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Direct observation of Eu atoms in AlN lattice and the first-principles simulations

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Abstract: Rare-earth metal (Eu) doped aluminum nitride has potential application as luminescence materials due to its unusual mechanical and physical properties, as well as high chemical stability. Here we investigate the energetics, local structure and optical and electronic properties by means of a combination of experimental observations (XDR, SEM, HR-TEM and XANES) and first-principles simulations. Present study has revealed that Eu ions are likely to be co-doped with O in the form of Eu-O pairs. Eu ions or Eu-O pairs favor participation at the surfaces of the AlN crystallites. Our analyses show dependences of the Eu valence and electronic/optical properties on the local chemical composition and structure. The obtained information helps us to realize tuning of the optical properties of the luminescent materials via composition and site occupation modification.

Keywords: AlN, Eu site, phosphor, first-principle calculation.

I. Introduction

Light-emitting-diodes (LEDs) are replacing conventional lighting sources due to their multiple advantages, such as high light conversion ratios, long lifetime, low energy consumption, high reliability, and environmental-friendliness [1,2]. (Oxy)nitrides phosphors have a strong absorption in the UV-blue band, adjustable emission color and good thermal quenching and therefore, at present are developed increasingly [3,4]. Among them, aluminum nitride (AlN) has been of particular interest due to its high electrical insulation (energy gap of

6.2 eV), high thermal conductivity, low thermal expansion coefficients as well as high chemical stability [5,6], and is considered as a potential host for photoluminescence and electroluminescence devices and for LED and FED devices [7].

There have been experimental efforts to understand the luminescent properties of AlN based phosphors [8-14]. It was demonstrated that Eu, Si co-doped AlN phosphor shows a strong blue luminescence by UV or electron excitation [13,15]. This co-doping which remains the chemical valence balance, promotes Eu incorporation into the AlN lattice and the obtained phosphor remains the wurtzite structure. In our previous study, we prepared Eu solely doped AlN samples by different synthesis methods (solid-state reaction (SSR), carbothermal reduction (CR) and gas-reduction nitridation (GRN)). The experimental observations showed that the luminescence properties are highly dependent on the oxygen content in the final samples [16-18]. Structural analysis showed that the AlN: Eu phosphor with a low oxygen content is dominated by the AlN wurtzite structure via the CR and GRN methods. In general, the large radius mismatches between the Al^{3+} (0.39 Å, 4CN) and Eu^{2+} (1.17 Å, 6CN) or Eu^{3+} (0.95 Å, 6CN) ions [19] indicate high energy costs for the replacements of Al^{3+} by Eu ions in the doped samples. Up to now, knowledge about these materials, e.g. the site occupations of Eu ions in the wurtzite AlN lattice is still limited. In this aspect, theoretical methods, especially parameters-free first-principles approaches are helpful. First-principles calculations have been applied successfully to analyze the electronic structure of aluminum nitride [20] and to investigate the structural models of aluminum oxynitride [21]. Pentaleri and co-workers studied substitutional impurities in zinc-blende aluminum nitride [22]. Recently *ab initio* density functional theory was applied successfully in study of the doping of Eu in scintillation and

luminescent materials [23,25]. In the current paper, we prepared the high-pure AlN: Eu phosphors by gas-reduction-nitridation (GRN) method and investigated the preferred sites of Eu ions in the AlN samples by a combination of multiple experimental techniques (SEM, EXAFS/XANES, STEM) and first-principles calculations. The *ab initio* simulations were performed for Eu doped in (wurtzite) AlN bulk and at its (110) and (0001) surfaces. The influence of oxygen on the Eu doping was addressed, considering the fact that oxygen is always unavoidable in the sample preparations. The obtained information here is helpful/useful to understand the mechanism of the luminescence properties, to obtain inspiration for AlN based phosphors doped with other large (rare-earth) ions and further to search new luminescence materials of desirable properties.

II. Experimental Sections and First-Principle Simulations

2.1. Synthesis. Phosphors with a chemical composition of AlN: 0.5mol% Eu were prepared by the gas-reduction-nitridation method. The powder mixture of γ-Al$_2$O$_3$ and Eu$_2$O$_3$ were fired in a horizontal alumina tube furnace at 1400 ^{o}C for 3 h under a flowing gas mixture of 1 l/min NH$_3$ and 15 ml/min CH$_4$. The as-prepared products were post-annealed at 1900 ^{o}C for 2 h in a carbon furnace under flowing nitrogen gas, to further improve its crystallinity.

