Magnetic study of the transition elements doped binary compound SrAs with hexagonal Na_2O_2-type structure

M. TORRICHI*, N. ZIANI, M. BELMEKKI
Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf, Département de Physique, Faculté de Physique, Oran, Algérie

Using the calculation based on the functional density theory, we find the existence of the magnetism of the binary compound SrAs doped with transition elements Ti, V, Cr, Mn, Fe, Co and Ni in its non-magnetic Na_2O_2 type hexagonal structure. We studied the stability of undoped binary SrAs in the absence (NM) and in the presence (FM) of spin polarization by a calculation of their cohesion energies. The hexagonal Na_2O_2-type in non magnetic phase is found to be energetically the most stable. It is interesting to note that the doping of the compound SrAs by the elements Ti, V and Cr induces a strong magnetism while the elements Fe, Co, and Ni introduce a weak magnetic moment. The element Mn gives a zero magnetic moment. The partial density of states indicates that ferromagnetism emerges fundamentally from the coupling between the states of the X-d states of the doping atom X, Sr-d states and As-p states of the Sr and As host atoms. These theoretical results make the binary compound SrAs doped withthe elements Ti, V, Cr, Fe, Co and Ni a good material for magnetism.

(Received October 10, 2020; accepted October 7, 2021)

Keywords: Magnetism, SrAs binary compound, Hexagonal Na_2O_2-type, Density functional theory

1. Introduction

Fert's research group observed the giant magneto resistance (GMR) in Fe/Cr multilayer's in 1988 [1]. Before the discovery of GMR, researchers were not interested to explore the correlation between charge and spin. The development of spin-based electronics, or spintronics, seeks to correlate the electron charge degree of freedom and the spin of the charges. Through a ferromagnetic material, the technology can make a spintronic device to generate a spin-polarized current and to inject the current. It makes it possible to read information stored in the magnetization of magnetic materials. The materials for spintronics must retain the fundamental characteristics of magnetic semiconductors doped at room temperature. Making magnetic semiconductors resides in the ability to dope the nonmagnetic semiconductor with impurities to change their properties. Ohno and his group [2] introduced the magnetic element Mn into the nonmagnetic host-lattice of GaAs, and investigated the magnetic properties of this material. The researchers are now looking for identifying other semiconductors with different dopant to overcome problems encountered. Through the recent band structure calculations of CaAs, CaP, and CaN, the researchers show that II-V compounds that do not contain transition metal atoms are ferromagnet, and their Curie temperature is estimated to be of the order of the room temperature [3].The most common technology uses semiconductors doped with transition metals [4-5] such as binary materials based on arsenic (As) for example we cite compounds XAs (X = Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Ho, Er and Yb) [6]. All its XAs compounds crystallize in a cubic structure, moreover they are semiconductors with low energy gap [7] with the exception of the XAs materials (X = La, Pr and Nd) which are metallic. The first experimental works concerning the study of the structural properties of the binary compounds XAs (X = Ca and Sr) seem to have been carried out by Iandelli and Franceschi [8]. Indeed, they synthesized binary material XAs in the hexagonal structure of Na_2O_2 type by using the powder method. On the other hand, theoretical studies [9] have shown that the SrAs material is not magnetic in the hexagonal structure of Na_2O_2 type. It has been found that this material is semiconductor with a gap of 0.013eV. Since then, few studies have been interested in these binary materials in the cubic zinc-blende type phase although it is not their most stable phase. To our knowledge, the binary compounds SaAs is not synthesized experimentally in cubic zinc blende-type structure and all works are only theoretical. We cite the work of Mojtaba and al [10] based on the study of two cubic structures (rocksalt and zinc-blende) and four hexagonal structures (NiAs, wurtzite, anti-NiAs, and Na_2O_2). This study showed, by calculating the variation of the total energy as a function of the volume, that the hexagonal structure of Na_2O_2 type in the nonmagnetic phase is the most stable among the other structures studied. Certain II–V compounds do not exhibit a semi-ferromagnetic character in their fundamental states, but compression or expansion of their equilibrium structures can transform them into a semi-ferromagnetic metal [3]. For a value of the critical network parameter lower than that of equilibrium the binary compounds based on arsenic XAs (X = Sr, Ca and Ba) become ferromagnetic [3]. In this work, our aim, based on the density functional theory (DFT), is to find new materials for the application in the field of spintronics. We adopt the binary compound SrAs by doping the transition elements Ti, V, Cr, Mn, Fe,

Co and Ni. We looked for the most stable structure of the SrAs material in the hexagonal structure of Na_2O_2 type in the presence (FM) and in the absence (NM) of spin polarization. Next, we studied the doping of the SrAs material with the transition elements. Up to date, no experimental or theoretical study has been reported in the literature concerning our investigation.

