Nanocrystalline Nanowires: I. Structure

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Geometric constructions of possible atomic arrangements are suggested for inorganic nanowires. These are fragments of bulk crystals, and can be called "nanocrystalline" nanowires (NCNW). To minimize surface polarity, nearly one-dimensional formula units, oriented along the growth axis, generate NCNW's by translation and rotation.

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Introduction. Periodic one-dimensional (1D) motifs are common in nature. The study of single-walled carbon nanotubes (SWNT)[1,2] is maturing rapidly, but other 1D systems are at an earlier stage. Inorganic nanowires are the topic of the present two papers. There is much optimism in this field[3–6]. Imaging gives insight into self-assembled nanostructures, and incentives to improve growth protocols. Electron microscopy, diffraction, and optical spectroscopy on individual wires[7] provide detailed information. Device applications are expected. These systems offer great opportunities for atomistic modelling. Many specific calculations are reported, but have not greatly influenced the field. Theoretical difficulties include: (1) the precise atomic structure of inorganic nanomaterials is rarely known; (2) techniques to exploit rotational as well as translational symmetry are not much developed. The present paper (I) contains speculations about structure which should assist the construction of models. The subsequent paper (II)[8] shows by construction how rotational symmetry can be used to simplify both the numerical tasks and the conceptual understanding, with a particular example of vibrations worked out in detail.

If the surface and interior of a finite-diameter 1D nano-object is rigidly occupied by atoms, it is often called a nanowire or nanorod[9], and sometimes "quantum wire" or "quantum rod[10]." In this paper, the term nanowire is used; the root "wire" is **not** intended to imply metallic conductivity. Ordered nanowires fall into several structural classes: (1) helical nanowires, (2) molecular nanowires, and (3) nanocrystalline nanowires (NCNW). Helical nanowires are filled nanotubes[11]. Molecular nanowires may be fragments of quasi-1d crystals. For example, the materials[12,13] $M_2Mo_6X_6$, where M is an alkali and X is S or Se, may be made with nanoscopic transverse dimensions. The non-helical inorganic polymer $(Mo_6S_6)_N$ is an example which has been studied experimentally[12] and theoretically[14,15]. Finally, nanocrystalline nanowires are 1D fragments of bulk crystals where the bulk was a 3D (not a quasi-1D) material. These three categories are not exhaustive. There are also twinned[16]; "core-shell" (COHN)[4,17]; and longitudinally heterogeneous (LOHN) NCNW's.

Design principle. The remainder of this note is about NCNW's. It offers a possible design principle, which assists visualization of candidate atomic structures, and provides a template for arrangements that can be tested theoretically, for example by density functional theory (DFT). The basic idea is (1) choose a maximally linear, charge-neutral, and (if possible) dipole-free atomic cluster containing a single formula unit, and (2) using if possible the symmetry axis of this linear cluster as the growth axis, distribute by translations and screw rotations the atomic clusters to give a stoichiometric nanowire with some symmetry around the growth axis and minimal surface polarity.

For monatomic crystals like Ag or Si, there are obvious candidate NCNW structures. For diatomics of AB stoichiometry, constraints arise from the possible polarity of the exposed surfaces[18]. Consider the wurtzite structure, which occurs in popular nanowires like CdSe, GaN and ZnO. The lattice is hcp, with c/a not far from the ideal close-packed value of $\sqrt{8/3}$. If A atoms are on the hcp sites, then B atoms are placed "on top" (in the c direction) of A atoms, filling tetrahedral interstitial sites. A simple way to make a charge-neutral nanowire with non-polar surfaces, is by choosing the c-axis as the growth axis, and thinking of the wire as built from c-axis oriented AB pairs. In both hcp and wurtzite structures, wires may have an atom-centered C_3 axis, or a $(C_6|c/2)$ 6-fold screw axis passing through the vacant center of the puckered hexagon[19], with $c/2$ the screw displacement that accompanies each $2\pi/6$ rotation. Thus c-axis oriented wurtzite nanowires are an obvious choice for a NCNW structure, and very favorable for theoretical modelling because of the symmetry[20]. Nature often cooperates, with c-axis growth the most commonly reported morphology for wurtzite NCNW's. Akiyama *et al.*[21] compared, by computation, the energy of InP nanowires in the c-axis wurtzite geometry and the closely related (111)-axis zincblende geometry. Even though zincblende InP is more stable in bulk, the c-axis wurtzite nanowire is more stable for nanowires until the diameter exceeds a value near 12 nm. An explanation is that the (111)-axis zincblende structure, although equally charge-neutral, has extra corner dangling bonds not found in

