Terms Linear in k in the Band Structure of Zinc-Blende-Type Semiconductors

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A calculation of the coefficient C_k of the terms linear in **k** in the Γ_8 valence bands of several III-V semiconductors is presented. On the basis of the systematics of these results it is concluded that these terms arise from coupling by the linear momentum and the spin-orbit operators to the uppermost *d* levels of the core. A simple analytic expression to calculate C_k for all III-V, II-VI, and I-VII compounds with zinc-blende structure is proposed. The results are in good agreement with the few experimental data available.

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The existence of terms linear in \mathbf{k} in the band structure of zinc-blende-type semiconductors around the top Γ_8 valence bands has been known for a long time.^{1,2} They determine the position of the top of the light- and heavy-hole bands off $\mathbf{k} = 0$ and are important in magneto-optical³ and polariton scattering experiments.4,5 In spite of this, little experimental and theoretical information about C_k (the coefficient of the linear term as defined in Refs. 1 and 2) and its origin is available.³⁻⁷ In this Letter we present fully relativistic linear muffin tin orbital (LMTO) calculations⁸ of C_k for InP, InSb, GaAs, and GaSb. These calculations yield not only the magnitude but also the sign of C_k . (The latter is usually not obtained in experiments because of a lack of knowledge about the bond directions in the samples. These directions can, however, be determined.⁹) An analysis of the systematics of the calculated results suggests that the origin of C_k is the second-order interaction, bilinear in $\boldsymbol{k}\cdot\boldsymbol{p}$ and in the spin-orbit operator H_{so} , between the Γ_8 states and the uppermost d core levels, and not the k-dependent spin-orbit Hamiltonian, as usually believed.^{1,2} An interpolation-extrapolation procedure is suggested to estimate C_k for all materials of the family (including II-VI and I-VII compounds). The results agree rather well with the few experimental data available.³⁻⁷

The self-consistent band-structure calculations employ the local-density approximation to exchange and correlation. It is well known that this leads to substantial errors in the conduction bands. Since we need correct values for the gaps and the effective masses we have adjusted the unoccupied states by adding sharply peaked external potentials on the nuclear sites—also on the "empty-sphere" positions.¹⁰ In this way selfconsistent band structures with correct gaps at Γ , L, and X were calculated; also, the masses agree well with experiments. Pressure calculations show that this semiempirical adjustment does not spoil the good predictions of the ground-state properties¹⁰ obtained in the conventional local-density–approximation scheme.

The splittings of the light- and heavy-hole bands $(\Delta E_{\rm lh}, \Delta E_{\rm hh})$ calculated for InP vs k along the [110]

direction near k = 0 are shown in Fig. 1. These splittings represent the difference between angular momentum "up" and "down" states with [110] as the quantization axis when the anion is placed at the origin and the cation at $\frac{1}{4}a(111)$. This convention determines uniquely the sign of C_k . The splittings $\Delta E_{\rm lh}$ and $\Delta E_{\rm hh}$ for k along [110] are given by^{1,2}

$$\Delta E_{\rm hh} = (3\sqrt{3}/2) C_k k, \quad \Delta E_{\rm lh} = (\sqrt{3}/2) C_k k, \quad (1)$$

provided that the difference in the quadratic (i.e., ef-



FIG. 1. Splittings calculated with the LMTO method for the heavy-hole and light-hole bands of InP (ΔE_{hh} and ΔE_{1h}) along the [110] direction. The straight lines represent the linear terms [Eq. (1)]. The sign of the splittings is defined as follows: a positive sign means that the $(\frac{3}{2}, \frac{3}{2})$ or $(\frac{3}{2}, \frac{1}{2})$ states, referred to the [110] quantization direction, have higher energy than $(\frac{3}{2}, -\frac{3}{2})$ or $(\frac{3}{2}, -\frac{1}{2})$, respectively.