2. Method

We have performed calculations within the generalized gradient approximation (GGA), as parameterized by Perdew-Burke-Ernzerhof (PBE) [11] method as implemented in the Quantum ESPRESSO code [12]. The cutoff energy for plane waves is chosen to 80Ry and an energy cut-off of 400Ry was included for the charge density. A Gaussian smearing of 0.02 Ry has been applied. The integration on the Brillouin zone was calculated within 6×6×4 k-points Monkhorst-Pack [13] mesh for hexagonal structure. The internal atomic positions were fully relaxed until the maximum force on a single atom becomes less than 5meV/Å. Calculations proceeded self-consistently until the total energy converged to within

3. Results and discussion

In the hexagonal Na_2O_2-type, the structure of the binary SrAs contains six arsenic atoms (As) and six Sr atoms [9] (see Fig. 1). We calculated the cohesion energy (E_{coh}) to define the most stable structure among ferromagnetic (FM) and non magnetic (NM) hexagonal Na_2O_2-type structure. This energy is deduced from the expression $E_{coh}=E_{SrAs}-(6E_{Sr}+6E_{As})$, where E_{SrAs} is the total energy of the SrAs material. E_{Sr} and E_{As} represent the total energy of Sr and As atoms respectively. We have represented in figure 2 the variation of cohesion energies with volumes for FM and NM hexagonal Na_2O_2-type structure. We can see that NM Na_2O_2-type is more stable than FM Na_2O_2-type for the binary material SrAs. The structural parameters a_0, c/a, the compression modulus (B_0) which is deduced from the Murnaghan equation of state [14] are given in Table 1. Our result is in perfect agreement with another theoretical [9] and experimental [8] works. To study mechanical stability, we calculated the elastic constants of undoped-SrAs compounds in the stable hexagonal structure of Na_2O_2-type without spin polarization. The hexagonal structure has six elastic constants (C_{11}, C_{12}, C_{13}, C_{33}, C_{44} and C_{66}), five of which are independent because $C_{66} = (C_{11}-C_{12})/2$ [15]. These constants C_{ij} must fulfill the conditions of Born stability: $C_{11}>0$, $(C_{11}-C_{12})>0$, $C_{44}>0$ and $(C_{11}+C_{12})\ C_{33}-2C^2_{13}>0$ [16]. As shown in Table 2, the calculated constants C_{ij} are positive and clearly show that the Born stability conditions are satisfied. The binary material SrAs is mechanically stable in the hexagonal structure of the Na_2O_2 type. To our knowledge, no experimental and theoretically data on elastic constants are available for comparison.

Our doping consists in replacing a local atom As by a doping atom X. We obtain six possible substitutions noted S_i with i = 1, 6. In order to know the most stable structure among its 6 substitutions, we calculated their cohesion energies. For the calculation of this last physical quantity, we took the doping of SrAs with chromium (Cr) as prototype. In Table 3, we have represented the results of this calculation. We can notice that the substitution S_5 has the most stable structure. Taking into account the substitution S_5, all the results of the structural optimizations obtained from doping of SrAs by the elements Ti, V, Cr, Mn, Fe, Co and Ni are given in Table 3. It shows that all the systems studied are magnetic, except for the doping of SrAs by manganese (Mn). Doping with Cr induces the highest total magnetic moment. The values of the total magnetic moments introduced by the elements Cr and Fe are almost half whole, which makes compounds obtained by their doping like materials almost half metallic. While the materials obtained by doping with Ti, V, Co and Ni are metallic. The induced magnetic moment comes mainly from the doping X atom. In addition, the atoms As and Sr provide a small magnetic moment.

