Total energy calculation for high pressure selenium: the origin of incommensurate modulations in Se IV and the instability of proposed Se II

G J Ackland and H Fox

School of Physics and Centre for Science at Extreme Conditions, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

Abstract
We present calculations of the high pressure crystal structures in selenium, including rational approximants to the recently reported incommensurate phases. We show how the incommensurate phases can be intuitively explained in terms of imaginary phonon frequencies arising from Kohn anomalies in the putative undistorted phase. We also find inconsistencies between the calculated and experimental Se II phase—the calculations show it to be a metastable metal while the experiment finds a stable semiconductor. We propose that the experimentally reported structure is probably in error.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The group VI elements selenium and tellurium are semiconductors with a hexagonal crystalline structure at ambient pressure. Both elements undergo a series of phase transitions as pressure is increased, transforming to various complex structures denoted by roman numerals I, II, III, IV. The generally accepted crystal structures associated with these phases in selenium are hexagonal Se I; monoclinic Se II from 14 GPa; triclinic Se III from 23 GPa; orthorhombic Se IV from 28 GPa; and subsequently simple higher symmetry phases [1]. Note that this nomenclature does not correspond to that used in earlier work [2]. Tellurium undergoes a similar set of phase transitions at lower pressures, without the equivalent of Se II.

In 2003 combined powder and single-crystal x-ray diffraction [3] studies found that the Te III phase had a more complex structure than had previously been thought, involving a modulated distortion of the previously reported unit cell. It was suggested that Se IV had a similar structure experimental confirmation of this is in progress [4]. Sulfur is now believed to exhibit similar behaviour [5].

A theory of complex phases at intermediate pressures in sp-bonded elements has been advanced, based on the free electron picture [6–8]. Here a significant effect arises from

interactions between the Fermi surface and the Brillouin zone boundary which increase as the reciprocal of the volume (V^{-1}), compared with the $V^{-1/3}$ and $V^{-2/3}$ dependences of Coulombic and kinetic energy terms. The simplest effects are stabilizations of particular ratios of the lattice constants in group IV elements and their compounds such as Si, Ge, Sn, GaAs [9]. A more complex effect is stabilization of particular phonons in the bcc structure, or stabilization of lattices of self-interstitial defects [6]. The irrational ratio between lattice reciprocal vectors and the Fermi vector [10] can lead to incommensurate modulations as observed in Se, or even to exotic 'hotel' structures [11–14] where two interpenetrating lattices with incommensurate lattice constants adjust to the Fermi vector [14]. The signature of this effect is the presence of diffraction peaks slightly below the free electron Fermi vector, and the opening of a gap or pseudogap in the band structure. This has historically caused particular difficulties in solving crystal structures from powder diffraction—there may be overlapping diffraction peaks close to the Fermi surface, and the simplest crystal structure consistent with powder data may be found to have a metallic rather than semiconducting band structure. Here we show this to be the case with Se II.

Another common effect of interactions between the Fermi surface and the Brillouin zone boundary is a lowering of the frequency of particular phonons due to Fermi surface nesting—the Kohn anomaly. Phonon dispersion has not yet been investigated experimentally for intermediate pressure phases, on account of the difficulty of producing large single crystals and achieving recovery to ambient conditions. Nor have calculations been done, due to the large unit cells needed for direct methods [15] and very large k-point sampling for perturbation theory [16] necessary for probing mid-zone Kohn anomalies.

The case of selenium IV presents a more tractable problem. In the nearly free electron picture [6] the incommensurate modulation arises from Fermi surface–Brillouin zone interactions so strong that they reduce the phonon energy sufficiently that it can couple to a lattice strain and produce a negative energy distortion—a charge density wave arising as an extreme case of a Kohn anomaly. The extra stability gained from the lattice coupling means that this is a slightly more complicated picture than a simple freezing in of an imaginary frequency phonon—specifically, it is not necessary for the phonon frequency to become imaginary for the combined lattice–phonon distortion to be stable.

