PHYSICAL REVIEW VOLUME 137, NUMBER 4A 15 FEBRUARY 1965

Energy Bands in PbTe*

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(Received 11 August 1964)

The augmented-plane-wave method for calculating the band structure of a solid has been extended to include the relativistic terms of the two-component Hamiltonian which is obtained by two successive applications of the Foldy-Wouthuysen transformation to the Dirac Hamiltonian. Basis functions for the secular equation which are basis partners for the irreducible representations of the double group are constructed from the eigenfunctions of the nonrelativistic Hamiltonian. Expressions for the relativisitic matrix elements between these basis functions are found and numerically evaluated, and the resulting Hamiltonian matrix is diagonalized to give the energy levels for PbTe. The calculated bands, with only slight modification, appear to be consistent with available experimental information.

INTRODUCTION

THE large amount of experimental investigation of PbTe which has been done in the past few years[1–4] has brought to light many interesting properties of the material but has not led to a well-defined band structure which explains all the measured properties. For this reason, it was felt that a band-structure calculation done from first principles would be of value in understanding PbTe. Despite the lack of self-consistency, the resulting band structure should provide a basis for interpretation of the experimental data. The experimental data can then be used to suggest modifications of the calculated energies, to give a better picture of the actual band structure of the material. This approach has been used to obtain the band structure for PbTe which is reported here.

The calculation is based on the one-electron approximation for a solid and is done by means of the augmented-plane-wave (APW) method of Slater and his associates.[5–9] Because of the importance of relativistic corrections to the energies of PbTe and other heavy materials,[10,11] the Hamiltonian used for this calculation is not the nonrelativistic Hamiltonian which has been previously used for band calculations. It is rather the two-component relativistic Hamiltonian,[12–14]

$$\mathcal{H}=\frac{p^2}{2m}+V+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot[(\nabla V)\times\mathbf{p}]+\frac{\hbar^2}{8m^2c^2}(\nabla^2 V)-\frac{1}{8m^3c^2}p^4, \quad (1)$$

which is obtained from the Dirac Hamiltonian by two successive applications of the Foldy-Wouthuysen transformation. The third term of this Hamiltonian is the familiar spin-orbit term, which may split degenerate levels and cause mixing of levels, thus altering the band picture. The fourth and fifth terms (the Darwin and mass-velocity corrections, respectively) are invariant under the operations of the single group and therefore do not split levels. However, these terms may mix levels of the same single-group symmetry, and they may shift levels appreciably. Because the effects of all three of the relativistic terms are strongly dependent on the angular-momentum character of the wave functions, which varies from band to band and, for each band, from point to point in **k** space, these terms affect both the relative spacing of the bands and their shape.

In order to include the relativistic terms in the energy-band calculation for PbTe, it is necessary to extend the formalism of the APW method to include the spin dependence of the wave functions, and to calculate the matrix elements of the relativistic terms between the spinor wave functions. Because the nonrelativistic

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* Research supported by the U. S. Army Research Office and the U. S. Office of Naval Research.

† Based in part on this author's thesis submitted to the Department of Electrical Engineering, Massachusetts Institute of Technology, in partial fulfillment of the requirements for the degree of Doctor of Science, June, 1964.

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terms make the largest contribution to the energy, the following procedure is used: First, the eigenfunctions $\Phi_i^{\alpha n}(\mathbf{k};\mathbf{r})$ and the eigenvalues $E_n^0(\mathbf{k})$ of the nonrelativistic Hamiltonian

$$\mathcal{H}_0=(p^2/2m)+V \tag{2}$$

are found by the APW method described in the references.[5–9] Spinor basis partners for the irreducible "double-valued" representations of the double group of the $\mathbf{k}$ vector are formed by taking appropriate linear combinations of the products $\Phi_i^{\alpha n}\alpha$ and $\Phi_i^{\alpha n}\beta$, α and β being the pure spin functions. The matrix elements of the relativistic Hamiltonian [Eq. (1)] between these spinor functions are determined, and the resulting Hamiltonian matrix is diagonalized to give the relativistic energies and eigenfunctions.[15]

The calculated band structure is compared with experimental data about the PbTe band structure and revised slightly to improve its agreement with several experimentally determined features. The resulting band structure is examined with reference to other experimental information about PbTe.

EXTENSION OF THE APW METHOD

Nonrelativistic APW Functions

In the present APW method for solving the Schrödinger equation for a crystalline solid, the potential of an electron in the crystal is approximated in the following way: Within a spherical shell (the "APW sphere") about each nucleus, the potential is approximated by its spherical average (as in an atomic calculation), giving the Hamiltonian spherical symmetry within each of these APW spheres. Outside the spheres, the potential is approximated by a constant value, taken for this calculation to be the average of the crystal potential over the region outside the spheres. For this calculation, the radii of the Pb and Te spheres are determined by the requirement that the lead spheres touch the tellurium spheres without overlapping and that the spherically averaged potential within the Pb sphere, evaluated at the surface of the Pb sphere, equal the spherically averaged potential within the Te sphere, evaluated at the surface of the Te sphere. (The latter condition is only approximately fulfilled because of small modifications to the potential, made after the work began, which did not warrant modification of the sphere radii.) The potential used for this calculation is listed in compressed form in Table I, and other constants entering the calculation are given in Table II.

TABLE I. The spherically symmetric approximate PbTe crystal potential in rydbergs, multiplied by the radius in atomic units, is listed for a radial mesh twice as large as that used in the calculation. The values listed for radii greater than the appropriate sphere radii (see Table II) are used in the determination of the constant value of the approximate potential in the region outside the spheres (discussed in "Calculated Energies"). This value is given in Table II.

r	$-rV_{\rm Pb}(r)$	$-rV_{\rm Te}(r)$	r	$-rV_{\rm Pb}(r)$	$-rV_{\rm Te}(r)$
0.0012	162.40	103.14	0.4104	38.415	30.268
0.0024	161.26	102.56	0.4488	35.062	28.038
0.0036	160.11	101.97	0.4872	32.150	26.064
0.0048	158.98	101.38	0.5256	29.601	24.310
0.0060	157.85	100.79	0.5640	27.352	22.736
0.0072	156.74	100.21	0.6024	25.359	21.304
0.0084	155.64	99.625	0.6408	23.141	19.989
0.0096	154.56	99.048	0.6792	21.696	18.775
0.0108	153.49	98.475	0.7176	20.312	17.657
0.0120	152.44	97.908	0.7560	19.062	16.389
0.0144	150.38	96.791	0.8328	16.881	14.576
0.0168	148.39	95.699	0.9096	15.036	13.049
0.0192	146.44	94.630	0.9864	13.459	11.749
0.0216	144.22	93.586	1.0632	12.106	10.637
0.0240	142.36	92.211	1.1400	10.942	9.6796
0.0264	140.60	91.317	1.2168	9.9387	8.8530
0.0288	138.89	90.349	1.2936	8.8149	8.1376
0.0312	137.22	89.398	1.3704	8.1678	7.5180
0.0336	135.60	88.469	1.4472	7.5281	6.9783
0.0360	134.02	87.560	1.5240	6.9682	6.3928
0.0408	130.95	85.805	1.6008	6.4768	6.0168
0.0456	128.01	84.127	1.6776	6.0450	5.6718
0.0504	125.19	82.518	1.7544	5.6647	5.3664
0.0552	122.47	80.972	1.8312	5.3294	5.0940
0.0600	119.88	79.482	1.9080	5.0333	4.8494
0.0648	116.82	78.041	1.9848	4.7713	4.6285
0.0696	114.40	76.675	2.0616	4.5391	4.4282
0.0744	112.07	75.027	2.1384	4.3329	4.2462
0.0792	109.82	73.666	2.2152	4.1494	4.0806
0.0840	107.65	72.403	2.2920	3.9861	3.9300
0.0936	103.53	69.982	2.3688	3.8406	3.7934
0.1032	99.681	67.694	2.4456	3.7112	3.6700
0.1128	96.070	65.526	2.5224	3.5966	3.5592
0.1224	92.670	63.471	2.5992	3.4438	3.4607
0.1320	89.458	61.521	2.6760	3.3817	3.3743
0.1416	86.193	59.671	2.7528	3.3047	3.2997
0.1512	82.933	57.916	2.8296	3.2471	3.2373
0.1608	80.222	56.245	2.9064	3.2019	3.1869
0.1704	77.636	54.270	2.9832	3.1692	3.1478
0.1800	75.168	52.806	3.0600	3.1495	3.1133
0.1992	70.557	50.040	3.1368	3.1429	3.1120
0.2184	66.337	47.512	3.2136	3.1499	3.1203
0.2376	62.474	45.192	3.2904	3.1711	3.1433
0.2568	58.937	43.056	3.3672	3.2066	3.1810
0.2760	55.688	41.085	3.4440	3.2572	3.2336
0.2952	52.689	39.260	3.5208	3.3227	3.3017
0.3144	49.384	37.564	3.5976	3.4038	3.3855
0.3336	46.828	35.983	3.6744	3.5004	3.4856
0.3528	44.481	34.415	3.7512	3.6129	3.6022
0.3720	42.305	32.786	3.8280	3.7414	3.7362

Because of this choice of approximate potential, it is convenient to expand the eigenfunction with energy E in a linear combination of "raw APW functions," $\Phi(\mathbf{k};\mathbf{r})$, having the following properties: Outside the spheres, $\Phi(\mathbf{k};\mathbf{r})$ is a plane wave, $e^{i\mathbf{k}\cdot\mathbf{r}}$. Within the spheres $\Phi(\mathbf{k};\mathbf{r})$ is a linear combination of eigenfunctions with energy E of the spherically symmetric Hamiltonian, so chosen that $\Phi(\mathbf{k};\mathbf{r})$ is continuous across the APW spheres. These conditions require that the raw

TABLE II. Various constants used in the APW calculation for PbTe. All quantities are given in atomic units.

