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by:
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THEME

ab intio study of the magnetic order of some gadolinium-based compounds

Publicly defended before the jury consisting of:

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Dedication

I dedicate this work
To my dear mother and my dear father for their support and their
Sacrifices during my studies and in all my life
To all my sisters
To my dear brothers
To my fiancee
To the whole family
To all my friends
To the spirit of my uncle

Zakri ABISMAIL

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I would first like to thank my thesis advisor The door to Prof. [Bachir BENTRIA] office was always open whenever I ran into a trouble spot or had a question about my research or writing. He consistently allowed this paper to be my own work, but steered me in the right the direction whenever he thought I needed it.

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Abstract:

The main purpose of our study is to predict the magnetic ordering in some binary gadolinium based compounds, namely; GdN, GdB_2, $GdAl_2$, GdAl. In our calculation we used the pseudo potential method and LSDA, GGA and LSDA+U for Exchange and correlation interactions. Magnetic exchange interactions between first and second-nearest neighbors J1 and J2 respectively are derived from total-energy differences different magnetic configurations, then we used these exchange parameters to predict Curie-Weiss and Neel temperatures within mean field theory. These temperatures are compared with experimental data or others theoretical predictions. GdN, GdB_2, $GdAl_2$, GdAl are found to be ferromagnetic.

Key words: Density functional theory (DFT), exchange parameter , Ferromagnetic(FM), Antiferromagnetic(AFM)

ملخص

الهدف الرئيسي من دراستنا هو التنبؤ بطبيعة المغناطيسية للمركبات التالية GdAl, GdB2, GdAl2, GdAl أجريت الحسابات في إطار النظرية الكثافة الوظيفية باستخدام تقر يبات طاقة التبادل والارتباط LSDA, LSDA+U, GGA.

التفاعلات التبادل بين أقرب الجيران من الدرجتين الأولى و الثانية J1و J2 على التوالي هي مشتقة من فروق الطاقة الكلية بين FMوAFM المختلفة .نستخدم معاملات التبادل J1و J2للتنبؤ بدرجات حرارة Curie-Weissو Neel في mean-field theory وتم مقارنتها النتائج التجريبيةأو أعمال التي أجريت.

نتائج حساباتنا أثبتت بأن المركبات التالية GdAl, GdB_2, $GdAl_2$, GdAl لها طبيعة مغناطيسية FM

الكلمات المفتاحية :نظرية الكثافة الوظيفية (DFT) , معامل التبادل , فيرومغناطسية (FM), انتي فيرومغناطسية, (AFM)

Résumé

Le but principal de notre travail est l'étude ab-initio de l'ordre magnétique dans les composés à base de gadolinium GdN, GdB2, GdAl2 et GdAl. Tous nos calculs sont basés la méthode des pseudo potentiels dans le cadre de la théorie de la fonctionnel de la densité. On utilisé l'énergie échange corrélation GGA, LSDA et LSDA+U. Les énergies d'échange magnétiques entre les atomes du premier et deuxième plus proche voisins J1 et J2 sont dérivées des différences d'énergie totale entre les configurations ferromagnétiques FM et antiferromagnétiques AFM-I et AFM-II. Ces paramètres sont ensuite utilises pour prédire les températures de Curie-Weiss et de Neel. notre résultats sont comparés avec les valeurs expérimentales disponibles et autre résultats théorie.

notre résultat montre que les composants GdN, GdB_2, $GdAl_2$, GdAl sont ferromagnétique

Mots clés: la théorie de la fonctionnel de la densité(DFT), paramètre d'échange, ferromagnétique(FM), Antiferromagnétique (AFM).

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General Introduction:

This thesis deals with magnetic ordering calculations of four different binary gadolinium-based compounds; GdX (where X=N, Al) and GdX_2(where X=Al, B). In all our calculations we have used the Density Functional Theory which is the main underlying theory of treating many body problem. The effective valance electron potential is treated by pseudo potential.

Gadolinium elements has strongly localized f states and hence it requires, for the calculation of he ground state energy and others propriety, treatment beyond the Local spin Density Approximation (LSDA) in density functional theory. The so called LSDA+U approach is adapted for this kind of situations. It adds an orbital dependent Coulomb interaction term U, to the local density functional in order to treat strong correlation effects in cases where LSDA fails to deal with it. Furthermore, and for comparisons purposes, we used Generalized Gradient Approximation(GGA).

The main purpose of this study is to shed some light on the ordering magnetic in these systems, GdN GdAl and GdX_2(where X=Al, B). By calculating ground state energies for AFM and FM configurations in order to predict magnetic ordering of our compounds. GdN is used as trail case since its magnetic ordering and transition temperature are well known. We start this compound in order to test the validity of our calculation method. It will also enable us to evaluate the calculation cost in order to predict the magnetic order for others materials. We then apply the same method and rules, to study and predict the ground state configuration of our materials.

In order to study the magnetic ordering, one relies generally on some model Hamiltonian, such as the Heisenberg-Hamiltonian and our task in first-principles calculations is then to establish the parameters of such a model.

There are several ways in which one can calculate the exchange interaction parameters used to describe magnetic ordering and eventually estimate Curie-Weiss and Neel temperatures.

One is by finding total energy differences between FM and AFM configurations of the crystal structure which is then related to these exchange interaction parameters.

Chapter I

I. The Binary System basic of Gadolinium

I.1. Introduction:

The first chapter of this dissertation presents some basic concepts related to magnetic materials. Then we presented the classification of magnetic materials by giving the definition each class. The types of magnetic material as we well known are, Diamagnetic (DM), Paramagnetic (PM), Ferromagnetic (FM), Antiferromagnetic (AFM) and Ferrimagnetic (FIM).

The second part of this chapter is dedicated to some binary gadolinium based compounds. We start with the well-studied class of Gd-monopnictides (GdX, X=N, P, As, Sb, Bi). GdN is the only ferromagnetic material of this class, is taken as example for our study. Then we will present an exhausted literature survey on three binary compound that are less known and studied (GdAl, $GdAl_2$ and GdB2).

We describe GdAl compound in each of the three plausible phases. The magnetic ordering of GdAl compound is not known. Then we introduced GdX_2, (X = B and Al) compounds, we feature their structural an available magnetic data [1],[2].

I.2. Magnetic materials:

The vocabulary of magnetism has no strict rules, but for most people working in the field use the term *magnetic materials* to mean materials where spontaneous magnetic ordering takes place. The ground-state arrangement of the magnetic moments, and the process of ordering itself. The simple classification of ordered states into ferromagnetic, Antiferromagnetic and ferrimagnetic cannot do justice to the rich variety of possible ordered patterns of three dimensional vectors at the sites of all crystal lattices possible in three dimensions.

In the rare-earth – transition-metal ferromagnetic, the anisotropy energy of the rare earth component is much larger than that of the transition metal, because the spin-orbit coupling is an order of magnitude stronger except for gadolinium which has zero orbital moment. As the orientations preferred by these anisotropy energies can be different and so are their temperature dependences, the overall effect is also temperature dependent, so that the orientation of the net ferromagnetic moment changes with temperature[3].

I.2.1. Classification of Magnetic Materials:

All materials can be classified in terms of their magnetic behavior fall into one of five categories depending on their bulk magnetic susceptibility. The two most common types of magnetism are diamagnetic and paramagnetic. These elements are usually referred to as non-magnetic, whereas those which are referred to as magnetic are actually classified as ferromagnetic. The only other type of magnetism observed in pure elements at room temperature is Antiferromagnetic. Finally, magnetic materials can also be classified as Ferrimagnetic although this is not observed in any pure element but can only be found in compounds,

I.2.1.1. Diamagnetism

Diamagnetism is a weak magnetism and is the fundamental property of all matter. Diamagnetism is mainly due to the non-cooperative behavior of the orbital electrons under the application of external magnetic field. In diamagnetic substances, all the atoms have paired electrons and there are no unpaired electrons in the shells. Thus the net magnetic moment of the atom of a diamagnetic substance is zero. However, when an external magnetic field is applied on these substances, these materials are magnetized opposite to the field direction. Thus they have negative magnetization[4].This means for diamagnetic substances the susceptibility is negative. If we plot M vs. H, we see:

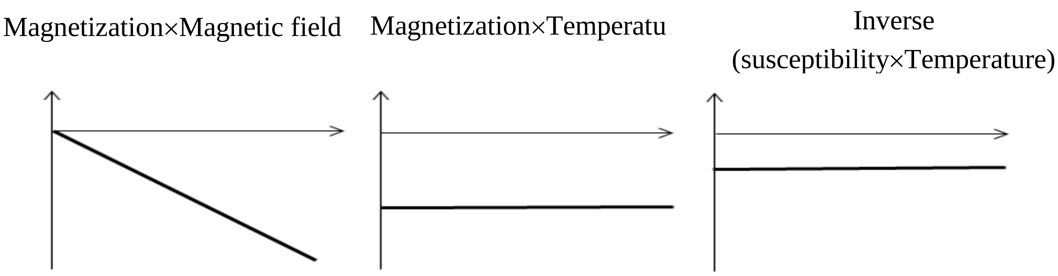

Figure I-1:Plot of M vs. H for diamagnetism

From the above plot it can be understood that the magnetization is zero when the applied is zero. The other characteristic behavior of diamagnetic substances is that their susceptibility is independent of temperature.

