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Half – metallic magnetism in light–rare earth nitrides

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Band structure calculations were performed on light-rare earth nitrides. LaN is a semiconductor and CeN shows a metallic-type conduction .We predict half metallicity for RN (R=Pr,Nd,Pm,Sm,Eu) nitrides with a gap for the minority spin and a metallic majority spin channel. The R(4f+5d) and N2p bands hybridize, and as a consequence, N2p anti-parallel polarization to 4f spin moment is induced. The determined spin moments per formula unit are integer numbers, confirming the half-metallicity. The computed results describe rather well the experimental data.

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Keywords: Rare-earth nitrides, Band structures, Magnetic properties

1. Introduction

Half-metals are characterized by metallic electronic structure for one spin channel, whereas for the opposite spin direction the Fermi level is situated within an energy gap [1]. There is a strong interest in these materials since they offer the opportunity to investigate the interplay between high polarization and band structure. In spite of growing evidence against a "pure" half–metallic character at finite temperatures [2–8], the attraction towards half–metals persist. Devices that exploit spin and charge of electrons operate at non–zero temperatures and consequently must involve systems having high magnetizations and also Curie temperatures. For these reasons many studies are focused on rare-earth (R) compounds which are characterized by their high magnetic moments. However, rare–earth atoms/compounds, still present controversies concerning their electronic structure. This is due to the 4f–orbitals which have different occupation numbers through the series, going from La to Lu, and it is still a challenging problem to obtain an accurate theoretical description of their electronic structure. Despite the fact that the 4f overlap with broad bands, forming narrow resonances, they are often treated as core states. The 4f moments cannot be generally quenched by the crystal field. The total magnetic moment has both orbital and spin components. In addition, spin–orbit interaction is particularly strong for many rare–earth elements. Because 4f bands are narrow, there is a strong on–site Coulomb repulsion between highly localized f electrons.

Different methods were used to compute the electronic structure of rare–earth compounds. Band structure calculations in the local–density approximation (LDA), underestimate band gaps. The local spin–density approximation (LSDA) to density functional theory, fails to describe the rare–earth 4f electrons correctly. The many body effects must be taken into account and more accurate approximation, as LSDA+U method, is considered. In this method, the LSDA is complemented with Hubbard–U corrections treated in a mean field approximation.

The broad range of behaviour of rare–earth nitrides (RN) from metallic or semimetallic to semiconductors make thse compounds very interesting to investigate. The emergence of the field of spintronics [9] provides new interest in this class of materials because of their unique magnetic and electronic properties, due to their unfilled and highly localized 4f orbitals. For example, GdN in pure state was predicted to be a narrow–gap semiconductor in bulk form [10] while others predicted it to be semimetal [11]. Despite its simplicity, the full understanding of electronic and magnetic properties of the RN compounds is still not complete. Petukhov et al [12]was the first to investigate the electronic structure of GdN, within the standard Linear Muffin Tin Orbital (LMTO) method considering a core description for the 4f–electrons. Later on, Self–Interaction Corrected, SIC–LSDA, calculations were performed by Aerts et al [13], showing that the electronic properties of RN include different classes of magnetic behaviour, especially the half–metallic light–rare–earth nitrides ferromagnets [14,15]. It is known that sometimes, the SIC–LSDA calculations overestimate the separation between occupied and non–occupied 4f states. More recently, LSDA+U calculations were performed by Larson. at al [16]. U corrections were considered for both the 4f and 5d. In this case the electronic structure of GdN turns out to be semiconducting, while the correction to 4f–only gave a half–metallic behaviour.

In all the above works the importance of R(5d)-N(2p) hybridization was less emphasized. However, this hybridization is important in establishing the overall physical properties, inducing a moment on N(2p) band which is responsible for the magnetic and transport properties. In addition, for the light–rare–earth compounds, it contributes significantly in the gap opening for the minority spins.

