Electronic structure of α-Sn and its dependence on hydrostatic strain

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The electronic structure of α-Sn is calculated within the local-density approximation. As a result of the inadequacies of this approximation for the description of excitation energies, the band structure is corrected to agree with energy differences at points of high symmetry by introducing additional external potentials on the atomic sites as well as on the interstitial positions of the diamond lattice. The resulting band structures are used to obtain effective masses as well as hydrostatic deformation potentials.

I. INTRODUCTION

The inverted band-structure model for α-Sn was first put forward by Groves and Paul.[1] In the Groves-Paul model, α-Sn is a semimetal (zero fundamental band gap) in which the ordering of the bands at Γ is Γ_{7v}^{+}, Γ_{7c}^{-}, Γ_{8vc}^{+}, increasing in energy, with the Fermi level lying at Γ_{8vc}^{+}. The $\mathbf{k}\cdot\mathbf{p}$ interaction[1] between the Γ_{7c}^{-} and one of the Γ_{8}^{+} levels gives the Γ_{8}^{+} band positive curvature. Two subsequent theoretical studies of the band structure, the nonlocal pseudopotential calculation of Chelikowsky and Cohen[2] and the relativistic orthogonalized-plane-wave calculation of Pollak *et al.*,[3] support the conjecture of Groves and Paul. In the present study the electronic structure of α-Sn is investigated self-consistently by the linear-muffin-tin-orbital (LMTO) method[4] within the local-density approximation (LDA) including the spin-orbit (SO) interaction as a perturbation. The treatment of relativistic effects, in particular the SO interaction, is essential to calculate accurate band structures for α-Sn.[5] We use the atomic-spheres approximation (ASA). Additional potentials are introduced in both the occupied and empty spheres in order to make up for the deficiencies of the LDA as discussed below.[6]

In Sec. II results for the band structure of the material with the equilibrium lattice constant are presented along with a discussion of the additional potentials. The energy levels at selected high-symmetry points are tabulated and are shown to agree well, in most cases, with previously published data. Section III contains a discussion of the band structure under hydrostatic strain. In Sec. IV we present the conclusions.

II. ENERGY BANDS

The calculations in this work are performed using the LMTO method[4] within the LDA including the SO interaction and empty spheres.[7] We include the combined-correction term in order to account for the overlap of the spheres.[4] It is well known[8] that LDA-based band-structure calculations on their own are inadequate to account for measured excitation energies in semiconductors. As a consequence of this inadequacy, the band gaps between valence and conduction bands are underestimated. In addition, the effective masses of all bands are in error.[6] The so-called scissors operator, which produces a rigid shift of the conduction bands, is an unsatisfactory solution to these problems as it does not correct the dispersion and thus leaves the effective masses in error. A solution to this problem is provided, within the microscopic theory, by the *GW* correction.[8] It is found that *GW* calculations give excitation energies close to the experimental values. The implementation of the *GW* correction, however, is computationally expensive. A semiempirical solution to the deficiency in the LDA mentioned above, adopted in this paper, is afforded by adding to the LDA potential V_{LDA} an extra potential V_{ext} localized at the spheres and possessing the full crystal symmetry. By varying the strengths and functional form of this potential in the empty and occupied spheres, control over the gaps is attained. V_{ext} is an additional, externally introduced potential which is included in the self-consistency iterations. We use the fact that the necessary gap corrections to be imposed on the LDA are known from experiment or more complete calculations such as those of Ref. 8.

We now describe the procedure by which the band structure is corrected. In Ref. 6 V_{ext} is composed of δ-like potentials $V_1 = V_o(R_o/r)\exp[-(r/R_o)^2]$, where r is the radial distance centered at each sphere. In the present work, V_1 is nonzero only in the occupied spheres. R_o is fixed at a small value and V_o is then adjusted for each distinct type of atom. Due to the δ-like nature of the potentials introduced in Ref. 6, mainly states possessing s character can be shifted by means of V_{ext}, i.e., via V_1, as it has hitherto been implemented.[6] Thus, in addition to V_1, potentials V_2 localized in the empty spheres growing rapidly toward the occupied spheres are introduced. V_2 is taken to be $V_2 = V_e(r/R_2)^{10}$ inside and zero outside the empty spheres where R_2 and $V_e > 0$ are parameters to be determined. This part of the potential should produce the necessary shift between bonding and antibonding wave functions of the valence and conduction bands, respectively, i.e., between wave functions of the same angular momentum, since the antibonding conduction-band wave functions have more weight towards (and in) the empty spheres than do the corresponding bonding valence-band

