

Size dependence of the bulk modulus of semiconductor nanocrystals from first-principles calculations

R. Cherian,^{1,*} C. Gerard,^{1,2} P. Mahadevan,^{1,†} Nguyen Thanh Cuong,³ and Ryo Maezono⁴

¹*Department of Material Science, SN Bose National Centre for Basic Sciences, Block JD, Sector III, Salt Lake, Kolkata 700 098, India*

²*Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*

³*Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology, Umezono 1-1-1, Tsukuba 305-8568, Japan*

⁴*School of Information Science, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan*

(Received 20 April 2010; revised manuscript received 22 October 2010; published 27 December 2010)

The variation in the bulk modulus of semiconductor nanoparticles has been studied within first-principles electronic-structure calculations using the local density approximation (LDA) for the exchange correlation. Quantum Monte Carlo calculations carried out for a silicon nanocrystal $\text{Si}_{87}\text{H}_{76}$ provided reasonable agreement with the LDA results. An enhancement was observed in the bulk modulus as the size of the nanoparticle was decreased, with modest enhancements being predicted for the largest nanoparticles studied here, a size just accessible in experiments. To access larger sizes, we fit our calculated bulk moduli to the same empirical law for all materials, the asymptote of which is the bulk value of the modulus. This was found to be within 2–10 % of the independently calculated value. The origin of the enhancement has been discussed in terms of Cohen's empirical law [M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985)] as well as other possible scenarios.

DOI: [10.1103/PhysRevB.82.235321](https://doi.org/10.1103/PhysRevB.82.235321)

PACS number(s): 62.25.-g, 71.15.Mb, 73.22.-f

I. INTRODUCTION

The physics and chemistry of size reduction has been a topic of intense research activity over the past two decades.¹ From a technological point of view, the interest has been spearheaded by the fact that the synthesized materials show dramatic enhancements in their optical properties,² enhanced mechanical properties among a long list of properties different from the bulk of the same material. Although the science of size reduction has seen a flurry of activity recently, the use of nanomaterials for enhanced strength of materials dates back hundreds of years to the medieval times. A recent study pointed out that the extreme strength of Damascus swords originated from the carbon nanotubes present in them.³

The specific aspect of enhanced mechanical properties in the nanoscale regime has thrown open several candidates. Enhanced Young's modulus of ZnO nanowires and nanotubes⁴ have been found. Enhanced bulk moduli have been observed in nanocrystals of AlN (Ref. 5) and CeO_2 .⁶ Semiconductor nanoparticles show structural phase transitions under pressure. It is found that these transition pressures also change between the bulk material and the nanocrystal. In addition, the bulk modulus of the high-pressure phase of the nanocrystal is found to be significantly different from the analogous bulk high-pressure counterpart.⁷ Considering the case of CdSe, the pressure at which there is a conversion from wurtzite to the rocksalt phase is 3–5 GPa for nanocrystals while it is 2 GPa for the bulk of the material.⁸

Although one finds several materials with enhanced mechanical properties at the nanosized limit, the microscopic origin of the enhanced properties have not been well established. Various models have been constructed either using direct atomistic simulation or continuum theory and various explanations have been offered. The elastic response of nanostructures has been explained by surface stresses and surface elasticity.⁹ By atomistic simulation, Miller and

Shenoy¹⁰ determined a proportionality constant associated with the surface elasticity for Si and Al which could explain the size-dependent Young's modulus. This model, however, failed to explain the physical origin of the softening or stiffening.

Extraction of the size dependence from experiments is usually clouded by various factors. These include the presence of passivating ligands introduced during the synthesis of colloidal nanoparticles, the pressure transmitting medium, defects, etc. Hence a theoretical approach handling certain limiting situations would be extremely useful in establishing trends. The question we asked was whether we could take a class of materials with similar bonding characteristics and examine the behavior in their bulk modulus as a function of size due to purely elastic effects. For this purpose we chose as our candidate test systems several semiconductors, both elemental as well as binary, and examined if we could use *ab initio* calculations to determine the bulk moduli as a function of size. To access sizes beyond those that can be handled within a first-principles approach, the calculated moduli were fit to an empirical relation. Not only did we find the same functional form across all materials studied, we also found that the bulk limit in each case which entered the model was captured within 10% of its independently calculated value. This gave us confidence in the predictability of our results. However, including elastic effects resulted in enhancements in the bulk moduli only in the very small size range—a regime barely accessible during synthesis for the largest particles studied here. By the time we reach the sizes found in experiments, there is no enhancement to talk about.

