



GEOMETRY OPTIMIZATION, COHESIVE ENERGY AND HARMONIC VIBRATION OF Al_9Cu_4 , $Cu_{12}Fe$ And $Al_{13}Fe$ ICOSAHEDRAL METALLIC ALLOYS

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ABSTRACT

Calculation of cohesive energies and IR-spectra of metallic alloy (Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$) clusters with icosahedral structure were reported using Fhi-aims program package based on quantum-mechanical first-principle. For the cohesive energy calculation, it was found that there is difference in energy between the two exchange functionals $pbe+vdW$ and pbe . It was found that For metallic alloy (Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$) there is difference of 0.066eV, 0.075eV and 0.071eV respectively, this shows that the $pbe+vdW$ is more accurate than pbe because of the correction in the short range forces. The Homo-Lumo gap for metallic alloys for all the functional were reported. However, the result of finite-difference method of harmonic vibration for metallic alloys was presented. Also the IR spectra of the metallic alloy produce the peaks observed for the metal as reported by M. Said and G. Babaji and some other peaks indicating that there is more absorption in the metallic alloys than in metal

Keys: Metallic alloys, Clusters, Cohesive energy and IR-spectrum

INTRODUCTION

Metals and Alloys have contributed more to the development of mankind over the millennia. Throughout the centuries, studies of metals belonged to one of the oldest branches of Applied Material Sciences-Metallurgy. This changed in the late 19th and early 20th centuries, when applications of metallic materials spread into other areas of science and technology including electronics, energy, aeronautics and space travel. Currently, it's impossible to imagine a world in which we could successfully function without metals and alloys. Traditionally, metals are portrayed as shiny solids, most of which are good conductors of heat and electricity. They are ductile and most will melt at high temperatures. The shapes of metals and alloys can easily be changed by mechanical processing (Viktor, 2007).

Clusters of alloys are interesting for novel nanomaterials as their atomic distributions and compositions could be quite different from bulk. Aluminum alloys are technologically important due to their building block (Pearson, 1982). Studies of the electronic structure and bonding in clusters provide a fundamental understanding of phenomena at the nanoscale and could give useful insight into the properties of complex alloys from a local point of view (Kumar, 2001).

Developments in nanoscale science enable scientists to atomically engineer and characterize clusters of any size and composition. The importance of these developments lies in the fact that clusters offer a novel class of materials with electronic, catalytic, and magnetic properties that are different from the bulk. Clusters are usually used to describe aggregates of atoms that are too large to be referred to as molecules and too small to resemble small pieces of crystals. Clusters generally do not have the same structure or atomic arrangement as a bulk

solid (Viktor, 2007). Clusters may be classified as metallic or nonmetallic according to the atoms they are made of in general some metallic character persists from small clusters to bulk matter of the same composition. Atoms are easily classified as metallic, nonmetallic or semiconducting purely in terms of their ionization potentials (Nusret *et al*, 2012).

Density-functional theory (DFT) is one of the most popular and robust theoretical approaches currently available for solving the electronic structures of solids and their surfaces. Although far from a panacea for all physical problems in this domain (or any other), no other theoretical approach has provided as much basic understanding of the electronic structures of surfaces, in general, and metal surfaces. In particular, DFT has proven capable of computing a host of properties of condensed matter and their surfaces to reasonable accuracy (Angelos and Scheffler, 2010).

Kumar, 2001 reported the study on $Al_{12}Cu$ that the structure has perfect icosahedral symmetry and magnetic moment of $3\mu_B$ and its interaction have led to an electronically closed shell magic cluster. Li *et al*, 2009 report study on small cluster of aluminum with atom at different adsorption site, suggested that both Al_3 and Al_6 on-top site is the most stable position for the doped Li element. Bowen, 2011 suggested that Al_{13} is the most highly stable for both electronic and geometrical icosahedral cluster. Mukul 2008 reported that the ground state geometries, binding energies, second differences in binding energy, Homo-Lumo gap energies and ionization potential of copper cluster with size range $2 \leq n \leq 55$. He concluded that icosahedral structure of copper cluster changes to decahedral when the number of atoms is between 40-44.

Fhi-aims computer program based on quantum-mechanical first-principle was used to investigating the electronic structure of metals and their alloys. The model is extracted from Cambridge energy land scape database and then modified with jmol molecular builder. We optimized the geometry, calculate the cohesive energy and the harmonic vibration of the found global minima of each cluster.

Density Functional Theory

The DFT is a method where the many-body problem is treated by the single-particle density through the Kohn-Sham equations. This was proposed by P. Hohenberg and W. Kohn in 1964. The total energy is a functional of the density. Thus all properties of the system can be considered to be unique functional of the ground state density. The number of degrees of freedom is now significantly reduced allowing for quick computations in comparison to other quantum chemical methods. As a result DFT has become a primary tool for calculation of electronic structure in condensed matter and is increasingly important for quantitative studies of molecules and other finite systems. The formulation of DFT as we use today, comes from the classic work of W. Kohn and L. J. Sham in 1965 and has become the basis of much of

$$\hat{H}^\sigma = -\frac{1}{2}\nabla^2 + \nabla^\sigma \quad (1)$$

For a system of N independent electrons with $N = N^\uparrow + N^\downarrow$ obeying this, the ground state has one electron in each of the N^σ orbitals ψ_i^σ with the lowest eigen values ε_i^σ of the Hamiltonian. The density of the auxiliary system is given by sums of squares of the orbitals for each spin.