wave functions. In this way, the p-to-p gaps are adjusted, and the Γ_8^- and Γ_6^- bands attain their correct positions with respect to the top of the valence band. The form chosen above for V_2 is not unique; a potential able to affect the uncorrected wave functions having significant weight near the empty-sphere boundaries must be chosen. The strength of V_2 in our calculations achieves a maximum of 0.153 Hartrees at the edge of the empty spheres. Similar to the small modification to the wave functions effected by the GW correction,[8] V_2 also leads to only small changes in the wave function.

The correction V_1 on occupied sites depends on the atom occupying the sphere; however, preliminary calculations show that the correction V_2 on empty sites is at most only weakly dependent upon the material with the following *caveat*. A scaling of the correction V_2 must be carried out whenever the radius of the empty spheres changes, such as from material to material or upon the application of stress. We chose it such that

$$\int d^3r\, V_2(r) = C, \tag{1}$$

where C is a constant and the integration is over the empty-sphere volume. Calculations show that deformation potentials for Ge using Eq. (1) are in significantly better agreement with experiment than other LMTO calculations using V_1 in all spheres.[9] In addition, V_1 automatically obeys a similar relationship due to its high degree of localization at the occupied-sphere centers.[6] With the corrections V_1 and V_2 the energy levels at L and X as well as at Γ attain values close to those measured experimentally; however, we have found a systematic tendency for the effective masses calculated from the corrected band structures at Γ to be overestimated, whereas they are close to the measured values at L. The warping of the valence bands is also slightly larger than found experimentally.

Crudely adjusting the energy levels results in effective masses in rough agreement with experiment. Further refinement might be possible. If the energy levels and effective masses are correct, one expects the details of the band structure, the momentum matrix elements, and consequently the optical properties, also to be correct. The adjusted potentials can be used in calculating deformation potentials, both hydrostatic and uniaxial (the latter provided the nonsphericity of the potentials can be neglected),[10] and, because C appears to be only weakly dependent upon the material, to calculate the energy bands of heterostructures.

The corrected band structure of α-Sn is shown in Fig. 1 along with the double-group symmetry labels at points of high symmetry. The values of the parameters for V_{ext} used are listed in Table I. The energy levels at selected high-symmetry points are given in Table II along with results from the nonlocal-pseudopotential calculations of Cohen and Chelikowsky[2] and available experimental values. In addition, the uncorrected, i.e., with $V_{\text{ext}}=0$, energy levels are included. We see that several of the energy gaps are in significant error before correction, most notably the ordering of the levels Γ_{7v}^+ and Γ_{7v}^-. SO splittings

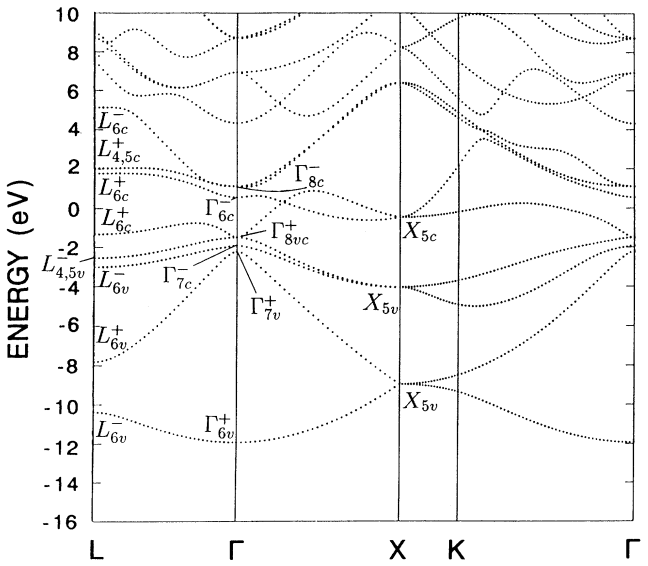

FIG. 1. Energy bands of α-Sn calculated with V_{ext} using the parameters of Table I.

and several other important energy differences calculated with the LMTO and nonlocal-pseudopotential methods as well as experimental results are also tabulated in Tables III and IV, respectively. We have not included the value $E(\Gamma_{8c}^-) = 2.72$ eV as given in Ref. 11 as it seems unreasonably high. Our adjustments are somewhat hampered by the lack of a complete and consistent set of experimental values for the energy gaps.