In order to understand the magnetic and electronic properties of these materials we have to correlate the experimental and theoretical data of the entire class of rare-earth nitrides. The electronic and magnetic properties of RN nitrides were computed by using LSDA+U method. In this paper we show that the the light–rare earth nitrides with R=Pr to Eu demonstrate a half–metallic behaviour. According to our calculations gaps are between 0.47 and 1.63 eV. Therefore, we believe that these compounds are possible material candidates for spintronics applications.

2. Electronic structure

We carried out electronic structure calculations for the light–rare–earth nitrides RN (R = La to Eu) , using the standard representation of the NaCl–structure. The space group is $Fm\bar{3}m$ (nr.225) in which the R occupies the (0,0,0) position and the N is situated in (1/2,1/2,1/2) one. As usual for non–closed–packed lattices, empty spheres are necessary. In our analysis, two empty sphere were introduced in the (1/4,1/4,1/4) and (3/4,3/4,3/4) positions. The lattice constants used in the calculations are present in Table 1.

Table 1. Lattice parameters and the values of the average Coulomb interaction U and exchange J. The last columns list the sphere radius in atomic units.

RE-N	a (Å)	U (eV)	J (eV)	r_R (a.u.)	r_N (a.u.)	r_E (a.u.)
LaN	5.30			3.45	2.27	1.50
CeN	4.87	7.470	0.898	3.14	2.13	1.40
PrN	5.17	7.276	0.941	3.31	2.27	1.55
NdN	5.15	7.609	0.987	3.29	2.27	1.55
PmN	5.19	7.992	1.030	3.32	2.30	1.55
SmN	5.04	8.220	1.07	3.20	2.25	1.52
EuN	5.00	8.506	1.109	3.17	2.24	1.52

The computed density of states of RN (R = La, to Eu) compounds are given in Fig.1 to 7. Values of U and J parameters similar as those given by Larson et al [16] were used in computing the band structures–Table 1.

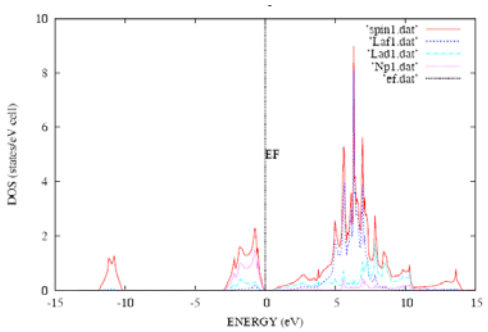

Fig.1. Density of states of semiconducting LaN.

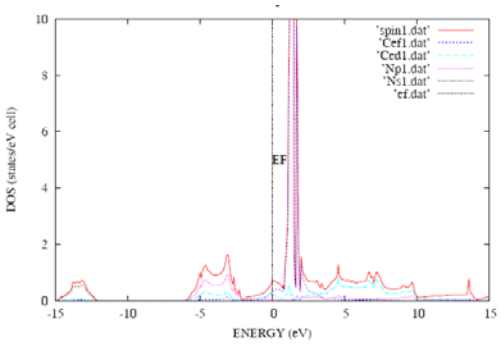

Fig. 2. Density of states of metallic CeN.

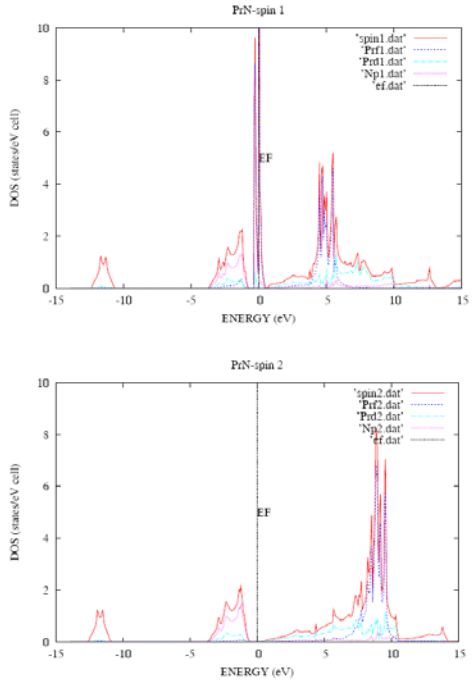

Fig. 3. Density of states of half metallic PrN. The majority spin bands (spin 1) and minority spin (sin 2) are ploted in Figs. 3-7.

