Calculation by Density functional theory of $FeNi_2Mo$ and $FeNi_2Nd$

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Abstract:

Our calculations were done with the help of density functional theory (DFT) and use the generalized gradient approximation (GGA), The pseudo-potential linearised augmented plane wave (PP-LAPW) method is applied to solve the Kuhn-Sham equations, in order to search for the structural, electronic and optical properties of the $FeNi_3$ original alloy, as well as the $FeNi_2Mo$ and $FeNi_2Nd$ alloys resulting from doping with (Mo, Nd) atoms in the original cell. The lattice parameters of the alloys were calculated and compared with previous theoretical and experimental results, the electronic properties such as energy bands and the total density of states showed the metallic property of the alloys and that the $FeNi_2Nd$ alloy has more magnetic moment. Also it was found that the contribution of the 3-*d* orbital is dominant, and this appears by comparing the density of partial states recorded in the two alloys, and this affects the electronic and magnetic properties of the two alloys. The general results of optical properties including absorption coefficient, refractive index, optical conductivity of $FeNi_2Mo$ and $FeNi_2Nd$ are discussed and compared with each other, our results show new and important optical properties.

Keywords: DFT, Siesta, Alloys, Properties structural, Properties Optic.
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1. INTRODUCTION

In recent years, nanomaterials have been revolutionizing the world as they offer new horizons in research and development, nanoparticles (NPs) are very small particles with lengths ranging from 1 to 100 nanometers, and they exist in many dimensions and at least one dimension, nanoparticles have a high surface area to volume ratio, thanks to which they can exhibit unique physical and chemical properties such as reactivity, versatility, and

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strength from their bulk counterparts [1-3].Among these types of nanoparticles, interest in magnetic nanoparticles (MNPs) has been increasing due to their unique physical, chemical and magnetic properties[4-6].These magnetic particles have many uses such as biomedicine [2], environmental remediation [1,5], catalysis [7], magnetic resonance imaging [8,9], data storage [10], and sensors [11], electromagnetic shielding [12], etc.

Iron-nickel alloys are an example of a metallic nanostructured magnetic alloy, which has received significant attention in recent years due to its desirable superiority in terms of magnetic and mechanical properties that make it applicable in many fields[13-15], One of the most important features of Fe-Ni alloys is that we can prepare them in different sizes, shapes and compositions, depending on the method used in preparation[13].Many researchers have been able to prepare a variety of morphological structures for iron-nickel alloys, including spherical particles [16], triangular particles [17], rods [18], platelets [19].

In this research paper, we will present a theoretical study on iron-nickel alloys doped with (Mo and Nd) atoms, and touch on an in-depth study on the structural, electronic and optical properties.This study is considered as the first theoretical study of this subject, which has not been addressed previously.

2. THEORETICAL APPROACH

$FeNi_3$ exists in face centered cube structure (fcc) and having lattice parameters, a=b=c=3.548Å, α = β = γ = 90.00° (space group: Pm3m). On Mo-doping and Nd-doping, the lattice relaxation and movement of all the atoms were allowed to obtain the optimized structure using Spanish initiative for electronic Simulations withthousands of atoms(Siesta) [20],within generalized gradient approximation (GGA), based on density functional theory (DFT) [21], in basics with four atoms defined by the following reduced coordinates: Fe (0, 0, 0) and three enumerated for the convenience nickelatoms Ni_1 (1/2, 1/2, 0), Ni_2 (0, 1/2, 1/2), Ni_3 (1/2, 0, 1/2), where it was compared with the results of previous theoretical and experimental work. The unit cell in $FeNi_2Mo$ and $FeNi_2Nd$ were built by substituting a Mo and Nd atom in place of a Ni atom by successive relaxation. Using the convergence criteria until the atomic forces were less than5 × 10^{-4}eV/Å. For the calculation of electronic ground state propertiesof these alloys, we used spin polarization with Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional within generalized gradient approximation (GGA). The Brillouin zone were sampled forthese cells by a Monkhorst-Pack k-grid of 3 × 3 × 3. The plane wave norm conserving pseudopotentials, created with the use of GGA-PBE approach, are obtained from library, withthe valence electron coverage of Fe, Ni, Mo and Nd atoms are$3d^64s^2$, $3d^84s^2$, $4d^55s^1$ and $4f^4$ $6s^2$, correspondingly. The energy band structures are sketched along the k-path built on data taken from Hinuma statistics [24]. We represented the projected density of states along atomic valence orbitals (PDOS) in order to compare and reveal the role of electrons in different atomic valence orbitals, on electronic properties, especially on x-polarization. And from it, the spin polarization is determined due to the different distribution of spin states (spin up and spin down) and from it determine the magnetic moment of the unit cell. Besides the two fcc crystals of $FeNi_3$ as a pure crystal as a reference, some relevant calculation data of $FeNi_2Mo$ alloy in comparison with $FeNi_2Nd$ alloy are also represented for similarity of electronic properties.