Lattice parameter a	=	12.1926
Pb sphere radius	=	3.1005
Te sphere radius	=	2.9958
Potential outside spheres	=	−0.80138

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[15] It would, of course, be possible to include the relativistic terms directly in the original secular equation, rather than solving two secular equations (one for the eigenfunctions of $\mathcal{H}_0$, and then one for the eigenfunctions of $\mathcal{H}$) as we have done. Programming considerations made the approach which was followed somewhat more appealing. However, it is perhaps slightly less accurate because the set of basis functions for the second secular equation is necessarily limited.

APW functions have the form

$$\Phi(\mathbf{k};\mathbf{r})=\delta e^{i\mathbf{k}\cdot\mathbf{r}}+\rho e^{i\mathbf{k}\cdot\mathbf{r}_p}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}4\pi i^l j_l(|\mathbf{k}|R_p)\times\frac{u_{plE}(r')}{u_{plE}(R_p)}[Y_l^m(\theta_{\mathbf{k}},\phi_{\mathbf{k}})]^*Y_l^m(\theta',\phi'),\qquad(3)$$

where $\delta=1$ outside the spheres and zero within the spheres, and $\rho=1$ within the spheres and zero outside them. The vector $\mathbf{r}_p$ is the vector from the origin of coordinates to the nucleus at the center of the APW sphere within which $\mathbf{r}$ terminates (the pth sphere). (Note that p and $\mathbf{r}_p$ depend on $\mathbf{r}$.) The vector from this nucleus to the point $\mathbf{r}$ is $\mathbf{r}'$, and it has length r' and angular coordinates θ' and ϕ'. R_p is the radius of the pth sphere, and j_l is the spherical Bessel function,

$$j_l(y)=(\pi/2y)^{1/2}J_{l+1/2}(y).\qquad(4)$$

The Y_l^m are the spherical harmonics,[16] with the phase conventions of Condon and Shortley,[16,17] so that they are properly related by the stepup and stepdown angular momentum operators. (The spherical harmonics are used for the sake of convenience in evaluating the spin-orbit matrix elements, but the raw APW function defined here is the same as that of Slater[5] and Wood.[6,7]) The radial functions u_{plE} are defined by the equation (in atomic units—see the discussion of the matrix elements of the relativistic terms)

$$\left[-\frac{d^2}{dr'^2}+V_p(r')+\frac{l(l+1)}{r'^2}\right]r'u_{plE}(r')=Er'u_{plE}(r'),\qquad(5)$$

where V_p is the approximate potential appropriate to the pth sphere. The angles $\theta_{\mathbf{k}}$ and $\phi_{\mathbf{k}}$ are the angular coordinates of the vector $\mathbf{k}$.

In order to take advantage of the rotational symmetry of the lattice, symmetrized APW functions, $\Phi_{i,(j)}{}^a$, are constructed from the raw APW functions, according to the formula[18]

$$\Phi_{i,(j)}{}^a(\mathbf{k};\mathbf{r})=\textstyle\sum_R\Gamma_a(R)_{i,j}{}^*[R\Phi](\mathbf{k};\mathbf{r}),\qquad(6)$$

where $\Gamma_a(R)_{i,j}{}^*$ is the complex conjugate of the i,j matrix element of irreducible representation a of the (single) group of the (reduced) $\mathbf{k}$ vector. R is one of the unitary operations of the group of the $\mathbf{k}$ vector, and the summation includes all such operations. The effect of R on a function is as defined by Wigner[19] and may be written symbolically

$$[Rf](\mathbf{r})=f(R^{-1}\mathbf{r}),\quad\text{or}\quad[Rf](R\mathbf{r})=f(r).\qquad(7)$$

Wood[7] has shown that the function $\Phi_{i,(j)}{}^a$ transforms as the ith basis partner of the representation a, so that standard group theoretical techniques may be used to reduce the nonrelativistic secular equation between these functions.[7] The raw APW functions and the symmetrized APW functions satisfy the Bloch condition,

$$\Phi_{i,(j)}{}^a(\mathbf{k};\mathbf{r}+\mathbf{T})=e^{i\mathbf{k}_0\cdot\mathbf{T}}\Phi_{i,(j)}{}^a(\mathbf{k};\mathbf{r}),\qquad(8)$$

where $\mathbf{k}_0$ is the reduced wave vector corresponding to $\mathbf{k}$, and $\mathbf{T}$ is a lattice translation vector. Thus, only APW functions corresponding to $\mathbf{k}=\mathbf{k}_0+\mathbf{K}$, where $\mathbf{K}$ is a translation vector of the reciprocal lattice, appear in the expansion for eigenfunctions with reduced wave vector $\mathbf{k}_0$.

It can be shown that, if R is any operation of the crystal point group,

$$[R\Phi](\mathbf{k};\mathbf{r})\equiv\Phi(\mathbf{k};R^{-1}\mathbf{r})=\Phi(R\mathbf{k};\mathbf{r}).\qquad(9)$$

The symmetrized APW function may thus be written [with the use of Eq. (3)]

$$\Phi_{i,(j)}{}^a(\mathbf{k};\mathbf{r})=\delta\textstyle\sum_R\Gamma_a(R)_{i,j}{}^*e^{i(R\mathbf{k})\cdot\mathbf{r}}+\rho\displaystyle\sum_{l=0}^{\infty}\sum_{m=-l}^{l}4\pi i^l j_l(|\mathbf{k}|R_p)\times(u_{plE}(r')/u_{plE}(R_p))Y_l^m(\theta',\phi')\textstyle\sum_R e^{i(R\mathbf{k})\cdot\mathbf{r}_p}\Gamma_a(R)_{i,j}{}^*[Y_l^m(\theta_{R\mathbf{k}},\phi_{R\mathbf{k}})]^*.\qquad(10)$$

The techniques for solving the nonrelativistic Schrödinger equation by means of a secular equation in these symmetrized APW functions have been discussed in the references[5–9] and are not repeated here. The results of such a calculation are the energies, $E_n{}^0(\mathbf{k})$, for the various bands, and the eigenfunctions of the nonrelativistic Hamiltonian, expressed as a linear combination of symmetrized APW functions,

$$\Phi_i{}^{an}(\mathbf{k}_0;\mathbf{r})=\textstyle\sum_{\mathbf{k},j}C_{\mathbf{k},j}(n)\Phi_{i,(j)}{}^a(\mathbf{k};\mathbf{r}),\qquad(11)$$

where the summation includes only $\mathbf{k}$ which differ from $\mathbf{k}_0$ by reciprocal lattice translation vectors, $\mathbf{K}$. It can also be shown that the set of symmetrized APW functions corresponding to $R\mathbf{k}$, where R is an operation of the group of the (reduced) $\mathbf{k}$ vector, is linearly related to the set corresponding to $\mathbf{k}$; hence, the summation also need include only one vector $\mathbf{k}$ from each set of vectors related by the operations of the group of the $\mathbf{k}$ vector.

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[16] See Ref. 12, Vol. 1, Appendix B, Sec. 10.

[17] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1951), Chap. III, Sec. 4.

[18] Note that both the raw APW functions and the symmetrized APW functions should carry an energy index. This is omitted only to ease notational difficulties.

[19] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, translated from the German by J. J. Griffin (Academic Press Inc., New York, 1959), Chap. 11.

Spin-Dependent Basis Functions for the Relativistic Problem

The eigenfunctions $\Phi_i^{an}(\mathbf{k}_0;\mathbf{r})$ of the nonrelativistic Hamiltonian are basis partners for the irreducible representation a of the single group of the $\mathbf{k}$ vector. Therefore the set of functions $\Phi_i^{an}(\mathbf{k}_0;\mathbf{r})\alpha$ and $\Phi_i^{an}(\mathbf{k}_0;\mathbf{r})\beta$, including all basis partners of representation a, is a basis set for that representation of the double group of the $\mathbf{k}$ vector which is the direct product of the representation a with the representation $D_{1/2}$ (for which the pure spin functions α and β form a basis set). If this product representation is not irreducible, it may be reduced to a direct sum of irreducible representations by a suitable unitary transformation.[20,21] The basis partners for these irreducible representations are the spinor basis functions for the relativistic problem. They are linear combinations of the functions $\Phi_i^{an}\alpha$ and $\Phi_i^{an}\beta$, the coefficients being the matrix elements of the unitary transformation matrix which reduces the product representation.[21]

In order to more conveniently use the spinor basis functions, it is helpful to express them in terms of normalized eigenfunctions, $(N_{an})^{-1}\Phi_i^{an}$, of the nonrelativistic Hamiltonian, where

$$N_{an}=\left[\int(\Phi_i^{an})^*\Phi_i^{an}dv\right]^{1/2}. \tag{12}$$

(The integral is independent of the partner index.[22]) The basis partners for the irreducible representations (the spinor basis functions for the relativistic problem), are then (with s as the partner index)

$$\begin{aligned}\psi_s^{d;\,an}(\mathbf{k}_0;\mathbf{r})&=\textstyle\sum_i U_{si}^{da}[(N_{an})^{-1}\Phi_i^{an}(\mathbf{k}_0;\mathbf{r})\alpha]\\&\quad+\textstyle\sum_i D_{si}^{da}[(N_{an})^{-1}\Phi_i^{an}(\mathbf{k}_0;\mathbf{r})\beta]\\&=\alpha\psi_s^{d;\,an+}+\beta\psi_s^{d;\,an-},\end{aligned} \tag{13}$$

where the summations include all basis partners of the single-group representation a from which the "double-valued" representation d arises. (Note that there are no summations over single-group representations or bands; each spinor function, $\psi_s^{d;\,an}$, contains eigenfunctions of the nonrelativistic Hamiltonian corresponding to only one single-group representation and only one nonrelativistic energy level. The index n cannot be used to label the energy levels of the relativistic problem, however, because more than one "double-valued" representation d may arise from a single, degenerate, nonrelativistic band, and these will be split by the spin-orbit term.) The coefficients U_{si}^{da} and D_{si}^{da} are determined entirely by the group-theoretical relationships between the "double-valued" representation d and the single-group representation a, and are thus independent of the nonrelativistic band index, n. If the spinor function is normalized, the coefficients must satisfy the relation

$$\textstyle\sum_i[|U_{si}^{da}|^2+|D_{si}^{da}|^2]=1 \tag{14}$$

because of the orthogonality and normalization of the functions involved.

