Electronic properties of silica nanowires

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G Bilalbegović

Department of Physics, University of Rijeka, Omladinska 14, 51000 Rijeka, Croatia

E-mail: goranka.bilalbegovic@zg.t-com.hr

Abstract
Thin nanowires of silicon oxide were studied by pseudopotential density
functional electronic structure calculations using the generalized gradient
approximation. Infinite linear and zigzag Si–O chains were investigated. A
wire composed of three-dimensional periodically repeated Si_4O_8 units was also
optimized, but this structure was found to be of limited stability. The geometry,
electronic structure, and Hirshfeld charges of these silicon oxide nanowires were
computed. The results show that the Si–O chain is metallic, whereas the zigzag
chain and the Si_4O_8 nanowire are insulators.

1. Introduction

Nanochains of metals [1], as well as of carbon, semiconductors and organic materials [2, 3],
have recently been the subject of experimental and theoretical studies. Similar chains of many
other chemical elements and compounds have not been studied. Because of the present interest
in nanotechnology these studies are important. Chains with particular properties are candidates
for preparation of nanostructures with chosen applications. It is also possible to deposit chains
on various substrates and to obtain one-dimensional conductors and quantum confinement.

There are many crystalline phases of bulk silica, for example, quartz, tridymite,
cristobalite, keatite, coesite, and stishovite [4]. In addition, amorphous SiO_2, which is abundant
in nature, has also been investigated and used in various technological applications. These silica
bulk phases have been studied by several experimental [5, 6] and theoretical [7–13] methods.
Silica is a very good electrical insulator. Macroscopic silica wires are used as waveguides in
the visible and near-infrared spectral ranges. Silica films are often applied in optics, and are
used as electric and thermal insulators in electrical devices [14]. SiO_2 substrates are important
in microelectronics, optics and chemical applications. Therefore silica surfaces have been also
investigated [15].

Much less study has been devoted to silica nanostructures. Various cylindrical
nanostructures of silica have recently been synthesized: nanowires, nanotubes, nanoflowers,
bundles, and brush-like arrays [16–19]. Their structural, mechanical, optical, and catalytic
properties have been examined. Silica nanowires, with diameters ranging from ten to several

hundred nanometres, have been produced using various experimental techniques. They have been proposed for use as high-intensity light sources, near-field optical microscopy probes, and interconnections in integrated optical devices.

The properties of infinite silica chains have not been theoretically investigated. However, several theoretical studies of silica clusters have been carried out using Gaussian [20–26], GAMESS [27], SIESTA [28] and DMOL [21] packages, as well as several other density functional theory (DFT) programs [29–32]. Nanotubes of SiO_x, $x = 1, 2$, have recently been studied using the VASP DFT program [33]. All these computational studies of silica nanostructures have shown that their properties are often different in relation to the bulk. Therefore, it is also important to study infinite silica nanochains where periodic boundary conditions are used along the axis. These one-dimensional structures of silica are interesting from the theoretical point of view, as well as models of very long real nanowires. They provide additional systems for investigating the structure and bonding in silica materials, and offer possibilities of designing new nanostructures. It is possible to prepare such thin silica wires on substrates. The one that is most interesting for applications is the assembly of silica chains on silicon surfaces and nanowires.

In this work, the structure, energetics and electronic properties of thin silica nanowires were investigated using a computational method. Infinite linear and zigzag chains, as well as a nanowire composed of periodically repeated Si_4O_8 structural units, were constructed and optimized using a plane-wave pseudopotential approach to the density functional theory. The rest of the paper is organized as follows. Section 2 presents the method. In section 3 the results and discussion are given. Conclusions are outlined in section 4.