3. RESULTS AND DISCUSSION

3.1. Alloys Structures

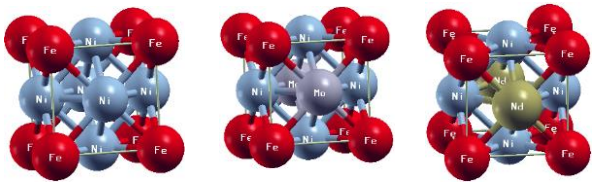
Structural parameters of an originally relaxed $FeNi_3$ cell with a Pm3m space group, formed by four atoms delimited by the following coordinates: Fe (0, 0, 0) and three relaxed Ni atoms Ni_1 (1/2, 1/2, 0), Ni_2 (0, 1/2, 1/2), Ni_3 (1/2, 0, 1/2).The lattice constants of $FeNi_3$ alloy over the past times have been verified many times, the primary structure of stable $FeNi_3$ alloy is the group structure of $Pm\bar{3}m$ and the lattice constants are estimated to be a = b = c = 3.528 Å, α = β = γ = 90.00°.Whereas in our present work, we find the lattice parameters for the new $FeNi_2Mo$alloy is a = b = c = 3.532 Å, while $FeNi_2Nd$alloy is a = b = c = 3.592 Å.

We based our calculations for this work on the Siesta code that was used to find the initial cell constants for $FeNi_3$, $FeNi_2Mo$ and $FeNi_2Nd$alloys, this is done by replacing one of the nickel atoms with molybdenum (Mo) atom in the first time and neodymium (Nd) atomin the second time to obtain

$FeNi_2Mo$ and $FeNi_2Nd$alloys.In this study, the results are compared with experiment data and previous theoretical work, and we present in Table 1 the structural parameters of the primary $FeNi_3$cell,we obtained the lattice parameters of the cell $FeNi_3$, $FeNi_2Mo$ and $FeNi_2Nd$ (see Fig. 1).

Tabel 1.Structural parameters of the optimized $FeNi_3$, $FeNi_2Mo$ and $FeNi_2Nd$ alloys and compared with theoretical and experimental result.

	work	a (Å)	b (Å)	c (Å)
$FeNi_3$	Our work	3.528	3.528	3.528
	Theor[22]	3.548	3.548	3.548
	Exep[23]	3.55	3.55	3.55
$FeNi_2Mo$	Our work	3.532	3.532	3.532
$FeNi_2Nd$	Our work	3.592	3.592	3.592



(a) (b) (c)

Fig. 1 – Structure of: (a) $FeNi_3$, (b) $FeNi_2Mo$, (c) $FeNi_2Nd$

It is observed from Table 1 that the obtained results are close to previous theoretical and experimental work, and that doping of the parent compound $FeNi_3$ with molybdenum (Mo) or neodymium (Nd) atoms changes the original cell dimensions and contributes to an increase in its volume.

