Negative compressibility of selenium chains confined in the channels of AlPO₄-5 single crystals

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Abstract. Pressure-induced structural and electronic variations of Se helical chains confined in nano-channels of zeolite single crystals are studied. Raman and optical absorption spectra provide us with evidence of softened vibration modes and band gap reduction under high pressure. We reveal that the Se chains elongate under hydrostatic compression by ab initio calculations. The changes in morphology lead to a softening of phonons and narrowing of energy gaps consistent with observations from optical measurements. The present investigation demonstrates negative compressibility of Se chains in one-dimensional channels of a zeolite framework.

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1. Introduction

Selenium is a group VI non-metallic element with a band gap of about 2 eV at ambient pressure. To realize metallization in bulk selenium with a concomitant structural phase transition, a large pressure of up to tens of GPa is necessary [1]–[3]. Such phase transition phenomena in polycrystalline selenium have been observed under high pressures by in situ measurements of Raman spectroscopy and x-ray diffraction. The metallization [4] and anomalous linear expansion coefficient under 20 GPa [5] have been examined for crystalline selenium using density functional calculations. Here, we investigate the properties of isolated Se chains under pressure to demonstrate that a much lower pressure is sufficient to induce detectable changes in the properties of confined Se chains inside the nano-channels of a zeolite framework. In this work, we have also taken the coexisting Se$_8$ rings into account, since both of these types of Se species are stabilized in the channels. The pressure-induced structural and electronic changes of Se chains confined in zeolite channels are measured by Raman spectroscopy and optical absorption spectroscopy. The experimental results indicate a trend toward metallization as we keep increasing the pressure. Detailed changes in electronic and structural parameters are calculated by the density functional theory (DFT) method, which models the hydrostatic pressures effect applied to the single trigonal helical chain of selenium. Comparison of the results from theory and experiment suggests an anomalous negative compressibility in these isolated Se chains confined in the zeolite pores.

2. Experiment and calculation methods

The zeolite template, AlPO$_4$-5 crystals (IUPAC code AFI; molecular formula Al$_{12}$P$_{12}$O$_{48}$), are synthesized using a hydrothermal method [6]. The crystalline framework with parallel one-dimensional channels is formed by alternating tetrahedra of [AlO$_4$]$^{-}$ and [PO$_4$]$^{+}$ units (space group: P6/mcc). The inner diameter of the channel is 7.3 Å, and the separation distance between two neighboring channels is 13.7 Å. As shown in figure 1(a), selenium species are incorporated into the AlPO$_4$-5 crystal channels by the vapor phase diffusion method as described previously [7]–[9]. Previous extended x-ray absorption fine structure (EXAFS) and photo-acoustic spectroscopy (PAS) studies on the Se–Se distances have confirmed that single chains of Se are indeed being confined in the assembling zeolite template [10, 11], mordenite with a channel diameter of 6.7 Å. The Se chains formed inside AFI with a diameter of 7.3 Å are studied by x-ray scattering, which determines the diameter of the chain to be 3.4 Å. If we consider that the van der Waals radius of the chain is 1.9 Å, only the formation of single chains is possible inside the channel of AFI [9].

Optical characterizations of selenium nanostructures formed inside AlPO$_4$-5 single crystals were measured by a Jobin–Yvon T64000 Raman spectrometer equipped with a CCD detector cooled by liquid nitrogen. The Raman scattering was excited by the 632.8 nm line from an He–Ne laser. A 100 W xenon lamp was used as the light source for the optical absorption spectroscopy. Using the confocal technique, optical absorption spectroscopy was measured within a light spot that was <20 μm in diameter with its center coinciding with the 1 μm light spot of the excitation laser for Raman scattering. Hydrostatic pressure was applied to the crystal by using a diamond anvil cell (DAC). The crystal was immersed in the transmitting medium: a ethanol–methanol mixture (1 : 4 ethanol and methanol in volume percentage) [12], together with a ruby grain that is used to determine the pressure inside the stainless steel gasket. The DAC is pressed in situ by a gas membrane without moving the sample.

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Figure 1. (a) Schematic representation of Se helical chains formed inside the AlPO$_4$-5 single crystal framework. (b) Raman scattering from Se species under the ZZ and YY polarized configurations. (c) Raman spectra of the trigonal selenium chain plotted as a function of applied pressure. When the pressure increases, two changes in Raman scattering take place: a gradual softening of Raman modes and a slight red shift in vibration frequency. The vertical dashed line indicates the frequency of the center of the $A_1$ Raman modes at 257 cm$^{-1}$ under ambient pressure. The dots denote the center of the $A_1$ mode at different pressures.