II. METHODOLOGY

The systems that we have considered are silicon (Si), germanium (Ge), gallium arsenide (GaAs), and cadmium selenide (CdSe). Si and Ge occur in the diamond structure

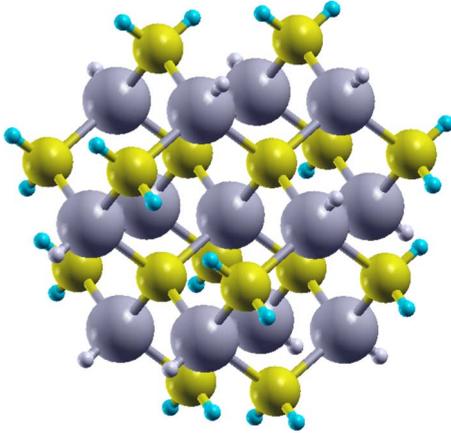


FIG. 1. (Color online) The structure of a typical nanocrystal considered by us with cations and anions (large spheres) shown in different colors. The surface layer is terminated by hydrogen denoted by small spheres.

while CdSe and GaAs could occur in the zinc-blende or the wurtzite structure. To keep the results independent of this structural aspect, we have considered only the zinc-blende polymorph in the case of GaAs and CdSe. Nanocrystals were constructed by taking a central atom, which could be a cation or an anion. Atoms were added keeping bulklike coordination and symmetry (see Fig. 1). The truncation condition used to terminate the cluster was to consider all atoms within a sphere of a desired radius. Further details may be found in Refs. 11 and 12. The surface atoms of the nanocrystal would have dangling bonds as a result of truncation. In order to make the comparison meaningful with experiment where passivants, usually organic molecules, are used to saturate the dangling bonds, we use hydrogen or pseudohydrogen¹³ for this purpose as has been used earlier.

The electronic and structural properties were calculated using a plane-wave pseudopotential implementation of density-functional theory (DFT) within VASP.¹⁴ Projected augmented wave¹⁵ potentials were used. The nanocrystal was simulated as a periodic unit cell with a vacuum between neighboring clusters at least 10 Å thick.¹⁶ For the plane-wave basis considered in these calculations, an energy cutoff of 312 eV was used in the case of Si, Ge, and GaAs. For bulk CdSe we used a cut-off energy of 500 eV which turned out to be computationally demanding. Consequently we used a cut-off energy of 342.8 eV for the nanocrystals. Increasing the cut-off energy by 200 eV or more did not change the total energies by more than 0.1 meV. The calculations for the electronic structure of the bulk crystals were carried out using a dense *k*-points grid of 8 × 8 × 8 in the Monkhorst-Pack scheme¹⁷ of division. The computations were performed for only Γ point for the nanocrystals. In the case of GaAs, the semicore 3*d* states in the Ga atom were treated as part of the core, following the conclusion obtained in a previous work.¹² On the other hand, the need to include the *d* states on Ge as a part of the basis were checked here. As the change in total energy is about 0.7 meV, the discrepancy in the lattice constant is equal to 0.37%, and in the bulk modulus is equal to 1.23%, we decided to treat the Ge *d* states as a part of the core in the calculations reported in this manuscript. Com-

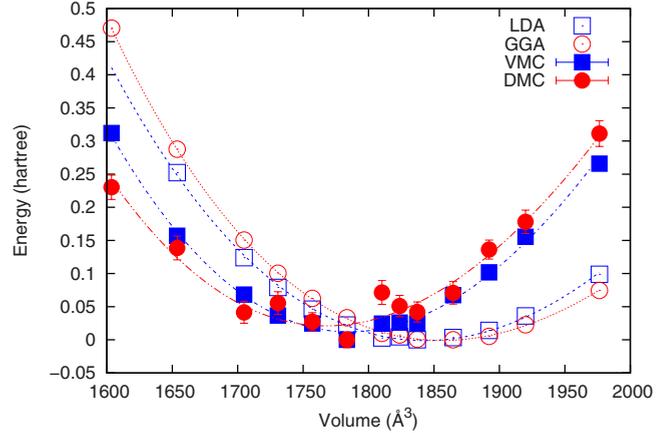


FIG. 2. (Color online) Energy-volume curves by DMC and variational Monte Carlo (VMC) for Si₈₇H₇₆. The energies are shifted for VMC by −383.339 hartree and DMC by −386.424 hartree, respectively, to have the same energy origin at equilibrium volume. Error bars for VMC are behind the symbol. Data are fitted by Vinet equation of state.