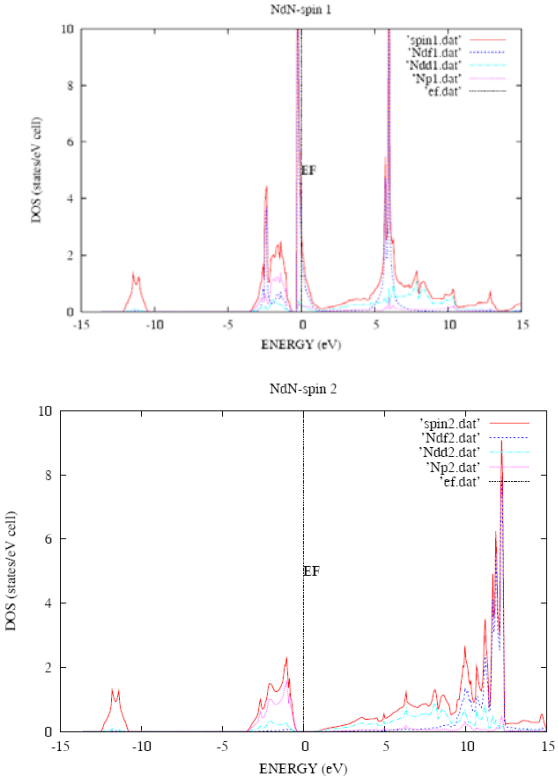

Fig. 4.Density of states of half metallic NdN

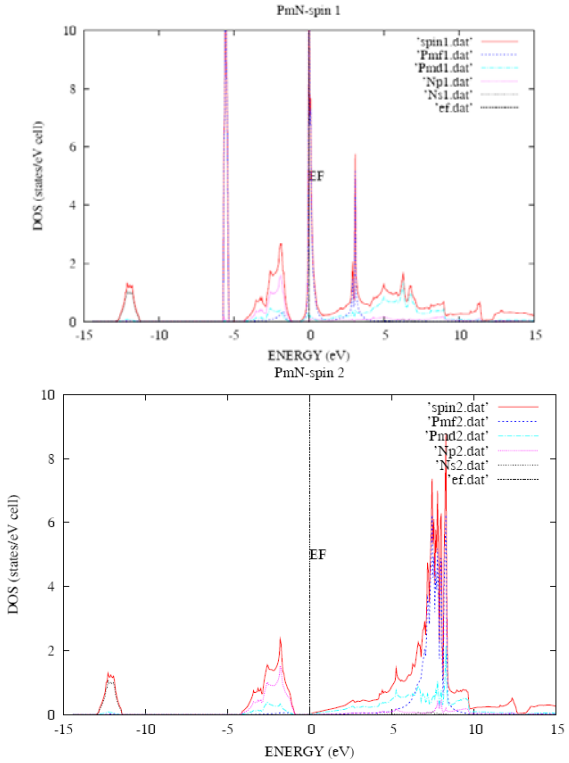

Fig. 5. Density of states of half metallic PmN

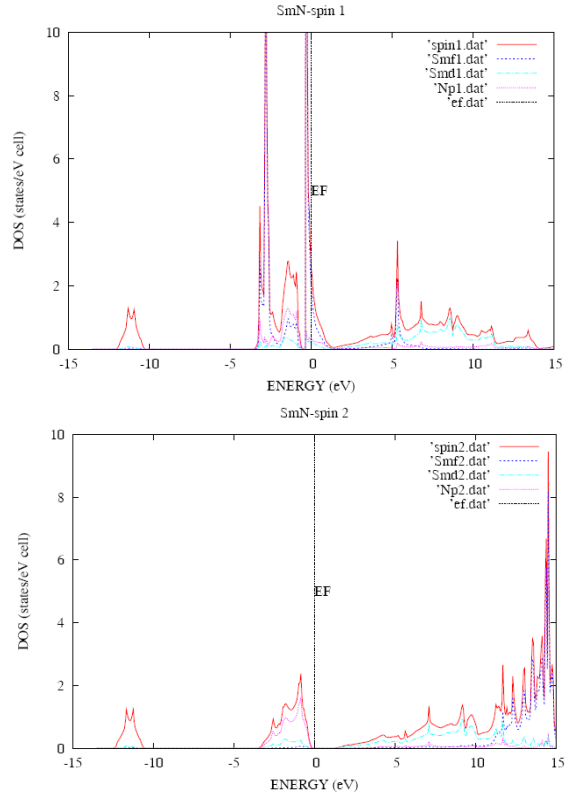

Fig. 6. Density of states of half metallic g SmN.

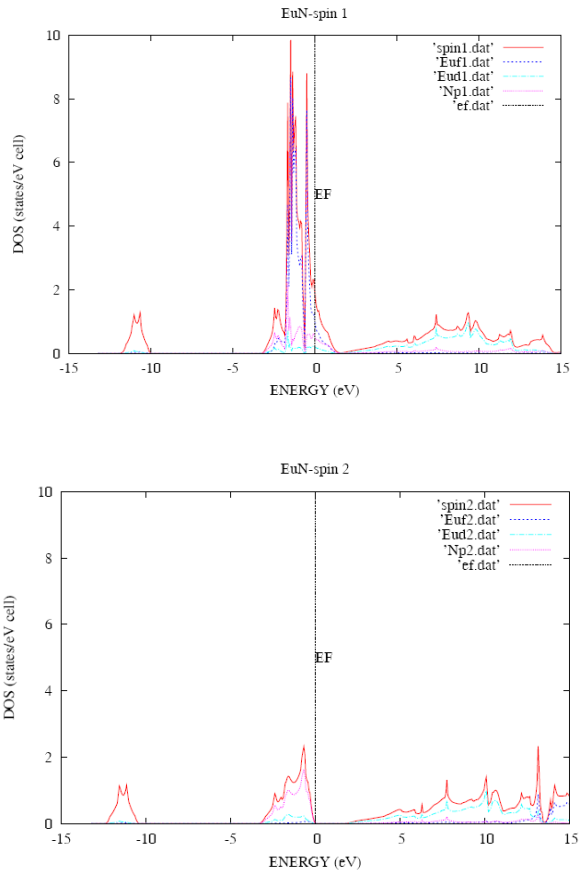

Fig.7. Density of states of half metallic EuN.

As a general feature, all RN compounds with light rare–earths have N–s states located at energies of ≅ 12 eV. These are very little hybridized with R(4f+5d) states. The center of gravity of the these bands are only little shifted to lower energies when increasing the atomic number of rare–earth.

The Ni–2p states are strongly hybridized with R4f and R5d states. The degree of hybridization increases from PrN to EuN. The center of gravity of N-2p bands are sifted to lower energies by ≅ 0.16 eV when increasing by one the electron occupations of 4f bands. The N–2p_x, N–2p_y and N–2p_z orbitals are non degenerate. The N–2p_y band, in LaN, cross the Fermi level in the X symmetry point–Fig.8. In case of EuN the N–2p_x and N–2p_z bands cross the Fermi level in the X and Γ symmetry points, while N–2p_y cross E_F in the Γ–point only –Fig. 9. A similar behaviour was shown for GdN. These data contradict the previous report [10] where N–2$p_{x,y}$ bands were showed to be degenerate.