2.2 Characterization. The phase was analyzed by an X-ray diffractometer (Model PW1700, Philips Research Laboratories, Eindhoven, the Netherlands) using Cu K$_\alpha$ radiation. Powder morphologies were observed by scanning electron microscopy (SEM) (Model JSM-6390LA, JEOL, Tokyo, Japan). The nitrogen/oxygen content was determined using a nitrogen/oxygen Analyzer (ModelTC-436, LECO, Tokyo, Japan. Elemental analysis was carried out using

Induced Couple Plasma Optical Emission Spectroscopy (ICP-OES, PerkinElmer Optima 5300, USA). Cathodoluminescence spectra (CL) were recorded in the Scanning Electron Microscope (SEM) equipped with a CL accessory (Sirion200, FEI, USA). The X-ray absorption near edge structure (XANES) of Eu L_3-edge was measured at the beamline of BL14W1 at Shanghai Synchrotron Radiation Facility with an electron beam energy of 3.5 GeV. Z-contrast Scanning transmission electron microscopy (STEM) was performed using high angle annular-dark field scanning electron microscopy (HAADF-STEM, JEM-ARM 200F). HAADF simulations were performed using Dr. Probe software.

2.3 Super cell method for first-principle simulations: To describe the effect of dilute Eu atoms/ions and Eu-O pairs in bulk AlN, we employed a supercell with dimensions of $4a_0 \times 4a_0 \times 2c_0$ (a_0, c_0 are the lattice parameters of a pristine unit cell of hexagonal AlN). This hexagonal supercell has axis lengths of about a= 12.51 and c=10.03 Å and contains 128 atoms (64 Al and 64 N). For the AlN (110) surface, we build a supercell which has in plane axis lengths of a= $4a_0$ and b=$2c_0$. This cell has 12 atomic layers (AL) and contains in total 192 atoms (96 Al and 96 N). A thick slab of vacuum (>17 Å) was used to avoid interface interactions. A single Eu atom replaced an Al a) in the center, b) at the surface and c) second layer of the surface (subsurface). Similarly, Eu and O co-doping replaced an Al-N pair a) at the center and at the surface of the slab. Test calculations for the polar AlN (0001) surfaces were performed for a supercell of a hexagonal lattice with $a = b = 2a_0$ in plane. There are 16 Al of atoms or 64 atoms (32 Al and 32 N) in total. The vacuum has a length of about 20 Å. One Eu atom replaces one Al in the center and at the two terminal surfaces to get some conceptual results about the preference of Eu occupation.

2.4 Computational technique and settings: We employed the first-principles code VASP (Vienna *Ab initio* Simulation Program) [26, 27], which is based on the density functional theory (DFT) within the Projector Augmented-Wave (PAW) method [28, 29]. The Generalized Gradient Approximation (GGA) was used for the exchange and correlation energy terms.[30] The cut-off energy of the wave functions was 550.0 eV. The cut-off energy of the augmentation wave functions was 700.0 eV. Such high cut-off energies provided reliability to describe the rather localized O/N 2s, 2p and Eu 4f orbitals. The energy differences were converged within 10^{-5} eV. The forces were converged within 10^{-3} eV/Å. The electronic wave functions were sampled on dense grids e.g. a 4×6×1 grid with 6 to 12 irreducible *k*-points depending on the symmetry, for the super cells of AlN(110) surface systems with Eu or Eu-O doping in the Brillouin zone (BZ) of the crystals using the Monkhorst and Pack method [31]. The localized Eu 4f states were described using the Hubbard U (*U*=2.5 eV) approach [24, 25]. Tests of *k*-mesh density and cut-off energies showed a good convergence (~ 1 meV/atom).

III. Results and Discussions

3.1 Experimental observations

3.1A. Phase, composition and morphology. As seen in Fig. S1 of the supporting information, our Rietveld refinement parameters (R_P=7.37%, R_{WP}=9.93%) confirm the phase purity of AlN: Eu powders. By using the induction coupled plasma method and the oxygen-nitrogen analysis, the actual chemical composition of AlN: Eu phosphor is determined as $Eu_{0.0033}Al_{0.9962}O_{0.0156}N_{0.9840}$. The particle size of the AlN: Eu sample is reflected by the SEM images seen in Fig. S2 of the supporting information. The size distribution is non-uniform and covers the range of 1-10um.