3.2. Electronic Properties

3.2.1 Bands Structure

In order to study the basic structure, we choose a specific region called the Brillouin zone, in order to find the electronic properties of the material. Fig. 2 shows the Brillouin zone of the cubic structure. It is worth noting that the study of properties in this region can be generalized later on both $FeNi_2Mo$ and $FeNi_2Nd$ alloys.

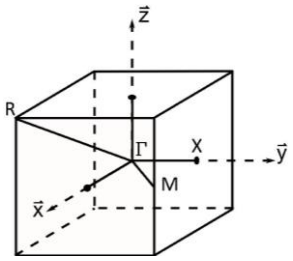
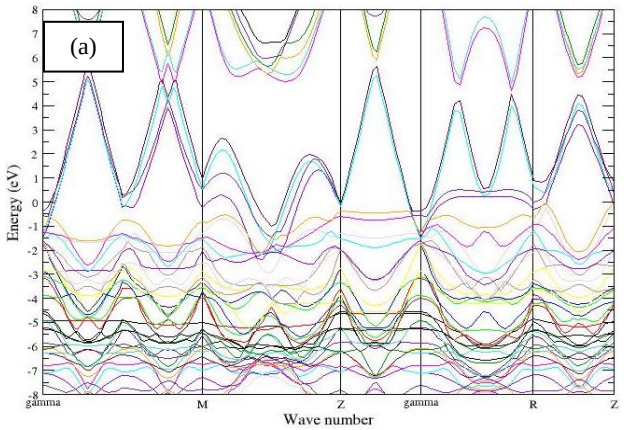


Fig. 2 –Brillouin zone of a cubic structure

In our study we used DFT theory and GGA approximation in order to determine the band gap of $FeNi_2Mo$ and $FeNi_2Nd$ alloys. This method has been relied upon because it is one of the most appropriate methods for studying the electronic structures of materials. Fig.3 shows the results of the structure of the energy bands for the alloys.



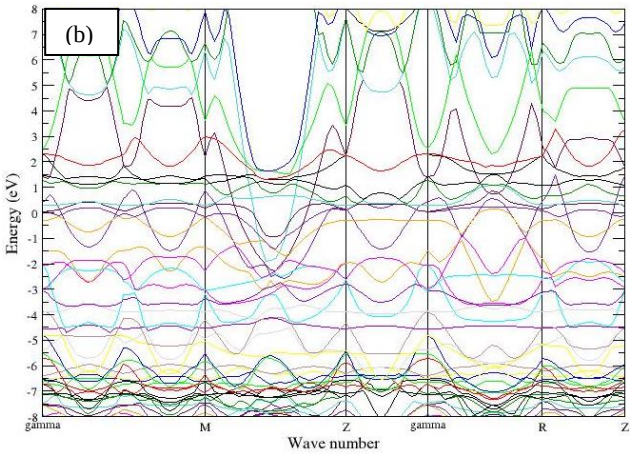


Fig. 3 – Energy bands structure of: (a) $FeNi_2Mo$,(b) $FeNi_2Nd$

As can be seen from Figs 3a and 3b, the highest valence bands overlap with the conduction bands, which is conclusive evidence of the metallicity of the two alloys,we also found that both alloys have ferromagnetic properties, with magnetic moments estimated to be 5.42µBand 5.53µB for $FeNi_2Mo$ and $FeNi_2Nd$alloys respectively.

3.2.2. Electronic Density of States (DOS)

We plotted both the total density of states (TDOS) and the partial density of states (PDOS) for $FeNi_2Mo$ and $FeNi_2Nd$ alloys using the GGA approximation, and then analyzed them to determine the reason for the presence of states that formed valence and conducive-bands, and to understand the nature of interactions between the atoms of the studied alloys, as is Shown in Fig. 4 and Fig. 5 respectively.