fective mass) energies is larger than ΔE , a condition which is fulfilled in most of the region of Fig. 1. To the linear splitting we must add, as shown in Fig. 1, a term cubic in k (γk^3) which is discussed elsewhere.^{1,2,10,11} It leads to the reversal of the sign of $\Delta E_{\rm lh}$ with increasing k. In fact, we have determined the sign of C_k by comparison with that of γ which is easily obtained by perturbation theory (third order in $\mathbf{k} \cdot \mathbf{p}$) from the matrix elements of \mathbf{p} between the Γ_8 valence states and the Γ_1 and Γ_8 conduction states. It can also be obtained through diagonalization of a 14×14 matrix involving these states and the spinorbit-split partners of Γ_8 (i.e., Γ_7).¹² In the case of InP, terms involving the spin-orbit coupling between the Γ_8 conduction and valence bands play a decisive role in the determination of the sign of γ , which turns out to be negative in InP (but positive for GaAs, GaSb, and InSb).¹⁰ This fact, and the sign convention above, leads in view of the data of Fig. 1 for $\Delta E_{\rm lh}$, to a negative sign for C_k ($C_k = -14.4$ meV Å) for InP. In a similar manner we obtain $C_k = -3.56$ meV Å for GaAs, $C_k = 0.7 \pm 0.3$ meV Å for GaSb, and $C_k = -9.2$ meV Å for InSb. For these materials experimental data are only available for InSb³ ($C_k = 9.3$ meV Å).

TABLE I. Values of the energies (electronvolts) required for the calculation of C_k with Eq. (3) and the resulting values of C_k (in meV Å) together with experimental values of the magnitude of this parameter when available. The energy values are taken to be those for the elements from Ref. 18, unless specified. [In the column giving C_k (calc.) we have also listed LMTO values.]

					C_{k}	$ C_k $
Material	$\Delta_{d,c}$	$\Delta_{\textit{d,a}}$	$E(\Gamma_8) - E_{d,c}$	$E(\Gamma_8) - E_{d,a}$	(Calc.)	(Expt.)
AlAs	0	0.53		40.95ª	-2.0	
AlSb	0	1.25		32.2 ^b	-6.0	· · ·
GaP	0.36	0	18.7°		-5.5	
GaAs	0.36	0.53	18.85 ^d	40.8 ^e	$-3.4, -3.6^{\rm f}$	
GaSb	0.36	1.25	18.95 ^d	31.75 ^e	$+0.7, +0.7^{f}$	
InP	0.88	0	17.4 ^d		$-14.4, -14.4^{\rm f}$	
InAs	0.88	0.53	17.2 ^d	40.65 ^e	-11.2	
InSb	0.88	1.25	17.4 ^d	31.35 ^e	$-8.2, -9.2^{\rm f}$	9.3 ^g
ZnS	0.4 ^h	0	9.03°		-15.5	
ZnSe	0.4 ^h	0.83	9.2 ^{h,i}	53.35 ⁱ	-13.8	1 2 ^j
ZnTe	0.4 ^h	1.51	9.6 ^k	40.0 ^k	-11.2	< 10 ¹
CdTe	0.79 ^h	1.51	10.3 ^k	40.2 ^k	-23.4	20.6 ^m
HgSe	1.8	0.83	7.93 ^k	53.4 ^k	-80.2	
HgTe	1.85 ^k	1.51	8.3 ^k	39.7°	-74.6	
CuCl	0.34 ^h	0	1.8 ⁿ	• • •	-78	
CuBr	0.34 ^h	1.0	2.0 ⁿ	70	-70	73°, 50°
CuI	0.34 ^h	1.87 ^h	2.1 ⁿ	50	-66	
AgI	0.48 ^h	1.87 ^h	4 ⁿ	50	-48	

^aEstimated from the values of GaAs and InAs.

^bN. J. Shevchik, J. Tejeda, C. M. Penchina, and M. Cardona, Solid State Commun. 11, 1619 (1972). ^cL. Ley, R. A. Pollak, F. R. McFeeley, S. P. Kowalczyk, and D. A. Shirley, Phys. Rev. B 9, 600 (1974).

^dReference 17.

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^fDerived directly from the LMTO calculations.

⁸Landoldt-Börnstein Tables, edited by O. Madelung, M. Schultz, and H. Weiss (Springer, Berlin, 1982), Vol. 17a; also Ref. 3.

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^mReference 5.

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They agree rather well with our calculations.