Koster *et al.*[21] have calculated the matrix elements of the unitary transformation matrices which reduce direct products of the $D_{1/2}$ representation with the single-group representations (or, equivalently, the "single-valued" representations of the double group) to direct sums of the irreducible representations of the double group. By relating their "single-valued" representations to those used in the nonrelativistic APW programs and expressing their spin functions in terms of spin functions quantized along the APW z axis, it is possible to use the results of Koster *et al.* to determine the coefficients U_{si}^{da} and D_{si}^{da}.

Group Theoretical Relationships

The relativistic Hamiltonian may be written

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_R+\mathcal{H}_{S-O}, \tag{15}$$

where $\mathcal{H}_0$ is the nonrelativistic Hamiltonian, $\mathcal{H}_R$ is the spin-independent part (the mass-velocity and Darwin terms) of the relativistic corrections, and $\mathcal{H}_{S-O}$ is the spin-orbit term. Because the total Hamiltonian and each of its parts are invariant under the operations of the double group, the selection rule[22]

$$\langle\psi_s^{d;\,an}|\mathcal{H}'|\psi_t^{f;\,bn'}\rangle=\langle\psi_u^{d;\,an}|\mathcal{H}'|\psi_u^{d;\,bn'}\rangle\delta_{df}\delta_{st} \tag{16}$$

holds for $\mathcal{H}'=\mathcal{H}$, $\mathcal{H}_0$, $\mathcal{H}_R$, or $\mathcal{H}_{S-O}$. (The partner index u may refer to any partner of the irreducible "double-valued" representation d, the matrix element being independent of it.) The spin-independent parts of the Hamiltonian are also invariant under the operations of the single group, so the additional selection rule[22]

$$\langle\Phi_i^{an}|\mathcal{H}''|\Phi_j^{bn'}\rangle=\langle\Phi_l^{an}|\mathcal{H}''|\Phi_l^{an'}\rangle\delta_{ab}\delta_{ij} \tag{17}$$

applies for $\mathcal{H}''=\mathcal{H}_0$ or $\mathcal{H}_R$. For $\mathcal{H}''=\mathcal{H}_0$ this selection rule may be replaced with the more restrictive one,

$$\langle\Phi_i^{an}|\mathcal{H}_0|\Phi_j^{bn'}\rangle=(N_{an})^2E_n^0\delta_{ab}\delta_{ij}\delta_{nn'}, \tag{18}$$

because the Φ_i^{an} have been chosen to be eigenfunctions of $\mathcal{H}_0$.

The nonvanishing matrix elements of the spin-independent terms of the Hamiltonian may thus be

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[20] See Ref. 19, Chap. 9.

[21] G. F. Koster, J. O. Dimmick, R. G. Wheeler, and H. Statz, *Properties of the Thirty-Two Point Groups* (MIT Press, Cambridge, Massachusetts, 1963).

[22] See Ref. 19, Chap. 12.

written

$$\begin{aligned}
&\langle\psi_u{}^{d;\,an}|\mathcal{H}''|\psi_u{}^{d;\,bn'}\rangle\\
&\quad=\int dv\,\textstyle\sum_{ij}[D_{ui}{}^{da}(N_{an})^{-1}\Phi_i{}^{an}]^*\mathcal{H}''[D_{uj}{}^{db}(N_{bn'})^{-1}\Phi_j{}^{bn'}]+\int dv\,\sum_{ij}[U_{ui}{}^{da}(N_{an})^{-1}\Phi_i{}^{an}]^*\mathcal{H}''[U_{uj}{}^{db}(N_{bn'})^{-1}\Phi_j{}^{bn'}]\\
&\quad=(N_{an}N_{bn'})^{-1}\textstyle\sum_{i,j}\{(D_{ui}{}^{da})^*D_{uj}{}^{db}+(U_{ui}{}^{da})^*U_{uj}{}^{db}\}\langle\Phi_i{}^{an}|\mathcal{H}''|\Phi_j{}^{bn'}\rangle\\
&\quad=(N_{an}N_{an}{}')^{-1}\delta_{ab}\textstyle\sum_i\{|D_{ui}{}^{da}|^2+|U_{ui}{}^{da}|^2\}\langle\Phi_l{}^{an}|\mathcal{H}''|\Phi_l{}^{an'}\rangle\\
&\quad=(N_{an}N_{an'})^{-1}\langle\Phi_l{}^{an}|\mathcal{H}''|\Phi_l{}^{an'}\rangle\delta_{ab}.
\end{aligned}\tag{19}$$

[Use has been made of Eqs. (13), (17), and (14).] If $\mathcal{H}''=\mathcal{H}_0$, the expression may be further reduced to

$$\langle\psi_u{}^{d;\,an}|\mathcal{H}_0|\psi_u{}^{d;\,bn'}\rangle=E_n{}^0\delta_{ab}\delta_{nn'}.\tag{20}$$

The matrix element of the relativistic Hamiltonian between two spinor basis functions is thus

$$\langle\psi_s{}^{d;\,an}|\mathcal{H}|\psi_t{}^{f;\,bn'}\rangle=\delta_{df}\delta_{st}\{[E_n{}^0\delta_{nn'}+\langle\Phi_l{}^{an}|\mathcal{H}_R|\Phi_l{}^{an'}\rangle(N_{an}N_{an'})^{-1}]\delta_{ab}+\langle\psi_u{}^{d;\,an}|\mathcal{H}_{S-O}|\psi_u{}^{d;\,bn'}\rangle\}.\tag{21}$$

The only part of the matrix element which need be directly calculated between the spinor functions is that arising from the spin-orbit term. The parts arising from the spin-independent terms are completely determined by the matrix elements of these terms between the eigenfunctions of the nonrelativistic Hamiltonian. The analytic expressions for the various matrix elements and the normalization are derived in the following section.

Matrix Elements of the Relativistic Terms

1. Matrix Elements of $\mathcal{H}_R$ between the Eigenfunctions of $\mathcal{H}_0$

In order to simplify the calculation of the matrix elements of $\mathcal{H}_R$, it is useful to re-express the form of the operators involved. The Hermitian character of the p^4 operator requires that[23]

$$\begin{aligned}
\langle\Phi_l{}^{an}|(8m^3c^2)^{-1}p^4|\Phi_l{}^{an'}\rangle&\equiv(8m^3c^2)^{-1}\int(\Phi_l{}^{an})^*p_{op}{}^4\Phi_l{}^{an'}dv\\
&=(8m^3c^2)^{-1}\int(p_{op}{}^2\Phi_l{}^{an})^*(p_{op}{}^2\Phi_l{}^{an'})dv\\
&=(2mc^2)^{-1}\int(E_n{}^0-V)(E_{n'}{}^0-V)(\Phi_l{}^{an})^*\Phi_l{}^{an'}dv.
\end{aligned}\tag{22}$$

The Darwin term may also be re-expressed in a more convenient form by using the relations (where the integrals are taken over the volume defined by the periodic boundary conditions),

$$\int\nabla\cdot[\Phi^*\Phi'(\nabla V)]dv=\int_{\text{encl. surf.}}(\Phi^*\Phi'\nabla V)\cdot d\boldsymbol{\sigma}=0,\tag{23}$$

$$\nabla\cdot[\Phi^*\Phi'(\nabla V)]=\Phi^*\Phi'(\nabla^2V)+(\nabla V)\cdot(\nabla\Phi^*)\Phi'+(\nabla V)\cdot(\nabla\Phi')\Phi^*.\tag{24}$$

Combining these equations leads to the result, with $\Phi=\Phi_l{}^{an}$ and $\Phi'=\Phi_l{}^{an'}$,

$$\langle\Phi_l{}^{an}|\hbar^2(8m^2c^2)^{-1}(\nabla^2V)|\Phi_l{}^{an'}\rangle=-\hbar^2(8m^2c^2)^{-1}\left\{\int(\Phi_l{}^{an})^*(\nabla V)\cdot(\nabla\Phi_l{}^{an'})dv+\int(\nabla\Phi_l{}^{an})^*\cdot(\nabla V)\Phi_l{}^{an'}dv\right\}.\tag{25}$$

In calculating these matrix elements, it is convenient to make use of atomic units, in which the unit of energy is the rydberg and that of length, the radius of the first Bohr orbit for hydrogen. The unit of mass is twice the electron mass, and the unit of angular momentum is $\hbar$. The velocity of light has the value $2/\bar{\alpha}$, where $\bar{\alpha}$ is the fine-

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[23] This may be proved through integration by parts over the volume defined by the periodic boundary conditions.

structure constant, $[137.0373]^{-1}$. In this system, the Hamiltonian operator is

$$\mathcal{H}=-\nabla^2+V-(\tfrac{1}{4}\bar{\alpha}^2)p^4+(\tfrac{1}{8}\bar{\alpha}^2)(\nabla^2V)+(\tfrac{1}{4}\bar{\alpha}^2)\boldsymbol{\sigma}\cdot[(\nabla V)\times\mathbf{p}], \tag{26}$$

$$\mathbf{p}_{op}=-i\nabla. \tag{27}$$

The nonvanishing matrix elements of $\mathcal{H}_R$ between the eigenfunctions of the nonrelativistic Hamiltonian are

$$\begin{aligned}\langle\Phi_l^{an}|\mathcal{H}_R|\Phi_l^{an'}\rangle&=\tfrac{1}{4}\bar{\alpha}^2\langle\Phi_l^{an}|(-p^4+\tfrac{1}{2}\nabla^2V)|\Phi_l^{an'}\rangle\\&=-\tfrac{1}{4}\bar{\alpha}^2\left\{\int(E_n{}^0-V)(E_{n'}{}^0-V)(\Phi_l^{an})^*\Phi_l^{an'}dv\right.\\&\qquad\left.+\frac{1}{2}\int[(\Phi_l^{an})^*(\nabla V)\cdot(\nabla\Phi_l^{an'})+(\nabla\Phi_l^{an})^*\cdot(\nabla V)\Phi_l^{an'}]dv\right\}.\end{aligned} \tag{28}$$

Because the approximate potential energy is constant in the region outside the APW spheres, the total contribution to the second integral comes from the region within the spheres. The contribution to the first integral from the region outside the spheres is just

$$(E_n{}^0-V)(E_{n'}{}^0-V)I_{al;\,nn'}, \tag{29}$$

where

$$I_{al;\,nn'}=\int_v(\Phi_l^{an})^*\Phi_l^{an'}dv, \tag{30}$$

V is the (constant) value of the potential in the region outside the spheres, and v is that region. Although this contribution is included in the present calculation, it should be so small as to be completely negligible. Since the relativistic terms have the translational symmetry of the crystal (and their matrices are thus diagonal in the reduced wave vector, ($\mathbf{k}_0$), the contributions to the matrix elements from each unit cell of the crystal must be equal. It is therefore sufficient to perform all integrations indicated (including those for the normalization) over the unit cell at the origin of coordinates, thus simplifying the calculation.