The Vienna $ab$ $initio$ simulations program [13] (VASP4.6.25) was used to perform the first-principles calculations. An energy cutoff of 194.0 eV(14.26 Ry)/Perdew–Wang(PW91) and a cutoff of 264.4 eV(19.43 Ry)/Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were applied. Infinite selenium trigonal chains (periodic along the chain axis) and finite selenium rings are simulated using the standard supercell approach. The Brillouin zone was sampled with $1 \times 1 \times 30$ $k$-points of a Monkhorst–Pack grid for chains. The supercell geometry is used and the chain–chain distance is chosen as 10 Å. At such a distance, interactions between adjacent chains are very weak, so the results can be interpreted as those for a single chain. For the phonon calculation, each Se chain structure of fixed repeat length was fully relaxed with respect to the other two dimensions according to the calculated force on the atoms. The Hellmann–Feynman forces converge to become $<0.005$ eV Å$^{-1}$. 

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3. Results

Visible light Raman spectra of our isolated selenium chains are shown in figures 1(b) and (c). Since Raman scattering from a pure zeolite single crystal is much weaker than that from the selenium species inside channels, the spectra contribution from the zeolite can be ignored [14]. From Se chains inside the channel, there are six optical phonon modes \( \Gamma_{\text{opt}} = A_1 + A_2 + 2E_1 + 2E_2 \). The highest frequency single mode (257 cm\(^{-1}\)), \( A_1 \), correspond to a vibration of symmetric chain radial expansion similar to the radial breathing mode in carbon nanotubes. The mode \( A_2 \) comes from the chain rotation mode, which is Raman-inactive. Both \( E \) modes are doubly degenerate; one of them is peaked at 233 cm\(^{-1}\), while the other (107 cm\(^{-1}\)) is well below the lower limit of our present frequency of Raman measurement (150 cm\(^{-1}\)). These Raman-active modes from Se chains can be identified in figure 1(b), under the ZZ configuration for both polarizations of the excitation and with the scattering light being parallel to the chain direction. For the YY configuration (both the excitation and scattering light are perpendicular to the chain axis), a peak from ring-shaped Se\(_8\) clusters at 267 cm\(^{-1}\) is dominant. This mode appears in both the ZZ and the YY configurations, which originate from the random orientation of the Se\(_8\) rings [15, 16].

A hydrostatic pressure of up to 6.42 GPa was applied to the channels through the pressure-transmitting media. As shown in figure 1(c), as the pressure increases, Raman modes are broadened with an increasing shoulder on the low-frequency side of the Raman mode with a slight red shift in frequency. Such a type of red shift of oscillator strength has been discussed before on the basis of chain–chain interaction [17]. Since there is no inter-chain coupling in Se chains isolated by the AlPO\(_4\)-5 zeolite frameworks, observations of pressure-induced changes in the line shape of the Raman modes are suspected to have a different origin.

Figure 2 shows the optical absorption peaks along different polarizations of the incident light. The polarized optical absorption spectra exhibit a clear anisotropy since the absorption measured in the \( E \parallel c \) (polarized along the channel direction) configuration is higher than that in the \( E \perp c \) (polarized perpendicular to the channel direction) configuration owing to the stronger dipole oscillation along the elongated direction of Se chains. For the ring-like Se\(_8\) cluster, the dependence on polarization is much weaker as no preferred absorption direction is present and the orientation of clusters is random inside the channel. Anisotropy in the absorption spectra provides strong evidence that most Se atoms are in the form of long chains inside the channels.

As we increase the pressure from 0 to 6.42 GPa, the absorption shifts monotonically to the lower energy side for the \( E \parallel c \) configuration from 2.55 to 2.05 eV, while a small shift to the higher energy side is observed in the \( E \perp c \) configuration from 2.86 to 2.95 eV. The two different variations of absorption spectra under pressure originate from two different species inside the channel. For the \( E \perp c \) configuration, the absorption is mostly from the ring-like Se\(_8\) structures. Since the contribution of absorption of chain structures is concentrated in the \( E \parallel c \) configuration, down shift of the absorption spectrum is consistent with the assumption that chain lengthening occurs with the increase of pressure. Electronic energy band structure calculations indicate that the longer the chains, the narrower the band gaps. The inset of figure 2(a) shows the band structure under local density approximation (LDA) of the Se chain for zero pressure (with \( k \) along the chain axis, 3 atoms per unit cell). The selenium atom has the electronic configuration of \( 4s^24p^4 \). As shown in the inset, two 4p electrons contribute to form covalent \( \sigma \) bonds with two neighboring atoms. The remaining two 4p electrons form the lone pair (LP) states and the highest valence bands. Above the Fermi level is the empty 4p anti-bonding
Figure 2. Optical absorption of Se species measured under a pressure from 0 to 6.42 GPa. (a) Red shift of absorption in the $E \parallel c$ configuration is shown, with the dots denoting the energy of the absorption edge. (b) Blue shift of the absorption peak in the $E \perp c$ configuration is shown, and the peak position is denoted by the dots. The inset shows the calculated LDA band structure where Fermi energy is equal to 0 eV.

