New magnetic semiconducting compounds: the rare earth oxynitrides $\text{Eu}_{2+1-x}\text{Ln}_{3+x}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$)

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NEW MAGNETIC SEMICONDUCTING COMPOUNDS : THE RARE EARTH OXYNITRIDES $\text{Eu}_{1-x}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$
($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$)

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Résumé.— Les oxynitrides de terres rares $\text{Eu}_{1-x}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) de structure type NaCl ont été préparés. Les domaines d'existence des phases riches en oxygène sont les suivants : $0 \leq x \leq 0,26$ à 1250°C avec Nd^{3+} , $0 \leq x \leq 0,30$ à 1200°C avec Eu^{3+} et $0 \leq x \leq 0,26$ à 1850°C avec Gd^{3+} . A basse température les moments magnétiques de Nd^{3+} et de Eu^{2+} sont antiparallèles dans les composés $\text{Eu}_{1-x}\text{Nd}_x^{3+}\text{O}_{1-x}\text{N}_x$. Une transition semiconducteur métal apparaît pour $x \approx 0,22$; elle résulte du croisement des niveaux $\text{Eu}^{2+}: 4f^7$ avec la bande de conduction $5d_{2g}-6s$. Les mesures magnétiques montrent clairement la présence de cations $\text{Eu}^{3+}: 4f^6$ dans les phases métalliques. Pour $x < 0,22$, la température de Curie T_C croît et l'énergie d'activation ΔE diminue lorsque x augmente. Les oxynitrides riches en oxygène $\text{Eu}_{1-x}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Eu}^{3+}, \text{Gd}^{3+}$) sont semiconducteurs ferromagnétiques et T_C augmente et ΔE diminue lorsque x croît. A 300K , deux raies caractéristiques de Eu^{2+} et Eu^{3+} apparaissent dans les spectres de résonance Mössbauer pour les oxynitrides $\text{EuO}_{1-x}\text{N}_x$. Les propriétés électriques et magnétiques des oxynitrides sont discutées à l'aide d'un diagramme d'énergie qualitatif déduit de celui des chalcogénures de terres rares. Ces propriétés sont comparées à celles de EuO étudié sous pression.

Abstract.— The R.E. oxynitrides $\text{Eu}_{1-x}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) with the NaCl type structure have been prepared. The homogeneity range of the oxygen rich system is the following : $0 \leq x \leq 0.26$ at 1250°C with Nd^{3+} , $0 \leq x \leq 0.30$ at 1200°C with Eu^{3+} and $0 \leq x \leq 0.26$ at 1850°C with Gd^{3+} . Lattice parameters, magnetic and electrical measurements have been carried out both as a function of x and temperature. The oxynitrides $\text{Eu}_{1-x}\text{Nd}_x^{3+}\text{O}_{1-x}\text{N}_x$ have a ferrimagnetic behaviour with antiparallel orientation of the neodymium and europium moments. A semiconducting metal transition appears for $x \approx 0.22$; it is explained by the crossing of the $\text{Eu}^{2+}: 4f^7$ levels and the $5d_{2g}-6s$ conduction band since the magnetic measurements show clearly the presence of Eu^{3+} ions for $x > 0.22$. In the semiconducting range ($x < 0.22$) the Curie temperature T_C increases and the activation energy ΔE decreases with increasing x . The oxygen-rich oxynitrides $\text{Eu}_{1-x}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Eu}^{3+}, \text{Gd}^{3+}$) are ferromagnetic semiconducting compounds for which T_C is greater than that of EuO ; ΔE decreases as x increases. The first Mössbauer resonance measurements in the $\text{Eu}^{2+}+\text{Eu}^{3+}\text{O}_{1-x}\text{N}_x$ system indicate two distinct Mössbauer lines for Eu^{2+} and Eu^{3+} at 300K . The electrical properties are discussed on the basis of a qualitative energy diagram deduced from those of the R.E. monochalcogenides. These properties are compared with those of EuO under pressure.