Density functional theory [17, 18], using pseudopotentials, plane waves and local exchange correlation functionals, has been the method of choice for theoretical study of selenium. Within the local density approximation (LDA) the p-bonded covalent chain structure and anomalous compression mechanism (one lattice parameter increases with pressure) was demonstrated [19]. The anisotropy showed that the LDA introduced an error equivalent to a pressure, which can be improved by including gradient corrections (GGA) [20, 21]. Since then band structures of the complex high pressure phases have been investigated using the experimental parameters without full relaxation of the crystal structure or incommensurate modulation [22], and the liquid phase has been investigated up to high pressures [23].

Although there are several papers on individual crystal structures, proposed transition mechanisms and the simple high symmetry structures at pressures above Se IV [24], we are not aware of published calculated phase transition pressures in Se I–IV[1]. This may be because of their structural complexity, because the enthalpy differences between the phases are extremely small or because of imperfect agreement with the reported sequence of transitions.

Here we report density functional calculations of the first four phases of selenium, identifying the stable structures over the pressure range to 40 GPa. Subsequently we

---

[1] Singh *et al* [28] report Se I to (metallic) Se II at 11.6 GPa in LMTO calculations. It is not clear whether atomic positions were optimized in this work. Moreover we find that their 8^3-k-point sampling is adequate for band structure calculations, but not for calculating the very small enthalpy differences needed for reliable transition pressures.

investigate the nature of the incommensurately modulated fourth phase of Se, approximating the incommensurate structure and showing it to be an extreme case of a Kohn anomaly.

2. Method

We used the computer program VASP [25], treating the exchange–correlation effect with a GGA [21] which is essential to obtaining accurate pressures for the low density structure [19, 20]. The wavefunctions are sampled using the method of Monkhorst and Pack, and the energies converged to 1 meV with respect to the k-point density and 0.2 meV with respect to the plane wave cut-off (194 eV). For Se I, Se II and Se IV a k-point mesh of 15^3 was sufficient, while for Se III we used 17^3. Each structure was fully relaxed with respect to lattice parameters and internal coordinates according to *ab initio* calculated forces and stresses. The core region is described with ultrasoft pseudopotentials [26]. For consistency, we performed calculations on reported structures of all phases I to IV. To calculate band structures a self-consistent calculation using the aforementioned meshes was first carried out, to obtain the ground state charge density, and then the single-particle states of the Kohn–Sham Hamiltonian were evaluated non-self-consistently on a finer mesh.

## 3. The phase sequence of Se

3.1. Se I

Se I is the ambient pressure phase of selenium. It has a hexagonal unit cell, with the atoms arranged in helical chains running parallel to the b axis. Each unit cell contains three atoms, in positions $(0, 0, u)$, $(u, \frac{1}{3}, 0)$, $(-u, \frac{2}{3} - u)$ with $u = 0.289$ at 20 GPa. The equilibrium lattice parameters at this pressure are $a = c = 4.256$ Å, $b = 5.135$ Å. In accordance with previous work [19, 20, 27], we find that as the pressure is increased, the size of the b parameter at first increases, then starts to contract at 10 GPa. However this change is a tenth smaller than the size of the reduction in the other two directions. Also, the value of u increases with pressure. Together, these findings mean that the chains are being pulled along their axis and squashed together as the bonding between neighbouring chains becomes stronger.

Experimental values for Se I [2] give $a = 4.366$, $c = 4.958$ at 0 GPa. At this volume the experimental bulk modulus and derivative are $B = 48.1$ GPa, $B' = 4.33$, compared with calculated values derived from a fit to a Murnaghan equation of states of $B = 39$ GPa and $B' = 4.1$. As has been previously noted [19], the agreement is better when comparing experiment with theory at the same volume than at the same pressure.

