The differences between the results using static and dynamic screening appear to be even smaller at low electron densities. Since our ansatz is identical to that of DK in absence of screening, the differences between our results and those of DK in the unscreened case are either due to the different numerical procedures employed in evaluating the integrals or to the difficulty in determining $\epsilon_2(\vec{k}, \omega_p)$ from the graph in DK.

As may be seen from Figs. 3 and 4 the asymptotic formulas agree quite well with the more detailed calculation for frequencies greater than twice the Fermi energy. The asymptote also fits well even for relatively low frequencies, though there is no *a priori* reason to expect it to be very good in that region. Consequently, Eqs. (19) and (20) may be used as interpolation formulas or to give order-of-magnitude estimates of the damping for frequencies as low as the Fermi energy. Such an approximation is desirable since the numerical calculation is quite difficult even with static screening. For very high frequencies where screening becomes unimportant the kinematic approximations assumed in deriving the asymptotic forms become exact and the closed form (19) gives the correct result for damping due to electron correlations.

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Valence-Band Parameters in Cubic Semiconductors

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A five-level $\vec{k}\cdot\vec{p}$ analysis is used to compute the principal effective-mass parameters at $k=0$ in diamond- and zinc-blende-type semiconductors. A semiempirical model is developed to describe the dependence of the momentum matrix elements on lattice constant, ionicity, and d-electron shells in the cores. Satisfactory agreement with available experimental data is achieved with six fitted parameters.

I. INTRODUCTION

A number of important semiconductor properties require for their analysis quite detailed knowledge of effective-mass values at the principal band extrema, but even for some of the most well-known materials it is at present rather difficult to make the best choice from the wealth of experimental and theoretical data existing in the literature. It should also be emphasized that even though simple formal expressions for the effective-mass parameters can readily be obtained from second-order $\vec{k}\cdot\vec{p}$ perturbation theory, the input parameters, notably the momentum matrix elements, have not been known with an accuracy sufficient to render the existing theoretical results reasonably reliable. The reason for this is connected with the fact that most of the theoretical work has stressed other aspects of the band structure, and, as shown recently for Si by Kane,[1] current methods of band-structure calculation may fit the over-all band structure while giving rather unsatisfactory values for the band-edge masses.

In the present work we propose a new procedure for evaluating the interband momentum matrix elements at $\Gamma(k=0)$. Otherwise, our effective-mass calculation is similar to that given by Cardona[2] except for a few details. Based on earlier observations, Cardona assumed that the covalent part of the p-matrix elements is independent of material, and others[3] have made use of the essentially equivalent empiricism that the actual interband momentum matrix elements are constant within a certain group of crystals, e.g., the III-V semiconductors. This feature has so far not been explained satisfactorily, because one would certainly expect some influence from the variation in lattice constant. Later work by Cardona *et al.*[4] used p-matrix elements derived from pseudopotential calculations, but, as already indicated, there are reasons to believe that this may not be an improvement.

Similar to the original work by Cardona,[2] our method is based on a five-level $\vec{k}\cdot\vec{p}$ model including various small correction terms. The basic parameters in the momentum matrix elements are obtained from the extremely accurate experimental valence-band parameters γ_1, γ_2, γ_3, and κ for Ge.[5] A proportionality factor describing the effect of core d electrons is determined from a fit to α-Sn, and a small, but important, higher-band contribution to the s-like conduction-band mass has been fixed to give the best over-all agreement with experiment for the III-V compounds. The present model thus contains six fitted parameters. The squared p-matrix elements so derived have then been combined with the most recent information on corresponding energy gaps to yield the principal effective-mass parameters pertaining to the band edges at Γ. A final comparison with available experimental data indicates that our results may be reliable to within a few percent.