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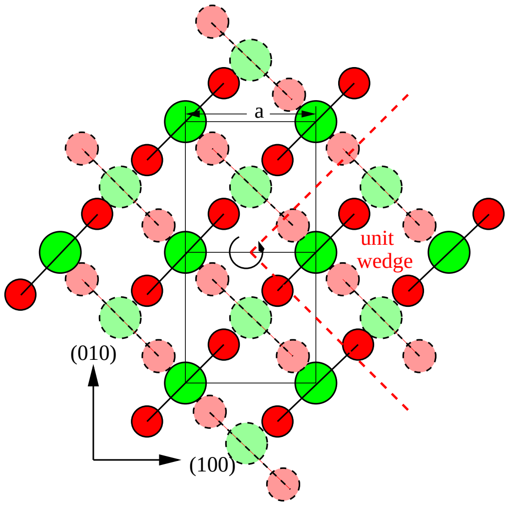

FIG. 1: (Color online) Atomic structure of a hypothetical rutile (001) NCNW, seen along the (001) growth axis. The structure has a C_4 screw axis with screw translation $c/2$, and four formula units of TiO_2 in the unit wedge. Ti atoms are in green, O in red; the lower layer has solid boundaries and bright colors. The upper layer is raised by $c/2$. This NCNW can be thought of as built from linear TiO_2 units, shown connected by black lines, solid or dashed. Half of them have (110) orientation, and half have $(1\bar{1}0)$ orientation.

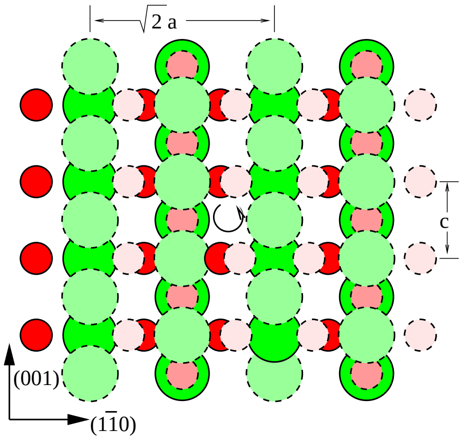

FIG. 2: (Color online) A hypothetical rutile (110) NCNW seen from the growth axis. The structure has both non-polar surfaces ±(001), and polar surfaces $\pm(1\bar{1}0)$. The central axis is a C_2 screw axis, with screw displacement $a/\sqrt{2}$, half of the translational periodicity. If the (001)-direction had been shortened to 8 instead of 9 TiO_2 rows, the central axis would also have C_2 screw symmetry. similarly, if the $(1\bar{1}0)$ direction had been changed from 4 to either 3 or 5 TiO_2 rows, the central axis would have simple C_2 symmetry.

wurtzite. However, nature is extremely subtle. ZnO grows often in c-axis NCNW's, but also can adopt a very complex twinned wurtzite-type "nanobelt"[22]. This form is then able to deform into "spring" geometry. The structure adopted by ZnO nanobelts is beyond what electronic structure theorists normally expect to predict.

Fluorite structure nanorods, such as CaF_2[23] grow in (111) orientation. This is an example of the design principle. Once one of the 4 equivalent (111) axes is chosen, a linear F-Ca-F unit along this axis makes a good choice for construction of a (111)-oriented nanorod by screw or simple 120° rotations around the growth axis, with non-polar surfaces exposed.

Anatase versus rutile. TiO_2 forms NCNW's in both its rutile and anatase forms. These provide an excellent example of the organizing principles. Each Ti has 6 oxygens in octahedral arrangement. Both structures have unique linear O-Ti-O unit; for each O atom, bonded to 3 Ti atoms, one of the 3 Ti's has a special relation, and a symmetry-equivalent O atom under inversion through the Ti The special O atoms of a Ti are "axial" and the other 4 are "equatorial." In rutile, equatorial rectangles orient with one side vertical (c-axis) and share their horizontal sides with vertically translated TiO_4. There are two symmetry-equivalent TiO_6 octahedra per rutile cell, rotated by 90° around c, and translated by $(1/2, 1/2, 1/2)$. The axial O's have Ti-O bonds along (110) and $(1\bar{1}0)$ for the two octahedra, and serve as equatorial O's for two other Ti's. None of the three nearly orthogonal Ti-O bond directions of one octahedron is parallel to any Ti-O bond direction of the other octahedron.