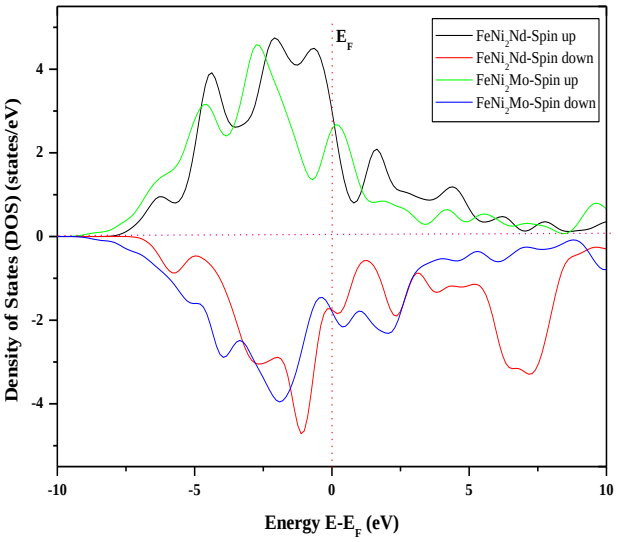
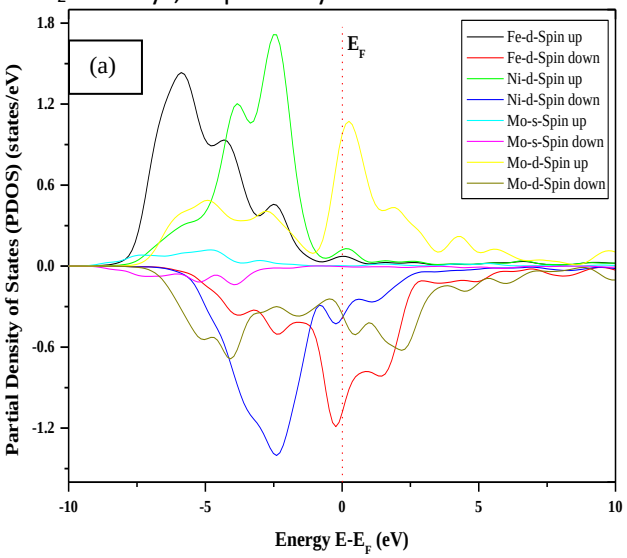


Fig. 4 –Total density of states (TDOS) for:(a) $FeNi_2Mo$, (b) $FeNi_2Nd$

Fig. 4 shows that the calculated TDOS for $FeNi_2Mo$ and $FeNi_2Nd$ alloys has high values with the GGA approximation in the region close to the Fermi level; we find that the TDOS value of $FeNi_2Nd$ is higher than that of $FeNi_2Mo$, and this indicates that its valence band is rich in electrons. Within the region close to the fermi level, we note that the highest peak density of states was recorded in $FeNi_2Nd$ alloy, which was estimated at 4.71 (state/eV), while the value 4.63 (state/eV) was recorded as the highest value for $FeNi_2Mo$. While we find exactly at the fermi level that the largest value for the density of states was recorded at the$FeNi_2Nd$ alloy with a value estimated 2.81 (states/eV).

3.2.3. Partial Density of States (PDOS)

In this work, we have calculated and analyzed the partial density of states (PDOS) of $FeNi_2Mo$ and $FeNi_2Nd$ alloys in order to understand the movement of electrons close to the fermi level. Figs. 5a and 5b show the PDOS of $FeNi_2Mo$ and $FeNi_2Nd$ respectively.
In this paper, we have calculated and analyzed the partial density of states (PDOS) of $FeNi_2Mo$ and $FeNi_2Nd$ alloys in order to understand the movement of electrons close to the Fermi level, where Figs. 5a and 5b show the PDOS of $FeNi_2Mo$ and $FeNi_2Nd$ alloys, respectively.