$$n(r) = \sum_\sigma n(r, \sigma) = \sum_\sigma \sum_{i=1}^{N^\sigma} |\psi_i^\sigma|^2 \quad (2)$$

the independent-particle kinetic energy T_s is given by

$$T_s = \frac{1}{2} \sum_\sigma \sum_{i=1}^{N^\sigma} \langle \psi_i^\sigma | \nabla^2 | \psi_i^\sigma \rangle = \frac{1}{2} \sum_\sigma \sum_{i=1}^{N^\sigma} |\nabla \psi_i^\sigma|^2 \quad (3)$$

and the classical Coulomb energy of the electron density $n(r)$ is defined as

$$E_{Hartree}[n] = \frac{1}{2} \int d^3r d^3r' \frac{n(r)n(r')}{|r-r'|} \quad (4)$$

The Kohn-Sham approach to the full interacting many-body problem is to rewrite the Hohenberg-Kohn expression of ground state energy functional in the form

$$E_{KS} = T_s[n] + \int dr V_{ext}(n)n(r) + E_{Hartree}[n] + E_H + E_{XC}[n] \quad (5)$$

where, V_{ext} is the external potential due to the nuclei and other external fields (assumed to be independent of spin), E_H : the interaction among the nuclei.

$$(H_{KS}^\sigma - \varepsilon_i^\sigma)\psi_i^\sigma(r) = 0 \quad (6)$$

where ε_i are the eigenvalues, and H_{KS} is the effective Hamiltonian

$$H_{KS}^\sigma(r) = -\frac{1}{2}\nabla^2 + V_{KS}^\sigma \quad (7)$$

where V_{KS}^σ consists of three terms, i.e.,

$$V_{KS}^\sigma = V_{ext}(r) + \frac{\delta E_{Hartree}}{\delta n(r, \sigma)} + \frac{\delta E_{XC}}{\delta n(r, \sigma)} = V_{ext}(r) + V_{Hartree} + V_{XC}^\sigma \quad (8)$$

The last three equations are the Kohn-Sham equations, with the electron density $n(r, \sigma)$ and total energy E_{KS} given in Eqs.5 and 8. If the exact $E_{XC}[n]$ functional is known, then the exact ground state density and energy can be calculated for the interacting system.

EXCHANGE CORRELATION FUNCTIONALS

Local Density Approximation (Lda)

In local density approximation (LDA) or more generally the local spin density approximation (LSDA), the exchange- correlation energy is an integral over all space with the exchange-correlation energy density at each point assumed to be the same as in a homogeneous electron gas with the density (Kohn and Sham, 1965).

$$E_{XC}^{LSDA}[n^\uparrow, n^\downarrow] = \int d^3r n(r) \varepsilon_{XC}^{hom}(n^\uparrow(r), n^\downarrow(r)) \quad (9)$$

Here, the spin quantization axis is assumed to be the same at all points in space. The LSDA is the most common local approximation for exchange and correlation. In the case of unpolarized systems, the LDA is found by setting $n^\uparrow(r) = n^\downarrow(r) = \frac{n(r)}{2}$. In LDA,

$$\delta E_{XC}[n] = \sum_\sigma \int dr \left[\varepsilon_{XC}^{hom} + n \frac{d\varepsilon_{XC}^{hom}}{dn^\sigma} \right]_{r, \sigma} dn(r, \sigma) \quad (10)$$

Hence the exchange-correlation potential V_{XC}^σ can be expressed as

present-day methods for treating electrons in atoms, molecules, clusters, surfaces, adsorbates and bulk. One of the landmark achievement of the DFT is the local-density approximation (LDA) as the exchange-correlation functional which is very successful in describing the material properties. Improvements over LDA, like generalized gradient approximation (GGA) is also mostly recommended in many cases. Below we present a brief theoretical description of the DFT following the description of (Martin, 2004).

The Kohn-Sham Approach

The assumption made behind this approach is that the ground state density of the original interacting system is equal to that of a non-interacting system, which leads to independent particle equations of the non-interacting system that can be considered exactly soluble with all manybody terms incorporated into an exchange-correlation functional of the density. By solving the equations one finds the ground state density and energy of the original interacting system with the accuracy limited by the approximations in the exchange-correlation functional. The Hamiltonian for the independent particle system has form (Kohn and Sham, 1965).

$$V_{XC}^{\sigma} = \left[\varepsilon_{XC}^{hom} + n \frac{d\varepsilon_{XC}^{hom}}{dn^{\sigma}} \right]_{r,\sigma} \quad (11)$$

Since $\varepsilon_{XC}^{hom}(n)$ scales $(n^{\sigma})^{-\frac{1}{3}}$ the LDA exchange terms are,

$$V_{XC}^{\sigma}(r) = \frac{4}{3} \varepsilon_X^{hom}(n(r,\sigma)) \quad (12)$$

Generalized-Gradient Approximation (GGA)

In generalized gradient approximation (GGA), the exchange-correlation potential is treated as a function of both electron density as well as the gradient of the density. The exchange-correlation functional in GGA has the form.

$$\delta E_{XC}[n] = \sum_{\sigma} \int dr \left[\varepsilon_{XC} + n \frac{d\varepsilon_{XC}}{dn^{\sigma}} + n \frac{d\varepsilon_{XC}}{d\nabla n^{\sigma}} \right]_{r,\sigma} dn(r,\sigma) \quad (13)$$

where, the term in the square brackets is the exchange-correlation potential.

$$\delta V_{XC}^{\sigma}[n] = \left[\varepsilon_{XC} + n \frac{d\varepsilon_{XC}}{dn^{\sigma}} + n \frac{d\varepsilon_{XC}}{d\nabla n^{\sigma}} \right]_{r,\sigma} \quad (14)$$

Density Functional Theory +vanderWaals (DFT+vdW)

Nowadays it is well known that most popular exchange functionals generally show unsatisfactory performance for vdW forces, which inherently arise due to nonlocal correlations (Biswajit *et al* 2008). In order to test if the lack of vdW forces is indeed responsible for the underestimation in the two body interaction we use a simple C_6R^{-6} correction for the DFT total energies. The C_6R^{-6} correction method was early proposed for correcting Hatree-Fock calculation (Ahlrich *et al*, 1977) and specifically applied to DFT by Wu and Yang (2002), Grimme (2004) and Jurecka *et al* (2007). certainly the C_6R^{-6} pairwise scheme is a simple one for incorporation dispersion interaction into DFT calculations in contrast to other approaches.