3.2. Se II

Se II is reported to have a monoclinic structure, with six atoms per unit cell, at positions $(0, 0, 0)$, $(u, 0, v)$, $(-u, 0, -v)$ and at $(\frac{1}{2}, \frac{1}{2}, 0)$ relative to these. At 22 GPa, $u = 0.147$ and $v = 0.339$. The equilibrium lattice parameters of the cell at this pressure are $a = 6.562$ Å, $b = 2.665$ Å, $c = 6.326$ Å, $\beta = 105.3°$. This is a layered structure, with each atom closely bonded to four other atoms. On pressure increase, the parameter a reduces much faster than b and c as the layers are being pushed together. The angle β changes very little over the calculated pressure range.

Figure 1 shows the density of electron states of Se II at 2 and 22 GPa. The effect of pressure is primarily to broaden the distribution. Consistently with previous work, there are
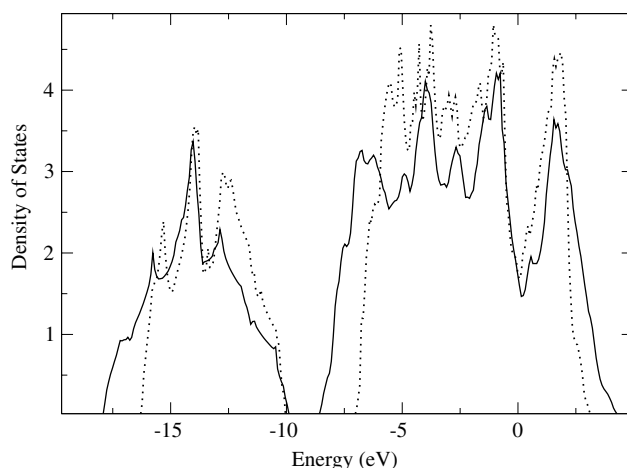
Figure 1. Calculated density of states for Se II structure from a 25^3-k-point grid at 2 GPa (dotted curve) and 22 GPa (solid curve) with ions and unit cell fully relaxed within the space group reported experimentally. The chemical picture outlined for Se I [19] is still applicable, with two low energy s electrons/atom still distinct; however the distinct 'covalent bond', 'lone pair' and unoccupied bands present now overlap to form a conduction band. The Fermi energy has been shifted to zero, no band gap is present and this structure would result in a metallic material (see footnote 1).

two sets of bands, corresponding to 4s and 4p electrons [28]. There is no band gap, showing that at either pressure the material is a metal[2].

Experimentally [29], the reported lattice parameters at 17 GPa are $a = 6.57$ Å, $b = 2.69$ Å, $c = 6.29$ Å, $\beta = 105.4°$.

3.3. Se III

Se III was initially indexed to a monoclinic structure [31, 29] but more recently a small distortion was identified and it is now reported to be triclinic, with six atoms per unit cell [32]. At 28 GPa, the equilibrium lattice parameters of the cell are $a = 3.460$ Å, $b = 12.240$ Å, $c = 2.624$ Å, $\alpha = 88.9°$, $\beta = 113.4°$, $\gamma = 90.4°$ and the calculated bulk modulus at this pressure is 154 GPa. This is in excellent agreement with recently found experimental values [32] at 26.5 GPa: $a = 3.465$ Å, $b = 12.088$ Å, $c = 2.648$ Å, $\alpha = 86.8°$, $\beta = 112.0°$, $\gamma = 91.3°$. Se III also has very anisotropic compression; the largest decrease in the cell is in the a direction, which decreases by 10% over a range of 20 GPa, compared with 5% for c and only 1.5% for b. Angles α, β, γ change little as the pressure is increased. At 24 GPa, the calculated atomic positions are: $(-0.003, -0.001, -0.024)$, $(0.465, 0.167, 0.389)$, $(0.030, 0.331, 0.064)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ relative to these. Band structure calculations show that Se III is metallic.