To know the nature of the undoped-SrAs and X-doped-SrAs binary compound in non-magnetic hexagonal Na_2O_2-type structure, the total densities of state (TDOS) is calculated in the majority spin bands (spin-up) and minority (spin-down) near the Fermi level (E_F). Fig. 3(a) shows that the TDOS of undoped-SrAs in non magnetic hexagonal Na2O2-type structure exhibits a semi conductor behavior with small gap of 0.023 eV. It is illustrated in Figs. 3(b, c, d) that the doping of the compound SrAs with the elements Cr, Fe and Co gives an almost half-metallic behavior. On the other hand, the TDOS illustrated in Figs. 4 (a, b, d) shows that the doping of the compound SrAs with the elements Ti, V and Ni exhibits a metallic behavior. The SrAs compound doped with Mn is non-magnetic. In order to analyze the contribution of the different states introduced by the doping atoms and the host atoms in the valence and conduction bands, we have represented the densities of partial states (PDOS) in Figs. 5 and 6. The latter show that the valence bands of the majority and minority spins of the materials obtained by doping with the elements Ti, V, Cr, Fe, Co and Ni are entirely occupied by the states X-d and As-p with a small contribution from Sr-d states. These results show that the appearance of magnetism in the doping of the compound SrAs with the transition elements comes from the coupling between the X-d states of impurity X and the Sr-d states of the Sr host atoms.

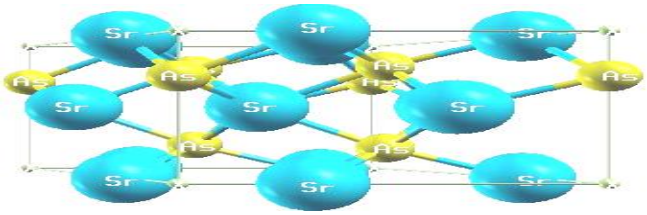

Fig. 1 Crystal structure of SrAs binary compound in hexagonal Na2O2-type structure (color online)

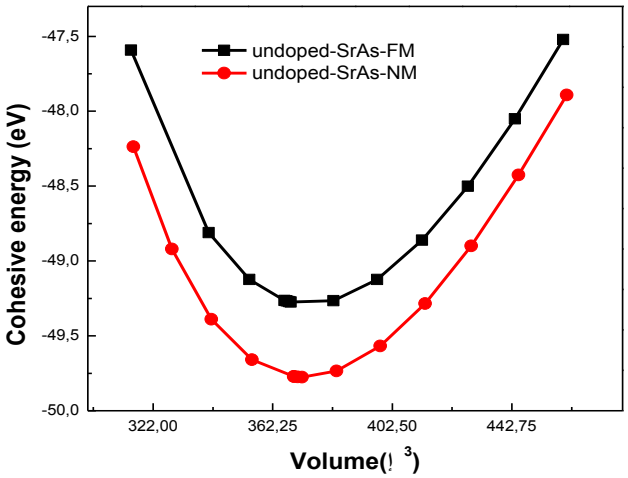

Fig. 2. Variation of cohesive energy versus volume of undoped-SrAs binary compound (color online)

Table 1. The structural parameters a_0, c/a, the compression modulus (B_0) and its pressure derivatives (B') of undoped SrAs binary material in hexagonal Na_2O_2-type structure

SrAs	a(Å)	c/a	B'	B_0 (GPa)
NM undoped-SrAs	8.315	0.756	2.14	47.4
	8.363[a]	0.744[a]		
	8.269[b]	0.749[b]		
FM undoped-SrAs	8.330	0.758	4.95	34.2

Table 2. Computed elastic constants (GPa) for undoped SrAs binary material in hexagonal Na_2O_2-type structure and non magnetic phase

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
SrAs	71.959	45.420	25.871	50.395	30.108	13.269

Table 3. The structural parameters a_0, c/a, the compression modulus (B_0) of Cr doped-SrAs binary material in hexagonal Na_2O_2-type structure

Cr doped-SrAs	a(Å)	c/a	B'	B_0(GPa)	E_{coh} (eV)	$M_{tot}(\mu_B)$
S_1	8,357	0.757	3.18	39.7	-49.89282	5.06
S_2	8,357	0.757	3.25	39.5	-49.89285	5.06
S_3	8,357	0.757	3.19	39.8	-49.89285	5.06
S_4	8,358	0.757	2.94	40.0	-49.89285	5.06
S_5	8,361	0.757	3.95	36.1	-49.93759	5.06
S_6	8,357	0.757	3.51	45.6	-49.92372	5.05

