Pressure dependence of the energy gaps in diamond-type semiconductors, and their III-V analogues such as InSb

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Abstract. In earlier work by March and Matthai [Phil. Mag. Lett. 84, 335 (2004)], the energy gaps \( E_g \) of the diamond-type semiconductors C, Si, Ge and \( \alpha \)-Sn were shown to correlate well with the mean interelectronic separation \( r_s \) of the 4 valence electrons per atom. Furthermore for the III-V analogues such as GaAs and InSb, it was demonstrated that a useful extension could be effected by introducing additionally the electronegativity difference between the constituent atoms. Here, we consider available experimental data, and their interpretation, for such energy gaps, as a function of pressure. The intensity of the X-ray forbidden reflections will also be discussed under pressure.

Key words: tetrahedral semiconductors; pressure dependence; lattice parameter dependence; energy gap; III-V compounds; X-ray spectroscopy.

The behavior of the diamond-structure semiconductors under pressure has been a topic of experimental and theoretical study for some time (see, e.g., Ref. [1]). Nathan et al. [2], e.g., carried out a thorough study of the pressure dependence in \( n \)-type Ge compared to, for example, Si, analyzing the effects of interband scattering. More recently, March and Matthai [3] have given a quantitative representation of the energy gap \( E_g \) in the diamond-structure semiconductors C, Si, Ge, and \( \alpha \)-Sn. They obtain a good fit of \( E_g \) at atmospheric pressure for these four materials by writing

\[
E_g = A \left( 1 - \sqrt{\frac{a}{a_c}} \right)^\gamma ,
\]

where \( a \) is the lattice parameter, and the fitting parameters are \( a_c = 6.7797 \) Å, \( A = 50.21 \) ev, and \( \gamma = 1.71675 \approx \frac{5}{2} \). Eq. (1) supports a description of the dependence of the band gap on the interelectron mean spacing in elemental tetravalent semiconductors in terms of a semiconductor-to-metal phase transition (SMT), in which \( E_g \) plays the role of the order parameter. Fig. 1 plots Eq. (1) against available experimental data (Tab. 1) for the four diamond-type elemental semiconductors mentioned above, as well as for several III-V analogues, both in zinc-blende and in wurtzite structures. Tab. 1 also records values for two selected II-VI compound

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Figure 1. Energy gap $E_g$ at atmospheric pressure against lattice parameter $a$ for diamond-type semiconducting elements C, Si, Ge, and $\alpha$-Sn (filled circles), and III-V, II-VI analogues in zinc-blende (open circles) and wurtzite structure (triangles), as listed in Tab. 1. Dashed line is March-Matthai fitting curve for diamond-type elements, Eq. (1) [3].

semiconductors (CdSe and CdTe), which have been recently employed in the construction of nanoscale electron devices [4, 5].

While Eq. (1) is more appropriate to describe a SMT close to the critical point, i.e. a vanishing band gap at a finite lattice parameter $a \sim a_c$, it is important to note that Litovchenko [6] has verified a correlation $E_g \propto 1/a^2$, which agrees with experimental data for $a \ll a_c$, and is justified by the asymptotic, low-$a$ power-law dependence of the energy matrix elements on the lattice parameter $a$ within the tight-binding approximation [7]. That an SMT transition is related to a change in lattice parameter is also confirmed by the empirical correlation between the transition pressure in semiconducting chalcogenides and an appropriate average of the cation and anion radii [8].

March and Matthai [3] proceed to generalize their results for the four monatomic diamond-structure semiconductors. However, they avoid undue size differences by relating AlP to Si, GaAs to Ge and InSb to $\alpha$-Sn. Their proposal was to express the energy gap in these three binary semiconductors as the sum of two parts, $E_g = E_g^e + E_g^{ed}$, where $E_g^e$ is the ‘elemental gap’ (e.g. Si for AlP etc.), while $E_g^{ed}$ expresses the electronegativity difference between the two atoms in the III-V semiconductors. They show (see Fig. 3 in Ref. [3]) that $\Delta E_g = E_g - E_g^e$ is proportional to the difference between the ionization potentials, say $\Delta I$, of the two atoms concerned. This is the approximate chemical estimate for electronegativity difference. As we expect $\Delta I$ to be insensitive to pressure, we expect $dE_g/dP|_{P=0}$ to be nearly the same for AlP as for Si, there being just a slight difference in their equilibrium lattice parameters $a$ (cf. Tab. 1 for Si and AlP, Ge and GaAs, and $\alpha$-Sn and InSb).

