

RELATIVISTIC CORRECTIONS TO THE BAND STRUCTURE
OF TETRAHEDRALLY BONDED SEMICONDUCTORS*

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(Received 13 November 1963)

Although our knowledge of spin-orbit splitting in the band structure of crystals is by now rather extensive,¹⁻⁴ the consequences of the closely related relativistic mass-velocity and Darwin (*s*-shift) corrections in this context have received scant attention.⁵ Since the direct solution of a relativistic crystal wave equation is a formidable undertaking, few attempts have been made in this direction. Recently, a perturbation treatment has been used to determine the relativistic corrections for PbTe.⁶ In this Letter, we shall attempt to estimate the magnitude of these corrections in a wide variety of crystals in a manner which avoids detailed crystal calculations. Our objective is to place the question of the importance of these corrections in specific applications on a semiquantitative basis.

By applying two successive canonical transformations of the Foldy-Wouthuysen (F-W) type,⁷ using the fine structure constant, α , as the expansion parameter (in contrast to F-W), the four-component Dirac Hamiltonian can be reduced to a four-component Hamiltonian in which positive and negative energy states are completely decoupled to order α^2 . This leads to the following two-component Hamiltonian for the positive-energy states:

$$H = -\nabla^2 + V(\vec{r}) - (\frac{1}{4}\alpha^2)\nabla^4 + (\frac{1}{8}\alpha^2)\nabla^2 V(\vec{r}) - i(\frac{1}{4}\alpha^2)\vec{\sigma} \cdot [\nabla V(\vec{r}) \times \nabla], \quad (1)$$

where energies are expressed in Rydbergs and distances in Bohr units, and where the electron rest energy, $2/\alpha^2$, has been dropped. The non-relativistic Hamiltonian H_0 is represented by the first and second terms, the relativistic mass-velocity correction by the third term, the relativistic Darwin correction by the fourth term, and the spin-orbit interaction by the final term. In a representation correct to order α^2 , the above mass-velocity term is equivalent to $-(\frac{1}{4}\alpha^2)[E_0 - V(\vec{r})]^2$, where E_0 is the nonrelativistic energy associated with H_0 , and the above Darwin term is equivalent to $-(\frac{1}{4}\alpha^2)\nabla V(\vec{r}) \cdot \nabla$.

In a book just published,⁸ relativistic and spin-orbit coupling corrections for free atoms obtained by a first-order perturbation treatment are reported. Starting with this information,

and applying three successive adjustments (*A, B, C*), we shall proceed to obtain estimates of these corrections for atoms embedded in crystals. The idea of estimating spin-orbit splittings in crystals from a knowledge of these splittings in the constituent free atoms was introduced by Kane.⁹ This procedure has proved quite successful.²⁻⁴ Our approach is an extension of this procedure which treats relativistic corrections on the same basis as spin-orbit splitting.

Adjustment *A* compensates for inadequacies in the perturbation treatment of the free atom corrections. Introducing an adjustment factor $A(Z)$ for each atom Z , we can establish its value for certain key atoms by comparing experimental¹⁰ and calculated⁸ spin-orbit splittings (Δ) for the outermost *p* orbitals in normal neutral atoms having the configurations $p^1 2P$ or $p^5 2P$ (atoms in columns IIIA and VIIA). Since these atoms have either one electron or one hole in the outermost *p* shell, the correspondence between experimental and calculated spin-orbit splittings is more clear-cut here than it is for atoms having more complicated configurations. We evaluate $A(Z)$ for these atoms from the definition: $A(Z) = \Delta_{\text{atom}}^{\text{exp}}(Z)/\Delta_{\text{atom}}^{\text{calc}}(Z)$. Using these values of $A(Z)$ as standards, we can obtain values of $A(Z)$ for neighboring atoms in the periodic table by linear interpolation or extrapolation. Since a study of relativistic and spin-orbit coupling corrections in the outermost orbitals of neutral and singly ionized atoms suggested that these corrections depend strongly on Z and only slightly on the state of ionization, we shall use only neutral atoms as our standards.

