Predicted half-metallicity with no net magnetization in Ca$_{0.75}$Cr$_{0.25}$As from a first-principles study

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The results of a first-principles study of the magnetic and half-metallic properties of ordered Ca-Cr-As alloy with zinc-blende like structure are presented. The full-potential linearized augmented plane wave method is used in order to resolve the electronic structure of Ca$_x$Cr$_{1-x}$As alloy, in which concentration of Ca atoms varies from 25% to 75% (x=0.25, 0.5, 0.75). The obtained results indicate that all the investigated compounds are half-metallic with magnetic moment determined by the Ca concentration. Particularly, it is found that Ca$_{0.75}$Cr$_{0.25}$As is a half-metallic antiferromagnet with no net magnetization. © 2009 American Institute of Physics.

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I. INTRODUCTION

Since half-metallicity was predicted by de Groot et al.$^1$ there have been growing interest in investigation of materials having this electronic property. In many cases novel materials were first designed computationally, and only later they were synthesized, as it was the case with zinc-blende (ZB) structured CrAs.$^2$ ZB half-metals attract considerable attention in the field of spintronics because they have large magnetic moment (MM), high Curie temperature, and they follow the structure and bonding of ZB semiconductors, which is of importance for applications.$^3$ An interesting compound of ZB structure that exhibits half-metallicity is CaAs. Like other compounds of Ca and group V elements it is predicted to be half-metallic ferromagnet (HM-FM) even though it does not contain a transition metal.$^4$

The frequent manifestation of ferromagnetism among half-metals does not exclude a possibility of existence differently magnetically ordered materials in the group. HM antiferromagnetism is a perfect form of ferrimagnetism with zero net magnetization. HM antiferromagnets (HM-AFMs) were predicted by van Leuken and de Groot.$^5$ HM-AFMs possibly have several advantages comparing to HM-FMs, among them: a high magnetic transition temperature, insensitivity to external fields, and the lack of stray fields.$^6$ Therefore, the search for the candidates for HM-AFMs has long been continued.$^6,7$ We have paid attention to the fact that ZB CrAs has a band gap in the minority spin channel$^8$ while ZB CaAs has the gap in the other one, and so a proper mixture of the two compounds could be a HM-AFM. In this paper we present the results of the first-principles electronic structure calculations of ordered Ca-Cr-As alloy with ZB structure, in which the concentration of Ca atoms in the Ca$_x$Cr$_{1-x}$As varied from 25% to 75% (x=0.25, 0.5, 0.75), and Ca$_{0.75}$Cr$_{0.25}$As reveals to be a HM-AFM.

II. COMPUTATIONAL METHOD

We performed the electronic structure calculations for ZB structured Ca$_x$Cr$_{1-x}$As (x=0.25, 0.5, and 0.75) alloy. The calculations were carried out by using the full-potential linearized augmented plane-wave (FLAPW) method as embodied in QMD-FLAPW code$^{8,10}$ within the generalized gradient approximation,$^11$ which allows to solve the Kohn-Sham equation$^{12}$ for the investigated system. Lattice harmonics with $l\leq 8$ were considered to describe the charge density, the potential and the wave functions inside each muffin-tin (MT) sphere within 2.20, 2.60, and 2.10 a.u. radii for Cr, Ca, and As, respectively. Integration inside the Brillouin zone was replaced by summation over at least 56 irreducible $k$ points inside the zone by the linear tetrahedron method. All core electrons were treated fully relativistically, while valence states were treated scalar relativistically without spin-orbit coupling.$^{13}$

III. RESULTS AND DISCUSSION

First, the equilibrium lattice constant for each of the three investigated compounds was determined from the total energy calculations. The obtained lattice parameters equal 11.20, 11.79, and 12.28 a.u. for $x=0.25, 0.5, 0.75$ in Ca$_x$Cr$_{1-x}$As, respectively. In Table I the $l$-like charges within the MT radii of the component atoms of the Ca-Cr-As alloys and the total MMs (TMMs) for each compound (per As atom) are presented. For comparison the results obtained for the binary CrAs and CaAs alloys with the identical set of input parameters are also presented. Since the calculated TMMs are all integer numbers, we can conclude that all the three alloys are half-metals. In particular, the Ca$_{0.75}$Cr$_{0.25}$As alloy has zero MM which implies that it is HM-AFM.

Due to the substitution of every fourth Cr atom with Ca, the polarization of both Cr and As in Ca$_{0.75}$Cr$_{0.25}$As becomes stronger than in CrAs. The calculated MMs of the Cr and As are 3.08$\mu_B$ and $-0.32\mu_B$, respectively. The changes are

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caused by the exchange of electrons between Cr, As, and the introduced Ca atoms. The MM on Ca atom is $-0.12\mu_B$. The increase in polarization of the three atoms in the alloy is sustained when the concentration of Ca with respect to Cr atoms is 50%. However, in this case the mechanism of electron flow may be different than that in $\text{Ca}_{0.25}\text{Cr}_{0.75}\text{As}$ since the polarization of $3d$ electrons of Cr atom in $\text{Ca}_{0.5}\text{Cr}_{0.5}\text{As}$ is stronger than in $\text{Ca}_{0.25}\text{Cr}_{0.75}\text{As}$.

When the ratio of Ca to Cr atoms in the alloy becomes 3:1 the magnetic properties change further. The polarization of all the atoms is reversed with respect to that in the Ca-

Cr-As alloys with the 25% and 50% concentrations of Ca with respect to Cr atoms. Cr is negatively polarized with the MM equal $-3.24\mu_B$, while As and Ca atoms are positively polarized and have MM equal $0.37\mu_B$ and $0.10\mu_B$, respectively. Such an arrangement of minority and majority electrons are close to the electronic properties of the binary CaAs alloy.