Making use of the Murnaghan equation of state (EOS) [16], one can estimate the pressure dependence of the lattice parameter as

$$a(P) = a(0) \left(1 + \frac{B'}{B} P\right)^{-\frac{1}{B'}}$$

(2)
Table 1. Relevant data for several elemental, III-V and II-VI compound semiconductors, in diamond-type structures (from Refs. [14, 15] and refs. therein, unless specified). For the two wurtzite compounds, the average lattice parameter $d$, defined as $d = \sqrt{3}a^2c/2$, is actually recorded.

|         | $a$ (Å) | $E_g$ (eV) | $\Delta I$ (eV) | $B$ (GPa) | $B'$ | $dE_g^{\text{exp}}/dP$ (meV/GPa) | $dE_g^{\text{calc}}/dP$ (meV/GPa) | $-P_c$ (GPa) |
|---------|---------|------------|----------------|----------|------|---------------------------------|---------------------------------|-------------|
| C       | 3.567   | 5.46       | 442            | 3.8      | 0.7 – 6.2 [9] | 9.3                                 | 116                                      |
| Si      | 5.431   | 1.12       | 97.82          | 4.4      | –14.1 | 27.9                                      | 21                                      |
| Ge      | 5.658   | 0.661      | 75             | 4.5      | 30    | 26.6                                      | 15                                      |
| α-Sn    | 6.4892  | 0.1        | 53             | 4.6      | –     | 24.4                                      | 6                                       |
| BN      | 5.9051  | 7.23       | 123.5          | 4.0      | 10.5  | 83.8                                      | 18                                      |
| BP      | 5.4510  | 2.45       | 86.5           | 4.1      | 94.2  | 70.3                                      | 21                                      |
| AlP     | 5.4512  | 2.26       | 4.88           | 4.7      | –     | 95                                          | 63.8                                     |
| GaAs    | 5.65325 | 1.424      | 75.6           | 4.8      | 126   | 59.6                                      | 15                                      |
| AlAs    | 5.6605  | 2.16       | 74.1           | 4.0      | 104.5 | 88.3                                      | 18                                      |
| InP     | 5.8686  | 1.35       | 4.99           | 4.8      | 4.8   | 72.7                                      | 14                                      |
| InAs    | 6.0584  | 0.36       | 4.025          | 4.9      | 48    | 30.7                                      | 10                                      |
| GaSb    | 6.0959  | 0.72       | 2.639          | 4.9      | 145   | 67.0                                      | 11                                      |
| AlSb    | 6.1355  | 1.58       | 2.655          | 4.5      | 140.8 | 148.9                                     | 13                                      |
| InSb    | 6.4794  | 0.17       | 2.854          | 4.9      | 137   | 45.2                                      | 6.4                                     |
| CdSe    | 6.050   | 1.713      | 0.759          | 53.0     | 0.48  | 43.1                                      | 158                                     |
| CdTe    | 6.481   | 1.6065     | 0.74           | 44.5     | 6.4   | 75.9*                                     | 153                                     |
| BN      | 2.86362 | 5.5        | 6.234          | 394 [10] | 3.68  | 3.8                                        | 7.4                                     |
| GaN     | 3.57434 | 3.36       | 8.53           | 210      | 4.6   | 41.4                                      | 12.1                                     |

*$^*$ Calculated at Γ point.

where $B$, $B'$ are the bulk modulus and its pressure derivative at $P = 0$. Eqs. (1) and (2) combined can then be used to calculate $dE_g/dP|_{P=0}$, which is confronted with experimental data in Tab. 1. With the notable exception of Si, for which a negative value of $dE_g^{\text{exp}}/dP$ is recorded, there is a quite clear correlation between calculated values and experiment, though the gap variation is underestimated substantially for GaSb and InSb, and overestimated for CdSe and CdTe.

Motivated by the correlation provided by Eq. (1) as shown in Fig. 1, we then seek a pressure counterpart of the ‘critical’ value of the lattice parameter $a_c$ at which an SMT takes place, with vanishing $E_g$. Since among diamond-type semiconductors larger lattice spacings are required for lower band gaps, it is clear that such a critical pressure, say $P_c$, at which a STM phase transition takes place, must be negative, thus implying some kind of lattice expansion, as can be e.g. brought about thermally, or by epitaxially growing films on a suitably lattice-mismatched substrate. In the latter case, a generalization of the Murnaghan EOS would then be required for strained layers, as in Ref. [17]. The last column of Tab. 1 then records our estimates for $-P_c$, from which it is seen that $-P_c$ shows a direct correlation with $E_g$ at ambient conditions.