It is now assumed, admittedly arbitrarily, that the value of $A(Z)$ as determined above can be used to adjust all the relativistic and spin-orbit corrections (X) associated with the outermost *s* and *p* orbitals for atom Z on the same basis. By this we mean that any adjusted correction for atom Z is given by $X_{\text{atom}}^{\text{adj}}(Z) = A(Z)X_{\text{atom}}^{\text{calc}}(Z)$, where $X_{\text{atom}}^{\text{calc}}(Z)$ is taken from reference 8. The critical assumption here, of course, is that corrections for *s* and *p* orbitals actually scale in the same manner. [In passing, we note that the average devi-

ation of $A(Z)$ from unity for all the atoms considered was about 0.2.]

Let us now direct our attention to the important and particularly simple class of s -like conduction-band states and p -like valence-band states at $\vec{k} = [000]$ in diamond-type [$s: \Gamma_{2'}; p: \Gamma_{25'}$] and sphalerite-type [$s: \Gamma_1; p: \Gamma_{15}$] crystals. Since the crystal wave functions for these states re-

semble the corresponding ns or np atomic orbitals in the core regions (which provide the principal contributions to the spin-orbit and relativistic correction matrix elements), we can make the passage from free atoms to crystals by introducing two further adjustment factors, $B(Z)$ and C . Both of these factors account for wave-function renormalization effects.²⁻⁴ For

Table I. Relativistic and spin-orbit coupling corrections in electron volts. The following quantities include the adjustments A and B described in the text. The adjustment C is not included here. Δ_p and δE_p^{vel} are the spin-orbit splitting and mass-velocity correction for the outermost p orbital. δE_s^{vel} and δE_p^{Dar} are the mass-velocity and Darwin corrections for the outermost s orbital. $\delta E_s = \delta E_s^{\text{vel}} + \delta E_s^{\text{Dar}}$. $\delta E_p = \delta E_p^{\text{vel}} + \frac{1}{3}\Delta_p$.

Atom	Δ_p	δE_p^{vel}	δE_s^{vel}	δE_s^{Dar}	δE_s	δE_p
Li 3			-0.001	0.001	-0	
Be 4	0.0005	-0	-0.004	0.003	-0.001	0
B 5	0.0020	-0.001	-0.015	0.010	-0.005	0
C 6	0.0059	-0.003	-0.038	0.025	-0.013	-0.001
N 7	0.0136	-0.007	-0.081	0.053	-0.028	-0.002
O 8	0.0274	-0.014	-0.153	0.100	-0.053	-0.005
F 9	0.0501	-0.025	-0.268	0.174	-0.094	-0.008
Ne 10	0.0851	-0.043	-0.440	0.285	-0.155	-0.015
Na 11			-0.036	0.022	-0.014	
Mg 12	0.0072	-0.004	-0.090	0.056	-0.034	-0.002
Al 13	0.0217	-0.013	-0.188	0.118	-0.070	-0.006
Si 14	0.0441	-0.027	-0.316	0.197	-0.119	-0.012
P 15	0.0753	-0.047	-0.484	0.307	-0.177	-0.022
S 16	0.1162	-0.074	-0.702	0.419	-0.283	-0.036
Cl 17	0.1704	-0.111	-0.978	0.511	-0.467	-0.054
Ar 18	0.2392	-0.157	-1.321	0.812	-0.509	-0.077
Cu 29			-0.695	0.416	-0.279	
Zn 30	0.074	-0.054	-1.061	0.609	-0.452	-0.029
Ga 31	0.171	-0.127	-1.640	0.978	-0.662	-0.070
Ge 32	0.290	-0.216	-2.241	1.283	-0.958	-0.119
As 33	0.426	-0.319	-2.923	1.737	-1.186	-0.177
Se 34	0.582	-0.438	-3.705	2.198	-1.507	-0.244
Br 35	0.763	-0.578	-4.596	2.623	-1.973	-0.324
Kr 36	0.9708	-0.739	-5.615	3.198	-2.417	-0.415
Ag 47			-1.954	1.140	-0.814	
Cd 48	0.227	-0.183	-2.787	1.624	-1.163	-0.107
In 49	0.458	-0.371	-3.997	2.327	-1.670	-0.218
Sn 50	0.709	-0.577	-5.149	2.993	-2.156	-0.341
Sb 51	0.973	-0.795	-6.381	3.568	-2.813	-0.471
Te 52	1.260	-1.033	-7.728	4.325	-3.403	-0.613
I 53	1.576	-1.296	-9.208	5.340	-3.868	-0.771
Xe 54	1.922	-1.587	-10.837	6.278	-4.559	-0.946
Au 79			-7.662	4.199	-3.463	
Hg 80	0.860	-0.750	-10.27	5.623	-4.642	-0.463
Tl 81	1.614	-1.411	-13.95	7.639	-6.315	-0.873
Pb 82	2.377	-2.083	-17.26	9.443	-7.814	-1.291
Bi 83	3.131	-2.750	-20.61	11.27	-9.334	-1.706
Po 84	3.908	-3.438	-24.12	13.22	-10.90	-2.135
At 85	4.725	-4.165	-27.84	15.25	-12.59	-2.590
Rn 86	5.588	-4.935	-31.79	17.37	-14.42	-3.072