1. Introduction.— Europium oxide EuO is a ferromagnetic semiconductor ($T_C=69.5\text{K}$, $\Delta E \approx 11\text{eV}$) with two main absorption bands located around 2 and 5 eV and corresponding respectively to the transitions $4f^7 \rightarrow 4f^6 5d_{2g}$ and $4f^7 \rightarrow 4f^6 5d_{eg}$. This compound exhibits large magneto-optic effects and has a relatively low absorption in the visible and near infrared region /1-4/. For example, the specific Faraday rotation for EuO at $0.7\text{ }\mu$ is as large as $5 \times 10^5\text{ deg./cm}$ ($T=4.2\text{ K}$ and $H=20\text{ kOe}$). The use of EuO films as the storage medium for a low temperature beam ad-

dressable memory has been previously proposed by G.Y. Fan and J.H. Greiner /5/. The ferromagnetic Curie temperature of EuO has been raised by selective doping with trivalent rare-earths in order to create a magnetic film available at the convenient cryogenic temperature of liquid nitrogen /6,7/. However we must emphasize that the trivalent R.E. introduce donor levels in EuO somewhat below the bottom of the conduction band. For instance gadolinium with the configuration $4f^7 5d^1$ when occupied acts as a localized donor with concentration $< 10^{20}\text{ cm}^{-3}$. At higher

concentration an impurity band forms and the Fermi level moves into the conduction band /8/.

To prevent the filling of the conduction band of EuO by electrons coming from the substitution of a trivalent rare earth, we have replaced simultaneously oxygen by nitrogen and obtained the oxynitrides with the formula $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) /9,11/.

The present paper reports the experimental results and their discussion concerning the preparation, the lattice parameter and the magnetic and electrical properties of the $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ system rich in oxygen.

2. Experimental results.-2.1.- Preparation and lattice parameter.- The R.E. oxynitrides $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) have been obtained by direct reaction of EuO with LnN, and quenched from the temperature of preparation. The reactions have been performed under purified argon in open molybdenum crucibles. The homogeneity range of the oxygen rich system is the following : $0 \leq x \leq 0.26$ at 1250°C with Nd^{3+} ; $0 \leq x \leq 0.30$ at 1200°C with Eu^{3+} and $0 \leq x \leq 0.26$ at 1850°C with Gd^{3+} .

At temperatures greater than 1250°C the reactions are carried out with an excess of europium metal in sealed molybdenum tubes in order to prevent the dissociation of the compounds. With this method we have prepared the phases in the $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ system, at 1650°C , in the entire range of homogeneity.

X-ray powder measurements performed between 300 K and 4,2K show that all the oxynitrides prepared have the NaCl type structure. Although the substitution of oxygen by nitrogen tends to expand the unit cell (since for the anionic radius $r_{\text{N}^{3-}} > r_{\text{O}^{2-}}$) (figs 1-2), the lattice parameter decreases with rising x and even more rapidly as the size of the Ln^{3+} ion is smaller ($r_{\text{Gd}^{3+}} < r_{\text{Eu}^{3+}} < r_{\text{Nd}^{3+}}$).

2.2. Magnetic properties.- Magnetization and susceptibility measurements have been performed between 300 K and 4.2 K on powder

samples.

Fig. 1 Lattice parameters vs compositions x for the $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ system rich in oxygen ($\text{Ln}^{3+}=\text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$).

Fig. 2 Lattice parameters vs composition for $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$.

2.2.1. The $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ system.- At high temperatures the susceptibility follows a Curie-Weiss law (fig 3). In the range $0 \leq x \leq 0.20$ the experimental molar Curie constant $C_m(\text{exp.})$ is in good agreement with the calculated one $C_m(\text{calc.})$ assuming that all Eu ions are divalent. For $x > 0.20$, $C_m(\text{exp.})$ is smaller than $C_m(\text{calc.})$ (Table I).

The deviation from the Curie-Weiss law at low temperatures is due to the crystal field splitting of the $^4\text{I}_{9/2}$ ground state of the Nd^{3+} ion. With rising x, up to $x=0.26$,

Fig.3 Temperature dependence of reciprocal susceptibility for six samples in the $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ system.

the paramagnetic Curie temperature θ_p remains constant and positive, then decreases to become negative and goes through a minimum at about $x = 0.80$ (Table I).

The saturation magnetization M_{sat} was not generally reached up to 20 kOe applied magnetic field at 4.2 K, except for Eu-rich compounds ($x \leq 0.50$). M_{sat} is consistent with the Nd^{3+} magnetic moments antiparallel to those of Eu^{2+} . As x increases the ferrimagnetic ordering temperature T_c shows a maximum at about $x \approx 0.22$ (Table I Fig. 4).