I.2.1.2. Paramagnetisme

In these materials, the atoms or ions have unpaired electrons in partially filled orbitals. That means each atom in a paramagnetic substance has a small net magnetic moment. But, there is no interaction between these atomic magnets. In the presence of an external magnetic field there will be a partial alignment of these atomic magnetic moments in the direction of applied magnetic field resulting in a net positive magnetization and positive susceptibility. When the applied field is zero, the magnetization also becomes zero.[4]

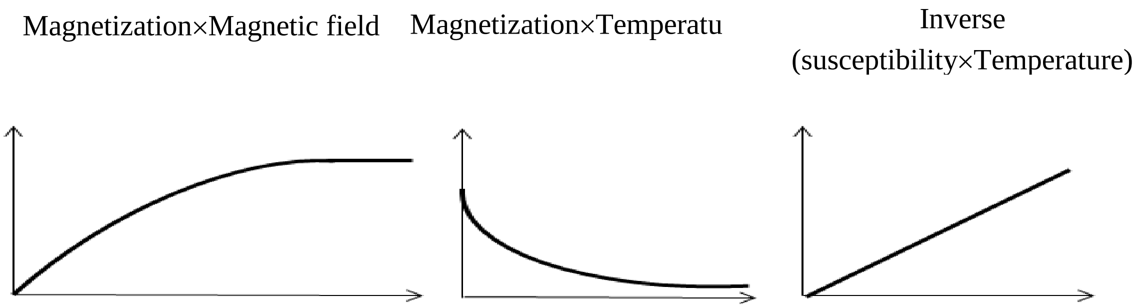

Figure I-2: Plot of M vs. H for paramagnetic

If the temperature of the paramagnetic substance increases, then alignment of the atomic magnets will be disturbed. That means the magnetic susceptibility depends on temperature. The magnetic susceptibility of is inversely proportional to the absolute temperature. This law is called curies law.

I.2.1.3. Ferromagnetism

When we think of magnetic materials, the most common materials that come into our mind are iron, nickel, and magnetite. These are generally called ferromagnetic substances. In these substances, there exists a strong interaction between the atomic magnets. These interaction forces are exchange type of forces. The interaction force between the atoms is due to exchange of electrons. The exchange type of forces is very large and is of magnitude 1000 Tesla[4]. This strength is almost 108 times the strength of the earth's magnetic field. Atomic magnets are aligned parallel to each other under the influence of these exchange forces.

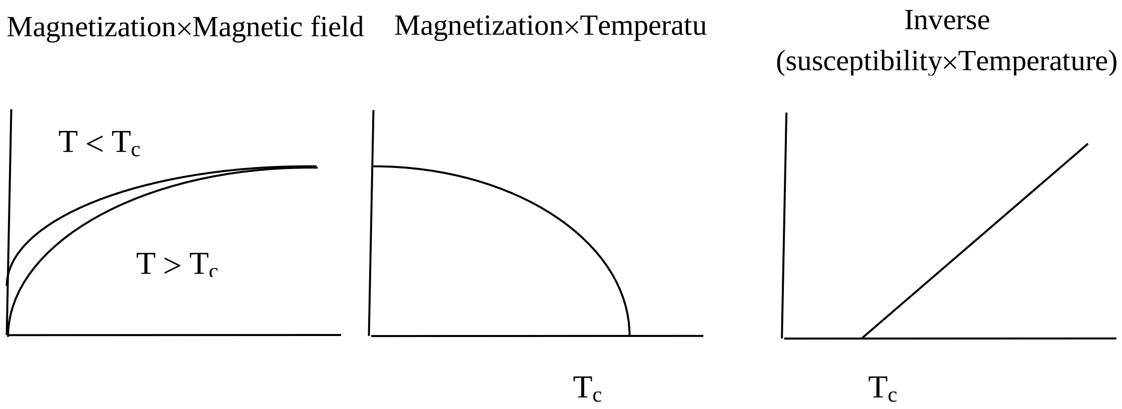

Figure I-3: Plot of M vs. H for ferromagnetic

I.2.1.4. Antiferromagnetism

If the magnetic moments of up and Down are equal in magnitude and opposite in direction, the net magnetic moment is zero. This type of magnetic alignment is called Antiferromagnetic. The main reason for Antiferromagnetic is the behavior of susceptibility above certain critical temperature, called the Neel temperature, denoted by (T_N). The susceptibility of paramagnetic substances obeys the Curie-Weiss law but with a negative intercept indicating the presence of negative exchange

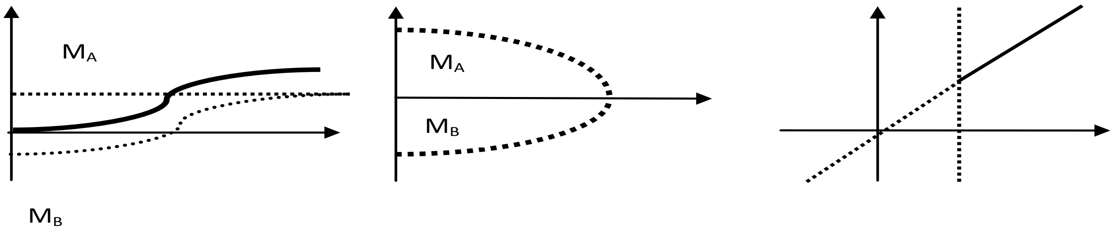

Figure I-4: Plot of M vs. H for Antiferromagnetic

I.2.1.4.1. Curie temperature:

The Curie temperature (T_C), or Curie point, is the temperature for ferromagnetic materials lose their permanent magnetic properties, to be replaced by induced magnetism. The Curie temperature is named after Pierre Curie, who showed that magnetism was lost at a critical temperature.[5]

I.2.1.5. Ferrimagnetism

In some ionic compounds (certain oxides of Fe) a complex form of magnetic ordering is observed due to crystal structure of these oxides. One such type of magnetic ordering is called ferrimagnetism. A simple orientation of magnetic spins in a ferrimagnetic oxide is shown in Fig
The magnetic structure in a ferrimagnetic oxide consists of two magnetic sub lattices separated by oxygen. The exchange interaction between the two sub lattices are communicated by oxygen anions and these interactions are called super exchange interactions. As a result of these super exchange interactions the spins of the sub lattices are aligned antiparallel. But, magnetic moments of sub lattices are not equal. Therefore there will be net magnetic moment.[4] Ferrimagnetic substance also exhibits spontaneous magnetization, Curie temperature, Hysteresis

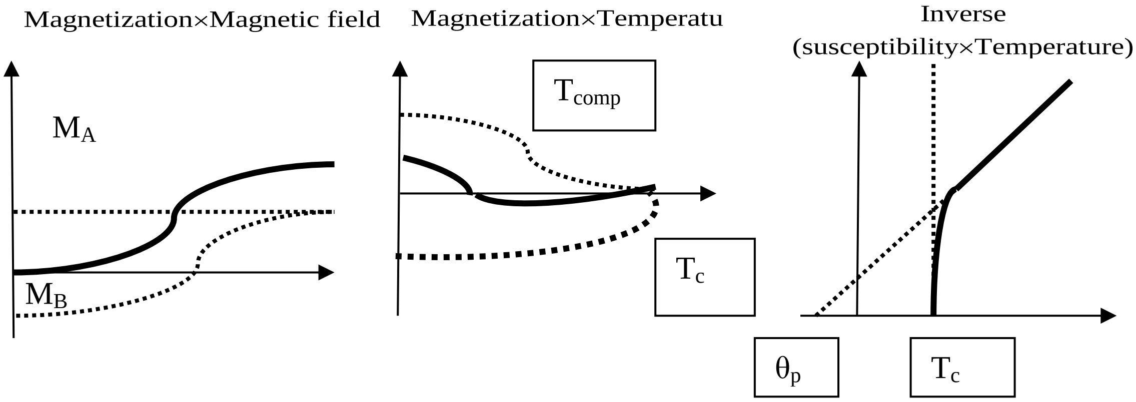

Figure I-5: Plot of M vs. H for ferrimagnetic

I.2.1.5.1. Neel temperature:

This is the transition temperature from Antiferromagnetic substances to paramagnetic phase (analogous to the Curie temperature for ferromagnetic).

I.3. About Gadolinium:

Gadolinium is chemical element, has the symbol Gd and it belongs to rare earth Group of the periodic table of elements.

Gadolinium is at the center of the lanthanide series and has a half-filled 4f orbital configurations.

Hence, it is to be expected that the 4f electrons will be strongly localized and magnetic properties will be dominated by the exchange interaction.[6]

It has same block f orbital of earth rare, we add also Gd has atomic number 64 we are going to added a tables below show us more detail about Gadolinium

Table I. 1: Some Data for Gadolinium[7]

Group	Lanthanides	Density (g/cm-3)	7.90
Block	F	Relative atomic masse (U)	157.25
State at 20^0C	Solid	Electronic configuration	[Xe] $4f^75d^16s^2$
Melting point	1313 °C		

Gadolinium was discovered in 1880 by Charles Glissade de Merignac at Genev, who detected its oxide by using spectroscopy. It is named after the mineral gadolinite, one of the minerals in which gadolinium is found, itself named after the chemist Johan Gadolin.

Gadolinium has found some use in control rods for nuclear reactors and nuclear power plants; it is used to make garnets for microwave applications and its compounds are used for making phosphorous for color TV tubes. Metallic gadolinium is rarely used as the metal itself, but its alloys are used to make magnets and electronic components such as recording heads for video recorders. It is also used for manufacturing compact disks and computer memory. Gadolinium is one of the more abundant rare-earth elements. It is never found as free element in nature, but it is contained in many rare minerals.

We added some physical end chemical properties of Gadolinium is a silvery-white malleable and ductile rare earth metal. It crystallizes in hexagonal; Gadolinium is believed to be ferromagnetic at temperatures below 20 °C and is strongly paramagnetic above this temperature. There is evidence that gadolinium is a helical Antiferromagnetic

I.4. **The Binary System basic of Gadolinium:**

I.4.1. **Binary System Gadolinium-Aluminum:**

[5]During studies of the influence of the free electron concentration on the strength of magnetic exchange, it became of interest to complete magnetic investigations of compounds in the system Gd-Al. the compounds $GdAl_3$, $GdA1_2$, GdAl, and Gd_3A1_2[7].

