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Enhanced stability of Eu in GaN nanoparticles: Effects of Si co-doping

Prabhsharan Kaur,^{1,2} S. S. Sekhon,^{2,3} J. M. Zavada,⁴ and Vijay Kumar^{1,5}

¹Dr. Vijay Kumar Foundation, 1969 Sector 4, Gurgaon 122001, Haryana, India

²Department of Physics, Guru Nanak Dev University, Amritsar 143005, Punjab, India

³Department of Physics, The University of the West Indies, St. Augustine, Trinidad and Tobago

⁴Department of Electrical and Computer Engineering, NYU Polytechnic School of Engineering, Brooklyn, New York 11201, USA

⁵Center for Informatics, School of Natural Sciences, Shiv Nadar University, NH91, Tehsil Dadri, Gautam Buddha Nagar 201314, Uttar Pradesh, India

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Ab initio calculations on Eu doped (GaN)_n (n = 12, 13, and 32) nanoparticles show that Eu doping in nanoparticles is favorable compared with bulk GaN as a large fraction of atoms lie on the surface where strain can be released compared with bulk where often Eu doping is associated with a N vacancy. Co-doping of Si further facilitates Eu doping as strain from an oversized Eu atom and an undersized Si atom is compensated. These results along with low symmetry sites in nanoparticles make them attractive for developing strongly luminescent nanomaterials. The atomic and electronic structures are discussed using generalized gradient approximation (GGA) for the exchange-correlation energy as well as GGA + U formalism. In all cases of Eu (Eu + Si) doping, the magnetic moments are localized on the Eu site with a large value of $6\mu_B$ ($7\mu_B$). Our results suggest that co-doping can be a very useful way to achieve rare-earth doping in different hosts for optoelectronic materials. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

Rare-earth (RE) doped compound semiconductor nanoparticles are of great interest for imaging and optoelectronic applications^{1–8} as the intra $4f$ level electronic transitions lead to intense luminescence.⁹ The host nanoparticles play a very important role in making intra $4f$ transitions possible as in a free RE ion, these are forbidden. Bulk GaN is a versatile host^{10–13} due to its wide band gap (3.4 eV) and chemical stability. By doping RE³⁺ ions in GaN, one can combine the electrical properties in GaN with optical transitions in the RE such as Eu which emits red light. In nanoparticles, there are low symmetry sites and this could lead to the possibility of strong luminescence. Eu doping in GaN powders,¹⁴ quantum dots,^{15–17} nanograins,¹⁸ and nanoparticles¹⁹ has been studied experimentally. However, there has been little progress on the theoretical understanding of the doping of RE in GaN nanoparticles. The size of the nanoparticles used in these experiments is at least a few nm in diameter which is difficult to treat from *ab initio* atomistic calculations. Theoretical studies on undoped small clusters or nanoparticles of III-V compounds have been reported²⁰ but to our knowledge no studies on doping of Eu in nanoparticles have been performed. Small nanoparticles often have structures different from the corresponding bulk material. In particular, GaN nanoparticles with ~ 1 nm diameter have fullerene-like structures²⁰ in contrast to the wurtzite structure in bulk. Here, we report the results of *ab initio* calculations on the atomic and electronic structure of Eu doped GaN nanoparticles and the effects of Si co-doping on their stability and electronic structure. The doping of RE atoms alone in bulk GaN is quite difficult due to the large size of Eu compared with Ga and is often accompanied with a N vacancy

formation but our results demonstrate that in nanoparticles, it may be energetically possible to dope Eu because of the presence of surface where strain can be released and that co-doping of, for example, Si could further facilitate it. Thus, co-doping is a useful approach to achieve this objective as also evidenced^{21,22} from the enhanced luminescence obtained in the case of Mg co-doping with Eu.

Doping of Eu as well as co-doping of Eu and Si in bulk GaN has been studied from *ab initio* calculations.^{23–26} When substituted on a Ga site, an Eu atom has C_{3v} symmetry which is non-centrosymmetric and the surrounding crystal field leads to hybridized mixed states. The large size mismatch between Ga and Eu ions leads to an outward relaxation around the Eu (3+) ion. This creates compression in neighboring GaN bonds and significant strain in GaN lattice that costs about 1.84 eV/atom in energy.²⁶ This makes it difficult to dope and retain RE atoms in GaN. Recently, Mitchell *et al.*²⁷ have reported that in bulk GaN size mismatch is accommodated to a large extent by the presence of nitrogen vacancies. The N vacancy can be on an adjoining C_{3v} symmetric site or another neighboring C_{1h} site. Also with a small probability there can be a Ga vacancy site which sits far enough so as not to disturb the Eu ion. The presence of defect sites (Ga and N vacancies) near and at some distance from Eu ion is important to have improved excitation efficiency. Co-doping of Si or Mg ions is further helpful in the creation of proper defect sites to improve excitation efficiency. However, in nanoparticles the behavior could be significantly different because a large fraction of atoms lie on the surface where strain can be significantly lower. Also, there could be a reduction in the local symmetry in a nanoparticle that could be beneficial for intra $4f$ electronic

transitions. The luminescence in Eu doped bulk GaN has been found to be site specific²⁸ and this is important as the atomic structure of small nanoparticles is generally very different from bulk. Small GaN nanoparticles are special as they have fullerene-like empty cage structures²⁰ and therefore all the atoms are on the surface. This could lead to sites with local environment very different from bulk as well as a high probability of doping RE atoms as the atoms lie on the surface. But also in small nanoparticles, Ga-N bonds are generally shorter compared with bulk and there is a distribution of interatomic distances. This would lead to site selectivity and its proper understanding is necessary.