The linear TiO_2 units are both charge-neutral and dipole-free. The difficulty with rutile is that there are two different orientations for the linear units. Therefore, unlike wurtzite or fluorite, the units cannot all align parallel to the growth axis to give non-polar surfaces. The simplest and worst case is a (001) nanowire, shown in Fig. 1. The simplicity is in the high symmetry. The undesirable part is the 4 equivalent polar (110) surfaces. The nanowire has no net dipole, but each surface has a dipole layer. As the nanowire grows outward, there are $(2n)^2$ TiO_2 units in each $\hat{z}$-periodic double layer, or $(2n+1)^2$ units if a Ti-atom centered (C_2) symmetry axis is used. It is also possible to make a C_4 screw-symmetric termination with $2n(n+1)$ TiO_2 units per double layer, but these expose the less favorable (100) surfaces. The (001) axis does not seem to be a preferred growth axis of rutile NCNW's.

Another way to make a NCNW from rutile is shown in Fig. 2. Here the growth axis is (110), parallel to an axis of half of the TiO_2 units. This causes 2 of the 4 surfaces to be non-polar (001), with 4-coordinated Ti's and 2-coordinated O's. The other two surfaces are polar $(1\bar{1}0)$, the same as in the (001) nanowire discussed above. Half of the $(1\bar{1}0)$ surface Ti's are 4-coordinated and half are 6-coordinated. These latter have 5 fully coordinated oxygen neighbors and one dangling 1-coordinated axial O atom. Real nanowires often have surfaces passivated by environmental ad-atoms, surfactant molecules, etc. It can be desirable for theoretical models to mimic[26] this passivation, often by artificial constructs[27]. The model polar $(1\bar{1}0)$ surfaces of (110)-axis rutile can be passivated in a natural way[28] by adding H_2O's in equal numbers to the dangling O's. Then one H would associate to each

O, and the other OH would occupy a vacant O position, since surface O sites are only half filled. Then the 4-coordinated surface Ti's would become 6-coordinated. The (110) axis is the reported growth direction for rutile NCNW's[29].

The anatase form of TiO_2 is less stable than rutile but is easily produced in nanocrystalline form. Its crystal structure is especially favorable from the present point of view. Unlike rutile, in anatase, TiO_6 octahedra all have a linear O-Ti-O unit oriented along the c (or $\hat{z}$) axis. In the square $a-b$ plane, there are alternate choices of O-Ti-O units which are not quite linear, but close enough, and always point in $\hat{x}$ and $\hat{y}$ directions. Therefore, any of these three choices of O-Ti-O units can be used to build a nanowire with non-polar surfaces. The c-axis growth direction has the appealing property of a $(C_4|c/4)$ screw axis, or an alternative C_2 simple axis, whereas for growth axes lying in the $a-b$ plane, the alternatives are $(C_2|a/2)$ or simple C_2 axes parallel to $\hat{x}$ or $\hat{y}$. The (110) axis also has a C_2 simple rotational choice, but no simple O-Ti-O unit to use for parallel construction of non-polar NCNW surfaces. Anatase structure TiO_2 nanowires indeed grow in (001)-axis orientation[30], although (110)[31] and (101)-orientation[32] is also reported. The favorable surfaces of anatase (001) NCNW's might explain why nanophase TiO_2 is so often found in anatase instead of the bulk ground state structure, rutile.