The magnetic characteristics of Gadolinium-Aluminum have received considerable attention in recent years. In the present work the inter metallic compounds of the Gadolinium-Aluminum system have been investigated, two compounds are $GdAl_2$ and GdAl, as well see later GdAl device into three phases

Table I. 2: Data for binary systems Gd- Al (space group, lattice constant, magnetic State). [8]

Compound	Magnetic State	Symmetry	Structure type	Lattice constant(Å)		
				a	b	c
Gd_3A1_2	unknown	Tetragonal	Hf_3A1_2	8.343		7.625
GdAl	unknown	Orthorhombic		5.66	5.89	11.53
$GdA1_2$	FM	Cubic	$MgCu_2$	7.897		
$GdAl_3$	unknown	Hexagonal	Mg_3Cd	6.359		4.619

I.4.2. **Binary System Gadolinium-Boron:**

The Gadolinium-borides are fascinating high-temperature materials with extremely interesting chemical and structural properties. In spite of this, detailed studies of Gd-B systems are rare. As a result, many fundamental as well as potentially useful properties of these materials have not been examined. One reason for this is that a solid coherent base of phase equilibrium information has been lacking, but is needed for preparing and understanding the behavior of these materials during studies of chemical, physical, and/or mechanical properties[9].

The rare-earth borides such as tetra borides GdB_4, hexaborides REB_6, and dodecaborides GdB_{12}, have attracted a lot of attention over the years as a rich class of materials which exhibit various phenomena of f-electron magnetism. Recently, new interesting aspects of the magnetism of these well-known borides have been discovered. GdB_2 was first described by[10]. However, the magnetism of the diborides, GdB_2, has not been as comprehensively reported[12].

Table I. 3: Data for binary systems Gadolinium-Bore (space group, lattice constant, State).

Compound	State	Symmetry	Space group	Structure type	Lattice constant		
					a	b	c
GdB_2[10]	unknown	hexagonal		AlB2	3.315		3.936
GdB_4[11]	AFM	Tetragonal	P4/mbm	ThB_4	7.148		4.050
GdB_6[11]	AFM	Cubic	Pm-3m	CaB_6	4.115		

I.5. The compound GdX(X=N,...Bi)

The binary system of Gadolinium- Azote ,Phosphor, Arsenic, Antimoine and Bismuth, namely the Gadolinium-mono-pnictides, Are all semi metallic. Furthermore, all these elements exhibit a rich variety in physical properties. The electronic, magnetic, and magneto-optical properties of such a system primarily depend on the behavior of f-electrons under the influence of the ling and the degree of localization and the position of f bands depend on the Gadolinium element and also on its chemical environment.

Gd-monopnictides(GdX, X=N, P, As, Sb and Bi) are known to exhibit unusual electric[14],and magnetic[15],[16],phenomena.GdN is a controversial semi metallic compound, which might be a very small-gap semiconductor. Other monopnictides, GdP to GdBi are semimetals.

For Gadolinium monopnictides, X-ray diffraction patterns show a single phase of NaCl-type for all the GdX samples. As we are going to present below. The room-temperature lattice constants are listed in the table

Table I. 4:Lattice Constant of GdX, (X=N, P, As, Sb and Bi)[15]

	GdN	GdP	GdAs	GdSb	GdBi
a(Å)	4.974	5.709	5.864	6.219	6.295

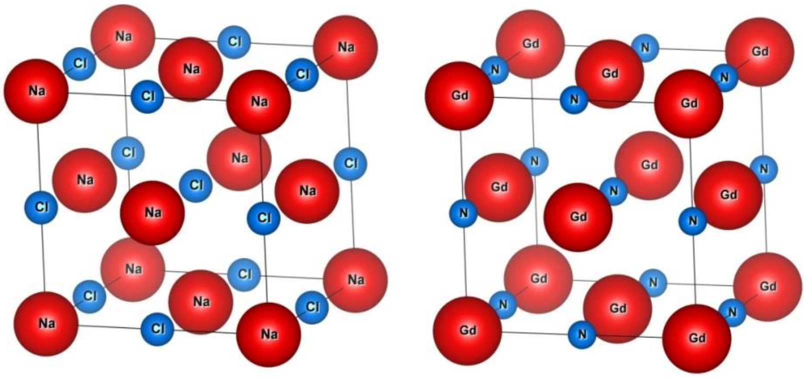

Figure I-6:The Gadolinium have same type structure of NaCl

Recently, there were several studies of the magnetic exchange interactions in the Gd-Pnictides: GdX, with X=N, P, As, Sb, Bi. These materials all share the rock salt structure and with the exception of GdN, all these compounds are semi metallic and Antiferromagnetic with the AFM-II structure as ground state, i.e. ferromagnetically ordered in (111) planes alter in spin orientation from layer to layer. We'll denote this as [111][17]

Finally, the Neel temperatures for the GdX with X=P, As, Sb, Bi, and Curie-Weiss temperature for GdN, are listed in table below

Table I. 5: Experimental Neel and Curie-Weiss temperatures (in K) for GdX(X=N, P, As, Sb and Si)[15].

T_C	GdN	81.0
T_N	GdP	15.9
	GdAs	18.7
	GdSb	23.4
	GdSi	25.8

I.6. The compound GdAl:

Examination of the published literature indicates that the Gadolinium-aluminum, GdAl, crystallizes with either b.c.c., CsCl type or one of two different orthorhombic structures, i.e. CeAl type, which belongs to the space group Cmc21 (van Vucht, 1957) or CrB type found for YA1 (Da-Gerhamn, 1963). All the lines in the GdA1 powder pattern could be indexed on the basis of the CeA1 type orthorhombic structure. Although Baenziger& Moriarty (1961) found some b.c.c, lines in their complex X-ray pattern for GdAl while none were found other works such as. This does not necessarily indicate that one of the results is incorrect. The difference could be explained by the existence of a high-temperature b.c.c, phase retained upon quenching by Baenziger& Moriarty (1961) but not retained in this research because of either too slow a cooling rate during quenching or too low an annealing temperature, i.e. below the orthorhombic b.c.c, transition temperature[18].

I.6.1. The first type Ortho1(CeAl):

For GdAl the lattice constants were obtained by the Nelson-Riley extrapolation method. The powder patterns of GdAl were quite complex which is in agreement with previous data. In the case of GdAl the lines for the b.c.c phase reported by baenziger and moriary(1961)[19] could not be identified in the powder pattern

The non-cubic phase in the GdAl powder patterns was indexed as having an orthorhombic structure.

Table I. 6: Lattice parameters and structural data for GdAl compound[19]

Compound	Lattice constant	Structure Type
GdAl	a = 9.274, b = 7.679, c = 5.584	CeAI

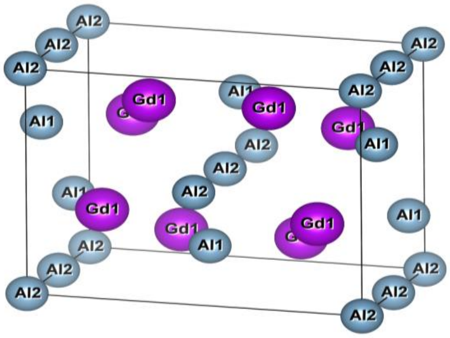

Figure I-7:Structure of GdAl on Type structure CeAl

I.6.2. The second type Otho2 (DyAl):

The systems neodymium-aluminum and gadolinium-aluminum have been investigated in the whole concentration range by metallographic and thermos analytical methods and by X-ray diffraction.[20]

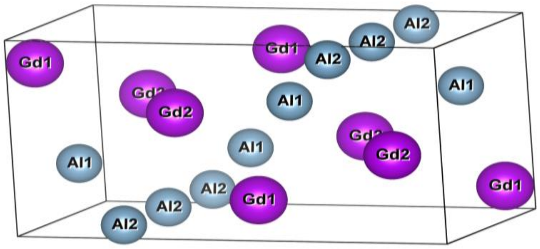

Figure I-8:Structure of GdAl on Type structure DyAl

The present X-ray experiments show that the phase is stable in orthorhombic, has structure type DyAl with space group Pbcm with lattice constants (a= 5.656; b= 5.888; c= 11.527Å)[20].

The alloy samples of this compound were prepared by melting the proper amounts of rare earth metal and Aluminum in an argon atmosphere by means of an arc furnace consisting of a movable tungsten electrode and a water-cooled copper hearth. To assure homogeneity each sample was remelted repeatedly. The purities of the metals used are 99.99% for Aluminum and 99.9% for Gadolinium. To obtain single-phase samples the alloy buttons were placed in a ThO_2 crucible and heated in an evacuated silica tube for about two weeks at a temperature below the peritectic point[21].

I.6.3. The third type CsCl:

The inter metallic compound investigated is GdAl, For a long time the RAl (With R is rare earth) compounds were thought to have the CsCl structure[22]. Most investigators, however, observed in the X-ray spectra additional reflections that could not be attributed to known impurities. It was recently shown that, as the CsCl structure is not stable at room temperature, the RAl compounds crystallize in orthorhombic structures[23]. Hence this phase is the less probable for GdAl.

CsCl structure has space group P m-3m,its number is 221,the lattice constant is (a=3.7208Å) and its volume of unit cell is Vol=51.51 $Å^3$.

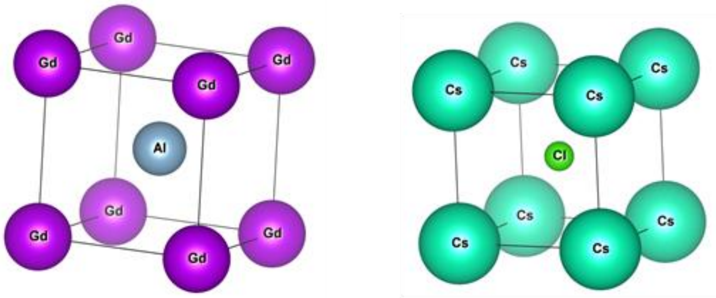

Figure I-9:Structure of GdAl on Type structure CsCl

I.7. The compound $GdAl_2$

In this section we are going to talk about the binary system Gadolinium-Aluminum, now we investing the compound $GdAl_2$, study its magnetic ordering, it is ferromagnetic or ant ferromagnetic. Firstly, we start by describe this compound. All the lanthanides combine with aluminum to form RAl_2 compounds with the same crystalline structure[24]namely the cubic $MgCu_2$. $GdAl_2$is no exception and powder X-ray diffraction patterns showed that the starting compound $GdAl_2$ had structure as well show below in Fig (C15, Laves phase) with space group Fd3m with lattice parameter a=7.899 Å,[25]. Magnetization measurements demonstrated that the compound is a ferromagnetic at lower temperatures with a Curie temperature of about 170K[26].

