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Prediction of rock salt structure of $(\text{InN})_{32}$ nanoparticles from first principles calculations

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

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

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

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

⁴*Center for Informatics, School of Natural Sciences, Shiv Nadar University, Chithera, Gautam Budh Nagar 203207, U.P., India*

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From first principles calculations, we show that $(\text{InN})_{32}$ nanoparticles favor rock salt structure compared with wurtzite structure in bulk. A phase transition from wurtzite to rock salt structure is known to occur in bulk InN at 12.1 GPa and higher values of pressure for AlN and GaN. However, at the nanoscale we show that this structural transition takes place in $(\text{InN})_{32}$ without applying pressure. The charge asymmetry value “g” and cation/anion size ratio in InN describe very well this behavior. Similar studies on nanoparticles of AlN and GaN as well as a few other binary compounds such as MgS, AgI, ZnO, and CdSe, however, do not show such a transition. Our results suggest $(\text{InN})_{32}$ to be a unique candidate as further calculations on a few larger size $(\text{InN})_n$ nanoparticles show that a filled cage (two shells) $(\text{InN})_{12} @ (\text{InN})_{48}$ structure of $(\text{InN})_{60}$ has higher binding energy compared with a rock salt structure of $(\text{InN})_{64}$ leading to the conclusion that other 3D structures are likely to become favorable over rock salt structure for larger sizes. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4795580>]

I. INTRODUCTION

The atomic structure of small nanoparticles with diameter of ~ 1 nm is often quite different from bulk as a large fraction of atoms lies on the surface and this generally leads to very significant size dependent reconstruction. In most cases, the lowest energy structure has little similarity to known crystalline phases. Moreover, the physical and chemical properties are size dependent due to quantum confinement and this makes small nanoparticles attractive to design materials with desired properties. Therefore, finding of novel species has been one of the important directions in cluster science. In most cases, however, it is still not known at what size nanoparticles start having bulk atomic structure. Recently, nanoparticles of $(\text{PbS})_n$ have been shown to attain bulk rock salt structure at a small size of $n = 32$. Accordingly $(\text{PbS})_{32}$ has been termed¹ as “magic baby crystal” because $n = 32$ is the critical size which can adopt bulk-like six-fold co-ordination and it can be replicated to form larger nanoparticles as well as bulk material. In this case, the atomic structure of nanoparticles is the same as in bulk. However, the mean bond distances in nanoparticles are generally shorter compared with bulk and along with surface tension this acts as compression of the bulk structure. As phase transitions often occur in bulk under pressure, an interesting question is whether such structural transition could occur in nanoparticles without applying pressure. In some cases, experimental studies^{2,3} have shown structural transitions in nanoparticles at a pressure which is suggested to be higher compared with the bulk value. Notably, a phase transition from wurtzite (four-fold coordination) to rock salt (six-fold coordination) structure has been shown⁴⁻¹⁶ to occur in III-V and II-VI compound semiconductors. In this pa-

per, however, we show that $(\text{InN})_{32}$ nanoparticle adopts rock salt structure as the lowest energy structure even without applying any pressure suggesting that in some cases nanoparticles may have structures that are observed under pressure in bulk.

Earlier studies⁷ have shown bulk InN to undergo a transition from wurtzite to rock salt structure, i.e., a transition from four-fold to six-fold coordination at 12.1 GPa pressure while for GaN and AlN, such a transition occurs at 52.2 GPa and 22.9 GPa, respectively.^{7,8} The magnitude of pressure reduces in the order $\text{GaN} > \text{AlN} > \text{InN}$. Phase transitions in such binary compounds have been correlated to the value of charge asymmetry factor “g” by Garcia and Cohen.¹⁷ It is a measure of the charge asymmetry along a bond $\rho_A = [\rho(\mathbf{r}) - \rho(-\mathbf{r})]/2$ (the origin of the coordinates being taken at halfway between the two atoms forming the bond) and $\rho(\mathbf{r})$ is the charge density at a point \mathbf{r} . It is related to the ionicity in a material. The value of g lies between 0 and 1. A value of zero corresponds to a homopolar material while strongly ionic materials will have value close to 1. Among III-N’s, the value of g (0.853) for InN (wurtzite structure) is the closest to the value of 0.958 for NaCl (rock salt structure) and it reduces to 0.794 and 0.780 for AlN and GaN, respectively. Clusters of alkali halides such as NaI (rock salt structure) are known¹⁸ to be cuboids. There is a possibility that InN could exhibit rock salt structure at the nanoscale even without applying pressure and if so, it would be an unusual result with wider implications for other nanomaterials. In our earlier study on III-V compound semiconductor nanoparticles,¹⁹ we have found that $n = 32$ size nanoparticles are magic for GaP, AlP, and as well as for their arsenides. But, most interestingly we found that among III-N nanoparticles, $(\text{InN})_{32}$ favored a filled cage structure with a