2. Computational method

Ab initio DFT calculations [34, 35] within the plane-wave pseudopotential method were performed to study silica chains. The pseudopotential approach has been very successful in describing the structural and electronic properties of various materials [36]. The ABINIT code was used [37]. The same method has already been applied to calculate various properties of bulk silica [9–13] and the (0001) α-quartz surface [15]. In this calculation the generalized gradient approximation and the exchange–correlation functional of Perdew *et al* were applied [38]. The pseudopotentials of Troullier and Martins [39] generated by the Fritz Haber Institute code [40] were used; these pseudopotentials were taken from the ABINIT web page [37]. They were tested by doing calculations for the bulk α-quartz, and these results were compared with experiments [41]. It was found that the computationally optimized structural parameters of quartz were very close to the experimental ones; the differences are below 0.1%. Several properties of silica nanowires were also calculated using the local density approximation (LDA) with the Teter extended norm-conserving pseudopotentials taken from the ABINIT web page [42, 37]. The results obtained using the Teter pseudopotentials were compared with experiments for bulk quartz structure, and differences of 0.1% have been obtained. Only minor quantitative differences were found between the LDA and GGA results for silica nanowires. The calculations were performed with a kinetic-energy cutoff of 35 Hartree. The wires were positioned in a supercell of side 30 au along the x and y directions. The axis of the wires was taken along the z direction, and periodic boundary conditions were applied. The Monkhorst–Pack method with 15 k-point sampling along the z direction was used in the integration of the Brillouin zone [43]. Structural relaxation for silica nanowires was carried out by performing a series of self-consistent calculations and computing the forces on atoms. The geometry optimizations were performed using the Broyden method of minimization

Table 1. The geometry and the binding energy of optimized structures. In this table a is the Si–O distance, while l is the Si–Si distance. The length unit is nm. Energies E are given in eV/atom.

Structure	Linear chain	Zigzag chain	Si_4O_8 nanowire
a	0.175	0.170	0.167
l	0.35	0.291	0.234; 0.235
E	−6.40	−5.51	−7.38

until the forces were less than 2.6×10^{-4} eV Å^{-1}. All atoms were allowed to relax without any imposed constraint.

Infinite Si–O chains were investigated. Two, four, and six atoms in a unit cell of a chain were studied to explore the possible dimerization and the existence of a zigzag structure. In previous studies of silica clusters it has been found that in stable structures there often exists a unit of two Si_2O_2 rhombuses sharing one silicon atom. This unit contains a tetrahedrally bonded Si atom and therefore shows the structural feature most often present in the bulk of SiO_2. Two adjacent rhombohedral rings in clusters are perpendicular to each other. It was calculated in this work that an optimized infinite silica wire forms if a Si_4O_8 unit is repeated periodically along a direction where the silicon atoms are positioned. The Si_4O_8 unit contains three whole Si_2O_2 rhombuses. Infinite tubular nanostructures of silica, similar to the finite MgO nanotubes studied recently [44], are not stable because their oxygen atoms are in four-fold coordinated configurations. However, calculations on silica clusters have shown that the oxygen atom prefers a lower coordination. In experimental studies of silica nanowires, much bigger structures having diameters 15–100 nm and lengths up to tens of millimetres have been prepared [16–19]. It has been shown that these silica nanostructures synthesized in the laboratories are amorphous. DFT-based studies of such already fabricated silica nanowires are not feasible within current computational power.

3. Results and discussion

The optimized distances and the binding energies of all nanowires are presented in table 1. The optimized geometries of silica chains are shown in figure 1. No dimerization was found for the linear chain. The zigzag chain is also stable and its energy is above that of the linear chain. Nonlinearity of the O–Si–O bonds is less favourable in a situation where there are no additional oxygen atoms, as in the case of bulk tetrahedral SiO_4 bonding. The optimized structure of the Si_4O_8 unit is shown in figure 2(a). It is well known that the Si–O distance in bulk silica is most often about 0.16 nm. It was calculated here that a larger Si–O distance of 0.175 nm exists in a linear chain, 0.170 nm in zigzag one, and 0.167 nm in a Si_4O_8 nanowire. In the zigzag chain the angles are $\alpha = 118°$. The width of the nanowire shown in figure 2(a) is up to about 0.24 nm. In the Si_4O_8 wire the oxygen atoms are bonded to two silicon atoms and the silicon atoms are bonded to four oxygen atoms. Such SiO_4 tetrahedra are typical for bulk materials involving silicon and oxygen. In the rhombuses of the Si_4O_8 wire the Si–O–Si angles are $\delta = 89.4°$ and $\gamma = 89.5°$, while the O–Si–O ones are $\beta = 90.4°$ and $\alpha = 90.6°$. The O–Si–O angle is $\epsilon = 119.7°$ when the oxygen atoms are in adjacent rhombuses. Thus, the coordination of the silicon atoms is distorted from an ideal tetrahedral geometry.