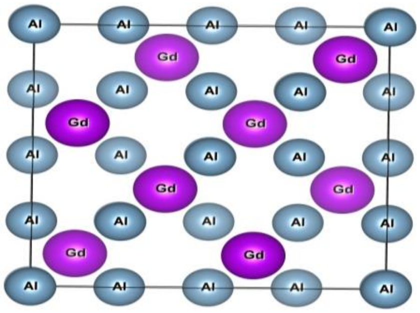

Figure I-10: MgCu2 Type Structure of GdAl2.

I.8. The compound GdB_2:

Twenty-four confirmed binary diborides phases with the hexagonal AlB_2-typestructure make this the most common phase type for binary metal-boron systems[27].The GdB_2 belong to this diborides group. A number of studiesexist in the literature dealing with lattice dynamical properties of diborides[28],[29]. The simple hexagonal AlB_2-type structure has the space group N°191,P6/mmm, and contains one formula-weight per unit cell. Fig1 illustrates the nature of the structure which was first reported in the 1930's[31],[32].The results of these works show that all these materials are dynamically stable in the AlB_2type structure [30].

The structure contains graphite-like boron layers which are separated by hexagonal close-packed (h.c.p.) layers of metals. The center of a hexagonal boron ring lies both directly above and below each metal[27].Each atoms of aluminum is situated in the center hexagonal polyhedral consisting of twelve boron atoms as shown below. For GdB2 belongs to the AlB2-type structure (Space group: No. 191,P6/mmm).The primitive cell contains one Gadolinium atom and two boron atoms occupy nonequivalent atomic positions of 1a (0,0,0) and 2d (1/3,2/3,1/2), respectively. We added here the crystallography data for GdB2: a=3.315Å and b=3.936Å[30].

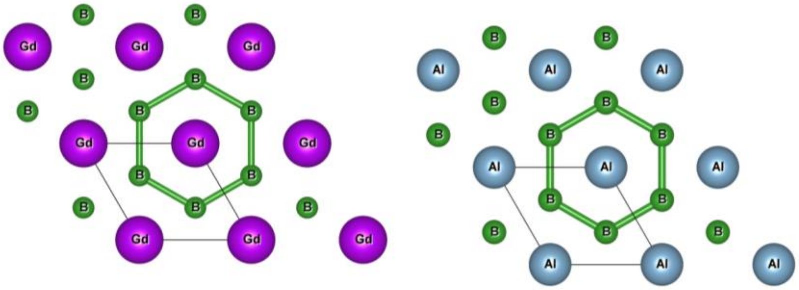

Figure I-11: Structure of GdB2 and AlB2 its type structure

Spin-polarized electronic structure calculations were carried out for the FM state of GdB2[33],[34],[35].We added here also, the rare earth borides have not been studied theoretically or experimental, one of by theme is GdB2. Systemic studies on lattice dynamics and thermodynamics of rare earth borides are of great importance and in demand[36].some experimental studies indicate that this compounds can be synthesized only at high pressures[37].

Conclusion:

Gd-monopnictides(GdX, X=N, P, As, Sb, Bi) have been extensively studied. The outcome of these investigations show that with the exception of GdN which is semiconductor and orders in ferromagnetic configuration at low temperature, all Gd-monopnictides compounds share the rock salt structure and are semi metallic and Antiferromagnetic with the AFM-II structure as ground state. On the other hand, Gd-Mx(M= B, Al; x=1, 2) have attracted less attention and their magnetic properties are not all known. Magnetic order can be predicted by means of ab-initio calculation together with magnetic exchange energies. The latter parameters can be used to predict transition temperatures.

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Chapter II

II. Result and Discussion:

II.1. Introduction:

In this chapter, we investigate four binary compounds based of gadolinium which are: GdN, GdAl, GdB_2 and $GdAl_2$.GdAl has three crystallographic phases. We investigate the much stable phase. The important thing we interested is the magnetic ground state for these compounds. Either Ferromagnetic or Antiferromagnetic. Furthermore, we are going to calculated total energy difference between Antiferromagnetic and ferromagnetic in order to extract the magnetic exchange parameters. The magnetic exchange interactions in the GdN, $GdX_{2,}$(X=B, Al),and GdAl series are analyzed from various points of view. First, a Heisenberg Hamiltonian between the 4*f* induced local moments on the Gd only is used and the corresponding exchange interactions between first and second-nearest neighbors are derived from total-energy differences between the ferromagnetic (FM) and Antiferromagnetic AFM_n, where n=I, II, configurations. These parameters are then used to directly estimate the Neel or Curie-Weiss transition temperatures.

In this work, we first start by GdN compound because of it is well known stable phase, lattice constants, magnetic order and transition temperatures. We start by it to test the validity of our calculation method. It will also enable us to evaluate the calculation cost in order to predict the magnetic order for others materials. Secondly, we apply the same method and rules, to study and predict the ground state configuration of GdAl, GdB2, and GdAl2.

We are going to present the results of our computation by using the CASTEP code. It is based on plane wave density functional theory (PW-DFT), with exchange correlation energy approximation, Generalized Gradient Approximation,(GGA), local spin density approximation (LSDA),but with orbital-dependent Coulomb and exchange integrals added, the so-called LSDA+*U*. in all our investigations, we use norm conserving pseudo potentials since they are most adapted precision calculations.

For completeness purpose, and due to lack of time, we will also present electronic density of states DOS of our compounds in different magnetic configurations without any comment. These data are in the annex. We believe that it may serve for future studies.

II.2. Magnetic Ordering of GdN:

The first step is the convergence study. The benefit of this study is looking for the minimum configuration (number of planes wave cut-off and number of grid in reciprocal space) in order to get the desired energy accuracy.

We are going to calculate ground state energy of ferromagnetic and three plausible Antiferromagnetic configurations in order to determine the ground state phase and magnetic order. The second aim of this study is the calculation of Curie-Wises temperature and compare it to experimental value and previous theoretical results of other groups. The first challenge is to build the adequate models for Antiferromagnetic phases. The second one is to determine which XC functional is best adapted for this type of calculations. Finally we wanted to know the cost of such calculations.

The experience gained from the study of GdN will be used for the study of other binary Gd compounds

II.2.1. Plane wave cut-off and K-points for GdN:

In practice, we have to look for the optimum number plane waves represented by the cut-off energy Ecut and K-point sampling of the first Brilouin zone. The strategy to do this is: firstly by calculating the energy with fixed K-points and we increase the Ecut from 100 ev to 900 eV. every once we take the Total energy, than we plot Energy in function Ecut, the reason behind that is choice E_{cut}, which after this values Energy total doesn’t augmented, as we will show below in figure

Next, we do the same way, so we done whit E_{cut}, like we seen previously but now we fixed E_{cut}, that we found above ,and we switch between them, the augmented K-point from (2 2 2) to
(10 10 10), and we plot Energy in function K-point,

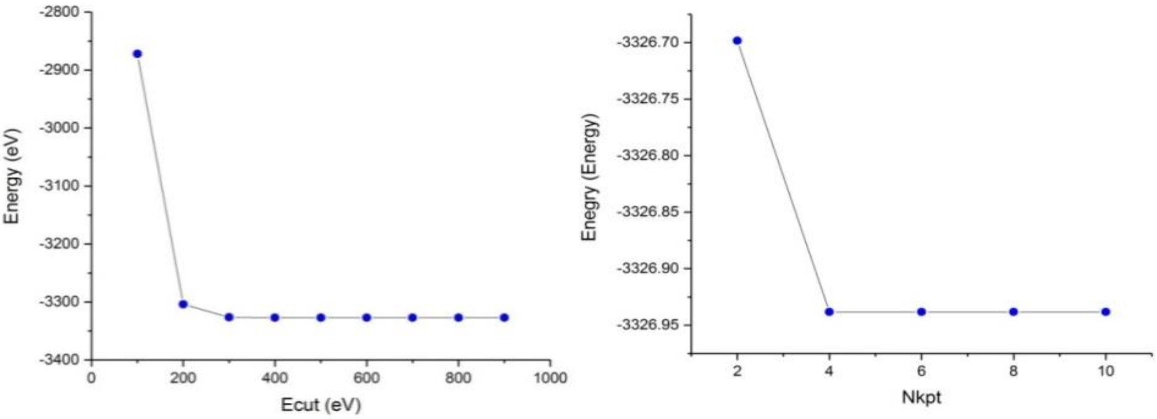

Figure II. 1: Energy function Ecut and Nkpt for GdN

II.2.2. Geometry optimization in case FM and AFM for GdN:

After convergence study, we launch our calculation for geometry optimization, by plane wave cut-off and K-point which we found above, the calculation was use Ecut 400 eV and K-point 4×4×4.the calculation divided into two section, the first for ferromagnetic and second for Antiferromagnetic there are many types for Antiferromagnetic Type I, type II and type III, different between them is describes alternating spins in the direction ,as we will show below.