convenience, we assume that $B(Z)$ is the same for all atoms in a given row of the periodic table, that C is the same for all atoms in a given column, and that C varies linearly across the periodic table. In effect, the C factor weighs the contri-

butions of different core regions in crystals containing more than one atomic species in the unit cell, while the B factor provides the average re-normalization over the unit cell.

With this in mind, we define $B(Z)$ as follows:

Table II. Estimated spin-orbit splittings (Δ_p^{est}) and net relativistic and spin-orbit coupling corrections for s -like conduction-band edges (δE_s^{est}) and p -like valence-band edges (δE_p^{est}) at $\vec{k} = [000]$ in diamond- and sphalerite-type crystals. Δ_p^{est} is compared with experimental values of the spin-orbit splitting of the p -like valence-band state at $\vec{k} = [000]$, Δ_0^{exp} , and with $\frac{3}{2}\Delta_1^{\text{exp}}$, where Δ_1^{exp} is the observed splitting of the p -like valence-band state at $\vec{k} = (\pi/a)[111]$. According to present theories, $\frac{1}{2}\Delta_1^{\text{exp}}$ should be approximately equal to Δ_0^{exp} , which is the direct experimental counterpart of Δ_p^{est} . Where not otherwise indicated, the experimental error is probably better than $\pm 10\%$; \sim denotes somewhat higher uncertainty. Averages were taken in cases where several independent results are available. Where the interpretation of the experimental data is doubtful, no experimental values are quoted. The experimental data for the III-V and II-VI compounds are contained in references 2, 3, and 4. All entries below are in electron volts.

Crystal	Δ_0^{exp}	$\frac{3}{2}\Delta_1^{\text{exp}}$	Δ_p^{est}	δE_s^{est}	δE_p^{est}
C	0.006 ± 0.001^a		0.006	-0.013	-0.001
Si	0.0441 ± 0.0004^b		0.044	-0.12	-0.013
Ge	0.290 ± 0.005^c	0.29 ± 0.02^d	0.290	-0.96	-0.12
α Sn		0.71 ± 0.05^e	0.71	-2.16	-0.34
BN			0.010	-0.046	-0.002
BP			0.051	-0.095	-0.015
BA _s			0.285	-0.43	-0.12
BS _b			0.65	-0.97	-0.31
AlN			0.016	-0.056	-0.003
AlP			0.057	-0.11	-0.017
AlAs			0.29	-0.44	-0.12
AlSb	~ 0.75	0.60	0.66	-0.98	-0.32
GaN			0.065	-0.45	-0.025
GaP	0.13		0.11	-0.50	-0.038
GaAs	0.34	0.35	0.34	-0.84	-0.14
GaSb		0.70	0.71	-1.38	-0.34
InN			0.16	-1.12	-0.074
InP		~ 0.21	0.20	-1.17	-0.088
InAs	0.43	0.40	0.44	-1.51	-0.19
InSb		0.81	0.80	-2.05	-0.39
ZnS			0.11	-0.42	-0.035
ZnSe	0.44	0.53	0.50	-0.63	-0.21
ZnTe		0.86	1.06	-0.94	-0.52
CdS			0.135	-1.02	-0.048
CdSe	0.43	0.42	0.52	-1.22	-0.22
CdTe		0.86	1.09	-1.54	-0.53
HgS			0.24	-3.91	-0.11
HgSe		~ 0.47	0.63	-4.12	-0.28
HgTe		0.98	1.19	-4.43	-0.56
CuCl			0.17	-0.28	-0.054
CuBr			0.76	-0.28	-0.33
CuI			1.58	-0.28	-0.77
AgI			1.58	-0.81	-0.77

^aC. J. Rauch, Proceedings of the International Conference on the Physics of Semiconductors, Exeter, July 1962 (The Institute of Physics and The Physical Society, London, 1962), p. 276.