(b)

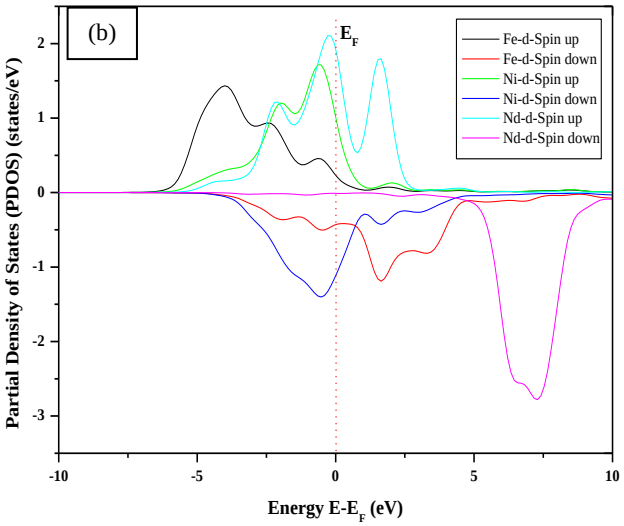


Fig. 5– Partial density of states (PDOS) for: (a) $FeNi_2Mo$, (b) $FeNi_2Nd$

In the figure above, we present the density of states on atomic valence orbital (PDOS) in order to compare them with each other and also reveal the role of electrons in different atomic valence orbital, and how they affect the electronic properties.From the different distributions of spin states (spin up and down) represented in the figure, the spin polarization is determined, starting with a single primitive cell and later generalizing to the entire alloys.In order to ascertain more deeply into the contributions of iron and nickel atoms that make up the $FeNi_2Mo$ and $FeNi_2Nd$ alloys, we calculated the expected density of states across electron orbitals as a function of energy ($E-E_F$).

Through the PDOS distributions, shown in Fig. 5a for $FeNi_2Mo$ alloy, it can be shown that the electronic states are mainly located in the active region, which extends from -7 eV to +7 eV around the Fermi levels. To give more detail, near the fermi level, Ni atoms have larger 3-*d*-orbital states than the Fe atom; also, the contributions that come from the up-spin Ni 3-*d* electrons are larger than those from the same down-spin 3-*d*elements.The3-*d*-orbitals contribution of all atoms is also dominant in the electronic distribution of $FeNi_2Mo$; the same note is made for $FeNi_2Nd$ alloy in Fig.5b.It is very clear by the two Figures. 5a and 5b that the molybdenum (Mo) or neodymium (Nd) atoms with which the original $FeNi_3$ alloy was doped have added a lot in the electronic distribution in the region near the fermi level, and $FeNi_2Nd$ alloy is considered the best in terms of chemical and catalytic activity from $FeNi_2Mo$ alloy .

3.3. Optical Properties

The study of the optical properties is very important, as its importance lies in obtaining information about the values of the optical constants of the material and its relationship to the photons falling on it. From this information, we can use it to design and manufacture optical blocks and optical pulses using different technologies.

3.3.1. Absorption coefficient

It is defined as the decreasing ratio of the spectrum of incident radiation energies with respect to the unit distance, in the direction of the direction of wave propagation within the material. The absorption coefficient is related to the energy of the incident photons, and from it it is possible to know the nature of the electronic transformations, and its equation is in the form:

$$\alpha = \frac{4\pi K}{\lambda} \quad (1)$$

Where α is absorption coefficient, k is the coefficient of extinction and λ is wave length (cm).
We have calculated the adsorption coefficient value of $FeNi_2Mo$ and $FeNi_2Nd$ alloys with GGA approximation, and they are shown in Fig. 6.