Selected effective masses are listed in Table V. We find that the effective masses at Γ are systematically higher than the experimental values. This is due to two reasons. First, the spherical charge symmetrization in the ASA leads to momentum matrix elements that are too small.[9] Second, our correction to the LDA is somewhat crude. We next consider the Luttinger parameters γ_1, γ_2, and γ_3 (Ref. 12) and momentum matrix elements (see Table VI[13]). The Luttinger parameters are calculated directly from the effective masses using

$$\frac{1}{m_{(100)}^{\text{LE,HH}}} = \gamma_1 \pm 2\gamma_2,$$

$$\frac{1}{m_{(111)}^{\text{LE,HH}}} = \gamma_1 \pm 2\gamma_3.$$

The superscript LE denotes light electrons. These states correspond to those which in cubic semiconductors with-

TABLE I. Best-fit correction-potential parameters in atomic units for α-Sn. The occupied- and empty-sphere radii are both 3.02 Bohr.

Occupied spheres:	$R_o = 0.015$ Bohr
	$V_o = 142$ Hartree
Empty spheres:	$R_2 = 2.7$ Bohr
	$V_e = 0.05$ Hartree

TABLE II. Selected energy levels in eV at points of high symmetry for α-Sn. The zero of energy is taken at the top of the valence band (Γ^+_{8vc}). The column labeled LDA contains values of the energy levels obtained self-consistently with $V_{\rm ext}=0$. The values in the column labeled "Corrected" include the additional potentials in $V_{\rm ext}$ using the parameters listed in Table I.

Level	LDA	Corrected	Nonlocal Pseudopotential[a]	Experiment
$E(\Gamma^+_{6v})$	−10.978	−10.432	−11.34	
$E(\Gamma^+_{7v})$	−0.744	−0.726	−0.80	−0.8[b]
$E(\Gamma^-_{7c})$[c]	−1.280	−0.406	−0.42	−0.413,[d] −0.634[e]
$E(\Gamma^-_{6c})$	+1.740	+2.055	+2.08	+1.98[d]
$E(\Gamma^-_{8c})$	+2.299	+2.610	+2.66	+2.48[d]
$E(\Gamma^+_{8vc})$	0.000	0.000	0.000	
$E(X_{5v})$	−7.961	−7.465	−7.88	
$E(X_{5v})$	−2.765	−2.560	−2.75	
$E(X_{5c})$	+0.569	+1.030	+0.90	
$E(L^-_{6v})$	−9.406	−8.880	−9.44	
$E(L^+_{6v})$	−6.749	−6.301	−6.60	
$E(L^-_{6v})$	−1.621	−1.508	−1.68	
$E(L^-_{4,5v})$	−1.148	−1.042	−1.20	
$E(L^+_{6c})$	−0.434	+0.175	+0.14	+0.115,[f] +0.09,[g] +0.092[h]
$E(L^+_{6c})$	+2.912	+3.288	+3.48	
$E(L^+_{4,5c})$	+3.150	+3.537	+3.77	
$E(L^-_{6c})$	+6.332	+6.637		

[a] From Ref. 2.
[b] Estimated from the energy splitting at L in Ref. 16.
[c] $E(\Gamma^-_{7c})\equiv E_0$.
[d] From Ref. 16.
[e] From Ref. 27.
[f] From Ref. 28.
[g] From Ref. 29.
[h] From Ref. 30.

out an inverted band structure are called light holes. HH stands for heavy hole. We find

$$\gamma_1=\frac{1}{2}\left(\frac{1}{m^{\rm HH}_{(111)}}+\frac{1}{m^{\rm LE}_{(111)}}\right)=-12.00,$$

$$\gamma_2=\frac{1}{4}\left(\frac{1}{m^{\rm LE}_{(100)}}-\frac{1}{m^{\rm HH}_{(100)}}\right)=-8.45,$$

$$\gamma_3=\frac{1}{4}\left(\frac{1}{m^{\rm LE}_{(111)}}-\frac{1}{m^{\rm HH}_{(111)}}\right)=-6.84.$$

(Alternatively, $\gamma_1=\frac{1}{2}[(m^{\rm HH}_{(100)})^{-1}+(m^{\rm LE}_{(100)})^{-1}]=-12.14$.) The signs of the Luttinger parameters have been chosen to conform with the standard convention. [In our discussion of the effective masses and momentum matrix elements, we use atomic units, i.e., $m_0=e=\hbar=1$, energy

TABLE III. Spin-orbit splittings in eV for α-Sn. The column labeled LDA contains values of the energy levels obtained self-consistently with $V_{\rm ext}=0$. The values in the column labeled "Corrected" include the additional potentials in $V_{\rm ext}$ using the parameters listed in Table I.

