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Theoretical study of small clusters of Iron-doped Group III antimonides- Fe (M-X) where M=Al, Ga & In and X-Sb

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ABSTRACT

Structure, electronic and vibrational properties of Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb are studied to investigate the changes in, when an electron is either added or removed from the corresponding neutral clusters by Density functional theory with the B3LYP exchange-correlation functional using DGDZVP as the basis set. Firstly geometrical optimizations of the nanoclusters have been done. Later on these optimized geometries are used to calculate the binding energy, HOMO–LUMO gap (band gap), electron affinity and ionization potential, chemical potential and chemical hardness of the clusters. The calculated results reveal that the any change in the configuration of clusters induces significant structural changes which might help in designing of new entities.

Keywords: Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb, Structure, Stability, DFT

INTRODUCTION

The subject of transition metal cluster chemistry has been the focus of research and importance for more than two decades and it continues to be a rapidly expanding area of chemical investigation[1]. The III-V binary compounds are of a great interest to the technological industry due to their applications in electro-optical devices. Aluminium, Gallium and Indium antimonides (AlSb, InSb, GaSb) are semiconductor of the group III-V family. Indium antimonide photodiode detectors are photovoltaic, generating electric current when subjected to infrared radiation. A layer of indium antimonide sandwiched between layers of aluminium indium antimonide can act as a quantum well. This approach is studied in order to construct very fast transistors [2]. GaSb can be used for infrared detectors, infrared LEDs and lasers and transistors, and thermo photovoltaic systems [3]. Iron being ferromagnetic in nature provided the necessary impetus to explore the structural and electronic changes by doping of iron on these antimonides.Doping of transition metals in group III antimonides are important and have practical uses. To the best of our knowledge no thorough study of Iron doped group III antimonides have been carried out so far in the literature.

MATERIALS AND METHODS

2. Computational Method

The electronic structure calculations were performed on AlSb, InSb and GaSb & Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb clusters, employing the Gaussian 09 code[4]. All calculations were carried out by solving the Kohn–Sham equations in the framework of the Density Functional Theory (DFT) [5]. The gradient corrected Density Functional Theory (DFT) with the three-parameter hybrid functional (B3) [6] for the exchange part and the Lee-Yang-Parr (LYP) correlation function [7] has been employed. The double zeta valence plus polarization

(DGDZVP) basis set optimized for the DFT-orbitals were used for these atoms [8]. To determine the ground state structures of these Fe doped clusters, we constructed as many initial structures as possible.The geometry optimizations were carried out with no symmetry constraint.For the lowest energy isomer, the vibrational frequencies under harmonic approximation were also computed.

RESULTS AND DISCUSSION

All the initial configurations of Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb are schematically represented in Figure 1. All the parameters like Symmetry, Bond Lengths (Å), binding energy and band gap for M-X and Fe-M-X clusters where [M-Al, Ga, In and X-Sb] are listed in Table 1.

3.1 Structural analysis

3.1.1 Neutral state [Fe (Al-Sb), Fe (Ga-Sb) and Fe (In-Sb) Clusters]

The ground state of Fe (AlSb) is predicted to be alluminium centered bend chain of Fe–Al–Sb (Fig.1 C) with FeAl and AlSb bond distances as 2.28 and 2.64 A °, respectively but in the monomer of AlSb, the bond length is 2.80 A ° which is much higher so it can be said that presumably because of the doping of Fe there is a decrease in the AlSb bond length.

The ground state of Fe (GaSb) is predicted to be triangular (Fig.1 D) with FeGa, GaSb and FeSb bond distances as 2.34, 2.70 and 2.36 A °, respectively but in the monomer of GaSb, the bond length is 2.82 A ° which is also much higher in comparison to the doped form. Doping of Fe also decreases the GaSb bond length.

Similarly,the ground state of Fe (InSb) is also predicted to be also triangular (Fig.1 D) with FeIn, InSb and FeSb bond distances being 2.63, 2.91 and 2.35 A °, respectively but in monomer of InSb, the bond length is 2.99 A ° which is much higher. Doping of Fe also decreases the InSb bond length considerably.