plete optimization of the internal coordinates was carried out to minimize the energy of the structure. This was determined to be the equilibrium structure at that size for which the bulk modulus was computed. The volume of the nanocrystal is needed for computing the bulk modulus. However, the volume of the nanocrystal has ambiguities associated with it and there could be several definitions. We choose the volume as being given by that of the convex hull¹⁸ formed by the outermost atoms making the structure. In order to compute the bulk modulus, we make expansions and contractions about the equilibrium geometry. Total energies of the expanded/contracted structure are computed for the structures in which the outermost atoms are kept fixed while those in the interior are optimized to minimize the total energy. The total energies at different volumes were fit to the Murnaghan equation of state.¹⁹ The bulk modulus was computed according to the equation

$$B = V \frac{\partial^2 E}{\partial V^2}, \quad (1)$$

where $E(v)$ is the total ground-state energy as a function of volume V . It should be noted that an error of $c\%$ in the volume, translates into an error of $(\frac{c}{1-c}) * 100\%$ in the bulk modulus.

It is well known that the generalized gradient approximation (GGA-DFT) exchange-correlation functional tends to

TABLE I. Elastic constants for Si₈₇H₇₆ evaluated by DFT and QMC. The constants are obtained by Vinet equation of state.

Method	B_0 (GPa)	V_0 (Å ³)	B'_0	E_0 (Ha)
LDA	105.91	1751.52	3.381	
VMC	125.1(4)	1785.2(2)	2.097	−212.742
DMC	113(9)	1768(4)	2.176	−252.514

TABLE II. A comparison of the calculated bulk moduli values using LDA and GGA functional with experimental references for columns entitled 3: Refs. 29 and 30 for GaAs value. 4: Refs. 31–33. 5: Refs. 34. The value of zinc-blende CdSe bulk modulus is estimated from the wurtzite structure in Ref. 35. Diff. represents the % deviation of the calculated value from the average experimental value.

Ref.		1 (LDA)	2 (GGA)	3 (Exp)	4 (Exp)	5 (Exp)	Average (Exp)
Si	Value (GPa)	97.0	89.3	98.8	98	97.9	98.2
	Diff. (%)	1.22	9.06	1.82	1.02	0.92	
Ge	Value (GPa)	72.3	59.3	77.2	77.2	68.9	74.4
	Diff. (%)	2.82	20.3	6.34	6.34	4.93	
GaAs	Value (GPa)	75.1	62.5	75.5	74.8/75	75.6	75.2
	Diff. (%)	0.13	17.0	0.66	0.40/0.13	0.79	
CdSe (w)	Value (GPa)	59.0	45.9			53.3	53.3
	Diff. (%)	10.7	13.9				

overestimate the equilibrium lattice constant by 1–3 % over the experimental value, whereas local-density approximation-DFT functional underestimates the same to a similar extent. So there is the need to calibrate the DFT exchange-correlation functionals by other reliable methods. In this research, the *ab initio* quantum Monte Carlo (QMC) (Ref. 20) method was used to calculate the bulk modulus of Si₈₇H₇₆ nanocrystal. We used the Slater-Jastrow form of many-body wave function,²⁰ for which the Slater-orbital functions are taken from Perdew-Burke-Ernzerhof (PBE)

GGA calculation with Gaussian basis sets²¹ for an isolated cluster. Si and H atoms are described by the pseudopotentials which are provided with properly tuned Gaussian basis sets, (9s1s9p, which represents s-type basis contracted from nine terms, an s-type uncontracted basis, and a p-type basis contracted from nine terms) for H and (9s1s9p1p1d) for Si.²² The form of Jastrow functions we used is the standard choice provided by CASINO QMC code,²³ in which electron-electron (*ee*) and electron-nucleus (*eN*) terms are expanded by power polynomials up to eighth order while the order for *eeN* (the

TABLE III. Bulk modulus calculated for different size of semiconductor nanoclusters. The deviation with respect to the bulk value is also given. The size of nanoclusters is given in term of the number of atoms and the volume.

Nanocluster	Cluster size (number of atoms)	Cluster volume (Å ³)	Bulk modulus (GPa)	Change with respect to the bulk (%)
Si	65	522.14	123.2	27.01
	71	651.32	117.0	20.62
	163	1751.52	105.8	9.07
	247	2995.34	102.6	5.77
	∞	∞	97.0	
Ge	65	577.81	106.9	47.86
	71	724.36	99.2	37.21
	163	1959.26	87.8	21.44
	247	3349.30	83.9	16.04
	∞	∞	72.3	
GaAs	65	577.72	100.1	33.29
	71	727.48	96.3	28.23
	163	1960.41	86.1	14.65
	247	3372.74	82.9	10.39
	∞	∞	75.1	
CdSe	65	718.21	65.3	13.57
	71	922.54	63.6	10.61
	163	2449.63	57.1	-0.69
	247	4234.44	55.0	-4.35
	∞	∞	57.5	