II.2.2.1. Unit cell for Ferromagnetic configuration:

The code CASTEP [20] allows us to simulate magnetic materials, as ferromagnetic by modifying formal spin direction. We have the choice, between spin up or spin down, in this section we selected spin up, for make it as materials ferromagnetic, as we will show below, in Figure II.2 we add notes spin just for elements of Gadolinium because it has ferromagnetic order magnetic, on the other hand we do not added spin for element of nitride because of it is Paramagnetic order magnetic,

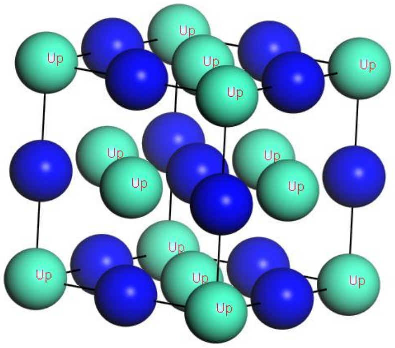

Figure II. 2:Ferromagnetic configuration of GdN compound

Table II. 1: calculated equilibrium lattice parameters a (Å) and magnetic ordering in many Works for GdN Compound

		E_{XC}	State	a= (Å)
GdN	Exp[1]			4.98
	This work	LSDA+U	FM	5.01
	This work	GGA	FM	5
	Ref[2]	FP-LMTO(LSDA+U)	FM	5.07
	Ref[3]	FP-LMTO(LSDA+U)	FM	5.08

From Table II.1 above we can see our result which calculated by pseudo potential is better than calculated by FP-LMTO with exchange-correlation energy LSDA+U, also it is nearest at experimental lattice constant. Difference potential and exchange-correlation energy gives the same result, that magnetic ordering of GdN compound is ferromagnetic.

II.2.2.2. Unit cell for Antiferromagnetic configurations:

Now we make GdN as Antiferromagnetic, as well now the Antiferromagnetic is anti-parallel of spin, has the same magnetic moment but opposite direction, we take this information than applied it in GdN, the different direction of spin in crystal can gives us different types of Antiferromagnetic configurations,

Here we have three types of Antiferromagnetic, The simplest AFM configurations have been described as AFM_I AFM_{II}, AFM_{III}, where AFM_I describes alternating spins in the (001) direction , AFM_{II} describes alternating spins in the (111) direction and AFM_{III} describes alternating spins inthe(011) as can be seen in figure below

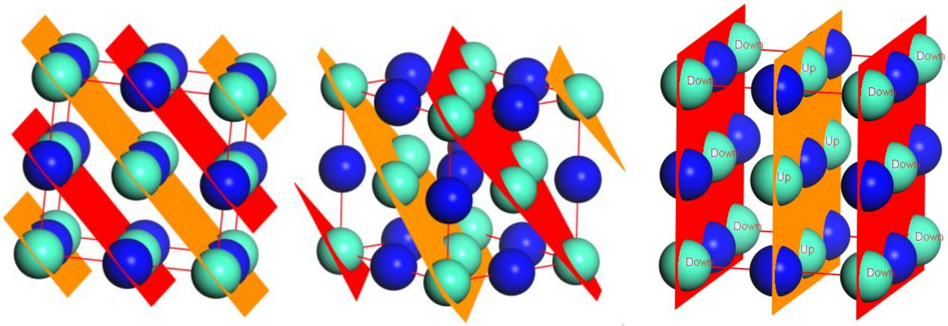

Figure II. 3: description of the types of AFM on left hand AFMI, the middle AFM_{II}, on the right hand AFM_{III}

Red color in the Figure above describe that plane has formal spin direction type down.

Table II. 2: Total energy calculated of GdN using LSDA+U for both types AFM_n ($n=_{I,\ II,III}$),and FM configurations

XC	order magnetic	Volume (Å^3)	Total Energy (eV)	$E_{(AFMN)}$-$E_{(FM)}$ (meV)	Magnetic moment (μ_B)
LSDA+U	FM	31.35	-2936.307	0	7
	$AFM_{I[0\ 0\ 1]}$	33.39	-2936.140	0.167	0.97E-05
	$AFM_{II[1\ 1\ 1]}$	33.62	-2935.966	0.341	-0.17E-11
	$AFM_{III[0\ 1\ 1]}$	33.60	-2936.137	0.17	0.38E-04
GGA	FM	31.21	-2997.374	0	7
	AFM $_{I[0\ 0\ 1]}$	31.28	-2997.353	0.021	-0.27E-06
	$AFM_{III[0\ 1\ 1]}$	31.28	-2997.354	0.02	-0.10E-05

We find that in all these compounds, the total energies of three AFM configurations have a consistent order $\mathbf{E_{FM} < E_{AFMI[0\,0\,1]} < E_{AFMIII[0\,1\,1]} < E_{AFMII[1\,1\,1]}}$.

FM-GdN does have the lowest energy while, for the others the AFM_I state has lowest energy. According to these calculations, GdN is indeed FM in its ground state in accordance with known results. We also checked that by using other exchange-correlation energy (GGA), which gives us the same result but with lower exchange energy. However, energy differences of GGA calculations are much lower than those obtained using LDA+U.

II.2.3. Exchange parameters

first of all we will recalculate the energy differences between the AFMI, AFMII, and FM states

We adopt a model with only nearest, J 1, and second nearest neighbor interactions, J_2. Positive coupling constants correspond to FM interactions. Using the magnetic structure of different configurations; we have calculated total energy as function of exchange parameters J_1 and J_2. The energies for the four relevant magnetic configurations are presented in Table II.3.We here adopted the quantum-mechanical Heisenberg Hamiltonian with S=7/2, corresponding to the total localized magnetic moment for Gd where the orbital momentum L=0. Alternatively, one could adopt a classical Heisenberg Hamiltonian with $S = \pm 1$ and this would simply renormalize the exchange interactions by a factor $S(S+1)$[4].

In the mean field treatment, the transition Neel temperature is given by the following relation[5] :

$$\mathbf{T_N = \frac{S(S+1)}{3k_B} \sum_{i=1,2} (Z^{\uparrow\uparrow} - Z^{\uparrow\downarrow}) J_i} \text{(Equation 1)}$$

Where z refers to the z-component of the spin, S is the total spin, k_B is the Boltzmann's constant, and J_i is the exchange coupling that runs over first and second neighbors, used as cutoff for the Hamiltonian.

On the other hand the Curie-Weiss temperature is:

$$\mathbf{T_{CW} = \frac{S(S+1)}{3k_B} \sum_{i=1,2} (Z^{\uparrow\uparrow} + Z^{\uparrow\downarrow}) J_i} \text{(Equation 2)}$$

The value of T_{CW} depends on the total number of neighbors in each neighbor shell and it is independent of the magnetic ordering in a given crystal.

Table II. 3 : relation between exchange parameter and The Curie-Weiss temperature

Compounds	The Curie-Weiss temperature
GdN[2]	$T_{CW} = (12J_1 + 6J_2)/3K_B$ (Equation 3)
GdAl	$T_{CW} = (J_1 + 2J_2)/3K_B$ (Equation 4)
GdB_2	$T_{CW} = (6J_1 + 2J_2)/3K_B$ (Equation 5)
$GdAl_2$	$T_{CW} = (4J_1 + 12J_2)/3K_B$(Equation 6)

The Curie-Weiss temperature T_{CW} for each compounds are given in table above

Table II. 4: Total-energy and energy differences AFM, FM in classical Heisenberg-Hamiltonian as function exchange parameters J_1 and J_2.

total-energy	classical Heisenberg Hamiltonian (CHH)
E_{FM} =	$E_0 + (-12J_1 - 6J_2)$
$E_{AFM[1\ 0\ 0]}$ =	$E_0 + (4J_1 - 6J_2)$
$E_{AFM\ II}$ =	$E_0 + (6J_2)$
$E_{AFM[0\ 1\ 1]}$ =	$E_0 + (-4J_1 - 2J_2)$
$\Delta E_I = E(AFM_{[1\ 0\ 0]}) - E(FM)$	$(6J_2)$
$\Delta E_{II} = E(AFM_{[0\ 0\ 1]}) - E(FM)$	$(+4J_2)$

With S=7/2 or S(S+1) =63/ 4. We extract J_1 and J_2 from the first-principles calculated energy differences, $\Delta E_I = E(AFM_{[0\ 0\ 1]}) - E(FM)$, $\Delta E_{II} = E(AFM_{[1\ 1\ 1]}) - E(FM)$ and $\Delta E_{III} = E(AFM_{[0\ 1\ 1]}) - E(FM)$the energy differences between different magnetic ordering statesis small (of the order of a few meV). The resulting energy differences and the extracted J1,J_2 and Curie-Weiss temperatures are given in Table II.4.

Table II. 5: Magnetic energy differences (in meV/pair), Heisenberg exchange parameters (in meV), except our work in eV and Curie-Weiss temperatures (in kelvins)

			ΔE_I	ΔE_{II}	J_1	J_2	T_C (K)
GdN	Exp[4],[6]				0.64	0.00	58
	This work	CHH	0.0419	0.09	0.0052	0.009	56
	Ref[4]		6.7	4.2	0.695	−0.322	67.3
	Ref[2]		3.4	0.4	0.42	-1.40	11

We note that the calculated J_2 parameters are fairly close to the experimental values and follow the same trend, the J_1interactions decreases much more rapidly in the experimentally extracted values.
As a further way to analyze the comparison with experiment, we have calculated the directly observable quantity Curie-Weiss temperature from our calculated parameters within mean field theory. This comparison is shown in Table II.4. The average of the experimental values for and T_{CW} (58 K), (28 K), is close to the mean-field value

The experimental value of T_c should be taken with some reserve as GdN is very difficult to make with low carrier concentrations, so part of the higher experimental Tc is from carrier mediated ferromagnetism.[ref*:* privet communication with Pr. Walter Lambrecht.*[Case Western Reserve University USA*].

II.3. Magnetic Ordering of GdAl:

As we said previously, GdAl compound has three stable phases, the first thing that we do is looking for stable phase then we launch our calculation in this phase. The magnetic order is unknown and the best of our knowledge no previous theoretical work has been carried out on this compound

II.3.1. Plane wave cut-off and K-points determination for GdAl:

Well-converged mesh based on division of the reciprocal unit cell for each one of these structures. It was as we will present in the tables below, in these group picture show us the energy does not minimized more than the critical that we, as we observed in these figures have a same plane wave cut-off (400ev) and K-point 7×7×4 divisions (the equivalent of separation 0.025 1/Å) .

