Journal of Magnetism and Magnetic Materials 374 (2015) 164–172

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Ab initio calculations of half-metallic ferromagnetism in Cr-doped MgSe and MgTe semiconductors

N.A. Noor [a], S.M. Alay-e-Abbas [b,c], M.U. Sohaib [d], S.M. Ghulam Abbas [e], A. Shaukat [b,*]

[a] Department of Physics, University of the Punjab, Quaid-e-Azam Campus, 54590 Lahore, Pakistan
[b] Department of Physics, University of Sargodha, Sargodha 40100, Pakistan
[c] Department of Physics, GC University Faisalabad, Allama Iqbal Road, Faisalabad 38000, Pakistan
[d] Lahore Development Authority, 54590 Lahore, Pakistan
[e] Department of Chemistry, University of Agriculture, Faisalabad 38040, Pakistan

ARTICLE INFO

Article history:
Received 1 May 2014
Received in revised form
8 August 2014
Available online 19 August 2014

Keywords:
Ab initio calculations
Ferromagnetic materials
Electronic properties
Doped semiconductors

ABSTRACT

The full-potential linear-augmented-plane-waves plus local-orbitals (FP-LAPW+lo) method has been employed for investigation of half-metallic ferromagnetism in Cr-doped ordered zinc-blende MgSe and MgTe semiconductors. Calculations of exchange and correlation (XC) effects have been carried out using generalized gradient approximation (GGA) and orbital independent modified Becke–Johnson potential coupled with local (spin) density approximation (mBJLDA). The thermodynamic stability of the compounds and their preferred magnetic orders have been analyzed in terms of the heat of formation and minimum total energy difference in ferromagnetic (FM) and anti-ferromagnetic (AFM) ordering, respectively. Calculated electronic properties reveal that the Cr-doping induces ferromagnetism in MgSe and MgTe which gives rise to a half-metallic (HM) gap at Fermi level (E_F). Further, the electronic band structure is discussed in terms of *s* (*p*)–*d* exchange constants that are consistent with typical magneto-optical experiment and the behavior of charge spin densities is presented for understanding the bonding nature. Our results demonstrate that the higher effective potential for the spin-down case is responsible for *p*–*d* exchange splitting. Total magnetic moment (mainly due to Cr-*d* states) of these compounds is $4\mu_B$. Importantly, the electronic properties and HM gap obtained using mBJLDA show remarkable improvement as compared to the results obtained using standard GGA functional.

1. Introduction

Light-emitting diodes (LED) and laser diodes operating in blue or ultraviolet (UV) spectral regions are important achievements in the field of optoelectronics. High ionicity of wide-gap II–VI compounds is of vital importance for electrochemical and optical coupling [1]. Apart from this, a growing effort has been directed toward the simultaneous manipulation of charge as well as spin degrees of freedom of electrons in semiconducting compounds for spintronic functionality. In this regard, the introduction of magnetic ions into a nonmagnetic semiconductor host material is an excellent solution for effective spin injection. Successful doping of considerable amount of Mn atoms into InAs and GaAs has proven to be a historic breakthrough for the establishment of spintronic devices [2,3]. To date, significant research efforts have been made toward studying the role of ferromagnetism in semiconducting compounds like Europium (Eu) chalcogenides and Cr-based spinels as well as anti-ferromagnetism in II–VI compounds [4,5]. Mn-doped II–VI compounds are highly appreciated in the opto-electronic field owing to the strong room temperature ferromagnetic interactions among localized spins with low carrier concentration. In addition, the induction of ferromagnetic behavior due to free holes in II–VI has also been reported [6,7].

The magnetic impurity-doped semiconductors are termed half-metallic (HM) ferromagnetic (FM) if the electronic states at the Fermi level are 100% spin-polarized [8,9]. One of the pioneering first principles works done by Groot et al. [10] formulates the concept of half-metallicity in terms of spin-polarization for NiMnSb semi-Heusler alloy. Consequently, tremendous number of theoretical investigations resulted in the predictions of many HM materials due to which an appreciable number of HM materials have been experimentally realized [11,12]. Considerable research attention has been devoted to probing the half metallicity and ferromagnetic ordering for their influence on various physical properties [13,14]. However, it is indispensable for the practical application of spintronic devices to investigate materials for HM ferromagnetic behavior having compatibility with important III–V and II–VI compounds. An upsurge of experimental and theoretical investigations has been directed toward

* Corresponding author. Tel.: +92 48 9230618; fax: +92 48 9230671.
E-mail address: schaukat@gmail.com (A. Shaukat).

http://dx.doi.org/10.1016/j.jmmm.2014.08.038
0304-8853/

magnetic semiconductors exhibiting spin-polarization with T_c above room temperature [15,16]. In these materials, *sp-d* exchange interaction is responsible for HM ferromagnetism for both doped semiconductors and dilute magnetic semiconductors (DMS) [17,18].

The principal difference between Mn-, Co-, Fe-doped semiconductors and Cr-doped semiconductors is that the former exhibit antiferromagnetic (AFM) *p–d* exchange interaction among anions and Mn-, Co- and Fe-ions, whereas the exchange interaction is ferromagnetic in case of Cr-ions [19]. Although some experimental reports on Cr-doped MgTe are available in the literature [20], so far no experimental studies have been undertaken for Cr-doped MgSe. Since large HM gap in the minority spin channel is an essential requirement for materials important in spintronic devices [21], in this paper we focus our attention on Cr-doped MgSe and MgTe and perform a thorough study of electronic and magnetic characteristics of these materials. Importantly, a comparison between the standard generalized gradient approximation (GGA) functional and specially devised exchange correlation (XC) functional for wide band gap semiconductors gives us a clear picture of the governing mechanism behind Cr dopant-induced HM ferromagnetism. The results presented in this paper may provide useful insight regarding the implementation of $Cr_xMg_{1-x}Se$ and $Cr_xMg_{1-x}Te$ in the field of spintronics.