three-body coalescence term in the Jastrow function) term is $(N_{eN}, N_{ee}) = (2, 2)$. The parameters of Jastrow functions are optimized by the self-consistent unweighted variance minimization using a variational Monte Carlo procedure.^{24,25} Finally, diffusion Monte Carlo (DMC) method is used to project out the ground-state component of the optimized Slater-Jastrow wave function. All QMC calculations were done by CASINO V3.0 CODE.²³ The bulk modulus of $\text{Si}_{87}\text{H}_{76}$ are evaluated by Vinet equation of state^{26,27} as follows:

$$E(V) = -\frac{4B_0V_0}{(B'_0 - 1)^2} \left[1 - f\left(\frac{V}{V_0}\right) \right] \cdot \exp\left[f\left(\frac{V}{V_0}\right) \right] + E_0, \quad (2)$$

where,

$$f(x) = \frac{3}{2}(B'_0 - 1)(1 - x^{1/3}). \quad (3)$$

Here B_0 and B'_0 are the bulk modulus evaluated for the equilibrium volume (V_0) structure, the first volume-derivative of the bulk modulus evaluated at V_0 . We tried other forms of the equation of state such as Birch-Murnaghan's²⁸ but for the present QMC data with statistical error bars only Vinet equation of state gives successful fitting. It should be noted that the local density approximation (LDA) value was the same using either Vinet or Murnaghan equation of state.

III. RESULTS AND DISCUSSION

To investigate the most reliable method for the evaluation of the bulk modulus of these materials we have first considered the case of a reasonably sized nanocrystal of Silicon. For this purpose, we consider a $\text{Si}_{87}\text{H}_{76}$ nanocrystal and evaluate its properties using QMC. The results of the energy vs volume are given in Fig. 2. The equilibrium lattice constant as well as the bulk modulus of $\text{Si}_{87}\text{H}_{76}$ nanocrystal evaluated by the Vinet equation of state are given in Table I. While the DFT calculations reported here treat the isolated system as the Γ point of large periodic boxes, the DFT cal-

culations that we use as trial wave functions for the QMC involve a purely isolated molecule treatment. The estimated equilibrium volume from the QMC calculations seems to agree with the LDA estimate. We obtain this result using either LDA- or GGA-based DFT wave functions as our starting point. Comparing the bulk moduli calculated within the different methods presented here, we find that LDA underestimates the bulk modulus—a feature consistent with its feature of underestimating bond strengths. In addition, a comparison of the calculated bulk moduli of bulk material with experiment^{29–34} is provided in Table II. The percentage deviations from experiment are provided in every case. It should be noted that the reported experimental value is for CdSe in the wurtzite structure.^{36,37} We have therefore made a comparison for the bulk wurtzite structure in this case. In every case the deviation between the calculated bulk modulus using LDA exchange and experiment is better than that between the GGA functional value and experiment. Bulk modulus for Si crystal evaluated recently by DMC, $B_0 = 103 \mp 7$,³⁸ 103 ∓ 10 ,³⁹ and 97.1 ∓ 3 ,⁴⁰ has also demonstrated good agreement between LDA and DMC and experimental results. We have therefore used the LDA functional for our computations for the nanocrystal.

The calculated bulk moduli of nanocrystals as a function of nanocrystal size are given in Table III. An enhancement is found as a function of decreasing size in every case with the enhancement going to several tens of percent at some sizes. The variation in the bulk moduli for bulk semiconductors in the diamond or zinc-blende structure has been found to follow a scaling law that depends just on the nearest-neighbor distance by Cohen.⁴¹ We examined whether this could explain the enhancement that we find. Naively speaking, atoms at the surface of the nanocrystal should have reduced coordination. They would therefore tend to lower their energy by forming shorter bond (increased nearest-neighbor interaction). So the question that we asked next was whether this deviation from bulk bond lengths could explain the enhancements we find. Examining the optimized geometry of the nanocrystals, we find that there is a distribution of bond lengths not only as a function of depth but also as a function

TABLE IV. Calculated bulk moduli (B_0) in GPa for different sizes of nanocrystals. The average nearest-neighbor distance (nn) in Å determined from our calculations as well as the material-dependent constant entering the empirical law given by Cohen are also shown.