(InN)₄ unit inside a (InN)₂₈ cage. On the other hand unlike (InN)₃₂, empty cage structures^{19,20} are favorable for (AlN)₃₂ and (GaN)₃₂. However, here we demonstrate that a rock salt structure of (InN)₃₂ is even more favorable than a filled cage. Therefore, a phase transition occurs in InN nanoparticles even without applying any pressure to a structure that bulk InN adopts under pressure. Accordingly our results suggest that nanostructures of some materials can have a different *crystal* structure than what they have in bulk. We discuss the reasons for the phase transition and also study a few clusters of InN with smaller as well as bigger sizes in order to study the range of the stability of cubic structure. Further, we explore the possibility of such a structural phase transition in nanoparticles of a few other binary compounds, e.g., MgS, ZnO, CdSe, and AgI.

In Sec. II, we present our computational approach while in Sec. III, results of our study are given. A summary is given in Sec. IV.

II. COMPUTATIONAL METHOD

The calculations have been performed using projector augmented wave pseudopotential plane wave method²¹ and generalized gradient approximation (GGA)²² for the exchange-correlation energy. The cut-off energy for the plane wave expansion is taken to be 400 eV. The nanoparticles are placed in a cube of side 20 Å with periodic boundary conditions. The ionic positions are optimized using only the Γ -point in the Brillouin zone until the force on each ion becomes less than 0.005 eV/Å and the energy is converged within 0.0001 eV. The cut-off energy for the plane wave expansion in other systems is taken as the default value for medium precision given in VASP.²¹ For bulk, calculations have been performed with high precision to optimize the cell volume. Bader analysis has been performed in order to obtain charges on different ions.

III. RESULTS

As recent studies¹⁹ on nanoparticles of III-V compound semiconductors have shown the stability of a filled cage structure for (InN)₃₂, to begin with we studied the atomic structure of (PbS)₃₂ by optimizing two structures: (i) a baby crystal structure (rock salt) which has been reported recently¹ and (ii) a filled cage structure which is built of a cage of (PbS)₂₈ with hexagons and four-membered rings similar to that of (BN)₂₈ and a (PbS)₄ unit inside that has been recently found¹⁹ to be favorable for (InN)₃₂ compound semiconductor nanoparticles. The optimized structures show that the rock salt structure is indeed 6.837 eV lower in energy than the filled cage structure. Also interestingly the optimized filled cage structure has an inherent tendency to relax towards the rock salt structure as the filled cage distorts completely with hexagonal units transforming to rhombus units. Thus, our results support the finding of baby crystals of PbS. With this check on (PbS)₃₂, we further compared the energies of both the rock salt and filled cage structures for (InN)₃₂. Both the optimized structures are shown in Fig. 1. Interestingly for this size of InN nanoparticles, the rock salt structure is not only stable but