Figure 1 also presents the bonding wells for the chains. The minima are rather pronounced and show a substantial stability of these nanowires. By contrast, it was not possible to obtain a similar figure for the Si_4O_8 wire. Even very small perturbations (∼1%) of the length along the wire axis destabilize the Si_4O_8 wire. A small difference between the angle within one
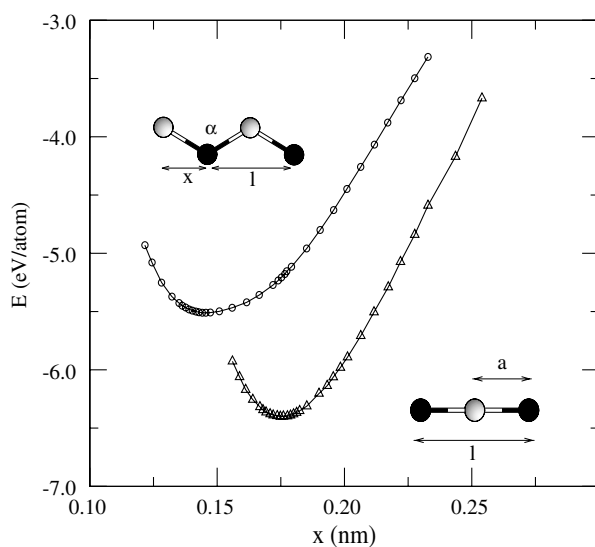
Figure 1. The binding energy as a function of $x = a$ for a linear chain (triangles), and $x = a \sin(\alpha/2)$ for a zigzag chain (circles), where a is the Si–O distance. The insets show the optimized geometries of the chains. Light and dark balls are used to represent the O and Si atoms respectively. These visualizations were performed using the Rasmol package [45, 46].
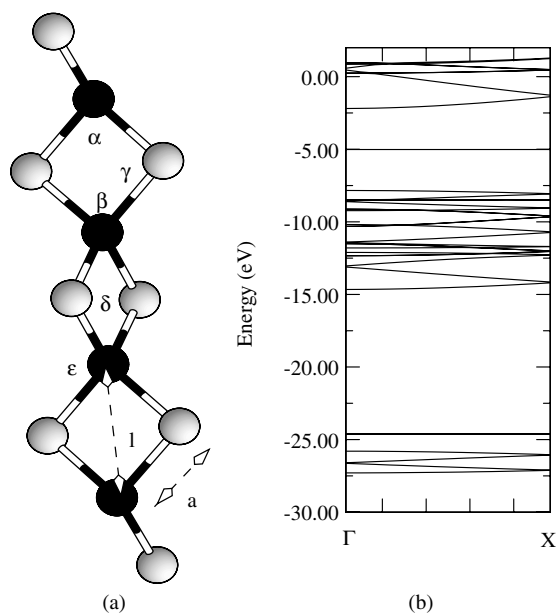

Figure 2. (a) The three-dimensional structural Si_4O_8 unit which repeats periodically along the wire axis and forms an optimized but almost unstable infinite nanowire (angles and lengths are given in the text). Light and dark balls are used to represent the O and Si atoms respectively. The middle rhombohedral ring is in the plane perpendicular to two edge rhombuses. (b) Electronic structure of the structure shown in (a). The Fermi level is denoted by the dashed line.
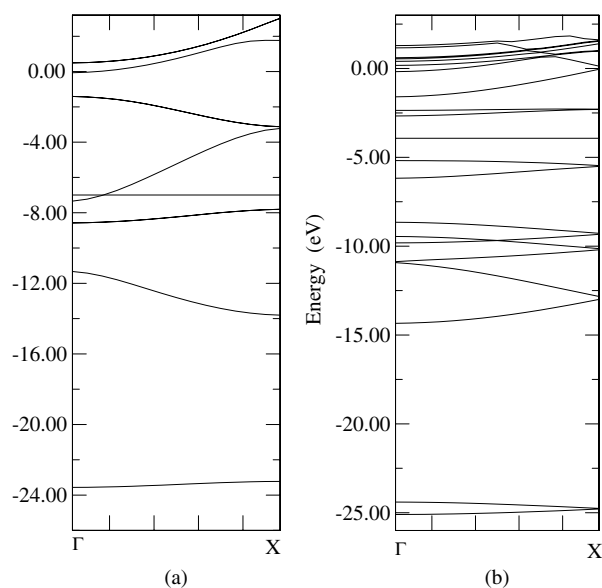
Figure 3. Energy band structures: (a) linear chain, (b) zigzag chain. The Fermi level is denoted by the dashed line.