$\sigma^*$ states for the lowest unoccupied conduction bands. Our calculations to be discussed indicate a band gap shrinkage (0.33 eV under a theoretical pressure of 6 GPa) when the chain is lengthened by 0.1 Å and thinned by 5%. Therefore the red shift of the absorption threshold is consistent with pressure-induced negative compressibility along the chain direction. Upon release of pressure, we have observed the absorption spectra recovered (not shown here) as selenium chains return to their original length.

4. Discussion

As mentioned earlier, cyclic Se molecules such as rhombohedral Se$_6$ or $\alpha$-monoclinic Se$_8$ rings may also exist in the channels. Electronically the ring clusters show a similar semiconducting band gap as the trigonal Se chain. Bulk Se chain and ring structures under high pressure have been investigated by x-ray and Raman spectroscopy measurements. The Raman modes showed a similar pressure-induced softening [18] due to the interference effect between inter- and intra-molecular bonds in the molecular crystals [17]. However, in the bulk material, the intra-chain Se–Se covalent bonds are much stronger than the inter-chain van der Waals interactions. The applied pressure tends to pack the chains denser so that chain–chain coupling increases rapidly. The bulk Se crystal can be viewed as an array of such helices with stronger inter-chain couplings.

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Figure 3. (a) Total energy (in eV) contour plot is shown with varying cross sectional radius and unit cell length along the chain axis. (b) The gradient of the total energy plot reveals the hydrostatic pressure line by finding vectors with equal components along the horizontal and vertical directions. The Se chain’s structural change as a result of an increase in the hydrostatic pressure should be unidirectional and located only in the second quadrant. The arrow in the circle indicates a theoretical pressure (∼6 GPa) that is close to our experimental value. (c) The contour map of calculated band gap values (in eV) for varying (δr, δc) parameters. Band gap reduction from (δr, δc) = (0, 0) can be found in the second quadrant as well.

For isolated Se chains, this mechanism is eliminated since interactions between chains are largely blocked by the walls between the zeolite pores. An isolated single trigonal helical Se chain is energetically more favorable than a linear or zigzag chain [19]. However, a trigonal Se helix is a semiconductor, while both of the hypothetical linear or zigzag chains are metallic (coordination number equals 2 in all cases).

To model the hydrostatic pressure applied to the Se chain in the confined channels, we have studied various compressed and decompressed chains. The Al, P and O atoms on the walls of AFI channels are not included in the simulation by assuming that the Se chains are unaffected by the weak van der Waals interaction with these framework atoms. In our simulation, the compression and decompression are applied along the chain axis with the symmetry preserved. Results of our calculation show that with an increase of pressure, compressed chains show no significant band gap modification, while decompressed chains show gradually narrowing band gaps. In comparison with the experimental observations, the decompression of the chain length with the increase of pressure is consistent with a gradual red shift of the absorption spectra as shown in figure 2.

