Electronic Band Structure of Gray Tin*

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The electronic energy band structure including spin-orbit coupling effects has been calculated for semi-conducting gray tin. The orthogonalized plane-wave method has been used to obtain the energy eigenvalues at the symmetry points Γ, X, and L in the Brillouin zone and to compute the spin-orbit splittings at these points. It is found that both the conduction and valence band edges are at the center of the zone. The effective masses for electrons and holes are calculated using our crystal wavefunctions and the experimental value for the energy gap. The effect of pressure on the energy band structure is also investigated.

I. INTRODUCTION

THERE has been some experimental interest in gray tin since single crystals of sufficient purity became available.[1] The electrical measurements[2,3] indicate that gray tin is a semiconductor with very small thermal-energy gap, but other details about its electronic energy band structure, such as location of its band edges and electron and hole effective mass values, are not definitely known. Therefore, we have attempted a theoretical calculation of the band structure in the hope that the results may supplement and interpret any future experimental information.

The method we adopted is essentially the orthogonalized plane wave (OPW) method.[4] However, the OPW method alone as it has been used for the light elements[5] is not sufficient to provide a description of the band structure of gray tin because in this case the spin-orbit splitting is larger than the energy gap. The OPW method, however, can be used as a starting point from which the spin-orbit splittings can be obtained in the way described by Liu.[6]

In Sec. II we describe the OPW calculation and present the results we obtain for the valence and the lowest conduction states, at the symmetry points Γ $[k=[0,0,0]]$, X $[k=(2\pi/a)(1,0,0)]$ and L $[k=(2\pi/a)(\frac{1}{2},\frac{1}{2},\frac{1}{2})]$ of the reduced zone. In Sec. III we derive the spin-orbit splitting at these three symmetry points. In Sec. IV we relate the present band structure to the experimental information. The values of electron and hole effective masses are computed and compared with experiment. An estimate of the pressure effect on the band structure is also given.

II. OPW METHOD APPLIED TO GRAY TIN

Gray tin is the allotropic modification of crystalline tin which has the diamond structure. It has been shown[5] that the OPW method is suitable to study electronic states of covalent crystals with the diamond structure. We carry out detailed calculations of the band structure of gray tin by constructing a crystal potential as a sum of atomic potentials, where the exchange contribution is taken as an average exchange potential in the approximation described by Slater.[7] For reasons of consistency discussed in Ref. 5 we use atomic eigenvalues and wave functions which have also been computed using the Slater approximation for exchange.[8] A selected choice of the parameters required for the OPW calculation are given in Table I, the additional parameters required for the calculations at points of the Brillouin zone different from $k=0$ have been computed but are not given because they could be obtained by interpolation from Table I. The value of $V^S(0)$ to be used in the calculation can be defined as the space average of the potential decreased by the shift in energy of the atomic core state eigenvalues due to the potential of the other atoms of the lattice near the nucleus of a particular atom. The space average of the potential as computed from Woodruff's prescription[9] yields the value -2.042 Ry, the core shift obtained from a plot of the Coulomb potential is about ~ -0.030 Ry so that the computed value to be used for $V^S(0)$ would be -2.01 Ry, which we used in the present calculation. The diagonalization of the secular equations of the OPW method with the parameters given in Table I gives the results listed in Table II for the valence states and the lowest conduction states at the symmetry points of interest. To visualize the significance of the results of Table II we present in Fig. 1 the energy band profiles in the symmetry directions Δ and Λ obtained by using the compatibility

[1] A. W. Ewald and O. N. Tufte, J. Appl. Phys. 29, 1007 (1958).
[2] G. Bush, J. Wieland, and H. Zoller, Helv. Phys. Acta 23, 528 (1950); 24, 49 (1951); G. Bush and J. Wieland, *ibid.* 26, 697 (1953).
[3] A. W. Ewald and E. E. Kohnke, Phys. Rev. 97, 607 (1955).
[4] C. Herring, Phys. Rev. 57, 1169 (1940).
[5] F. Bassani and M. Yoshimine, Phys. Rev. 130, 20 (1963). This paper contains reference to earlier work.
[6] L. Liu, Phys. Rev. 126, 1317 (1962).