2.2.2. The $\text{Eu}_{1-x}\text{O}_{1-x}\text{N}_x$ system.- Mössbauer spectra of three samples ($x = 0.05, x = 0.15, x \approx 0.25$) are shown in figure 5. They were recorded at room temperature using a source of 100mCi of ^{151}Sm as $\text{SmF}_3/12$. All three spectra consist of two distinct absorption lines, one near 0 mm/sec due to Eu^{3+} and the other near -12mm/sec due to Eu^{2+} . The measured intensity ratios of Eu^{3+} ;total europium are given in the table II, together with the values corrected for finite absorber thickness, assuming equal recoilless

TABLE I

x	θ_p (K)	T_c (K)	C_m		$\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$			M_{sat} (Hg/mole) at 4.2 K	
			exp.	calc.	Eu^{2+}	Eu^{3+}	Nd^{3+}	exp.	calc.
0	+ 77	69.5	7.88	7.90	1	0	0	6.77 ± 0.20	7
0.09	+ 73	80.5	7.41	7.34	0.91	"	0.09	6.29 ± 0.20	6.20
0.13	+ 75	82.5	7.11	7.08	0.87	"	0.13	5.74 ± 0.17	5.85
0.18	+ 74	85.5	6.52	6.77	0.82	"	0.18	5.15 ± 0.15	5.40
0.20	+ 74	87.5	6.36	6.64	0.76	0.04	0.02	4.70 ± 0.14	4.94
0.23	+ 74	87	6.08	6.46	0.71	0.06	0.23	4.45 ± 0.13	4.54
0.26	+ 74	85	5.73	6.26	0.66	0.08	0.26	4.18 ± 0.13	4.13
0.34	+ 72	80	4.96	5.77	0.54	0.12	0.34	3.16 ± 0.10	3.14
0.40	+ 70	76	4.43	5.38	0.44	0.16	0.40	2.55 ± 0.08	2.78
0.51	+ 44	66	3.97	4.69	0.36	0.13	0.51	1.6 ± 0.05	1.56
0.65	+ 26	-	3.03	3.83	0.22	0.13	0.65		
0.68	+ 13	-	2.74	3.64	0.17	0.15	0.68		
0.80	- 29	-	2.51	2.89	0.14	0.06	0.80		
0.90	- 25	-	2.15	2.26	0.07	0.03	0.90		
1	+ 20	25	1.61	1.64	0	0	1		

Table. 1 Magnetic data for $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$. C_m has been calculated assuming the presence of only Eu^{2+} and Nd^{3+} . The saturation magnetization has been calculated taking into account the Eu^{2+} , Eu^{3+} and Nd^{3+} ion concentration.

fractions for both ions. Within experimental error, the value of Eu^{3+} content agree with x .

Fig. 4. Magnetic ordering temperature T_C vs composition x for the $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ system rich in oxygen ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$).

This result means that the formula of the oxynitrides may be written: $\text{Eu}_{1-x}^{2+}\text{Eu}_x^{3+}\text{O}_{1-x}\text{N}_x$

Table. II Measured and corrected fraction of the total absorption in the Eu^{3+} line for three samples of $\text{Eu O}_{1-x}\text{N}_x$.

x	Eu^{3+} measured	Eu^{3+} (corrected)
0.05	0.11 (3)	0.08 (3)
0.15	.19 (3)	0.14 (3)
0.25	.30 (3)	0.24 (3)

There is a slight increase in isomer shift and line width of the Eu^{2+} resonance with increasing x , but as there is no complementary effect on the Eu^{3+} line, this must be attributed to an increase in the Eu^{2+} isomer shift of 0.2 mm/sec per nitrogen neighbor, rather to charge fluctuations. From the lack of line broadening attributable to electron hopping we deduce that any charge fluctuations are much slower than 10^{-8} sec. By comparison, the charge fluctuation

time found in Eu_3S_4 at 300 K was $3 \cdot 10^{-11}$ sec [13,14]. We, therefore, conclude that valence fluctuations are blocked in the europium oxynitrides.

Fig. 5 ^{151}Eu Mössbauer spectra for three samples of $\text{Eu O}_{1-x}\text{N}_x$ at room temperature.