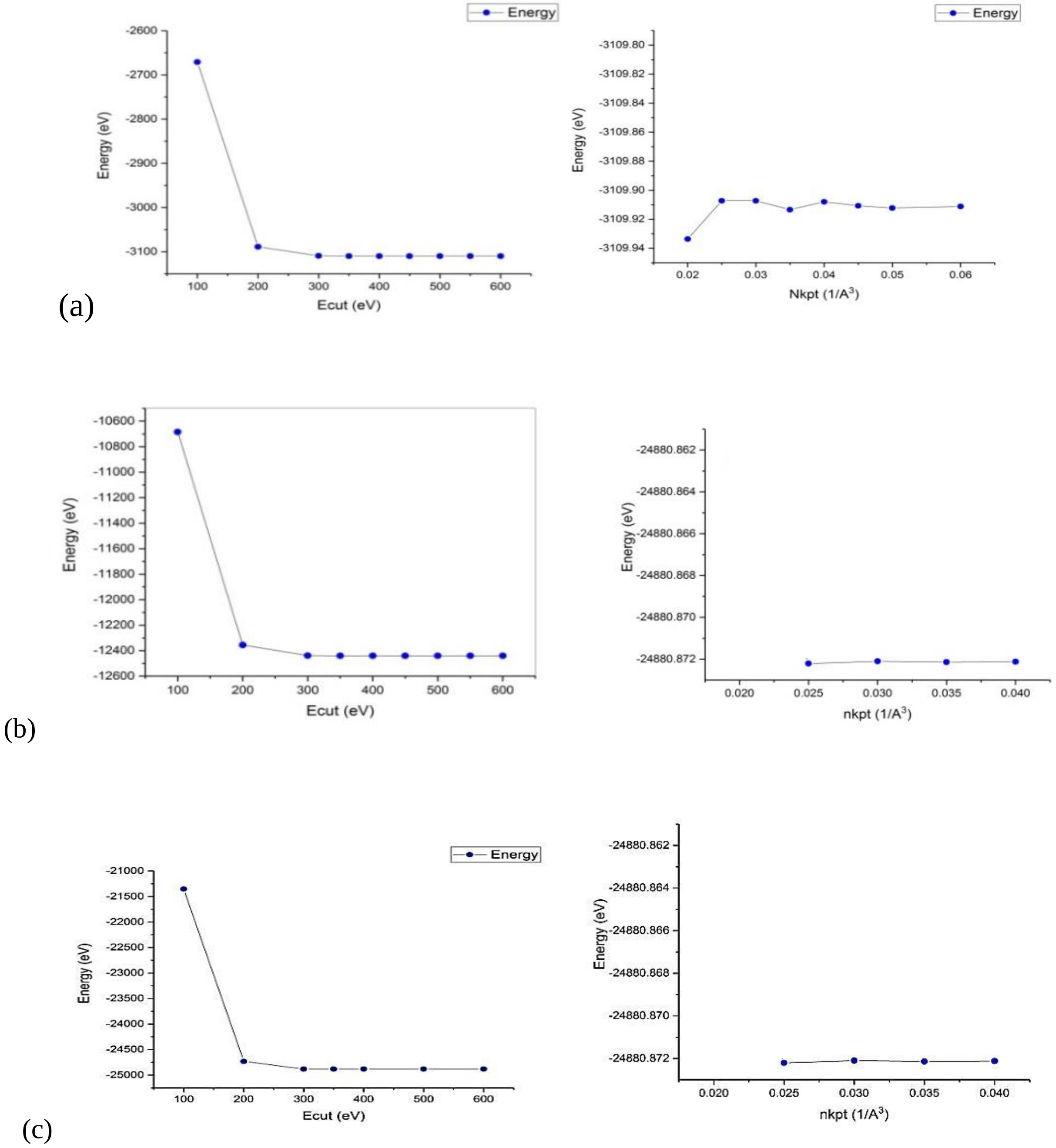

Figure II. 4: Convergence for GdAl type structure CsCl, CeAl and DyAl respectively

II.3.2. Geometry optimization in case FM and AFM for GdAl:

In this section, the first thing we investigated is to cheek which of the three structures of GdAl is more stable. The way to do that is by comparison the ground state energy for each one. As we said previously, we launch our optimization by the same plane wave cut-off and K-point.

Secondly, selected the ground state for GdAl, then we suppose for this structure, FM and AFM, compare again which is the ground state

II.3.2.1. Geometry-Optimization of both structure phases for FM configuration:

The selected structures in this study are optimized by the CASTEP code to compare their energies and Lattice constant. The relative stability of the CsCl (Cubic), CeAl (Orthorhombic1) and DyAl (Orthorhombic2) type structures. We suppose them as magnetic materials; the result obtained using LSDA is alsoshown in Figure below.

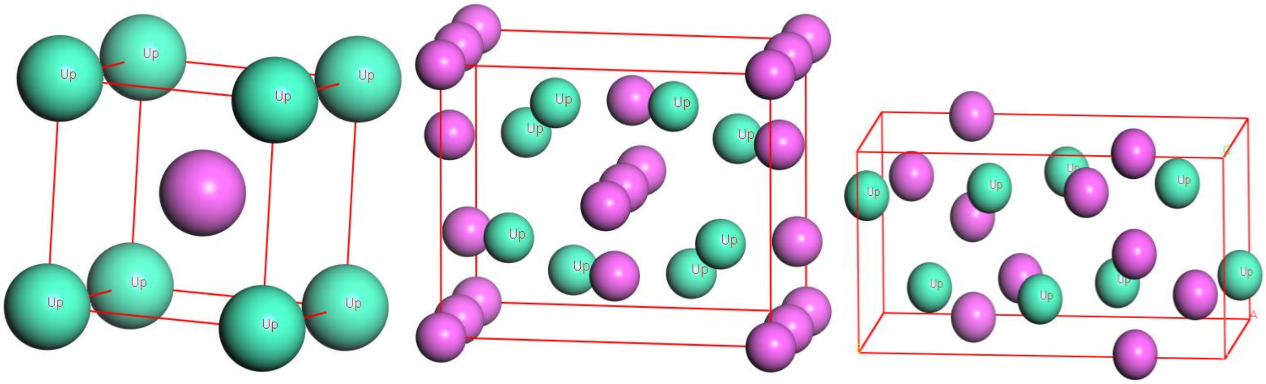

Figure II. 5: Structur phases of GdAl the first is CsCl in right, the scecond is CeAl in the middle of pictur, the third is DyAl in left

The unit-cell dimensions, space group and atom position of three inter metallic phases found in groups CsCl, CeAl and DyAl are presented in Table II.5below.

Table II. 6: structure information for both structure types SG, phase prototype and atom position

Compound	space group	Phase Prototype	atom position			
				x	y	z
GdAl	Pm-3m, N°: 221, [21]	CsCl: b.c.c.	Gd	0.50000	0.50000	0.50000
			Al	0.00000	0.00000	0.00000
	Cmcm, N°: 63,[8]	CeAl: Orthorhombic1	Gd1	0.32100	0.16100	0.25000
			Al1	0.00000	0.29000	0.25000
			Al2	0.00000	0.00000	0.00000
	Pbcm, N°: 57, [22]	DyAl:Orthorhombic2	Gd1	0.16040	0.51480	0.25000
			Al1	0.33200	0.10220	0.25000
			Gd2	0.59850	0.33290	0.25000
			Al2	0.06910	0.25000	0.00000

Total energy calculated by LSDA for both structure types are listed in table below

Table II. 7: total energy calculated by LSDA for both structure types

Compound	Space group	Total energy (eV/Number de formula)	Lattice constant (Å)	
			This work	Exp
GdAl type structure CsCl	Pm-3m, N°: 221	-3110.037	a=3.58	a=3.72 Ref[7]
GdAl type structure CeAl	Cmcm, N°: 63	-3110.122	a=8.98, b= 7.36 c= 5.52	a=9.27 Ref[8] b=7.68 c= 5.54
GdAl type structure DyAl	Pbcm, N°: 57	-3110.142	a=5.81 b=11.43 c=5.54	a=5,89 Ref[9] b=11,53 c=5,66

As can be shown in table above, the energy stability favorable to the Orthorhombic2 (DyAl) structure(Pbcm) followed by the Orthorhombic1 (CeAl) structure (Cmcm), then the Cubic (CsCl) structure (Pm-3m).

II.3.2.2. Geo-Opt the case AFM for GdAl structure type DyAl:

In the compound GdAl structure type, has two types of AFM configuration, the first is AFM$_{[1\ 0\ 0]}$ describes alternating spins in the[1 0 0]direction, the second is AFM$_{[0\ 0\ 1]}$ describes alternating spins in the[0 0 1] direction.

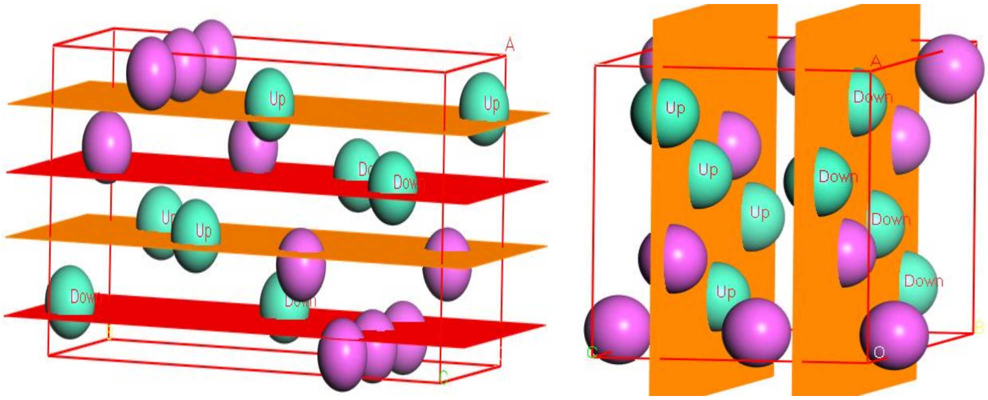

Figure II. 6: Antiferromagnetic configuration of GdAl compound AFM$_{[1\ 0\ 0]}$Fig AFM$_{[0\ 0\ 1]}$

Figure II.6presentsthe types of AFM; onleft hand AFMI, on the right hand AFM_{II}. Red color in the figure above describe that plane has formal spin direction type down. We consider two different magnetic ordering configurations: ferromagnetic (FM) and two Antiferromagnetic(AFM).