Table 4. The structural parameters a, c/a, the compression modulus (B_0) of X doped SrAs binary material in hexagonal Na_2O_2-type structure

X-doped-SrAs	a(Å)	c/a	B_0(GPa)	M_{Sr} (μ_B)	M_{As} (μ_B)	M_X (μ_B)	M_{Tot} (μ_B)
Ti-doped-SrAs	8,413	0.756	49.5	0.5217	-0.0125	1.8639	4.86
V-doped-SrAs	8,678	0.735	31.6	0.2081	-0.0688	2.6784	4.14
Cr-doped-SrAs	8.361	0.757	36.1	0.1518	-0.0101	3.7627	5.06
Mn-doped-SrAs	8,195	0.745	79.3	-0.0000	0.0000	0.0000	0 .00
Fe-doped-SrAs	8,361	0.745	32.8	-0.0531	0.1060	2.816	2.99
Co-doped-SrAs	8,307	0.740	22.7	0.1769	0.0912	-0.0575	1.54
Ni-doped-SrAs	8,355	0.735	18.7	0.0700	0.0910	0.4426	1.02

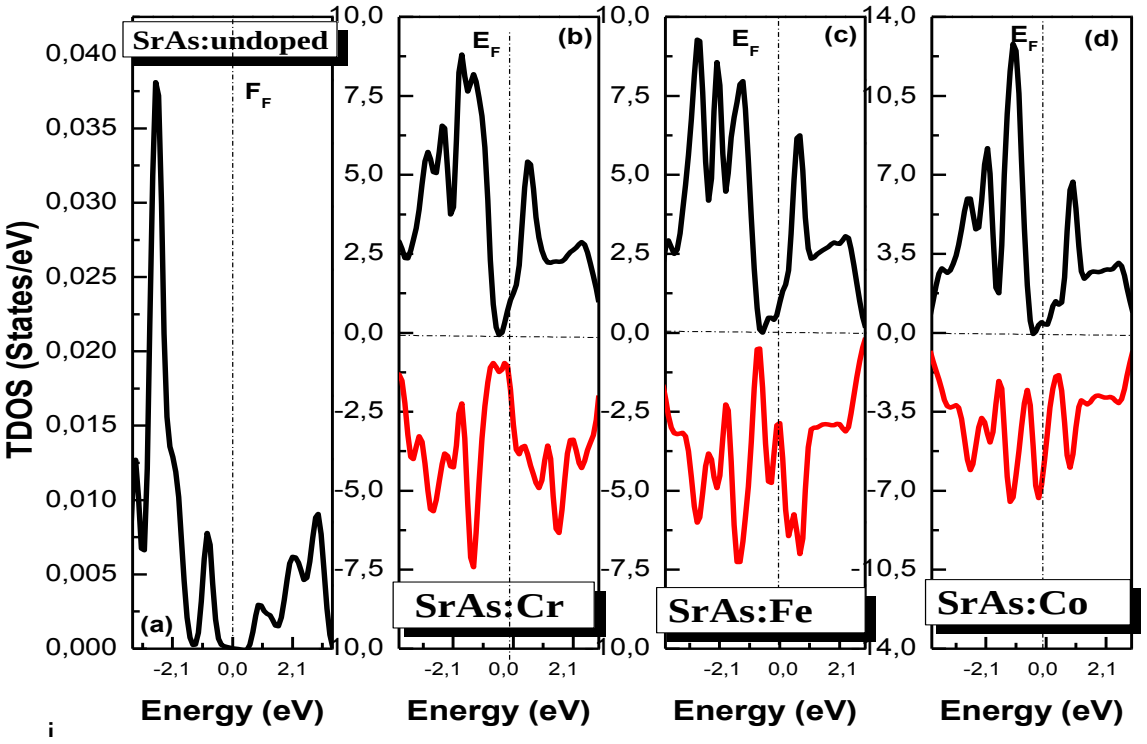

Fig. 3. Calculated total density of state (a) undoped-SrAs (b) Cr-doped-SrAs (c) Fe-doped (d) Co-doped (color online)