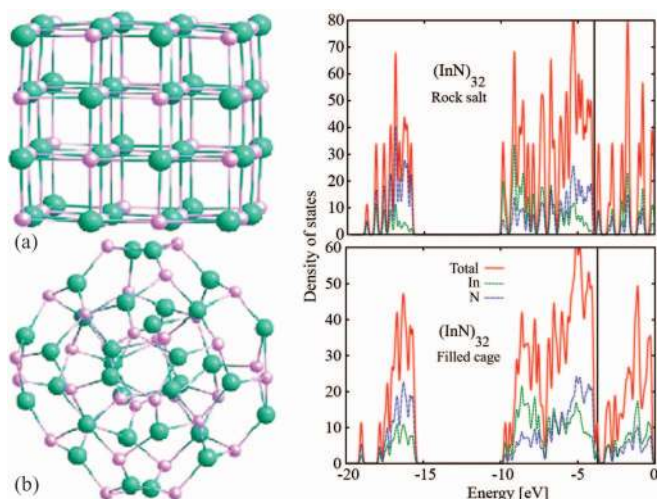


FIG. 1. (a) Rock salt structure and (b) filled cage structure of (InN)₃₂ nanoparticle with (InN)₂₈ cage and (InN)₄ inside. The (InN)₃₂ rock salt isomer is 2.072 eV lower in energy than the filled cage isomer. Green (pink) balls represent In (N) atoms. The total (red curve) and partial (blue curve for N and green curve for In) densities of states obtained by Gaussian broadening of the electronic states are shown for (InN)₃₂ rock salt structure as well as for filled cage isomer.

also it is 2.072 eV lower in energy than the filled cage structure predicted earlier.¹⁹ Therefore, (InN)₃₂ does transform to rock salt structure even without applying any pressure.

In order to explore the stability of the rock salt structure for other sizes of InN nanoparticles, we further calculated the energies of both the rock salt and cage structures of (InN)_n, for $n = 4, 8, 16,$ and 64 , i.e., smaller and bigger sizes than $n = 32$. Note that in the earlier studies¹⁹ on (InN)₁₂, empty cage structure has been found to be favorable. The optimized structures are shown in Fig. 2. $n = 4$ is the smallest size that could form a cubic unit of (InN)₄. However, we find that (InN)₄ has a ring structure (4a in Fig. 2) with alternate In and N atoms and it is 0.58 eV lower in energy compared with a rock salt

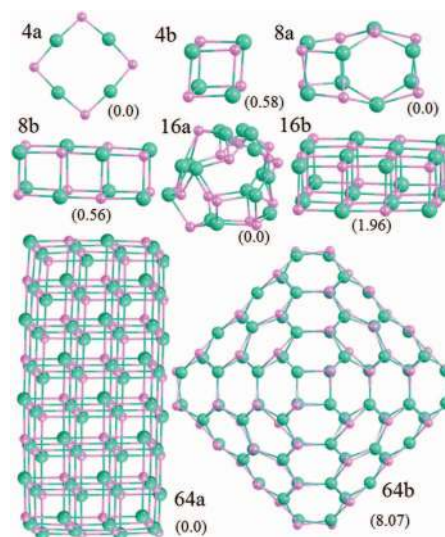


FIG. 2. The atomic structures of isomers of (InN)₄, (InN)₈, (InN)₁₆, and (InN)₆₄ nanoparticles. The energy difference between the lowest energy structure (taken as reference) and the other isomer is given in brackets. All the energy values are in eV. Green (pink) balls represent In (N) atoms.

isomer which is stable as shown in Fig. 2, 4b. For $(\text{InN})_8$, $(\text{InN})_{16}$, and $(\text{InN})_{64}$ nanoparticles, we have considered empty cage structures following earlier work^{19,20} as well as rock salt structure such that $(\text{InN})_8$ is formed of two cubes and $(\text{InN})_{16}$ nanoparticle has the structure in which two such units are joined together or it is half the portion of $(\text{InN})_{32}$ as shown in Fig. 2, 16b. Similarly for $(\text{InN})_{64}$, we considered two $(\text{InN})_{32}$ units joined together. It is found that after optimization the isomers with rock salt structure retain the atomic structure with some relaxation but cage structure is favorable for $n = 8$ and 16 over the rock salt structure. The cage corresponding to $n = 8$ (8a in Fig. 2) is made of a structure corresponding to $n = 6$ which is favored by clusters of many II-VI and III-V compounds and a rhombus is attached on it. The initially cage structure of $(\text{InN})_{16}$ with hexagons and rhombi distorts after optimization and the hexagonal units tend to transform to rhombus units (Fig. 2, 16a). The energy of the cage structure is 1.96 eV lower than the respective rock salt structure (16b in Fig. 2). On the other hand, a cage structure for $n = 16$ is stable for both AlN and GaN without distortion. It indicates that the behavior of InN nanoparticles is different from those of AlN and GaN and that the structure of $n = 16$ corresponds to an intermediate stage between cage structures and rock salt crystal structure of InN nanoparticles. In Table I, the energies of various considered atomic structures of InN nanoparticles are presented.