Further even in large three dimensional (3D) GaN nanoparticles, the surface atomic structure could be quite different from bulk. There can be significant sp^2 bonding character on the surface as it has been found in small nanoparticles. Note that even on some surfaces of bulk GaN, one finds²⁹ a tendency to have sp^2 bonding character. Therefore, an understanding of RE doping in small GaN clusters could also give useful information for large nanoparticles. In the latter case, the doping could be inside or on the surface of the nanoparticles and it needs to be properly understood. Further, co-doping with, for example, a smaller atom such as Si can facilitate Eu doping as it has been reported for bulk GaN.²⁶ Is the behavior of the co-dopant in nanoparticles similar to bulk GaN? Being tetravalent, Si would behave as an intrinsic donor on a Ga site in GaN nanoparticles and the question would be how an extra electron is distributed in a small system? The co-doping would also have the effect of further reducing the local symmetry around the Eu ion. It is interesting to note that in experiments on thin films, Si co-doping has been reported to increase the photoluminescence lifetime and the excitation efficiency.³⁰

Here, we report results of *ab initio* calculations on the doping of an Eu atom in $(\text{GaN})_n$ ($n = 12, 13, \text{ and } 32$) nanoparticles which are considered as representatives of small sizes. In particular, we focus on the following aspects: (1) if Eu doping in GaN nanoparticles becomes energetically favorable in contrast to bulk, (2) if it would lead to a transition from an empty cage to a 3D filled cage structure of GaN nanoparticles and, if so, whether Eu goes inside the nanoparticles or on the surface, and (3) the effect of Si co-doping on the stability, charge distribution, and the electronic structure.

In Sec. II, we report our method of calculations while the results have been presented in Sec. III. Our conclusions are summarized in Sec. IV.

II. METHOD OF CALCULATIONS

We used projector augmented wave pseudopotential plane wave method³¹ with generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof³² for the exchange-correlation energy. The ionic pseudopotentials have been generated³³ by including scalar relativistic effects. The cut-off energy for the plane wave expansion is taken to be 400 eV. The nanoparticles are placed in a cubic cell of side 20 Å with periodic boundary conditions. Some

calculations were also repeated with a cubic unit cell of side 25 Å and the results of the atomic structure and energy were almost the same. The Brillouin zone integrations are performed using only the Γ point. For large unit cells as considered here, Γ point calculations are sufficient. The ionic positions are relaxed until the force on each ion becomes less than 0.005 eV/Å and the energy is converged within 0.0001 eV. The valence configuration for Ga, N, Si, and Eu atoms is taken to be $4s^24p^1$, $2s^22p^3$, $3s^23p^2$, and $5s^25p^64f^76s^2$, respectively. We also performed several calculations by taking 13 valence electrons on Ga including the 3d states and the overall trend of the stability of different structures is similar, though the binding energy improves by about 0.05 eV/atom. Here, we shall discuss the results obtained by considering three valence electrons on Ga and mention the results of calculations with 13 valence electrons on Ga where relevant.

For the Eu doped nanoparticles, we performed spin-polarized calculations due to partially occupied 4f states. Also, GGA + U calculations have been done to study the effects of on-site Coulomb interaction on the localized 4f states of Eu. The value of the effective on-site Coulomb interaction parameter U has been taken¹³ to be 6.0 eV. The binding energy per atom, E_b , of different nanoparticles has been calculated from $(n_A E(A) + n_B E(B) + n_C E(C) + n_D E(D) - E(ABCD))/(n_A + n_B + n_C + n_D)$, where $E(X)$ ($X = A, B, C, \text{ and } D$) is the energy of an isolated X atom and $E(ABCD)$ is the energy of the nanoparticle with $n_A, n_B, n_C, \text{ and } n_D$ atoms of type A, B, C, and D, respectively. To begin with, we calculated the binding energy of GaN and EuN dimers and the values are 2.57 eV and 3.00 eV, respectively. The corresponding bond length is 1.86 Å and 1.84 Å with the magnetic moments of $2\mu_B$ and $6\mu_B$, respectively. Therefore, EuN dimer has a higher E_b compared with GaN. In these free dimers, there is no strain and the EuN dimer is even shorter than GaN dimer. However, in nanoclusters, the Eu-N bond length is generally longer compared with the value for Ga-N bond and the substitution of Eu on a Ga site generally leads to some strain (compression) in Ga-N bonds around the Eu site. Also, substitution of Si on a Ga site creates some strain (dilation) in the surrounding Ga-N bonds as the Si-N bond is shorter than Ga-N. Further, we calculated the formation energy for Si co-doping in nanoparticles from the formula $\Delta H_{\text{Si}} = E(\text{Ga}_{n-x-y}\text{N}_n\text{Eu}_x\text{Si}_y) - E(\text{Ga}_{n-x}\text{N}_n\text{Eu}_x) - yE(\text{Si}_N)/N + yE(\text{Ga}_N)/N$, where $N = 2n$ is the total number of atoms in the nanoparticle. Here, $E(\text{Si}_N)$ and $E(\text{Ga}_N)$ are, respectively, the energies of the pure Si and Ga nanoparticles with N atoms. As we shall discuss below, our results show large formation energy for Si co-doping, making it highly favourable. We performed calculations for one and two Eu atoms doped in $(\text{GaN})_n$ nanoparticles and also for Eu atoms co-doped with a Si atom in $(\text{GaN})_n$ nanoparticles ($n = 12, 13, \text{ and } 32$). The optimized structures for the case of two Eu doping show a small decrease in the binding energy compared with one Eu doping as it was also found³⁴ for Gd and Nd doping in small GaN nanoparticles. Therefore, it is expected that clustering of Eu atoms may not occur in nanoparticles, though the doping may not be limited to one Eu ion per nanocrystal.

