PHYSICAL REVIEW B VOLUME 58, NUMBER 8 15 AUGUST 1998-II

Theoretical study of the structural and electronic properties of GaSe nanotubes

Michel Côté and Marvin L. Cohen
Department of Physics, University of California at Berkeley and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

D. J. Chadi
NEC Research Institute, 4 Independence Way, Princeton, New Jersey 08540

(Received 6 March 1998)

We predict the formation of GaSe nanotubes from an energetic argument which employs pseudopotential density functional theory methods. The strain energy of GaSe nanotubes is found to be comparable to existing carbon nanotubes. Based on this energetic comparison, we expect GaSe nanotubes with diameters of 40–48 Å to form. The energy gap of these nanotubes is predicted to decrease from the bulk value as the nanotubes get smaller. These calculations demonstrate that the synthesis of GaSe tubes would yield interesting new materials which would allow further studies of the properties of nanotubes and expand their applications.
[S0163-1829(98)51532-9]

The existence of tubular forms of matter with nanoscale diameters has opened an exciting field of research in physics. These tubes provide the opportunity to study the physics of systems with reduced dimensionality. At present, only a few compounds, such as carbon,[1] boron nitride,[2] MoS_2,[3,4] and WS_2,[5] exhibit the ability to form tubular structures. It is important to continue the search for compounds which might form nanotubes since they will offer new materials with new and possibly useful properties.

In this paper, we propose that the GaSe layered compound be explored to form nanotubes. The structure of this compound makes it an ideal candidate for tube formation. In order to validate our proposal, we have conducted *ab initio* calculations of the strain energies needed for rolling the GaSe sheet into a tube. We find that the energetic requirement is comparable to those of existing carbon nanotubes. Interestingly, the dependence of the energy gaps with respect to the size of these GaSe nanotubes is found to behave oppositely to one might think due to quantum confinement, meaning that it decrease as the radii of the nanotubes gets smaller. However, this effect can be understood by considering the pressure dependence of the bulk band structure. According to the strain energy, it is likely that nanotubes as small as 40 Å in diameter can be formed and these tubes would have an energy gap in the range of 0.8–1.0 eV. We also propose a way to reduce the strain energy by combining different elements that form this layered structure which will induce curvature into the sheet. The GaSe compound has been intensively studied because of the large exciton binding energies. Since the exciton binding energy increases as the dimensionality of the system decreases, GaSe nanotubes offer the possibility to study excitons in a one dimensional system.

Throughout this study, we have used different methods to calculate the properties of these nanotubes. For the structural properties, we performed *ab initio* calculations using a plane-wave basis pseudopotential total-energy scheme[6,7] within the density functional theory where the local density approximation (LDA) is used for the exchange-correlation energy.[8] To determine the energy gap, we employed a total-energy tight binding method,[9] where the tight binding parameters have been fit to the bulk structure to give the experimental equilibrium structural properties and energy gap. In both methods, the results are reported for the fully relaxed system.

It is possible for III-VI compounds to be semiconductors if some of the electrons form bonds between the metal atoms and those bonds do not run continuously in the structure.[10] In Fig. 1, a single layer of the GaSe compound is shown. We see that in this structure the bond between the Ga atoms is perpendicular to the plane of the sheet. These Ga-Ga dimers are then connected together by the Se atoms which form three bonds with the Ga atoms. Experimentally, the Ga-Ga bond length is 2.35 Å and the bond length between the Se and the Ga atoms is 2.47 Å. The unit cell is hexagonal with a lattice constant of 3.75 Å. The bulk is made by superposing two layers shifted with respect to each other. The layers which have a thickness of 4.73 Å (from Se atoms to Se atom) interact through a van der Waals potential and the distance between Se atoms on different layers is 3.0 Å. The tube is made by rolling up the GaSe sheet onto itself. By analogy with the carbon nanotubes, we use the notation (n,m) which

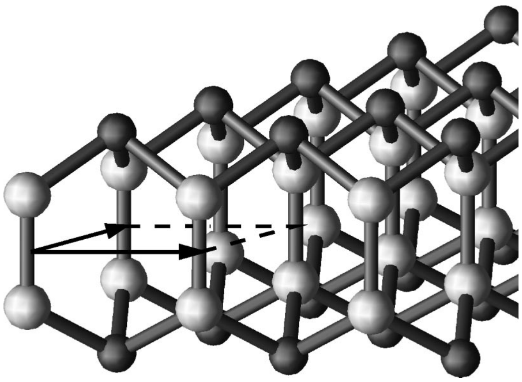

FIG. 1. A single layer of the GaSe compound. The light color atoms correspond to Ga and the dark color atoms are Se. The arrows represent the lattice vectors of the hexagonal cell.