3.1.2 Cationic state

The ground state of Fe (AlSb) is predicted to be alluminium centered linear chain of Fe–Al–Sb (Fig.1 A) with FeAl and AlSb bond distances as 2.34 and 2.66 A °, respectively whereas in monomer of AlSb, the bond length is 3.23 A ° which is much higher. Doping of Fe in this case too, decreases the AlSb bond length.

The ground state of Fe (GaSb) is predicted to be triangular (Fig.1 D) with FeGa, GaSb and FeSb bond distances are 2.87, 2.82 and 2.58 A °, respectively but in monomer of GaSb, the bond length is 3.243 A ° which is much higher. Doping of Fe also decreases the GaSb bond length.

The ground state of Fe (InSb) is predicted to be antimony centered linear chain (Fig.1 F) with FeSb and InSb bond distances are 2.53 and 3.22 A °, respectively but in monomer of InSb, the bond length is 3.447 A ° which is much higher. Doping of Fe also decreases the InSb bond length.

3.1.3 Anionic state

The ground state of Fe (AlSb) is predicted to be antimony centered bend chain of Fe–Sb-Al (Fig.1 F) with FeSb and SbAl bond distances are 2.48 and 2.64 A °, respectively but in monomer of AlSb, the bond length is 2.62 A ° which is lower. Doping of Fe increases the AlSb bond length.

The ground state of Fe (GaSb) is predicted to be trigular (Fig.1 D) with FeGa, GaSb and FeSb bond distances are 2.60, 2.64 and 2.55 A °, respectively but in monomer of GaSb, the bond length is 2.646 A ° which is higher. Doping of Fe also decreases the GaSb bond length.

The ground state of Fe (InSb) is predicted to be triangular (Fig.1 D) with FeIn, InSb and FeSb bond distances are 2.76, 2.86 and 2.47 A °, respectively but in monomer of InSb, the bond length is 2.668 A ° which is much lower. Here the striking feature is that the doping of Fe increases the InSb bond length.

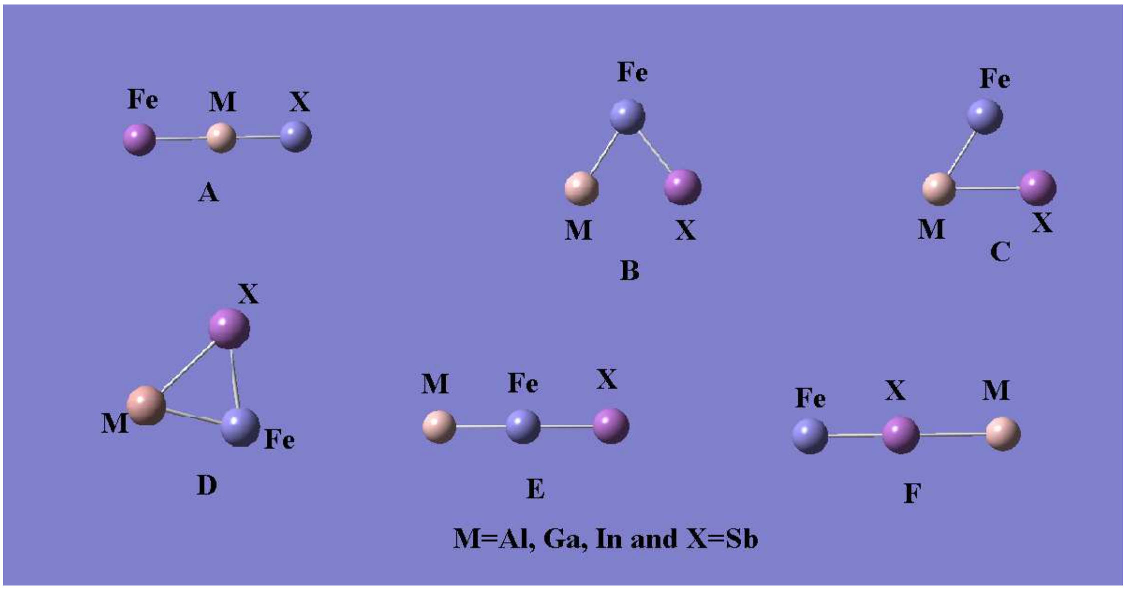

Fig-1 Different cluster combinations of Fe doped group III antimonides

Table 1 Symmetry, Bond Lengths (Å), binding energy and band gap for M-X and Fe-M-X clusters where [M-Al, Ga, In and X-Sb]