With this approach the pairwise vdW interaction (E_{dis}) is calculated by (Biswajit *et al* 2008),

$$E_{disp} = - \sum_{j>i} f_{damp}(R_{ij}, R_{ij}^0) C_{6ij} R_{ij}^{-6} \quad (15)$$

where C_{6ij} are the dispersion coefficients for an atom pair ij , R_{ij} is the interatomic distances, R_{ij}^0 is the sum of equilibrium vdW distances for the pair and damping function. The damping function is needed to avoid the divergence of the R^{-6} term at short distances and reduces the effect of the correction on covalent bonds (Biswajit *et al*, 2008).

VIBRATION AND VIBRATIONAL FREE ENERGY OF CLUSTERS

The dynamic behavior of a cluster is described by a set of coordinates (Ahmad *et al* 2013);

$$[r_1, r_2, \dots, r_N] \quad (16)$$

which are treated as time dependent variable. The particles within the cluster are assumed to interact via binary potential v which depends only on their relative position;

$$v(r_i, r_j) = v(|r_i - r_j|) \quad (17)$$

The total potential energy of the cluster, v_p is assumed to be given by the summation of binary interactions over all the pair particles in the cluster

$$v_p([r_1 \dots r_N]) = \sum_{i>j} v(|r_i - r_j|) \quad (18)$$

where the dependence of the potential energy on the cluster configuration has been emphasized. The configuration of a cluster which minimizes the potential energy function can be denoted by the set of coordinates

$$[r_1^0, r_2^0 \dots r_N^0] \quad (19)$$

which denoted by mean static position of N particle within the cluster.

Assuming that;

$$U_i = r_i - r_i^0; |U_i| \ll |r_i^0 - r_j^0| \forall i, j \in \{1, \dots, N\} \quad (20)$$

the displacement of particles from their equilibrium position are small, one can expand the total potential energy of the cluster in Tylor series up to the second order as

$$v_p([r_1 \dots r_N]) = v_p([r_1^0, \dots, r_N^0]) + \frac{1}{2} \sum_{i,j} \sum_{\alpha,\beta} U_i^{\alpha} U_j^{\beta} \left(\frac{d^2 v_p}{dr_i^{\alpha} dr_j^{\beta}} \right) \quad (21)$$

where α and β denote the Cartesian component (X, Y and Z) of vectors. The first derivatives of v_p with respect to atom coordinate are assumed to vanish that is, the cluster is assume to be minimum potential energy configuration and this is well known as harmonic approximation and it serves as starting point for calculation of cluster normal mode of vibration (i.e a set of linear combination of $\{U_i \dots U_N\}$ variables or eigenmodes each of which correspond to a vibration of the system with single frequency). The Hamiltonian of the problem when written in terms of normal mode coordinates represent a set of independent harmonic oscillation whose both quantum and classical dynamic are well known. There are $3N - 6$ such oscillations with characteristic frequency ω_p with $p = 1, \dots, 3N - 6$. Six degree of freedom that does not represent vibrations is the three rotations and three translation of the whole system.

Once a set of eigen frequencies are calculated one can proceed to calculate the Helmholtz free energy of the cluster F which is given as (Ahmad *et al* 2013);

$$F = -K_B T \ln Z \quad (22)$$

where K_B is Boltzmann constant T is temperature and Z is quantum partition function of the system of $3N - 6$ independent oscillators. Equation 22 can be express in term of eigenmodes frequencies as;

$$F = v_p^0 + \sum_{p=1}^{3N-6} \frac{\hbar \omega_p}{2} + K_B T \sum_{p=1}^{3N-6} \ln \left[1 - e^{-\left(\frac{\hbar \omega_p}{K_B T}\right)} \right] \quad (23)$$

where

$$v_p^0 = v_p [r_1^0 \dots r_N^0] \quad (24)$$

The above equation is the minimum of classical potential energy of the cluster (ground state energy). The sum of the first two terms in equation 23 represents the quantum ground state of the cluster, E_0 calculated in the harmonic approximation.

At constant temperature, the state which represents the thermodynamical equilibrium of the system is the one which minimizes the Helmholtz free energy. (Not that even at zero temperature, the cluster free energy has a quantum zero-point energy contribution). Thus even at zero temperature the thermodynamical equilibrium state of the cluster need not to be the same as the state which minimizes the classical potential energy of the cluster (Ahmad *et al* 2013).

COMPUTATIONAL METHODE

FHI-AIMS CODE

Fhi-aims(Fritz Haber Institut ab-initio molecular simulation) is a computer program package for computational material science based on quantum-mechanical first principles. The main production method is density functional theory(DFT) to compute the total energy and derived quantities of molecular, cluster or solid condense matter in its electronic ground state. In addition FHI-aims allows to describe electronic single quasiparticle excitations in molecules using different self-energy formalisms, and wave-function base molecular total energy calculation based on Hartree-Fock and manybody perturbation theory (Blum *et al* 2009).

The focus here is on density functional theory(DFT) in the local and semi-local (generalized gradient) approximations but an extension on hybrid functional, Hartree-Fock theory, and MP2/GW electron self-energies for local energies and excited states is possible with the same underlying algorithms. An all electron/full-potential treatment that is both computationally efficient and accurate is achieved for periodic and cluster geometries on equal footing, including relaxation and ab initio molecular dynamics (Havu *et al*, 2009). The construction of transferable, hierarchical basis set is demonstrated, allowing the calculation to range from qualitative tight-binding like accuracy to meV-level total energy convergence with basis set. Together with scalar-relativistic treatment, the basis sets provide access to all elements from light to heavy. Both low-communication parallelization of all real-space grid based algorithms and a scalapack-based, customized handling of the linear algebra for all matrix operations are possible, guaranteeing efficient scaling (CPU time and memory) up to massively parallel computer system with thousand of CPUs(Havu *et al*, 2009).