III. RESULTS

A. Atomic structure

For the undoped small GaN nanoparticles, earlier studies^{20,35} have shown empty cage structures to be most favorable. The general tendency is similar to the cage structures of BN which have been well understood.³⁶ BN cages have 4-membered and 6-membered rings as compared to pentagons and hexagons in carbon fullerenes because of the presence of two types of atoms and polar bonding character. The 4-membered rings are isolated similar to pentagons in carbon fullerenes. As one goes down in the periodic table, such as from carbon to silicon, then instead of empty cage structures, filled fullerene cages become favorable.³⁷ A similar behavior has been shown for the nanoparticles of CdSe.³⁸ Doping can affect the atomic structure and therefore, for the doped nanoparticles we studied empty cage as well as filled cage isomers composed of hexagons (6-membered rings) and rhombi (4-membered rings). In Figs. 1 and 2, we have shown the optimized atomic structures of the different isomers of the $n=12$, 13, and 32 nanoparticles doped with one Eu atom and also co-doped with Si. For each case (empty and filled cage structures), we doped Eu and Si at different Ga sites in hexagonal and rhombus units that could lead to different environments around the dopant, which is important for intra 4f shell transitions and applications.³⁹ In general at a hexagonal site, the bonding tends to be predominantly sp^2 type,

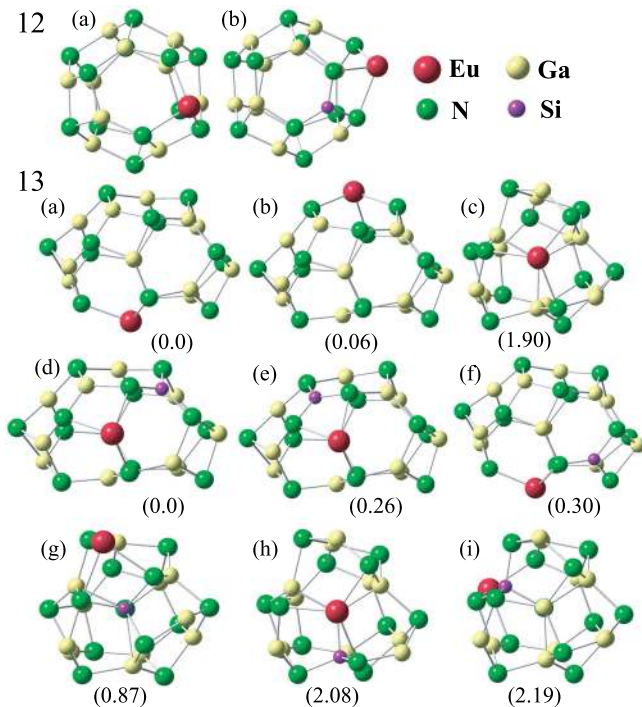


FIG. 1. Different isomers of empty and filled cage structures for $(\text{GaN})_n$ ($n=12$ and 13) nanoparticles doped with one Eu atom and co-doped with Eu + Si. For $(\text{GaN})_{12}$, all Ga sites are equivalent and therefore for Eu doping only one case is shown in 12(a). Co-doping of Eu and Si is favored on Ga sites on the same rhombus as shown in 12(b). For $n=13$, the lowest energy isomer is shown in 13(a) and the energy of the other isomers is given in brackets in eV. The energy of the lowest energy isomer has been taken as the reference. Cage structures 13(b) to 13(f) are favored over 3D structures (filled cage isomers) shown in 13(g) to 13(i).