Parameters (Symmetry)	R (Fe-M) (Å)	R (M-X) (Å)	R (Fe-X) (Å)	B.E. (ev)	BandGap (ev)
AlSb	-	2.80	-	2.44	0.585
FeAlSb (Cs)	2.28	2.64	-	2.353	2.405
$AlSb^+$	-	3.23	-	1.63	α=0.79 β=0.84
$FeAlSb^+$ (C_{inf})	2.34	2.66	-	2.137	α=2.688 β=3.389
$AlSb^-$	-	2.62	-	2.72	α=2.17 β=1.11
$FeSbAl^-$(Cs)	-	2.64	2.48	1.832	α=2.130 β=2.243
GaSb	-	2.82	-	2.44	0.585
FeGaSb(Cs)	2.34	2.70	2.36	2.267	2.433
$GaSb^+$	-	3.243	-	1.36	α= 0.93 β=0.93
$FeGaSb^+$(Cs)	2.87	2.82	2.58	2.136	α=2.516 β=2.879
$GaSb^+$	-	2.646	-	3.53	α=2.9 β=1.18
$FeGaSb^-$(C_{inf})	2.60	2.64	2.55	1.633	α=1.823 β=1.880
InSb	-	2.9948	-	2.17	0.571
FeInSb(Cs)	2.63	2.91	2.35	2.169	2.290
$InSb^+$	-	3.447	-	1.36	α=0.80 β=0.84
$FeSbIn^+$(C_{inf})	-	3.22	2.53	2.133	α=2.458 β=2.688
$InSb^-$	-	2.668	-	2.72	α=2.63 β=1.12
$FeInSb^-$(Cs)	2.76	2.86	2.47	1.733	α=1.982 β=2.159

3.2 Stability:

In this sub section the relative stability of Fe doped antimonide clusters are analysed based on the average binding energy.

Binding energy (E_b) and HOMO–LUMO gap (E_g)-

Binding energy per atom of the (M-X) Fe clusters is defined as follows-

$$\text{For neutral clusters } E_{BE} = (E\,[M\text{-}X] + E\,[Fe] - E\,[(M\text{-}X)\,Fe])/\,(2)$$

For cationic clusters $E_{BE} = (E\,[M\text{-}X^{+}] + E\,[Fe] - E\,[(M\text{-}X)\,Fe^{+}])/\,(2)$

For anionic clusters $E_{BE} = (E\,[M\text{-}X] + E\,[Fe^{-}] - E\,[(M\text{-}X)\,Fe^{-}])/\,(2)$

The values of binding energy per atom and forbidden band gap (HOMO-LUMO gap) of all clusters are given in Table 1. The variation of binding energy per atom of all clusters shows the same trend for neutral and ionic states as shown in Figure 2. For FeAlSb like clusters, HOMO-LUMO gap of anionic FeAlSb cluster is the lowest of them all ie. 2.13 eV. For FeGaSb like clusters, HOMO-LUMO gap of anionic cluster is also lowest ie. 1.82 eV. For FeInSb like clusters, HOMO-LUMO gap of anionic cluster is 1.98 eV. So anionic FeGaSb cluster is most reactive among them all having the lowest band gap. The variation of Band gap shows same trend for neutral and ionic states of all clusters is given in Figure 3. HOMO-LUMO plots for all the clusters are given in Figures 4, 5 and 6.