CONSTRUCTION OF GEOMETRY

The geometry of the icosahedron clusters were obtained from the Cambridge University Landscape Database (<http://www-wales.ch.cam.ac.uk/CCD.html>, 2016). Jmol molecular viewer was used to arrange the clusters into the FHI-aims format for the alloys. For Al_9Cu_4 , $Al_{12}Fe_1$ and $Cu_{12}Fe_1$ a Metropolis Monte Carlo approach was employed for finding the best configuration setting for the structures.

GEOMETRY OPTIMIZATION

The exchange functional (pbe+vdW), spin (collinear), default_initial_moment (hund) and zeroth-order regular approximation (atomic_zora scalar) were kept fixed. The parameters optimized are; Occupation_type_gaussian, charge_mix_param, sc_accuracy_rho, sc_accuracy_eev, sc_accuracy_etot,sc_accuracy_forces,empty_states and relax_geometry.). Each parameter chosen, a number of values were selected until the lowest energy was found. The structure was relaxed again by putting the optimized values found. The procedure was repeated for each Alloys (AlCu, CuFe and AlFe) and for each time the total energy was recorded.

CALCULATION OF BASIS SIZE

After obtaining the converged geometry, the calculation of basis size was employed for both metal and alloy. Each element has different basis set. For Al_9Cu_4 ; there are 19 basis size for tier_1, 28 basis size for tier_2, and 37 basis size for tier_3. For $Cu_{12}Fe_1$; there are 22 basis size for tier_1, 32 basis size for tier_2, and 46 basis size for tier_3. There are 19 basis size for tier_1, 32 basis size for tier_2, and 41 basis size for tier_3. For each set of tiers the total energy was calculated and recorded.

Calculation of Cohesive Energy

After finding converged basis size we now revisit the phase stability of cluster. The cohesive energy (E_{coh}) of a cluster is the energy per atom needed to separate it into its constituent of atoms. E_{coh} is defined as

$$E_{cohesive} = -\frac{1}{N} [E_{total} - \sum(aE_{al} + bE_{cu})] \quad (25)$$

were $N = a + b$, E_{total} = total energy of the cluster, E_{al} and E_{cu} = total energy of free atom of aluminum and copper respectively.

VIBRATION

After the geometry of the metals were obtained, the Harmonic vibration using finite difference method used for the spectral analysis of the cluster was set by commenting the relax_geometrybfgs 1.0E-5 and adding the tags; the vibrations free_energy vibrations trans_free_energy into the *control.in* for calculating the vibrational and rotational energies at different temperature was chosen for this work. The procedure was repeated for Al_9Cu_4 , $Al_{12}Fe_1$ and $Cu_{12}Fe_1$.

RESULTS AND DISCUSSION

Optimization of Key Parameters

GEOMETRY OPTIMIZATION WITH INCREASE BASIS SIZE

Table 1: Optimized parameters of for Al_9Cu_4 , $Al_{12}Fe_1$ and $Cu_{12}Fe_1$ clusters with icosahedral structure

Parameter	Optimized Values								
	Al_9Cu_4			$Al_{12}Fe_1$			$Cu_{12}Fe_1$		
	Optimize values	Energy (eV)	Time(s)	Optimize values	Energy (eV)	Time(s)	Optimize values	Energy (eV)	Time(s)
occupation_type Gaussian	0.4	-240499.9108744670	39374.61	0.1	-577704.0564425050	34591.95	0.2	-114124.4743298140	12.345
charge_mix param	0.006	-240499.9108744670	39374.61	0.002	-577704.4253033220	17407.87	0.004	-114124.4743298140	12.345
sc_accuracy rho	0.0001	-240499.7256474620	10827.37	0.00002	-577704.4253033220	17407.87	0.0001	-114124.4743298140	12.345
sc_accuracy eev	0.0005	-240499.7256474620	10827.37	0.00005	-577704.4253033220	17407.87	0.0005	-114124.4743298140	12.345
sc_accuracy etot	0.00001	-240499.5137392700	37859.87	0.00001	-577704.4253033220	17407.87	0.0001	-114124.2743298140	3902.684
sc_accuracy forces	0.0001	-240499.9108744670	39374.61	0.00002	-577704.4253033220	17407.87	0.00004	-114124.4743298140	12.345
empty_states	10	-240499.9108744670	39374.61	8	-577704.2627250350	16835.4	8	-114124.2743298140	6.987
relax_geometry	0.00001	-240499.9108744670	9241.434	0.0001	-577704.4253033220	17407.87	0.00001	-114124.3584912300	2579.661