3.4. Se IV

3.4.1. Unmodulated. We modelled the simple orthorhombic Se IV cell by relaxing ions and lattice parameters from the cell reported experimentally [3] without the incommensurate

---

[2] DFT is known to underestimate band gaps because the excited state does not contribute to the charge density. It is conceivable that this could cause a spurious band gap closure as occurs in strongly correlated materials. However, this would have the effect of overstabilizing the Se II phase by *lowering* the enthalpy, the opposite of what is observed in figure 5.
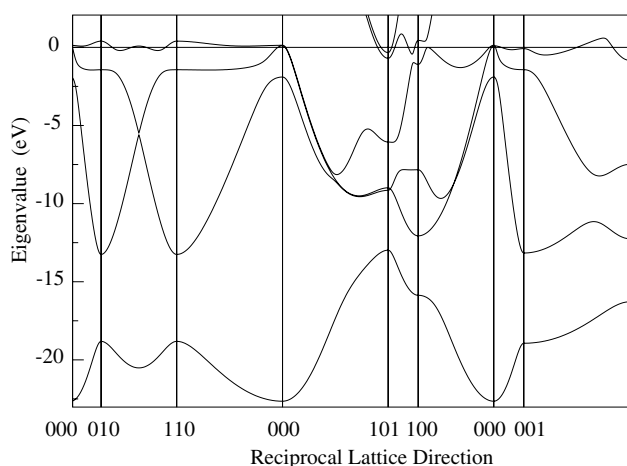
Figure 2. Band structure of one-atom 'unmodulated Se IV' at 35 GPa as described in the text—the actual incommensurate structure can be regarded as a modulation of this along the (010) direction, with both atomic motion and lattice strain. The Fermi energy has been shifted to zero to emphasize the flat band along (000)–(010)–(110)–(000). The instability of this structure arises from $(0q0)$ wavevectors linking the nested Fermi surface which arises from these flat bands: the large region across which the bands are flat suggests that a range of possible distortion wavevectors could lower the energy. While experiment will pick out the one giving largest energy reduction, our calculations show that $(0, \frac{1}{4}, 0)$, $(0, \frac{2}{7}, 0)$ and, by implication, all vectors in between including the experimentally observed ones lead to a lowering of energy.
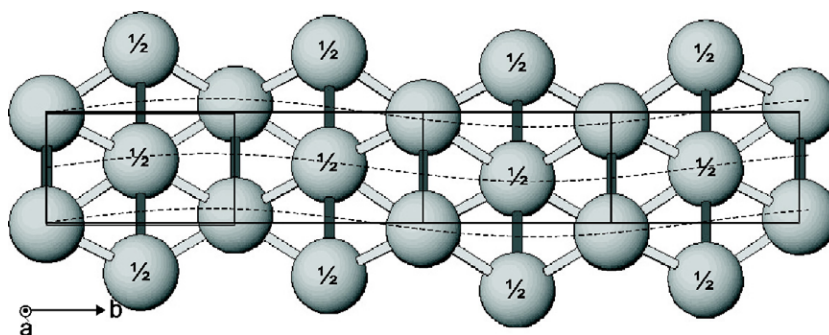
Figure 3. Four cells of the modulated body-centred monoclinic cell of Se IV viewed down the a axis. The dashed line shows the modulation at the experimental value of $q = 0.28$; the calculations were done on cells with this modulation adjusted to $q = \frac{1}{3}$ and $\frac{1}{4}$ corresponding to a modulation wavelength of three and four cells respectively. Atoms labelled with $\frac{1}{2}$ lie at that fractional coordinate in the c direction; others lie in the plane. (Figure courtesy of M I McMahon.)

distortion (figure 3). At 35 GPa, the equilibrium lattice parameters were $a = 3.383$ Å, $b = 4.071$ Å, $c = 2.613$ Å and $\beta = 115.6°$. This compares with the experimental results: $a = 3.299$ Å, $b = 3.996$ Å, $c = 2.587$ Å and $\beta = 113.105°$. The calculated unit cell parameters are about 2% larger than the experimental value at the same pressure. This is typical for the GGA. In this setting Se IV has four atoms per unit cell.