For $(\text{InN})_{64}$, we considered a symmetric octahedral cage²⁰ and an isomer with rock salt crystal structure comprised of two $(\text{InN})_{32}$ stacked cubic units as shown in Fig. 2. Interestingly, for this size also the isomer with rock salt crystal structure lies lower in energy than the empty cage isomer with a significant energy difference of 8.07 eV. Further,

TABLE I. Energy difference between isomers considered (favorable is shown with asterisk, positive value means rock salt crystal structure is favorable while negative value means the other respective structure is favorable) for each size, binding energy per atom, and the HOMO-LUMO gap of $(\text{InN})_n$, $n = 4, 8, 16, 32$, and 64 nanoparticles. The corresponding values for $(\text{MgS})_{32}$, $(\text{CdSe})_{32}$, $(\text{ZnO})_{32}$, and $(\text{AgI})_{32}$ nanoparticles are also given.

System	Atomic sizes	Isomers	Δ (eV)	BE/atom (eV)	Gap (eV)
InN	4	Rock salt	-0.58	2.32	0.06
		Ring*		2.40	1.00
	8	Rock salt	-0.56	2.72	0.57
		Empty cage*		2.76	0.18
	16	Rock salt	-1.96	2.98	0.04
		Empty cage*		3.04	0.42
32	Rock salt*	2.07	3.17	0.48	
	Filled cage		3.14	0.59	
64	Rock salt*	8.07	3.27	0.02	
	Empty cage		3.20	0.49	
MgS	32	Rock salt*	2.31	3.69	2.81
		Filled cage		3.65	3.13
CdSe	32	Rock salt	-8.90	2.10	0.73
		Filled cage*		2.23	1.99
ZnO	32	Rock salt	-6.01	3.30	1.23
		Empty cage*		3.39	1.83
AgI	32	Rock salt	-0.67	2.16	2.09
		Filled cage*		2.17	2.14

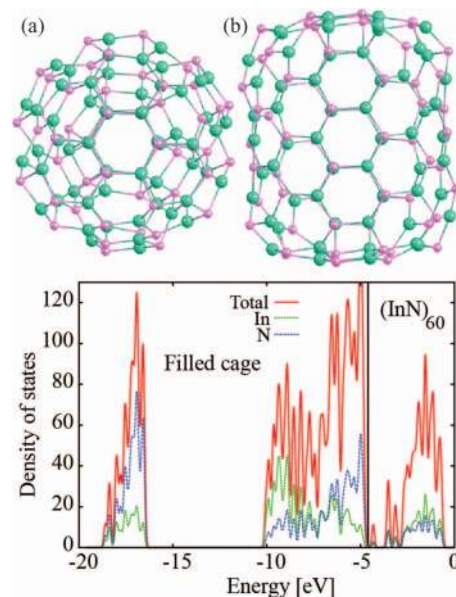


FIG. 3. The atomic structures of (a) filled cage $(\text{InN})_{12} @ (\text{InN})_{48}$ and (b) empty cage isomer of $(\text{InN})_{60}$. The empty cage isomer lies 8.07 eV higher in energy than the filled cage isomer. The Gaussian broadened total and the partial densities of states for the filled cage isomer are also given. Other details are as in Fig. 1.