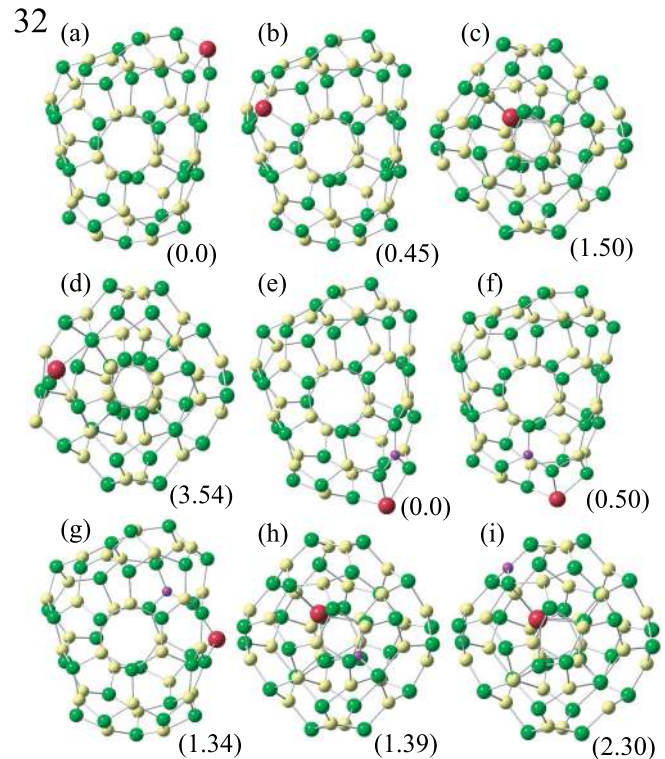


FIG. 2. Different empty ((a), (b), (e), (f), and (g)) and filled ((c), (d), (h), and (i)) cage isomers of $(\text{GaN})_{32}$ doped with one Eu atom ((a)–(d)) and co-doped with Eu and Si ((e)–(i)). Other details are the same as in Fig. 1.

while at a rhombus site the bonding is more sp^3 like. Note that the GaN bond length is shorter for sp^2 bonding configuration compared with the value in sp^3 configuration. This is important and is likely to affect the preference for substitution of Eu and Si on Ga sites.

Similar to $(\text{BN})_{12}$, undoped $(\text{GaN})_{12}$ has a highly symmetric cage structure with eight hexagons and six rhombi.²⁰ All Ga sites are equivalent and only one case is shown for Eu doping in Fig. 1. The optimized structure, 12(a), shows that the cage is only slightly distorted due to the larger size of Eu as compared to Ga (ionic radius of $\text{Ga}^{3+} = 0.62 \text{ \AA}$ and $\text{Eu}^{3+} = 0.95 \text{ \AA}$). The Eu-N bond is much longer (2.286 \AA) than Ga-N and it leads to an outward relaxation around the Eu ion and a contraction of the nearest neighbor Ga-N bonds. The latter lies in the range of $1.876\text{--}1.938 \text{ \AA}$ compared with the value of $1.879\text{--}1.954 \text{ \AA}$ for the undoped $(\text{GaN})_{12}$. Further, the Eu-N bond is slightly longer compared to 2.25 \AA in Eu doped bulk GaN²⁶ and it indicates that the outward relaxation due to Eu doping in nanoparticles is greater because the strain can be better released at the surface of the cage. Most interestingly, Eu doping in GaN nanoparticles becomes energetically favorable by 0.40 eV (see Table I) in contrast to bulk where it costs 1.84 eV . The binding energy of the Eu doped nanoparticles also increases indicating enhanced chemical bonding by Eu doping.

We further studied co-doping of Si with one Eu atom on Ga sites considering both hexagonal and rhombus locations in $(\text{GaN})_{12}$. The optimized lowest energy isomer (Fig. 1, 12(b)) is the one in which Si occupies a Ga site that is nearest neighbor to the site occupied by the Eu atom such that both Si and Eu are on the same rhombus. The main reason of this

TABLE I. The total binding energy, E (eV), the HOMO-LUMO gap, E_g (eV), and the binding energy, E_b (eV/atom) calculated within GGA (GGA + U) for the different undoped $(\text{GaN})_n$ nanoparticles as well as doped with one Eu and co-doped with Eu and Si atoms. The GGA + U calculations have been done only for the Eu doped nanoparticles.

n	System	E , GGA (GGA + U)	E_g , GGA (GGA + U)	E_b , GGA (GGA + U)
12	GaN	86.19	1.55	3.59
	GaN:Eu	86.58 (85.74)	0.03 (0.17)	3.61 (3.57)
	GaN:Eu + Si	90.85 (90.40)	0.10 (0.93)	3.79 (3.77)
13	GaN	91.97	0.96	3.54
	GaN:Eu	92.52 (91.80)	0.05 (0.11)	3.56 (3.53)
	GaN:Eu + Si	96.96 (96.40)	0.15 (0.59)	3.73 (3.71)
32	GaN	242.54	1.45	3.79
	GaN:Eu	242.95 (242.27)	0.17 (0.39)	3.80 (3.79)
	GaN:Eu + Si	247.24 (247.22)	0.02 (0.89)	3.86 (3.86)

favorable doping configuration is that the bonding in a rhombus is more sp^3 -like as mentioned before with longer Ga-N bonds compared with predominantly sp^2 bonding in hexagons. Therefore, strain due to an over-sized Eu atom is lower at such a site. Furthermore, Si-N bond distance is short (1.692 Å) which is the reason why both *Eu and Si favor nearest neighbor Ga sites so that the strain due to an over-sized Eu and an under-sized Si can be compensated.* After Si co-doping, the Eu-N bond length increases slightly to 2.337 Å due to charge transfer from Si (as we shall show later) and the Si-N bond distance remains nearly unchanged (1.692 Å). The Ga-N bonds in the neighborhood of the doping sites are in the range of 1.883–1.928 Å. Therefore, the compressed Ga-N bonds become slightly elongated. Si co-doping with Eu in nanoparticles leads to a large gain of 4.27 eV (see Table I) making the system energetically more favorable compared with Eu doping alone.