	Cluster size (number of atoms)	Cluster volume (\AA^3)	nn (\AA)	B_0 (GPa)
Si (LDA) ($A=1905.182$)	65	522.14	2.3314	98.46
	71	651.32	2.3293	98.78
	163	1751.52	2.3312	98.49
	247	2995.34	2.3349	97.95
	∞	∞	2.3414	97.0
Ge (LDA) ($A=1651.924$)	65	577.81	2.4130	75.69
	71	724.36	2.4144	75.54
	163	1959.26	2.4199	74.94
	247	3349.30	2.4253	74.36
	∞	∞	2.4448	72.3

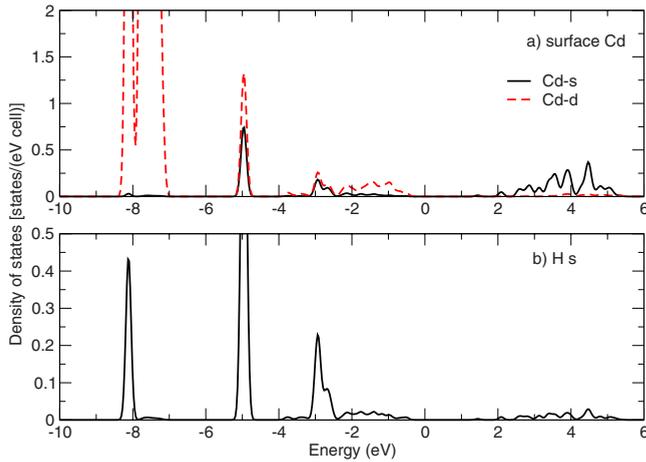


FIG. 3. (Color online) (a) The Cd *s* (solid line) and *d* (dashed line) projected partial density of states for a surface Cd atom and (b) the H *s* (solid line) projected partial density of states for the pseudohydrogen attached to the surface Cd atom in the case of the largest size CdSe nanocrystal considered in our study. The Fermi energy is set to zero.

of surface coordination. We therefore calculate an averaged bond length as defined earlier.⁴² We use this value in the scaling relation given by Cohen,⁴¹ where the bulk modulus is given by $B=A/d^{3.5}$. The material-dependent constant A is determined by taking the bulk modulus value as well as nearest-neighbor bond length obtained from the DFT calculations at the bulk limit. Using this value with the average bond length that we find in our calculations, for two prototypical examples Si and Ge (Table IV), we find an enhancement of just a few percent. Apart from the bond-strain effect discussed above, there is the additional enhancement of the band gap in the size regime that we are examining the nanocrystals. However, we find that although there are significant enhancements in the band gap for the largest sizes consid-

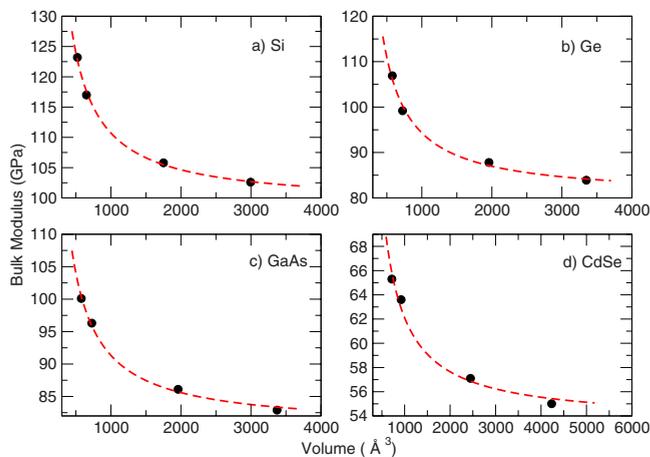


FIG. 4. (Color online) The calculated bulk modulus (solid circles) from *ab initio* calculations as function of nanocrystal sizes for Si, Ge, GaAs, and CdSe using LDA as the exchange-correlation functional. The dashed line through the data points denotes the best fit for the phenomenological rule where the bulk modulus varies as $\exp(k/V)$.

TABLE V. Results of the fit performed on *ab initio* computations of the Si, Ge, GaAs, and CdSe bulk modulus for different nanocluster sizes using LDA as the exchange-correlation functional. Bulk limit bulk modulus (B_{∞}^{fit}) and k are obtained after the fitting. B_{∞} is the bulk modulus for the bulk material, computed by DFT calculations. The last column presents the deviation between B_{∞}^{fit} and B_{∞} .