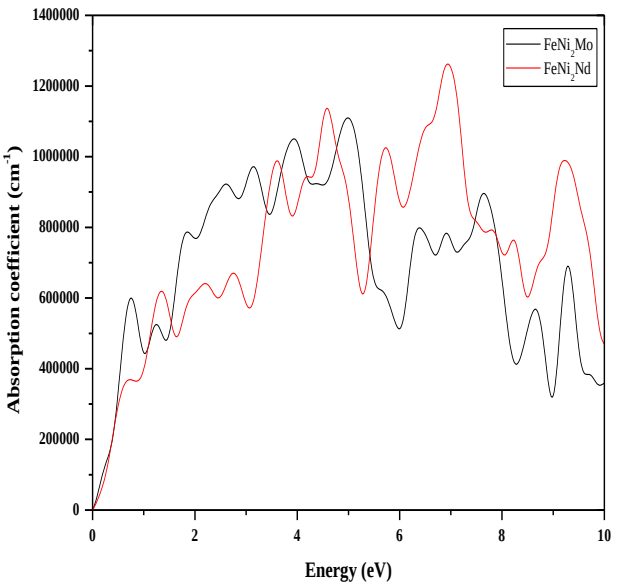


Fig. 6 – Absorption coefficient of $FeNi_2Mo$ and $FeNi_2Nd$

Fig.6 shows the change in the absorption coefficient as a function of the energy of the incident photon on $FeNi_2Mo$ and $FeNi_2N$dalloys.It is clear from the figure that the absorption coefficient in general begins to increase gradually and in an oscillating manner with the increase in the energy of the photons of light, until the energy value 5 eV for the $FeNi_2M$oalloyand the value 4.5 eV for $FeNi_2Nd$ alloy, after which the value of the absorption coefficient decreases significantly with the increase in the energy of the incident photons. In general, the behavior of both alloys in absorption is almost the same, except that higher values are recorded sometimes in $FeNi_2N$dalloy, this is especially when the amount of energy 6.92eVwith a peak value of 1231000 cm^{-1}.This indicates that the change in the energy of the incident photons leads to different optical behaviors in this material. This result is close to work [25].

3.3.2. Optical Conductivity

It is a physical property that relates the current density to the electric field, and is given by the following equation:

$$\sigma(\omega) = \frac{J(\omega)}{E(\omega)} \qquad (2)$$

Where σ is optical conductivity (Sm/m), J is current density (A/m^2) and E is electric field (N/C).
The optical conductivity values of $FeNi_2Mo$ and $FeNi_2Nd$ alloys have been calculated with approximations GGA, and the results are written in Fig. 7.

