PHYSICAL REVIEW B **79**, 153203 (2009)

Pressure variation of the valence band width in Ge: A self-consistent GW study

P. Modak,[1,*] A. Svane,[1] N. E. Christensen,[1] T. Kotani,[2] and M. van Schilfgaarde[3]
[1]*Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark*
[2]*Department of Applied Physics and Mathematics, Tottori University, Tottori 680-8552, Japan*
[3]*School of Materials, Arizona State University, Tempe, Arizona 85287-6006, USA*

(Received 29 January 2009; revised manuscript received 10 March 2009; published 29 April 2009)

Analyzing x-ray emission spectra (XES) of germanium under pressure Struzhkin *et al.* [Phys. Rev. Lett. **96**, 137402 (2006)] found that the valence band width of diamond Ge does not vary with pressure. This contradicts the usual experience and also what is predicted by density-functional calculations. In the present work we report results of *quasiparticle self-consistent GW* (QSGW) band calculations for diamond- as well as β-tin-type Ge under pressure. For both phases we find that the band width increases with pressure. For β-tin Ge this agrees with experiment and density-functional theory, but for diamond Ge neither the local density approximation nor the QSGW calculations agree with the conclusions drawn from the XES data.

DOI: 10.1103/PhysRevB.79.153203 PACS number(s): 78.70.En, 62.50.−p, 71.20.Mq, 71.15.Qe

I. INTRODUCTION

Band structure models based on a simple tight-binding approximation relate the band widths to the orbital overlaps, and a reduction in the interatomic distances, a compression of the solid, increases the overlaps and leads to an increase in the band width. This trend has until recently also been generally assumed to apply to the valence bands of covalently bonded semiconductors, and it was therefore very surprising that Struzhkin *et al.*[1] found that x-ray emission spectroscopy (XES) indicated that this is not the case for the valence band in diamond-type germanium. For pressures up to ~10 GPa, where the structure changes to that of β tin, the band width did not change with pressure. In the β-tin phase, however, a "normal" broadening was observed.[1]

The most common theoretical methods for obtaining total energies are based on the density-functional theory (DFT).[2] Also, although it is not "designed" for that purpose, the formal one-electron energies give energy bands, even in the local density approximation (LDA),[3] which agree well with spectroscopic data (except for the band gap in semiconductors). The method has been very successful for calculating band widths and it also gives very reasonable band dispersions though there is no theoretical justification of this remarkable property of LDA, and several examples of successful applications to semiconductor valence bands are known, including the LDA calculation in Ref. 1 of the band width of diamond Ge at ambient pressure.

Maybe the experiment in Ref. 1, in fact, detects details in the *quasiparticle* (QP) electronic structure which even for the rather wide valence band of Ge cannot be properly described by the LDA and that it is necessary to take the many-body effects better into account. This could be done, for example, by including many-body corrections via the electron self-energy as first carried out by Hybertsen and Louie[4] as a perturbation to LDA. Starting from LDA eigenvalues and eigenfunctions they calculated *ab initio* QP states within Hedin's GW approximation (G is the Green's function and W is the screened Coulomb interaction).[5] The perturbation approach in Ref. 4 is often referred to as "GW-LDA." Since then many groups published the results of GW-LDA calculations or its extensions but few works studied the many-body effects on the valence band width. For prototype metals such as Na, the GW calculations[6–8] give a narrower occupied band than DFT-LDA, whereas for the prototype insulator LiF they give a larger valence band width.[9,10] Also for semiconductors, QP calculations give slightly larger valence band widths than those of DFT-LDA.[9] All these QP calculations are "one-shot" GW calculations and results for the same quantities are not consistent among different groups. This may be because of further approximations involved in this type of calculations, and further, the results are very much dependent on the quality of the initial LDA calculation. Hence some type of self-consistency is required to calculate quasiparticle states which are consistent in the sense that they do not depend on a particular one-electron scheme such as an LDA calculation. Recently van Schilfgaarde *et al.*[11,12] implemented a self-consistent GW method which they call the *quasiparticle self-consistent GW* (QSGW) method. This method is not a fully many-body self-consistent approach but may be considered as iteration to self-consistency in the nonlocal energy dependent self-energy $\Sigma(\mathbf{r},\mathbf{r}',\omega)$. A mapping of the noninteracting Green's function, G^0, onto the dressed Green's function, G, is obtained by calculating the polarization function from G^0 and then calculating W and Σ. A new Hamiltonian, including a new nonlocal effective potential derived from Σ, is then used to derive a new G^0, defining a *reverse* approximate mapping, $G \rightarrow G^0$. Then the sequence $G^0 \rightarrow G \rightarrow G^0 \rightarrow \cdots$ can be iterated to self-consistency. At self-consistency the quasiparticle energies in G^0 correspond to those in G. The final results are independent of the very first Hamiltonian (or G^0), which in practice can be obtained from an LDA calculation. van Schilfgaarde and co-workers[11,12] applied their method for a number of weakly and moderately correlated materials and showed that this method gives values of the fundamental gaps for semiconductors which agree very well with experiments. They further showed that for some stronger correlated systems their method gives little larger error but the results are systematic.