rhombus exists ($\beta = 90.4°$ versus $\alpha = 90.6°$). It was not possible to stabilize such a three-dimensional thin wire using a smaller Si_2O_2 cell. The Si_4O_8 nanowire is at the border of instability. However, it was also found that the calculation where the LDA approximation to the DFT theory with the Teter extended norm-conserving pseudopotentials [42] was used produced a similar optimized Si_4O_8 infinite wire. For example, in this LDA approximation the Si–Si distance is $l = 0.232$ nm, whereas the Si–O distances are $a = 0.164; 0.165$ nm. It should be possible to assemble silica chains on the surfaces, using various nanotubes and nanowires, or long channels in porous materials. The role of the substrate is to increase the stability of very thin silica nanowires.

The band structure of silica chains is shown in figure 3. The plot of the electronic structure of a linear chain (presented in figure 3(a)) shows that one band crosses the Fermi level; therefore this system is metallic. The electronic structure of a zigzag chain is shown in figure 3(b). This wire is an insulator. The band plot in figure 2(b) shows that the Si_4O_8 nanowire is also an insulator. When the number of neighbours in Si–O nanowires increases, the electronic behaviour goes from metallic to insulating, as in the bulk. At the Gamma-point, the difference between the valence and conduction band is 5.646 eV for the Si_4O_8 nanowire, and 2.514 eV for the zigzag chain. Tetrahedral SiO_4 clusters exist in the Si_4O_8 nanowire. This structure is similar to the fragments of the cristobalite bulk lattice. The three-dimensional Si_4O_8 wire behaves as an insulator, and a similar electronic behaviour and a band gap value exist in the cristobalite crystal [8]. Table 1 shows that the Si–O and Si–Si distances are smaller in the zigzag chain than in the linear one. This compression of bonds as a result of the rearrangement of atoms into the zigzag chain removes a crossing band from the Fermi level, and an insulating behaviour arises in this structure. The Si–O distance in the linear chain is larger than in the majority of silica bulk phases, as well as in the zigzag and Si_4O_8 wires. That decreases the extent of π-bonding between silicon and oxygen atoms in the linear wire. The weak metallic behaviour arises in the linear silica chain as a consequence of this weaker bonding and a small coordination.
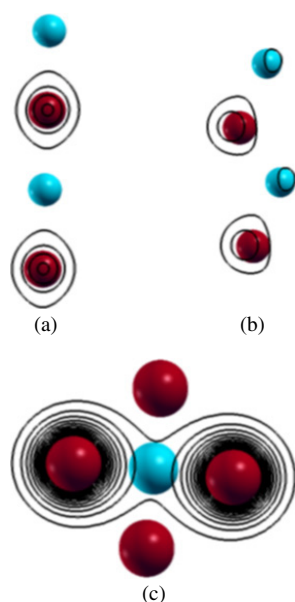
Figure 4. Charge density contour plots drawn using 0.4 e/a_0^3 isovalues. The dark spheres are O, whereas the light ones are Si atoms. Side views of unit cells for: (a) linear chain, (b) zigzag chain. (c) A top view of the cell for the Si_4O_8 nanowire: isolines around two top oxygen atoms are shown and the central ball represents the strand of Si atoms.

(This figure is in colour only in the electronic version)

Table 2. The Hirshfeld atomic charges. The calculated average charge transfers δQ are shown.