Splitting	LDA	Corrected	Nonlocal Pseudopotential[a]	Experiment
$\Delta_0(\Gamma^+_{8vc}-\Gamma^+_{7v})$	0.744	0.726	0.80	0.8[b]
$\Delta_1(\Lambda_{4,5v}-\Lambda_{6v})$	0.483	0.472	0.48[c]	0.482[d]
$\Delta'_0(\Gamma^-_{8c}-\Gamma^-_{6c})$	0.559	0.555	0.58	0.300,[d] 0.50[e]
$\Delta'_1(L^+_{4,5c}-L^+_{6c})$	0.238	0.250	0.29	0.228[d]

[a] From Ref. 2.
[b] Estimated from the energy splitting at L in Ref. 16.
[c] Actually the energy splitting at L in Ref. 2.
[d] Reference 11.
[e] From energy levels given in Ref. 16 as listed in Table II.

TABLE IV. Other energy gaps in eV for α-Sn. The values in the column labeled "Corrected" include the additional potentials in V_{ext} using the parameters listed in Table I.

Gap	Corrected	Nonlocal Pseudopotential [a]	Experiment
$E(\Lambda_{6c}-\Lambda_{4,5v})=E_1$	1.209		1.316[b]
$E(\Lambda_{6c}-\Lambda_{6v})=E_1+\Delta_1$	1.681		1.798[b]
$E(\Gamma_{6c}^--\Gamma_{8vc}^+)=E_0'$	2.055	2.08	1.98,[c] 2.25[d]
$E(\Gamma_{8c}^--\Gamma_{8vc}^+)=E_0'+\Delta_0'$	2.610	2.66	2.48[c]
$E(\Delta_{6c}-\Delta_{7v})$	3.040		2.94[b]
$E(X_{5c}-X_{5v})=E_2$	3.590	3.65	3.681[b]
$E(L_{6c}^+-L_{4,5v}^-)=E_1'$	4.330	4.68	4.28[b]
$E(L_{4,5c}^+-L_{4,5v}^-)=E_1'+\Delta_1'$	4.579	4.97	4.51,[b] 4.8,[d] 4.20,[d] 4.4,[e] 4.39[f]
$E(L_{4,5c}^+-L_{6v}^-)$	5.045	5.45	4.89[f]

[a] From Ref. 2.
[b] From Ref. 11.
[c] From Ref. 16.
[d] From Ref. 31.
[e] From Ref. 32.
[f] From Ref. 33.

in Hartree units, and Luttinger parameters in units of $\hbar^2/(2m_0)$.]

The momentum matrix elements P and Q are defined as

$$P=i\langle\Gamma_{25',x}^v|p_x|\Gamma_{2'}\rangle,$$
$$Q=i\langle\Gamma_{25',x}^v|p_y|\Gamma_{15,z}^c\rangle$$

using single-group notation. (The phases of the wave functions which correspond to the values of the matrix elements given here are defined in Fig. 1 of Ref. 9.) From $\mathbf{k}\cdot\mathbf{p}$ theory, P and Q are related to the $\mathbf{k}\cdot\mathbf{p}$ parameters F and M by[13–17]

$$F=-\frac{2P^2}{E_0},$$
$$M=H_1+H_2,$$
$$H_1=-\frac{2Q^2}{E_0'+\frac{2}{3}\Delta_0'},$$
$$q=-\frac{2}{9}H_1\frac{\Delta_0'}{E_0'+\frac{2}{3}\Delta_0'},$$
$$\kappa=-\frac{1}{6}(F-G-M)-\frac{1}{3}-\frac{9}{4}q,$$
$$G=-2\frac{\sum_j^{\Gamma_{12'}}|\langle x|p_x|u_j\rangle|^2}{E_{\Gamma_{12}'}}.$$