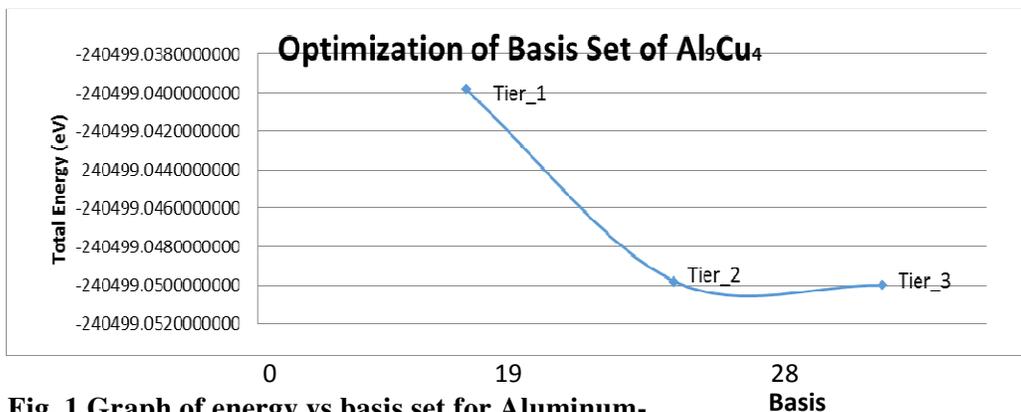


Fig. 1 Graph of energy vs basis set for Aluminum-

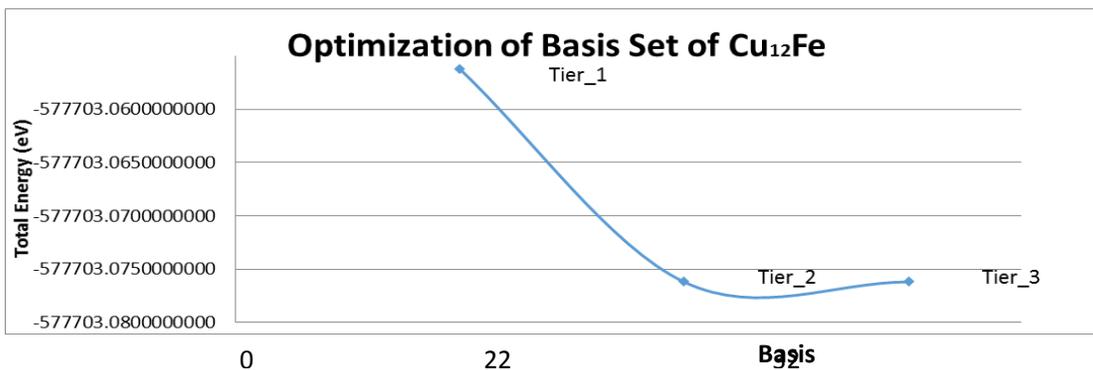


Fig. 2 Graph of energy vs basis set for Copper

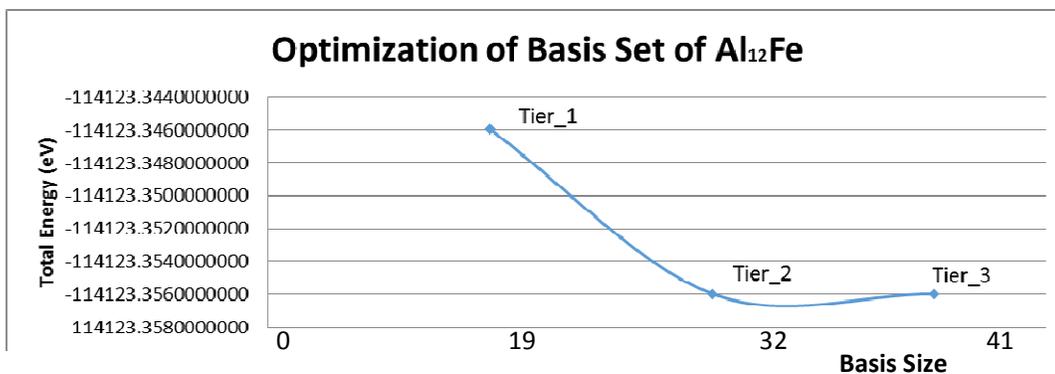


Fig. 3 Graph of energy vs basis set for Aluminum Iron

4.3 COHESIVE ENERGY

Table 2: Calculated value of the cohesive energy of a pure Al, Cu and Fe Icosahedron cluster using pbe and pbe+vdW

S/N	Metal	Total Energy(eV)	Method	Cohesive Energy(eV)	References (eV)	Homo-Lumo (eV)
1.	AlCu	-240499.049799384	pbe+vdW	2.619599346	2.595eV(Kumar and Kawazoe, 2001)	0.61815649
2.	AlCu	-240499.910874467	pbe	2.685835891		0.48762530
3.	CuFe	-577703.076190273	pbe+vdW	2.261454565		0.14326813
4.	CuFe	-577704.055970726	pbe	2.336822303		0.13596176
5.	AlFe	-114123.355962386	pbe+vdW	2.711292328		0.33438081
6.	AlFe	-114124.273957468	pbe	2.781907345		0.32175020