we performed preliminary studies on $(\text{InN})_{60}$ nanoparticles for which a filled cage isomer with two shells was also considered. We compared the binding energies of $(\text{InN})_{60}$ empty and filled cages (Fig. 3) with $(\text{InN})_{64}$ empty cage as well as rock salt structures. The values are 3.20, 3.29, 3.20, and 3.27 eV/atom, respectively. These results show that in empty cage structures the binding energy per atom changes slowly and that is expected. But such structures are not favorable for InN nanoparticles in this size range. The binding energy per atom is higher for $(\text{InN})_{60}$ filled cage among all the structures we studied. Shevlin *et al.*²⁰ have also predicted higher stability of 60 filled cage of nanoparticles of III-nitrides. The two shell filled cage to be referred to $(\text{InN})_{12} @ (\text{InN})_{48}$ is very symmetric and is comprised of a $(\text{InN})_{12}$ symmetric unit fitted inside a symmetric $(\text{InN})_{48}$ cage.²⁰ Our results support this finding. The binding energy of the rock salt isomer of $(\text{InN})_{64}$ is lower compared with the value for the filled cage isomer of $(\text{InN})_{60}$. Generally, the binding energy per atom is expected to increase with increasing size of the nanoparticles and converge to the bulk value. As InN has wurtzite structure in bulk, a structural transition from rock salt to other structures is very likely with an increasing size unlike in nanoparticles of PbS for which the crystal structure is rock salt. Therefore, our preliminary results on larger size nanoparticles of InN suggest that already around $n = 60$ a structural transition may occur where rock salt structure is either not favorable or other structures become very competitive. Further detailed study of nanoparticles around these sizes would be required to understand properly this transition.

The above results suggest that in the growth behavior of InN nanoparticles, $n = 32$ is a critical size for which a symmetric rock salt crystal structure is favorable and a structural transition may occur around the size of $n = 60$ such that the atomic structures may have similarity to those that may be

avored by other compound semiconductors with wurtzite bulk structure such as CdSe and this would require more detailed studies.

For $n = 32$, we also optimized the same structures of iso-valent $(\text{AlN})_{32}$ and $(\text{GaN})_{32}$, but unlike $(\text{InN})_{32}$ these compound nanoparticles favor empty cage structures that were predicted earlier.^{19,20} We find that the empty cage structures for $(\text{AlN})_{32}$ and $(\text{GaN})_{32}$ are, respectively, 1.839 eV and 12.964 eV lower in energy than the rock salt structure. Therefore, energetically the tendency to transform to rock salt structure in nanoparticles of III-N compound semiconductors is in the order of $\text{GaN} < \text{AlN} < \text{InN}$. This trend is consistent with the value of pressure under which these compound semiconductors undergo a transition^{7,8} to rock salt structure in bulk, i.e., GaN (52.2 GPa) $<$ AlN (22.9 GPa) $<$ InN (12.1 GPa) as mentioned above except that in $(\text{InN})_{32}$ nanoparticles this transition occurs without applying pressure.

It is to be noted that in bulk InN , our calculations give the nearest neighbour bond distance to be 2.21 Å while in the filled cage isomer which has the bonding characteristics similar to bulk, the nearest neighbour bond distances lie in the range of 2.00–2.40 Å. Therefore, there is a compression of bond distances in nanoparticles while some bond distances also expand. A compression in bond lengths is also found in the rock salt structure as for $(\text{InN})_{32}$ nanoparticle the nearest neighbour bond distances lie in the range of 2.23–2.299 Å while in the bulk rock salt structure of InN we obtained the value of 2.36 Å. A larger value of the nearest neighbour bond distance in the rock salt structure is due to higher coordination number of atoms. Our results suggest that this compression is large enough in $(\text{InN})_{32}$ to lead to a structural transition to a denser phase in order to reduce the surface energy. As the nanoparticle size increases, the nearest neighbour bond distance tends to increase towards the bulk value. Then we expect a transition from rock salt structure to other isomers with an increase in size. In AlN and GaN nanoparticles, the bond shortening is not sufficient to lead to a transition to cubic rock salt structure.