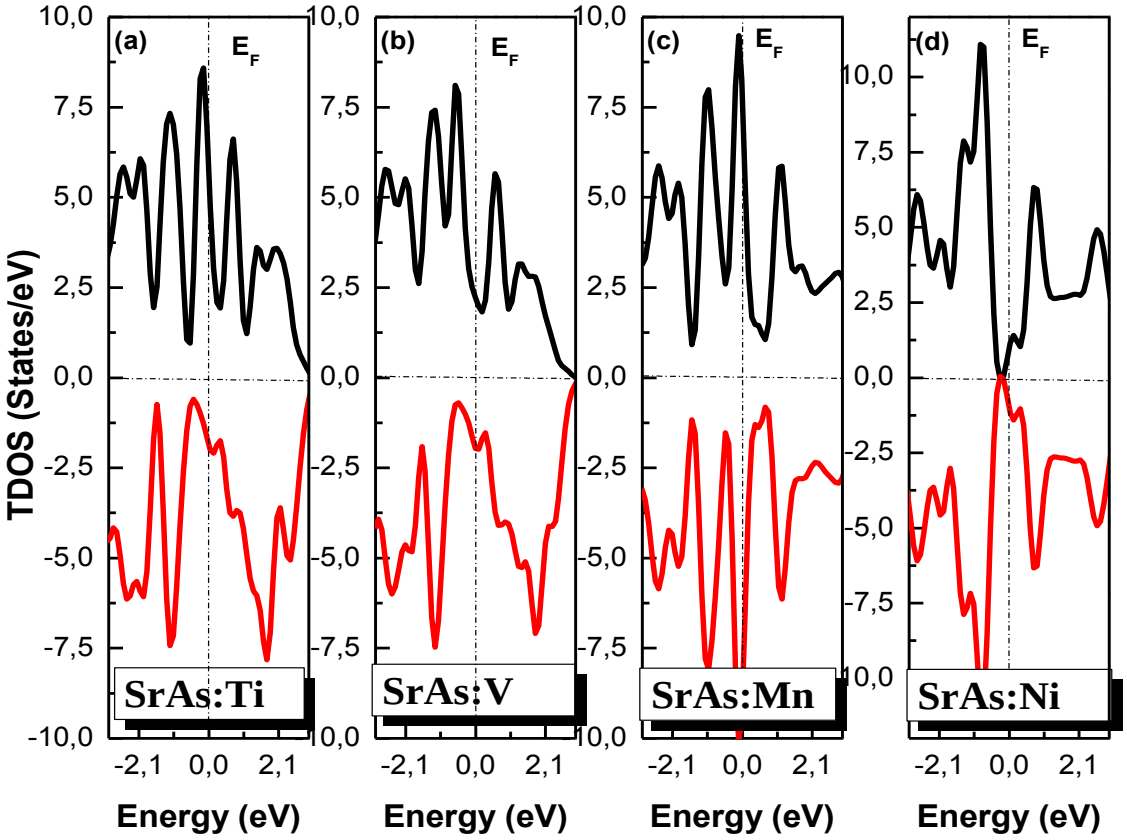

Fig. 4. Calculated total density of state (a) Ti-doped-SrAs (b) V-doped-SrAs (c) Mn-doped-SrAs (d) Ni-doped-SrAs. (color online)