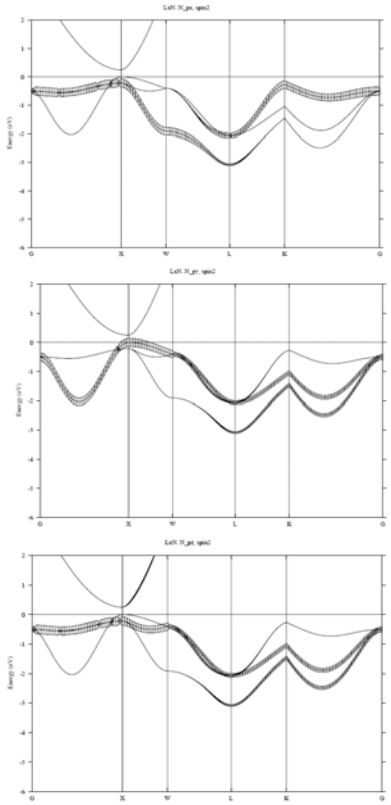

Fig. 8. The band structure of N-2p in LaN

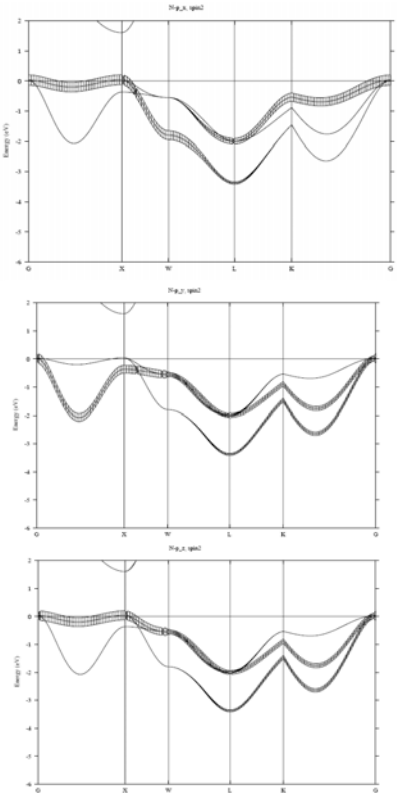

Fig. 9. The band structure of N-2p in EuN.

The LaN nitride is shown to have an energy gap of 0.22 eV both in spin majority and spin minority bands – Fig.10. Thus, LaN is semiconductor.

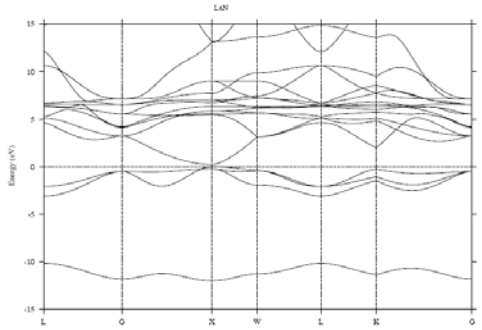

Fig.10. *The band structure of semiconducting LaN.*

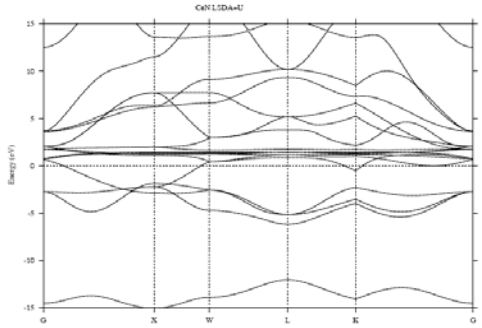

Fig. 11. The band strucure of metallic CeN.

The analysis of CeN band structure, shows a strong hybridization of Ce–4f and Ce–5d+6s states. There is also a relative weak hybridization with N2p states. The 4f states are situated in the conduction band, close to the Fermi level –Fig.11. The 4f states are occupied by 0.315 electrons both in spin majority and spin minority bands. The dominant character at the Fermi level is 4f mixed also with 5d+6s bands showing that CeN is a mainly a 4f band system. The cerium nitride has a metallic behaviour.

The RN compounds with R = Pr,Nd,Pm,Sm,Eu have a close related behaviour. All the compounds are half metallic. The gap in the minority spin bands increase from Pr to Eu. In the majority spin bands at least one of R4f occupied band is situated close to the Fermi level and hybridize with the R(5d+6s) and N–2p bands–Fig. 3–7.