It is possible to represent a prototype 'unmodulated Se IV' in a one-atom unit cell. For this, we choose axes such that the modulation direction will still lie along $\mathbf{b}' = 3.997$, with $\mathbf{a}' = (\mathbf{a} + \mathbf{b} + \mathbf{c})/2 \, \mathbf{c}' = \mathbf{c}$. The band structure calculated for this cell is shown in figure 2.

Table 1. Details of frozen phonons at $q = \frac{1}{4}$ and $q = \frac{2}{7}$ at various pressures: amplitudes of modulations in the xz plane for $q = \frac{1}{4}$ correspond to maximum displacement u, intermediate displacement v and two atoms fixed at unmodulated positions. For $q = \frac{1}{4}$ we have chosen the frozen phonon to be in phase with the unmodulated cell: within error the ratio $u/v = \sqrt{2}$ implies that the distortion can be described as a single harmonic phonon. For $q = \frac{2}{7}$ the displacement pattern is again harmonic, u_x and u_z represent the amplitude of a fitted sine wave, but the phase of the modulation is not locked. Enthalpy differences are of order 2–3 meV/atom (10–30 meV/cell) from the unmodulated Se IV calculated with the same size, k-point sampling and supercell. The similarity between modulated and unmodulated cells and use of identical k-point sets leads to cancellation of errors and means that these small enthalpy differences are significant: the existence of an instability depends only on the *sign* of the change in energy with appropriate coupled distortion. Such small energy differences would not be significant in comparing very different structures, such as Se I and Se IV.

P (GPa)	$q = \frac{1}{4}$					$q = \frac{2}{7}$		
	u_x	v_x	u_z	v_z	ΔH	u_x	u_z	ΔH
25	0.017	0.012	0.057	0.040	−3	0.021	0.077	−4
30	0.016	0.011	0.057	0.040	−3	0.018	0.070	−3
35	0.014	0.010	0.057	0.040	−3	0.015	0.065	−3
40	0.012	0.008	0.055	0.038	−2	0.012	0.060	−2

The electronic instability of this structure arises from the splitting of the flat band of electrons close to E_F in the Γ–(010) branch.

3.4.2. Modulated. It is impossible to do calculations on an incommensurate cell using periodic boundary conditions; however one can use a rational approximant [14] assuming that a distortion close to the observed q will also be stable relative the undistorted structure. Here we approximated the distorted structure with tripled, quadrupled or heptupled cells corresponding to $q = \frac{1}{3}$, $\frac{1}{4}$ and $\frac{2}{7}$. In each case the calculation was started with frozen-in values of the incommensurate wave displacement vector taking Te III data $u_x = 0.0249$ and $u_z = 0.1026$ as initial symmetry breaking displacements. Both these internal parameters and the lattice parameters were allowed to relax.

For $q = \frac{1}{4}$ calculations were done at four different pressures: 25, 30, 35 and 40 GPa. In all cases, the displacement remained, and the enthalpy of each atom in the distorted structure is 3 meV smaller, with the distorted structure being slightly larger than the undistorted one. Table 1 shows a summary of results found. The energy differences from the undistorted phase are small, but lie within k-point and cut-off convergence. We tested this to greater accuracy which can be obtained by eliminating sampling errors for the crucial energy *differences* by comparing cells with and without the distortion, using identical k-points and cut-offs [30].

The calculated distortions at $q = \frac{1}{4}$ and $\frac{2}{7}$ are smaller than those found experimentally at 35 GPa. This is to be expected since the calculated distortions are not the most favoured ones. Likewise, the very small enthalpy difference (-3 meV/atom) is a lower bound on the stability of the incommensurate wave. The displacement eigenvector (transverse, $u_z/v_z = 0.22 \pm 0.04$ at 40 GPa), is in excellent agreement with the experimental value (0.26 at 42 GPa [4]).