II. ELEMENTAL SEMICONDUCTORS

A. $\vec{k}\cdot\vec{p}$ Model

In the homopolar materials the states at $k=0$ have either even or odd parity, and the $\vec{k}\cdot\vec{p}$ perturbation only couples states of opposite parity. For the valence-band edge Γ_8^+ with energy zero we follow Dresselhaus, Kip, and Kittel[6] and introduce the parameters

$$\begin{aligned}
F &= -\frac{2}{m}\sum_j \frac{|\langle X|P_x|\Gamma_2', j\rangle|^2}{E_j}\,,\\
G &= -\frac{2}{m}\sum_j \frac{|\langle X|P_x|\Gamma_{12}', j\rangle|^2}{E_j}\,,\\
H_1 &= -\frac{2}{m}\sum_j \frac{|\langle X|P_y|\Gamma_{15}, j\rangle|^2}{E_j}\,,\\
H_2 &= -\frac{2}{m}\sum_j \frac{|\langle X|P_y|\Gamma_{25}, j\rangle|^2}{E_j}\,,
\end{aligned} \tag{1a}$$

where $|X\rangle$ is the yz-type wave function of the Γ_{25}' valence-band states in the case where spin-orbit coupling is neglected, and j runs over various conduction bands with the electron energy E_j and of the indicated symmetry. Furthermore, the spin-orbit splitting Δ_0' of the Γ_{15} states yields the additional parameter q,[5]

$$q \approx \frac{4}{9m}\sum_j \frac{|\langle X|P_y|\Gamma_{15}, j\rangle|^2 \Delta_{0j}'}{E_j^2}\;. \tag{1b}$$

From this we derive the Luttinger valence-band parameters[7] γ_1, γ_2, γ_3, κ, and q, where[8]

$$\begin{aligned}
\gamma_1 &= -\tfrac{1}{3}(F+2G+2H_1+2H_2)-1+\tfrac{1}{2}q\,,\\
\gamma_2 &= -\tfrac{1}{6}(F+2G-H_1-H_2)-\tfrac{1}{2}q\,,\\
\gamma_3 &= -\tfrac{1}{6}(F-G+H_1-H_2)+\tfrac{1}{2}q\,,\\
\kappa &= -\tfrac{1}{6}(F-G-H_1+H_2)-\tfrac{1}{3}-\tfrac{9}{4}q\,.
\end{aligned} \tag{2}$$

Following the usual approach, we shall confine the index j in Eq. (1) to include only the nearest state of the indicated symmetry because of the larger energy denominators for more distant bands and because the momentum matrix elements themselves decrease with increasing E_j. Let

$$\begin{aligned}
E_P &\equiv 2/m\,|\langle X|P_x|\Gamma_2'\rangle|^2\,,\\
E_P' &\equiv 2/m\,|\langle X|P_y|\Gamma_{15}\rangle|^2
\end{aligned} \tag{3}$$

be the energy equivalents of the principal interband momentum matrix elements. We then have

$$F = -E_p/E_0\,, \quad H_1 = -E_p'/E_0'\,, \tag{4}$$

where E_0 is the fundamental direct p-s energy gap and E_0' the p-p gap at Γ. The comparatively small parameters G and H_2 will not be factorized because we know too little about the corresponding band gaps. q is simplified to[5]

$$q = -\tfrac{2}{9}H_1\,\Delta_0'/E_0'\,. \tag{5}$$

The band gap E_0 is rather accurately known from numerous experiments, but E_0' must essentially be calculated from band theory. This simplest approach is that due to Van Vechten,[9] who finds

$$E_0' = (3.40\text{ eV})\,(a/a_{\mathrm{Si}})^{-1.92}\,, \tag{6}$$

where a is the lattice constant. The spin-orbit splitting Δ_0' is only known for Ge, where $\Delta_0' \approx 0.18$ eV.[5,10] Based on this result, we shall assume the general approximation

$$\Delta_0' \approx 0.64\,\Delta_0\,, \tag{7}$$

where Δ_0 is the well-known spin-orbit splitting of the valence band at Γ. It follows that the calculated values of q are hardly more than estimates. Since q is always small, this will have very little effect on the parameters γ_1, γ_2, γ_3, and κ as calculated from Eq. (2).