From Eqs. (6) and (11), the eigenfunctions of $\mathcal{H}_0$ have the form

$$\Phi_l^{an}(\mathbf{k}_0;\mathbf{r})=\textstyle\sum_{\mathbf{k},t}C_{\mathbf{k},t}(n)\sum_R\Gamma_a(R)_{l,t}{}^*[R\Phi^n](\mathbf{k};\mathbf{r}), \tag{31}$$
$$\mathbf{k}=\mathbf{k}_0+\mathbf{K},$$

where the energy dependence of the raw APW functions has been indicated by the superscript n. The nonvanishing matrix element of $\mathcal{H}_R$ between two such eigenfunctions is

$$\langle\Phi_l^{an}|\mathcal{H}_R|\Phi_l^{an'}\rangle=\textstyle\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}{}^*(n)C_{\mathbf{k}',t'}(n')\sum_{R,R'}\Gamma_a(R)_{l,t}\Gamma_a(R')_{l,t'}{}^*\displaystyle\int[R\Phi^n]^*(\mathbf{k};\mathbf{r})\mathcal{H}_R[R\Phi^{n'}](\mathbf{k}';\mathbf{r})dv. \tag{32}$$

The work of Wood[6,7] shows that, because $\mathcal{H}_R$ is invariant under the operations of the (single) point group, this may be reduced to the form

$$\begin{aligned}\langle\Phi_l^{an}|\mathcal{H}_R|\Phi_l^{an'}\rangle&=(g/n_a)\textstyle\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}{}^*(n)C_{\mathbf{k}',t'}(n')\sum_R\Gamma_a(R)_{t,t'}{}^*\displaystyle\int[\Phi^n(\mathbf{k};\mathbf{r})]^*\mathcal{H}_R[R\Phi^{n'}](\mathbf{k}';\mathbf{r})dv\\&=(g/n_a)\textstyle\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}{}^*(n)C_{\mathbf{k}',t'}(n')\sum_R\Gamma_a(R)_{t,t'}{}^*\displaystyle\int[\Phi^n(\mathbf{k};\mathbf{r})]^*\mathcal{H}_R\Phi^{n'}(R\mathbf{k}';\mathbf{r})dv,\end{aligned} \tag{33}$$

where g is the order of the group of the $\mathbf{k}$ vector and n_a the dimensionality of the representation a. [Use has been made of Eq. (9).]

Within the pth sphere, the raw APW functions Φ^n have the form [Eq. (3)]

$$\Phi^n(\mathbf{k};\mathbf{r})=\textstyle\sum_{l,m}A_{lm}(n,\mathbf{k})u_{pln}(r')Y_l{}^m(\theta',\phi'), \tag{34}$$

where the subscript n, rather than E, has been used to indicate the energy dependence of the radial function $u_{pln}(r')$. Because of the spherical symmetry of the approximate potential, the operator $\mathcal{H}_R$ involves only the radial dependence of the wave functions. The integral within the sphere thus factors into the product of a radial integral times an angular integral, and the latter reduces to $\delta_{l,l'}\delta_{m,m'}$ because of the orthonormality of the spherical harmonics. The contribution from the pth sphere to the matrix element of $\mathcal{H}_R$ is then

$$-(g/n_a)\tfrac{1}{4}\bar{\alpha}^2\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}^*(n)C_{\mathbf{k}',t'}(n')\sum_R\Gamma_a(R)_{t,t'}^*\sum_{l,m}[A_{lm}(n,\mathbf{k})]^*A_{lm}(n',R\mathbf{k}')$$
$$\times\int_0^{R_p}\left\{u_{pln}(r)[E_n{}^0-V_p][E_{n'}{}^0-V_p]u_{pln'}(r)+\tfrac{1}{2}u_{pln}(r)\frac{dV_p}{dr}\frac{d}{dr}u_{pln'}(r)+\tfrac{1}{2}u_{pln'}(r)\frac{dV_p}{dr}\frac{d}{dr}u_{pln}(r)\right\}r^2dr. \quad (35)$$

With the complete expressions for the A_{lm}'s, this becomes

$$-\tfrac{1}{4}\bar{\alpha}^2(g/n_a)\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}^*(n)C_{\mathbf{k}',t'}(n')\sum_R\Gamma_a(R)_{t,t'}^*\sum_{l,m}e^{-i(\mathbf{k}-R\mathbf{k}')\cdot\mathbf{r}_p}(16\pi^2)j_l(|\mathbf{k}|R_p)j_l(|\mathbf{k}'|R_p)$$
$$\times Y_l{}^m(\theta_{\mathbf{k}},\phi_{\mathbf{k}})[Y_l{}^m(\theta_{R\mathbf{k}'},\phi_{R\mathbf{k}'})]^*[u_{pln}(R_p)u_{pln'}(R_p)]^{-1}\int\Big\{u_{pln}(r)[E_n{}^0-V_p][E_{n'}{}^0-V_p]u_{pln'}(r)$$
$$+\tfrac{1}{2}u_{pln}(r)\frac{dV_p}{dr}\frac{d}{dr}u_{pln'}(r)+\tfrac{1}{2}u_{pln'}(r)\frac{dV_p}{dr}\frac{d}{dr}u_{pln}(r)\Big\}r^2dr=-\bar{\alpha}^2\pi(g/n_a)\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}^*(n)C_{\mathbf{k}',t'}(n')$$
$$\times\sum_l(2l+1)j_l(|\mathbf{k}|R_p)j_l(|\mathbf{k}'|R_p)[u_{pln}(R_p)u_{pln'}(R_p)]^{-1}\int_0^{R_p}\Big\{u_{pln}[E_n{}^0-V_p][E_{n'}{}^0-V_p]u_{pln'}$$
$$+\tfrac{1}{2}u_{pln}\frac{dV_p}{dr}\frac{d}{dr}u_{pln'}+\tfrac{1}{2}u_{pln'}\frac{dV_p}{dr}\frac{d}{dr}u_{pln}\Big\}r^2dr\sum_R\Gamma_a(R)_{t,t'}^*e^{-i(\mathbf{k}-R\mathbf{k}')\cdot\mathbf{r}_p}P_l\left(\frac{\mathbf{k}\cdot[R\mathbf{k}']}{|\mathbf{k}|\,|\mathbf{k}'|}\right). \quad (36)$$

(The addition theorem for spherical harmonics has been used to eliminate the summation over m.)

The contribution from the unit cell to the matrix element is the sum of the contributions from the Pb sphere and the Te sphere, plus the small contribution to the mass-velocity matrix element from the region outside the spheres.

2. *Normalization and Overlap of the Eigenfunctions of $\mathcal{H}_0$*

A derivation completely analogous to that given for the matrix elements of $\mathcal{H}_R$ shows that the contribution from the pth sphere to the overlap integral between two eigenfunctions of the nonrelativistic Hamiltonian is

$$S_p(al;nn')\equiv\int_{p\text{th sphere}}[\Phi_l{}^{an}(\mathbf{k}_0;\mathbf{r})]^*\Phi_l{}^{an'}(\mathbf{k}_0;\mathbf{r})dv$$
$$=4\pi(g/n_a)\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}^*(n)C_{\mathbf{k}',t'}(n')\sum_l(2l+1)j_l(|\mathbf{k}|R_p)j_l(|\mathbf{k}'|R_p)[u_{pln}(R_p)u_{pln'}(R_p)]^{-1}$$
$$\times\int_0^{R_p}u_{pln}(r)u_{pln'}(r)r^2dr\sum_R\Gamma_a(R)_{t,t'}^*e^{-i(\mathbf{k}-R\mathbf{k}')\cdot\mathbf{r}_p}P_l(\mathbf{k}\cdot[R\mathbf{k}']/|\mathbf{k}|\,|\mathbf{k}'|). \quad (37)$$

The integral over a unit cell of $e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}}$, if $\mathbf{k}$ and $\mathbf{k}'$ both correspond to the same reduced $\mathbf{k}$ vector, is $\Omega\delta_{\mathbf{k},\mathbf{k}'}$, where Ω is the volume of the unit cell. The integral over the volume enclosed by a sphere of radius R_p, of $e^{-i\mathbf{k}\cdot\mathbf{r}}e^{i\mathbf{k}'\cdot\mathbf{r}}$ is

$$4\pi e^{-i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}_p}R_p{}^2[|\mathbf{k}-\mathbf{k}'|]^{-1}j_1(|\mathbf{k}-\mathbf{k}'|R_p), \quad (38)$$

if the center of the sphere is at the point $\mathbf{r}_p$ from the origin. Thus the contribution from the region outside the spheres to the overlap integral (over a unit cell) between two eigenfunctions of $\mathcal{H}_0$ which correspond to the same reduced $\mathbf{k}$ vector is

$$I_{al;\,nn'}=(g/n_a)\sum_{\mathbf{k},t}\sum_{\mathbf{k}',t'}C_{\mathbf{k},t}^*(n)C_{\mathbf{k}',t'}(n')$$
$$\times\sum_R\Gamma_a(R)_{t,t'}^*[\Omega\delta_{\mathbf{k},R\mathbf{k}'}-\sum_{p=1}^{2}4\pi e^{-i(\mathbf{k}-R\mathbf{k}')\cdot\mathbf{r}_p}R_pj_1(|\mathbf{k}-R\mathbf{k}'|R_p)/|\mathbf{k}-R\mathbf{k}'|]. \quad (39)$$

(The double summation over operations of the group has been reduced to a single sum by the technique used with the matrix elements of $\mathcal{H}_R$.)