We discuss now the origin of C_k . Three contribu-tions are proposed in the literature.^{1,2} The first one, C_a , is a first-order perturbation term produced by the **k**-dependent spin-orbit Hamiltonian $H_{so}(\mathbf{k})$ $= (4c^2)^{-2} (\nabla V \times \mathbf{k}) \cdot \boldsymbol{\sigma}$. This term has been estimated to be 50 meV Å for InSb.¹ We believe, however, that this estimate, based on the spin-orbit splitting of Γ_8 , is not correct. In fact, the spin-orbit splitting of Γ_8 is given by the $(4c^2)^{-1}(\nabla V \times \mathbf{p}) \cdot \boldsymbol{\sigma}$ part of the H_{so} Hamiltonian which diverges more rapidly near the atomic cores and thus has much larger matrix elements between Γ_8 states than $H_{so}(\mathbf{k})$, where **p** has been replaced by the constant k. We note that if nonrelativistic orbital functions are used, the matrix elements of $H(\mathbf{k})$ between Γ_8 states should be zero.¹³ The structure of $H(\mathbf{k})$ is the same as that of the Hamiltonians involved in deformation-potential calculations.¹⁴ It is known that relativistic effects do not significantly affect these calculations.¹⁵ A simple estimate of the matrix elements of $H(\mathbf{k})$ based on these considerations yields less than 10^{-2} meV Å.

The other two contributions to C_k are second-order terms involving matrix elements of **p** and H_{so} to Γ_{12} (*d* like) and Γ_{25} (*f* like) intermediate states. The former are expected to be larger than the latter. We suggest here that the main contribution to the former, and thus to C_k , is via the Γ_{12} components of the uppermost *d* core states of the two constituent atoms. By use of Eq. (57) of Ref. 2 it is easy to derive the contribution of the cation *d* levels to C_k ,

$$C_{k} = 4\sqrt{3}\Delta_{dc}S\beta/5[E(\Gamma_{8}) - E_{dc}], \qquad (2)$$

where $\Delta_{d,c}$ is the spin-orbit splitting of the core levels of the cation and $E_{d,c}$ their energy, β is the admixture coefficient of these levels in the valence band, and S the corresponding matrix element of p [defined as $\langle \Gamma_{15}^{x} | p_x | (x^2 - y^2) \rangle = -iS$]. With our sign convention we find from the LMTO calculations $\beta \approx -0.26$ and, from Cardona,¹⁶ $S \approx 0.13$ bohr⁻¹. Taking $E(\Gamma_8)$ $-E_{d,c} = 17.4 \text{ eV}^{17}$ and $\Delta_d = 0.88 \text{ eV}$,¹⁸ we find C_k = -11 meV Å, in satisfactory agreement with the LMTO calculation.

In view of this we propose for C_k the following expression, which also includes the smaller effect of the *d* core levels of the anion:

$$C_{k} = -A \frac{\Delta_{d,c}}{E(\Gamma_{8}) - E_{d,c}} + B \frac{\Delta_{d,a}}{E(\Gamma_{8}) - E_{d,a}}, \qquad (3)$$

where A and B are positive parameters which we take to be the same for all III-V compounds. Using the values of C_k calculated for InP and GaSb and those of Δ_d and E_d from Table I, we find A = 285 meV Å and B = 155 meV Å, and $C_k = -3.4$ for GaAs and -8.2 for InSb, in rather good agreement with those given above. We now extend Eq. (3) to the II-VI and I-VII compounds. For Ge, A should be equal to B and approximately equal to the average of their III-V counterparts: (255+155)/2=220 meV Å. Linear extrapolation of the values of A and B found for Ge and the III-V's leads for the II-VI's to A = 350 meV Å, B = 90 meV Å, and similarly, for the I-VII's, A = 415 meV Å, B = 25 meV Å.

With these values of A and B and those of Δ_d and $E(\Gamma_8) - E_{d,c}$ given in Table I we obtain the values of C_k listed in this table. In the cases where reliable experimental data are available (given also in Table I), such as for CuBr, CdTe, and ZnSe, the agreement between them and the calculated ones is excellent.

In conclusion, we have calculated C_k for a few III-V compounds. We have interpreted the mechanism responsible for C_k and we have given a scheme to estimate C_k for all zinc-blende-type semiconductors. In the few cases for which experimental data are available, they agree very well with our calculations.

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