[7] J. C. Slater, Phys. Rev. 81, 385 (1951).
[8] F. Herman and S. Skillman, Bull. Am. Phys. Soc. 7, 214 (1962). The authors are grateful to Dr. Herman for providing them with the atomic self-consistent results for tin prior to publication.
[9] T. O. Woodruff, Phys. Rev. 103, 1159 (1956).

TABLE I. Orthogonality coefficients and Fourier constants of the crystal potential defined with the same conventions as in Ref. 5. Energy eigenvalues for the atomic core states are also given in the last row. All energies are expressed in Rydberg units.

| $|k+h|^2(a^2/4\pi^2)$	$A_{1s}(|k+h|)$	$-A_{2s}(|k+h|)$	$-iA_{2p}(|k+h|)$	$A_{3s}(|k+h|)$	$iA_{3p}(|k+h|)$	$A_{3d}(|k+h|)$	$-A_{4s}(|k+h|)$	$-iA_{4p}(|k+h|)$	$-A_{4d}(|k+h|)$	$V_{Total}(|h|)$
0	0.00192	0.01254	0	0.04780	0	0	0.17222	0	0	-1.0209
3/4	0.00192	0.01251	0.00053	0.04733	0.00631	0.00045	0.16286	0.06276	0.02947	...
1	0.00192	0.01251	0.00062	0.04718	0.00727	0.00060	0.15986	0.07117	0.03778	...
2	0.00192	0.01248	0.00087	0.04656	0.01016	0.00118	0.14844	0.09373	0.06510	...
11/4	0.00192	0.01246	0.00102	0.04610	0.01182	0.00160	0.14043	0.10430	0.08061	...
3	0.00192	0.01245	0.00106	0.04595	0.01231	0.00174	0.13786	0.10707	0.08502	-0.4957
4	0.00192	0.01243	0.00123	0.04535	0.01406	0.00229	0.12806	0.11547	0.09959	-0.4375
8	0.00191	0.01232	0.00172	0.04304	0.01904	0.00436	0.09532	0.12584	0.12696	-0.3193
11	0.00191	0.01224	0.00201	0.04139	0.02162	0.00578	0.07619	0.12272	0.13110	-0.2733
12	0.00191	0.01221	0.00210	0.04085	0.02234	0.00623	0.07064	0.12076	0.13095	-0.2615
16	0.00191	0.01211	0.00240	0.03877	0.02472	0.00792	0.05181	0.11069	0.12628	-0.2248
19	0.00191	0.01203	0.00260	0.03729	0.02611	0.00907	0.04058	0.10213	0.12051	-0.2044
	E_{1s}	E_{2s}	E_{2p}	E_{3s}	E_{3p}	E_{3d}	E_{4s}	E_{4p}	E_{4d}	
	-2069.1	-307.8	-288.8	-60.07	-52.09	-37.16	-9.761	-7.060	-2.526	
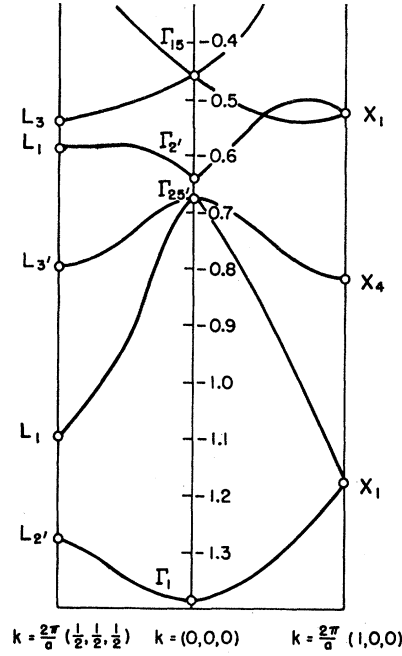
FIG. 1. Profiles of valence and conduction bands of gray tin in the directions Δ and Λ. The computed points are indicated by circles. Energies are in Rydbergs.

$k = \frac{2\pi}{a}(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ $k = (0,0,0)$ $k = \frac{2\pi}{a}(1,0,0)$

relations.[10] It may be noticed that the present band structure is very similar to the one obtained for Ge in the same approximation. However, the absolute minimum of the conduction band at $\Gamma_{2'}$ is now lower than the minimum at L_1 by a large enough value (about 0.05 Ry) to indicate that this may be the real situation in gray tin. Herman[11] previously reported a schematic band structure for gray tin, which he obtained from preliminary calculations and from extrapolation of the results for diamond and germanium. The essential features of his band structure are the same as the ones obtained here.