Structure	Linear chain	Zigzag chain	Si_4O_8 nanowire
$\delta Q(Si)$	0.212	0.275	0.446
$\delta Q(O)$	−0.212	−0.275	−0.225

Atomic charges were calculated using the Hirshfeld partitioning of the electron density [47–49]. The Hirshfeld method (or 'stockholder' partitioning) uses the charge density distribution to determine atomic charges in the molecule or nanostructure. First, the reference state of the promolecule density is defined as $\rho^{\mathrm{pro}}(\vec{r}) = \Sigma_A \rho_A(\vec{r})$, where $\rho_A(\vec{r})$ is the electron density of the isolated atom A placed at its position in the molecule. The atomic charge is

$$q_A = -\int \delta\rho_A(\vec{r})\, d\vec{r}, \tag{1}$$

where $\delta\rho_A(\vec{r})$ is the atomic deformation density given by

$$\delta\rho_A(\vec{r}) = w_A(\vec{r})\Delta\rho(\vec{r}). \tag{2}$$

In equation (2), $w_A(\vec{r})$ is the relative contribution ('share') of the atom A in the promolecule, whereas $\Delta\rho(\vec{r})$ is the molecular deformation density. The sharing factor is a weight that determines the relative contribution of atom x to the promolecule density at point r. It is defined as

$$w_A(\vec{r}) = \frac{\rho_A(\vec{r})}{\rho^{\mathrm{pro}}(\vec{r})}. \tag{3}$$

The molecular deformation density (used in equation (2)) is

$$\Delta(\vec{r}) = \rho(\vec{r}) - \rho^{\mathrm{pro}}(\vec{r}), \tag{4}$$

where $\rho(\vec{r})$ is the molecular electron density. The Hirshfeld partitioning is almost insensitive to the basis set and it minimizes missing information [47–49]. The Hirshfeld charges are presented in table 2. The calculations show that for all silica wires charge transfer occurs from Si to O atoms. This indicates ionic bonding. All oxygen atoms get similar amounts of the electron density, regardless of the structure.

The character of the bonding was also analysed using the electronic charge density. In figure 4 the charge density isosurface plots are presented. This visualization was performed by the XCrySDen package [50]. The well-defined spherical charges are located and accumulated on the oxygen atoms. Similar charge density plots that show a predominantly ionic bonding have been, for example, obtained for bulk α-quartz [7].

4. Conclusions

Three configurations of infinite silica nanowires were optimized and studied using *ab initio* DFT calculations in the pseudopotential approximation. The structural properties of these wires were investigated. It was found that a linear chain is energetically more favourable than a zigzag wire. The calculations of the bonding wells showed that both chains are stable, whereas the infinite Si_4O_8 wire is at the border of instability. The Hirshfeld charges were calculated and the results show that a similar transfer of a charge to oxygen atoms exists for all wires. It was found that the zigzag chain and the Si_4O_8 wire are insulators, while a single state crosses the Fermi level in the band plot of the linear chain. The existence of a metallic state offers the possibility to use simple long silica chains in conducting nanodevices without doping. It is possible to deposit and assemble these chains on various surfaces, nanotubes, or inside the long and wide pores of suitable bulk materials.

Acknowledgments

References

[1] Agraït N, Levy Yeyati A and van Ruitenbeek J M 2003 *Phys. Rep.* **377** 81
[2] Tongay S, Durgun E and Ciraci S 2004 *Appl. Phys. Lett.* **85** 6179
[3] Service R F 2001 *Science* **294** 2442
[4] Wyckoff R W G 1965 *Crystal Structures* (New York: Wiley)
[5] Nithianandam V J and Schnatterly S E 1988 *Phys. Rev.* B **38** 5547
[6] DiStefano T H and Eastman D E 1971 *Solid State Commun.* **9** 2259
[7] Chelikowsky J R and Schlüter M 1977 *Phys. Rev.* B **15** 420
[8] Xu Y N and Ching W Y 1991 *Phys. Rev.* B **44** 11048
[9] Gonze X, Allan D C and Teter M P 1992 *Phys. Rev. Lett.* **68** 3603
[10] Gonze X, Charlier J C, Allan D C and Teter M P 1994 *Phys. Rev.* B **50** R13035
[11] Lee C and Gonze X 1995 *Phys. Rev.* B **51** 8610
[12] Detraux F and Gonze X 2001 *Phys. Rev.* B **63** 15118
[13] Donadio D, Bernasconi M and Tassone F 2003 *Phys. Rev.* B **68** 134202
[14] Miyata H, Suzuki T, Fukuoka A, Sawada T, Watanabe M, Noma T, Takada K, Mukaide T and Kuroda K 2004 *Nat. Mater.* **3** 651