The effective mass m_c^* at the Γ_2' conduction-band edge is given by[2]

$$m/m_c^* = 1 - F(1-y) + F'\,, \tag{8}$$

where the second term results from the interaction with the valence bands Γ'_{25} ,

$$y = \Delta_0/3(E_0+\Delta_0) \ , \tag{9}$$

and the last term stands for the contribution from higher-lying states of even parity. Since detailed information is not available, we shall assume that F' is constant, and from an over-all fit to experimental values of m_c^* we find

$$F' \approx -2.0, \tag{10}$$

which is not unreasonable.

The effective mass m^*_{so} of the spin-orbit split-off valence band Γ_6^+ can also be determined from the above quantities[2]:

$$m/m^*_{so} = \gamma_1 + Fy \ . \tag{11}$$

Finally, we can calculate the g factors. The hole g factors at the valence-band edge are described by κ and q (cf. Ref. 5); the conduction-band g factor g_c is given by[2]

$$g_c = 2(1+Fy) \tag{12}$$

and that of the split-off hole by[8]

$$g_{so} = -2(1+2\kappa+Fy). \tag{13}$$

g_{so} will not be computed explicitly since it is observed that

$$g_{so}+g_c = -4\kappa, \tag{14}$$

and this relation also holds quite well for the ionic materials (cf. Sec. III A).

The basic formalism having thus been discussed, we turn our attention to the central problem: Evaluation of the momentum matrix elements, in particular the quantities E_P and E'_P.

B. Momentum Matrix Elements

From simple considerations of the momentum operator one would expect its matrix elements to be inversely proportional to the lattice constant. However, values of E_P deduced from Eq. (8) and experimental conduction-band masses show no correlation with lattice constant. Relativistic contributions are estimated to be very small on the basis of the linear k terms present in crystals without inversion symmetry.[11] In a reasonably simple picture, the only other possibility is the influence on the valence-band wave functions of d-electron core states. We now show how this effect can be accounted for quantitatively without detailed band-structure calculations.

In the dipole approximation, the oscillator strength for an optical transition from a valence-band state i to a conduction-band state i' is given by[12]

$$f^x_{ii'} = \frac{2}{m} \ \frac{|\langle i|P_x|i'\rangle|^2}{E_i' - E_i} \ , \tag{15}$$

where x signifies light polarized in the x direction. In particular, for the transition from a state at the valence-band edge to the Γ_2' conduction band we find

$$f^x_{ii'} \equiv f_{cv} = E_P/3E_0. \tag{16}$$

The oscillator strengths satisfy the sum rule[12]

$$\sum_{ii'} f^x_{ii'} = 4\pi^3 N_{\rm eff} \ , \tag{17}$$

where $N_{\rm eff}$ is the effective concentration of valence electrons. In the Penn model[13] of the low-frequency dielectric constant $\epsilon(0)$, one finds[14]

$$\epsilon(0) = 1 + 4\pi e^2\hbar^2 N_{\rm eff}/mE_g{}^2, \tag{18}$$

in which E_g is an average electronic band gap that scales as a power function of the lattice constant for homopolar materials.[14] With no d electrons in the core, $N_{\rm eff}=N$, where N corresponds to eight electrons per diatomic volume. In order to account for the d electron effects, Van Vechten[14] introduced the enhancement factor $D \equiv N_{\rm eff}/N$, and its values were deduced from Eq. (18) and experimental evidence on $\epsilon(0)$.

Although the sum rule (17) only deals with the totality of oscillator strengths, it is reasonable to propose that essentially the same enhancement factor applies to the individual $f_{ii'}$. Thus, for example,

$$E_P = E_P(\mathrm{Si})\,\delta \ , \tag{19}$$

with

$$\delta = [1+\alpha(D-1)]\ (a_{\rm Si}/a)^2, \tag{20}$$

where α is a constant of order unity. From γ_1, γ_2, γ_3, κ, and q for Ge,[5] we can deduce $E_P(\mathrm{Ge})$, and $E_P(\alpha\text{-Sn})$ is also known rather accurately.[8] Combining this with D values found by Van Vechten,[14] we find

$$\alpha = 1.23 \ . \tag{21}$$

Since Γ is the point of highest symmetry in the Brillouin zone, it is not surprising that the influence of d electrons is slightly larger than average here (α>1). It should be noted that both the lattice constant and D tend to increase with atomic number, and so these effects compensate somewhat in the scaling factor δ. This is the reason why no definite trends are observed in E_P.