Since the energy difference between different magnetic ordering states is small (of the order of a few meV), using we use 4000 *k* points in the Brilouin zone to obtain the total energy accuracy of 0.1 meV[10].

Table II. 8: total energy used LSDA for both types of order magnetic in this work for GdAl compound

order magnetic	space group	Volume ($Å^3$)	Total Energy (eV)	E(AFM)-E(FM) meV	Magnetic moment (μ_B)
FM	Pbcm, N°: 57	368.01	-24881.139		7.52
$AFM_{I[1\ 0\ 0]}$	P $mc2_1$, N°: 28	366.48	-24881.022	0.117	0
$AFM_{II[0\ 0\ 1]}$	P ma2,N°: 26	366.10	-24880.908	0.231	0

We find that in all these configurations, the total energies of two AFM configurations have a consistent order, $E_{FM}<E_{AFM[1\ 0\ 0]}<E_{AFM[0\ 0\ 1]}$. The observations that GdAl compounds studied here has the FM structure.

Remark: we have investigated magnetic order of GdAl in the CsCl type structure using norm conserving pseudo potentials and ultrafine calculations and both GGA and LDA+U for the XC potentials. We also explored two AFM configurations; $AFM_{[001]}$and $AFM_{[110]}$.

The results show that this phase orders in the Antiferromagnetic configuration $AFM_{[001]}$. This demonstrates that the FM order is not systemic in the Gd based binary compounds.

II.3.3. :Exchange parameters

Using the three magnetic structures, we have formulated the total energy as function of the exchange parameters. The relation between total-energy differences and exchange interactions are listed in table below

Table II. 9: total-energy and energy differences AFM, FM in CHH

total-energy	classical Heisenberg Hamiltonian
E_{FM} =	E_0 +($-J_1$-$2J_2$)
$E_{AFM[1\ 0\ 0]}$ =	E_0 + (J_1)
$E_{AFM[0\ 0\ 1]}$ =	E_0 + ($-J_1$+$2J_2$)
ΔE_I=E($AFM_{[1\ 0\ 0]}$) –E(FM)	($2J_1$+$2J_2$)
ΔE_{II}=E($AFM_{[0\ 0\ 1]}$) –E(FM)	(+$4J_2$)

The Heisenberg model is then used to predict Curie-Weiss temperatures using (Equation 4)and compared with experimental data. The calculated total energy differences and the resulting exchange parameters are listed in Table II.9.

Table II. 10: Magnetic energy differences per unit formula and Heisenberg exchange parameters in (eV), and Curie-Weiss temperatures (in kelvins).

	ΔEI	ΔEII	J_1	J_2	T_{CW}(K)
CHH	0.029	0.015	0.231	0.684	97.4

In principle, our procedure in which the exchange parameters are directly given in terms of the energy differences is more direct since no mean-field approximation is involved.[11]

II.4. Magnetic phases of GdB_2:

In this section, we performed density functional calculations to investigate the magnetic phase stability of GdB_2within the CASTEP code. The exchange and correlation functional was treated by the Generalization Gradient Approximation (GGA),local density approximations, LSDA and LSDA+U, since our material are strongly correlated.

II.4.1. Plane wave cut-off and K-points for GdB_2:

Very careful step analysis is done to ensure convergence of the total energy in terms of the vibration cutoff-energy parameter. At the same time, we have used an appropriate set of k-points to compute the total energy.

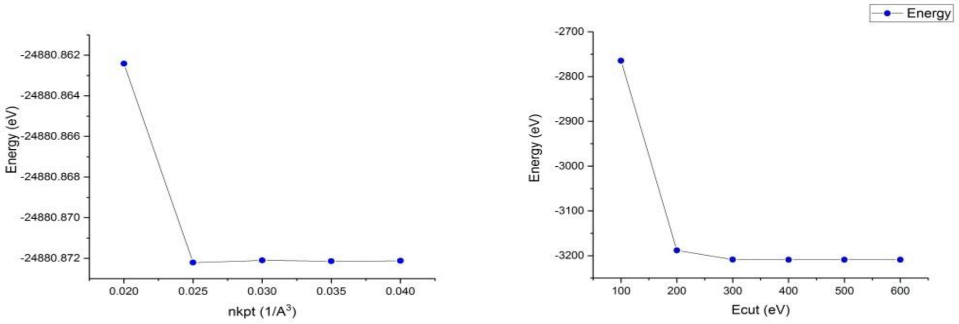

Figure II. 7: Convergence for GdB_2

The total energy was minimized using a set 0.03(1/Å^3) separation in the irreducible sector of the Brilouin zone, and the value of 400 eV for the cutoff energy was used. The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal converged to less than 1 meV.

II.4.2. Geometry optimization in case FM and AFM for GdB_2

The checked ground state of GdB_2, by suppose the compound in Ferromagnetic then Antiferromagnetic configuration. The ground state has lower energy, after that we extract exchange interactions between first and second-nearest neighbors are derived from total-energy differences, between the FM and AFM-I and AFM-II configurations.

II.4.2.1. Unit cell for Ferromagnetic configuration:

The crystallographic AlB_2-type structure of $GdB_2$is presented in table II.10.The primitive cell contains one Gadolinium atom and two Boron atoms occupying non equivalent atomic positions of 1a (0, 0, 0) and 2d (1/3, 2/3, 1/2), respectively with the equilibrium lattice parameters (a=3.32,c=3.396 in Å).

Table II. 11: Structure information for GdB_2 (SG, phase prototype and atom position)

Compound	space group	Phase Prototype	atom position			
				x	y	z
GdB_2	P 6/mmm	AlB_2	B	1/3	2/3	0.5
			Gd	0	0	0

Including spin up in all atoms of Gadolinium, allowed us to present our compound in the case FM configuration.

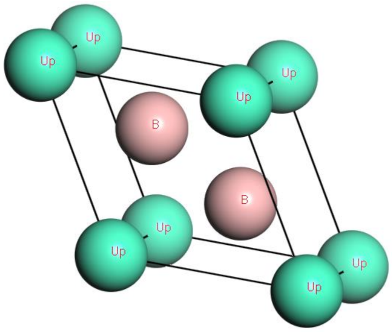

Figure II. 8: Ferromagnetic configuration of GdB_2 compound

Also we compute the equilibrium lattice constants, by different exchange-correlation energies, tables II.11.

Table II. 12 : calculated equilibrium lattice parameters a (Å) and magnetic ordering in many Works for GdB_2 Compound

		E_{XC}	State	Lattice constant (Å)
GdB_2	Exp			a=3.32,c=3.936 Exp[12] a=3.32, c=3.944 Exp[13]
	This work	GGA	FM	a =3.31, c=4.06
		LSDA	FM	a = 3.25, c=3.94
		LSDA+U	FM	a = 3.31,c=3.97
	Ref[14]	(LSDA+U)	FM	a=3.25, c=3.89
	Ref[15]	GGA	FM	a=3.32, c=3.94

The most important result, evident from Table II.11 is that our calculations predict the FM ordering of GdB_2 in accordance with previous theoretical investigations [13], [14]. From table II.11, observed that LSDA+U increased the volume of structure and nearest experimental lattice constant than LSDA and GGA.

II.4.2.2. Unit cell for Antiferromagnetic configurations:

The simplest FM and AFM configurations have been described as FM, AFM where $AFM_{[1\ 0\ 0]}$describes alternating spins in the [001]direction, $AFM_{[1\ 1\ 0]}$describes alternating spins in the [110]direction.

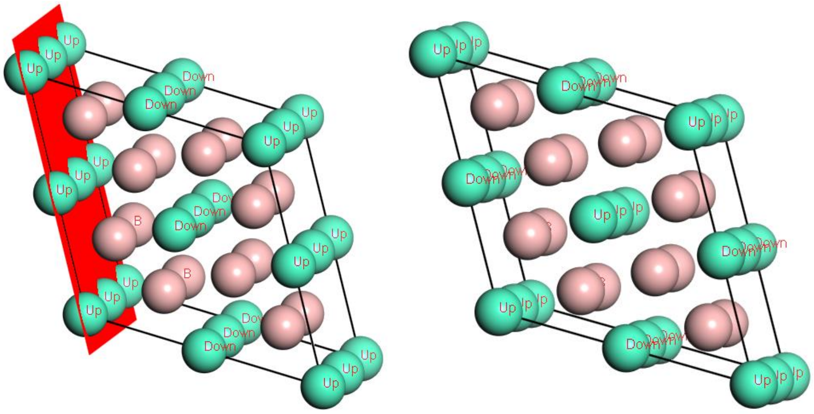

Figure II. 9: Antiferromagnetic configuration of GdB_2 compound $AFM_{[1\ 0\ 0]}$ and $AFM_{[110]}$

The magnetism of the diborides, GdB_2, has not been as comprehensively reported[16]. For that we add suppose it also as AFM, then compare between FM and AFM.(Table II.12)

Table II. 13: total energy for both types of order magnetic in this work for GdB_2 compound calculated with LSDA

order magnetic	Total Energy (eV)	Volume (Å)	Magnetic moment (μ_B)
FM	-3209.004986074	36.21	7.38
$AFM_{I[1\ 0\ 0]}$	-3208.971373422	36.31	0
$AFM_{II[1\ 1\ 0]}$	-3208.752678507	39.50	0.027

As shown in table the total energies indicate that the GdB_2 compound is Ferromagnetic. The total energy was calculated by LSDA. We obtain the same result when we us another Exchange-Correlation energy, like GGA and LSDA+U

From table above, we notice that the volumes determined by the LSDA+U are higher in comparison with those calculated by the LSDA and GGA. The existing differences in our results may be attributed to the poor description of the exchange-correlation interaction by both the LSDA, GGA and LSDA+U approaches in density functional theory.