Magnetization and susceptibility measurements indicate that the europium oxynitrides are ferromagnetic for $0 \leq x \leq 0.30$ (Table III - Fig. 6). Saturation magnetization measurements are consistent with the fact that only Eu^{2+} spins order ($J = 7/2$), while the Eu^{3+} ($J = 0$) sublattice bears no moment.

Table. III Paramagnetic and ferromagnetic Curie temperature θ and T_C and saturation magnetization M_{sat} per Eu^{2+} ion of $\text{Eu O}_{1-x}\text{N}_x$ ($0 \leq x \leq 0.30$).

x	θ (K)	T_C (K)	M_{sat} at 4.2 K (μ_B/Eu^{2+})
0	77	53.5	6.77 ± 0.23
0.05	87	69.5	6.55 ± 0.23
0.10	87	69.3	6.75 ± 0.20
0.15	88	69.9	7.07 ± 0.21
0.20	89	71.6	7.2 ± 0.22
0.25	91	74.4	7.16 ± 0.21
0.30	93	77	7.23 ± 0.22

The molar susceptibility χ_{tot} above T_C is interpretable as a simple sum of Van Vleck type (Eu^{3+}) and Curie-Weiss type (Eu^{2+}) con-

tributions :

$$\chi_{\text{tot}} = (1-x) \chi_{\text{C.W.}}(\text{Eu}^{2+}) + x \chi_{\text{V.V.}}(\text{Eu}^{3+})$$

The ferromagnetic Curie temperature T_C increases with x (Fig. 4).

Fig. 6 Thermal variation of the spontaneous magnetization for EuO and two samples of $\text{EuO}_{1-x}\text{N}_x$.

2.2.3. The $\text{Eu}_{1-x}\text{Gd}_x\text{O}_{1-x}\text{N}_x$ system.- The molar Curie constant is consistent with the presence only of Eu^{2+} and Gd^{3+} ions (Table IV) (9).

Table. IV Paramagnetic and ferromagnetic Curie temperature θ and T_C , molar Curie constant C_m and saturation magnetization M_{sat} per formula unit of $\text{Eu}_{1-x}\text{Gd}_x\text{O}_{1-x}\text{N}_x$ ($0 \leq x \leq 0.26$).

Table IV

x	θ (K)	T_C (K)	C_m calc.	C_m exp.	M_{sat} at 4.2 K (10^3 G/formula unit)
0	77	69.5	7.9	7.89	6.77 ± 0.20
0.06	128	126	7.9	7.55	6.30 ± 0.19
0.10	170	129	7.9	7.31	6.23 ± 0.19
0.12	118	116	7.9	7.8	6.55 ± 0.23
0.21	114	103	7.9	7.84	6.50 ± 0.20
0.26	100	100	7.9	7.72	6.75 ± 0.16

The saturation magnetization is in agreement with the fact that Eu^{2+} ($J=7/2$) and Gd^{3+} ($J=7/2$) magnetic moments are parallel below T_C (Table IV). A ferromagnetic ordering temperature T_C is found for $0 \leq x \leq 0.26$. The variation of T_C as a function of x shows a maximum at $x \approx 0.10$ (Fig. 4).

2.3. Temperature dependance of the lattice parameter between 300K and 4.2 K. X-ray measurements of the lattice parameter as a function of temperature for EuO and $\text{Eu}_{1-x}\text{Ln}_x\text{O}_{1-x}\text{N}_x$ system ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) reveal a volume reduction when these compounds are cooled through the Curie temperature (Fig. 7). These contraction can be assigned to the exchange striction and the relative volume variation is proportional to the spin-spin correlation function. As indicated previously no symmetry change of the lattice has been observed down to 4.2 K.

2.4. Electrical properties.- Four point probe d.c; resistivity measurements and Seebeck effect have been carried out on sintered samples having a compactness of 80%. The oxynitrides being hygroscopic, the handling of the samples has been performed in a dry box under purified argon.

2.4.1. Resistivity measurements.- Resistivity measurements have been performed between 800 K and 4.2 K.

a) The $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ system ($0 < x < 1$)

A semiconducting behavior is observed at high temperatures for $x < 0.22$. The activation energy ΔE deduced from the high temperature range, decreases almost linearly with rising x and vanishes at about $x \approx 0.22$ (Figs 8,9). At low temperatures below T_C a semiconductor-metal transition occurs as for $\text{EuO}_{1-\delta}$ (Fig. 10) /15-17/.