Since the above d-electron enhancement is a property of the wave functions at the valence-band edge, the same scaling applies to all the momentum matrix elements in our calculation. The scaling factor δ should therefore be used also for E'_P, G, and H_2.

The actual values of E_P, E'_P, G, and H_2 as normalized to Si [cf. Eq. (19)] are determined from the valence-band parameters measured by Hensel and Suzuki[5] for Ge because these are the most accurate mass parameters available. From[5] $\gamma_1 = 13.38 \pm 0.02$, $\gamma_2 = 4.24 \pm 0.02$, $\gamma_3 = 5.69 \pm 0.02$, $\kappa = 3.41 \pm 0.03$, $q = 0.06 \pm 0.01$, and the band gaps listed in Table I, we find by means of Eq. (2)

$$\begin{aligned} &E_P(\mathrm{Si}) = 21.6\ \mathrm{eV}, \quad E'_P(\mathrm{Si}) = 14.4\ \mathrm{eV}, \\ &H_2(\mathrm{Si}) = -0.19, \qquad G = -0.75\ . \end{aligned} \tag{22}$$

Together with $F' = -2.0$ and $\alpha = 1.23$ discussed above, these six parameters constitute the basis of our calculation. Of course, when we presently extend the formalism to the ionic semiconductors, there will be new parameters describing the mixing of even and odd wave functions by the antisymmetric ionic potential, but this will essentially be expressed in terms of quantities determined elsewhere.

III. III-IV AND II-VI COMPOUNDS

A. Effect of Ionicity

For the present purpose, the effects of ionicity have the following four aspects: (a) The lack of inversion symmetry results in nonzero first-order $\vec{k}\cdot\vec{p}$ intraband matrix elements giving rise to linear k terms in the dispersion relations; (b) the principal band gaps are increased; (c) even and odd wave functions of the same basic symmetry (e.g., p symmetry) are mixed so that the momentum matrix elements are modified; and (d) d-electron core shifts with ionicity strongly affect the s-like conduction band. The linear k terms will be neglected because they are very small and connected with relativistic spin-orbit effects.[11] Furthermore, experimental evidence is not very consistent on this point. The three other effects will be considered in some detail.

For the simple bonding-antibonding band gaps, Van Vechten[9,14] has shown more or less empirically that the influence of ionicity can be described quantitatively through the electronegativity C which is derived from the dielectric constant and Eq. (18) by assuming[14]

$$E_g^2 = E_h^2 + C^2, \tag{23}$$

where E_h is the average covalent band gap and is a function of the bond length only. By analogy, the E'_0 gap between Γ_{15v} and Γ_{15c} states can be expressed as[9]

$$E'_0 = (E'^2_{0h} + C'^2)^{1/2}, \tag{24}$$

with the homopolar part E'_{0h} calculated from Eq. (6). Van Vechten[9] assumed $C' = C$, but stated later that somewhat larger values should be used for p-p gaps. This is also in agreement with recent pseudopotential band calculations by Walter and Cohen,[15] and we find that

$$C' = 1.25C \tag{25}$$

gives a reasonable fit to these calculations. For the E_0 gap, we shall use the experimental values.

Once the symmetric and antisymmetric components of the E'_0 gap known, it is straightforward to describe the admixture of the homopolar wave functions. Other bands of p symmetry are assumed to be very remote. The behavior of the wave functions has already been treated by Cardona,[2] and so we leave out the details here. In this way we find that H_1 is still given by Eq. (4) and that

$$\begin{aligned} &H_2 \approx H_2(\mathrm{Si}) z\delta\ , \\ &G \approx G(\mathrm{Si}) z\delta\ , \end{aligned} \tag{26}$$