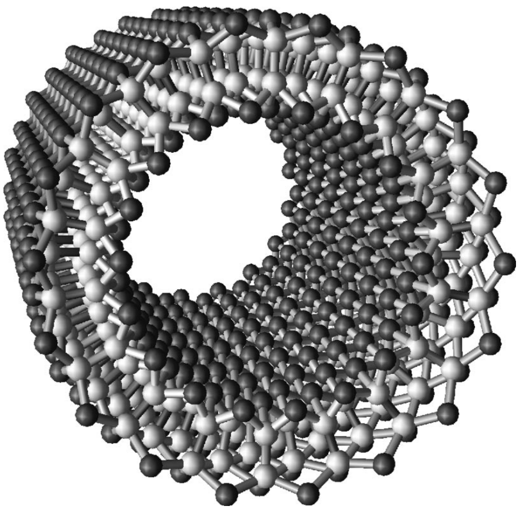

FIG. 2. GaSe nanotube. This tube corresponds to a (18,0) nanotube. The light color atoms are Ga and the dark color atoms are Se.

corresponds to the circumference of the tube onto the sheet. An example of such a tube is shown in Fig. 2. In the tubular form, the Ga-Ga bonds are in the radial direction with Se atoms on the inside and outside part of the tube wall.

In order to assess the likelihood for the formation of GaSe nanotubes, we have calculated the strain energy which is defined as the energy difference between the tube and the planar configuration for several sizes of tubes. The results are plotted in Fig. 3. For comparison, we also show the strain energy for carbon nanotubes.[11] Carbon nanotubes with diameters as small as 7–8.5 Å have been observed.[12] Such nanotubes would have between 9 to 11 unit cells around the circumference. Their strain energy is around 0.1 eV per atom corresponding to a temperature of 1000 °C which is typical of the environment during the growth process of nanotubes. If we use the strain energy as an indication for the likelihood of synthesizing nanotubes, then it should be expected that GaSe nanotubes which have between 34–40 unit cells around the circumference would be able to form. These tubes have diameters in the range of 40–48 Å. The growth of such tubes would certainly depend on other experimental parameters, but clearly the strain energy results support the possibility for these tube to exist.

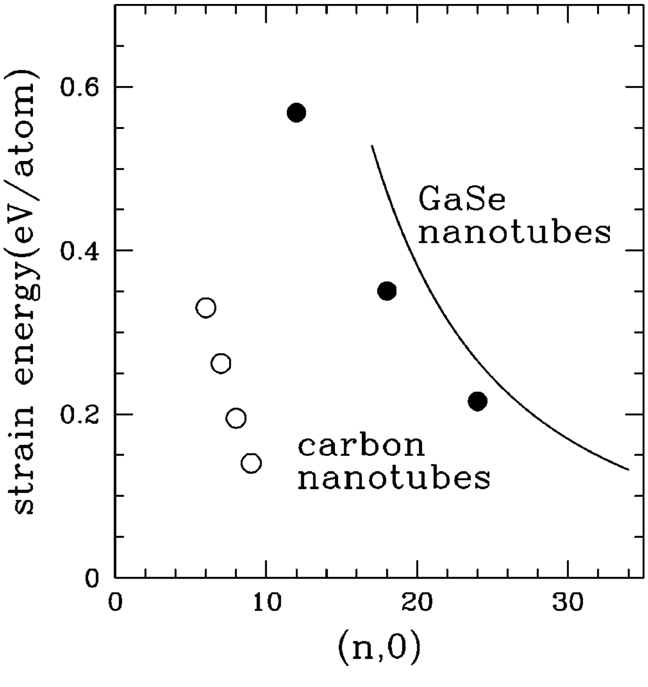

FIG. 3. Plot of the strain energy vs nanotube size which is given by the number of unit cells around the circumference. All values are for $(n,0)$ type tubes; the open circles correspond to carbon nanotubes and the solid circles correspond to GaSe nanotubes. The values are obtained using LDA where the structure has been fully relaxed. The line shown in the graph represents the estimated values for the GaSe nanotubes according to the model described in the text which does not have any fitting parameter.