The total and the partial electronic densities of states for the rock salt and filled cage isomers of $(\text{InN})_{32}$ are also shown in Fig. 1. The partial densities of states of In and N atoms show significant covalent bonding in nanoparticles and a larger contribution from nitrogen $2p$ valence states indicating ionic character due to the charge transfer from In to N. Bader charge analysis shows charge transfer of ~ 0.88 e– 1.18 e from In to N (on N sites charge varies from -0.96 e to -1.19 e). A similar analysis for the filled cage isomer shows 1.05 e to 1.24 e charge transfer from In to N sites (on N sites the charge varies from -0.84 e to -1.26 e). The variation in the charge transfer is due to different environment of ions. The rock salt isomer has smaller HOMO-LUMO gap (0.48 eV) as compared to the value (0.59 eV) for the filled cage isomer, though in both the isomers it is small. The density of states in the rock salt isomer shows sharper peaks as compared to that of the filled cage isomer mainly because of the higher symmetry in the rock salt structure. However, the overall features in the two cases appear to be similar. The total and partial densities of states for the filled cage isomer of $(\text{InN})_{60}$ are shown in Fig. 3.

The overall features are similar to those obtained for the $n = 32$ case as shown in Fig. 1 and the HOMO-LUMO gap is quite small.

This behavior of nanoparticles of III-N compound semiconductors could be correlated with the value of the charge asymmetry parameter “ g ” as suggested by Garcia and Cohen¹⁷ for the bulk systems. Traditionally, the ionic radii of cations and anions have been used to understand the phase stability of ionic solids with the idea of close packing. According to Pauling’s rules,²³ if the cation (R_+)/anion (R_-) radius ratio of any system lies in the range of $0.414 > R_+/R_- > 0.225$, then it favors four coordination in its atomic structure with the cation occupying a tetrahedral interstitial site. On the other hand, if the radius ratio lies in the range of $0.732 > R_+/R_- > 0.414$, then the system favors six coordination, i.e., rock salt structure with the cation occupying an octahedral site. The R_+/R_- ratio for AlN , GaN , and InN is 0.366, 0.424, and 0.548, respectively. Therefore from Pauling’s criterion, InN should exhibit rock salt structure, and GaN is at the boundary line to exhibit rock salt structure while AlN will have four-fold coordination of cations. However, InN has wurtzite structure in bulk and not the rock salt. Therefore, Pauling’s criterion is not satisfactorily obeyed in these compounds as the bonding also has significant covalent contribution. What we find is that in nanoparticles, $(\text{InN})_{32}$ does transform to rock salt structure but this is not the case for $(\text{GaN})_{32}$, as the rock salt structure is 12.964 eV higher in energy and for $(\text{AlN})_{32}$, it is 1.839 eV higher in energy than the empty cage. Thus, phase transitions in such compounds containing first row elements such as N cannot be explained on the basis of their ionicity values alone. The lack of core p states makes their pseudopotential for valence $2p$ orbitals strongly attractive and there are large electronegativities and charge asymmetries.¹⁷ Accordingly the “ g ” value prescription of Garcia and Cohen¹⁷ that takes in to consideration charge asymmetry reasonably explains the behavior of III-N in bulk and this trend is also obeyed in their nanoparticles. The “ g ” value is the largest (0.853) for InN while for GaN and AlN this has the value of 0.78 and 0.794, respectively. In nanoparticles, these values are likely to change slightly due to change in the interatomic bond distances as well as the hybridization. However, the dominant bonding character remains nearly the same and our interest to use the “ g ” values here is to understand the structural trend which comes out in the right direction. The pressure needed for transition to rock salt structure in InN bulk is the least and because of the larger “ g ” value for AlN , it undergoes transition to rock salt phase at a lower pressure than GaN . For nanoparticles, we find that the rock salt structure is favored even without pressure for $(\text{InN})_{32}$ while for $(\text{GaN})_{32}$ the energy difference between the rock salt and empty cage structures is higher than in $(\text{AlN})_{32}$. The latter two systems do not adopt rock salt structure in nanoparticles at zero pressure. Thus, the contraction in the bond lengths as well as surface tension is sufficient to cause a transition in InN but not in GaN and AlN . It is possible that the bond shortening in nanoparticles also causes some changes in the charge transfer in these systems as compared to bulk. However, our results suggest that charge asymmetry factor “ g ” as obtained for bulk systems is a reasonable factor to explain the