4.4 HARMONIC VIBRATION

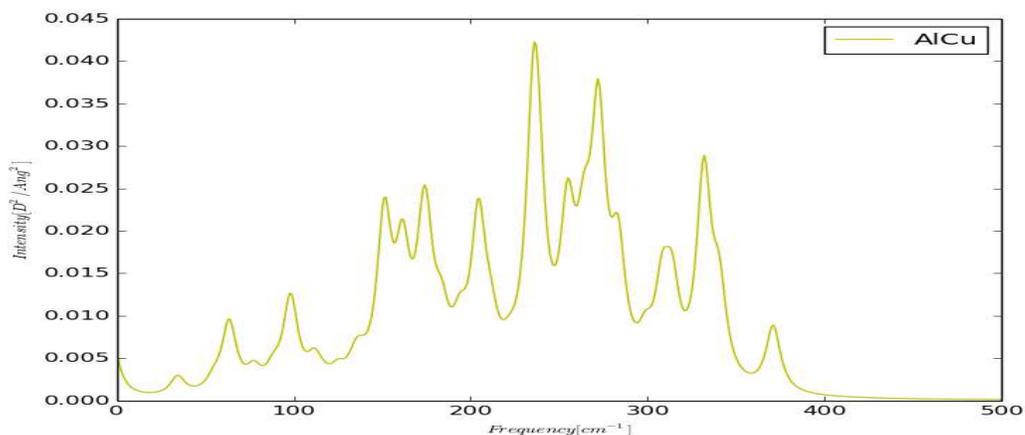


Figure 4: IR spectra of Aluminum Copper cluster with icosahedron structure

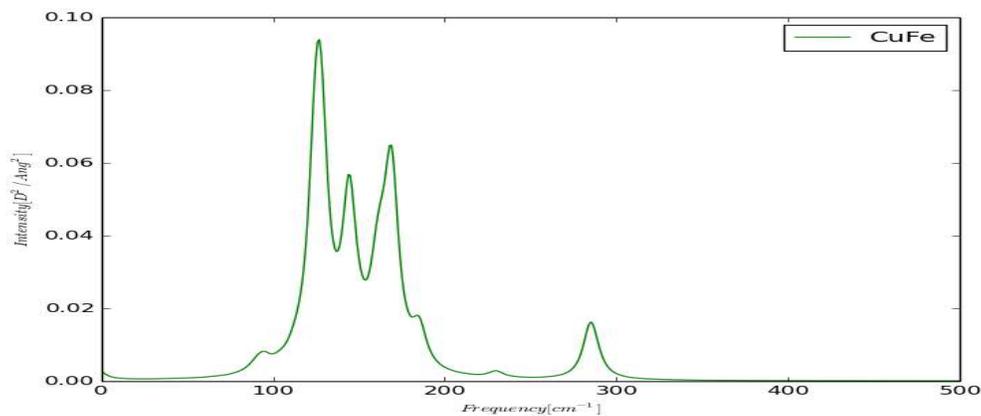


Figure 5: IR spectra of Copper Iron cluster with icosahedron structure

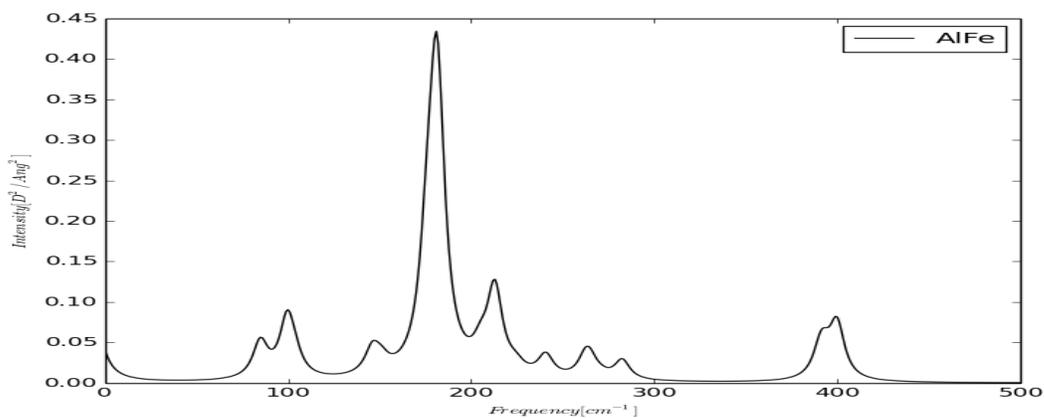


Figure 6: IR spectra of Aluminum Iron cluster with icosahedron structure

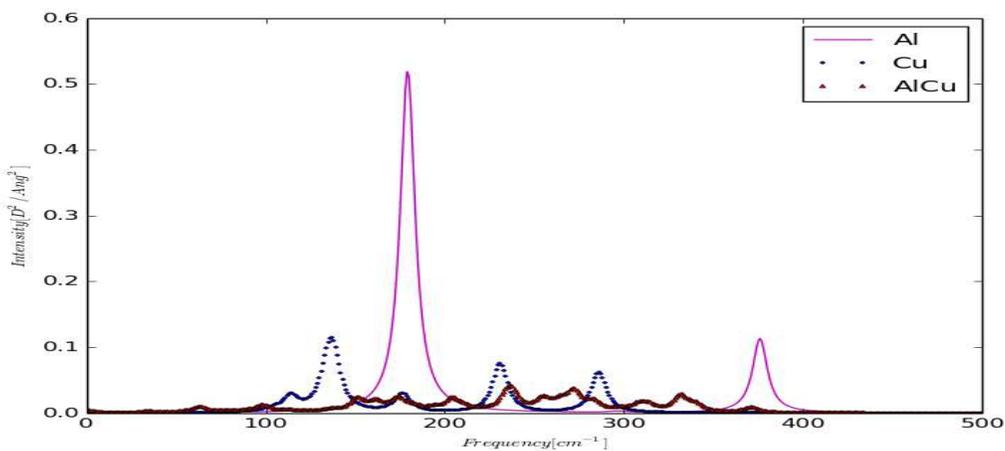


Figure 7: Comparisons of Aluminum, Copper and Aluminum Copper alloy Clusters with Icosahedral structure

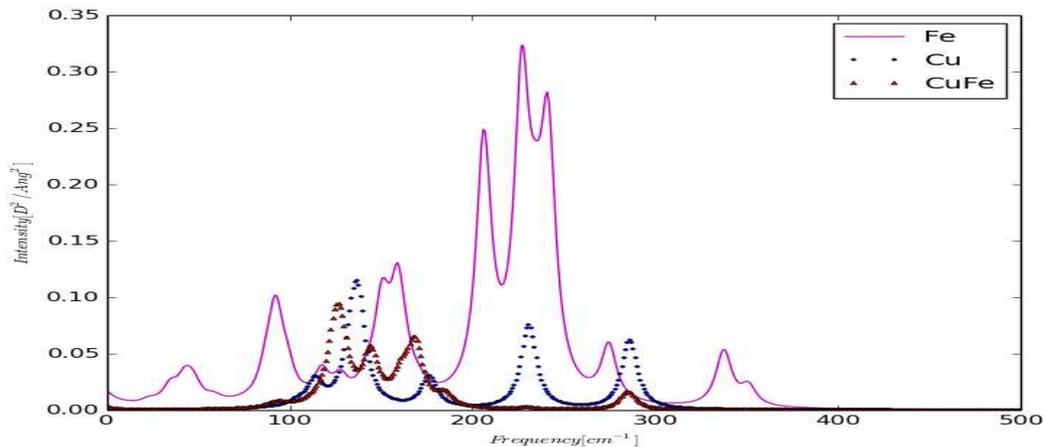


Figure 8: Comparisons of Copper, Iron and Copper iron alloy Clusters with Icosahedral structure