For $q = \frac{1}{3}$ we carried out calculations at six different pressures: 10, 20, 25, 30, 35 and 40 GPa, the last three when Se IV was predicted earlier to be stable. At all six pressures, the structure relaxed back to the unperturbed structure, as did calculations with $q = \frac{1}{7}$.

3.4.3. Fermi surface effects. While DFT is clearly a sufficient theory for explaining the incommensurate modulation, a more intuitive explanation exists: modulation arises from a
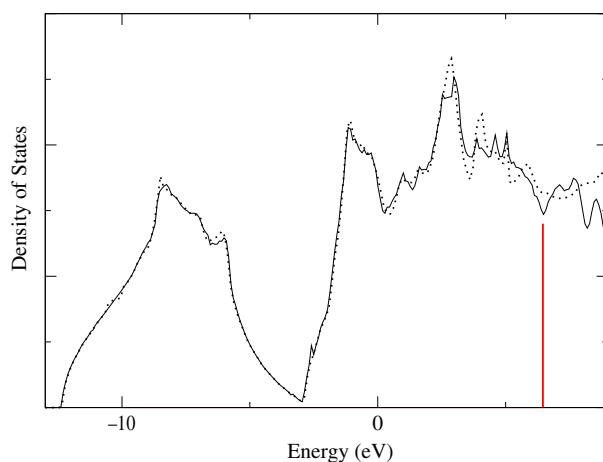
Figure 4. The calculated Kohn–Sham band structure and density of states for Se IV at 35 GPa with (solid curve) and without (dotted curve) the modulation at $q = \frac{1}{4}$. The Fermi energy $E_F = 6.46$ eV in both cases is shown by the vertical line. The Kohn anomaly arises because the distortion perturbs states at $(0, \frac{1}{4}, 0)$ which lie close to E_F, leading to the drop in the density of states at E_F.

Kohn anomaly (interaction between the nested Fermi surface and a phonon) so large that the phonon energy becomes negative and the soft mode 'freezes in' and is further stabilized by a lattice distortion. This type of effect is common in compounds but has only recently been explored in high pressure elements—the key point being that the energy associated with the freezing in of the anomaly increases and scales more rapidly with compression (as V^{-1}) than do the Coulomb, kinetic and exchange–correlation energies [6].

Experimentally [3], the incommensurate q-vector drops from 0.31 to 0.28 between 30 and 50 GPa, remaining at 0.28 until 70 GPa is reached [4]. A standard Kohn anomaly in the free electron picture would occur at $q = 2k_F$, and soften (i.e. reduce the frequency of) the phonon at that wavevector. Here the softening of the mode is so great that it freezes in (i.e. the frequency is imaginary), lowering the symmetry of the unit cell and allowing coupling to the unit cell parameters. The stability arises because the phonon mode opens a pseudogap at the Fermi energy, which can been seen as a dip in the electronic density of states: figure 4 shows that the distortion has exactly this effect.

3.5. Phase stability

Figure 5 shows the phase stability deduced from our calculations of enthalpy of each phase from 1 to 40 GPa. The stable structure of selenium at each pressure is that with the lowest enthalpy, and although the differences in enthalpy are small throughout the whole pressure range they are above our convergence errors.