For $n = 13$, there are empty and filled cage isomers as shown in Fig. 1. We ask the question if an isomer with a cage composed of 13 Ga and 12 N atoms and one N atom inside the cage (filled cage) becomes favorable after Eu doping compared with an empty cage doped with Eu. In the filled cage isomer, Eu atom can bind with four N (three on the cage and one inside) compared with three in an empty cage. The latter has a GaN dimer attached to the $n = 12$ cage and it becomes an elongated structure with some distortions. In this empty cage isomer (Fig. 1(13a), (13b)), we substituted Eu on Ga sites in both a hexagon and a 4-membered ring. The optimized structures show that the difference in energies of the two configurations is only 0.06 eV with the site on a distorted hexagon slightly more favorable. For the $(\text{GaN})_{13}$ filled cage, we placed Eu at different Ga sites on the cage such that Eu has one bond with N inside the cage. The lowest energy isomer is shown in Fig. 1(13c). However, the Eu doped empty cage is 1.90 eV more favorable than the lowest energy isomer of the Eu doped filled cage. This is due to the strong tendency of small GaN nanoparticles to form empty cage structures. Note that the undoped empty cage of $(\text{GaN})_{13}$ is 2.158 eV lower in energy²⁰ than the filled cage. This is a large energy. Therefore, with Eu doping although this difference in energy is slightly reduced, yet it is not sufficient to transform the $(\text{GaN})_{13}$ nanoparticle into a filled cage 3D structure. The Eu-N bond distance in an empty cage isomer is 2.336 Å (nearly the same as in $n = 12$ case), and

the neighboring Ga-N bond distances are in the range of 1.878–1.929 Å.

For the case of Si co-doping, we again explored empty and filled cage isomers and the optimized structures are shown in Fig. 1(13d-i). Among the different doping sites we explored, the empty cage isomer with Eu at a rhombus site and Si at a distorted hexagonal site has the minimum energy (13d). The isomer with both Eu and Si doped on the same rhombus (13e) is only 0.26 eV higher in energy than the minimum energy configuration. Different filled cage isomers (13g-i) are significantly higher in energy (0.87 eV to 2.19 eV) than the empty cage isomers but the energy difference reduces significantly as compared to only Eu doping. Therefore, Si co-doping can induce transition to 3D structures for larger nanoparticles and this can be expected as in a 3D structure the bonding would be close to sp^3 type, which is favored by Si. The Eu-N and Si-N bond distances for the lowest energy $(\text{GaN})_{13}$ filled cage isomers are 2.347 Å and 1.691 Å, respectively, while the Ga-N bond distances nearest neighbor to them are in the range of 1.884 Å–1.961 Å. These values are similar to those in an empty cage isomer but Eu-N and Ga-N bonds are slightly elongated.

Figure 2(32a-i) shows the optimized empty and filled cage isomers for $(\text{GaN})_{32}$. In this case also, empty cage isomers (32a, b, e, f, and g) are favorable over the filled cage isomers (32c, d, h, and i). In the empty cage isomer, Eu doping has the lowest energy at a rhombus site (32a) and there is a gain of 0.40 eV (see Table I) compared with the undoped cage. The Eu-N bond length is 2.296 Å and the Ga-N bonds nearest neighbor to the doping site are in the range of 1.888–1.906 Å. The isomer with Eu doped at a hexagonal site (32b) is 0.45 eV higher in energy. The filled cage has a distorted cuboidal unit inside $n = 28$ cage,²⁰ and it is only 0.576 eV higher in energy than the empty cage isomer. In this isomer, we explored doping of Eu on a Ga site both inside and on the surface of the filled cage (32c, d). However, these isomers are 1.50 eV (32c) and 3.54 eV (32d) higher in energy than the minimum energy Eu doped empty cage isomer. Furthermore, the isomer with Eu doping on the surface of the filled cage (32d) is much higher (3.54 eV) in energy compared with the isomer with Eu doped on a site inside the cage (1.50 eV) as shown in Fig. 2(32c).

This may be due to more Eu-N bonds inside the cage and the fact that the cage is not tightly filled. This result

could be very significant for doping large 3D nanoparticles since the most favorable Eu doping site generally has sp^3 bonding, whereas bulk GaN surfaces tend to have sp^2 bonding and consequently shorter bonds. Therefore, doping at subsurface sites could be very likely. For the case of Si co-doping with Eu (32e-i), the empty cage isomer with both Eu and Si substituting Ga (32e) on the same rhombus has the minimum energy. In this case, again the Eu-N bond distance is elongated to 2.378 Å and the Si-N bond distance is 1.680 Å. This compensates the strain in the nanoparticle. An empty cage isomer with Eu at a rhombus site and Si at a hexagon site (32f) is 0.50 eV higher in energy, and another isomer with both Eu and Si co-doped in a hexagon (32g) is 1.34 eV higher in energy. The filled cage isomer shown in Fig. 2(32h) has Eu and Si both in the core. It is 1.39 eV higher in energy than the lowest energy isomer. Another filled cage isomer is also shown in Fig. 2(32i) in which Eu is doped on a Ga site inside the cage and Si is doped on a Ga site on the surface. This is 2.30 eV higher in energy than the minimum energy empty cage isomer. We find that Si co-doping with Eu in $(\text{GaN})_{32}$ nanoparticles lowers the energy by 4.573 eV and therefore Si co-doping increases the stability (see Table I) of the nanoparticles. As we shall show, an extra electron from Si changes Eu into a +2 charge state with $4f^7$ configuration. In general, Si co-doping with Eu in GaN nanoparticles leads to less symmetric structures that could further facilitate intra $4f$ transitions.

