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Role of semicore *d* electrons in quasiparticle band-structure calculations

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We have investigated the role of semicore *d* electrons in the calculation of quasiparticle band structures within the *GW* approximation for a number of elemental and compound semiconductors, as well as for a semimetal. The systems studied comprise Ge, GaN, ZnS, CdS, and α-Sn. Semicore *d* states are explicitly taken into account as valence states in our investigations. Overall, they have a strong influence on the band structure of the compounds, but not on that of the elemental semiconductor Ge or of the semimetal α-Sn. Nevertheless, there is a distinct influence on the Ge band structure to be noted, as well, in that the gap changes from direct to indirect by the inclusion of the semicore *d* states. Our band-structure results are in very gratifying agreement with available experimental data. [S0163-1829(98)01511-2]

I. INTRODUCTION

Within the last decade, the *GW* approximation[1,2] has been established as the standard approach to calculate quasiparticle (QP) band structures from first principles. QP band structures have been obtained for group-IV semiconducters and a number of group III-V semiconductors, in excellent agreement with experimental data.[3–6] The calculations are usually carried out in the framework of pseudopotential theory, i.e., only the valence electrons are taken into account explicitly, while all deeper states are treated as core states, thus being effectively eliminated from the calculations.

More recently, QP band structures have also been calculated for II-VI semiconductors, as well as, for group III-nitrides.[7–11] These semiconductors are of particular technological interest for optical applications because of their large fundamental gap. A very careful treatment of their cationic semicore *d* electrons, i.e., of the *d* electrons in the highest fully occupied atomic shell below the valence states, is required. Both in II-VI compounds and in group-III nitrides, the semicore *d* states have relatively high band-structure energies. They therefore have a strong influence on the electronic properties of the valence states and the band structure. Simply treating the semicore *d* states as core states when constructing pseudopotentials for the cations leads to distinct disagreement between theory and experiment with respect to structural properties, as well as to QP band-structure energies, as was shown, e.g., in Refs. 10 and 12.

In this work we fully include the cationic semicore *d* states as *valence states* in our *GW* QP band-structure calculations. It was shown in Refs. 12 and 13 that explicit inclusion of the semicore *d* states in the valence shell yields structural properties of II-VI compounds, in very good agreement with experimental data. For cubic CdS, we have shown in addition[10] that the calculated QP band-structure energies result in good agreement with experiment when the semicore states are explicitly taken into account as valence states.

In the present paper, we systematically discuss the influence of cationic *d* electrons on the band structure of a number of wide-band-gap semiconductors. To this end, we consider the II-VI semiconductors ZnS and CdS, as well as the group III-nitride GaN. We include results for the elemental semiconductor Ge, as well, to cover a wider range of systems and to show the respective trends in the impact of the *d* electrons. In addition, we investigate the influence of the semicore *d* states on the band structure of a group-IV semimetal, α-Sn, which to the best of our knowledge has not been studied by *GW* QP calculations before.

Our approach may be considered as a systematic step toward an all-electron QP band-structure calculation within GW approximation. However, we do not include all core electrons but restrict ourselves to including only the electronic states of the semicore shell which couple efficiently to the valence states and which therefore should not be treated as core states. This way we obtain reliable band-structure results. The numerical effort, nevertheless, is considerably smaller than that of a full all-electron calculation.

The paper is organized as follows. In Sec. II we briefly address the theoretical framework of our QP calculations, and discuss our method of including the complete semicore shell in the construction of the respective pseudopotentials. In Sec. III we present our QP band-structure results for the compound semiconductors ZnS, CdS, and GaN, and systematically discuss the influence of the semicore *d* electrons on the band structures of these compounds. In Sec. IV we discuss respective results for the elemental semiconductor Ge and the semimetal α-Sn. In the latter materials the influence of the semicore states on the band structure turns out to be much smaller than in the compounds. A short summary concludes the paper in Sec. V.

II. THEORETICAL FRAMEWORK

Our computational approach was presented in detail in Ref. 14. Here we only summarize a few formal aspects which are of particular importance for the systems addressed in this work.

A. LDA and *GW* approximation calculations

GW quasiparticle calculations are usually based on the results of preceding local-density-approximation (LDA) calculations that have to be performed first. For these, we employ norm-conserving *ab initio* pseudopotentials[15,16] which

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include the semicore electrons in the valence shell (see Sec. II B). The exchange-correlation energy is taken into account in the form as given in Refs. 17 and 18. For the representation of the wave functions we use a Gaussian orbital basis set. At each atom, s, p, d, and s^* orbitals with different decay constants are taken into account. The respective decay constants for the materials addressed in this work are given in Ref. 19. From these calculations, we obtain the LDA wave functions and LDA band-structure energies.