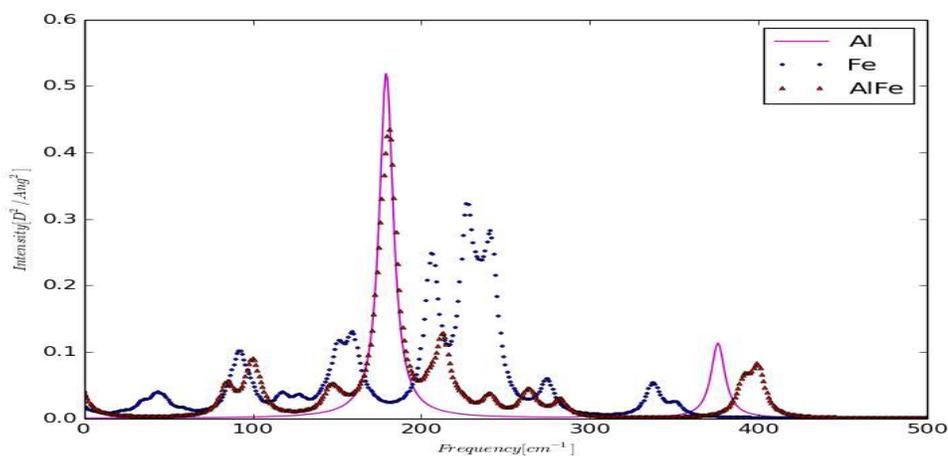


Fig.9 Comparisons of Aluminum, Iron and Aluminum iron alloy Clusters with Icosahedral structure

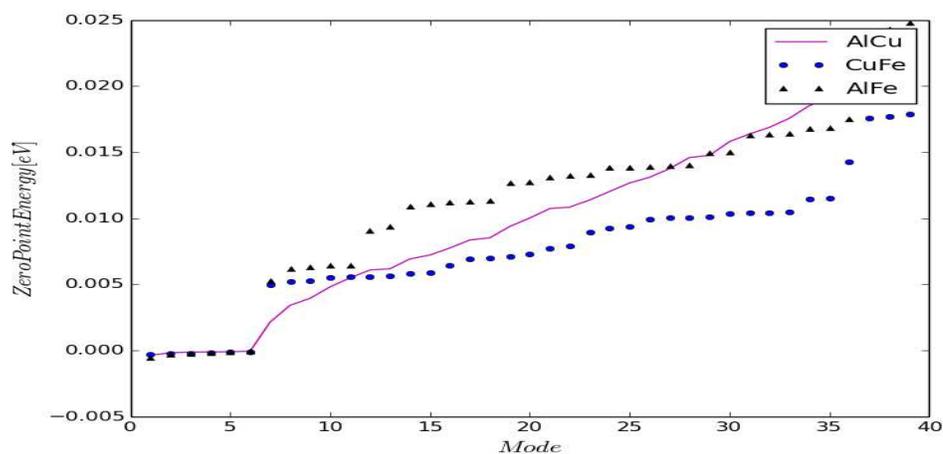


Fig.10 Vibration of Zero point Energy of AlCu(solid), CopperFe (circle) and AlIron (angel) with icosahedron structure



Figure 11: Geometry of Al_9Cu_4 (a) Before relaxation and (b) After relaxation (produce by Jmol molecular viewer)

DISCUSSION

Table 1 shows the result of the optimized parameters of metallic alloys Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$ respectively with GGA+vdW exchange functional. Similar behavior were observed as in metal (Sa'ïd and Babaji, 2016). However, there was increase in the total energy for the metallic alloys. This increase was due to the difference in the electronic property between metal and metallic alloy. Similar behavior was observed for exchange functional GGA. It was observed that there were -0.861075083, -0.979780453 and -0.917995082 eV difference between pbe+vdw and pbe for Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$ respectively. In fig. 11, Al_9Cu_4 was found to be non-icosahedral sturcture after optimization because of the increase in number of copper the alloy. Similar to the report by kumaret al, 2008 only $Al_{12}Fe_1$, $Al_{11}Cu_2$ and $Al_{10}Cu_3$ have perfect icosahedron structure. $Cu_{12}Fe$ and $Al_{12}Fe$ have perfect icosahedral structure. For the basis size, it was observed that there were rapid decrease in energy from tier_1 to tier_2 and almost constant from tier_2 to tier_3.

After finding the converged computational setting, Table 2. shows the calculated values of total energy, cohesive energy and homo-lumo gap using pbe+vdW and pbe exchange functional for phase stability checking and it was observed that the values obtained using pbe+vdW is more accurate as compared with the result obtained by Muku et al, 2008, Philipsen&Baerends, 1996 and Kumar & Kawazoe, 2001. This is due to correction of short range forces done by the approach as incorporated in the code by Tkatchenko and Scheffler, 2009.

Highest Occupy Molecular Orbital to Lowest Unoccupied Molecular Orbital (HOMO-LUMO) gap is another sensitive quantity used to prove the stability of the structure, this energy gap depends on the material as found in this work, that Aluminum-iron

REFERENCES

- Ahlich R., Penco R. and Scoles G. (1977) chem.phy **19** 119
- Ahmad N. Hassan A.K. and Keishav N.S. (2013). DFT calculation of vibration in the clusters of zinc and oxygen atoms: sainsmalaysiaiana **42**(5) pp 649-654

and Copper-Iron are have higher stability than Aluminum-copper alloy due to the HOMO-LUMO gap observed.