where

$$z = (E'_0 + E'_{0h})/2E'_0\ . \tag{27}$$

For the Γ_{1c} conduction band, the situation is a little different because this state is strongly influenced by the presence of d electrons in the core combined with ionicity. For the isoelectronic series Ge, GaAs, ZnSe, calculations by Walter and Cohen[16] of the pseudocharge density associated with this state have shown that the initially antisymmetric state (for Ge) tends to concentrate on the anion (Se) site. This means that the Γ_{1c} and Γ_{15v} wave functions, behave in the same way with ionicity, and so the corresponding interband momentum matrix element is rather insensitive to the antisymmetric ionic potential. For such materials, the homopolar formulas for F [Eq. (4)], m/m_c^* [Eq. (8)], and g_c [Eq. (12)] are still valid. On the other hand, if d electrons are absent as in AlP, the Γ_{1c} wave function is unaffected by ionicity because there are no levels of similar symmetry within reasonable distance. In that case, there is no matching between Γ_{1c} and Γ_{15v} states, and Cardona's formulas[2] should be valid. In skew compounds containing d electrons, the differences in core properties are expected to lead to incomplete matching. It is therefore convenient to introduce a matching parameter β which is zero for no d electrons, 1 for isoelectronic compounds with d electrons, and somewhere in between otherwise. The defining equation is

$$E_P = E_P(\mathrm{Si})\delta[\beta + (1-\beta)z]\ . \tag{28}$$

Then Eq. (4) gives the relevant F, and the conduction-band mass is given by a modification of (8):

$$m/m_c^* = 1 - F(1 - y - x) + F', \tag{29}$$

where x stands for the contribution from the Γ_{15c} band and is approximately

$$x \approx \frac{\beta}{\beta + (1-\beta)z}\ \frac{E_0}{E'_0 - E_0}\ \frac{E'_0 - E'_{0h}}{2E'_0}\ . \tag{30}$$

This term may contribute up to 15% in the worst case. Similar to Eq. (28), the formula for g_c, Eq. (12), must be modified to include the Γ_{15c} interaction. We then find

$$g_c = 2[1 + F(y + y')] \ , \qquad (31)$$

where

$$y' \approx \Delta_0'/3(E_0' - E_0) \ . \qquad (32)$$

y' is usually insignificant. The values of the

TABLE I. Principal band gaps in eV at 0 K used in the mass-parameter calculation. E_0' is computed from Eq. (24). β is the matching factor for the ionicity behavior of the wave function of the Γ_{1c} and Γ_{15v} band-edge states. δ is the scaling factor for the squared momentum matrix elements as calculated from Eq. (20) using lattice constants and D factors listed in Ref. 14. For HgTe, HgSe, and HgS, D was estimated to be 1.30, 1.28, and 1.19, respectively, from experimental data on E_P and the fact that these materials are contracted (see Ref. 18).

Crystal	E_0	Δ_0	E_0'	β	δ
C	13.04[a]	~0[b]	7.63	···	2.31
Si	4.07[a]	0.04[c]	3.40	···	1.00
Ge	0.89[d]	0.29[e]	3.16	···	1.22
Sn	−0.413[f]	0.77[b]	2.40	···	1.10
AlP	5.12[a]	0.05[b]	5.18	0	0.99
AlAs	3.06[g]	0.28[g]	4.66	0.5	1.06
AlSb	2.30[h]	0.75[i]	4.73	0.5	0.96
GaN	3.62[j]	−0.01[b]	9.12	0.5	1.66
GaP	2.87[k]	0.08[k]	5.33	0.5	1.13
GaAs	1.52[l]	0.34[h,e]	4.81	1	1.19
GaSb	0.81[m]	0.77[b,h,m]	3.69	0.5	1.11
InP	1.42[n]	0.13[h,o]	5.10	0.5	1.05
InAs	0.42[p]	0.38[q]	4.40	0.5	1.13
InSb	0.237[r]	0.81[h,g]	3.49	1	1.07
ZnO	3.40[s]	−0.02[s]	13.60	0.5	1.56
ZnS	3.80[t]	0.07[t]	8.47	0.5	1.11
ZnSe	2.82[u]	0.43[v]	7.67	1	1.12
ZnTe	2.39[w]	0.92[h]	6.23	0.5	1.03
CdS	2.56[s]	0.07[s]	7.85	0.5	1.00
CdSe	1.84[s]	0.42[s]	7.39	0.5	1.02
CdTe	1.60[x]	0.91[h]	6.01	1	0.96
HgS	−0.15[b]	0.07[b]	9.56	0.5	1.05
HgSe	−0.24[y]	0.45[b]	6.80	0.5	1.06
HgTe	−0.303[z]	1.00[z]	5.58	0.5	0.97