The reason for the higher strain energy of the GaSe nanotubes as compared to the carbon nanotubes is due to the structure of the GaSe layers. Since the layer has a finite thickness, when it is rolled into a tube the circumference of the inner part of the tube layer is smaller than the outer one. This means that bonds in the inside part of the wall will be compressed and those outside will be stretched. For this reason, we have chosen to consider $(n,0)$ nanotubes in this study because these tubes have one of their Ga-Se bonds lying on the axis of the nanotube which means that it will not suffer from the size difference of the inner and outer part of the tube wall.

It is possible to understand this increase in strain energy by modeling the nanotube using elastic theory and the Young modulus of a single layer. We note that the GaSe, MoS_2, and WS_2 compounds all have similar structures since they all have their metal atoms in the middle of the layer which form bonds with the group VI atoms located on both side of the layer. The energy required for the formation of the tube comes from the expansion and contraction of these bonds. Therefore the same analysis can be employed for all these compounds. We attempt to model the layer by two elastic sheets separated by a given distance d which should roughly be the thickness of the layer [see Fig. 4(a)]. When the tube is formed the inner sheet will be contracted and the outer one will be expanded [see Fig. 4(b)]. The energy involved in stretching an elastic sheet is given by $\Delta E = AY(\Delta L)^2/2L$ where Y is the Young modulus, A is the cross section area, and L is the length of the sheet. Since we do not know the Young modulus of a single layer for any of these compounds, we make use of total energy calculations in order to assess this quantity. We can relate the energy cost per atom for uniformly stretching the layered compound, ΔE_{layer} with the Young modulus by the following expression:

$$\Delta E_{\text{layer}} = 2\times 2\times \frac{StY(\Delta S)^2/2S}{S^2N} = 2\frac{Yt}{N}\left(\frac{\Delta S}{S}\right)^2,$$

where S is the length of the layer, t is the thickness of the layer and N is the number of atoms per unit area. In the above expression, one of the factors of 2 arises because we are expanding the sheet in two directions and the other arises because there are two sheets in the compound. We calculate the total energy of a single layer within LDA as it is compressed and expanded. From the curvature of the graph of the total energy per atom versus the lattice constant, we evaluate the ratio Yt/N. Since there is no good way of determining the thickness of a sheet and there is no need to do it, we

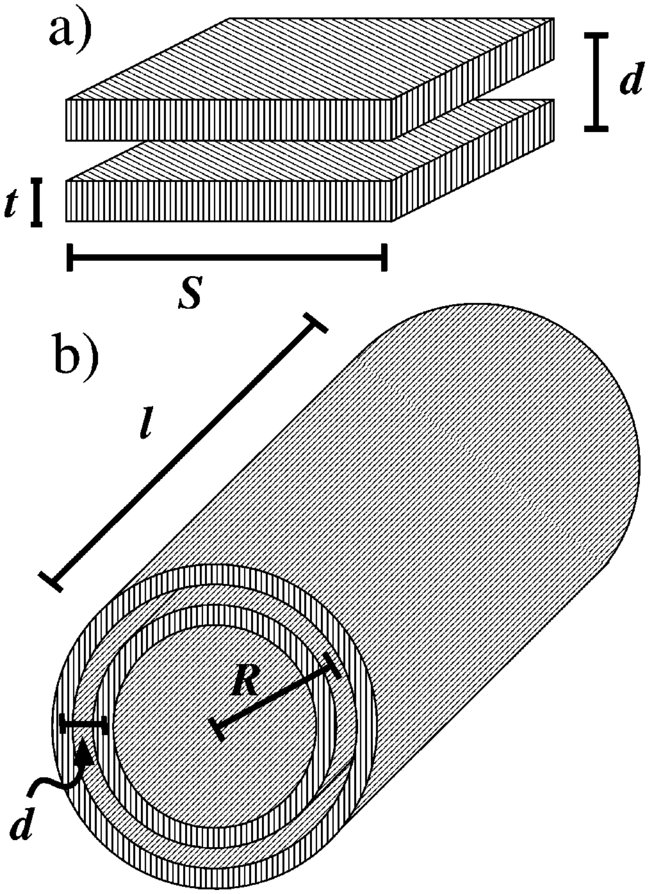

FIG. 4. Model used to assess the strain energy in the nanotubes: (a) shows the two elastic sheets used in the model of the layer and (b) corresponds to a nanotube.

calculate the ratio Yt/N which is found to be 9.85 eV/atom for GaSe.