Fig 4, 5 and 6 shows the spectra of metallic alloys Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$ respectively. Fig 7, 8 and 9 shows a direct comparison between the pure spectrum of metal and metallic alloys and it was observed due to the absorption strong peak appears in AlCu cluster more than that of Aluminum and Copper clusters. For CuFe cluster there less peaks when compared with Copper and Iron separately and finally more peaks appear in the AlFe cluster than spectra of Alumimun and Iron. Fig 7, 8 and 9 Show the peak related to each element in the alloy by comparing the peaks with that of pure metal. However there is decrease in the intensity in alloy.

Fig. 10 shows the propagation of zero point energy at different modes. As it predicted in the above paragraph Aluminum has higher vibrational energy follows by Iron then Copper.

CONCLUSION

In this work, geometry optimization, cohesive energy and IR spectra of metallic alloys with icosahedron structure were reported. The result shows $Cu_{12}Fe$ and $Al_{12}Fe$ have good surface but Al_9Cu_4 did not have a good surface. This change in the shape shows how easily of cluster by increasing number of atoms not like in bulk. It was found that the cohesive energy calculated with pbe+vdW give more accurate value for cohesive energy than pbe alone when compared with other work reported by Kumar, 2001, Mukul, 2008 and Philipsen&Baerends, 1996. However, IR-spectra of and there alloys Al_9Cu_4 , $Cu_{12}Fe$ and $Al_{12}Fe$ were also reported and it was observed that at ZPE copper cluster have less vibrational energy than Iron and Aluminum.

- Alonso J. A., (2005). Structure and properties of atomic nanoclusters, Imperial college press, London.
- Angelos M. and Scheffler M., (2008). An Introduction to the theory of metal surface. *Journal of chemical physics* **128**

- Biswajit S., Angelos M., Martin F., Alexandre T., Claudia F. and Matthias S. (2008). On the accuracy of density functional theory exchange-correlation function for H. bond in small clusters.II the water hexamer and vanderwaals interaction. *Journal of chemical Physics* **129**, 194111
- Blum V., Gehrke R., Hanke F., Havu P., Havu V., Ren V., Reuter K., Scheffler M.,(2009). The Fritz Haber Institute ab initio molecular simulations package (FHI-aims), <http://www.fhi-berlin.mpg.de/aims>.
- Bowen K.H., (2011), Toward the development of Aluminum cluster containing materials for propulsion application. Airforce office of scientific research 875 North Randolph.str.
- Fermi E., (1930).Un metodostatistico per la determinazione di alcunepriorieta dell atome, Rend. Accad. Naz. Lincei 26, 376.
- Grimme S. (2004). J.comput. **25** 1463
- Havu V., Blum V., Havu P., and Scheffler M.(2009). Efficient O(N) integration for all-electron electronic structure calculation using numerical basis functions. J. comp.phys.
- Hofmann O. T andNemec L., (2014), Hands-on Summer School: Electronic Structure Theory for Materials and (Bio)molecules. Fritz-Haber-Institut der Max-Planck-Gesellschaft
- Hohenberg and W. Kohn, Inhomogeneous electron gas, Phys. Rev. 136, B864 (1964). <http://education.jlab.org/itselemental/ele029.html>, 2016
- <http://www-wales.ch.cam.ac.uk/CCD.html> , 2016
- Jurecka P., Cerny J., Hobza P. and Salahub D.R. (2007). J. Comput. Chem. **28** 555
- Knight W. D., Clemenger K., de Heer W. A., Saunders W. A., Chou M. Y., and Cohen M. L., (1984), Electronic shell structure and abundances of sodium clusters, Phys. Rev. Lett. 52, 2141
- Kohn P. W. and Sham L. J.,(1965). Self-Consistent equations including exchange and correlation effects, Phys. Rev. 140, A1133.
- Kumar V. and Kawazoe Y., (2001).,Hund's rule in metal cluster; prediction of high magnetic moment state of $Al_{12}Cu$ from first-principle calculation. Physical Review B vol. 64 115405.
- Li D., Xiong Q. and Liu G. W, (2009) Theoretical study of small Aluminum cluster absorption on surfaces. Power and engineering conference. Appeec Asia Pacific
- Martin R. M., (2004) Electronic Structure: Basic Theory and Practical Methods, (Cambridge University Press, Cambridge.
- Mukul K., Abhijit M., and Bhattacharya A.K.,(2008). Structure and stability of copper: A tight-binding molecular dynamics. ar.xiv:physics|0310144vi
- Nusret, D., Mehmet, F. F. and Isik, O. (2012). Ni55 nanocluster: density functional theory study of binding energy of nickel and ethylene adsorption. Turk. J. chem. **36**55-67.
- Philipsen P.H.T and Baerends E.J., (1996), Cohesive energy of $3d$ transition metals; Density functional theory atomic and bulk calculations. Physical Review B vol 54 No.8
- Sa'íd M. and Babaji G. (2016) Geometry Optimization, Cohesive Energy and Harmonic Vibration of Al_{13} , Cu_{13} and Fe_{13} Icosahedral Metals Using Fhi-aims Code. Bayero Journal of Mathematics and Physics (Accepted)
- Tkatchenko A. and Scheffler M., (2009), Accurate Molecular Van Der Waals Interactions from Ground-State Electron Density and Free-Atom Reference Data. Physical Review LettersPrl 102, 073005
- Thomas L. H., (1927). The calculation of atomic fields, Proc. Cambridge Phil. Roy. Soc. 23, 542.
- Viktor Balema.,(2007). Advance Metals and Alloys. *Material Matters 2(4) Aldrich chemistry*.
- Wu Q. and Yang W. (2002) chem. Phys. 116 515