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matching factor β for the intermediate cases cannot be obtained from simple arguments. In order to minimize the error we shall fix it at 0.5. To take $\beta = 1$ for the isoelectronic compounds is, of course, also an approximation. It is evident that the arbitrariness in this parameter is one of the principal sources of uncertainty in our calculation. The subsequent comparison with experiments shows, however, that the inclusion of $\beta \neq 0$ is a definite improvement over Cardona's method,[2] which corresponds to $\beta = 0$.

B. Polaron Effects

It is a well-known feature that the band structure as deduced from experiments contains corrections to the simple one-electron band structure because of the electron-phonon interaction. For the present discussion we shall distinguish between the nonpolar short-range (SR) and the polar long-range (LR) interactions.

The SR self-energy arises from interaction with a broad spectrum of phonons, and recent theoretical developments[17] indicate that it can be considered as a local vibrational effect on the one-electron potential. In that case, its over-all influence on the effective-mass parameters is described by conventional $\vec{k} \cdot \vec{p}$ theory using the "renormalized" band gaps and momentum matrix elements. Typical SR band-gap self-energies are less than 0.1 eV and are probably representative of actual potential changes. It is therefore reasonable to assume that the squared momentum matrix elements (e.g., $E_P \sim 20$ eV) undergo changes of similar absolute magnitude, and such changes are thus negligible.

The important part of the LR interaction couples the carrier to the polarization associated with long-wavelength optical vibrations in ionic crystals. The self-energy of the band edges (i.e., the polaron binding energy) is small compared to the important energy gaps, and the polaron mass renormalization must usually be dealt with separately because it depends strongly on the type of experiment involved.

We conclude that our calculation gives the mass parameters at zero temperature renormalized with respect to the SR interaction and bare relative to the LR interaction. An extension to finite temperatures is in principle possible now that the lattice-constant dependence of the squared momentum matrix elements is prescribed [cf. Eqs. (19) and (20)], but more knowledge of the D factor in Eq. (20) will be needed.

IV. DISCUSSION OF RESULTS

A. Results

In Table I we list the relevant input parameters for our calculations. Some of these are directly experimental, whereas others, notably E_0' and δ, have been calculated from lattice constants, D factors, and C values tabulated by Van Vechten[9,14] and supplemented by other sources for the Hg-chalcogenides,[18] GaN,[19] and ZnO.[19] Our results for the principal effective-mass parameters at

TABLE II. Calculated band parameters for diamond- and zinc-blende-type semiconductors. All effective masses are in units of the free-electron mass. The signs have been chosen positive for a normal band structure like that of Ge.