2. Method of calculations

For high performance electronic and optical device applications, first-principles material modeling is commonly used to predict electronic structure of the target material. In this work Density functional theory is employed for computing the structural, electronic and magnetic properties of $Cr_xMg_{1-x}Se$ and $Cr_xMg_{1-x}Te$ ($0 \le x \le 1$) using the full-potential linear-augmented-plane-waves plus local orbitals (FP-LAPW+lo) method [22]. For structural properties, the XC potential has been constructed using the Wu–Cohen GGA parameterization scheme (WC-GGA) [23]. A recently formulated functional by Tran and Blaha [24] has been employed for electronic properties, which uses exchange potential from modified Becke–Johnson functional and the correlation potential from local density approximation (mBJLDA) to provide better description of electronic properties of semiconductor. The choice of using mBJLDA for computing the electronic properties is based on its success in predicting the electronic structures of ferromagnets which are consistent with experimental results [25].

The end binary compounds MgSe, MgTe, CrSe and CrTe have been modeled in the cubic zinc-blende (ZB) structure with space group $F\bar{4}3m$ (space group number 216), whereas the calculations for alloys are based on a supercell (SC) model [21,26,27]. For $Cr_xMg_{1-x}Se$ and $Cr_xMg_{1-x}Te$ alloys the limiting case of infinitesimal SCs compatible with the constituents in percentage is therefore used which result in periodically repeated SCs with preferred compositions in ordered structures. For compositions $x=0.25$, 0.5 and 0.75 this is achieved by constructing an eight atom cubic $1 \times 1 \times 1$ SC of the ZB structure. In case of $x=0.25$ and 0.75, the resulting structure after the introduction of dopant is a simple cubic lattice with eight atoms belonging to space group $P\bar{4}3m$ (space group number 215) which has the cation with lowest concentration at the simple cubic lattice site. On the other hand, the structure obtained for 50% doping is a four-atom tetragonal cell with space group $P\bar{4}m2$ (space group number 115). In spite of the fact that ordered structures considered in this study are small to represent a random alloy, our calculated test results for 16 atoms $1 \times 1 \times 2$ SC indicate that larger SC structures have little influence on overall band structure profile.

The core electron states are treated fully relativistically by solving Dirac equations, while the valence states are treated semi-relativistically. All ferromagnetic (FM) calculations for electronic properties are done by using our computed lattice parameters, which have been optimized using WC-GGA and are compared with the experimental data in Table 1. The plane wave cutoff parameters $R_{mt} \times K_{max}$ have been set to 8, where K_{max} is plane wave cutoff and R_{mt} is radius of the smallest muffin-tin spheres. $G_{max}=18$ a.u.$^{-1}$ is used for Fourier expansion of the potential in the interstitial region. The MT radii (in atomic units) for Cr, Mg, Se and Te are taken as 2.5, 2.5, 2.25 and 2.44, respectively. Brillouin zone integration is performed over a $10 \times 10 \times 10$ uniform Monkhorst–Pack **k**-mesh. The convergences of the total energy of crystal and charge are chosen as 10^{-4} Ry and $10^{-3}e$, respectively, and the Hellman–Feynman forces are minimized by allowing the atomic positions to relax at the optimized lattice volume until forces on atoms are below 2 mRy/a.u.

Table 1
Calculated ground state lattice parameter, bulk modulus, heat of formation and minimum total energy difference between AFM and FM ordering in $Cr_xMg_{1-x}Se$ and $Cr_xMg_{1-x}Te$ ($x=0.0$, 0.25, 0.5, 0.75 and 1.0) alloys.

	Lattice constant a_0 (Å)					Bulk modulus B (GPa)			ΔH (eV)	ΔE (meV)
	x	This work		Exp.	Other works	This work		Other works	This work	This work
		GGA	LDA			GGA	LDA			
$Cr_xMg_{1-x}Se$	0	5.90	5.88	5.89[a]	5.90[b], 5.87[c]	45.86	50.96	45.86[b], 50.5[c]	−13.52	–
	0.25	5.88	5.82			49.08	53.73		−11.83	12.82
	0.50	5.83	5.75			53.08	58.83		−9.64	25.33
	0.75	5.78	5.71			58.38	68.62		−7.55	45.22
	1.0	5.74	5.62	–	5.8[d], 5.77[e]	61.5	45.6	59.5[g]	−5.16	68.02
$Cr_xMg_{1-x}Te$	0	6.43	6.37	6.36[a]	6.51[b], 6.38[c]	36.72	38.54	34.1[b], 38.7[c]	−11.27	–
	0.25	6.38	6.31			38.14	41.63		−10.40	34.20
	0.50	6.3	6.22			54.14	45.65		−7.90	48.60
	0.75	6.24	6.15			52.64	51.86		−6.41	75.86
	1.0	6.17	6.09	6.21[f]	6.44 [d], 6.24[e]	50.44	57.32	50.9[g]	−3.3	123.99

[a] Ref. [40].
[b] Ref. [41].
[c] Ref. [42].
[d] Ref. [43].
[e] Ref. [44].
[f] Ref. [45].
[g] Ref. [15].