The most notable feature is that our structure for Se II, reported experimentally at 14 GPa [33, 34, 29], is not predicted to be stable at any pressure. It is higher in energy by around 8 meV/atom than that of Se III, which is greater than the convergence of the calculation. This may be because of an entropic effect: a symmetry breaking distortion may have lower energy with Se II a dynamically stabilized phase with a transition below room temperature [35, 36] (8 meV corresponds to a temperature of 100 K). However, this would not explain the band structure observed in the calculation—along with previous authors [22, 37] we predict that Se II is metallic while experimentally it is a semiconductor (see footnote 1).
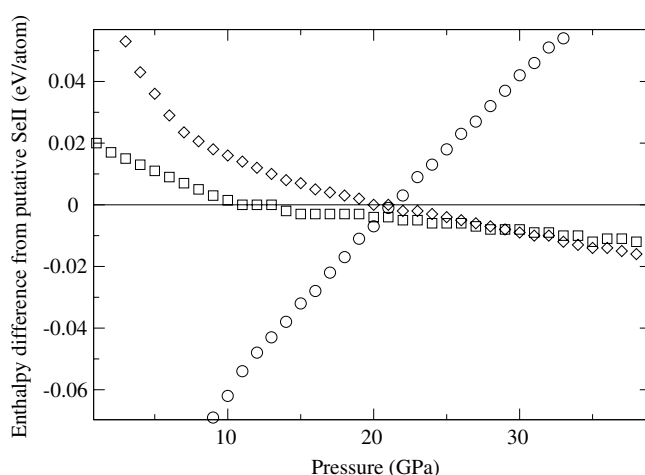
Figure 5. Calculated enthalpy differences between Se II and other phases. The stable structure is the one with the lowest enthalpy at each pressure. Circles denote Se I, squares Se III and diamonds unmodulated Se IV. Errors are of order the size of the symbols.

This is a strong indication that the atomic positions used in the calculation (starting from the experimental ones, and relaxing to the nearest equilibrium) are incorrect and we conclude that there may be an error in the experimentally reported crystal structure.

We predict a phase transition from hexagonal Se I direct to monoclinic Se III at 21.5 GPa accompanied by a volume reduction of 5.5%; experimentally Se III is observed at 23 GPa [34, 1]. The transition from Se III to Se IV is predicted at 27.5 GPa, compared to the experimental value of 28 GPa [33, 2, 29]. These excellent agreements give us confidence that our method correctly describes high pressure selenium.

4. Conclusions

To summarize, *ab initio* total energy and band structure calculations on four different phases of selenium are reported. The generally accepted sequence of phase transitions is not reproduced although unit cell and internal parameters are in good agreement with experiment. The calculated instability of the experimentally reported Se II structure, combined with our prediction that it should be metallic, leads us to suspect that this phase may have been characterized, and there is very recent evidence for unexplained diffraction peaks for Se II [38].

Body-centred monoclinic Se IV is unstable against a phonon modulation with $q = \frac{1}{4}$ or $\frac{2}{7}$. Inspection of the band structure of the undistorted phase leads us to conclude that this instability arises from a Kohn anomaly in the phonon spectrum of sufficiently large magnitude that the phonon eigenenergy is negative (i.e. the mode is unstable). The wavevector of the nested Fermi surface is incommensurate with the crystal structure and varies with pressure. This gives a theoretical picture of the recent unexplained experimental observation of an incommensurate Se IV.