Crystal	E_p (eV)	f_{cv}	m_c^*	g_c	γ_1	γ_2	γ_3	κ	q	m_{hd}^*	m_l^*	m_{so}^*
C	49.8	1.27	0.36	2.00	4.62	−0.38	1.00	−0.63	0.00	a	a	0.36
Si	21.6	1.77	0.23	1.96	4.22	0.39	1.44	−0.26	0.01	0.53	0.16	0.24
Ge	26.3	9.9	0.038	−2.86	13.35	4.25	5.69	3.41	0.07	0.35	0.043	0.092
Sn	23.8	(19.2)	−0.058	84.4	−14.97	−10.61	−8.52	−11.84	0.30	0.29	−0.029	0.038
AlP	17.7	1.15	b	b	3.47	0.06	1.15	−0.54	0.01	0.63	0.20	0.29
AlAs	21.1	2.30	0.22	1.52	4.04	0.78	1.57	0.12	0.03	0.76	0.15	0.24
AlSb	18.7	2.71	0.18	0.52	4.15	1.01	1.75	0.31	0.07	0.94	0.14	0.29
GaP	22.2	2.58	0.17	1.85	4.20	0.98	1.66	0.34	0.01	0.79	0.14	0.24
GaAs	25.7	5.63	0.067	−0.06	7.65	2.41	3.28	1.72	0.04	0.62	0.074	0.15
GaSb	22.4	9.2	0.045	−7.12	11.80	4.03	5.26	3.18	0.13	0.49	0.046	0.14
InP	20.4	4.80	0.080	1.20	6.28	2.08	2.76	1.47	0.01	0.85	0.089	0.17
InAs	22.2	17.6	0.023	−14.8	19.67	8.37	9.29	7.68	0.04	0.60	0.027	0.089
InSb	23.1	32.5	0.014	−48.4	35.08	15.64	16.91	14.76	0.15	0.47	0.015	0.107
ZnS	20.4	1.79	0.28	1.94	2.54	0.75	1.09	0.17	0.00	1.76	0.23	0.40
ZnSe	24.2	2.86	0.14	−5.74	3.77	1.24	1.67	0.64	0.02	1.44	0.149	0.30
ZnTe	19.1	2.66	0.18	0.44	3.74	1.07	1.64	0.42	0.05	1.27	0.154	0.33
CdTe	20.7	4.32	0.096	−1.12	5.29	1.89	2.46	1.27	0.05	1.38	0.103	0.28
HgS	18.8	(41.8)	−0.006	−70.6	−41.28	−21.00	−20.73	−21.54	0.00	2.78	−0.012	−0.013
HgSe	19.4	(26.9)	−0.042	117.4	−25.96	−13.69	−13.20	−14.29	0.02	1.36	−0.019	0.031
HgTe	18.0	(19.8)	−0.031	59.0	−18.68	−10.19	−9.56	−10.85	0.06	1.12	−0.026	0.102

[a] Formalism invalid because γ_2 and γ_3 have opposite sign.

[b] Unreliable because $E_0 \approx E_0'$.

TABLE III. Comparison of calculated and experimental conduction-band masses and values of $m/m_c^* + m/m_{so}^*$. For ZnO and ZnSe, the experimental value of m_c^* includes an appreciable polaron renormalization.

Crystal	m_c^*/m Theory	m_c^*/m Expt.	$m/m_c^* + m/m_{so}^*$ Theory	$m/m_c^* + m/m_{so}^*$ Expt.
Ge	0.038	0.038[a]	37.1	36.8[a]
Sn	−0.058	−0.058[b]		
GaN	0.14			
GaAs	0.067	0.066[c]	21.5	21.5[d]
GaSb	0.045	0.045[e]	29.1	29.8[f]
InP	0.080	0.077[g]		
InAs	0.023	0.024[g,h]		
InSb	0.0141	0.0137[i]	81.0	79[j]
ZnO	0.15	0.19[k]		
ZnS	0.28	0.28[l]		
ZnSe	0.14	0.17[m]		
ZnTe	0.18	0.16[n]		
CdS	0.18	0.20[o]		
CdSe	0.13	0.13[p]		
CdTe	0.096	0.096[q]		

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Γ are shown in Table II, where we include values of E_P which may be useful when a small E_0 gap makes it necessary to consider the s-p $\vec{k}\cdot\vec{p}$ interaction more accurately.[11] Furthermore, we also show the computed values of the fundamental oscillator strength f_{cv} given by Eq. (16).[20]

Although the valence-band parameters γ_1, γ_2, and γ_3 give a complete description of the parabolic band structure near the edge, the effective masses in specific directions are certain functions of these parameters. For the heavy holes, this involves a considerable cancellation, and so γ_1, γ_2, and γ_3 are shown with a larger number of significant figures than their accuracy warrants. To facilitate comparison between materials we have evaluated the average light-hole mass m_l^* and the density-of-states heavy-hole mass m_{hd}^* calculated in the following way according to Lax and Mavroides.[21] Define the light-to-heavy-hole (average) splitting parameter (B' in the notation of Ref. 21)

$$\bar{\gamma} \equiv (2\gamma_2^2 + 2\gamma_3^2)^{1/2} \tag{33}$$

and the heavy-hole anisotropy factor[21]

$$\gamma_h \equiv 6(\gamma_3^2 - \gamma_2^2)/\bar{\gamma}\,(\gamma_1 - \bar{\gamma})\,, \tag{34}$$

then

$$m_l^*/m = (\gamma_1 + \bar{\gamma})^{-1}, \tag{35}$$

$$m_{hd}^*/m \approx (\gamma_1 - \bar{\gamma})^{-1}\,(1 + 0.05\gamma_h + 0.0164\gamma_h^2)^{2/3}. \tag{36}$$