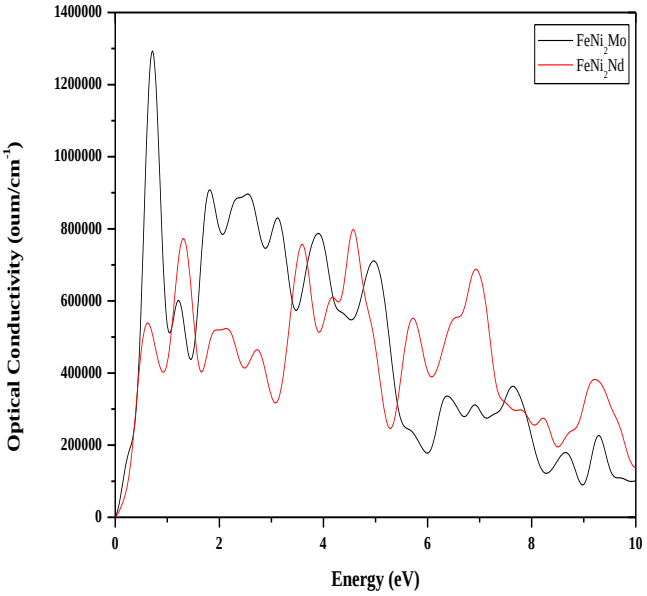


Fig. 7 – Optical conductivity of $FeNi_2Mo$ and $FeNi_2Nd$

Fig.7 represents the optical conductivity changes in terms of the energy of photons falling on the $FeNi_2Mo$ and $FeNi_2N$dalloys using the GGA approximations, in general, we notice that the value of photoconductivity increases with increasing energy of the two alloys, the values fluctuate between increasing at times and decreasing at other times, where we recorded the largest value of photoconductivity in $FeNi_2Mo$ alloy with an estimated value of 1300000 Oum/cm^{-1}, while the highest value of the $FeNi_2N$dalloy reached the value 750000oum/cm^{-1}.By comparing the two alloys with each other, $FeNi_2Mo$ alloy appears to be more optically conductive in the infrared and visible ranges. What can be concluded from the analysis of each of the absorption and optical conductivity curves is that $FeNi_2M$oalloyhas a good absorption value that allows their use in optoelectronics and photovoltaic compounds.

3.3.3. Refractive Index

It is the ratio between the speed of light in free space and its speed in the matter, and the refractive index can be found according to the following equation:

$$n_0 = \left[\left(\frac{1+R}{1-R}\right)^2 - (k_0^2 + 1)\right]^{\frac{1}{2}} + \frac{1+R}{1-R} \qquad (3)$$

Where R is reflectivity, $K_0$is extinction coefficient.

The refractive index values for $FeNi_2Mo$ and $FeNi_2Nd$ were calculated using the GGA approximations as shown in Fig.8.

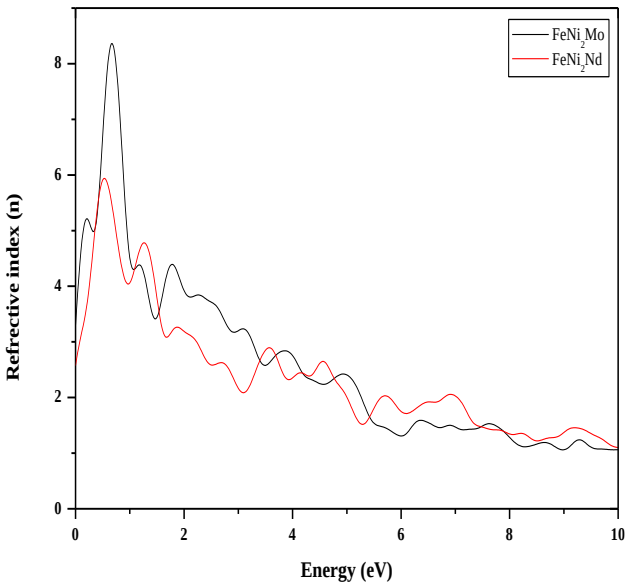


Fig. 8 – Refractive index of $FeNi_2Mo$ and $FeNi_2Nd$

By Figure 8, which expresses the refractive index in terms of incident photons, we noticed that the refractive index n_0 for the $FeNi_2Mo$ and $FeNi_2Nd$ are 4, 2.84Respectively.Whereas, with the increase in the energy of the incident photons, the value of the refractive index began to increase to reach its maximum value at the energy 1.78 eV and 0.87 eV after that, the values of the refractive index began to decrease sharply, due to the increase in the energy of the incident photons.

4. CONCLUSION

Proceeding from the calculations made according to the density function theory (DFT) and using an approximation, and using the Siesta program, the results obtained for the $FeNi_2Mo$ and $FeNi_2Nd$ alloys, whether structural, electrical or optical, were compared, and the following was concluded:

- There is a clear difference between the structural parameters of the two alloys ($FeNi_2Mo$ and $FeNi_2Nd$) from the structural parameters of the original alloy ($FeNi_3$).
- The results of the density of states showed that each of the two alloys has metallic properties, in addition to that the $FeNi_2Nd$ alloy has a greater magnetic moment
- It was found that the contribution of the 3-*d* orbital is dominant, and this appears by comparing the density of partial states recorded in the two alloys, and this affects the electronic and magnetic properties of the two alloys.
- The differentiation in the optical properties of the two alloys favors each of them for specific technological uses.

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