used the Vosko, Wilk and Nusair parametrization<sup>16</sup> for the local density approximation (LDA) to the exchange-correlation potential to solve the Kohn-Sham equations within the full-potential screened Korrington-Kohn-Rostoker method.<sup>17</sup> I have used the experimental lattice constants of GaAs and InAs for all the calculations; I do not present the results for the AlAs lattice constant since the latter one is practically the same as the GaAs lattice parameter. I simulated the surface by a slab consisting of 15 CrAs layers, so that I have two equivalent surfaces. For the screening I took for all compounds interactions up to the sixth neighbors into account leading to a tight-binding (TB) cluster around each atom of 65 neighbors. To calculate the charge density, I integrated along a contour on the complex energy plane, which extends from the bottom of the band up to the Fermi level,<sup>18</sup> using 42 energy points. For the Brillouin zone (BZ) integration I have used a  $\mathbf{k}$ -space grid of  $30 \times 30 \times 30$  in the full BZ for the bulk calculations and a  $\mathbf{k}_{\parallel}$ -space grid  $30 \times 30$  in the two-dimensional full BZ for the surface calculations. In addition I used a cutoff of  $l_{\max}=6$  for the multipole expansion of the charge density and the potential and a cutoff of  $l_{\max}=3$  for the wavefunctions.

In the Zb structure there is a gap in the paramagnetic materials which is separating the bonding from the antibonding states. While in a semiconductor like GaAs only the bonding states are occupied and the semiconducting phase is stable, in the case of CrAs there are also occupied antibonding states. Due to the very high DOS at the Fermi level the paramagnetic phase is not stable and the ferromagnetic state is stabilized. This stabilization is not followed by a change in the charge transfer. For the GaAs lattice constant the Cr atom loses about 0.9 electrons and the As atom about 0.8 electrons for both the paramagnetic and ferromagnetic phases and this charge is gained by the vacant sites. The KKR calculated ferromagnetic DOS presented in the left panel of Fig. 2 is similar to the one obtained using the FLAPW by Akinaga *et al.*<sup>14</sup> for the same lattice constant but the Fermi level in the FLAPW calculation was at the middle of the gap while in my calculations it is at the right edge of the gap. In the ferromagnetic phase the Cr moments are well localized due to the exclusion of the spin-down electrons at the Cr site, similar to the localized Mn moments in the Heusler alloys,<sup>19</sup> and the Cr spin moment is more than  $3\mu_B$  as can be seen in Table I. The As atom possesses a small induced spin magnetic moment that is antiferromagnetically coupled to the Cr spin moment, while the contribution of the two vacant sites to the total moment is negligible.

GaAs is not the only possible buffer for the growth of CrAs as InAs is also widely used in experiments. In Fig. 2 I have drawn the atomic and spin-projected DOS for CrAs for the case of the experimental GaAs and InAs lattice constants (left and right panel, respectively). In both cases the system remains half-metallic with a pretty large band gap (a width of  $\sim 2$  eV) compared to the NiMnSb that has a band gap that is only  $\sim 0.5$  eV wide.<sup>10,11</sup> The  $d$  states of Cr are well localized and in the case of the GaAs lattice constant it is mainly the  $p$  states of As which are squeezed compared to the larger InAs lattice constant. As they are squeezed they move higher in energy pushing also the Fermi level higher in energy and

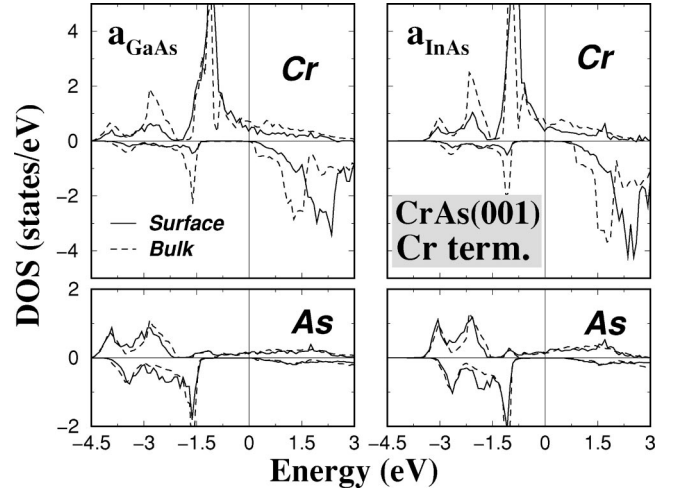


FIG. 2. Spin- and atom-resolved DOS of the Cr-terminated (001) surface for the Cr atom at the surface layer and the As atom at the subsurface layer for both the GaAs and InAs lattice constants. The As  $s$  states are located at around 10 eV below the Fermi level and are not shown in the figures. The surface DOS are compared to the bulk calculations (dashed lines).