Acknowledgments

References

[1] Akahama Y, Kobayashi M and Kawamura H 1992 *Solid State Commun.* **84** 803
[2] Parthasarathy G and Holzapfel W B 1988 *Phys. Rev.* B **38** 10105
[3] Hejny C and McMahon M I 2003 *Phys. Rev. Lett.* **91** 215502
Hejny C and McMahon M I 2004 *Phys. Rev.* B **70** 184109
[4] McMahon M I, Henjy C, Loveday J S, Lundegaard L F and Hanfland M 2005 *Phys. Rev.* B submitted
[5] McMahon M I and Henjy C 2005 *Phys. Rev. Lett.* at press
[6] Ackland G J and Macleod I R 2004 *New J. Phys.* **6** 138
[7] Hafner J and Heine V 1986 *J. Phys. F: Met. Phys.* **16** 1429
[8] Heine V and Weaire D 1970 *Solid State Phys.* **24** 249
[9] Ackland G J 2001 *Rep. Prog. Phys.* **64** 483
[10] Lambert J H 1796 *Proc. Berlin Academy* Berlin
[11] Nelmes R J, Allan D R, McMahon M I and Belmonte S A 1999 *Phys. Rev. Lett.* **83** 4081
[12] McMahon M I, Bovornratanaraks T, Allan D R, Belmonte S A and Nelmes R J 2000 *Phys. Rev.* B **61** 3135
[13] McMahon M I, Rekhi S and Nelmes R J 2001 *Phys. Rev. Lett.* **87** 055501
Schwarz U, Grzechnik A, Syassen K, Loa I and Hanfland M 1999 *Phys. Rev. Lett.* **83** 4085–8
[14] Reed S K and Ackland G J 2000 *Phys. Rev. Lett.* **84** 5580
[15] Ackland G J, Warren M C and Clark S J 1997 *J. Phys.: Condens. Matter* **9** 786
[16] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 *Rev. Mod. Phys.* **73** 515
[17] Hohenberg P, Kohn W and Sham L J 1964 *Phys. Rev.* **136** B864
[18] Kohn W and Sham L J 1965 *Phys. Rev.* **140** A1133
[19] Akbarzadeh H, Clark S J and Ackland G J 1993 *J. Phys.: Condens. Matter* **5** 8065
[20] Kresse G, Furthmuller J and Hafner J 1994 *Phys. Rev.* B **50** 13181
[21] Perdew J P, Chevary J A, Vosko S H, Jackson K A, Pederson M R, Singh D J and Fiolhais C 1992 *Phys. Rev.* B
46 6671
[22] Geshi M, Oda T and Hiwatari Y 1998 *J. Phys. Soc. Japan* **67** 3141
Geshi M, Oda T and Hiwatari Y 1999 *J. Phys. Soc. Japan* **68** 3341
Geshi M, Oda T and Hiwatari Y 2001 *J. Phys.: Condens. Matter* **13** 9401
Geshi M, Oda T and Hiwatari Y 2002 *J. Phys.: Condens. Matter* **14** 10885
[23] Stadler R, Kresse G and Gillan M J 1999 *J. Phys.: Condens. Matter* **11** 10211
Stadler R, Kresse G and Gillan M J 1993 *J. Phys.: Condens. Matter* **5** 8065
[24] Rudin S P, Liu A Y, Freericks J K and Quandt A 2001 *Phys. Rev.* B **63** 224107
[25] Kresse G and Furthmuller J *VASP The Guide* http://cms.mpi.univie.ac.at/vasp/vasp/vasp.html
[26] Vanderbilt D 1990 *Phys. Rev.* B **41** 7892
[27] Clark S J, Ackland G J and Akbarzadeh H 1995 *J. Phys. Chem. Solids* **56** 329
[28] Singh D, Bandyopadhyay A K, Rajagopalan M, Sadu P C, Yousef M and Rajan K G 1999 *Solid State Commun.*
109 339
[29] Ohmasa Y *et al* 1995 *J. Phys. Soc. Japan* **64** 4766
[30] Kelsey A A and Ackland G J 2000 *J. Phys.: Condens. Matter* **12** 32
[31] Akahama Y, Kobayashi M and Kawamura H 1992 *Phys. Rev.* B **47** 20
[32] Hejny C and McMahon M I 2004 *Phys. Rev.* B **70** 184109
[33] Akahama Y, Kobayashi M and Kawamura H 1992 *Solid State Commun.* **83** 269
[34] Bundy F P and Dunn K J 1980 *Phys. Rev.* B **22** 3157
[35] Ackland G J 2002 *J. Phys.: Condens. Matter* **14** 2975
[36] Drummond N D and Ackland G J 2001 *Phys. Rev.* B **65** 184104
[37] Ikawa A 1997 *J. Phys. Soc. Japan* **66** 676
[38] McMahon M I 2004 private communication