III. SPIN-ORBIT INTERACTION

The results of Table II are used to compute the spin-orbit splitting at the symmetry points following the procedure discussed in a previous paper.[6] We first compute the spin-orbit splitting of the atomic core states from the same atomic Coulomb potential used in Sec. II. Since the behavior of valence and conduction wavefunctions near the nuclei is given by their core parts, the spin-orbit splitting can be expressed in terms of the spin-orbit splittings of the core states. The results for both core states and higher energy states are given in Table III; the experimental results which are available are also listed. The comparison between the computed and experimental values of spin-orbit splittings is, in general, satisfactory except for the d states where there is a disagreement of a factor of about 2. We do not understand the reason for such a disagreement, which may be due to the neglect of exchange in

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[10] L. P. Bouckaert, R. Smoluchowski, and E. Wigner, Phys. Rev. 50, 58 (1936).
[11] F. Herman, J. Electron. 1, 103 (1955).

TABLE II. Eigenvalues (in Ry) and eigenvector coefficients for the valence states and the lowest conduction states. The eigenvector coefficients are listed for the symmetrized combination of OPW's in order of increasing wave numbers. The pertinent symmetrized combinations are given in Ref. 5.

	Γ_1	$L_{2'}$	X_1	L_1	X_4	$L_{3'}$	$\Gamma_{25'}$	$\Gamma_{2'}$	$L_1(2)$	L_3	$X_1(2)$	Γ_{15}
E	−1.386	−1.278	−1.174	−1.079	−0.818	−0.807	−0.671	−0.641	−0.594	−0.541	−0.527	−0.461
c_1	1.004	1.069	0.925	0.860	0.955	1.002	0.839	1.052	0.420	0.829	0.450	1.010
c_2	−0.556	−0.330	0.653	0.720	0.429	−0.212	0.648	0.807	−0.965	−0.467	−0.847	0.338
c_3	−0.159	0.312	0.176	0.159	0.059	0.225	0.127	−0.093	0.479	−0.035	−0.422	0.041
c_4	−0.043	−0.001	0.186	−0.043	−0.162	−0.197	−0.003	−0.063	0.217	0.477	0.020	0.103
c_5	0.027	−0.120	0.158	−0.116	0.085	−0.207	−0.153	−0.009	−0.055	0.354	0.278	−0.071
c_6	−0.005	0.104	−0.010	0.130	−0.011	0.152	−0.107		−0.021	−0.005	−0.050	0.025
c_7	−0.015	−0.007	0.094	0.067	0.022	−0.006	−0.031		−0.070	0.056	−0.025	−0.050
c_8		−0.050	0.047	−0.056	−0.085	−0.001	−0.027		−0.076	0.103	−0.066	−0.021
c_9		−0.007	0.026	0.019	−0.023	−0.057			0.024	−0.033	−0.035	
c_{10}		0.010	0.054	0.003	−0.025	0.092			0.031	−0.089	0.068	
c_{11}		−0.020	0.028	−0.024	−0.006	0.077			−0.004	−0.082	−0.033	
c_{12}		−0.007	−0.008	−0.023	−0.030	−0.010			−0.028	−0.012	−0.046	
c_{13}		0.006	−0.005	−0.004		−0.065			0.003	−0.052	−0.019	
c_{14}		0.005	0.006	0.017		−0.017			−0.013	−0.003	0.012	

the calculation of the spin-orbit integral

$$\zeta = (2m^2c^2)^{-1} \int (1/r)(\partial V/\partial r)\,|P_{nl}(r)|^2 dr. \quad (1)$$

This uncertainty in the splittings of the d states has, however, a negligible effect on the spin-orbit splittings of valence and conduction states because the contribution of the d core states to the valence and conduction wave functions are small and furthermore their spin-orbit splittings are much smaller than those of the corresponding p core states. The convergence of the spin-orbit splitting values as function of the number of plane waves used in the expansion of the crystal wave functions is satisfactory as was the case for Ge.[6]