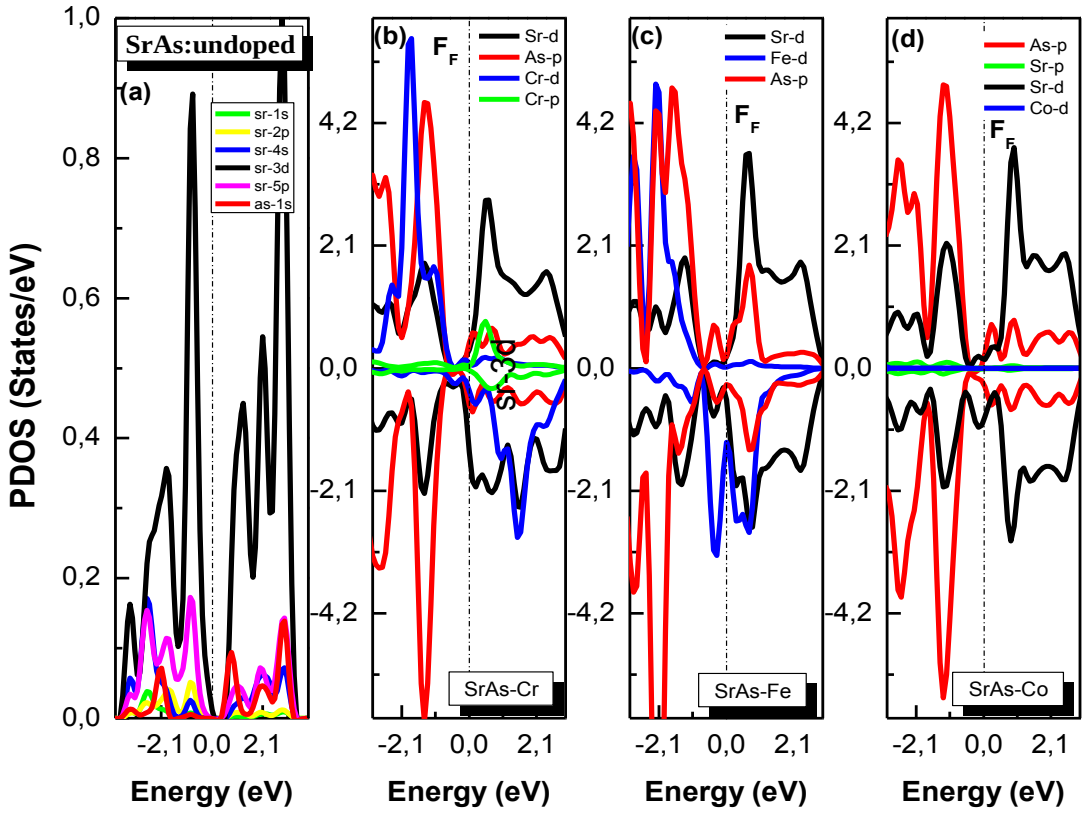

Fig. 5. Calculated partial density of state (a) undoped-SrAs (b) Cr-doped-SrAs (c) Fe-doped (d) co-doped (color online)