Nanocluster	B_{∞}^{fit} (GPa)	k (Å ³)	B_{∞} (GPa)	$ B_{\infty}^{fit} - B_{\infty} / B_{\infty}$
Si	99.0	112.95	97.0	0.0206
Ge	80.2	162.18	72.3	0.1093
GaAs	80.2	129.94	75.1	0.0679
CdSe	53.5	148.77	57.5	0.0696

ered here, we already enter the size regime where bulk modulus enhancements are modest. Hence the two have different origins. Hence the bond-strain mechanism or the quantum confinement effects that enhance the band gap from the bulk value cannot explain the observed enhancements in the bulk moduli of the nanocrystals. This suggests that there is some other effect, beyond the bond-strain effect required to explain the bulk moduli of the nanocrystals that we find in our calculations. There are some clues of this when we look at the partial density of states associated with the hydrogen/pseudohydrogen atoms that we use to simulate the passivating layer. In Fig. 3 we have plotted the Cd *s* and *d* projected partial density of states due to the surface Cd atoms. The H *s* contribution is also provided. A passivant should merely serve the purpose of being a site to which electrons are transferred to or from which electrons are transferred out. Here, we find that it interacts very strongly with the atoms of the semiconductor (Fig. 3). Thus it is this strong interaction we believe that is responsible for the enhanced moduli that we find in our calculation. Further work will be carried out on well-controlled passivants.

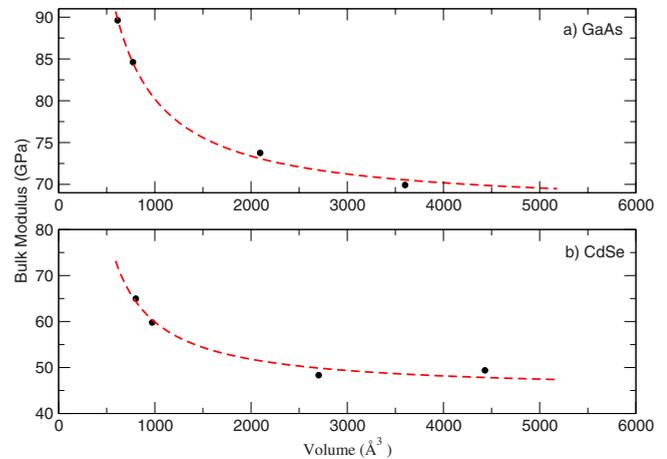


FIG. 5. (Color online) The calculated bulk modulus (solid circles) from *ab initio* calculations as function of nanocrystal sizes for GaAs and CdSe using GGA as the exchange-correlation functional. The dashed line through the data points denotes the best fit for the phenomenological rule where the bulk modulus varies as $\exp(k/V)$.

TABLE VI. Prediction of the size dependence for a 10 nm³ nanocrystal using the phenomenological law. The value of the bulk modulus for the 10 nm³ nanocrystal (B_V) is compared with the fitted bulk modulus for the bulk B_∞ .

Nanocluster	B_V (GPa)	B_∞^{fit} (GPa)	$ B_V - B_\infty^{fit} /B_\infty$
Si	100.1	99.0	0.011
Ge	81.5	80.2	0.016
GaAs	81.2	80.2	0.012
CdSe	54.3	53.5	0.015

The size regime in which we see the enhancement is much smaller than most of the sizes realized during growth of nanoparticles in experiment. In order to make our comparison meaningful to experiment, we examined if the results for various systems could be fit to an empirical law. This would enable us to examine the sizes beyond the limitations of our computational scheme. A fit of all the available data allows us to extract a dependence describable by the phenomenological rule $B_0 = B_\infty^{fit} \exp(k/V)$, where B_0 is the bulk modulus of the material, B_∞^{fit} is the corresponding value for the bulk and k a material parameter. The best fit curve along with the data used for the fitting is presented in Fig. 4. The parameter k also has a physical significance, it gives an estimate of the volume of a particular nanocrystal below which the enhancement of bulk modulus is greater than 170%. We have not included the bulk modulus of the extended solid in our fitting but we compare it to the asymptote of our fit function. Table V gives the fit details. The deviation between the asymptote of function proposed here and the bulk value is the largest for Ge and its about 10%. All curves allow an asymptote very close to the bulk value. This gives us greater confidence in our volume computation of the nanocrystals by convex hull method and thus a much better confidence in the phenomenological relation that we have derived here.

The nanocrystal size studied here is evidently a little small compared with those more often experimentally observed. On the other hand, defining a phenomenological law enables us to predict the behavior of bigger sizes, more difficult to calculate due to the numerical cost. Thus, Table VI shows the size dependence expected for a 10 nm³ nanocrystal. The deviation from the bulk value is very small, possibly within the error bars of our calculations. Although our earlier analysis suggested the LDA form of the exchange correlation gave a good description of the elastic properties of these materials, we also examined the GGA form. This was done to see if the trend observed here in the variation in the bulk modulus is not a result of the exchange-correlation functional used. Here too we were able to fit the bulk modulus variation (Fig. 5) for the binary nanocrystals using the same phenomenological rule as described earlier. The fitted details are given in Table VII. Here again the enhancements for 10 nm³ particles is small.