The compounds are metallic for $x \geq 0.22$ (Fig. 11).

b) -The $\text{Eu}_{1-x}\text{Ln}_x\text{O}_{1-x}\text{N}_x$ system ($\text{Ln}^{3+} = \text{Eu}^{3+}, \text{Gd}^{3+}$)

The phases studied in these two systems have a semiconducting behavior at high temperatures (Figs 12-13) and show a semiconductor-metal transition below the ferromagnetic Curie temperature T_C as for example

$\text{EuO}_{1-\delta}$ and $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ (Fig. 14).

Fig. 7 Thermal variation of the lattice parameter between 300 and 4.2 K for : a) EuO b) three samples of $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$, c) $\text{EuO}_{1-x}\text{N}_x$ ($x = 0.30$), d) $\text{Eu}_{1-x}\text{Gd}_x\text{O}_{1-x}\text{N}_x$ ($x = 0.10$).

In all cases the activation energy ΔE deduced from the high temperature range decreases as x increases (Fig. 9).

2.4.2. Seebeck effect.— Seebeck effect temperature dependence has been studied between 77 K and 380 K only for the samples having the lowest resistivity in the systems $\text{Eu}_{1-x}^{2+}\text{Eu}_x^{3+}\text{O}_{1-x}\text{N}_x$ and $\text{Eu}_{1-x}^{2+}\text{Nd}_x^{3+}\text{O}_{1-x}\text{N}_x$

(Figs. 15, 16).

The negative Seebeck coefficient α observed, for all the samples studied, indicates that electrical conductivity is dominated by the electron contribution.

3. Discussion and conclusions.— To interpret the electrical and magnetic properties of the oxynitrides $\text{Eu}_{1-x}\text{Ln}_x^{2+3+}\text{O}_{1-x}\text{N}_x$ rich in

Fig. 8 Conductivity as a function of temperature between 77 and 800 K for $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ ($x < 0.22$)

Fig. 9 Variation of the activation energy ΔE vs x for the $\text{Eu}_{1-x}\text{Ln}_x\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$) system

oxygen we propose a qualitative energy diagram for these compounds. The magnetic, electrical and crystallographic properties of the semiconducting oxynitrides are very

similar to those of EuO . The aim is to know the relative positions of the $\text{Eu}^{2+}4f^7$ and $\text{Ln}^{3+}4f^n$ localized levels with respect

Fig. 10 Resistance vs temperature between 4.2 K and 300 K for $x = 0.10$ and $x = 0.20$ in the $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ system.

Fig. 11 Resistivity vs temperature for $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$ ($x = 0.24$).

Fig. 12 Conductivity as a function of temperature between 300 and 800 K for EuO and five samples of $\text{Eu}_{1-x}\text{N}_x$.

Fig. 13 Conductivity as a function of temperature between 300 and 800 K for EuO and five samples of $\text{Eu}_{1-x}\text{Gd}_x\text{O}_{1-x}\text{N}_x$.

Fig. 14 Resistance vs temperature between 4.2 and 300 K for $\text{EuO}_{0.70}\text{N}_{0.30}$

to the empty conduction band and the valence band. An energy level scheme can be deduced from those of the europium oxides EuO and Eu_2O_3 , the latter comprises both the divalent and trivalent states of europium ($\text{Eu}^{2+}:4f^7$ and $\text{Eu}^{3+}:4f^6$) (Fig. 17), /18.19/.

Fig. 15 Seebeck effect temperature dependence between 77 and 380 K for two samples of $\text{Eu}_{1-x}\text{N}_x$.

A qualitative energy level scheme of the stoichiometric semiconducting oxynitrides is given in Fig. 18. The valence band which derives from the anionic p levels is separated by an energy gap from the empty $5d_{2g}$ - $6s$ conduction band.

Fig. 16 Seebeck effect temperature dependence between 77 and 380 K for four samples of $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$.

Fig. 17 Energy level diagram of EuO and Eu_3O_4 , ref /16/.

Fig. 18 Qualitative energy level diagram of the semiconducting oxynitrides $\text{Eu}_{1-x}\text{Ln}_x\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$).

With increasing x , we can expect that the top of the valence band moves up due to the fact that nitrogen has a smaller nuclear charge than oxygen.