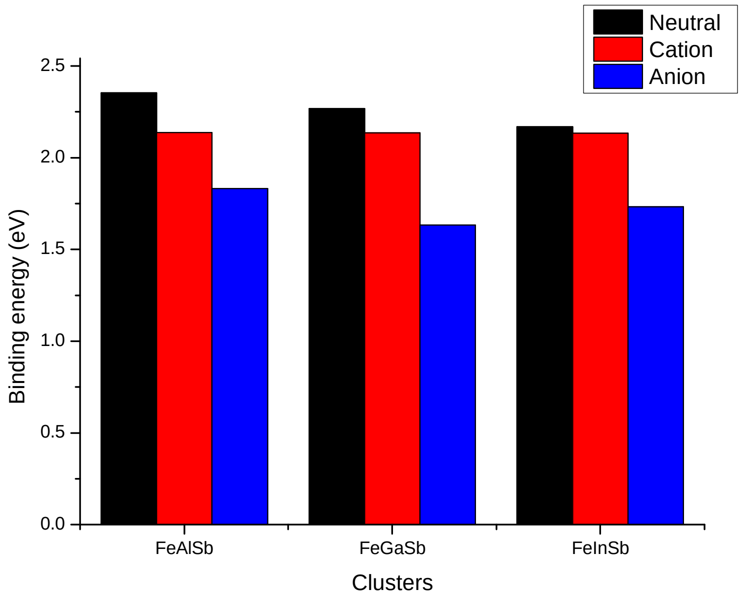

Fig-2 Variation of Binding Energy per atom for neutral, cationic and anionic clusters

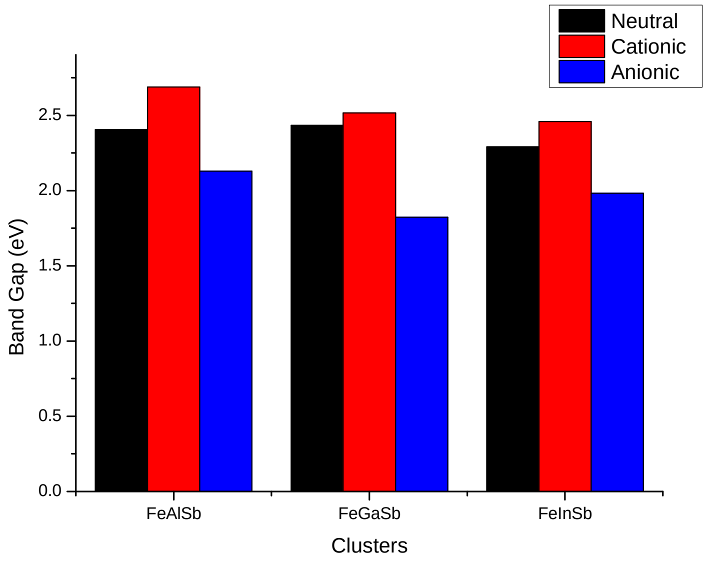

Fig-3 Variation of HOMO-LUMO gap with different combinations for neutral, cationic and anionic clusters