Also we have optimized the lattice parameters for each magnetic configurations to perform a detailed analysis on the energy dependence of the magnetic systems using the LSDA, GGA and LSDA +U approaches.

II.4.3. Exchange parameters

The resulting energy differences and the extracted, and Curie-Weiss temperatures are given in Table below.

Table II. 14: total-energy and energy differences AFM, FM in classical Heisenberg-Hamiltonian.

total-energy	classical Heisenberg Hamiltonian
E_{FM}	$E_0 +(-6J_1-2J_2)$
$E_{AFM[1\ 0\ 0]}$	$E_0 +(-6J_1+2J_2)$
$E_{AFM[0\ 0\ 1]}$	$E_0 +(2J_1-2J_2)$
ΔE_I=E($AFM_{[1\ 0\ 0]}$) –E(FM)	$(4J_1)$
ΔE_{II}=E($AFM_{[0\ 0\ 1]}$) –E(FM)	$(+8J_2-4J_2)$

Table below shows the results obtained. We extract *J*1and *J*2from the first-principles calculated energy differences ΔE_I=E($AFM_{[1\ 0\ 0]}$) –E(FM) and ΔE_{II}=E($AFM_{[0\ 0\ 1]}$) –E(FM).

The calculation the Curie-Weiss temperature by using (Equation 5)

Table II. 15 : Calculated total energy differences per formula between FM and three AFM configurations for GdB_2, The exchange parameters, J_1, J_2.

GdB_2		ΔE_I(V)	ΔE_{II} (eV)	J_1(eV)	J_2(eV)	T_C(K)
	CHH	0.034	0.252	-0.008	0.021	195

II.5. Magnetic Ordering of $GdAl_2$:

in this section we well check the ground state of $GdAl_2$,by supposing it as FM and AFM. Then we calculate total energy difference between AFM and FM. We use this difference to extract exchange parameter, finally we predict Curie-Weiss temperature.

II.5.1. Find the plane wave cut-off and N-point of $GdAl_2$:

As can be show in figure below, Convergence study show us the $GdAl_2$ optimum in plane wave cut-off 400 eV and separation 0.03 (1/Å^3).

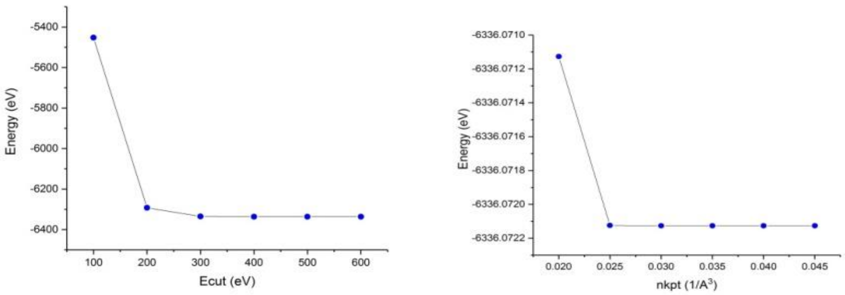

Figure II. 10: Energy function Ecut and k-point for $GdAl_2$

II.5.2. Geometry optimization in case FM and AFM for $GdAl_2$:

II.5.2.1. Unit cell for Ferromagnetic configuration:

The $GdAl_2$ compound crystallizes in the cubic Laves structure. Its atomic basis comprises six atoms (two formula units) and the primitive translations form an fcc Bravais lattice. We present also space group, atom position as we can see in table below. The total energy was minimized using a set of 0.03Å^{-1}separations in the irreducible sector of the Brilouin zone for the $GdAl_2$ as Ferromagnetic.

The lattice constant of $GdAl_2$is (a=7.75) from Table II.16 below.

Table II. 16: structure information for both structure types SG, phase prototype and atom position

Compound	space group	Phase Prototype	atom position			
				x	y	z
$GdAl_2$	P 6/mmm ,N°:227	$MgCu_2$, Cubic, fcc	Al	0.00000	0.00000	0.00000
			Gd	0.37500	0.37500	0.37500

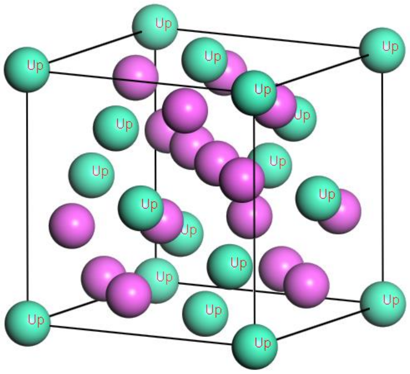

Figure II. 11: describe $GdAl_2$ in ferromagnetic configuration

The calculated results are listed in Table. It can be seen that all theoretical equilibrium lattice parameters and the experimental value.

Table II. 17: calculated equilibrium lattice parameters a (Å) and magnetic ordering in Exp Works for $GdAl_2$ Compound

		State	E_{XC}	Lattice constant
$GdAl_2$	Exp[17]	FM		a=7.75
	Exp[18]	FM		a=7.9
	This Work	FM	LSDA	a=7,80
		FM	LSDA+U	a=7,91

We notice that from Table II.16, lattice constant determined bythe LSDA+U and LSDA nearest to that calculated in experimental.

II.5.2.2. Unit cell for Antiferromagnetic configurations:

The simplest FM and AFM configurations have been described as FM, $AFM_{[1\ 0\ 0]}$ and $AFM_{[1\ 1\ 0]}$ where $AFM_{[1\ 0\ 0]}$describes alternating spins in the [100] direction, $AFM_{[1\ 1\ 0]}$describes alternating spins in the [110] direction.$GdAl_2$ was found by our calculations to have a lower energy in the FM than in any of the AFM configurations. The energies of the different configurations, given with respect to the FM state are given in table below

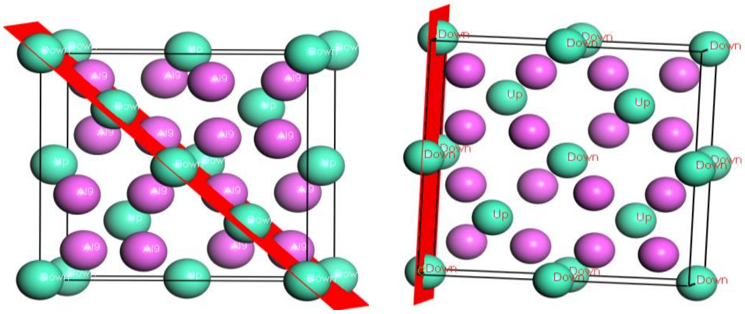

Figure II. 12: AFM configuration for $GdAl_2$, in the right AFM[1 0 0] and the left AFM[1 1 0]

It can be seen in table the $GdAl_2$ compound has lower energy. The calculations also confirm the preference for a ferromagnetic of ground state in $GdAl_2$

Table II. 18: calculated equilibrium lattice parameters a (Å) and magnetic ordering in many Works for $GdAl_2$ Compound

order magnetic	Total Energy	Volume (Å)	Magnetic moment(μ_B)
FM	-6336.156	475,25	15.05
$AFM_{I[1\ 0\ 0]}$	-6336.031	476,29	0
$AFM_{II[1\ 1\ 0]}$	-6336.105	476.28	0

The result show that the$GdAl_2$isferromagnetic in its ground state, also found to crystallize inthe cubic $MgCu_2$fcc structure, in agreement with previous experimental descriptions.

II.5.3. Exchange parameters

Table II. 19: total-energy and energy differences AFM, FM in quantum and classical Heisenberg-Hamiltonian.

total-energy	classical Heisenberg Hamiltonian
E_{FM} =	$E_0 +(-6J_1-2J_2)$
$E_{AFM[1\ 0\ 0]}$ =	$E_0 +(-6J_1+2J_2)$
$E_{AFM[1\ 1\ 0]}$ =	$E_0 +(2J_1-2J_2)$
$\Delta E_I=E(AFM_{[1\ 0\ 0]})-E(FM)$	$(8J_1)$
$\Delta E_{II}=E(AFM_{[1\ 1\ 0]})-E(FM)$	$(4J_2)$

For our structure we extracted the relations between exchange parameters and total energy. They are presented in table below. From total energy difference, we can extract exchange parameter J1 and J2 describe first nearest neighbors and second nearest neighbors respectively. Then we can predict Curie temperature by using (Equation 6).As can be seen from table below.

Table II. 20: Magnetic energy differences (in eV/pair), Heisenberg exchange parameters (in meV), and Curie-Weiss temperatures (in kelvins)

			ΔEI(eV)	ΔE_I (eV)	J_1(meV)	J_2(meV)	T_C(K)
$GdAl_2$	This work	CHH	0.016	-0.006	1.95	-1.55	41.7
	Exp[19]						170

A previous study shows that crystalline $GdAl_2$ has ferromagnetic (FM) transition at Curie Temperature T =170 K(as in Table II.19).Finally, the net result of our study is that gives a severe underestimate of the Curie temperature in GdB_2. This indicates that the experimental Curie temperatures in that system may be influenced by defects or other extrinsic causes.

II.6. Conclusion

We have investigated the magnetic structures of four binary gadolinium compounds namely GdN, GdAl, $GdAl_2$ and GdB_2.

Ground state energies of our compounds were calculated with high precision in order to distinguish between FM and AFM states. We used LSDA, GGA and LDA+U. furthermore we established the relations between total energies differences and exchange parameters J_1 and J_2 in order to extract them. These parameters were then used to predict transition Curie-Weiss or Neil temperatures.

We started with the well-known compound GdN in order to test and validate our approach. Both GGA and LAD+U give the right prediction of the magnetic order for this compound.

All our compounds have ferromagnetic ordering ground state.

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