Using these LDA results, we construct the GW self-energy operator, $\Sigma = iGW$, where G is the LDA Green's function and W is the screened Coulomb interaction.[1,2] In the evaluation of W we employ the random-phase approximation[1,2] and a plasmon-pole model[20] to include the dynamics of the screening. The difference between the self-energy operator and the LDA exchange-correlation (XC) potential constitutes a perturbation operator. Evaluating its contribution to first order results in the quasiparticle (QP) band structure

$$E^{\mathrm{QP}}_{m\mathbf{k}} = E^{\mathrm{LDA}}_{m\mathbf{k}} + \langle \psi_{m\mathbf{k}} | \Sigma(E^{\mathrm{QP}}_{m\mathbf{k}}) - V^{\mathrm{LDA}}_{\mathrm{XC}} | \psi_{m\mathbf{k}} \rangle. \tag{1}$$

The self-energy operator and a number of other functions entering Σ are spatial two-point functions depending on $(\mathbf{r},\mathbf{r}')$. For their description, we employ a Gaussian-orbital basis set, as well, which is similar to that used in the LDA calculations (for details, see Ref. 14). This allows for an accurate treatment of the strongly localized semicore states with a moderate computational effort.

B. Pseudopotentials

The use of appropriate potentials is a crucial point in any pseudopotential approach. In particular, a careful treatment of the semicore shell is necessary when semicore d electrons are involved. As an example, we discuss the Zn pseudopotential (PP) that we employ for the calculations of ZnS. For the construction of this pseudopotential we follow the prescription as given by Hamann.[16]

The electronic configuration of the Zn atom is (Ne)$3s^2 3p^6 3d^{10} 4s^2$. When the complete third shell is treated as a core shell, one arrives at a Zn^{2+} PP which incorporates the $4s$ electrons only.[15] It is our aim to include the $3d$ electrons explicitly as valence states in our calculations for ZnS. This could be done[15] by employing a Zn^{12+} PP containing the $3d$ and $4s$ valence states, only, while the $3s$ and $3p$ states are treated as core states. Such a separation of the atomic semicore shell into core and valence states leads, however, to uncontrolled shortcomings in the QP band structure.[21] The respective QP energies deviate from experiment by up to several eV, as we showed recently for cubic CdS (cf. Ref. 10). The physical origins for these deviations were discussed in detail in that reference. It turned out that one should avoid the division of the semicore shell into valence and core states, and should include the $3s$ and $3p$ states in the valence shell, as well.[22] For ZnS this leads to a Zn^{20+} PP.

The inclusion of the complete semicore shell in the valence shell requires particular care in the construction of the norm-conserving pseudopotentials. For the Zn^{20+} PP, pseudo-wave-functions are required for both the $3s$ and $4s$ states. These two pseudo-wave-functions have to be orthogonal to each other, and therefore cannot be chosen independently. In particular, the $4s$ wave function should have a node at the same radius at which the true $4s$ wave function has its outermost node. To this end, we do not construct our pseudopotentials for the neutral Zn atom but for a Zn *ion* whose $4s$ state is unoccupied. The latter has the electronic configuration (Ne)$3s^2 3p^6 3d^{10}$. Thus we obtain a Zn^{20+} PP. When this PP is then used for the *neutral* Zn atom with the 4 s state occupied, a wave function for the $4s$ state is obtained automatically which is orthogonal to the other valence states. We found that this $4s$ pseudo-wave-function agrees with the true atomic $4s$ wave function outside the core region. This holds for the $3s$, $3p$, and $3d$ pseudo-wave-functions, as well. Furthermore, the energies of the $3s$, $3p$, $3d$, and $4s$ states of the pseudoatom agree with those of a respective atomic all-electron calculation. This way we obtained a Zn^{20+} PP which reproduces all relevant properties of the $3s$, $3p$, $3d$, and $4s$ states, and can thus be employed in the calculation for ZnS.

The results reported in this paper were obtained using pseudopotentials which treat all states of a given atomic semicore shell on equal footing, i.e., either as core or valence states. In particular, we employ Zn^{2+}, Cd^{2+}, Ga^{3+}, Ge^{4+}, and Sn^{4+} PP's for reference calculations without d electrons, and Zn^{20+}, Cd^{20+}, Ga^{21+}, Ge^{22+}, and Sn^{22+} PP's for the final calculations including the d electrons and the complete respective semicore shell in the valence shell. For the anions (N and S) of the compounds we employ conventional N^{5+} and S^{6+} PP's throughout this work, i.e., their semicore states are treated as core states.[15] This is reasonable since the anionic semicore states are much lower in energy than the cationic semicore states. The influence of the anionic semicore states on the band structures is therefore very small. In the following sections we discuss our results for the studied solids.

III. COMPOUND SEMICONDUCTORS

In this section we discuss the QP band structures of the wide-band-gap compound semiconductors ZnS, CdS, and GaN to identify the role of the semicore d electrons on their band structures. We restrict ourselves to the cubic zinc-blende modifications of the materials. All calculations are carried out at the respective experimental lattice constants[23,24] for a more meaningful comparison with experimental data and theoretical results from the literature.