Further, we calculated the formation energy for Si co-doping. Our calculations for $n=12, 13,$ and 32 Eu doped nanoparticles support that the Si co-doping with Eu in GaN nanoparticles is favorable. For this, we calculated the energies of the pure Ga and pure Si clusters with 24, 26, and 64 atoms. The atomic structures of Ga and Si clusters have been studied earlier and we followed the results of Joshi and coworkers⁴⁰ for Ga, while for Si_{24} and Si_{26} , we used the structures obtained by Zeng and coworkers.⁴¹ We derived the atomic structure of Si_{64} from the one given by Zhou and coworkers⁴² for Si_{60} by adding four atoms on the surface. All the structures were optimized without any symmetry constraint. The optimized structures are shown in Fig. 3 and these are very different from those obtained for GaN nanoparticles. The calculated binding energies of $N=24, 26,$ and 68 nanoparticles are 3.933 eV/atom, 3.977 eV/atom, and 4.029 eV/atom for Si_N and 2.371 eV/atom, 2.369 eV/atom, and 2.467 eV/atom for Ga_N (with 13 valence electrons),

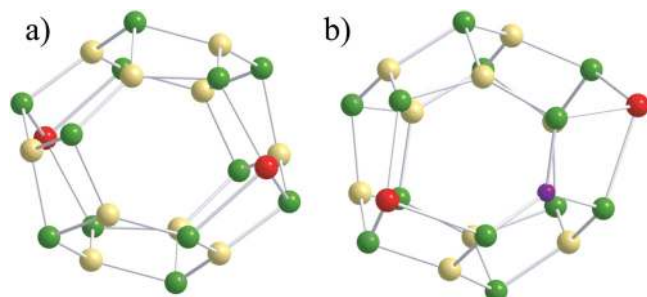


FIG. 3. Atomic structures of (a) two Eu doped $(\text{GaN})_{12}$ and (b) two Eu + Si co-doped $(\text{GaN})_{12}$ nanoparticles. Yellow, green, red, and violet balls show Ga, N, Eu, and Si atoms, respectively.

respectively. The values of the formation energy are -2.715 eV, -2.841 eV, and -3.024 eV, respectively, for $n=12, 13,$ and 32 GaN nanoparticles doped with one Eu and codoped with a Si atom considering three valence electrons on Ga. These results suggest that Si co-doping is strongly favorable in GaN nanoparticles.

We also investigated the effects of including 3d electrons of Ga as valence electrons on the properties of Eu and Eu + Si co-doped GaN nanoparticles. It has been found that 3d electrons could have significant effect on the properties of bulk GaN.⁴³ However, our calculations on pure GaN nanoparticles as well as doped nanoparticles show that the conclusions of the present work remain intact. In all cases, we find an increase in E_b by about 0.05 eV/atom. In Table II, we have compared the values of the binding energy for $n=32$ case and the change in going from three valence electrons to thirteen valence electrons on Ga is small. Also, we calculated the formation energy of the Si co-doping in the case of $n=12$ GaN nanoparticle doped with a Eu atom and it is -2.570 when 13 electrons are considered as valence on Ga as compared to the value of -2.715 eV when three valence electrons are considered on Ga. Therefore, the effect of the inclusion of 3d electrons on Ga as valence is small.

Earlier studies³⁴ on doping of two RE atoms such as Gd and Nd in small GaN nanoparticles have shown that the binding energy decreases slightly when two Gd or two Nd atoms are doped in $n=12$ and 22 nanoparticles as compared to a case where only one RE atom is doped. This suggests that if possible, RE atoms will tend to be away from each other. We performed some calculations on the doping of two Eu atoms in $(\text{GaN})_{12}$ nanoparticles as shown in Fig. 3 and the binding energy is 3.648 eV/atom and 3.661 eV/atom in the case of one and two Eu atoms, respectively, considering 13 valence electrons on Ga. Therefore, there is a small increase in the binding energy for the doping of two Eu atoms and the coupling is ferromagnetic with the total magnetic moments of $12\mu_B$. However, in the case of $n=32$ nanoparticle, the binding energy decreases slightly to 3.846 eV/atom (2 Eu atoms doped) from the value of 3.849 eV/atom (1 Eu atom doped). We conclude that there is only a small change in the binding energy when two Eu atoms are doped and therefore it is possible that small nanoparticles could be also doped with more than one Eu atom. If a Si atom is co-doped with two Eu atoms, then again there is a large gain in the binding energy and for $n=32$ nanoparticle the binding energy becomes 3.933 eV/atom with the magnetic moment of $13\mu_B$ and a large heat of formation of -4.027 eV.

TABLE II. A comparison of the binding energies (E_b) of $(\text{GaN})_n$, $n=32$ pure, Eu, and Eu + Si co-doped nanoparticles by considering 3 and 13 valence electrons on Ga.

System	E_b (eV/atom)	
	3e	13e
GaN	3.790	3.844
GaN:Eu	3.796	3.849
GaN:2Eu	3.794	3.846
GaN:2Eu + Si	3.882	3.933

Therefore, Si doping in such nanoparticles is highly favorable.