In forming the tube, the inner (outer) sheet will be compressed (expanded) by a length equal to $2\pi(R+d/2)-2\pi R=\pi d$ for a tube of radius R. Therefore, the strain energy per atom for a tube of length l is

$$\Delta E_{\text{tube}}=2\times\frac{ltY(\pi d)^2/2(2\pi R)}{(2\pi R)Nl}=\frac{1}{4}\frac{Yt}{N}\left(\frac{d}{R}\right)^2,$$

where the first factor of 2 arises because the strain energy is the same for the inner and outer sheets. Using the last expression for the (24,0) GaSe nanotube which has a radius of $R=24\times3.75/(2\pi)=14.3$ Å and using $d=4.7$ Å we obtain $\Delta E_{\text{tube}}=0.265$ eV. This estimate is in good agreement with our first principles calculation which yields a strain energy per atom of 0.215 eV. This supports the claim that indeed the strain energy involved in the nanotube is due to stretching and compression of the bonds. In Fig. 3 we see that the strain energy for (18,0) and (24,0) nanotubes fit well to a $1/R^2$ dependence but our result for the (12,0) falls significantly lower than the expected trend. However, we should not expect elastic theory based on the unstrained layer to hold for this size of tubes since the compression of bonds is very severe.

We can also estimate the size of MoS_2 and WS_2 nanotubes which should form using the last expression. The ratio Yt/N is calculated to be 15.2 and 16.0 eV/atom for the MoS_2 and WS_2 respectively. These tubes are synthesized at a temperature of roughly 1000 °C (Ref. 5) which corresponds to an energy of 0.1 eV. Assuming that this energy is the maximum strain energy per atom that a tube can support and using a d of 3.2 Å which is the distance between the sulfur atoms in both MoS_2 and WS_2, we obtain a radius of 20 Å. This value is in good agreement with the smallest WS_2 nanotubes which have diameters of 4 nm (Ref. 5) and with the smallest internal radius of fullerenes of MoS_2 at 1.5 nm.[3]

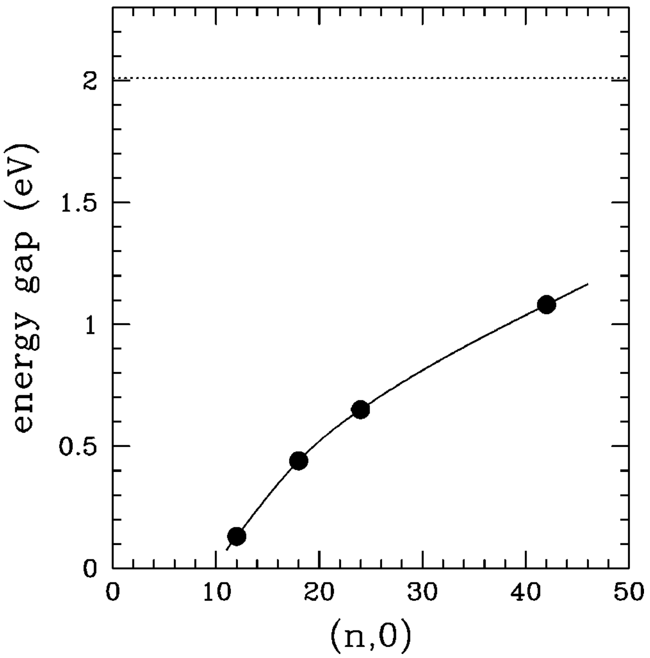

FIG. 5. Energy gaps (eV) for the GaSe nanotubes calculated within the tight binding approach. The solid circles correspond to tight binding energy gaps where the tight binding parameters have been fit to the experimental value of the bulk.