The normalization factor N_{an} is thus

$$N_{an}=\{[\sum_{p=1}^{2}S_p(al;nn)]+I_{al;\,nn}\}^{1/2}. \quad (40)$$

3. *Matrix Elements of $\mathcal{H}_{S-O}$ between the Spinor Basis Functions*

The spin-orbit term is not invariant under the operations of the single group, since they do not transform the spin coordinates. Thus the double summation over operations of the single group, which appears in the expressions for the matrix elements because of the symmetrization of the APW functions, cannot be reduced to a single summation as in the case of the matrix elements of $\mathcal{H}_R$. The fastest way to calculate the matrix elements of $\mathcal{H}_{S-O}$ is therefore to generate each spinor function in the form

$$\psi_s{}^{d;\,an}=\alpha\sum_l u_{pln}(r')\sum_m A_{ds}{}^{an}(lm;p)Y_l{}^m(\theta',\phi')+\beta\sum_l u_{pln}(r')\sum_m B_{ds}{}^{an}(lm;p)Y_l{}^m(\theta',\phi') \tag{41}$$

within each sphere, and store the coefficients $A_{ds}{}^{an}(lm;p)$ and $B_{ds}{}^{an}(lm;p)$ in the computer memory. The spinor functions are then available as often as necessary for the calculation of the spin-orbit matrix elements, and little additional calculation is necessary, so that the amount of computer time required for this part of the calculation is appreciably reduced. Use of Eqs. (10), (11), and (13) gives

$$A_d{}^{an}(lm;p)=4\pi(N_{an})^{-1}i^l[u_{pln}(R_p)]^{-1}\sum_{\mathbf{k},j}C_{\mathbf{k},j}(n)j_l(|\mathbf{k}|R_p)\sum_R e^{i(R\mathbf{k})\cdot\mathbf{r}_p}[Y_l{}^m(\theta_{R\mathbf{k}},\phi_{R\mathbf{k}})]^*\sum_i U_{si}{}^{da}\Gamma_a(R)_{i,j}{}^*. \tag{42}$$

The expression for $B_{ds}{}^{an}(lm;p)$ is obtained from Eq. (42) by substituting $D_{si}{}^{da}$ for $U_{si}{}^{da}$. Because the approximate potential is constant in the region outside the spheres, this region gives no contribution to the spin-orbit matrix elements, and it is not necessary to generate the spinor wave functions for this region.

The spherical symmetry of the approximate potential within each sphere allows the spin-orbit operator to be written in terms of the operator for angular momentum about the center of the sphere:

$$\mathcal{H}_{S-O}=\frac{\bar{\alpha}^2}{4}\boldsymbol{\sigma}\cdot[(\nabla V)\times\mathbf{p}]=\frac{\bar{\alpha}^2}{4}\frac{1}{r'}\frac{dV}{dr'}\boldsymbol{\sigma}\cdot\mathbf{L}=\frac{\bar{\alpha}^2}{4}\frac{1}{r'}\frac{dV}{dr'}[\tfrac{1}{2}\sigma_+L_-+\tfrac{1}{2}\sigma_-L_++\sigma_zL_z], \tag{43}$$

in atomic units. The effect of the spin operators on the functions α and β is the following:

$$\begin{aligned}&\sigma_+\beta=2\alpha,\quad \sigma_-\beta=0,\quad \sigma_z\beta=-\beta;\\&\sigma_+\alpha=0,\quad \sigma_-\alpha=2\beta,\quad \sigma_z\alpha=\alpha.\end{aligned} \tag{44}$$

The effect of the angular momentum operators on the spherical harmonics is

$$\begin{aligned}&L_zY_l{}^m(\theta',\phi')=mY_l{}^m(\theta',\phi'),\\&L_\pm Y_l{}^m(\theta',\phi')=[l(l+1)-m(m\pm1)]^{1/2}Y_l{}^{m\pm1}(\theta',\phi');\end{aligned} \tag{45}$$

they do not affect the radial part of the wave function. Thus the integral of $\psi^\dagger\mathcal{H}_{S-O}\psi'$ is factored into the product of a radial and an angular integral, as was the case with the matrix elements of $\mathcal{H}_R$. Use of the relations (44) and (45), together with the orthogonality and normalization of the spin functions α and β and of the spherical harmonics, allows the angular integration to be performed analytically to give

$$\begin{aligned}\langle\psi_s{}^{d;\,an}|\mathcal{H}_{S-O}|\psi_s{}^{d;\,bn'}\rangle=\frac{\bar{\alpha}^2}{4}\sum_{p=1}^{2}\sum_{l=0}^{\infty}\left[\int_0^{R_p}r^2dr\frac{1}{r}\frac{dV}{dr}u_{pln}(r)u_{pln'}(r)\right]\sum_{m=-l}^{l}\{m\{[A_{ds}{}^{an}(lm;p)]^*A_{ds}{}^{bn'}(lm;p)\\-[B_{ds}{}^{an}(lm;p)]^*B_{ds}{}^{bn'}(lm;p)\}+[l(l+1)-m(m+1)]^{1/2}[A_{ds}{}^{an}(lm;p)]^*B_{ds}{}^{bn'}(l,m+1;p)\\+[l(l+1)-m(m-1)]^{1/2}[B_{ds}{}^{an}(lm;p)]^*A_{ds}{}^{bn'}(l,m-1;p)\}.\end{aligned} \tag{46}$$

Since the expression vanishes for $l=0$, the summation may equally well start with $l=1$.

Because of the very strong dependence of the relativistic corrections on the angular-momentum character of the wave functions, which appears in the strong dependence of the radial integrals on l, only the $l=1$ term of the above expression gives a significant contribution to the matrix element. Thus it is adequate to compute and store only the $l=1$ coefficients of the spinor basis functions and to calculate only the $l=1$ term in the above expression, which drastically reduces both the computer time and the memory required for these calculations. The error caused by this truncation appears to be less than one percent in the spin-orbit matrix elements between most of the states. Only in the case of states having no $l=1$ part about either atom is the percentage error in the matrix elements appreciable, and the matrix elements for such states have negligibly small effect on the band structure. For the same reason, it is only necessary to include the $l=0$, 1, and 2 terms in the expression for the matrix elements of $\mathcal{H}_R$.

THE BAND STRUCTURE

Calculated Energies

The energy levels of PbTe have been calculated for several points of the Brillouin zone by the technique

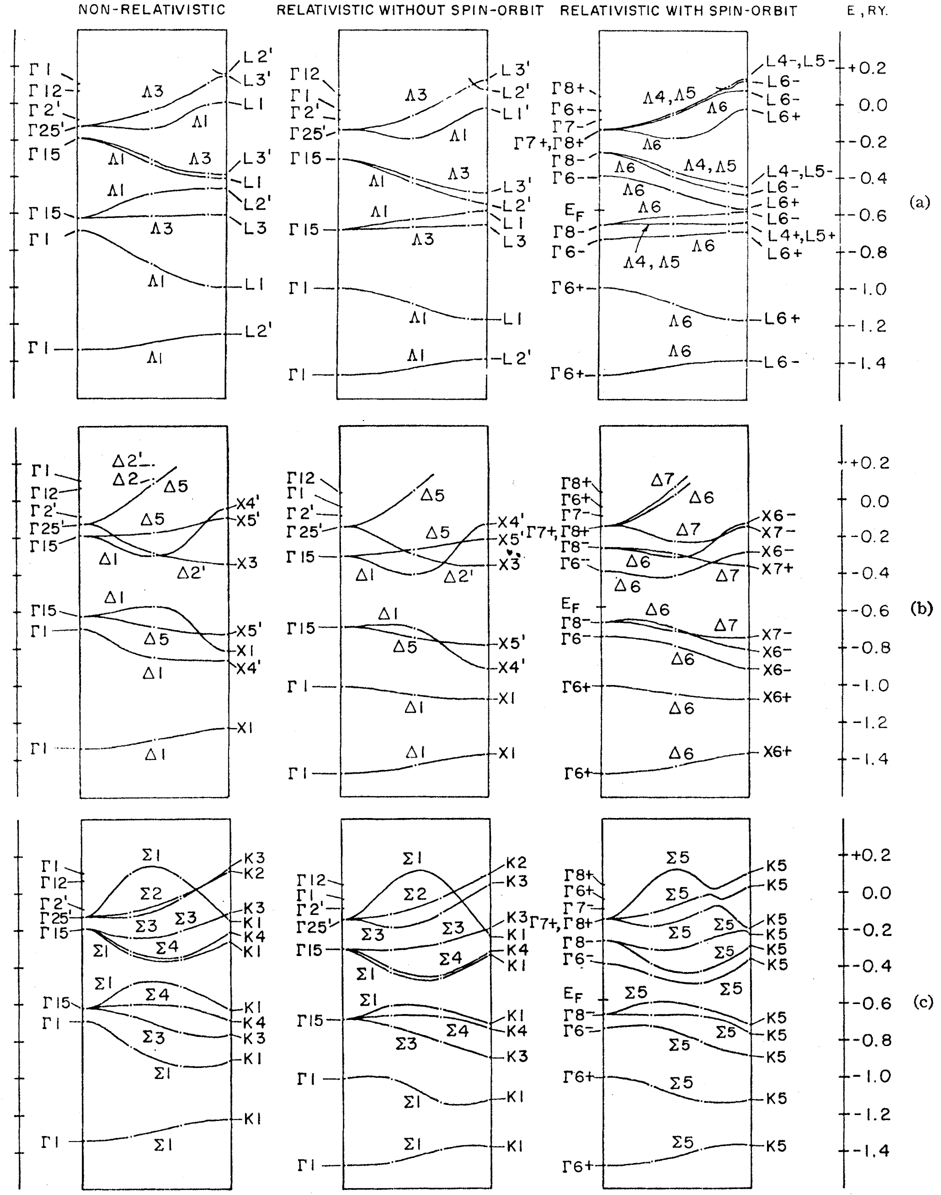

FIG. 1. Calculated bands of PbTe in the ⟨111⟩, ⟨010⟩, and ⟨110⟩ directions of **k** space (top, center, and bottom, respectively) for the nonrelativistic, spin-independent relativistic, and full relativistic Hamiltonians. The symmetries indicated are for rotations about the Pb nuclei.

just outlined, which has been programmed for the IBM 709 computer. The calculated eigenvalues of the nonrelativistic Hamiltonian, of the relativistic Hamiltonian without the spin-orbit term, and of the full relativistic Hamiltonian are shown in Fig. 1 for several points in the Brillouin zone. The calculated points have been connected by solid lines to indicate the estimated shape of the energy bands in the ⟨111⟩, ⟨010⟩, and ⟨110⟩ directions of **k** space. The calculated energies are also compared in Table III. Representative nonzero matrix elements of the relativistic terms between the spinor functions corresponding to the eigenstates of the nonrelativistic Hamiltonian are given in Table IV for the points L and Γ. The distribution of charge for the various nonrelativistic eigenstates is given in Table V; this corresponds roughly to the distribution of charge in the final, relativistic solutions and gives an indication of the linear-combination-of-atomic-orbitals characteristics of the various levels.