A. II-VI compounds: ZnS and CdS

II-VI Zn and Cd compounds were addressed in a number of LDA and GW calculations.[7,10–13,25–29] These LDA band structures exhibit a number of deficiencies when compared with experiment. The gap is systematically underestimated, a well-known shortcoming of standard LDA band-structure calculations for semiconductors. The band-structure energies of the semicore d states, if included in the LDA calculations, result to be too high in energy by several eV. One way to obtain reliable band structures in good agreement with experiment is to calculate QP energies within the GW approximation. However, an appropriate treatment of the semicore d states in the respective calculations is very important.

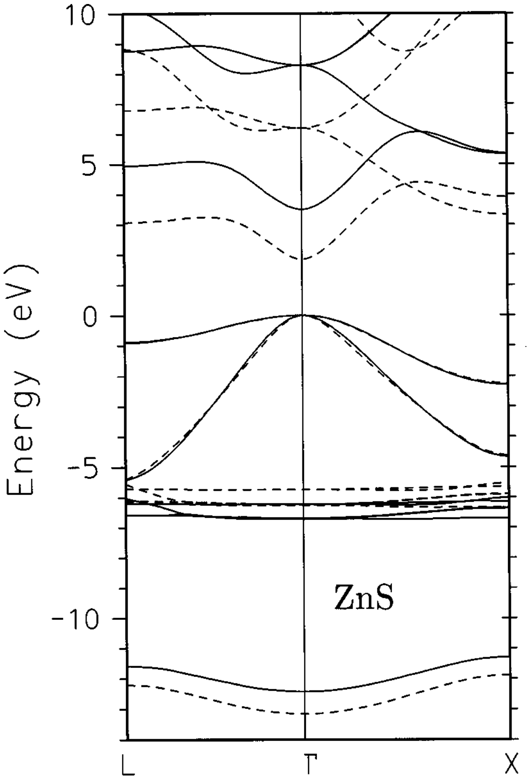

FIG. 1. Band structure of cubic ZnS as calculated with explicit inclusion of the Zn 3*d* semicore states, i.e., using a Zn^{20+} PP. The solid lines denote *GW* QP energies, while the dashed lines denote LDA energies.

TABLE I. *GW* QP band-structure energies (in eV) of cubic ZnS, CdS, and GaN, as calculated with the semicore states treated as core electrons (2+ and 3+ PP, respectively) and with explicit inclusion of the semicore states as valence states (20+ and 21+ PP), respectively. We present results for the gap energy E_g, for the band width W of the upper valence bands, as well as, for the semicore *d* energy E_d. The Zn and Ga 3*d* energies that would result from a self-consistent *GW* approach including satellites in the self-energy (labeled SAT) were estimated on the basis of the respective results for Cd 4*d*, Ge 3*d*, and Si 2*p* (see Refs. 21 and 30). We include *GW* results from Ref. 7 for ZnS and CdS, as well as, from Refs. 8 and 9 for GaN, that have been obtained employing the NLCC.

		2+/3+	20+/21+	SAT	GWA incl. NLCC	Exp.
ZnS	E_g	4.97	3.50		3.98[a]	3.8[b]
	W	4.70	5.42		5.20[a]	5.5[b]
	E_d		−6.4	−7.9[c]		−9.0[b]
CdS	E_g	3.70	2.45		2.83[a]	2.48[d]
	W	3.90	4.75		4.33[a]	4.18[e]
	E_d		−8.1	−9.1		−9.2[e]
GaN	E_g	3.59	2.88		3.1[f],2.76[g]	3.3[h]
	W	6.88	7.33		7.8[f],7.68[g]	
	E_d		−15.7	−17.3[c]		−17.7[i]

[a] Reference 7.
[b] Reference 23.
[c] Reference 30.
[d] Reference 32.
[e] Reference 33.
[f] Reference 8.
[g] Reference 9.
[h] Reference 24.
[j] Reference 34.

The group-IIB–VI Zn and Cd compounds are characterized by a relatively small energy difference between the *d* electrons of the semicore shell and the anion *p* and cation *s* electrons of the valence shell. Therefore, the influence of the semicore *d* states on the valence- and conduction-band structures is very strong in compounds of these elements. They thus form prototype systems for the investigation of the role of *d* electrons on QP band structures. In Ref. 10, we reported QP band-structure calculations for cubic CdS. In the present work we address the band structure of cubic ZnS (see Fig. 1 and Table I), in addition, which is similar to that of CdS. The respective data[10] for CdS are included in Table I to allow for a direct comparison. For further comparison, the LDA band structure of ZnS is included in Fig. 1 (dashed lines). The QP corrections to the LDA results, i.e., the differences between the QP and LDA band-structure energies, show a typical behavior: the conduction bands are shifted to higher energies, and the gap energy is increased. The cationic semicore *d* states, on the other hand, experience negative QP corrections.