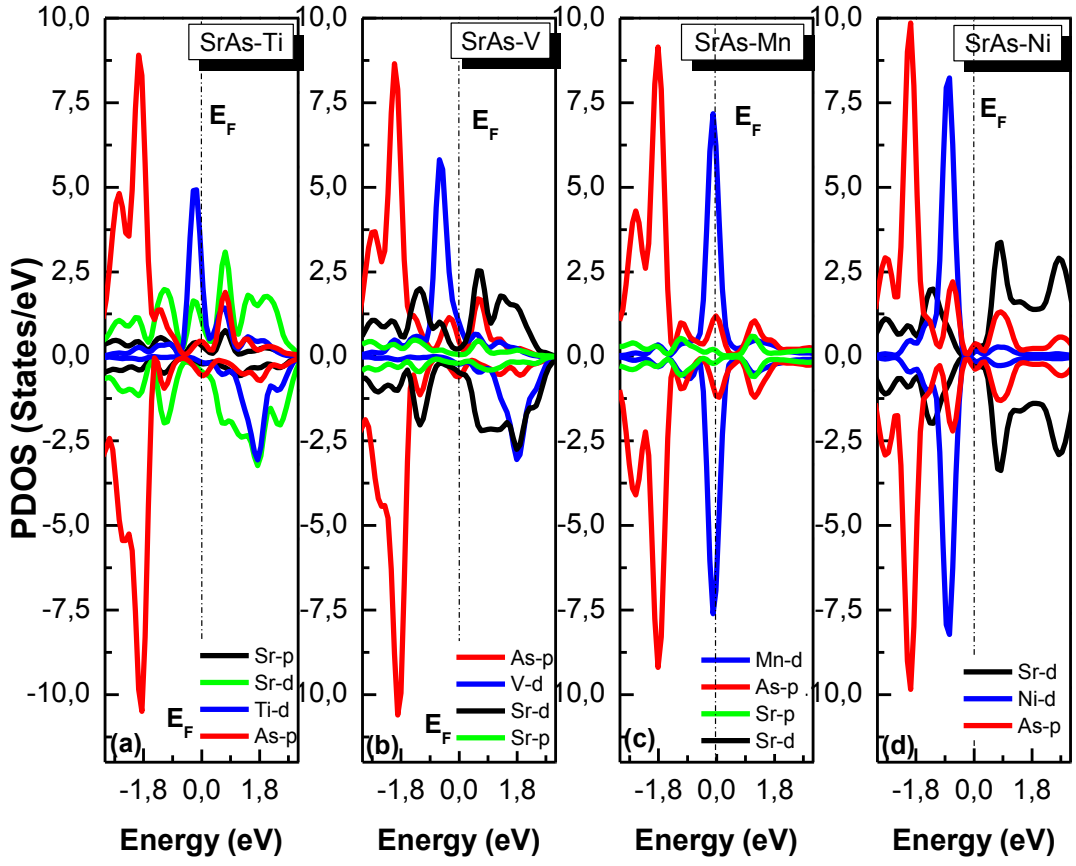

Fig. 6. Calculated partial densitie of state (a) Ti-doped-SrAs (b) V-doped-SrAs (c) Mn-doped-SrAs (d) Ni-doped-SrAs. (color online)

4. Conclusion

Based on the density functional theory, we studied the SrAs binary materials in hexagonal Na_2O_2-type structure doped with transition element X (X=Ti, V, Cr, Mn, Fe, Co and Ni). In the absence of spin polarization study, undoped-SrAs binary compound crystallize in the non magnetic hexagonal Na_2O_2-type structure and our lattice constants are in good agreement with other experimental and theoretical works. Our calculations based on X-doped-SrAs predicted that magnetism can be induced in these binary materials. We found that X (X= Cr, Fe and Co)-doped-SrAs are almost half metallic, whereas (X= Ti, V and Ni)-doped-SrAs are found to be metallic. The induced magnetic moment comes mainly from the doped X atom. In addition, the atoms As and Sr provide a small magnetic moment. Magnetism emerges fundamentally from the coupling between impurity s X-d states and host Sr-d and As-p states.

Acknowledgments

The author wishes to thank laboratory IBN BAJA "intensive computing" technical platform of the University of Science and Technology-MB- of Oran Algeria.

References

[1] M. N. Baibich, J. M. Broto, A. Fert, F. Nguyen Van Dau, P. Etienne, G. Creuzet, A. Friederich, J. Chazelas, Phys. Rev. Lett. **6**, 2472 (1988).
[2] H. Ohno, Science **281**(5379), 951 (1998).
[3] O. Volnianska, P. Jakubas, P. Boguslawski, Journal of Alloys and Compounds **423**, 191 (2006).
[4] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, D. Ferrand, Science **287**, 1019 (2000).
[5] P. Mahadevan, A. Zunger, Phys. Rev. B **69**, 115211 (2004).
[6] S. Ono, J. G. Despault. L. D. Calvert, J. B. Taylor, J. Less-Common Metals. **22**, 51 (1970).
[7] S. E. R. Hiscocks, J. B. Mullin, J. Mater. Sci. **4**, 962 (1969).
[8] A. Iandelli, E. Franceschi, J. Less-Common Metals **30**, 211 (1973).
[9] Persson Kristin, Materials Data on SrAs (SG:189) by Materials Project, 2 (2015).
[10] Seyed Mojtaba Rezaei Sani, Omid Khakpour, School of Nano Science, Institute for Research in Fundamental Sciences (IPM), 19395-5531.
[11] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[12] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcion, I. Dabo, A. Dal Corso, S. D. Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J. Phys. Condens. Matter. **21**, 395502 (2009).
[13] H. J. Monkhorst, J. D. Pack, Phys. Rev. B **13**, 5188 (1976).
[14] F. D. Murnaghan, Proc. Natl. Acad. Sci. **30**, 244 (1944).
[15] J. F. Nye, Physical Properties of Crystals, Oxford, Clarendon Press (1957).
[16] M. Born, K. Huang, Dynamical Theory of Crystal Lattices, Oxford, Oxford University (1954).

*Corresponding author: torrichi@yahoo.fr