B. Electronic structure

The density of states (DOS) for the doping of one Eu atom as well as co-doping of Eu and Si in $(\text{GaN})_{12}$ nanoparticles is shown in Fig. 4. Eu on a Ga site is in a +3 state and the net magnetic moment on this cluster is $6\mu_B$. The spin-up $4f$ states lie close to the top of the GaN valence states and there is a hole. On the other hand, the spin-down states lie in the unoccupied region and hybridize with the states of Ga and N. In the case of Si co-doping, the electronic configuration of Eu ion tends to be a +2 state and there is a net magnetic moment of $7\mu_B$ with all the spin-up $4f$ states fully occupied. The $4f$ states shift upward due to effectively less positive charge on the Eu ion and the spin-up $4f$ states lie in the HOMO-LUMO gap above the valence states of GaN nanoparticle. This leads to a reduction in the hybridization between the Eu $4f$ spin-up states and the GaN bonding states making the spin-up Eu $4f$ states peak sharper. The magnetic moments are mostly localized on Eu ions as shown in the insets in Fig. 4. There is some spin-down polarization on the neighboring sites. The larger magnetic moment with Si co-doping is in agreement with the experimental finding⁴⁴ of enhanced magnetism in Si and Eu co-doped films of GaN compared with only Eu doped films.

As the $4f$ states are localized, we further studied the effect of on-site Coulomb interaction within the GGA + U formalism by taking an effective U value of 6 eV for Eu $4f$ electrons. The total and partial DOS using GGA + U formalism are also given in Fig. 4. For one Eu doping in $(\text{GaN})_{12}$, the $4f$ spin-up states shift deeper in the valence states of GaN nanoparticles and the spin-down states shift upward in the conduction states of GaN so that there is more hybridization between Eu $4f$

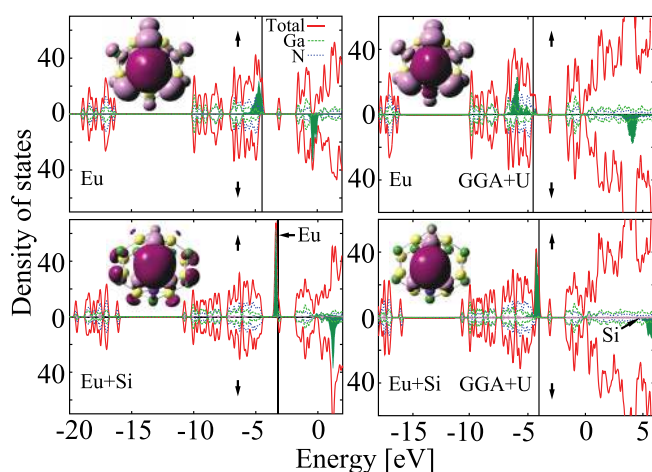


FIG. 4. The total density of states (DOS) obtained by Gaussian broadening of the energy states (red color) for Eu doped and Eu + Si co-doped $(\text{GaN})_{12}$ nanoparticles using GGA and GGA + U formalisms. Up and down arrows show the spin-up and spin-down states, respectively, and the vertical line shows the HOMO. Green color filled regions represent Eu $4f$ states, while pink curve shows Si partial DOS. The brown (full line) and blue (broken line) curves show, respectively, the Ga and N partial DOS. The insets show the spin-polarization iso-surfaces with dark (light) color showing spin-up (spin-down) distribution.

states and the GaN states. This leads to the broadening of the distribution of $4f$ states. In the case of Si co-doping, the spin-up Eu $4f$ states lie close to the top of the valence states of GaN and are fully occupied while the spin-down $4f$ states are shifted significantly upwards as shown in Fig. 4. In this case also the distribution of the $4f$ states is broadened. There are some changes in the distribution of the spin-polarization when GGA + U is used, but the main feature that the spins are mainly localized on Eu site remains the same.

For the purpose of comparison, the total and partial DOS for the doped nanoparticles ($n = 13$ and 32) are shown in Fig. 5 using the GGA + U formalism. The main features of the electronic states are similar to those discussed above for the $n = 12$ case. The distribution of the $4f$ states is slightly different in nanoparticles of different sizes (see Figs. 4 and 5) due to the different local environments but they appear at similar energies and the main features are also quite similar. The partial DOS shows the dominant contributions of Ga and N states in the occupied and unoccupied regions and therefore the bonding is polar covalent. The HOMO-LUMO gap and E_b have been calculated and the values are given in Table I. Within GGA, Eu doping in GaN nanoparticles is energetically favorable, but in GGA + U calculations it costs 0.45 eV for $(\text{GaN})_{12}$, 0.16 eV for $(\text{GaN})_{13}$, and 0.28 eV for $(\text{GaN})_{32}$. This is a relatively small energy compared with the cost in bulk GaN. The slight change in the results from energy gain within GGA in doping Eu in nanoparticles as compared to a cost within GGA + U is also consistent with the behavior²⁶ in bulk GaN, where Eu doping costs 1.84 eV in GGA, while in GGA + U, the energy cost increases to 2.02 eV. Even considering the results obtained from GGA + U calculations, the important point is that it costs much less energy to dope Eu in GaN nanoparticles compared with bulk GaN. Accordingly, Eu doping can be better achieved in nanoparticles compared with bulk GaN. Co-doping with Si further facilitates Eu doping in nanoparticles as obtained both within GGA and GGA + U calculations.