3.1B. Optical properties. Instead of photoluminescence, cathodoluminescence measurement owns a powerful excitation source and can motivate the phosphor to exhibit plentiful emission. Fig. 1 shows the CL spectra of the AlN: Eu powder. As seen, AlN: Eu phosphors show broad green emission band at about 530 nm under electron irradiation, which is undoubtedly ascribed to the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+}. The full width at half maximum (FWHM) of the band is quite broad (~92 nm), which greatly exceeds the value in AlN: Eu, Si (55 nm) [13]. As shown in Fig. 1, the brightness of AlN: Eu increase as the anode voltage increases from of 5 kV to 20 KV. This enhanced intensity as a function of anode voltage is ascribed to the increased number of excited Eu^{2+} ions resulting from an increase in the penetration depths of the electron beam as the applied voltage is increased.

In Fig. 1, there are two red emissions around 630 and 660 nm in the CL spectrum. These emissions can be assigned to Eu^{3+} and Eu^{2+} intra-4f transitions. Unlike the absence of Eu^{3+} in AlN with Eu, Si co-doping samples [32], our results indicate that there are Eu^{3+} ions companying Eu^{2+} in the crystal lattice. The coexistence of Eu^{2+} and Eu^{3+} is clearly identified by the XANES analysis as shown in Fig. 2, where two peaks can be clearly seen at about 6977 and 6984eV due to the divalent and trivalent oxidation states of Eu, respectively [33] as well as the coexistence of Eu^{2+} and Eu^{3+} in the Eu doped polycrystalline *c*-BN specimens [34]. The simultaneous presence of Eu^{2+} and Eu^{3+} results in the overlapping green/red emission spectra.

3.1C. Direct observation of Eu sites.

For a low doping crystal (0.5% Eu), the exact doping structure could only be resolved via direct viewing in the atomic scale. By taking advantage of the atom-resolved Cs-corrected STEM, we are able to observe individual heavy atoms, such as the rare-earth atoms in the crystal lattice which can be highlighted in the Z-contrast HAADF (High-angle annular dark-field) images. Fig. 3 (a) shows a typical atomic-resolution STEM image of AlN: Eu. The scattering strength of nitrogen is relatively weak but along the (010) plane, the atomic dumbbell consisting of Al and N atoms is still clearly recognized. Thus, we can directly determine the atomic site of the Eu dopants from the images. The atomic columns containing Eu dopants are observed as the brighter spots, and one can see that the Eu dopants are dispersed along the boundary. In the high-magnification atomic resolution STEM image of Fig. 3 (b), the single Eu dopant evidently substitutes the Al site in edge of the AlN crystallites. As shown in Fig. 3 (c), the arrangement of atoms in AlN: Eu matches with the intensity file from the box in Fig. 3 (b). This bright feature at the Al site is quantitatively reproduced in the simulated image (Fig. 2 (d)), where a single Eu atom has been substituted for an Al atomic site. In addition to the Eu sites along the boundary, Eu ions can also replace Al ions close to the boundary, as seen in Fig. 3 (e, f). This may origin from the easily released crystal strain near the boundary.

Overall, our experiments have shown that there are simultaneous presence of Eu^{2+} and Eu^{3+} in the AlN: Eu sample. To get insight into the phenomenon, we performed first-principles simulations.

3.2 Theoretical simulations

3.2A. Bulk AlN, EuO and EuN. Our calculation results for the bulk properties of the related compounds, AlN, EuO and EuN are shown in Table I.

(Some references are present in Table 1 [23, 24, 25, 35, 36]).

As shown in Table I, the obtained lattice parameters for the bulk AlN, EuO and EuN are close to the experimental values within 1% error. The present calculations show that wurtzite AlN is more stable than the cubic phase with an energy difference of about 0.45 eV/AlN. The calculations also show that EuO with table salt structure has a local magnetic moment of $s=7$, whereas the spin state is $s=6$ for the EuN. In order to have a good understanding about the spin states of Eu in EuO and EuN, we performed spin-polarization calculations using the fixed spin approach for both EuO and EuN with table salt structure. The calculated relationship between the cohesive energy and local magnetic moment is shown in Fig. 4. Clearly, the most stable spin state is $s = 7/2$ for EuO, whereas, it is $s=6/2$ for EuN. These results agree with the ionic model: Eu^{2+} with $4f^7$ configuration in EuO and Eu^{3+} with $4f^6$ configuration in EuN.