transition in InN nanoparticle to rock salt structure as well as the trend in the behavior of III-N nanoparticles. Besides (AlN)₃₂, (GaN)₃₂, and (InN)₃₂, we also optimized rock salt crystal structure for III-P and III-As with $n = 32$. But unlike (InN)₃₂, no other compound we studied undergoes a transition from wurtzite to rock salt phase at zero pressure.

In order to check a few other cases if we can find a different crystal structure of a material at the nanoscale than what it has in bulk, we have considered (MgS)₃₂, (CdSe)₃₂, (ZnO)₃₂, and (AgI)₃₂ nanoparticles. In Table I, we have included the energies of the nanoparticles of these four binary compounds along with the values for the nanoparticles of InN. MgS is an interesting candidate to explore as in bulk it is at the boundary line of four-fold to six-fold coordination transition.¹⁷ The energies of the optimized empty as well as filled cage structures, and the rock salt baby crystal structure of (MgS)₃₂ show that the rock salt structure is 2.314 eV lower in energy than the filled cage isomer and further the empty cage is 5.398 eV higher in energy than the rock salt structure. (MgS)₃₂ rock salt structure has higher binding energy as well as smaller HOMO-LUMO gap than the filled cage isomer (Table I). It is to be noted that in bulk, MgS has rock salt structure. So this case is similar to PbS and there is no transition.

Next, we considered filled cage and rock salt structure isomers for (CdSe)₃₂. For this system, earlier studies²⁴ have shown filled cage isomer to be the most favorable structure. We also find that a filled cage isomer is 8.899 eV lower in energy than the rock salt structure. Therefore, CdSe is not the right candidate. We further explored (ZnO)₃₂ and (AgI)₃₂ binary nanoparticles. For (ZnO)₃₂, an empty cage is 6.005 eV lower in energy than the rock salt structure. On the other hand for (AgI)₃₂, the filled cage structure is 0.67 eV lower in energy than the rock salt structure. All the three compounds CdSe, ZnO, and AgI have wurtzite structure in bulk. The lowest energy atomic structures of (CdSe)₃₂, (ZnO)₃₂, and (AgI)₃₂ also have larger HOMO-LUMO gaps than the respective higher energy structure as it is clear from Table I. For (AgI)₃₂, the rock salt structure has an inherent tendency to transform to filled cage structure as the rhombus units relax to form hexagonal rings. It is to be noted that this behavior of (AgI)₃₂ is opposite to that of (PbS)₃₂, in which the filled cage structure undergoes transition to rock salt structure. Therefore at the nanoscale, the phase transition is material specific and it is important to understand this behavior. Our studies on nanoparticles of a few systems suggest that (InN)₃₂ is unique in showing a structural transition to rock salt crystal structure at zero pressure.

IV. SUMMARY

In summary, we have shown from first principles calculations that (InN)₃₂ nanoparticle favors a rock salt crystal structure though in bulk, InN crystallizes in wurtzite structure. Accordingly, a structural transition occurs even without applying any pressure in nanoparticles while in bulk such a transition occurs at 12.1 GPa. Further, in nanoparticles of a few other compounds that we studied, this transition does not take place at zero pressure. The cation/anion size ratio as well

as charge asymmetry factor “g” supports this phase transition in (InN)₃₂. Further preliminary studies on larger sizes of InN nanoparticles suggest that already around $n = 60$ the rock salt structure will transform to other structures as the bulk structure is wurtzite. We believe that the result of our study is important in the context of compound semiconductors as well as other systems because of applications in electronic, optical, and magnetic devices as well as in catalysis. It would be interesting to further explore larger nanoparticles and if rock salt structure would continue to be favored for some other sizes. Also capping with different ligands can throw further possibilities of structural transition which should be explored from the applications point of view as often nanoparticles are capped in order to protect them.

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