Perovskite. The final example is perovskite, *e.g.* $BaTiO_3$. We have little direct experimental evidence of where atoms go in the nanowire. The (100) surface has two terminations, BaO and TiO_2. Both are nominally non-polar, Experimental reports of (100)-oriented nanowires with probable (010) surfaces[24] and (110)-oriented nanowires[25] exist. A problem arises for candidate small (100) NCNW's. The standard symmetric cubic unit cell can be chosen with Ti (nominally 4+) at the center of a cube, 8 nominally 2+ Ba ions on the corners, of which 1/8th of each is in the unit cell, and 6 nominally 2− oxygen ions on cube face centers, with half of each oxygen ion in the cell. By simple cubic translations, this unit is distributed to make an infinite crystal. But nature does not give fractional atoms or ions, so we cannot distribute this charge-neutral unit by translation to give a **finite**, locally charge-neutral nanosystem. Let us ignore charge-neutrality in favor of symmetry, letting ad-ions or spare electrons provide the missing charge that unequally distributed ionic species require. Square $n \times n$ layers built from repeats of the square BaO and TiO_2 units yield (001) NCNW's with large deviations from stoichiometry when n is small. If we start from the Ba-cornered 2×2 unit, and add layers by symmetric outward growth, we get the sequence of stoichiometries $Ba_9Ti_4O_{16}$, $Ba_9Ti_{16}O_{40}$, $Ba_{25}Ti_{16}O_{56}$, etc. If instead we start from a Ti-cornered 2×2 unit, and grow symmetrically out, the sequence is $Ba_4Ti_9O_{21}$, $Ba_{16}Ti_9O_{33}$, $Ba_{16}Ti_{25}O_{65}$. In all cases, the oxygen concentration is 1 shy of the stoichiometric Ba plus twice Ti concentration, and the Ba to Ti ratio converges to 1 slowly, like $2/n$.

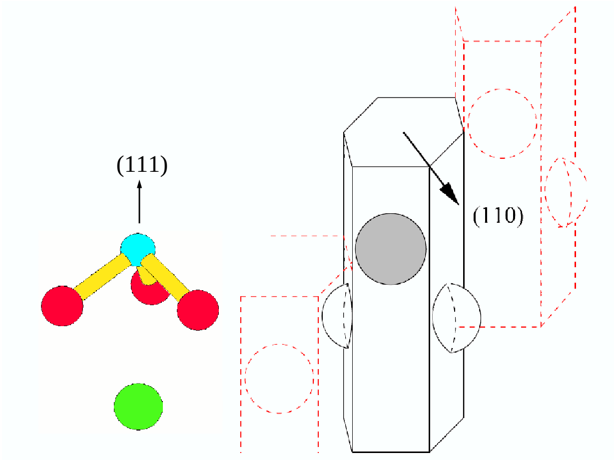

FIG. 3: (Color online) The cubic perovskite structure can be generated by translations of the formula unit shown on the left. This represents, for example, $BaTiO_3$, with the TiO_3 unit shown on top, with Ti on a C_3 rotational axis, and Ba below, on the same axis. The corresponding unit cell is shown to the right. It has three hemispherical protrusions (on alternate faces) to hold the formulaic oxygens, and three hemispherical holes, elevated by $c/3$ and rotated by 60°, to hold three virtual oxygens, which will appear under translations, to complete the TiO_6 octahedron. The translation rule is illustrated in Fig. 4. Vertical translations by $c/3$ are enforced by the hemispheres. The dashed red lines indicate how stacking may terminate on a $(1\bar{1}0)$ oxygen-terminated surface, with oxygen sites half occupied and half empty.

Any small (100) perovskite NCNW has a large fraction of either highly undercoordinated Ba or Ti edge atoms. Modeling with adsorbed species like H^+ or OH^- may help[33].

Unconventional translational cells. Consider cubic $BaTiO_3$ at temperatures above the ferroelectric distortive transitions. The aim is to pick a formula unit (one Ba, one Ti, and three O's) with maximal axial symmetry, and distribute them in an axially symmetric way. The answer is shown in Fig. 3. It has the important property of being not only charge neutral, but also having no net electrical dipole. This is important in $BaTiO_3$, which distorts at temperatures below 400K in bulk crystals to a sequence of distorted phases whose separate domains each carry a spontaneous electrical polarization. The polarization can be organized by an external field, including reversal of direction, which is the hallmark of ferroelectricity. If the translational unit used to build the crystal or nanowire had a net dipole, the structure would be pyroelectric rather than ferroelectric, and the polarity would not be reversible. The stability of the spontaneous polarity in nanowires of $BaTiO_3$ is a subject of debate[33,34].