II. CALCULATIONS AND RESULTS

We used the QSGW formalism[11,12] implemented within the *linear muffin tin orbital* (LMTO) method[13] in a full-

TABLE I. Calculated equilibrium properties of Ge within DFT formalism.

	Lattice constant (Å)	Bulk modulus (GPa)
Present LDA	5.630	71
GGA[a]	5.7627	76
Expt.[a]	5.6569	77

[a] Reference 1.

potential version.[14] The screened Coulomb interaction is represented in a mixed basis comprised of products of radial waves inside muffin tin spheres and plane waves in the interstitial region. In the present calculations we have applied two sets of muffin tin orbitals with s, p, d, and f angular shape, with two different decay energies. In addition, local orbitals of $3d$ character were included to describe the semicore states.

For the accurate determination of energies we further included floating orbitals[14] centered on interstitial sites. For the mixed basis we have used $l=4$ as angular momentum cutoff inside muffin tin spheres and $G_{\max}=4$ a.u. as cutoff in the interstitial region. The calculations used the tetrahedron method for Brillouin zone (BZ) integrations which were carried out on a regular $8\times 8\times 8$ k-point mesh.

First a brief description of our DFT calculations for germanium is given. The calculated zero-pressure lattice constant and bulk modulus (diamond structure) are given in Table I, where they are compared to the calculation and experiment in Ref. 1. Our equilibrium volume is underestimated by $\sim$1.4%. As usual, LDA leads to some overbinding, and we did not include the energy contribution from the ionic zero-point motion.

The calculation in Ref. 1 was performed within the *generalized gradient approximation* (GGA), and as often observed, this leads to a somewhat larger equilibrium volume in the present case larger than measured. This is not unusual, and it does not affect the bands and has no consequences for the discussion of the DFT bands and their variation with volume in Ref. 1.

We carried out the LDA calculations for a series of volumes, for diamond, as well as β-tin germanium. From the total energies, the pressures as well as enthalpies were derived. From the structural enthalpy difference vs the theoretical pressure, we find that the diamond→β-tin transition in Ge occurs at $\sim$9 GPa. This agrees well with experiments, 10.5 ± 0.2 by Qadri *et al.*[15] and from 8.1 ± 0.3 to 10.6 ± 0.5 GPa, depending on the choice of pressure transmitting medium by Menoni *et al.*[16]

There are several other theoretical and experimental studies (see, for example, Refs. 17–22) of Ge, including pressure effects, pressure-induced structural transformations, and changes in the band structure. The theoretical works, in particular those where the effects of applying external pressure are included, are mainly based on LDA methods. Therefore we decided to study the bands vs pressure using a method that goes beyond LDA, and below the results of our QSGW calculations are summarized.

TABLE II. Band gaps and valence band width (in eV) of Ge at ambient pressure.

	Indirect gap: Γ-L	Direct gap: Γ-Γ	Indirect gap: Γ-X	Valence band width
Present (LDA)	0.06	−0.19	0.67	12.81
Present (QSGW)	1.02	1.32	1.25	13.02
Expt.[a]	0.78	1.0	1.3	12.6
SCGW[b]	0.79	1.51	0.71	14.77
GW-LDA[b]	0.51	1.11	0.49	13.12
GW-LDA[c]	0.75	0.7	1.2	12.9
GW-LDA[d]	0.75	0.71	1.23	12.86
GW-LDA[e]	0.77	1.11	1.23	13.06
GW-LDA[f]	0.61	0.39	1.33	13.07

[a] Reference 23.
[b] Reference 24.
[c] Reference 25.
[d] Reference 4.
[e] Reference 26.
[f] Reference 27.