Computed values of m_l^* and m_{hd}^* are included in Table II. γ_h is not shown because it turns out (somewhat as a property of our model) that γ_h varies but little; i.e., the relative anisotropy of the heavy-hole band is essentially the same for most of the materials studied here. However, for diamond and some other first-row compounds not shown, the anisotropy is found to be much smaller.

B. Comparison with Experiment

One of the principal purposes of the present work has been to produce effective-mass parameters in better agreement with experiment than previously achieved.[2,3,22] In Table III, we compare our values of the conduction-band mass m_c^* with available experimental data including the wurtzite compounds GaN, ZnO, CdS, and CdSe to which the theory also applies.[2] The general agreement is rather encouraging, in particular since the important basic parameters of the calculations have been derived from the *valence-band* parameters of Ge. We also compare the mass parameter $m/m_c^* + m/m_{so}^*$ with recent magneto-optical data.

Since our calculation is in no respect based on Si (except as a hypothetical reference material), a crucial test of the validity of the momentum matrix element scaling, Eq. (20), is provided by accurate cyclotron resonance data on γ_1, γ_2, and γ_3 for this material. Previous ambiguities about these parameters have now been settled by Hensel[23] and Owner-Petersen and Samuelsen.[24] Hensel finds (γ_1, γ_2, γ_3) = (4.28, 0.375, 1.45) as compared to our values (4.22, 0.39, 1.44). Less accurate cyclotron resonance data for holes are available for GaSb,[25] InSb,[26] and ZnTe.[27] In general, we find good agreement for the light-hole mass and for the heavy-hole mass in the ⟨100⟩ direction, whereas our anisotropy of the heavy-hole band is somewhat larger. This might indicate that our crude treatment of the G term associated with Γ_{12c} levels in Eqs. (1) and (2) is insufficient for the more ionic materials. However, for InSb the density-of-states heavy-hole mass $m^*_{hd} = 0.47m$ compares favorably with that deduced directly from experiments: $m^*_{hd} = 0.43m$.[28]

Accurate experimental evidence exists for a few g factors. Thus, for InSb,[29] $g_c = 48$, and for InAs,[30] $g_c = -14.7$, while our results are -48.4 and -14.8, respectively. Since experiment and theory agree on the value of m^*_c, the above results are not really a critical test of our calculation for these materials.

C. Conclusion

An important aspect of the present semiempirical mass-parameter calculation is the new treatment of the principal momentum matrix elements, in particular their dependence on d electrons in the cores. This influence shows up in the scaling of the covalent part with Van Vechten's D factor as expressed in Eq. (20) and in the "matching factor" β which for ionic semiconductors describes the effect of core-shift-induced transfer of the conduction-band s-state pseudocharge density towards the anion site. The general agreement between experiment and the results of the present theory supports the physical significance of the D factor and, through $N_{eff} = DN$ in Eq. (18), the relevance of scaling with lattice constant of the average covalent band gap E_h.[14] This seems to be one of the most questioned[31] features of Phillips and Van Vechten's ionicity theory. Furthermore, the scaling of momentum matrix elements in Eq. (20) includes a natural lattice-constant dependence.

As already pointed out, the combined effects of lattice-constant variation and core d electrons more or less cancel so that E_P turns out roughly independent of material in agreement with previous empirical observations. However, when high accuracy is wanted, the detailed behavior of E_P must be included, and all first-row compounds exhibit very high values of E_P as a consequence of the small lattice constant. Thus for Zn0 we find $E_P = 28$ eV, which eventually leads to the unexpectedly small value of $m^*_c = 0.15m$. It would be of considerable interest to test this result by more direct experimental evidence than presently available.

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