IV. DISCUSSION AND COMPARISON WITH EXPERIMENTAL RESULTS

The agreement between the experimental energy gap (0.085 eV)[3] and the computed energy gap (0.2 eV) is satisfactory if we consider that the $\Gamma_{2'}$ state is very sensitive to the crystal potential and to the value of $V^S(0)$ in particular. It would be sufficient to take $V^S(0) = -2.03$ instead of our -2.01 to obtain a practically exact agreement without appreciable change in the other states because the other eigenvalues are much less sensitive to the details of the potential and to the value of $V^S(0)$. Another important point which has been brought to our attention by Herman,[12] is that other relativistic corrections besides the spin-orbit splitting may be of significance. He estimated[12] the mass-velocity correction and the s-shift correction to atomic valence states; he found that the energies of both s and p states are decreased, the s states having a larger shift (perhaps 1 eV larger). We have not attempted to include these corrections in a band calculation since the appropriate core states are not yet available. On the basis of the present results it appears that the minimum of the conduction band is at $\Gamma_{2'}$ and

[12] F. Herman (private communication).

recent magnetoresistance experiments[13] indicate that this is the case. Other experiments on Knight shift in gray tin powder[14] have been interpreted to indicate that the conduction band minimum cannot be at Γ because a small positive Knight shift is observed. The conduction electrons at Γ would have a large negative g value[15] and thus produce a negative Knight shift. We argue that the quoted experiment does not necessarily exclude that the conduction minimum be at Γ because it is not clear whether the experimental effect is due to electrons or holes, and furthermore, the temperature is large enough that conduction electrons may be raised to the second minimum at L.

Cardona and Greenway[16] observed peaks in the reflectivity, which they attribute to interband transitions at symmetry points. Our results are basically in agreement with their interpretation, but our computed energy for the $L_{3'} - L_1$ transition is 2.8 eV while the observed reflectivity peaks which they attribute to this transition are at 1.29 and 1.73 eV. The neglect of the relativistic shifts may be partly responsible for the disagreement and it is also possible that the observed peaks are due to $\Lambda_3 - \Lambda_1$ transitions as in the case of Ge.[17] The value of the spin-orbit splitting of 0.44 eV is in agreement with the value we computed at $L_{3'}$; we have not computed the value of the splitting along Λ_3 which should increase continuously from 0 to its value at $L_{3'}$.[18] The interpretation of the 3.65-eV peak as due

[13] E. D. Hinkley and A. W. Ewald, Bull. Am. Phys. Soc. 8, 245 (1963).
[14] W. E. Blumberg and J. Eisinger, Phys. Rev. 120, 1965 (1960). The authors are grateful to Dr. Y. Yafet for bringing this paper to their attention.
[15] L. M. Roth, B. Lax, and S. Zwerdling, Phys. Rev. 114, 90 (1959).
[16] M. Cardona and D. L. Greenway, Phys. Rev. 125, 1291 (1962).
[17] D. Brust, J. C. Phillips, and F. Bassani, Phys. Rev. Letters 9, 94 (1962).
[18] In Ref. 6 it was indicated that a crossover occurs in the Λ direction between the two states which split from Λ_3. The argument then given depends upon a particular approximation to the wave function and is not valid in general.

TABLE III. The calculated spin-orbit splittings of atomic states and several crystal states, expressed in Rydberg units. The corresponding experimental values for atomic core states are obtained from x-ray data[a] and that for the atomic $5p$ state is obtained from an analysis of spectroscopic data for the $5p^2 \, {}^3p$ configuration.[b] As in the case for atomic p states the states Γ_8 and $\Gamma_{8'}$ which have degeneracy 4 are higher than the original states $\Gamma_{25'}$ and Γ_{15} by $\frac{1}{3}$ of the spin-orbit splitting. At the point L instead the original states $L_{3'}$ or L_3 are midway between the two doubly degenerate states which are separated by the spin-orbit splitting.