Trigonal chalcogen bulk phases (Se and Te) are known to show unusual negative linear compressibility [20] as the spiral selenium chain diameter contracts and the chain length expands under pressure. Figure 3(a) shows the total-energy map of the Se chain as a function
of helical radius \( r \) and lattice constant \( c \). Using the DFT method, we first obtain the equilibrium structure of the helical Se chain located in the center of the plot. Structural contraction or expansion of chains in all three dimensions gives very high energies in the landscape (lower left corner of the contour plot), so the anisotropic structural deformation is more favorable under pressure. Away from equilibrium, the Se chains can minimize the deformation energy either by elongating in length with contraction in radius or by shortening in length with expansion in radius simultaneously. We will see that the chain tends to elongate in length and shrinks in radius in reaction to the hydrostatic external pressure. Once the structural parameters are different from their equilibrium values, there are finite energy gradients along structural coordinates (i.e. \( \frac{\partial E}{\partial r} \neq 0 \) and \( \frac{\partial E}{\partial c} \neq 0 \)), and when properly normalized by area, these gradients correspond to a pressure. In order to deform the Se chain away from the equilibrium position, a corresponding external pressure tensor has to be applied to the chain. The pressure in a fluid can be considered as a measure of energy per unit volume or energy density. The hydrostatic pressure applied in the experiment sets the boundary condition to have equal pressures along the radial and longitudinal directions: \( P(V) = \frac{\partial E(V)}{\partial V} = -\frac{1}{2\pi r_0 c \pi} \frac{\partial E}{\partial r} \) and \( P(V) = -\frac{\partial E(V)}{\partial V} = -\frac{1}{\pi r_0^2 c} \), where \( r_0 = 0.976 \text{Å} \) and \( c_0 = 4.962 \text{Å} \) are the chain radius and length under zero pressure. The quantities \( -\frac{1}{2\pi r_0 c \pi} \frac{\partial E}{\partial r} \) and \( -\frac{1}{\pi r_0^2 c} \) can be regarded as the pressure along the radial and tangential directions that are required to maintain the chain deformation. The pressure vector components \( \left(-\frac{1}{2\pi r_0 c \pi} \frac{\partial E}{\partial r}, -\frac{1}{\pi r_0^2 c}\right) \) are illustrated in figure 3(b) in a vector map. The arrows at 45° give the unidirectional pressure line and their magnitudes determine the hydrostatic pressure applied.

We note that there are four quadrants in figures 3(a) and (b), corresponding to the four possible combinations of changes in structural parameter: \((\pm \delta r, \pm \delta c)\) about the equilibrium point at \((\delta r, \delta c) = 0\) for a freely standing spiral chain. If we impose any external condition of equal pressure on the radial and tangential directions, the chain will be changed from the equilibrium condition of \( \frac{\partial E}{\partial r} = \frac{\partial E}{\partial c} = 0 \) to a compressed configuration such that \( -\frac{1}{2\pi r_0 c \pi} \frac{\partial E}{\partial r} = -\frac{1}{\pi r_0^2 c} \) and arrow vectors in figure 3(b) should be along 45°. We found that such a condition can only be found in the quadrant \( \delta r < 0, \delta c > 0 \), corresponding to configurations in which the spiral chain becomes ‘slimmer’ and ‘elongated’. The configuration corresponding to the pressure of 6 GPa (the experimental nominal pressure is up to 6.42 GPa) is found to be \((\delta r, \delta c) = (-0.0488, 0.1)\) in Angstroms (see the arrow in the circle in figure 3(b)). Our theoretically estimated pressure coefficient \((d\omega/dP)\) for the A1 mode \(-0.529 \text{ cm}^{-1} \text{ GPa}^{-1}\) is reasonably close to the experimental observed value \(-0.573 \text{ cm}^{-1} \text{ GPa}^{-1}\).

We examined the change in electronic and lattice vibrational properties when the chains are elongated under pressure. Figure 3(c) shows the LDA band gaps of the Se chains for different values of \((\delta r, \delta c)\). The contour plot clearly shows that deformations in the second quadrant lead to a reduced band gap. In the extreme case, the top left corner corresponds to a metallic state with zero band gap, corresponding to the \( \delta r < 0, \delta c > 0 \) quadrant that we identified. Interestingly, the isotropic contractions \( \delta r < 0, \delta c < 0 \) under pressure would lead to a dramatically enlarged band gap. This ‘normal’ pressure dependence of the structural parameters, which transforms the Se chains to an insulator, is in contradiction to our experimental observations of hydrostatically compressed selenium chains.

For the effect of elongation of the chain on phonon frequencies, we expect that when the chains are elongated under the pressure, the weakening atomic interaction between neighboring atoms leads to reduction in phonon frequencies. Such softening effects in tensile strain response are well known in quasi-one-dimensional systems such as carbon nanotubes [21]. Similar
Figure 4. Phonon frequencies are calculated for the structures under pressure by varying the lattice constant for the single Se chains. The highest mode (black squares) for Se helical chains corresponds to the $A_1$ mode. Red shift in phonon frequency is found for the elongated chains ($\delta c > 0$). The Se$_8$ ring’s phonon frequencies are indicated by the short bars.