Several experimental results are available in the literature on particle size of 10 nm implying a volume of around

TABLE VII. Results of the fit performed on *ab initio* computations of GaAs and CdSe bulk modulus for different nanocluster sizes using GGA as the exchange-correlation functional. Bulk limit bulk modulus (B_∞^{fit}) and k are obtained after the fitting. B_∞ is the bulk modulus for the bulk material, computed by DFT calculations. The last column presents the deviation between B_∞^{fit} and B_∞ .

Nanocluster	B_∞^{fit} (GPa)	B_∞ (GPa)	k	$ B_\infty^{fit} - B_\infty /B_\infty$
GaAs	67.1	62.5	177.98	0.074
CdSe	44.8	45.1	290.50	0.067

525 nm³. The enhancement of bulk modulus was observed for AlN,⁵ CeO₂,⁶ and γ -Fe₂O₃.⁴³ The size effect on AlN is found equal to 63% while γ -Fe₂O₃ and CeO₂ bulk modulus enhancement are, respectively, reported equal to 52% and 50%. We therefore conclude that the mechanism behind this size effect is not the same as that found here. The phenomenon studied here may be considered to be restricted to very small nanostructures with a perfect structure.

IV. CONCLUSIONS

We have studied the size dependence of the bulk modulus nanoclusters of Si, Ge, CdSe, and GaAs. An enhancement is seen in the small size regime and we attribute this to the strong interaction with the passivant. A phenomenological law is derived which in most cases has the correct magnitude in the asymptotic limit. We use the phenomenological law to extrapolate the results to larger clusters of 10 nm³ volume. A modest enhancement of 1–3 % is found at these sizes, which could be placed as lying within the error bars of our computational scheme.

ACKNOWLEDGMENTS

We acknowledge D. D. Sarma for useful discussions. P.M. thanks Department of Science and Technology, India for funding. The computation in this work has been partially performed using the facilities of the Center for Information Science in JAIST. Financial support was provided by Bilateral Joint Projects/Seminars between India and Japan “Novel magnetic oxide nanomaterials investigated by spectroscopy and *ab initio* theories” (Japanese Ministry of Education, Culture, Sports, Science, and Technology, MEXT), by Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency (PRESTO-JST), and by a Grant-in-Aid for Scientific Research in Priority Areas “Development of New Quantum Simulators and Quantum Design” under Grant No. 17064016 (Japanese Ministry of Education, Culture, Sports, Science, and Technology; KAKENHI-MEXT) for R.M. C.G. thanks Association Française des Femmes Diplômées d’Université (AFFDU) for its support.

*Present address: Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany.

†Corresponding author.