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^cM. V. Hobden, J. Phys. Chem. Solids **23**, 821 (1962).

^dF. Lukeš and E. Schmidt, reference 4.

^eM. Cardona and D. L. Greenaway, reference 2.

$$B(Z) = X_{\text{crystal}}^{\text{tent}}(Z) / X_{\text{atom}}^{\text{adj}}(Z),$$

where the numerator is a tentative estimate of quantity X for atom Z embedded in a crystal, and the denominator is the adjusted value of X for atom Z as given by adjustment A . We shall establish our B scale by matching experimental spin-orbit splittings for the $\Gamma_{25'}$ state in diamond-type crystals with the adjusted spin-orbit splittings for the corresponding free atom orbitals. This matching procedure yields $B(6) = 1.00$ (diamond); $B(14) = 1.56$ (silicon); $B(32) = 1.67$ (germanium); and $B(50) = 1.67$ (grey tin). In accordance with our model, we set $B(Z) = 1.00$ for all row 2 atoms, $B(Z) = 1.56$ for all row 3 atoms, and $B(Z) = 1.67$ for all row 4 and 5 atoms. In the absence of a suitable experimental guidepost, we arbitrarily set $B(Z) = 1.67$ for all row 6 atoms as well.

Table I summarizes the essential results we obtain after applying the A and B (but not the C) adjustments to all the atoms encompassed in our study. δE_s is the net shift of the s -like conduction-band edge, and δE_p is the net shift of the p -like valence-band edge, i. e., the upper member of the spin-orbit split p -like valence-band state. Although Table I is intended for use primarily in the study of diamond- and sphalerite-type crystals, it can probably be applied without serious modification to other tetrahedrally bonded semiconductors (wurtzite, chalcopyrite, etc.), where the renormalization problem is analogous. In order to apply Table I to other types of crystals, it would be necessary to re-examine the renormalization problem, and to change the B scale accordingly.

Returning to the diamond- and sphalerite-type crystals, our model yields the following C factors for the s -like conduction-band state: IV-IV compound: $C = 1/2$; III-V compound: $C(\text{III}) = 2/3$, $C(\text{V}) = 1/3$; II-VI compound: $C(\text{II}) = 5/6$, $C(\text{VI}) = 1/6$; I-VII compound: $C(\text{I}) = 1$, $C(\text{VII}) = 0$. For the p -like valence-band state, we have, similarly, $C(\text{IV}) = 1/2$; $C(\text{III}) = 1/3$, $C(\text{V}) = 2/3$; $C(\text{II}) = 1/6$, $C(\text{VI}) = 5/6$; $C(\text{I}) = 0$, $C(\text{VII}) = 1$. The total correction for the quantity X for the III-V compound Z_1Z_2 , for example, is given by: $X(Z_1Z_2) = X(Z_1) \times C(\text{III}) + X(Z_2)C(\text{V})$, where $X(Z_1)$ and $X(Z_2)$ are given in Table I. A diamond-type crystal would be treated here as the IV-IV compound Z_1Z_1 .

Our final estimates (including the C factor) for the relativistic and spin-orbit corrections are presented in Table II. Our estimates for

the spin-orbit splittings are in somewhat better agreement with experimental values than are similar estimates previously given.²⁻⁴ The estimates given in Table II for the relativistic corrections represent the principal original contribution of the present work.