pressure dependences are found in our numerical results on helical Se chains. Figure 4 shows the calculated phonon frequencies as a function of change in the lattice constant $\delta c$. For each value of $\delta c$, atoms are relaxed to their zero force position, and zone-center phonon frequencies are calculated by diagonalizing the force matrix. We also computed the phonon frequencies of an isolated Se$_8$ atomic ring (fully relaxed, the see inset of figure 4 for the atomic geometry) and have plotted them in figure 4 for comparison. The highest two Raman active modes of the equilibrium ($\delta c = 0$) Se chains are slightly below the highest frequency mode of the Se$_8$ rings, which is qualitatively consistent with the experimental results shown in figure 1(b). When the lattice constant is changed, there is a decrease (increase) of phonon frequencies as the chain is elongated (shortened). Regarding Raman scattering as shown in figure 1(c), there is an overall reduction of signal intensity, but the signal strength is skewed towards the low-frequency side of the spectra with a slight decrease of the Raman frequency. At the pressure of around 6 GPa, the calculated change of $\delta c = 0.1$ corresponds to a red shift of the vibration modes for about 3.2 cm$^{-1}$. For the Raman scattering centered around 257 cm$^{-1}$ at the ambient pressure, we experimentally find that the Raman mode red shift is around 4 cm$^{-1}$ in the pressure range from 0 to 6.42 GPa. This frequency shift agrees with the mode softening for $\delta c > 0$ predicted by LDA calculations reasonably well.

The volume compression actually results in contraction of chain radius, longer Se–Se bond length and larger bond angle. Thus, this somewhat counter-intuitive result makes all the experimental and theoretical data consistent. Brief mention should be made of the marked directional negative compressibility, which have been found previously in a class of compounds and biological systems [22]. But to our knowledge, it has not been reported in the single element-like Se chains.
5. Conclusion

In conclusion, we investigated the properties of Se atomic chains under pressure inside one-dimensional nano-channels. Using this template material, a moderate external pressure can induce quite a conspicuous change in the structure of Se chains which modifies its electronic, optical and vibrational properties. The confined geometry allows us to investigate the effect of pressure on a single chain. A combination of the density functional calculations and optical spectroscopy shows that the Se chains are elongated under pressure along with a narrowing of the band gap and softening of the phonon modes.

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References

[1] Degtyareva O, Hernandez E R, Serrano J, Somayazulu M, Mao H-k, Gregoryanz E and Hemley R J 2007 J. Chem. Phys. 126 084503
[2] Nakano K, Akahama Y, Kawamura H, Takumi M and Nagata K 2001 Phys. Status Solidi b 223 397
[3] Degtyareva O, Gregoryanz E, Somayazulu M, Dera P, Mao H-k and Hemley R J 2005 Nat. Mater. 4 152
[4] Yonezawa F, Ohtani H and Yamaguchi T 2001 J. Non-Cryst. Solids 293–295 199
[5] Akbarzadeh H, Clark S J and Ackland G J 1993 J. Phys.: Condens. Matter 5 8065
[6] Qiu S, Pang W, Kessler H and Guth J-L 1989 Zeolites 9 440
[7] Tang Z K, Loy M M T, Goto T, Chen J and Xu R 1997 Solid State Commun. 101 333
[8] Tang Z K, Loy M M T, Chen J and Xu R 1997 Appl. Phys. Lett. 70 34
[9] Li I L, Zhai J P, Launois P, Ruan S C and Tang Z K 2005 J. Am. Chem. Soc. 127 16111
[10] Khouchaf L, Tuilier M H, Guth J L and Elouadi B 1996 J. Phys. Chem. Solids 57 251
[11] Tamura K, Hosokawa S, Endo H, Yamasaki S and Oyanagi H 1986 J. Phys. Soc. Japan 55 528
[12] Rafailov P M, Maultzsch J, Machon M, Reich S, Thomsen C, Tang Z K, Li Z M and Li I L 2002 Structural and Electronic Properties of Molecular Nanostructures: XVI International Winterschool on Electronic Properties of Novel Materials (AIP, Kirchberg, Tirol, Austria) p 290
[13] Kresse G and Furthmuller J 1996 Phys. Rev. B 54 11169
[14] Goldbach A and Saboungi M L 2003 Europ. Phys. J. E: Soft Matter Biol. Phys. 12 185
[15] Poborchii V V, Kolobuz A V, Caro J, Zhuravlev V V and Tanaka K 1997 Chem. Phys. Lett. 280 17
[16] Li I L, Ruan S C, Li Z M, Zhai J P and Tang Z K 2005 Appl. Phys. Lett. 87 071902
[17] Martin R M, Luovsky G and Helliwell K 1976 Phys. Rev. B 13 1383
[18] Nagata K, Ishikawa T and Miyamoto Y 1983 Japan. J. Appl. Phys. 22 1129
[19] Springborg M and Jones R O 1988 J. Chem. Phys. 88 2652
[20] Baughman R H, Stafström S, Cui C and Dantas S O 1998 Science 279 1522
[21] Wu G, Zhou J and Dong J 2005 Phys. Rev. B 72 115411
[22] Kornblatt et al 1998 Science 281 143a

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