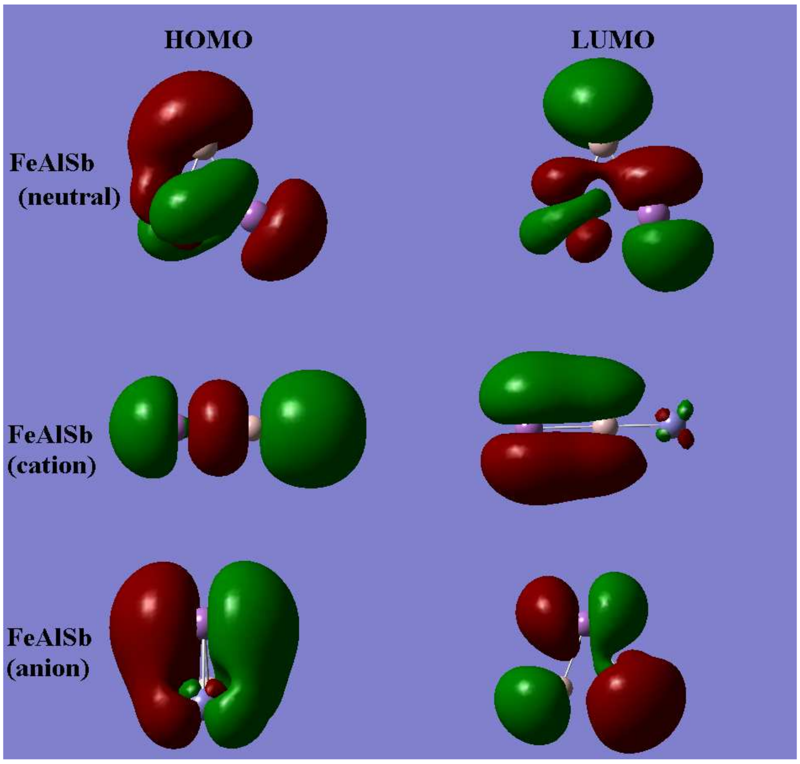

Fig-4 HOMO LUMO pictures of FeAlSb in neutral, cationic and anionic states

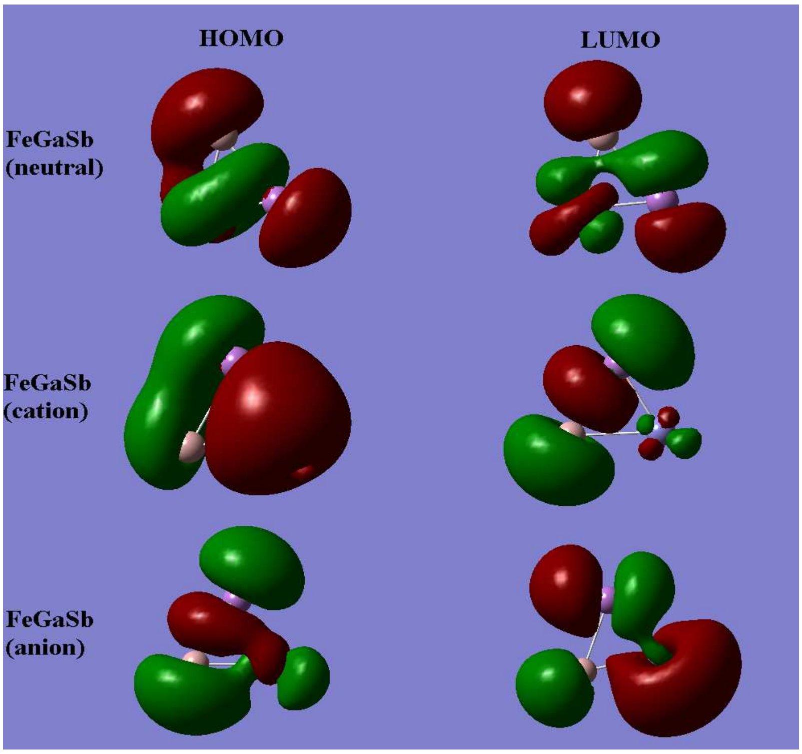

Fig-5 HOMO LUMO pictures of FeGaSb in neutral, cationic and anionic states

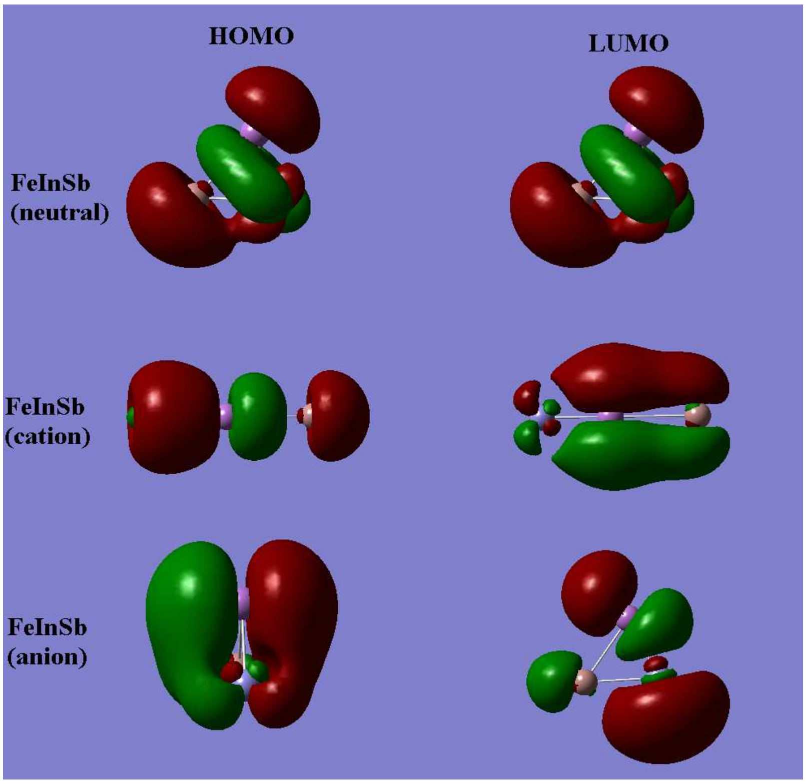

Fig-6 HOMO LUMO pictures of FeInSb in neutral, cationic and anionic states

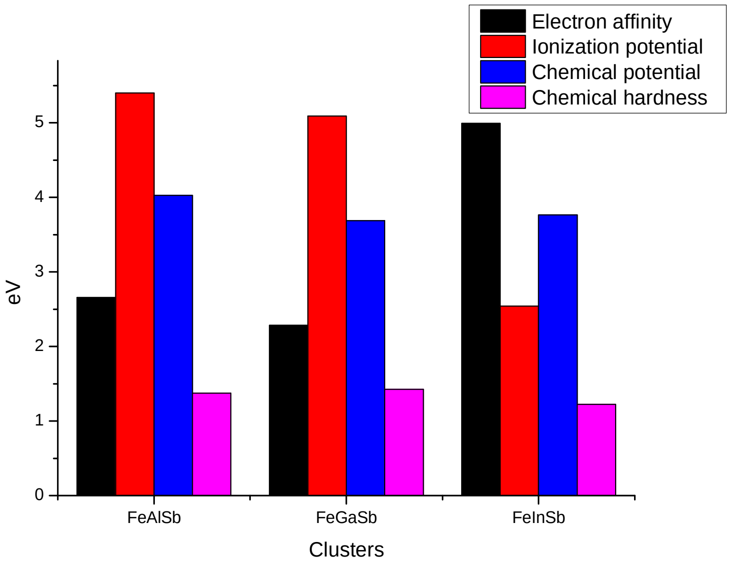

Fig-7 Variation of Electron Affinity, Ionization Potential, Chemical Potential and Chemical Hardness with different combinations for neutral, cationic and anionic clusters

3.3 Electron Affinity, Ionization potential, chemical potential and chemical hardness for Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb

The calculated electron affinity, the ionization potential, chemical potential and chemical hardness for all clusters are listed in Table 2. We define the electron affinity to be EA = E (neutral) – E (anion) and the ionization potential to be IP = E (cation) – E (neutral). We define the chemical potential to be μ = - (IP+EA)/2and chemical hardness to be η = (IP-EA)/2. As far as the chemical hardness is concerned it often acts as a good benchmark of the stability of the system.The variation of Electron Affinity, Ionization potential, chemical potential and chemical hardness of all clusters for neutral and ionic states is given in Figure 7.

Table 2 Electron Affinity and Ionization potential, chemical potential and chemical hardness for FeMX clusters where [M-Al, Ga, In and X-Sb]

Structures	Electron Affinity (ev)	Ionization potential (ev)	Chemical potential (ev)	Chemical Hardness (ev)