	$2p$	$3p$	$4p$	$5p$	$3d$	$4d$	$\Gamma_{25'}$	Γ_{15}	L_3	$L_{3'}$
Calc.	15.7	2.88	0.524	0.0346	0.651	0.0830	0.0439	0.0362	0.0351	0.0310
Exptl.	16.7	3.10		0.0309	0.32	0.06				

[a] Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1950), 6th ed., Vol. I.
[b] C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D. C., 1952).

to an $X_4 - X_1$ transition is in agreement with the result of our calculation. It would be of great help to the final assignment of the reflectivity peaks to obtain their pressure dependence. We have decreased the lattice constant in our calculations by an amount $0.0265a$ and have found that relative to $\Gamma_{25'}$, the state $\Gamma_{2'}$ moves up by ~ 0.05 Ry and the conduction state L_1 by ~ 0.02 Ry while the conduction state X_1 is practically unchanged. To confirm the current interpretation of the reflectivity peaks, under the effect of pressure the peaks at 1.29 and 1.73 eV should shift toward higher energies much more than the peak at 3.65 eV.

From the results of Sec. II and Sec. III it is also possible to compute the effective masses of electrons and holes. The general formalism for the case of small energy gap zincblende compounds has been developed by Kane.[19] Let us consider the case of very low temperature and impurity content, when only a few states near $k=0$ are occupied by electrons and holes. Three effective masses can then be defined, one electron effective mass m_e^* corresponding to the minimum of the conduction band at $\Gamma_{2'}$ and two hole effective masses m_{hh}^* and m_{lh}^* corresponding to the maximum at $\Gamma_{25'}{}^{3/2}$. We can use the approximation

$$|k| \times |\langle \Gamma_{2'}|p_z|\Gamma_{25'}{}^{xy}\rangle|\hbar/m < E_g < \Delta, \qquad (2)$$

where E_g is the energy gap $\Gamma_{2'}-\Gamma_{25'}{}^{3/2}$ and Δ is the spin-orbit splitting $\Gamma_{25'}{}^{3/2}-\Gamma_{25'}{}^{1/2}$. The expressions for the effective masses become in the three-band model[19]:

$$\frac{1}{m_e^*}=\frac{1}{m}+\frac{2}{3}\frac{|\langle\Gamma_{2'}|p_z|\Gamma_{25'}{}^{xy}\rangle|^2}{m^2}\left(\frac{2}{E_g}+\frac{1}{E_g+\Delta}\right),$$

$$\frac{1}{m_{lh}^*}=\frac{1}{m}-\frac{4}{3}\frac{|\langle\Gamma_{2'}|p_z|\Gamma_{25'}{}^{xy}\rangle|^2}{m^2 E_g}, \qquad (3)$$

$$1/m_{hh}^*=1/m.$$

The nonzero matrix element of the momentum operator p_z can be estimated by considering only the plane-wave

part of the crystal wave functions. From the coefficients of Table II and the appropriate combinations of plane waves we obtain $|\langle\Gamma_{2'}|p_z|\Gamma_{25'}{}^{xy}\rangle|\simeq 0.78$ au. Using the experimental energy gap $E_g=0.085$ eV and the value given in Table III for the spin-orbit splitting Δ we obtain:

$$m_e^*/m\simeq 0.0036,$$

$$m_{lh}^*/m\simeq 0.0038.$$

The electron effective mass value recently measured by Hinkley and Ewald[18] from magnetoresistance experiments is about 5 times larger than the above value. Since the momentum matrix element is not sensitive to the details of the wave function we cannot understand the reason for such a discrepancy. Relativistic corrections to the effective mass formalism should introduce corrections to the effective mass but it is unlikely that these corrections could produce a difference of a factor of 5 in the final result. This point certainly deserves further investigation. It is also possible that the conduction state L_1 is really much closer to $\Gamma_{2'}$ than our results indicate in which case a number of electrons could populate the L_1 minimum. There would then be two additional electron effective masses at L_1, m_t^* and m_l^*. We have computed their values from the k.p. perturbation theory[20] as was previously done for Ge.[6] We obtain the values $m_t^*\simeq 0.1m$ and $m_l^*\simeq 1.6m$ using the results of Table II. The value of the momentum matrix element which occurs in m_t^* as computed from Table II is the same as that which Cardona and Greenway[16] inferred from the experimental data on InSb. They obtained $m_t^*=0.057m$ because they used the value 1.51 eV for the $L_{3'}-L_1$ energy difference instead of our computed value of 2.8 eV.

ACKNOWLEDGMENTS

[19] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).

[20] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).