this is clearly seen in Fig. 2 where the Fermi level for the InAs lattice constant is at the middle of the gap while for the smaller GaAs lattice constant is at the right edge of the gap. The theoretical lattice constant is inbetween these two values.<sup>15</sup> So bulk CrAs is a stable half-metallic ferromagnet over a large range of lattice constants.

It is interesting also to mention that the total spin magnetic moment in a half-metallic material should be an integer number as the total number of spin-down occupied states is an integer number. As shown in Table I the total spin-moment of bulk CrAs should be  $3\mu_B$ . In the KKR method the charge density is calculated by integrating on the complex energy plane. The numerical accuracy of this integration combined with the finite  $l$ -cutoff are responsible for the non-integer value of the total bulk spin moments presented in Table I. The explanation of why there are exactly three uncompensated spin states is similar to the one for the half-metallic Heusler alloys which is discussed in detail in Ref. 20. The As atom in the minority band offers one  $s$  band and three  $p$  bands that lie low in energy and can accommodate four electrons. There are practically no occupied minority  $d$

TABLE I. Spin magnetic moment in  $\mu_B$  for CrAs in the bulk case and for the surface and subsurface layers in the case of the Cr and As terminated (001) surfaces for both the GaAs and InAs experimental lattice constants.

$m^{\text{spin}}(\mu_B)$		Cr	As	Void1	Void2	Total
$a_{\text{GaAs}}$	Bulk	3.017	-0.198	0.005	0.122	2.946
	(001)Cr	3.961	-0.177	0.078	0.170	
	(001)As	2.407	-0.388	-0.044	0.014	
$a_{\text{InAs}}$	Bulk	3.269	-0.382	-0.029	0.080	2.937
	(001)Cr	4.138	-0.333	0.044	0.124	
	(001)As	2.941	-0.618	-0.067	0.003	

states. The total number of uncompensated spins should be just the total number of valence electrons 11 minus two times the number of occupied minority states,  $2 \times 4 = 8$ , and the total spin moment in  $\mu_B$  would be also  $(11-8) \mu_B = 3 \mu_B$ . In the case of the InAs lattice constant the Cr spin moment is larger than for the GaAs lattice constant. When the lattice is expanded, the Cr electronic structure becomes more atomic-like and its spin-magnetic moment increases. This is also reflected on the charge transfer which is smaller for the InAs lattice parameter (the Cr atom loses 0.8 electrons and the As atom 0.6). Although this means that the hybridization with As states should decrease, the larger Cr moment induces a larger spin polarization of the As  $p$  states, so that the total magnetic moment remains  $3 \mu_B$ .

As the last part of this contribution I have studied the (001) surfaces of CrAs taking into account both the Cr and As terminations. I present in Fig. 2 the atomic projected DOS for the Cr atom at the surface and the As atom at the subsurface layer for the Cr-terminated surface and for both the GaAs and InAs lattice constants. There are no surface states within the gap, so this surface is half-metallic. To my knowledge this is the first case that electronic structure calculations predict a surface of an intermetallic compound to present 100% spin-polarization at the Fermi level. The As atom at the subsurface layer has the same tetrahedral environment as in the bulk and the amount of electronic charge, which it loses, is similar to the bulk case. The DOS of the surface atoms is slightly different than the bulk DOS. The Cr atoms at the surface lose electronic charge towards the vacuum and their magnetic moment increases considerably by about  $\sim 0.95 \mu_B$  for both the GaAs and InAs lattice constants as can be seen in Table I. On the other hand the absolute value of the magnetic moment of the As atom at the subsurface layer decreases compared to the bulk case. Note that in agreement with the half-metallicity of this surface also the total spin moment remains an integer number. If the total spin moments of the atoms in the surface and subsurface layers are added the total spin moment is slightly larger than  $4 \mu_B$ , but if also the negative moment of the vacuum is added then the total moment is exactly  $4 \mu_B$  for both the GaAs and InAs lattice constants.