We have calculated quasiparticle states for four volumes in diamond structure within the pressure range between 0 and 18 GPa and for four volumes for the β-tin structure in the range of 9–20 GPa. In Table II we compare our calculated band gaps with earlier experimental and theoretical results.[23–27] In contrast to LDA calculations, the QSGW gives the correct ordering of the conduction band minima at the Γ, L, and X points when compared to experiments. The values of the gaps obtained by the QSGW method are somewhat larger than those measured, and this agrees with the general trend found in the study[11] of many semiconductors. However, the QSGW results include neither vertex corrections, exciton states in the gap, nor the gap renormalization caused by electron-phonon interaction. Further, zero-point motion of the Ge atoms can reduce the gap by 0.1–0.2 eV.[28] The lower part of Table II lists results of other GW calculations. The label "SCGW" in Ref. 24 refers to a many-body self-consistent calculation, i.e., it uses a kind of self-consistency which is quite different from that of QSGW. The other GW calculations (GW-LDA) are perturbations to LDA band structures. (The results in Ref. 27 were taken from the thesis by Hott, not the PRB paper).

Now, consider the pressure variation of quasiparticle states at the L, Γ, and X points of the BZ. From Fig. 1 it is clear that the bands broaden as the applied pressure is increased. The valence band maximum is chosen as a reference, and on that scale the next upper valence states only moved slightly, whereas the lowest valence state moves down by $\sim$1 eV when the pressure grows from 0 to 10 GPa (the diamond→β-tin structural transformation). The direct band gap at Γ and the indirect Γ-L gap increase with pressure whereas the Γ-X gap remains constant, and around 4 GPa this gap becomes lowest in magnitude. These findings are consistent with earlier pseudopotential calculations.[29]

The response of the band structure of (cubic) Ge to application of external pressure is further illustrated in Table III,

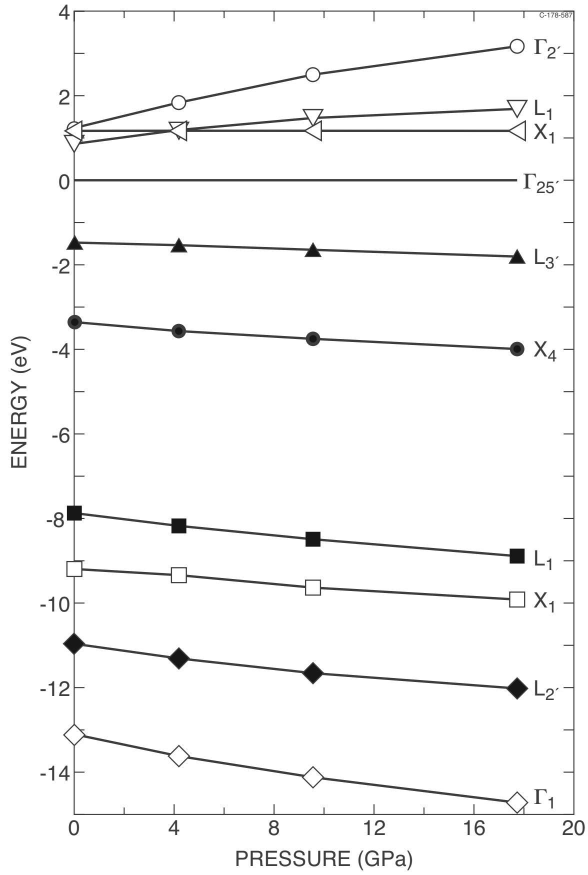

FIG. 1. Pressure variation of the valence states and the three lowest conduction states in Ge as calculated by the QSGW method at the Γ, *L*, and *X* symmetries points in the Brillouin zone. (Zero energy is at the valence band maximum, Γ'_{25}, i.e., $-\varepsilon(\Gamma_1)$ gives the valence band width.)

TABLE III. Deformation potentials, $\gamma = d\varepsilon / d\ell nV$, in eV. (Experiments: converted, using a bulk modulus $B=77$ GPa (Ref. 1), from measured pressure coefficients (Refs. 30 and 31) and cited in Ref. 32.

	QSGW	LDA	Experiment
Γ_{1v}-$\Gamma_{25'v}$	9.4	8.3	
$\Gamma_{2'c}$-$\Gamma_{25'v}$	−11.6	−9.8	-11.8 ± 0.4,[a] −9.3 [b]
$L_{2'v}$-$\Gamma_{25'v}$	6.6	5.6	
L_{1v}-$\Gamma_{25'v}$	6.0	5.1	
$L_{3'v}$-$\Gamma_{25'v}$	1.8	1.7	
L_{1c}-$\Gamma_{25'v}$	−4.6	−3.3	−3.9
X_{1v}-$\Gamma_{25'v}$	5.0	4.1	
X_{4v}-$\Gamma_{25'v}$	4.0	3.8	
X_{1c}-$\Gamma_{25'v}$	1.0	1.4	1.3
X_{1c}-X_{4v}	−3.0	−2.4	−4.2
L_{1c}-$L_{3'v}$	−6.4	−5.0	−5.8

[a] Reference 30.