We begin our discussion with the band structure of cubic ZnS as calculated without including the Zn 3*d* electrons, i.e., employing a simple Zn^{2+} PP, only. The *GW* approximation QP gap energy resulting from this calculation amounts to 4.97 eV, and is thus much larger than the experimental value of 3.8 eV.[23] Furthermore, the QP band width of the upper valence bands amounts to 4.70 eV only which is smaller than the experimental value of 5.5 eV.[23] These deviations are caused by neglecting the influence of the Zn 3*d* semicore states. Different from more strongly bound core states, the atomic semicore *d* electrons relax when the Zn atoms are incorporated into the ZnS solid. This relaxation affects the structural and electronic properties of ZnS.[10,12] In particular, the gap energy is strongly influenced, since the *d* states have band-structure energies that are only a few eV below the valence-band maximum (VBM) and thus couple strongly with the states near the gap, in particular with the *p*-like VBM states. The bandwidth of these upper valence states is very sensitive to the *p*-*d* hybridization, as well.

When using the Zn^{20+} PP instead of the Zn^{2+} PP, a much smaller gap energy results. We find a *GW* approximation QP gap energy of 3.50 eV, in good agreement with the measured gap of 3.8 eV. In addition, the QP bandwidth of the upper valence bands is increased by including the semicore shell. It now amounts to 5.42 eV, in very good agreement with experiment.

Within the LDA we obtain an average band-structure energy of −5.9 eV for the Zn 3*d* states which is too high if compared to experiment. By QP corrections, this energy is lowered by −0.5 eV, resulting in a QP band-structure energy of −6.4 eV. This value, however, is still too high as compared to the measured value of –9.0 eV. The remaining deviation of 2.6 eV is related to self-consistency effects in Σ that are not included in our present *GW* approach. A QP energy of approximately −7.9 eV can be expected to result[30] from a self-consistent treatment including satellites in the self-energy, as presented in Ref. 21. The effect of self-consistency on the fundamental band gap, on the other hand, is much smaller than for the semicore states.[31]

The measured energy position of the *d* states in ZnS and CdS is quite similar (−9.0 and −9.2 eV, respectively).

Therefore, the strength of the *p*-*d* coupling to the states near the gap is very similar in both compounds, as well. Concomitantly, the explicit inclusion of the *d* states in the calculation has nearly the same influence on the gap energy of the two systems, i.e., the QP gap energy is lowered by −1.47 and −1.25 eV, respectively.

One alternative to include the influence of the semicore *d* states on the structural properties and band structures to a certain extent is to take nonlinear core corrections (NLCC's) into account that are constructed within the LDA.[7–9,26,35] Respective *GW* band-structure results for ZnS and CdS by Zakharov *et al.*,[7] as well as, for GaN by Rubio *et al.*[8] and Palumno *et al.*,[9] are included in Table I.

Another more pragmatic alternative to include the influence of the semicore *d* electrons is to use self-interaction corrected (SIC) and self-interaction- and relaxation-corrected (SIRC) pseudopotentials, as discussed in detail in Refs. 36–38. These yield excellent structural results and band structures for the compounds by taking self-interaction and relaxation corrections approximately into account.

B. III-V compound GaN

The III-V compound GaN is a wide-band-gap semiconductor, as well, with a gap energy of 3.3 eV (Ref. 24) in the zinc-blende modification and 3.5 eV (Ref. 23) in the wurtzite modification. In this work we restrict ourselves to the cubic zinc-blende modification. GaN has been addressed by a number of theoretical investigations. The system was studied in Ref. 39, as well as in Ref. 40, within the LDA including the Ga 3*d* states explicitly. Vogel, Krüger, and Pollmann presented a self-interaction-corrected LDA calculation for GaN.[38] Jenkins, Srivastava, and Inkson[41] carried out LDA calculations for GaN, and included QP corrections to the gap energy using the Sterne-Inkson model.[42] Rubio *et al.*[8] and Palumno *et al.*[9] calculated QP band structures of GaN within *GW* approximation. The *d* states were, however, not explicitly included in their approaches. Instead, NLCC's were taken into account.

In this work we present a *GW* QP calculation for GaN, in which the semicore *d* states are fully included as valence states by employing a Ga^{21+} PP. The respective *GW* QP band structure is displayed in Fig. 2 together with the respective LDA band structure. In Table I, the results are compared to those of a Ga^{3+} PP calculation in which the *d* states are kept in the core.

Due to the larger nuclear charge of Ga, as compared to Zn, the 3*d* states have lower band-structure energies in GaN than in ZnS. Therefore their coupling to the states near the gap, as well as their influence on the gap energy, is much weaker in GaN than in ZnS. But now the *s*-*d* coupling of the anion 2*s* states to the 3*d* states is more important. Within the Ga^{3+} PP calculation, the QP gap energy of 3.59 eV is larger than the measured gap of 3.3 eV.[24] By inclusion of the *d* states in the calculation, the QP gap energy is reduced by −0.71 eV. This reduction is smaller than the respective reduction of −1.47 eV in the case of ZnS, as was to be expected from the larger binding energy of the 3*d* states in GaN. The resulting QP gap energy amounts to 2.88 eV, which is now lower than experiment.