3.2B. Dilute Eu doping and Eu-O co-doping in bulk AlN. We first address the calculations, where a single Eu atom doping and an Eu-O pair co-doping in AlN bulk are discussed, respectively. The calculated results are shown in Table II. Fig. 5 shows the calculated total density of states (tDOS) for the related systems, and the partial density of the related Eu 4f states. The tDOS of wurtzite AlN is included for comparison.

As shown in Table II, the calculations show that replacing one Al by Eu costs about 2.6 eV with respect to the parent binaries AlN and EuN. A Eu-O co-doping costs about 4.5 eV when Eu and O are set far-away and about 3.6 eV when Eu and O is nearby in AlN.

As shown in Fig. 5 (top row), AlN is calculated to be a wide gap insulator with the calculated energy gap being about 4.2 eV, which is smaller than the experimental value. This is not unusual for the density functional theory.[37] The N 2s states form a broad band in the energy range between -13.1 eV to -10.5 eV (Fermi level is set to be zero eV). The valence band which is dominated by N 2p states is in the energy range between -5.1 eV to zero eV, whereas the conduction band is about 4.2 eV above the valence band. The present results agree with the former theoretical calculations [21,22].

The tDOS curves of the Eu and Eu-O doped systems are very similar to that of AlN bulk. For EuO co-doped system (Eu-O is close), there is a sharp peak at about 2.1 eV above the valence band. This peak is occupied by electrons. Eigencharacter analysis shows that this peak belongs to the Eu $4f^7$ states for the majority electrons. Meanwhile, the unoccupied Eu 4f states are at upper energy (about 10 eV) above the Fermi level (not shown). This result corresponds well to the Eu^{2+} configuration (Table II). The partial density of the Eu 4f states for the Eu doping system (Fig. 5) is more complicated and showed disperse nature. The pDOS of the Eu 4f states for the majority electrons (black lines in third row) consists mainly of two parts. The lower part is in the valence band, ranging from about -2.5 eV to -0.5 eV, whereas the upper part is unoccupied and positioned at 0.4 eV above the valence band. There are also some small Eu 4f contributions just below the Fermi level. These disperse nature of the Eu 4f states indicates strongly interaction between Eu 4f and N 2p states, in contrast to the case with Eu-O co-doping where the Eu 4f states are strongly localized.

3.2C. Eu at the AlN surfaces. As mentioned before, the ground state of AlN has the wurtzite structure (Fig. S3a) with a hexagonal lattice with a_0 =3.11 Å, c_0 =4.98 Å [38]. In this structure each Al is in a tetragonal coordination by four N. It is possible to obtain non-polar surfaces by cleaving the crystal along (110) orientation (Fig. S3b) [38]. A smooth cleavage of AlN along its (0001) orientation produces one Al-terminated and one N-terminated surface. Therefore, a smooth AlN (0001) surface is polar. Both experimental and theoretical studies showed reconstruction of the Al (0001) surfaces [38-41]. Our goal here is for understanding the Eu preference in the bulk or at the surfaces of AlN. We first chose the non-polar AlN (110) surface as the example. Furthermore, we also investigate the Eu preferred sites using a slab containing smooth AlN (0001) surfaces considering the fact that the surfaces are composed of Al-N or N-Al double atomic layer and, therefore, are weak/moderate in polarity.

Figure 6 shows the single Eu replacements of Al and Eu:O co-doping at different site. The calculated energetics for one Eu atom/ion and one Eu-O pair at different positions at/in AlN (0001) surfaces and (110) are shown in Table III.

First we discuss the calculations for the non-polar AlN (110) surface. As shown in Table III, the total energy calculations show that Eu prefers the surfaces site. The energy difference is about 3.05 eV for one Eu doping at the AlN surface, which is notably larger than that of one Eu doping at the subsurface. Moreover, Eu-O co-doping at the AlN (110) surface is much favored with an energy difference as 3.2 eV. This type of Eu preferential behavior at the surface is understandable considering the large Eu ionic size as compared with an Al ion. Meanwhile, the Eu in the center of the slab is connected to four N with Eu-N bond-length 2.24 (×2), 2.27 and 2.30 Å which are just slightly different from those (Eu-N: 2.22 (×3), 2.26 Å) for the Eu in AlN

bulk, which comes from the broken symmetry and the surface influence. The calculations show that the local magnetic moments or spin states of the Eu in the center, at the second layer and at the surface of the AlN slab. The Eu at the center of the AlN slab has its spin state $s = 6.26/2$, which is slightly larger than that in Eu in AlN bulk (6.04/2).