To construct a nanowire with this unit, one should use the (111) unit axis as the growth axis. This is not

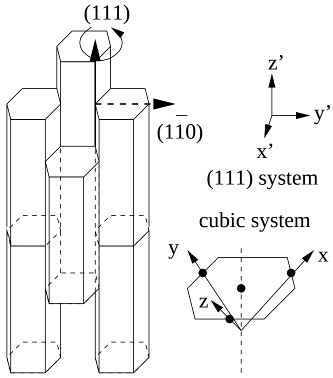

FIG. 4: The simple cubic and related structures can be generated from the hexagonal prism unit cell shown, under cubic translations $n_1\vec{a}_1 + n_2\vec{a}_2 + n_3\vec{a}_3$ where $\vec{a}_1$,$\vec{a}_2$,$\vec{a}_3$ are x, y, z in the "cubic system," or $\hat{a}_n = a\sqrt{2/3}[\cos(2\pi n/3)\hat{x}' + \sin(2\pi n/3)\hat{y}'] + a\sqrt{1/3}\hat{z}'$, in the "(111)-system." The fcc and related structures can be similarly generated, except that $\vec{a}_1$ is $(a/2)(\hat{y}+\hat{z})$ and so forth. A nanowire with (111) growth direction is generated by terminating in transverse directions, with vertical facets formed by the sides of the hexagonal prisms, and a constant transverse cross-section. If the termination is symmetric around the (111) axis, there are two choices for the symmetry axis. The axis shown has $(C_3|c/3)$ screw symmetry, with screw translation $(c/3)\hat{z}$, where the c parameter is $\sqrt{3}a$ for perfect cubic angles. Alternately, a simple C_3 symmetry is found around an axis through the center of a hexagon.

the reported growth direction, but perhaps perovskite nanowires with (111) growth can be made in the future. The "unit wedge" for such a nanowire, with $(C_3|c/3)$ screw rotational symmetry, is shown in Fig. 4. The exposed surfaces of such a nanowire are necessarily polar, because the $BaTiO_3$ unit is not linear. The likely surface is (110), shown in Fig. 5. Underneath this surface are alternating BaTiO and O_2 layers, with the top surface being a half-occupied O_2 layer. As in the rutile $(1\bar{1}0)$ surface, this can be passivated by addition of a molecule like H_2O. One H goes on the existing O, and the remaining OH fills the site of the missing O atom. The surface is still polar, but has dangling bonds satisfied. It is not obvious that nature will like this solution to the nanowire construction problem, but it offers a simple NCNW for theoretical modeling, and more satisfying solutions do not easily come to mind.

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[9] Neither "nanowire" nor "nanorod" appears in the 2006 AIP PACS (Physics and Astronomy Classification Scheme) index. It has become common in the literature to find the designation "nanowire (nanorod)." The implication is that nanowire is the preferred terminology, and nanorod means nothing different.
[10] The qualifier "quantum" applied to dots, wires, or rods, is ambiguous, not indicating whether the system is a free standing fragment of a crystal, or a region embedded in a host crystal, as in gate-patterned regions of a two-dimensional layer in a 3-D crystal. It would be preferable not to use "quantum" except for the latter case, or unless the ambiguity is intentional.
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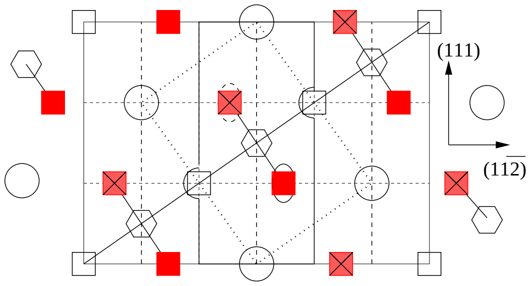

FIG. 5: The perovskite (1$\bar{1}$0) surface obtained by tiling the units of Fig. 3 according to the rules of Fig. 4. Ti atoms are denoted as hexagons, Ba atoms as circles, and oxygens as squares. Empty figures represent the subsurface BaTiO layer, and filled figures represent the top O_2 layer. This layer is half-filled according to the tiling rules of Figs. 1 and 2. The missing atoms have 'X' drawn through them. The diagonal rectangle shows the conventional primitive unit cell of the (1$\bar{1}$0) surface. Vertical dashed lines are topmost edges of the hexagonal prisms. The central hexagonal prism, with protrusions and hollows indicated, is drawn in bold outline, and represents an alternate primitive surface cell. A few atoms to the left and right indicate how the surface would continue.

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