In PrN there are occupied spin majority bands, at –0.3 eV and near the Fermi level. The empty bands are situated at energies between 4.43 and 5.70 eV. In NdN, there are filled bands at -2.60; -2.35; -0.24 eV two empty bands close to the Fermi level, at 0.24 and 0.5 eV as well as two situated at ≅5.8 eV. The filled 4f bands in PmN are located at -5.6 eV and at -0.03 eV and empty bands between 0.1 and 1.74 eV. In SmN the occupied 4f bands are situated between -3.16 and -0.32 eV and empty 4f bands at 0.50 and 5.4 eV. The 4f bands in EuN are located at-1.7 and -0.5 eV and the empty band close to Fermi level.

In minority spin bands there is a mixture of R4f with

R5d+6s and N2p bands. The conduction bands are shifted to higher energies as the R4f bands are gradually filled. As example, in PrN the empty 4f states are located between 7.34 and 9.55 eV, while in EuN, at energies above 13 eV.

The band gaps in the minority spin bands increase from 0.47 eV in PrN to 1.63 In EuN. The band gaps are located in symmetry points X – Figs. 12 and 13.

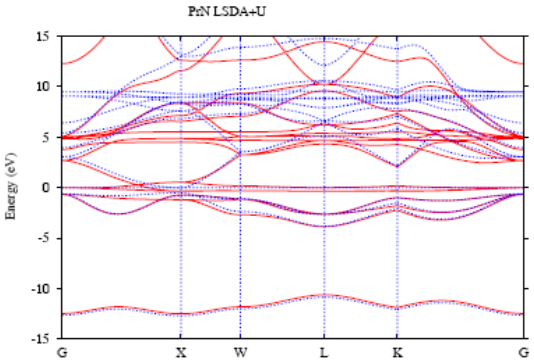

Fig.12. The band structure of half metallic PrN.

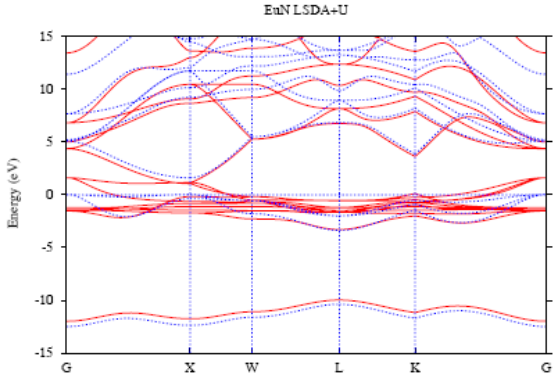

Fig. 13. The band structure of half metallic EuN.

3. Magnetic properties

The magnetic properties of light–earth nitrides, determined from band structure calculations are listed in Table 2. The R4f spin moments were determined both by using LSDA and LSDA+U methods. The LSDA+U method describes better the magnetic properties of the half–metallic systems.

Table 2. Electronic and Magnetic Properties of Light Rare-Earths Nitrides

Nitride	Energy gap (eV)		Type of conduction	$M_s(4f)(\mu_B)$		$M(5d)(\mu_B)$	$M_N(2p)(\mu_B)$	$M_s(total)(\mu_B)$	$M_l(4f)(\mu_B)$
	majority spin band	minority spin band		LSDA	LSDA+U	LSDA+U	LSDA+U	LSDA+U	
LaN	0.22	0.22	semiconductor	0	0	0	0	0	0
CeN	0	0	metallic	0	0	0	0	0	0
PrN	0	0.47	half metallic	1.80	2.00	0.15	- 0.16	1.99	- 5.0
NdN	0	0.83	half metallic	3.00	3.01	0.06	- 0.08	2.99	- 6.0
PmN	0	0.80	half metallic	3.90	3.99	0.12	- 0.16	3.95	- 6.0
SmN	0	1.04	half metallic	5.10	5.30	0.05	- 0.36	4.99	- 5.0
EuN	0	1.63	half metallic	6.00	6.48	0.03	- 0.51	6.00	- 3.0