- ¹M. Sheik-Bahae, D. J. Hagan, and E. W. Van Stryland, *Phys. Rev. Lett.* **65**, 96 (1990); J. R. Heath, *Science* **270**, 1315 (1995).
- ²Y. Kayanuma, *Phys. Rev. B* **44**, 13085 (1991); M. B. Mohamed, C. Burda, and M. A. El-Sayed, *Nano Lett.* **1**, 589 (2001); J. Hu, L. Li, W. Yang, L. Manna, L. Wang, and A. P. Alivisatos, *Science* **292**, 2060 (2001); A. Shabaev and Al. L. Efros, *Nano Lett.* **4**, 1821 (2004); M. Simurda, P. Nemeč, F. Trojanek, K. Neudert, T. Miyoshi, K. Kasatani, and P. Maly, *Physica E* **36**, 205 (2007).
- ³M. Reibold, P. Paufler, A. A. Levin, W. Kochmann, N. Pätzke, and D. C. Meyer, *Nature (London)* **444**, 286 (2006).
- ⁴C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, and Y. J. Yan, *Phys. Rev. Lett.* **96**, 075505 (2006).
- ⁵Z. Wang, K. Tait, Y. Zhao, D. Schiferl, C. S. Zha, H. Uchida, and R. T. Downs, *J. Phys. Chem. B* **108**, 11506 (2004).
- ⁶Z. Wang, S. K. Saxena, V. Pischedda, H. P. Liermann, and C. S. Zha, *Phys. Rev. B* **64**, 012102 (2001).
- ⁷S. H. Tolbert and A. P. Alivisatos, *Science* **265**, 373 (1994); *Annu. Rev. Phys. Chem.* **46**, 595 (1995); J. Z. Jiang, L. Gerward, D. Frost, R. Secco, J. Peyronneau, and J. S. Olsen, *J. Appl. Phys.* **86**, 6608 (1999); J. Z. Jiang, L. Gerward, R. Secco, D. Frost, J. S. Olsen, and J. Trukenbrodt, *ibid.* **87**, 2658 (2000).
- ⁸S. H. Tolbert and A. P. Alivisatos, *J. Chem. Phys.* **102**, 4642 (1995).
- ⁹G. Ouyang, W. G. Zhu, C. Q. Sun, Z. M. Zhu, and S. Z. Liao, *Phys. Chem. Chem. Phys.* **12**, 1543 (2010).
- ¹⁰R. E. Miller and V. B. Shenoy, *Nanotechnology* **11**, 139 (2000).
- ¹¹G. M. Dalpian, M. L. Tiago, M. L. Puerto, and J. R. CheLIKowsky, *Nano Lett.* **6**, 501 (2006).
- ¹²R. Cherian and P. Mahadevan, *Phys. Rev. B* **76**, 075205 (2007).
- ¹³K. Shiraishi, *J. Phys. Soc. Jpn.* **59**, 3455 (1990).
- ¹⁴G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996); *Comput. Mater. Sci.* **6**, 15 (1996).
- ¹⁵G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁶The thickness of the vacuum was determined by evaluating total-energy differences for smaller unit cells as a function of the vacuum layer. The total energies by themselves do not converge fast enough but the differences converge fast.
- ¹⁷The convergence with respect to k points was tested by increasing the mesh density from $8 \times 8 \times 8$ to $12 \times 12 \times 12$. The total energies changed by 0.02 meV.
- ¹⁸C. B. Barber, D. P. Dobkin, and H. T. Huhdanpaa, *ACM Trans. Math. Softw.* **22**, 469 (1996).
- ¹⁹F. D. Murnaghan, *Proc. Natl. Acad. Sci. U.S.A.* **30**, 244 (1944).
- ²⁰B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
- ²¹GAUSSIAN 03, REVISION E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT (2004).
- ²²M. Burkatzki, C. Filippi, and M. Dolg, *J. Chem. Phys.* **129**, 164115 (2008).
- ²³R. J. Needs, M. D. Towler, N. D. Drummond, and P. López Ríos, *J. Phys.: Condens. Matter* **22**, 023201 (2010).
- ²⁴N. D. Drummond, M. D. Towler, and R. J. Needs, *Phys. Rev. B* **70**, 235119 (2004).
- ²⁵N. D. Drummond and R. J. Needs, *Phys. Rev. B* **72**, 085124 (2005).
- ²⁶P. Vinet, J. H. Rose, J. Ferrante, and J. R. Smith, *J. Phys.: Condens. Matter* **1**, 1941 (1989).
- ²⁷R. Maezono, A. Ma, M. D. Towler, and R. J. Needs, *Phys. Rev. Lett.* **98**, 025701 (2007).
- ²⁸F. Birch, *Phys. Rev.* **71**, 809 (1947).
- ²⁹C. Kittel, *Introduction to Solid State Physics*, 8th ed. (Wiley, New York, 2005).
- ³⁰S. Adachi, *J. Appl. Phys.* **58**, R1 (1985).
- ³¹R. W. G. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), Vol. 1.
- ³²*Crystal and Solid State Physics*, edited by O. Madelung, Landolt-Börnstein, New Series, Group III (Springer, Berlin, 1984).
- ³³H. J. McSkimin, A. Jayaraman, and Jr. Andreatch, *J. Appl. Phys.* **38**, 2362 (1967).
- ³⁴O. Madelung and M. Schultz, Landolt-Börnstein, New Series, Group III Vol. 22 (Springer-Verlag, Berlin, 1987).
- ³⁵H. Sowa, *Solid State Sci.* **7**, 1384 (2005).
- ³⁶G. Simmons and H. Wang, *Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook*, 2nd ed. (MIT Press, Cambridge, 1971).
- ³⁷W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980).
- ³⁸X.-P. Li, D. M. Ceperley, and R. M. Martin, *Phys. Rev. B* **44**, 10929 (1991).
- ³⁹D. Alfè, M. J. Gillan, M. D. Towler, and R. J. Needs, *Phys. Rev. B* **70**, 214102 (2004).
- ⁴⁰R. Maezono, N. D. Drummond, A. Ma, and R. J. Needs, *Phys. Rev. B* **82**, 184108 (2010).
- ⁴¹M. L. Cohen, *Phys. Rev. B* **32**, 7988 (1985).
- ⁴²R. Cherian and P. Mahadevan, *Appl. Phys. Lett.* **92**, 043130 (2008).
- ⁴³J. Z. Jiang, J. S. Olsen, L. Gerward, and S. Mørup, *Europhys. Lett.* **44**, 620 (1998).