A theoretical energy level diagram based on an ionic model as well as experimental data indicate that in EuO and Eu_3O_4 the localized divalent $\text{Eu}^{2+}:4f^7$ states are the highest occupied valence states and are located between the bottom of the conduction band and the top of the anionic valence band. As in the case of Eu_3O_4 , the $\text{Eu}^{3+}:4f^6$ level in $\text{Eu}_{1-x}^{2+}\text{Eu}_{1-x}^{3+}\text{O}_{1-x}\text{N}_x$ would be separated from the $\text{Eu}^{2+}:4f^7$ level by a large electron-electron electrostatic energy (≈ 5.7 eV in Eu_3O_4), which would place it below the top of the valence band /16/. It would be likewise for the position of the $\text{Nd}^{3+}:4f^3$ and $\text{Gd}^{3+}:4f^7$ levels in the other oxynitrides.

As found for the R.E. monochalcogenides the 5d states in the oxynitrides split into 5 dt_{2g} and 5 de_g levels due to the action of the crystal field. The crystal symmetry is such that the 5 dt_{2g} level is lower in energy than the 5 de_g level. Due to the reduced spatial extent of the 5d charge density distribution, overlap of the 5d wave functions is small, resulting in rather narrow 5d subbands.

To understand the variation with x of the intrinsic activation energy of the solid solutions $(\text{EuO})_{1-x}(\text{LnN})_x$, we refer to the band structure proposed for the gadolinium nitride GdN . A recent band calculation using the APW method indicates that GdN is semiconductor with a small gap between the 5d-6s conduction band and the 2p valence band (< 1 eV) /20/. Electrical measurements suggest also that GdN may be a semiconductor but it does not seem, however, that a precise value of the energy gap has been determined /21/. On the contrary, a rough energy level diagram established from a simple ionic tight binding model indicates that between the 5d and 2p bands there is hardly any energy gap and an overlap at certain points in the Brillouin zone can be expected; furthermore, according to this model the $\text{Gd}^{3+}:4f^7$ level is located at about 7 eV below the 5d band and appreciably below the 2p valence band /19/.

Whatever may be the band structure proposed for the RE nitrides it seems well

established that the energy gap between the 5d and the 2p bands is smaller than that found in EuO (>2eV). Consequently, we can expect, with increasing x, a decrease of the gap between the 5d-6s conduction band and the 2p valence band in the solid solutions $(\text{EuO})_{1-x}(\text{LnN})_x$. This effect is enhanced by the shrinking of the lattice parameter which increases both the 5d ligand field splitting $\Delta 5d$ and the width of the 5d band. All these effects explain the decrease of the intrinsic gap ΔE between the $\text{Eu}^{2+}:4f^7$ levels and the 5d-6s conduction band, as x increases in the oxynitrides.

In order to determine the maximum contribution to $-\frac{d\Delta E}{dx}$ from a smaller lattice parameter we have plotted the variation of ΔE as a function of the volume of the unit cell for both EuO under pressure and the $\text{Eu}_{1-x}^{2+}\text{Eu}_x^{3+}\text{O}_{1-x}\text{N}_x$ oxynitrides (Fig. 19). For EuO under pressure the shrinking of the distances $\text{Eu}^{2+}-\text{Eu}^{2+}$ involves an increase of the 5d ligand field splitting $\Delta 5d$ and a broadening of the $5d_{2g}$ conduction band which both tend to decrease ΔE /22,23/. It is worthwhile to point out that the decrease with x, of the lattice parameter plays a minor role in the variation of ΔE in the oxynitrides.

The semiconductor-metal transition observed with rising x in the $\text{Eu}_{1-x}^{2+}\text{Nd}_x^{3+}\text{O}_{1-x}\text{N}_x$ system could be explained by crossing of the $\text{Eu}^{2+}:4f^7$ levels with the conduction band, involving a change from the divalent state to the trivalent state of europium. Comparing the experimental molar susceptibility to the calculated one by the expression $\chi_m = (1 - x - y) \chi_{\text{Eu}^{2+}} + y \chi_{\text{Eu}^{3+}} + x \chi_{\text{Nd}^{3+}}$ we have determined the Eu^{3+} ion content (Table I). The sharp shrinking of the unit cell is closely related to the Eu^{3+} ion content ($r_{\text{Eu}^{3+}} < r_{\text{Eu}^{2+}}$) (Fig. 2). The fact that the semiconductor-metal transition appears simultaneously with the change in the valence of europium, confirms that the first occupied states just below the conduction band are the $\text{Eu}^{2+}:4f^7$ levels in the stoichiometric semiconducting phases.