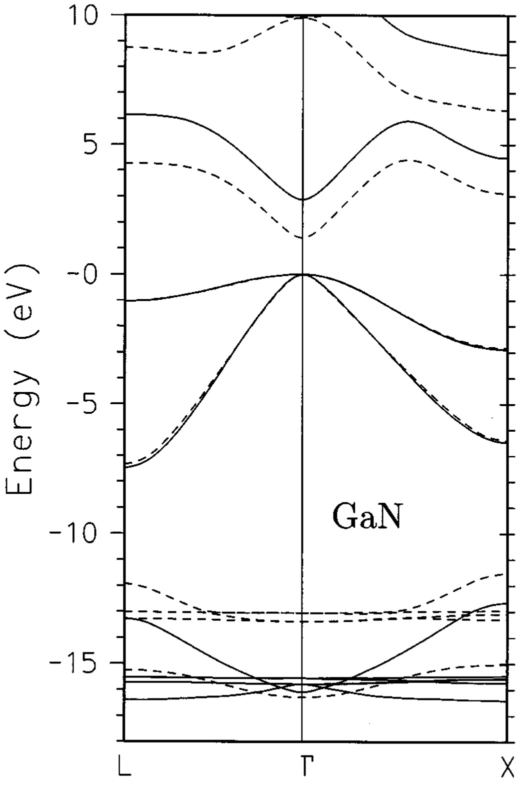

FIG. 2. Same as Fig. 1, but for cubic GaN explicitly including the Ga 3*d* semicore states, i.e., using a Ga^{21+} PP.

The character of the *s*-*d* coupling between the Ga 3*d* states and the N 2*s* states depends sensitively on the energy difference between the two. In the standard LDA, the *s*-*d* coupling is not correctly described, since the level order of Ga 3*d* and N 2*s* is not in agreement with experiment. The *GW* self-energy operator, which is based on LDA wave functions and energies has to be constructed with particular care, therefore (for details, see Ref. 19). Within the LDA, the Ga 3*d* states result some 2.5 eV higher in energy than in our *GW* QP band structure (see Fig. 2). In addition, the LDA dispersion of the Ga 3*d* states is different from that of the QP band structure. Furthermore, the bandwidth of the N 2*s* band is much smaller in the LDA than in the *GW* approximation.

In our QP band structure the energies of the N 2*s* band range from −16.1 to −12.7 eV. For Ga 3*d* bands, we obtain an average energy of −15.7 eV. In the photoemission spectrum of Ding *et al.*, two emission peaks are observed at −17.7 and at −14.2 eV.[34] From the relative intensities the authors attribute the lower band-structure energy to Ga 3*d*, and the higher one to N 2*s*. This is the same order of states as we find in our calculation. The difference of 2 eV between our calculated Ga 3*d* energy and the measured 3*d* level can be explained by the effect of renormalizing the Green's function, which is not included in the present calculation. From this effect we expect an additional lowering of the Ga 3*d* energy by approximately −1.6 eV, which would lead to a final 3*d* energy of approximately −17.3 eV.[30]

In Fig. 3 we compile the QP band structures of ZnS, CdS, and GaN near the fundamental gap. The dotted lines were calculated with the cationic semicore states kept in the core, i.e., by employing the respective 2+/3+ PP's. The solid

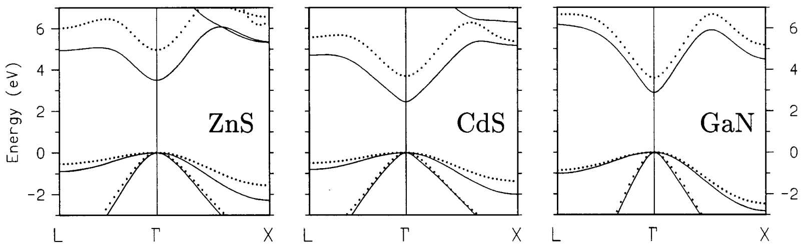

FIG. 3. Sections of calculated QP band structures of ZnS, CdS, and GaN near the fundamental gap. The dotted lines denote energies resulting when the cationic semicore electrons are treated as core electrons, i.e., using 2+/3+ PP's, respectively. The solid lines result when the semicore electrons are treated explicitly as valence electrons by employing 20+/21+ PP's, respectively.

lines show the results of our calculations in which the semicore states have been explicitly included (20+/21+ PP's). From Fig. 3 we observe the following general trend in the influence of the semicore *d* states on the band structures. In all cases, the conduction bands are lowered due to explicit inclusion of the semicore *d* states, and the fundamental gap energy is reduced. This effect is similar in ZnS and CdS. In GaN, on the other hand, the reduction of the gap is smaller, since the 3*d* states have larger binding energy in the group-III element Ga than in the group-II elements Zn and Cd. Therefore, the influence of the *d* states on the gap is weaker in GaN. The dispersion and bandwidth of the upper valence bands is increased when the semicore states are explicitly included in the calculation. This effect is more pronounced in ZnS and CdS than in GaN, as well.