Beyond specific measurements of $E_g$ as a function of pressure, it seems of interest to summarize here some studies, both theoretical and experimental, relating to X-ray diffraction for diamond-lattice semiconductors under compression. Briefly, the study of March and Flores [18] discussed the significance of the forbidden 222 reflection as one approaches a metallic phase as a
result of applying pressure to an originally diamond-structure semiconductor. They considered that the X-ray intensity at this forbidden 222 reflection should be useful in discussing such a transition to a metallic phase. Earlier work of Zunger and Freeman [19] calculated the 222 reflection for diamond under pressure. From an experimental point of view, Yoder-Short et al. [20] performed X-ray diffraction studies of Si and also InSb as they were compressed near the transition to a metallic \(\beta\)-Sn structure. In both cases, the intensity of the 222 reflection was observed to undergo a sharp decrease just before the structural transition, which occurs at \(\sim 125\) kbar [21, 22] for Si, and close to 30 kbar for InSb [23].

Summarizing, we have obtained a gross estimate of the variation of the energy gap \(E_g\) with lattice parameter in diamond-type semiconductors C, Si, Ge, and \(\alpha\)-Sn. Using the Murnaghan EOS, this is converted to a result for \(\frac{dE_g}{dP}|_{P=0}\), which is confronted with experimental data. The III-V analogues AlP, GaAs, and InSb of Si, Ge, and \(\alpha\)-Sn respectively are predicted to have largely similar values for \(dE_g/dP\) to their monatomic counterparts. We have also discussed X-ray diffraction results on the 222 forbidden reflection in the diamond structure from both theory and experiment as a metallic phase is approached by application of pressure. As for directions for future studies, it may be worth mentioning what Cohen [24] calls a ‘dramatic difference’ between the pressure dependence of the band gaps of elemental and compound semiconductors, and those of carbon nanotubes. While for most semiconductors the fundamental gap increases with applied pressure, for carbon nanotubes there appears to be a dependence on chirality \((n, m)\). According to a recent theoretical study [25], the sign of \(dE_g/dP\) should depend on \(q = (n - m)\mod 3\), with \(dE_g/dP < 0\) for \(q = 2\), and \(dE_g/dP > 0\) for \(q = 1\), in agreement with experimental data [26].

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References
[1] Paul W and Warschauer D M 1963 Solids under pressure (New York: McGraw-Hill)
[2] Nathan M I, Paul W and Brooks H 1961 Phys. Rev. 124 391
[3] March N H and Matthai C C 2004 Phil. Mag. Lett. 84 335
[4] Merad A E, Kanoun M B, Cibert J and Merad G 2003 J. Elec. Devices 2 31
[5] Shan W, Walukiewicz W, Ager III J W, Yu K M, Wu J and Haller E E 2004 Appl. Phys. Lett. 84 67
[6] Litovchenko V G 2002 Phys. Rev. B 65 153108
[7] Harrison W A 1980 Electronic structure and the properties of solids (New York: Dover)
[8] Syassen K 1985 phys. stat. sol. (a) 91 11
[9] Van Camp P E, Van Doren V E and Devreese J T 1988 Phys. Rev. B 38 12675
[10] Albe K 1997 Phys. Rev. B 55 6203
[11] Lam P K, Cohen M L and Martinez G 1987 Phys. Rev. B 35 9190
[12] Mujica A, Rodríguez-Hernández P, Radescu S, Needs R J and Muñoz A 1999 phys. stat. sol. (b) 211 39
[13] Wang S Q and Ye H Q 2002 J. Phys.: Condens. Matter 14 9579
[14] Levinstein M, Rumyantsev S and Shur M, eds. 1999 Handbook Series on Semiconductor Parameters (London: World Scientific). Mostly available online at http://www.ioffe.ru/SVA/NSM
[15] Weast R C and Astle M J, eds. 1974 CRC Handbook of Chemistry and Physics (Palm Beach FL: CRC Press), 59 edition
[16] Murnaghan F 1944 Proc. Natl. Acad. Sci. U.S.A. 30 244
[17] Frohley M D, Downes J R and Dunstan D J 2000 Phys. Rev. B 62 13612
[18] March N H and Flores F 1984 Solid State Commun. 49 649
[19] Zunger A and Freeman A J 1977 Phys. Rev. B 15 5049
[20] Yoder-Short D R, Colella R and Weinstein B A 1982 Phys. Rev. Lett. 49 1438
[21] Minomura S, Samara G A and Drickamer H G 1962 J. Appl. Phys. 33 3196
[22] Piermarini G J and Block S 1975 Rev. Sci. Instrum. 46 973
[23] Okai B and Yoshimoto J 1975 J. Phys. Soc. Japan 45 1880
[24] Cohen M L 2005 *Physica E* **29** 447
[25] Capaz R B, Spataru C D, Tangney P, Cohen M L and Louie S G 2004 *physica status solidi (b)* **241** 3352
[26] Shan W, Wu J, Walukiewicz W, Ager III J W, Yu K M, Haller E E, Kissell K, Bachilo S M, Weisman R B and Smalley R E 2004 *phys. stat. sol. (b)* **241** 3367