According to Table II, for example, the net relativistic and spin-orbit correction for the $\vec{k} = [000]$ gap in germanium is $-0.96 + 0.12 = -0.84$ eV, which is to be compared with the observed gap (0.80 eV), the observed spin-orbit splitting of $\Gamma_{25'}$ (0.29 eV), and the observed conduction-band edge separations $\Delta_1 - \Gamma_{2'}$ (0.85 - 0.80 = 0.05 eV) and $\Gamma_{2'} - L_1$ (0.80 - 0.66 = 0.14 eV). (All values quoted refer to 300°K.¹¹)

Since the magnitude of the relativistic and spin-orbit corrections is strongly dependent on the atomic orbital character of crystal wave functions in the ion core regions,¹² these corrections can be expected to vary considerably from band to band at a given \vec{k} , and from point to point in the reduced zone for a given band. If sufficiently large, these corrections can affect the detailed form of the band structure appreciably. In the case of germanium, we may conclude, on the basis of our estimates, that the band structure in the important region bordering the forbidden band will be significantly affected by relativistic effects. It is unlikely that a nonrelativistic energy-band calculation for such a crystal can correctly predict the order of the various conduction-band minima, let alone the width of the forbidden band at any value of \vec{k} . A nonrelativistic calculation for germanium would have to yield a $\vec{k} = [000]$ forbidden gap of 1.64 eV if the net correction of -0.84 eV is to reduce this to the observed value of 0.80 eV. In crystals such as grey tin,¹³ the relativistic corrections become so large (see Table II) that the relativistic band structure would bear slight resemblance to its nonrelativistic counterpart. The situation in other crystals can be ascertained with the aid of Tables I and II.

*Work supported in part by the U. S. Office of Naval Research, and in part by the Lockheed Independent Research Fund.

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tions (with free electron exchange) for all normal neutral atoms in the periodic table from He through Lw. Relativistic and spin-orbit coupling corrections are presented for all even-Z atoms in this range. In subsequent work [F. Herman (unpublished)], these corrections were also obtained for many odd-Z atoms. In Table I of the present work, results given for the np orbital for column II atoms refer to an excited p orbital; all other results refer to occupied orbitals.

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ELECTRONIC PARAMAGNETIC RELAXATION TIMES OF METAL-AMMONIA SOLUTIONS*

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(Received 18 October 1963)

Electronic paramagnetic relaxation times of potassium-ammonia solutions have been measured over a range of concentrations and temperatures both by the continuous-wave saturation method¹ and by the use of pulsed radiofrequency fields.² Hutchison and O'Reilly¹ found that the spin-lattice (T_1) and spin-spin (T_2) relaxation times were equal for concentrated K solutions ($>0.2M$ at $25^\circ C$) but that T_1 is as long as two times T_2 in more dilute solutions. Pollak reported from pulse measurements that T_1 and T_2 are equal over the entire range of concentration (0.004 to 0.8 mole liter⁻¹) and temperature ($+30^\circ C$ to $-50^\circ C$) studied. T_2 values measured by Pollak are in good agreement with those measured by the cw method. It is the purpose of this note to point out that the above results are consistent with one another and are a consequence of the nature of the relaxation mechanism^{2,3} of the unpaired electrons. This mechanism has been proposed^{2,3} to proceed via the hyperfine interactions between the unpaired electrons and nitrogen-14 nuclei of the ammonia molecules.

Let us assume, for the moment, that both the nuclear and the electronic relaxation proceed via an isotropic hyperfine interaction and denote the total nuclear (N^{14}) spin by \vec{I} , total unpaired electron spin by \vec{S} , nuclear relaxation times by T_{1n} and T_{2n} , and electronic relaxation times by T_{1e} and T_{2e} . The equations of motion of the various components of spin are as follows:

$$\frac{d\langle S_z \rangle}{dt} = \frac{-1}{T_{1e}} (\langle S_z \rangle - S_0) + \frac{1}{T_{1n}} (\langle I_z \rangle - I_0), \quad (1)$$

$$\frac{d\langle I_z \rangle}{dt} = \frac{-1}{T_{1n}} (\langle I_z \rangle - I_0) + \frac{1}{T_{1e}} (\langle S_z \rangle - S_0), \quad (2)$$

$$d\langle S_\mu \rangle / dt = (-1/T_{2e}) \langle S_\mu \rangle, \quad (3)$$

$$d\langle I_\mu \rangle / dt = (-1/T_{2n}) \langle I_\mu \rangle; \quad (4)$$

where $\mu = x$ or y , $\langle \rangle$ means the canonical ensemble average, and S_0 and I_0 are the thermal equilibrium values of $\langle S_z \rangle$ and $\langle I_z \rangle$, respectively. Equations