The explicit inclusion of the cationic semicore *d* electrons reduces the gap energies by -1.47, -1.25, and -0.71 eV for ZnS, CdS, and GaN, respectively. This reduction is due to the fact that the *p*-*d* interaction shifts the anionic *p* bands energetically closer to the cationic *s* conduction bands. Since the binding energy of the semicore *d* states increases from ZnS over CdS to GaN the *p*-*d* interaction decreases along the row, and the gap shrinkage decreases accordingly.

IV. ELEMENTAL MATERIALS

In this section we present results for the group-IV elements Ge and α- Sn, having diamond structure. For these systems, the influence of the semicore *d* states can be expected to be much less pronounced than in the compound semiconductors discussed above, since the semicore *d* states are much stronger bound in Ge and Sn than in Zn, Cd, and Ga, respectively.

A. Group-IV semiconductor Ge

As far as the influence of the 3*d* electrons on the band structure is concerned, two major aspects have to be addressed for Ge in comparison with GaN. First, Ge has one additional proton in the nucleus as compared to Ga. Therefore, the energy of the 3*d* states is considerably lower in Ge than in Ga. We obtain a QP binding energy of -30.0 eV (Ref. 21) for the Ge 3*d* semicore states in bulk Ge, in good agreement with the experimental value of -29.5 eV.[43,44] Concomitantly, the influence of the 3*d* states on the band structure of Ge is much weaker than in GaN. Second, Ge is an elemental semiconductor, while GaN is a compound. In the latter, the valence-band maximum and conduction-band minimum states are composed of orbitals from different elements. The VBM is more anionlike, while the conduction-band minimum (CBM) is cation dominated. Therefore the influences of the cationic *d* states on the VBM and CBM are different, leading to the sensitivity of the gap energy as discussed in Secs. III A and III B. In the case of the elemental semiconductor Ge there is no difference between the ''cation'' and ''anion.'' Although the VBM and CBM states have different orbital characters, being *p* like and *s* like, respectively, they are equally distributed over atoms of the unit cell. In addition, the energy separation between VBM and CBM, i.e., the gap energy is very small as compared to the Ge 3*d* binding energy. This is opposite to the case of the wide-band-gap semiconductors, in which the gap is large and the *d*-state binding energy is relatively small. In consequence, both band edges in Ge are influenced by the 3*d* states in a similar way. In consequence, a much smaller influence of the *d* states on the gap energy results as compared to the compound semiconductors discussed above.

In our respective QP calculations for Ge, we found that the influence of the 3*d* states on the QP band structure is at most on the order of 0.1 eV, and is thus an order of magnitude smaller than in the compound semiconductors ZnS, CdS, and GaN. We refrain from showing the LDA and *GW* approximation band structures of Ge anew, since they were given in Ref. 6 already. Here we focus, for the sake of brevity, on the direct-gap energy at the Γ point and on the indirect gap energy between the Γ and *L* points of the Brillouin zone (see Table II). These results were obtained using a Ge^{4+} PP or a Ge^{22+} PP, i.e., without or with the 3*d* states in the valence shell, respectively. Within the Ge^{4+} PP calculation, we obtain a direct gap of 0.68 eV at Γ. Including the 3*d* electrons in the calculation, the band-structure energies of the lowest conduction band are raised near the Γ point and lowered near the *L* point. The resulting QP band structure shows an *indirect* gap of 0.71 eV between Γ and *L*, in good agreement with the measured gap of 0.744 eV between Γ and *L*.[23] The direct gap of Ge as resulting from the

TABLE II. *GW* QP gap energies (in eV) for Ge as calculated with the semicore states kept in the core (Ge^{4+} PP) and with explicit inclusion of the semicore states in the valence shell (Ge^{22+} PP), respectively. The results from Ref. 45 were obtained including core-polarizability corrections.