The variation of the resistivity at low temperatures in the oxynitrides appears to be similar to that found in $\text{EuO}_{1-\delta}$, especially in the case of $\text{Eu}_{1-x}^{2+}\text{Nd}_x^{3+}\text{O}_{1-x}\text{N}_x$ and $\text{Eu}_{1-x}\text{O}_{1-x}\text{N}_x$ oxynitrides. This observation would suggest that our samples are oxygen-deficient. The semiconductor-metal transition observed in the oxynitrides, below the Curie temperature, could be interpreted as that observed in $\text{EuO}_{1-\delta}$ /15,16,17,24,25,26,27/.

The saturation magnetization measurements indicate that: 1) the magnetic moments order ferromagnetically in $\text{EuO}_{1-x}\text{N}_x$ and $\text{Eu}_{1-x}\text{Gd}_x\text{O}_{1-x}\text{N}_x$ 2) the magnetic moments of Nd^{3+} are antiparallel to those of Eu^{2+} in $\text{Eu}_{1-x}\text{Nd}_x\text{O}_{1-x}\text{N}_x$. From the expression given the magnetic moment of a R.E. cation $\vec{\mu} = [g_j / (g_j - 1)] \mu_B \vec{S}$ we deduce that the spin-spin interactions are ferromagnetic in all the oxynitrides since $g_j = 2$ for Eu^{2+} and Gd^{3+} and $g_j = 8/11$ for Nd^{3+} .

The magnetic superexchange mechanisms proposed by J. B. Goodenough and T. Kasuya for the R.E. chalcogenides are valid for the oxynitrides /28,29/. The exchange interaction between the 12 nearest neighbors is ferromagnetic and involves a virtual transfer of a 4f electron to the empty $5d_{2g}$ excited state of a neighbor cation.

The ferromagnetic interactions become stronger as the transfer integral, which is proportional to the orbital overlap, is higher and the excitation energy ($4f^7 \rightarrow 5d_{2g}$) is weaker. Thus the ferromagnetic interaction $\text{Ln}^{3+} - \text{Ln}^{3+}$ is negligible due to the large excitation energy required (Figs 17,18).

The 180° superexchange interaction between the 6 next nearest neighbors is antiferromagnetic and involves an overlap of the antibonding $5d_{eg}$ orbital of the cations with the p orbitals of the anion. Since the $5d_{eg}$ charge distribution extends in the direction of the anions. The antiferromagnetic interaction increases with the covalency.

Fig. 19 Variation of the activation energy ΔE as a function of the ratio V/V_0 for EuO under pressure and for $\text{EuO}_{1-x}\text{N}_x$ (V_0 and V being respectively the volume of the unit cell of EuO ($P=1 \text{ atm.}; 300\text{K}$) and of $\text{EuO}_{1-x}\text{N}_x$).

In all the oxynitrides studied, rich in oxygen, the Curie temperature is always greater than that of EuO (Fig. 4). The evolution of T_c with rising x is the consequence of the competition between several parameters: 1) the decrease of both the cation-cation distances and the excitation energy (energy separation $4f^7 - 5d_{2g}$) enhance the ferromagnetic interaction. 2) the increase of both the number of Ln-Ln^{3+} magnetic interactions and the covalency with nitrogen which favor the antiferromagnetic exchange coupling, tend to diminish T_c .

We have compared the variation of the Curie temperature of EuO under pressure with those of $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ ($\text{Ln}^{3+} = \text{Nd}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}$), as a function of the unit cell volume (Fig. 20) /30/. We conclude that the diminution of the cation-cation distances plays a minor role in the rise of T_c in comparison to that of the magnetic cations Nd^{3+} and Gd^{3+} ; Eu^{3+} behaves as a diamagnetic-like cation.

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Fig. 20 Variation of the magnetic ordering temperature as a function of the ratio V/V_0 for EuO under pressure and for the $\text{Eu}_{1-x}^{2+}\text{Ln}_x^{3+}\text{O}_{1-x}\text{N}_x$ oxynitrides (V_0 and V have the same meaning that in figure 19).

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