Since bulk GaSe is a semiconductor with a gap of around 2 eV, it is interesting to study how this energy gap changes with the size of the nanotube. In Fig. 5 is shown a plot of the calculated energy gap for different GaSe nanotubes. The values are computed using tight binding parameters which have been fit to the experimental value of the bulk. This figure shows that the energy gap decreases as the nanotube gets smaller. This result is interesting and surprising since at a first glance one would expect the gap to increase due to quantum confinement. However, this behavior can be understood when considering the pressure dependence of the electronic states in this compound. The fundamental energy gap in the bulk is from Γ to M with the conduction states at K and Γ only slightly above the M state. When the layer is compressed, the states at M and K come down in energy with respect to the valence state at Γ whereas the direct gap is roughly constant. The K states come down faster than the M states so that the fundamental gap becomes from Γ to K. Assuming the states in the tube can be derived by a ''folding'' scheme of the band structure of the bulk, since the curvature of a layer is like a compression of a layer, the more curved the layer is the further down the K states become closing the gap in the nanotube. It is interesting that the nature of the lowest unoccupied molecular orbital (LUMO) state in the nanotube should change depending on the size of the tube. Larger tubes should have a LUMO state that corresponds to M states in the bulk whereas in smaller tubes the LUMO should be more like K states. For the size range where strain energy is favorable to tube formation, we would expect energy gap of 0.8–1.0 eV for the smallest tubes. We also do not expect the gap to vary much with the chirality of the tube. Because of the energetic requirement, only tubes with a relatively large number of unit cells around its circumference are expected. This means that according to a band folded scheme, the allowed k-states of the nanotube will sample most of the Brillouin zone of the bulk band structure.

This particular layered structure is not unique to the GaSe compound, e.g., GaS and InSe also form this arrangement. The formation of tubular structures is also expected for these compounds. Interestingly, the possibility of combining these compounds might provide a natural way to reduce the stress in the nanotube. Since the Ga-S bond length is shorter than the Ga-Se bond length, one could use sulfur atoms for the inner side of the layer in the nanotube and selenium atoms for the outside. The different bond lengths will naturally curve the sheet reducing considerably the strain energy needed to form the nanotube. Crystals of GaSe doped with In have already been grown.[13]

In conclusion, our theoretical analysis shows that the energy requirement for the formation of GaSe nanotubes should allow tubes with radii between 40–48 Å to form. It is predicted that the energy gap of these nanotubes will decrease as the size of the tubes becomes smaller. Since the energy gaps of these nanotubes is in between those of carbon or boron-nitride nanotubes, they could permit nanotube technology to widen its range of applications. We also discussed how the structural and electronic properties of GaSe nanotubes can be understood by the compression of the GaSe layer compound. Finally, the possibility of mixing other elements might provide an easy way of inducing curvature in these systems.

We would like to thank U. Varadarajan, A. Zettl, P. Y. Yu, J. C. Grossman, and A. Mizel for useful discussions. The work at Berkeley was supported by National Science Foundation Grant No. DMR-9520554 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational resources have been provided by NCSA and by NERSC. One of us (M.C.), acknowledges the support of the Natural Sciences and Engineering Research Council of Canada.

---

[1] S. Iijima, Nature (London) **354**, 56 (1991).

[2] N. Chopra *et al.*, Science **269**, 966 (1995).

[3] Y. Feldman, E. Wasserman, D. J. Srolovitz, and R. Tenne, Science **267**, 222 (1995).

[4] M. Remskar *et al.*, Appl. Phys. Lett. **69**, 351 (1996).

[5] R. Tenne, L. Margulis, M. Genut, and G. Hodes, Nature (London) **360**, 444 (1992).

[6] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[7] M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[8] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[9] D. J. Chadi, Phys. Rev. B **19**, 2074 (1979).

[10] W. B. Pearson, Acta Crystallogr. **17**, 1 (1964).

[11] X. Blase, A. Rubio, S. G. Louie, and M. L. Cohen, Europhys. Lett. **28**, 335 (1994).

[12] S. Iijima and T. Ichihashi, Nature (London) **363**, 603 (1993).

[13] D. R. Suhre, N. B. Singh, and V. Balakrishna, Opt. Lett. **22**, 775 (1997).