	Ga^{4+}	Ge^{22+}	Ref. 45	Exp.
$E_{\rm gap}^{\rm dir}$ (Γ-Γ)	0.68	0.81	0.85	0.89
$E_{\rm gap}^{\rm ind}$ (Γ-L)	0.75	0.71	0.73	0.744

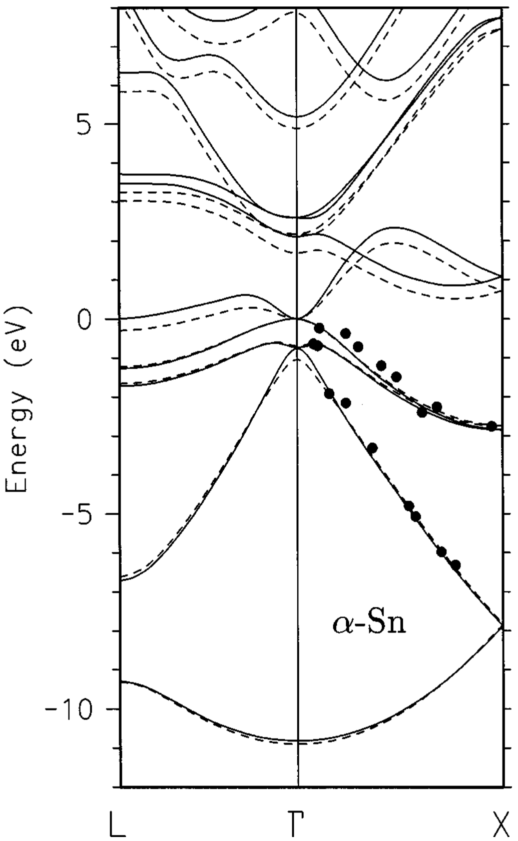

FIG. 4. Calculated band structure of α-Sn. The solid lines denote GW QP energies, while the dashed lines denote LDA energies. For these band structures, the Sn semicore states are treated as core electrons, i.e., a Sn^{4+} PP is used. The spin-orbit coupling was included in the calculations (see text). The experimental ARPES data were measured by Höchst and Hernańdez-Calderoń (Ref. 50).

conventional Ge^{4+} PP approach can thus be identified to be an artifact of neglecting the $3d$ semicore states in the valence shell.

The same transition from a direct to an indirect semiconductor was observed in Ref. 45 by taking the core polarizability into account, as well as in Ref. 46 by the inclusion of self-interaction corrections. The latter authors explained the transition as resulting from the contraction of the core states when self-interaction corrections are included. In our Ge^{22+} PP calculation, however, we do not observe any contraction of the semicore states as compared to the isolated Ge atom.

B. Group-IV semimetal α-Sn

As the last system we address the metastable α modification of Sn (grey tin), which has the diamond structure. Different from the other group-IV elements C, Si, and Ge, α-Sn is a semimetal, i.e., it has a semiconductorlike band structure but the gap is exactly zero (see Fig. 4). Its electronic properties are, nevertheless, rather semiconductorlike than metallic due to the vanishing density of states at the Fermi level and due to a vanishing Fermi surface. Band-structure results for α-Sn were presented by Chelikowsky and Cohen,[47] as well as by Brudevoll *et al.*[48] Here we discuss the first QP band structure for this material as calculated within GW approximation.

TABLE III. Optical transition energies (in eV) for α-Sn resulting from the GW QP band structures, as calculated with the semicore states treated as core electrons using a Sn^{4+} PP and with explicit inclusion of the semicore states in the valence shell using the Sn^{22+} PP, respectively. We focus on the dipole-allowed lowest-energy transitions at the high-symmetry points L, Γ, and X.

	Sn^{4+}	Sn^{22+}	Exp.[a]
at L	4.7	4.6	4.1–4.2
at Γ	2.1	1.9	2.0–2.4
at X	3.9	3.7	3.6–3.7

[a] Reference 23.

For the band structures discussed so far, we neglected spin-orbit interaction. In the case of α-Sn, on the other hand, spin-orbit interaction is important for an accurate determination of the topology of the bands at the valence-band maximum and for a meaningful comparison of the band-structure results with experimental data. We take the spin-orbit interaction into account by employing respective pseudopotentials.[15,49] The matrix size of the Hamiltonian is doubled when the electronic spin is taken into account explicitly.

We first discuss the results obtained with a Sn^{4+} PP leaving the semicore states in the core. In Fig. 4 we display the resulting LDA and GW QP band structures. Within the LDA the lowest conduction band has negative band-structure energies near the L point (-0.30 eV at L). Concomitantly the Fermi level is at negative energy (about -0.2 eV), leading to a metallic band structure with a nonzero Fermi surface and a density of states which is nonzero at all energies. At the Γ point the highest valence band and lowest conduction band are degenerate, both of them having p-type symmetry.

By the QP corrections the metallic character of the band structure is removed. The QP corrections for the lowest conduction band depend strongly on the wave vector. The band is shifted to higher energies by some 0.3 eV for most of the wave vectors of the Brillouin zone, except for the region near the Γ point. The final QP band-structure energy at the L point amounts to 0.01 eV, in good agreement with the measured value of 0.11 eV.[23] The QP band structure is indeed semimetallic. At Γ, the QP correction of the lowest conduction band tends to zero, and the degeneracy of the VBM and CBM states at Γ is maintained. Thus the QP corrections of the lowest conduction band are completely different from those for many semiconducting systems where the conduction bands show a more or less rigid shift without a **k** dependence.