The potential used for the calculation, as mentioned earlier, is constant outside the APW spheres and spherically symmetric within each sphere. The potential is based on Slater's simplification of the Hartree-Fock scheme,[24] in which the one-electron potential is taken

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[24] J. C. Slater, Phys. Rev. **81**, 385 (1951).

TABLE III. The calculated eigenvalues for the nonrelativistic Hamiltonian, the single-group relativistic Hamiltonian (no spin-orbit term), and the full relativistic Hamiltonian. The coordinates of the wave vectors are in units of π/a. The states at L and Γ are numbered for identification in Table IV.

		Single-group states		Double-group states	
		Nonrel.	Rel.	Full rel.	
	$L(1,1,1)$				
1	$L_{3'}$	$+0.149$	$+0.126$	$+0.132$	L_4^-, L_5^-
$\overline{1}$				$+0.125$	L_6^-
2	$L_{2'}$	$+0.151$	$+0.073$	$+0.072$	L_6^-
3	L_1	$+0.016$	-0.029	-0.029	L_6^+
4	$L_{3'}$	-0.394	-0.485	-0.451	L_4^-, L_5^-
$\overline{4}$				-0.495	L_6^-
5	$L_{2'}$	-0.465	-0.553	-0.582	L_6^-
6	L_1	-0.406	-0.579	-0.573	L_6^+
7	L_3	-0.604	-0.660	-0.640	L_4^+, L_5^+
$\overline{7}$				-0.686	L_6^+
8	L_1	-0.995	-1.173	-1.173	L_6^+
9	$L_{2'}$	-1.253	-1.385	-1.385	L_6^-
	$\Lambda(\frac{7}{8},\frac{7}{8},\frac{7}{8})$				
	Λ_1	-0.012	(no convergence)		Λ_6
	Λ_3	$+0.110$	$+0.083$	$+0.095$	Λ_4, Λ_5
				$+0.074$	Λ_6
	Λ_3	-0.388	-0.478	-0.423	Λ_4, Λ_5
				-0.478	Λ_6
	Λ_1	-0.467	-0.522	-0.559	Λ_6
	Λ_1	-0.400	-0.590	-0.600	Λ_6
	Λ_3	-0.605	-0.661	-0.651	Λ_4, Λ_5
				-0.681	Λ_6
	Λ_1	-0.985	-1.171	-1.171	Λ_6
	$\Lambda(\frac{1}{2},\frac{1}{2},\frac{1}{2})$				
	Λ_3	-0.040	-0.063	-0.060	Λ_4, Λ_5
				-0.064	Λ_6
	Λ_1	-0.140	-0.188	-0.187	Λ_6
	Λ_3	-0.315	-0.406	-0.372	Λ_4, Λ_5
				-0.478	Λ_6
	Λ_1	-0.334	-0.436	-0.397	Λ_6
	Λ_1	-0.499	-0.631	-0.619	Λ_6
	Λ_3	-0.615	-0.674	-0.651	Λ_4, Λ_5
				-0.709	Λ_6
	Λ_1	-0.875	-1.083	-1.084	Λ_6
	$\Gamma(0,0,0)$				
10	Γ_{12}	$+0.068$	$+0.041$	$+0.041$	Γ_8^+
11	Γ_1	$+0.105$	-0.039	-0.039	Γ_6^+
12	$\Gamma_{2'}$	-0.086	-0.086	-0.086	Γ_7^-
13	$\Gamma_{25'}$	-0.127	-0.144	-0.144	Γ_8^+
$\overline{13}$				-0.144	Γ_7^+
14	Γ_{15}	-0.192	-0.305	-0.262	Γ_8^-
$\overline{14}$				-0.390	Γ_6^-
15	Γ_{15}	-0.622	-0.684	-0.659	Γ_8^-
$\overline{15}$				-0.735	Γ_6^-
16	Γ_1	-0.698	-1.001	-1.001	Γ_6^+
17	Γ_1	-1.339	-1.473	-1.473	Γ_6^+
	$X(0,2,0)$				
	$X_{4'}$	-0.041	-0.136	-0.132	X_6^-
	$X_{5'}$	-0.097	-0.215	-0.143	X_7^-
				-0.283	X_6^-
	X_3	-0.345	-0.359	-0.359	X_7^+
	$X_{5'}$	-0.725	-0.780	-0.747	X_7^-
				-0.816	X_6^-
	X_1	-0.814	-1.074	-1.074	X_6^+
	$X_{4'}$	-0.865	-0.910	-0.914	X_6^-
	X_1	-1.223	-1.367	-1.367	X_6^+
	$\Delta(0,1,0)$				
	$\Delta_{2'}$	$+0.196$	(not included)		
	Δ_2	$+0.115$	(not included)		
	Δ_5	$+0.087$	$+0.045$	$+0.066$	Δ_7
				$+0.030$	Δ_6
	Δ_5	-0.176	-0.274	-0.226	Δ_7
				-0.311	Δ_6
	$\Delta_{2'}$	-0.286	-0.299	-0.299	Δ_7
	Δ_1	-0.295	-0.401	-0.405	Δ_6
	Δ_1	-0.578	-0.697	-0.700	Δ_6
	Δ_5	-0.681	-0.742	-0.706	Δ_7
				-0.788	Δ_6
	Δ_1	-0.845	-1.048	-1.049	Δ_6
	Δ_1	-1.292	-1.429	-1.429	Δ_6
	$\Delta(0,1,0)$				
	Σ_1	$+0.103$	(not included)		
	Σ_2	-0.101	-0.118	-0.118	Σ_5
	Σ_3	-0.128	-0.188	-0.188	Σ_5
	Σ_3	-0.241	-0.309	-0.309	Σ_5
	Σ_1	-0.334	-0.431	-0.453	Σ_5
	Σ_4	-0.313	-0.410	-0.387	Σ_5
	Σ_1	-0.499	-0.607	-0.599	Σ_5
	Σ_4	-0.601	-0.661	-0.670	Σ_5
	Σ_3	-0.663	-0.723	-0.723	Σ_5
	Σ_1	-0.829	-1.043	-1.043	Σ_5
	Σ_1	-1.315	-1.449	-1.449	Σ_5
	$\Sigma(1,1,0)$				
	Σ_1	$+0.085$	(not included)		
	Σ_2	-0.021	-0.034	-0.034	Σ_5
	Σ_3	-0.025	-0.107	-0.107	Σ_5
	Σ_3	-0.211	-0.274	-0.274	Σ_5
	Σ_1	-0.359	-0.461	-0.486	Σ_5
	Σ_4	-0.353	-0.452	-0.426	Σ_5
	Σ_1	-0.504	-0.631	-0.624	Σ_5
	Σ_4	-0.616	-0.672	-0.680	Σ_5
	Σ_3	-0.757	-0.811	-0.811	Σ_5
	Σ_1	-0.934	-1.133	-1.133	Σ_5
	Σ_1	-1.259	-1.394	-1.394	Σ_5
	$K(\frac{3}{2},\frac{3}{2},0)$				
	K_2	$+0.115$	$+0.105$	$+0.105$	K_5
	K_3	$+0.124$	$+0.040$	$+0.040$	K_5
	K_3	-0.109	-0.200	-0.200	K_5
	K_1	-0.147	-0.220	-0.215	K_5
	K_4	-0.218	-0.320	-0.299	K_5
	K_1	-0.269	-0.335	-0.361	K_5
	K_1	-0.627	-0.730	-0.718	K_5
	K_4	-0.695	-0.752	-0.775	K_5
	K_3	-0.767	-0.886	-0.886	K_5
	K_1	-0.914	-1.119	-1.119	K_5
	K_1	-1.224	-1.365	-1.365	K_5

to be the sum of a Coulomb potential and an approximate exchange potential. The Coulomb potential is that arising from the nuclei plus the charge density of all the electrons; the exchange potential is equal to $-6[3\rho(r)/8\pi]^{1/3}$, where $\rho(r)$ is the charge density from all the electrons, in units of the electronic charge. In summing the contributions to the potential from several atoms, these terms were calculated as follows: The Coulomb potentials and the charge densities arising from all the atoms were separately summed, the total Coulomb potential being set equal to the sum of the atomic Coulomb potentials. The total exchange potential was evaluated from the expression above, with ρ set equal to the total charge density from all the atoms. A similar procedure was followed in the averaging required to obtain the approximate potential for the calculation. The atomic charge densities and Coulomb potentials were obtained from a Hartree-Fock-Slater self-consistent calculation using the programs of Herman and Skillman.[25] To obtain the potential within the spheres, the contributions from a given atom, its nearest unlike neighbors, and its nearest like neighbors were included. To obtain the constant value of potential for the region between the spheres, an integration was performed which is equivalent to summing the contributions from all the atoms of the crystal and averaging over the volume outside the spheres.[26]

It must be noted that this calculation takes into account only what might be termed the "direct" relativistic effect, that is, the additional terms in the one-electron Hamiltonian which arise from relativistic considerations. However, there is also an "indirect" effect arising from the corrections to the wave functions of the core electrons. Since the potential energy of the valence electrons arises in part from the charge of the core electrons, the changes in their charge distributions cause corresponding modifications in the potential-energy term appearing in the one-electron Hamiltonian. In a nonself-consistent calculation such as that reported here, the appropriate way to include the "indirect" relativistic effect would be to use relativistically self-

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[25] F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[26] This program was devised by L. Ferreira.