Structural optimization and electronic structure calculations show that for a Eu-O pair in the center or at the surface of AlN, the spin state for Eu is $s=7/2$, corresponding to the Eu^{2+} model.

Fig. 7 shows the calculated total density of states for Eu (first row) and Eu-O (third row) at AlN surface. The related partial densities of the Eu 4f states are also included. Clearly, in the Eu-O pair co-doped case, the Eu 4f states are fully spin-polarized. The occupied Eu $4f^7$ states for majority electrons form a sharp peak at about 2 eV above the valence band, whereas the unoccupied Eu 4f states also form a sharp peak at about 4.5 eV above the occupied 4f states. There are surface states in the range between about 2.3 eV to above the valence band to the bottom of the conduction band of the bulk AlN.

3.3 Discussions and summary

Our study by means of a combination of multiple experimental observation and first-principles simulation has shown that Eu ions or Eu-O pairs favor at the surface of the grain boundary of the AlN particles. O bonded to Eu is a key point to determine the valence and electronic/optical properties of Eu. Single Eu substitution is 3+ valent while Eu ions exhibit a 2+ valence for Eu-O pairs which was confirmed by the analysis of the oxygen content that 0.60 wt % of oxygen amount is present in AlN: Eu phosphor.

Overall, single Eu doping exhibits a 3+ valence, which is responsible for the sharp red emission in AlN: Eu phosphor. Eu ions are likely to get bounded to form Eu-O pair. With the help of Eu-O codoping, Eu^{2+} is stable as it has a full filled 4f orbitals ($4f^7$), which results in the broad green emission band of 4f-5d electron transitions. Based on the crystal field theory, the split of 5d orbitals of Eu^{2+} is affected by the type of ligands and the arrangement of the ligands around the Eu^{2+}. Owing to the higher formal charge of N^{3-} compared with O^{2-} and the lower electronegativity of nitrogen (3.04) compared with oxygen (3.44), some Eu^{2+} doped pure nitride phosphors show emission peaks situated in the red region, such as 610 nm for Eu doped $SrAlSiN_3$(Sr-N: $\sim$2.7 Å, C.N. = 10) and 620 nm for Eu doped $Sr_2Si_5N_8$ (Sr-N: $\sim$2.8 Å, C.N. = 8-9) [42, 43]. Regarding to the preferable Eu-O co-doping at the boundary of AlN: Eu phosphor, low coordination number, asymmetry coordination and O defects would possibly result in a weaker crystal-field splitting and consequently a green emission. Note that it cannot be concluded that Eu stay in the center or subsurface of AlN crystal due to possible local defects around Eu^{2+}, as seen in Fig. 3 (e). Here we briefly summarize our investigations into a schematic diagram of Fig. 8.

IV. Conclusions

Our findings indicate that even dopant atoms with extremely large size mismatch can be incorporated into host crystal lattice through Eu substitution Al at or near the surface. Single Eu prefers to remain 3+ valent due to its large ionic size while Eu owns a 2+ valence when Eu-O co-doping is achieved as Eu^{2+} has fully filled 4f orbitals ($4f^7$). Expectedly, we may be

able to control unique functionalities in largely mismatched systems by tuning the Eu^{2+}/Eu^{3+} ratios in the lattice via manipulating samples' particle size distribution, chemical composition and site occupation modification.

Acknowledgements

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Figure captions:

Figure 1. Cathodoluminescence spectra of the AlN: Eu phosphor.

Figure 2. Eu L$_{III}$-edge XANES spectrum of the AlN: Eu sample.

Figure 3. (a) HAADF image along [010] zones showing Eu sites along the boundary. (b)
Enlarged HAADF image. (c) Intensity profile corresponding to the box in (c). (d) Simulated
HAADF image showing that the intensity difference between different atoms. (e, f) another
region showing Eu sites close to the boundary.

Figure 4. Relationships between the calculated energies of EuX (X=O, N) crystals on the
magnetic moment per Eu. The energies for moment =7 are used as the references. Clearly, for
X = O, the state with s=7/2 is most stable while for X=N, s=6/2 is the ground state. That
corresponds well to the ionic model: Eu^{3+}N^{3-} and Eu^{2+}O^{2-}.