In the case of the As-terminated (001) surface the situation is not as ideal as in the case of the Cr terminated surface as can be seen in Fig. 3. Now there are states within the gap that destroy the half-metallic character. In the case of the InAs lattice constant the gap is only partially destroyed but the Fermi level is below the remaining fully spin-polarized region. Contrary to the Cr termination the DOS of both the As surface atom and the Cr subsurface atom present large deviations from the bulk case. The As atom at the surface loses  $\sim 0.4$  more electrons than in the bulk CrAs. Its spin magnetic moment is practically doubled. Although the Cr atoms at the subsurface layer present a charge transfer comparable to the bulk calculations, the changes in their DOS are pronounced, the spin imbalance decreases and their magnetic moment is  $0.3-0.4 \mu_B$  lower than in the bulk CrAs.

The different behavior of the two terminated surfaces is possibly arising from the different origin of surface states in the  $3d$  transition metals and the  $sp$  elements. The As atoms

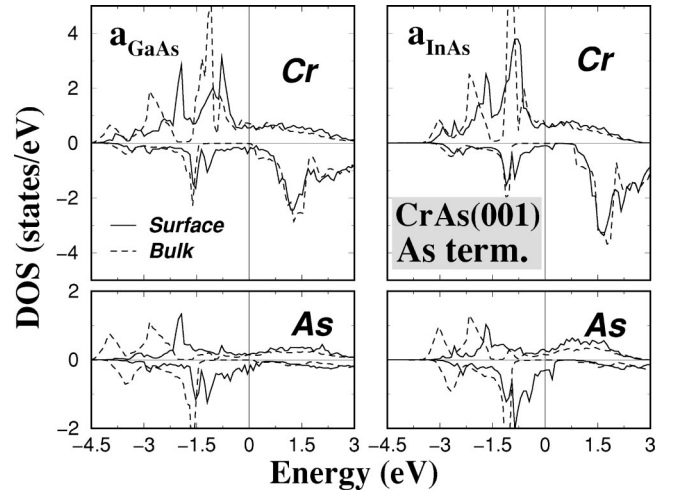


FIG. 3. Similar to Fig. 2 for the As-terminated (001) surface.

have mainly  $s$  and  $p$  type electrons which can participate in directional bonding similar to what happens in a semiconductor like GaAs. In a simple model we can assume that As atoms interact through directional bonds made up of some kind of  $sp$  hybrids. When we open the As terminated surface an As atom at the surface loses 4 from its 12 nearest As neighbors (note that the As atoms sit on a fcc lattice) and so dangling bonds are created. These dangling bonds create a surface band within the minority spin-down gap. In the case of a transition metal, the surface states arise from  $d$ -type atomiclike states, which are pinned near the Fermi level acting like a virtual bound state.<sup>21</sup> These states, except in the case of the most close-packed surfaces, are not enough broadened by the interaction between the surface atom and its neighbors and they form a surface band. In the case of Cr in CrAs the exchange splitting of its  $d$  states is very large and thus when we open the Cr-terminated surface there is no  $d$ -like atomic state that can be found within the minority gap and the surface remains half-metallic. Contrary to Cr, the Ni terminated (001) surface in the case of the NiMnSb compound loses its half-metallicity<sup>12</sup> because both the gap and the exchange splitting of the Ni  $d$  states are very small and when the Ni surface is opened there is a  $d$ -like state of the Ni atom at the surface that is slightly shifted in energy compared to the continuum of the  $d$  states and is pinned at the Fermi level.

I have shown using first-principles calculations that the Cr-terminated (001) surface of CrAs in the zinc blend structure should be half-metallic for both the GaAs and InAs experimental lattice constants. Contrary to the Cr-terminated, the As-terminated surface loses its half-metallicity due to surface states within the gap. The bulk CrAs shows a total spin magnetic moment of  $3 \mu_B$  and its properties can be explained similarly to the ones of the half-metallic Heusler alloys.

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