In Fig. 1 the total and atom-projected density of states (DOS) of $\text{Ca}_{x}\text{Cr}_{1-x}\text{As}$ ($x=0.25$, 0.5, and 0.75) are shown. The DOS values of spin-down electrons are multiplied by $-1$ and the Fermi levels are set to zero. The HM properties of the

### TABLE I. I-decomposed electrons inside MT spheres of component atoms in Ca-Cr-As alloys, MM on the atoms, and the TMM per As atom.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Atom</th>
<th>$s(\uparrow/\downarrow)$</th>
<th>$p(\uparrow/\downarrow)$</th>
<th>$d(\uparrow/\downarrow)$</th>
<th>MM ($\mu_B$)</th>
<th>TMM/As ($\mu_B$/As)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CrAs</td>
<td>Cr</td>
<td>0.13/0.09</td>
<td>0.09/0.09</td>
<td>3.42/0.49</td>
<td>2.99</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>0.59/0.60</td>
<td>0.66/0.90</td>
<td></td>
<td>$-0.24$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}<em>{0.25}\text{Cr}</em>{0.75}\text{As}$</td>
<td>Ca</td>
<td>0.08/0.09</td>
<td>0.09/0.13</td>
<td>0.18/0.25</td>
<td>$-0.12$</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.12/0.08</td>
<td>0.07/0.07</td>
<td>3.39/0.35</td>
<td>3.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>0.60/0.60</td>
<td>0.60/0.92</td>
<td></td>
<td>$-0.32$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}<em>{0.50}\text{Cr}</em>{0.50}\text{As}$</td>
<td>Ca</td>
<td>0.07/0.08</td>
<td>0.07/0.10</td>
<td>0.13/0.20</td>
<td>$-0.13$</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.11/0.07</td>
<td>0.06/0.06</td>
<td>3.40/0.29</td>
<td>3.16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>0.60/0.61</td>
<td>0.56/0.92</td>
<td></td>
<td>$-0.36$</td>
<td></td>
</tr>
<tr>
<td>$\text{Ca}<em>{0.75}\text{Cr}</em>{0.25}\text{As}$</td>
<td>Ca</td>
<td>0.07/0.07</td>
<td>0.08/0.06</td>
<td>0.17/0.10</td>
<td>0.10</td>
<td>$-0.09^a$</td>
</tr>
<tr>
<td></td>
<td>Cr</td>
<td>0.06/0.11</td>
<td>0.05/0.05</td>
<td>0.25/3.44</td>
<td>$-3.24$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>0.60/0.60</td>
<td>0.90/0.53</td>
<td></td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>CaAs</td>
<td>Ca</td>
<td>0.06/0.07</td>
<td>0.07/0.04</td>
<td>0.17/0.10</td>
<td>0.09</td>
<td>$-1.09^a$</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>0.60/0.60</td>
<td>0.91/0.54</td>
<td></td>
<td>0.37</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Minus sign is put in order to underline that the band gap is in the spin-up channel.

FIG. 1. The total and atom-projected DOS obtained for $\text{Ca}_{0.25}\text{Cr}_{0.75}\text{As}$ (left), $\text{Ca}_{0.5}\text{Cr}_{0.5}\text{As}$ (middle), $\text{Ca}_{0.75}\text{Cr}_{0.25}\text{As}$ (right). Spin-down values are multiplied by $-1$ and Fermi levels are set to zero.
three investigated compounds manifest through the clearly seen band gaps in the total DOS pictures. The compounds containing 25% and 50% of Ca atoms have the band gap in spin-down channel, while the alloy containing 75% of Ca atoms has the gap in spin-up channel, which is exactly the case in the binary ZB CaAs. The spin dependent band structure reflects the properties of binary CrAs and CaAs. A small amount of Ca atoms substituting Cr in CrAs does not change the overall electronic properties of the binary CrAs material, and the DOS of Ca0.25Cr0.75As resembles that of CrAs. Comparing the obtained DOS with that of CrAs one can see that the only effect of the presence of 25% of Ca atoms in the compound is a slightly larger delocalization of Cr and As electrons contributing to the bands in the energy range from −3 to 4 eV. This is the effect of a week hybridization between Ca d and Ca p orbitals with As 4p and Cr 3d. Due to the exchange of electrons between the Ca, Cr, and As atoms, Ca 3d empty states accept electrons on the cost of Cr atoms. There are majority states at the Fermi level contributed from both Cr 3d and As 4p electrons. Similar effect is observed in Ca0.5Cr0.5As. However, due to the larger concentration of Ca atoms, the majority spin d bands contributed by Cr are even more delocalized. There is also a larger number of As 4p states at the Fermi level.

IV. CONCLUSION

The first-principles calculations were performed in order to investigate the magnetic properties of ZB structured CaCr1-xAs (x=0.25, 0.5, 0.75) alloys. We have found that all the three compounds were half-metals. The alloys with 25% and 50% concentrations of Ca atoms have the energy band gap in the spin-down channel, while the one with 75% of Ca atoms has the gap in the spin-up channel. The TMM calculated per As atom also depends on the concentration of Ca atoms in the alloys and it is 2.0µB, 1.0µB, and 0µB for Ca0.25Cr0.75As, Ca0.5Cr0.5As, and Ca0.75Cr0.25As, respectively. Since the calculated total magnetization of the latter compound is zero, we found that Ca0.75Cr0.25As is a HM-AFM. This finding may be important for the applications of Ca-Cr-As alloys in spintronics.

ACKNOWLEDGMENTS

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