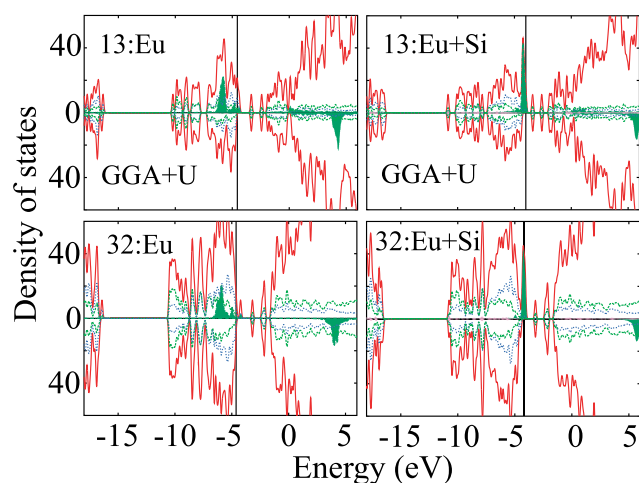


FIG. 5. The total DOS (red curve) and the partial DOS for Ga (brown full line), N (blue broken line), Eu (green filled curve), and Si (pink curve) obtained by using GGA + U method for Eu and Eu + Si doped in $(\text{GaN})_{13}$ and $(\text{GaN})_{32}$ nanoparticles.

In Fig. 6, we have shown the DOS for a $(\text{GaN})_{12}$ nanoparticle doped with one Eu atom as well as for the case of co-doping with one Eu and a Si atom by considering 13 valence electrons on Ga. When compared with the DOS in Fig. 4, one can see that the main features in DOS near the HOMO and the LUMO remain intact. There are sharp peaks near -18 eV and this arises from the 3d states of Ga. These results reassure that the results of the calculations performed with three valence electrons on Ga are quite good and describe the important states near the HOMO and LUMO quite well.

IV. SUMMARY

In summary, we have shown that Eu doping in GaN nanoparticles is easier to achieve compared with Eu doping in bulk GaN. The strain is significantly reduced in GaN nanoparticles because of the presence of surface than its bulk counterpart where Eu is associated with N vacancy as a neighbor. The Eu-N bond is longer than Ga-N bond and Eu generally favors sp^3 bonding site (rhombus site) that has longer Ga-N bond lengths in nanoparticles. Si co-doping further facilitates Eu doping with a large energy gain due to compensation of strain from an over-sized and an under-sized dopant. Therefore, co-doping is an interesting strategy to stabilize rare earths in GaN and other hosts. Nanoparticles form an important route to develop efficient luminescent materials and Eu occupies less symmetric sites in nanoparticles

compared with bulk and that can facilitate intra $4f$ level transitions. The structural transition from empty to filled cage due to Eu doping in GaN nanoparticles is, however, not observed in the size range we have studied in the present work due to strong preference for sp^2 bonding and shorter Ga-N bonds present in nanoparticles compared with bulk GaN. However, the energy difference between the empty cage and filled cage structures of the doped nanoparticles is significantly reduced compared with the corresponding isomers of undoped nanoparticles. Co-doping of Si also helps to reduce the difference. It is therefore expected that with an increase in size, the doped nanoparticles may attain 3D structures faster than the undoped nanoparticles. Our results also suggest that in larger nanoparticles Eu doping may occur on a subsurface site as the surface atoms may continue to prefer sp^2 type of bonding in which the GaN bond length is contracted.

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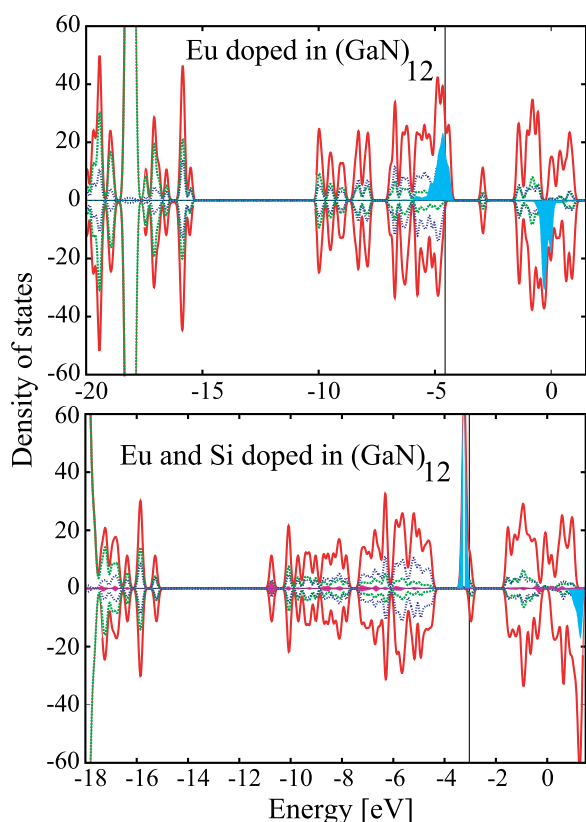


FIG. 6. The total (red curve) and partial DOS (green curve for Ga and blue curve for N) for the doping of one Eu and co-doping of one Eu and a Si atom in $(\text{GaN})_{12}$ nanoparticle by considering 13 valence electrons on Ga. The Eu states are shown in greenish blue filled curve. The vertical line shows the HOMO.

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