$M_s(4f)$ – R4f spin magnetic moment; M(5d) – R5d band polarization; $M_N(2p)$ – N(2p) band polarization;
$M_s(total)$ – total spin magnetic moment; $M_l(4f)$ – orbital magnetic moment

The magnetic susceptibilities, χ, of LaN and CeN were experimentally investigated [17-20]. Generally, at low temperatures (T<20-30 K), the χ values are strongly affected by the presence of magnetic impurities. Thus, the comparison of the computed values from band structures with those experimentally ones, obtained at low temperatures, is questionable. According to Didchenko and Gortsema [20], the magnetic susceptibilities of LaN is small and temperature independent. Schumacher and Wallace [17], reported a value of $4.6 \cdot 10^{5}$ emu/mol at 200 K. The higher χ values, determined at low temperatures, were ascribed to magnetic impurities. We obtained a value of $\cong 2 \cdot 10^{-5}$ emu/mol.

The magnetic susceptibilities of CeN, at 78 K, are between 3.85×10^{-4} and 6.1×10^{-4} emu/mol [18,20]. Schumacher and Wallece [17] reported a value of 5.5×10^{-4} emu/mol at 50 K. These data are in good agreement with our determined value of 5.4×10^{-4} emu/mol. We note that a magnetic susceptibility of 2.2×10^{-4} emu/mol was previously computed [24].

Schumacher and Wallace [17] analysed the temperature dependence of the magnetic susceptibilities up to 300K. A nonlinear temperature dependence was reported. The studies were then extended up to 1300 K[18]. Above 300 K the susceptibilities increase, having a maximum around 900 K. A temperature dependent effective moment was suggested. At T>1200 K an effective cerium moment close to that of Ce^{3+} ions was obtained. A similar behaviour was reported latter [19]. Since cerium is very susceptible to oxidation, the data obtained above 300 K, can be influenced by this effect. Thus, reliable data are expected to be obtained only by measurements below room temperature. Anomalies in temperature dependences of the lattice parameter [18] and resistivities [20] above room temperature were observed. An electronic configuration of cerium in CeN at 5K, of +3.43 and +3.32 at 500 K was suggested [21,22]. Analysing by XANES, the $Ce_xGd_{1-x}N$ system [23], showed that for $x \geq 0.7$ cerium has $[X_c]4f^o$ configuration. Thus, there is not an agreement between valence state of cerium, given by various authors. Consequently, we compared our

data only with those obtained at 90 K $\leq$ T $\leq$ 300 K, where no oxidation effect are present [17]. According to our

data the electronic configuration of cerium, at low temperatures is +3.68, more close to the +4 value than previous studies. Since cerium is in mixed valence state there are contributions to the magnetic susceptibilities of Van-Vleck χ_v and Curie-types. Consequently, we analyzed the temperature dependence of the magnetic susceptibilities [17] considering both terms $\chi=\chi_v + C\cdot T^{-1}$, where C is the Curie constant. We obtained an effective magnetic moment per cerium atoms of 1.41 μ_B, corresponding to an electronic configuration Ce^{+365} close to our theoretical result. A Van–Vleck contribution $\chi_v \cong 2\cdot 10^{-3}$ emu/mol was also determined. The present data agree with that suggested by Delin et al [24] which reported that a more appropriate picture of CeN is a 4f–band type nitride. The high specific heat coefficient, γ, of CeN, as compared to LaN, can be correlated with the presence of high amount of 4f states at the Fermi level as showed in Fig.2.

The RN compounds with R = Pr,Nd,Pm,Sm,Eu are magnetically ordered at low temperatures. The determined magnetic moments from band structure calculations are listed in Table 2. The R(5d) bands are polarized. Their magnetic contributions are paralelly oriented to 4f spin moment.