[b] Reference 31.

where the deformation potentials of level differences are listed. LDA as well as QSGW results are given, and also some experimental results are included. These were obtained from measured pressure coefficients, Refs. 30 and 31 plus data listed in Table II of Ref. 32 (the results without a reference in Table III). Both sets of calculations agree equally well (or equally poorly) with the measured values.

Figure 2 shows the calculated valence band width for both the diamond and *β*-tin phases of Ge together with the experimental data of Struzhkin *et al.*[1] We find that in both phases the band width increases with pressure according to the QSGW as well as the LDA calculations. The QSGW band widths are slightly larger than those from the LDA. Also for the *β*-tin phase the QSGW valence bands are wider. This is consistent with earlier findings.[9] The present calculations do not include spin-orbit splitting. But since the pressure coefficient of the splitting, Δ_0, at the valence band maximum in Ge is extremely small, ~ 1 meV/GPa,[32,33] this does not affect our conclusions. Also, it should be noted that we calculate the valence band width, in the diamond structure, as the difference between the valence band maximum ($\Gamma_{25'}$) and the lowest level (Γ_1). The former is *p*-like, but the latter has *s* character, and transitions from the Γ_1 state to the 1*s* core state with photon emission is not allowed. But the experiment will also sample states somewhat above Γ_1 where some *p* character has been mixed in. As follows from Fig. 1, also these states move down relative to the valence band top when pressure is applied. Although the downshifts of these states are smaller, it is clear from Fig. 2 that the experimental resolution is so good that such smaller shifts would have been observed. Hence our QSGW calculations do not reproduce the experimental pressure variation of the valence band width in Ge.

III. CONCLUSIONS

We have carried out QSGW calculations for Ge both in cubic diamond and high pressure *β*-tin phases in order to examine whether *ab initio* calculations, which go beyond LDA and GW-LDA, can explain the experimentally ob-

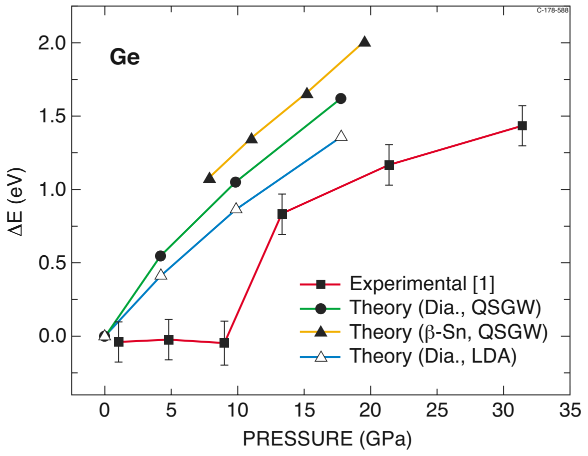

FIG. 2. (Color online) Pressure variation of the valence band width in Ge. The valence band width in *β*-tin Ge is defined as the difference between the Fermi level and the lowest valence state level at Γ.

served anomalous pressure variation of the valence band width in the semiconducting phase. The QSGW method used here is fundamentally different from a one-shot GW perturbation on top of an LDA calculation (GW-LDA) (the kind of calculation referred to in Ref. 1). Using the QSGW, we avoid that the pressure-induced band broadening can be “inherited” from an initial LDA (or GGA) calculation. But also our calculations were unable to reproduce the lack of pressure sensitivity of the valence band width deduced from the experiment.[1] It is unknown whether self-consistent QSGW calculations taking into account vertex corrections can lead to results which agree better with the experiments. As mentioned in Ref. 1, the final-state rule[34] should exclude that core-hole effects influence the XES spectra, and even if final-state relaxation effects were important, it is difficult to imagine that they could exactly cancel the band broadening in the insulating phase. Nevertheless, a new investigation of the theoretical basis of x-ray emission spectroscopy may be useful. We shall not pretend to know how to avoid complications of nonuniform pressure distribution[35] and nonhydrostatic pressure components in the diamond cell better than the experimentalists in Ref. 1. On the other hand, it would be interesting if further experimental data, also on other semiconductors, could be stimulated by this discussion.

ACKNOWLEDGMENTS

M.v.S. and T.K. acknowledge support by ONR under Contract No. N00014-7-0479 and NSF under Contact No. QMHP-0802216. The project was further supported by the Danish Agency for Science and Innovation under Contract No. 272-08-0257, and the calculations were carried out at the Center for Scientific Computing in Aarhus (CSC-AA), supported by the Danish Center for Scientific Computing (DCSC).