Figure 5. Total density of states (tDOS) for bulk AlN with wurtzite structure (a), for Eu doped
system (b) and for Eu-O co-doped AlN system (d). The partial density of Eu 4f for Eu in AlN (c)
and for Eu (f) and O (e) in the co-doped Eu-O (pair) system. The Fermi levels are indicated by
the dotted lines respectively. The present study shows the Eu^{3+} (4f^6 configuration) in the single
doping system and Eu^{2+} (4f^7 configuration) for the Eu-O coped system.

Figure 6. Schematic structure of Eu at the center (a), subsurface (b) and at surface (c) of the
AlN slab, and one Eu-O pair replacing an Al-N pair near the surface (d). The small silvery
spheres for Al, small yellow for N, large oranges for Eu, and middle blue for O.

Figure 7. The calculated total density of states (tDOS) for Eu at AlN(110) surface (a) and the
related Eu 4f states (b); total density of states (tDOS)for Eu-O at AlN(110) surface (c) and the
related Eu 4f states (d). The dotted redline means Fermi level. The positive values means for
spin-up (majority) electrons and the negative values for the spin-down (minority electrons).
Clearly, the Eu at AlN (110) surface has Eu^{3+} valence and corresponding to spin states ~6.1/2,
whereas at the surface Eu^{2+} with spin state s = 7/2 for the Eu-O pair.

Figure 8. A schematic diagram showing the origin of the observed green and red emissions in AlN: Eu phosphor.

Table 1. Calculated results for binary AlN, related EuO and EuN phases using the PBE / PBE+U (U=2.5 eV for Eu 4f) method [23, 24, 25]. The experimental values of AlN, EuN and EuO from literature are included in parentheses. SG in column 2nd represents for space group, Mag in 5th column for magnetic moment in the Eu sphere.

Phases	Lattice (SG)	Parameter	Bonds/charges	Local moment
Hex_AlN	P6$_3$mc (nr. 194)	a=3.128 (3.112) [35] c=5.017 (4.982) [35]	Al-N:1.90(×3),1.91	0
EuN*	Fm-3m (nr.225)	a=5.131 (5.144) [36]	Eu-N: 2.56(×6)	M$_{mag}$=6μ$_B$/Eu
EuO*	Fm-3m (nr.225)	a=5.130 (5.141) [36]	Eu-O: 2.55(×4)	M$_{mag}$=7μ$_B$/Eu

Table 2. The calculated results (formation energy, ΔE= E(Al$_{64-x}$Eu$_x$N$_{64-y}$O$_y$) $-[E$(Al$_{64-x}$Eu$_x$N$_{64-y}$O$_y$) $+ xE$(EuN)+y E(EuO)], and local chemical bonding and local spin state). Column 1 of rows 3 and 4, the symbol f-/c- represents the co-doped O and Eu being far away/being close (Eu-O pair).

Configuration	Eu bonds	ΔE(eV/Eu) spin per Eu
Al$_{63}$EuN$_{64}$	Eu-N:2.22(×3), 2.26	+2.646 eV/EuN s=6.04/2
f-Al$_{63}$EuN$_{63}$O	Eu-N:2.28(×3), 2.33	+4.510 eV/EuO s=7/2
c-Al$_{63}$EuN$_{63}$O	Eu-N:2.26(×3),O:2.33	+3.635 eV/EuO s=7/2

Table 3. The calculated energetics for one Eu atom/ion and one Eu-O pair at different positions at/in AlN (0001) surfaces and (110).

Position of Eu	*Spin state s*= (Bohr unit)	Bond (Å)	ΔE(eV) *
AlN(110) (non-polar)			
Eu at center	6.26/2 / 7/2*	Eu-N:2.24(×2),2.27,2.30	0.000 / + 0.49**
Eu at 2nd layer	6.29/2 / 7/2*	Eu-N: 2.26(×2),2.31,2.40	-0.52 / -0.31**
Eu at surface	5.92/2 / 7/2 *	Eu-N: 2.33,2.366(×2)	-3.05 / -3.02**
EuO at surface	7/2	Eu-N:2.26,2.29 -O: 2.59	-3.22/(EuO)**
EuO at center	7/2	Eu-N:2.27,2.29,2.31 -O: 2.31	0.0
AlN(0001) (polar)			
Eu at center	/ 7/2*	Eu-N:2.16(×3), 2.37	0.0
Eu at Al_surf	/ 7/2*	Eu-N: 2.41(×3)	-4.72**
Eu at N_surf	/ 7/2*	Eu-N: 2.16(×3)	-1.91**

* indicates the spin is fixed to s = 7/2 and **is the related energy differences with respect to the ones of zero eV.