FeAlSb	2.657	5.401	4.029	1.372
FeGaSb	2.284	5.089	3.686	1.424
FeInSb	4.991	2.540	3.765	1.225

3.4 Vibrational analysis of Different clusters

Analysis of the normal vibrational modes of Fe (M-X) is carried out in this subsection. The study of the normal modes was used to judge the stability of the lowest lying isomers for the Fe (M-X) clusters. We have considered six different structures (linear, bend, triangular in different combinations) for Fe (M-X) configuration, In Table 3 the vibrational frequencies and their dipole moments of all clusters are collected.

Table 3 Vibrational frequencies and Dipole moment of Different FeMX clusters where [M-Al, Ga, In and X-Sb] most stable structures [cm^{-1}]

Structures	Frequency Values [cm^{-1}]	Dipole moment (Debye)
FeAlSb	2.15, 259, 342	2.14
$FeAlSb^{+}$	83, 84, 152, 409	6.90
$FeSbAl^{-}$	205, 207, 308	2.61
FeGaSb	148, 201, 304	2.19
$FeGaSb^{+}$	81, 114, 200	3.60
$FeGaSb^{-}$	109, 171, 221	1.78
FeInSb	122, 154, 302	2.30
$FeSbIn^{+}$	15, 16, 89, 207	0.32
$FeInSb^{-}$	99, 145, 237	1.79

CONCLUSION

The geometrical structures, stability and the electronic properties etc of the Fe doped (M-X) clusters where M=Al, Ga & In and X-Sb clusters have been studied by Density functional theory with the B3LYP exchange-correlation functional using DGDZVP as the basis set. The descriptors like chemical potential, chemical hardness and binding energy of the clusters provide additional information for the experimentalists to build new materials of industrial importance.

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