By employing a Sn^{22+} PP, we included the Sn semicore states into the calculations explicitly. In order to reduce the numerical effort, we analyzed the respective effects on the band structure without including spin-orbit interaction. Thereafter, the respective semicore corrections are added to the band structure, including spin-orbit coupling. This has only a small influence on the band structure, as was to be expected from the respective results for Ge. The changes in the band-structure energies are, nevertheless, in the order of 0.2 eV (see Table III). They are thus somewhat larger than for Ge. Along column IV of the Periodic Table from C to Sn, the energy difference between the semicore and valence states becomes increasingly smaller, and the spatial separation between the respective states becomes less pronounced. Concomitantly the explicit influence of the semicore states on the valence states is very weak for C and stronger for Sn. For the band structures of diamond and Si it turns out that it does not make any difference whether the semicore states are described as core states or are included in the valence shell.

The correction of the valence bands due to inclusion of the semicore d states in the valence shell is quite small for α-Sn. The valence bands were investigated by Höchst and Hernández-Calderón using angle-resolved photoemission spectroscopy (ARPES).[50] Their results are included in Fig. 4 as full dots. Our QP band-structure results are in very gratifying agreement with these data.

For the conduction bands, no direct band-structure data have been reported so far, to our knowledge. A number of experiments addressed optical transition energies (see Ref. 23 and references therein). For a comparison of our calculated results with these data, we concentrate on the lowest dipole-allowed direct transitions at the L, Γ, and X points (see Table III). The band-structure energies of the conduction bands are lowered due to including the $4d$ semicore states of Sn in the valence shell, while the valence bands remain more or less unchanged. Concomitantly the optical transition energies are reduced by some 0.2 eV. The final Sn^{22+} PP results are in reasonable agreement with the measured data. One exception is the L point, where the transition energy is somewhat larger than the measured value.

V. SUMMARY

In this paper we investigated the role of semicore d states on quasiparticle band structures of compound and elemental semiconductors, as well as of the semimetal α-Sn. In particular, we addressed the question of whether these states can be treated as core states when constructing respective pseudopotentials or should explicitly be included in the valence shell. To resolve this question and arrive at general trends, we discussed the respective QP band structures for ZnS, CdS, GaN, Ge, and α-Sn.

The band structures of the three compounds ZnS, CdS, and GaN are very sensitive to the treatment of the semicore states. The gap is drastically reduced, and the bandwidth of the upper valence bands is increased when the semicore d states are explictly included in the calculation as valence states. This effect is most distinct in ZnS and CdS, where the semicore states have relatively small binding energies, allowing for a strong p-d coupling to the valence states.

For the group-IV systems Ge and α-Sn, on the other hand, the influence of the semicore d states on the band structure is much smaller due to the homopolar character of the materials preventing a spatial separation of electronic valence- and conduction-band states, and due to the large binding energy of the semicore d states. Nevertheless, the gap of Ge changes from direct to indirect when the semicore states are explicitly treated as valence electrons. Our results for the gap energies are in very good agreement with experiment. For the semimetal α-Sn, we also observe slight improvements in optical transition energies due to inclusion of the semicore states.

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[22] By employing the respective Cd^{20+} PP (see Ref. 10) for cubic CdS, we arrived at QP band-structure results and Cd $4d$ semicore QP energies, in particular, which are in very good agreement with experiment, indeed. When the Cd semicore shell is divided into core and valence states, the Cd $4d$ QP energy differs by as much as 3 eV from the result of the Cd^{20+} PP calculation.

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[30] In principle, the self-energy operator should be constructed using the resulting QP energies in a self-consistent manner instead of employing the LDA energies (see Ref. 21). This has nearly no effect on the valence- and conduction-band structures. The energy of localized semicore states, on the other hand, observe a downward shift. In the case of Zn $3d$, this shift would amount to approximately -0.1 eV. In our QP band structure for GaN, this type of self-consistency effect on Ga $3d$ is already included. Furthermore, taking the renormalization and satellites of the Green's function into account when constructing the self-energy operator results in an additional lowering of the band-structure energy of localized states (Ref. 21). We observed shifts of -2.5, -1.8, and -0.9 eV for the states Si $2p$, Ge $3d$, and Cd $4d$, having mean radii $\langle r\rangle$ of 0.54, 0.74, and 1.29 a.u., respectively. For the Zn $3d$ (Ga $3d$) state, having a mean radius of 0.91 a.u. (0.81 a.u.), by interpolation we thus expect an energy shift of approximately -1.4 eV (-1.6 eV) due to this effect. The final result for the Zn $3d$ (Ga $3d$) state would amount to -7.9 eV (-17.3 eV) which is a reasonable expectation for the results of a QP calculation as presented in Ref. 21. These final results would then be in gratifying agreement with the measured data.

[31] The gap energy of, e.g., ZnS would be increased by several 0.1 eV when self-consistency effects were included. It should be noted, however, that this increase of the gap would be partly compensated for when vertex corrections to the self-energy were included, as well (see the discussion in Ref. 21).

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