---

*Permanent address: High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India.

[1] V. V. Struzhkin, H.-K. Mao, J.-F. Lin, R. J. Hemley, J. S. Tse, Y. Ma, M. Y. Hu, P. Chow, and C.-C. Kao, Phys. Rev. Lett. **96**, 137402 (2006).
[2] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964).
[3] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[4] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).
[5] L. Hedin, Phys. Rev. **139**, A796 (1965).
[6] J. E. Northrup, M. S. Hybertsen, and S. G. Louie, Phys. Rev. Lett. **59**, 819 (1987).
[7] E. L. Shirley, Phys. Rev. B **54**, 7758 (1996).
[8] E. Jensen and E. W. Plummer, Phys. Rev. Lett. **55**, 1912 (1985).
[9] M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett. **55**, 1418 (1985).
[10] F. J. Himpsel, L. J. Terminello, D. A. Lapiano-Smith, E. A. Eklund, and J. J. Barton, Phys. Rev. Lett. **68**, 3611 (1992).
[11] M. van Schilfgaarde, T. Kotani, and S. V. Faleev, Phys. Rev. Lett. **96**, 226402 (2006).
[12] T. Kotani, M. van Schilfgaarde, and S. V. Faleev, Phys. Rev. B **76**, 165106 (2007).
[13] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[14] M. Methfessel, M. van Schilfgaarde, and R. A. Casali, *Electronic Structure and Physical Properties of Solids: The Uses of the LMTO Method*, Lecture Notes in Physics Vol. 535 (Springer, Berlin, 2000).
[15] S. B. Qadri, E. F. Skelton, and A. W. Webb, J. Appl. Phys. **54**, 3609 (1983).
[16] C. S. Menoni, J. Z. Hu, and I. L. Spain, Phys. Rev. B **34**, 362 (1986).
[17] S. Minomura and H. G. Drickamer, J. Phys. Chem. Solids **23**, 451 (1962).
[18] M. J. Baublitz and A. L. Ruoff, J. Appl. Phys. **53**, 5669 (1982).
[19] N. Moll, M. Bockstedte, M. Fuchs, E. Pehlke, and M. Scheffler, Phys. Rev. B **52**, 2550 (1995).
[20] R. J. Nelmes, H. Liu, S. A. Belmonte, J. S. Loveday, M. I. McMahon, D. R. Allan, D. Hausermann, and M. Hanfland, Phys. Rev. B **53**, R2907 (1996).
[21] K. Takemura, U. Schwarz, K. Syassen, M. Hanfland, N. E. Christensen, D. L. Novikov, and I. Loa, Phys. Rev. B **62**, R10603 (2000).
[22] F. J. Ribeiro and M. L. Cohen, Phys. Rev. B **62**, 11388 (2000).
[23] *Zahlenwerte und Funktionen aus Naturwissenschaften und Technik*, Landolt-Börnstein, New Series, Vol. III, Pt. 23a (Springer-Verlag, New York, 1982).
[24] W. Ku and A. G. Eguiluz, Phys. Rev. Lett. **89**, 126401 (2002).
[25] G. E. Engel and W. E. Pickett, Phys. Rev. B **54**, 8420 (1996).
[26] W. von der Linden and P. Horsch, Phys. Rev. B **37**, 8351 (1988).
[27] R. Hott, Ph.D Thesis, Max-Planck-Institut für Festkörperforschung, Stuttgart, 1990; R. Hott, Phys. Rev. B **44**, 1057 (1991).
[28] M. Cardona and M. L. W. Thewalt, Rev. Mod. Phys. **77**, 1173 (2005).
[29] F. Bassani and D. Brust, Phys. Rev. **131**, 1524 (1963).
[30] B. Welber, M. Cardona, Y. F. Tsay, and B. Bendow, Phys. Rev. B **15**, 875 (1977).
[31] A. R. Goñi, K. Syassen, and M. Cardona, Phys. Rev. B **39**, 12921 (1989).
[32] S. Lee, J. Sanchez-Dehesa, and J. D. Dow, Phys. Rev. B **32**, 1152 (1985).
[33] P. J. Melz and I. B. Ortenburger, Phys. Rev. B **3**, 3257 (1971).
[34] U. von Barth and G. Grossmann, Phys. Rev. B **25**, 5150 (1982).
[35] N. E. Christensen, A. L. Ruoff, and C. O. Rodriguez, Phys. Rev. B **52**, 9121 (1995).