As a result of the hybridization of N2p and R4f+5d states, the N2p states are also polarized. The magnetic contributions of N2p states increase generally from PrN to EuN – Table 2. This behaviour is connected with a higher degree of hybridization, as the atomic number of rare-earth increases. The resultant magnetic spin moments have integer values in agreement with a half–metallic behaviour suggested from band structure analysis.

Table 3.Magnetic Properties of Light Rare-Earths Nitrides.

Nitride	M_s (μ_B/f.u.)	T_C (K)	θ (K)	M_{eff} (μ_B)	Magnetic behaviour	Reference
LaN					paramagnet	17
CeN					paramagnet	18
PrN		< 4K	0	3.66	ferromagnet	20,25
NdN	3.1	32	24		ferromagnet	26
NdN		35	15	3.70	ferromagnet	17
SmN	0.4	41				27
SmN	0.07[a)]				ferromagnet or antiferromagnet	28
SmN		18[b)]				29
SmN		15			ferromagnet or antiferromagnet	26,30
SmN		13				17
EuN			-200			26

a) neutron diffraction data; b)specific heat data

The magnetic properties of light–earth nitrides, experimentally determined are listed in Table 3. For NdN a saturation moment of 3.1 μ_B/f.u. was reported [26]. The above value agrees well with a magnetic moment of 3.01 μ_B as determined from band structure calculations, considering also the orbital contribution.

The magnetic properties of SmN are more disputed since of a very small magnetic moment determined from magnetic measurements (0.4μ_B) [27] or neutron diffraction studies (0.07 μ_B) [28]. Up to now it is difficult to decide if the above nitride is ferromagnetic or antiferromagnetically ordered. The present analysis show that there is a total spin contribution of 4.99 μ_B and an orbital contribution of –5.00 μ_B. These near cancel. Generally, it is very difficult to obtain stoichiometric compositions. Small variations in the 1:1 stoichiometry can influence the result of measurements. For SmN, at low temperatures, there is a peak in temperature dependence of magnetic susceptibilities at 15–18K [17,20]. Also the specific heat data show a λ–type anomaly at 18.2 K [29] From the temperature dependence of the magnetic susceptibilities a value of $T_C \cong 40$ K can also be obtained if we do not consider that the peak at 15 K has an important significance. Studies are in the progress in order to obtain more information on the magnetic behaviour of this compound.

The present data show that RN (R = Pr, to Eu) nitrides are half metallic, CeN shows a metallic behaviour and LaN is a semiconductor.

Half–metallicity occurs when the exchange splitting is large enough to form a gap in one spin channel and at the same time the other spin channel should be partially occupied. So, the gap formation is determined by the interplay between the exchange splitting and the details of the electronic structure. Thus, in case of CeN the electronic structure, resulting from mixed cerium valence state is mainly the reason in determining the metallic behaviour. The RN (R = Pr to Eu), in which the rare earth has +3 valence state are half metallic. By increasing the occupation of 4f states, the exchange splittings increase enlarging gradually the band gaps.

4. Conclusions

The band structure calculations show that LaN is a semiconductor and CeN has a metallic behaviour. The RN (R = Pr,Nd,Pm,Sm,Eu) nitrides are half–metallic. In these systems the exchange splitting is large enough to form a gap in the minority band while the majority spin channel is metallic. The band gaps increase when going from PrN to EuN, from 0.47 eV to 1.63 eV.

The N2p bands are strongly hybridized with R4f+5d bands. As a result of charge transfer, these bands are polarized. Their magnetic moments are antiparallely oriented to R4f spin moments and increase when atomic number of rare-earth is higher. A small polarization is also induced in R5d bands, paralelly oriented to spin moments. The contributions of N–$2p_x$, N–$2p_y$, N–$2p_z$ orbitals were analyzed and these orbitals are found to be non–degenerate.

The computed spin–moments are integer numbers and confirm the half–metallicity of RN nitrides. A comparative analysis of the experimental data with computed magnetizations was also made. A rather good agreement between the two sets of data is shown.

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