[15] Rignanese G M, DeVita A, Charlier J C, Gonze X and Car R 2000 *Phys. Rev.* B **61** 13250
[16] Gole J L, Wang Z L, Dai Z R, Stout J and White M 2003 *Colloid Polym. Sci.* **281** 673
[17] Yu D P, Hang Q L, Ding Y, Zhang H Z, Bai Z G, Wang J J, Zou Y H, Qian W, Xiong G C and Feng S Q 1998
    Appl. Phys. Lett. **73** 3076
[18] Zhang M, Ciocan E, Bando Y, Wada K, Cheng L L and Pirouz P 2002 *Appl. Phys. Lett.* **80** 491
[19] Tong L, Gattass R R, Ashcom J B, He S, Lou J, Shen M, Maxwell I and Mazur E 2003 *Nature* **426** 816
[20] Wang L S, Nicholas J B, Dupuis M, Wu H and Colson S D 1997 *Phys. Rev. Lett.* **78** 4450
[21] Nayak S K, Rao B K, Khanna S K and Jena P 1998 *J. Chem. Phys.* **109** 1245
[22] Bromley S T, Zwijnenburg M A and Maschmeyer Th 2003 *Phys. Rev. Lett.* **90** 035502
[23] Sun Q, Wang Q and Jena P 2004 *Phys. Rev. Lett.* **92** 039601
[24] Bromley S T, Zwijnenburg M A, Flikkema E and Maschmeyer Th 2004 *Phys. Rev. Lett.* **92** 039602
[25] Sun Q, Wang Q, Kawazoe Y and Jena P 2004 *Nanotechnology* **15** 260
[26] Sun Q, Wang Q, Rao B K and Jena P 2004 *Phys. Rev. Lett.* **93** 186803
[27] Lu W C, Wang C Z, Nguyen V, Schmidt M W, Gordon M S and Ho K M 2003 *J. Phys. Chem.* A **107** 6936
[28] Zhao M W, Zhang R Q and Lee S T 2004 *Phys. Rev.* B **69** 153403
[29] Chelikowsky J R 1998 *Phys. Rev.* B **57** 3333
[30] Chu T S, Zhang R Q and Cheung H F 2001 *J. Phys. Chem.* B **105** 1705
[31] Song J and Choi M 2002 *Phys. Rev.* B **65** R241302
[32] Bromley S T and Flikkema E 2005 *Phys. Rev. Lett.* **95** 185505
[33] Singh K A, Kumar V and Kawazoe Y 2005 *Phys. Rev.* B 155422
[34] Hohenberg P and Kohn W 1964 *Phys. Rev.* **136** B864
[35] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[36] Martin R M 2004 *Electronic Structure* (Cambridge: Cambridge University Press)
[37] Gonze X, Beuken J M, Caracas R, Detraux F, Fuchs M, Rignanese G M, Sindic L, Verstraete M, Zerah G, Jollet F,
    Torrent M, Roy A, Mikami M, Ghosez Ph, Raty J Y and Allan D C 2002 *Comput. Mater. Sci.* **25** 478
    http://www.abinit.org
[38] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[39] Troullier N and Martins J L 1991 *Phys. Rev.* B **43** 1993
[40] Fuchs M and Scheffler M 1999 *Comput. Phys. Commun.* **119** 67
[41] Levien L, Prewitt C T and Weidner D 1980 *Am. Mineral.* **65** 920
[42] Teter M 1993 *Phys. Rev.* B **48** 5031
[43] Monkhorst H J and Pack J D 1976 *Phys. Rev.* B **13** 5188
[44] Bilalbegović G 2004 *Phys. Rev.* B **70** 045407
[45] Sayle R and Milner-White E J 1995 *Trends Biochem. Sci.* **20** 374
[46] Bernstein H J 2000 *Trends Biochem. Sci.* **25** 453
[47] Hirshfeld F L 1977 *Theor. Chim. Acta* **44** 129
[48] De Proft F, Van Alsenoy C, Peeters A, Langenaeker W and Geerlings P 2002 *J. Comput. Chem.* **23** 1198
[49] Nalewajski R F and Parr R G 2000 *Proc. Natl Acad. Sci. USA* **97** 8879
[50] Kokalj A 1999 *J. Mol. Graphics Modelling* **17** 176 http://www.xcrysden.org