TABLE IV. Matrix elements at L and Γ for the mass-velocity plus Darwin corrections, $\mathcal{H}_R$, and for $\mathcal{H}_R+\mathcal{H}_{S-O}$ between the normalized spinor functions corresponding to the eigenstates of the nonrelativistic Hamiltonian. Matrix elements which are rigorously zero or which were computed to be less than 10^{-4} are not listed. The key to the numbering of the nonrelativistic states is given in Table III. (All the relativistic matrix elements are real for the choice of basis functions used.)

i,j	$\langle i\|\mathcal{H}_R\|j\rangle$	$\langle i\|\mathcal{H}_R+\mathcal{H}_{S-O}\|j\rangle$	i,j	$\langle i\|\mathcal{H}_R\|j\rangle$	$\langle i\|\mathcal{H}_R+\mathcal{H}_{S-O}\|j\rangle$
1, 1	+0.9238	+0.9314	7, 7	+0.1414	+0.1612
1, 4	−0.0412	−0.0254	$\bar{7}, \bar{7}$	+0.1414	+0.1216
$\bar{1}, \bar{1}$	+0.9238	+0.9162	$\bar{7}$, 8		−0.0138
$\bar{1}$, 2		−0.0204	8, 8	−0.3420	−0.3420
$\bar{1}, \bar{4}$	−0.0412	−0.0571	9, 9	−0.5807	−0.5807
$\bar{1}$, 5		+0.0163	10, 10	+0.8424	+0.8424
$\bar{1}$, 9		−0.0051	11, 11	+0.7248	+0.7248
2, 2	+0.8648	+0.8648	11, 16	−0.1636	−0.1636
2, $\bar{4}$		−0.0425	11, 17	−0.1159	−0.1159
2, 5	+0.0770	+0.0770	12, 12	+0.7154	+0.7154
3, 3	+0.7716	+0.7716	13, 13	+0.6569	+0.6569
3, 6	−0.0010	−0.0010	$\overline{13}, \overline{13}$	+0.6569	+0.6569
3, $\bar{7}$		−0.0232	14, 14	+0.4953	+0.5389
4, 4	+0.3183	+0.3512	14, 15	+0.0175	+0.0114
$\bar{4}, \bar{4}$	+0.3183	+0.2854	$\overline{14}, \overline{14}$	+0.4953	+0.4082
4, 5		+0.0339	$\overline{14}, \overline{15}$	+0.0175	+0.0296
$\bar{4}$, 9		−0.0105	15, 15	+0.1175	+0.1420
5, 5	+0.2548	+0.2548	$\overline{15}, \overline{15}$	+0.1175	+0.0684
5, 9	−0.0504	−0.0504	16, 16	−0.1832	−0.1832
6, 6	+0.1923	+0.1923	16, 17	−0.0189	−0.0189
6, $\bar{7}$		+0.0227	17, 17	−0.6646	−0.6646
6, 8	−0.1304	−0.1304			

consistent atomic potentials and charge densities as the basis for computing the crystalline one-electron potential. Because the programs of Herman and Skillman are nonrelativistic, it was not possible to do this in the present calculation. Future investigations, however, should be able to use the results of programs by Waber and Liberman,[27] which do give relativistically self-consistent results, as a starting point for relativistic band calculations. Neglect of the "indirect" effect in the present work should result in a lowering of the calculated levels from the energies which would have been obtained had the "indirect" effect been included.

Since there is as yet no clear indication of the ionicity of PbTe, the atomic potentials of neutral Pb and Te were used to compute the approximate crystal potential for this calculation. Consideration of the charge distributions of the states at L seems to indicate that the effect of increased ionicity would be to move the (single-group) $L_{3'}$ level (at -0.485 Ry) and the L_3 level (at -0.660 Ry) together toward the gap. The $L_{2'}$ level (at -0.553 Ry) would be shifted slightly downward, and the L_1 level (at -0.579 Ry) would remain almost at its calculated level. The double-group levels would be affected accordingly. The use of an approximate crystal potential which is spherically symmetric within the spheres and constant outside them has undoubtedly also affected the calculated energies. This source of error is currently being investigated.[28] The indications are that, with careful choice of the value of the constant potential outside the spheres, the effect of this approximation is small, but the investigation is not yet complete.

Inaccuracies in the eigenvalues and eigenfunctions of the nonrelativistic Hamiltonian because of the numerical techniques used should be quite small. Summations in l have been carried to $l=12$, and summations in $\mathbf{k}$ include all $\mathbf{k}$ for which $|\mathbf{k}| \leqq (80)^{1/2}\pi/a$; these limits have been found to be adequate for convergence in nonrelativistic calculations. A program limitation that the number of distinct $\mathbf{k}$ in the summations for the relativistic matrix elements be less than or equal to ten, however, has caused convergence errors in these matrix elements which may be as large as 10 or 20% of their value, for points of low symmetry. These errors have been estimated, however, for all points of interest, and they should cause no appreciable change in the band structure, because the relativistic contributions to the energies, though important, are only a small fraction of the total energies.

Comparison with Experiment

As was suggested in the Introduction, a calculated energy-band structure such as this one can often be modified in the light of experimental information to obtain a more accurate description of the one-electron energies of the material. In the case of PbTe, a definite indication of the character of the bands is given by the reported Pb Knight shift[29] in p-type PbTe, which implies that the valence band edge has s-like character about the Pb nuclei. This, in turn, implies that the closely spaced L_6^+ and L_6^- levels at about -0.58 Ry should be interchanged. (The L_6^+ functions arising from the L_1 single-group state are s-like about the Pb; the L_6^- functions arising from the $L_{2'}$ state, on the other hand, are s-like about the Te and p-like about the Pb, containing no s-like character about the Pb.) Investiga-

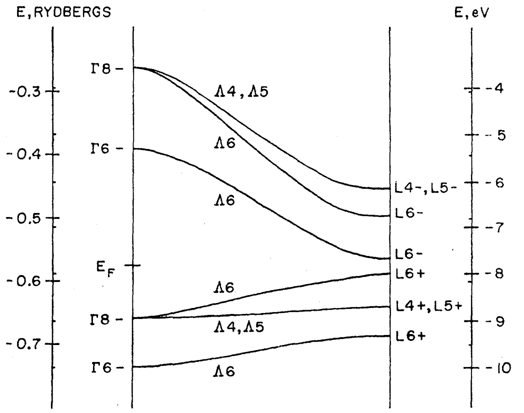

FIG. 2. Revised energy bands in the ⟨111⟩ direction near the forbidden gap.

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[27] See Ref. 25, Chap. 3, pp. 3–11 ff.

[28] P. DeCicco *et al.*, Solid State and Molecular Theory Group, MIT (unpublished).

[29] I. Weinberg and J. Callaway, Nuovo Cimento **24**, 190 (1962).

TABLE V. Charge distributions for representative eigenstates of the nonrelativistic Hamiltonian. Although the relativistic corrections mix these somewhat, their charge distributions correspond roughly to those of the relativistic eigenstates, especially to those of the Hamiltonian without the spin-orbit term. The $\int \Phi^* \Phi dv$ has been separated into its contribution from the region outside the spheres ("plane wave") and from within each sphere ("Pb" and "Te"). The contributions from within each sphere have been further separated by the quantum number for angular momentum about the center of the sphere, in order to indicate the atomic-like character of the eigenfunctions. (Note, however, that there is not a one-to-one correspondence between the figures given here and the makeup of eigenfunctions in terms of the appropriate atomic functions of Pb and Te.)

			$l=0$		$l=1$		$l=2$		$l=3$		
	Energy	Plane wave	Pb	Te	Pb	Te	Pb	Te	Pb	Te	Remainder
$L(1,1,1)$											
L_3'	+0.149	0.452	0	0	0.090	0	0	0.341	0.110	0	0.007
L_2'	+0.151	0.452	0	0.039	0.327	0	0	0.106	0.063	0	0.013
L_1	+0.016	0.543	0.009	0	0	0.316	0.080	0	0	0.040	0.013
L_3'	−0.394	0.311	0	0	0.555	0	0	0.125	0.006	0	0.002
L_2'	−0.465	0.484	0	0.124	0.309	0	0	0.064	0.018	0	0.001
L_1	−0.406	0.177	0.365	0	0	0.411	0.025	0	0	0.019	0.002
L_3	−0.604	0.202	0	0	0	0.735	0.060	0	0	0.001	0.003
L_1	−0.995	0.282	0.464	0	0	0.246	0.006	0	0	0.002	0.001
L_2'	−1.253	0.142	0	0.805	0.048	0	0	0.001	0.004	0	0.000
$\Lambda(\frac{1}{2},\frac{1}{2},\frac{1}{2})$											
Λ_3	−0.040	0.571	0	0	0.043	0.017	0.131	0.201	0.021	0.012	0.004
Λ_1	−0.140	0.617	0.051	0.020	0.094	0.051	0.064	0.047	0.023	0.032	0.002
Λ_3	−0.315	0.304	0	0	0.496	0.067	0.022	0.091	0.004	0.014	0.002
Λ_1	−0.334	0.353	0.094	0.014	0.226	0.232	0.000	0.033	0.027	0.020	0.001
Λ_1	−0.499	0.239	0.212	0.037	0.136	0.337	0.014	0.016	0.002	0.001	0.006
Λ_3	−0.615	0.197	0	0	0.073	0.687	0.024	0.003	0.012	0.001	0.003
Λ_1	−0.875	0.178	0.351	0.224	0.022	0.209	0.004	0.001	0.008	0.002	0.001
$\Gamma(0,0,0)$											
Γ_{12}	+0.068	0.416	0	0	0	0	0.242	0.338	0	0	0.003
Γ_1	+0.105	0.662	0.260	0.054	0	0	0.000	0.000	0	0	0.025
Γ_2'	−0.086	0.834	0	0	0	0	0	0	0.092	0.075	0.000
Γ_{25}'	−0.127	0.609	0	0	0	0	0.160	0.226	0	0	0.006
Γ_{15}	−0.192	0.241	0	0	0.576	0.125	0	0	0.013	0.045	0.000
Γ_{15}	−0.622	0.161	0	0	0.118	0.696	0	0	0.022	0.003	0.001
Γ_1	−0.698	0.142	0.622	0.232	0	0	0.000	0.000	0	0	0.005
Γ_1	−1.339	0.197	0.160	0.641	0	0	0.000	0.000	0	0	0.002
$X(0,2,0)$											
X_4'	−0.041	0.231	0	0	0.216	0.516	0	0	0.032	0.003	0.003
X_5'	−0.097	0.178	0	0	0.462	0.307	0	0	0.020	0.031	0.002
X_3	−0.345	0.722	0	0	0	0	0.124	0.153	0	0	0.000
X_5'	−0.725	0.280	0	0	0.180	0.530	0	0	0.008	0.002	0.000
X_1	−0.814	0.161	0.731	0.054	0	0	0.002	0.050	0	0	0.001
X_4'	−0.865	0.395	0	0	0.202	0.402	0	0	0.000	0.000	0.000
X_1	−1.223	0.113	0.036	0.821	0	0	0.028	0.001	0	0	0.001
K_2	+0.115	0.566	0	0	0	0	0.072	0.217	0.083	0.056	0.006
K_3	+0.124	0.357	0	0	0.397	0.075	0.060	0.040	0.012	0.052	0.007
K_3	−0.109	0.272	0	0	0.112	0.530	0.004	0.042	0.033	0.001	0.005
K_1	−0.147	0.388	0.002	0.038	0.346	0.091	0.064	0.037	0.002	0.029	0.002
K_4	−0.218	0.191	0	0	0.431	0.260	0.028	0.076	0.001	0.007	0.005
K_1	−0.269	0.457	0.007	0.007	0.058	0.302	0.048	0.090	0.029	0.000	0.002
K_1	−0.627	0.271	0.203	0.032	0.150	0.297	0.014	0.031	0.001	0.000	0.002
K_4	−0.695	0.240	0	0	0.153	0.576	0.015	0.006	0.006	0.003	0.002
K_3	−0.767	0.351	0	0	0.197	0.443	0.004	0.003	0.001	0.000	0.001
K_1	−0.914	0.241	0.532	0.003	0.017	0.188	0.003	0.012	0.002	0.002	0.001
K_1	−1.224	0.107	0.005	0.854	0.017	0.000	0.012	0.001	0.002	0.000	0.002

tion of the effective masses by $\mathbf{k}\cdot\mathbf{p}$ perturbation theory also indicates that the L_6^+ state should be the top of the valence band and the L_6^- state the bottom of the conduction band. This ordering of the levels at L is also required in order for the deformation potential calculated by Ferreira[30] (see below) to agree with experiment. There seems to be no experimental evidence that the other levels at L or the levels calculated for the other directions of $\mathbf{k}$ should be appreciably altered. Thus it seems clear that the energy bands in the ⟨111⟩ direction near the forbidden gap should be those pictured in Fig. 2 (rather than those of Fig. 1) and the other levels those shown in Fig. 1.

The experimental data most easily compared with this revised energy band structure are the optical data for PbTe found by Cardona and Greenaway.[31] For convenient comparison with this data, the allowed transitions between the energy levels at the points L, X, and Γ are shown with their energies in Fig. 3. These are to be compared with the energies of the maxima of $\epsilon_2 E^2$ (ϵ_2 is the imaginary part of the dielectric constant), which should be roughly proportional to the joint density of states for the transitions. These maxima, as obtained by Cardona and Greenaway, are tentatively identified in Fig. 3. The identifications give agreement between the experimental and theoretical energies to within 0.1 eV for all but the two largest energies, which differ from the experimental values by about 0.3 eV. The good agreement with experiment found in the levels identified is an encouraging sign, but it cannot be taken as conclusive. The number of possible transitions is sufficiently large and covers a sufficient range of energies that, for several of the experimentally observed transitions, it would be possible to make more than one identification without shifting the theoretical levels by more than the expected error of the calculation. A con-

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[30] L. G. Ferreira, Ph.D. thesis, Department of Electrical Engineering, Massachusetts Institute of Technology, 1964 (to be published).

[31] M. Cardona and D. L. Greenaway, Phys. Rev. **133**, A1685 (1964).

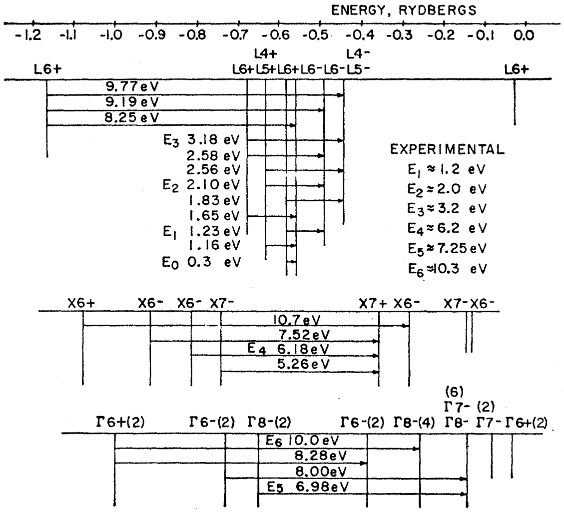

FIG. 3. Allowed optical transitions between levels of the calculated bands at L (revised), X, and Γ. The experimental energies of Cardona and Greenaway are tentatively identified.

clusive test would require calculation of the densities of states and the matrix elements for the optical transitions between the energy levels.

A further, and perhaps more conclusive, check on the validity of the calculation comes from the use of the calculated wave functions in perturbation calculations for the various electronic properties of the material. The correction which was made to the calculated levels at L is not one which should cause large mixing of the wave functions for the various levels. Therefore, the calculated wave functions should be approximately correct, and perturbation calculations using these wave functions as an approximation to the correct wave functions should give reasonable results. This procedure has been used by Ferreira[30] to calculate the properties of strained PbTe, and his calculated deformation potential agrees quite well with the experimental deformation potential obtained from studies of PbTe under hydrostatic pressure. It has also been used by Pratt and Ferreira[32] in a $\mathbf{k}\cdot\mathbf{p}$ calculation for the effective masses and g factors for PbTe. Their results are shown in Table VI, together with the experimental effective masses for PbTe, and the agreement is seen to be quite good. These calculations would seem to indicate, at least for the levels at L near the energy gap, that the calculated wave functions are a good approximation to the actual one-electron wave functions for PbTe, which, in turn, points strongly toward the accuracy of the calculation as a whole.[33,34]

TABLE VI. Effective masses and g-factors obtained by Pratt and Ferreira using the calculated wave functions and the calculated energies, shifted slightly to give the 0°K gap of 0.2 eV. Experimentally determined low-temperature effective masses are given for comparison.

	(m_t/m)	(m_l/m)	$g_{\parallel}$	$g_{\perp}$	
Valence	0.034	0.426	31.4	2	Calc.
	0.043±0.006	0.274	...	...	Exp.[a]
Cond.	0.031	0.238	−29.2	2	Calc.
	0.030±0.005	0.165	...	...	Exp.[b]

[a] P. J. Stiles, E. Burstein, and D. N. Langenberg, J. Appl. Phys. Suppl. **32**, 2174 (1961).
[b] K. F. Cuff, M. R. Ellett, and C. D. Kuglin, J. Appl. Phys. Suppl. **32**, 2179 (1961).

It is of interest that the calculation shows no indication of the secondary valence band maximum at Γ which has been proposed to account for some of the experimental measurements of PbTe. There is a secondary maximum in the $\langle 110\rangle$ direction of k space, but it is unlikely that the constant energy surfaces of such a maximum would have the desired spherical symmetry of a $\mathbf{k}=0$ maximum. The large g factor calculated by Pratt and Ferreira, however, is in agreement with tentative explanations of anomalous oscillatory magnetic effects in PbTe.

CONCLUSIONS

It has been shown that the inclusion of the relativistic terms in the Hamiltonian can be done in a straightforward manner in the context of the APW method. When these terms are included in the calculation of the energy bands and wave functions for PbTe, the resulting band structure requires only slight modification to bring it into agreement with the available experimental data. Furthermore, the wave functions obtained from such a calculation are sufficiently accurate to be used in perturbation calculations for electronic properties of the material which give good agreement with experimental measurements of these properties. This may be ranked, not only as a success for the techniques employed, but for the energy band approximation itself.

ACKNOWLEDGMENTS

We are grateful to the members of the Solid State and Molecular Theory Group at MIT and to Dr. L.G Ferreira for valuable assistance and suggestions during this work. We also wish to thank the staff of the Cooperative Computing Laboratory at MIT for their cooperation in preparing the numerical computations.

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[32] G. W. Pratt, Jr., and L. G. Ferreira, *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie, Paris, 1964).

[33] The calculation by Pratt and Ferreira has also led to the very significant conclusion that the interaction between nearest bands alone is not necessarily sufficient for a $\mathbf{k}\cdot\mathbf{p}$ calculation. This is especially true for PbTe, where this approximation gives very poor results for the effective masses, but where inclusion of the next nearest interacting band in the calculation gives quite good agreement with experiment.

[34] It has come to our attention since the completion of this work that L. Kleinman and P. J. Lin have arrived at a band structure for PbTe which is very similar to that reported here, by use of a pseudopotential calculation. Their work is reported in the *Proceedings of the International Conference on the Physics of Semiconductors* (Dunod Cie, Paris, 1964). K. F. Cuff, M. R. Ellett, C. D. Kuglin, and L. R. Williams have also arrived at an ordering of the energy levels at L, based on a $\mathbf{k}\cdot\mathbf{p}$ analysis of experimental data, which agrees with that proposed in this paper. Their work is reported in the proceedings of the same conference. Their value of the effective g factor agrees to within a factor of 2 with that obtained by Pratt and Ferreira (Ref. 32) using the results of this calculation.