The energies are referred to as Γ_{8vc}^+. See also the definitions of E_0, E_0', and Δ_0' in the tables. The $\mathbf{k}\cdot\mathbf{p}$ parameters are related to the Luttinger parameters by[16,17]

$$\gamma_1=-\frac{1}{3}(F+2G+2M)-1+\frac{1}{2}q,$$
$$\gamma_2=-\frac{1}{6}(F+2G-M)-\frac{1}{2}q, \quad (2)$$
$$\gamma_2-\gamma_3=-\frac{1}{6}(3G-2M)-q.$$

Since we do not include f orbitals in our LMTO calculation, we take $H_2=0$, i.e., the $\mathbf{k}\cdot\mathbf{p}$ coupling to the high-energy f-like Γ_{25} band is neglected. We find $F=46.366$ and $P=0.588$. We also have $M=-5.48$, $q=0.279$, $Q=0.494$, and $G=-0.992$. The value of q is close to that calculated in Ref. 13. A formula for the inverse mass of the split-off valence band can be obtained by noting that this quantity is essentially γ_1 modified by the appropriate gap in F, G, and M,[15] and including the effect of q.[17] One finds

$$\frac{1}{m^{\text{SO}}}=1+\frac{1}{3}\left(\frac{E_0F}{E_0+\Delta_0}+\frac{2E_{\Gamma_{12}'}G}{E_{\Gamma_{12}'}+\Delta_0}+\frac{2(E_0'+\frac{2}{3}\Delta_0')M}{E_0'+\frac{2}{3}\Delta_0'+\Delta_0}\right)+q. \quad (3)$$

$E_{\Gamma_{12}'}$, not given in the tables, is $E_{\Gamma_{12}'}(\Gamma_8^-)=8.435$ eV. Solving Eq. (3) for F, we can check our numerical band-structure results for consistency by comparing with the value of F obtained from Eq. (2). We find from Eq. (3) that $P=0.555$, representing a deviation of ~ 6 % between the two values of P. This indicates that the $\mathbf{k}\cdot\mathbf{p}$ theory, including the bands mentioned above as intermediate states, has a minor difficulty in fitting the numerical results for α-Sn. A possible explanation is that the SO band, lying lower in energy than Γ_{8vc}^+, has a slightly stronger $\mathbf{k}\cdot\mathbf{p}$ coupling to the $4d$ core levels. This effect has not been included in the parameters above. Considering the energy difference involved, however, the effect does not appear to be large enough to account for the entire discrepancy.

III. DEFORMATION POTENTIALS

The absolute hydrostatic deformation potential is defined as the logarithmic volume derivative of a given en-

ergy level with respect to an absolute energy reference, (discussed next) while relative hydrostatic deformation potentials are given by the logarithmic volume derivative of band gaps and splittings at constant temperature. Usual optical experiments measure energy gaps and splittings and thus only relative deformation potentials are directly accessible by these means. Nevertheless, absolute deformation potentials have important implications as discussed in Ref. 18. Our absolute deformation potentials are obtained using as the energy zero the reference of the LMTO-ASA energy scale, where the potential outside a single atomic sphere with charge Q is Q/r, with r here the distance from the sphere center.[19] The ones relevant to scattering by longitudinal phonons in transport effects must actually be referred to the dielectric midgap energy (DME).[19] In order to convert the values of Table VII to those referred to the DME, one must add to them 5.9 eV.[19]

Selected absolute and relative hydrostatic deformation potentials are listed in Table VII together with calculated values from Refs. 19 and 20. The data in the literature are rather sparse, so a critical examination of our values is difficult. One notes, however, qualitative agreement for the absolute hydrostatic deformation potentials closest to the Fermi level of the three levels at Γ with the calculations of Ref. 20 which were obtained using the

TABLE V. Effective masses from the corrected band structures in units of the free-electron mass m_0 for α-Sn.

	This work	Experiment
Electrons		
Γ_{8vc}^{+} (Light electrons)		
$m_{(100)}^{\mathrm{LE}}$	0.0344	0.0233[a]
$m_{(110)}^{\mathrm{LE}}$	0.0377	0.0244,[a]0.028[b]
$m_{(111)}^{\mathrm{LE}}$	0.0389	0.0251[a]
L_{6c}^{+} (Heavy electrons)[c]		
$m_{\mathrm{DOS}}^{\mathrm{d}}$	0.202	0.21[e]
$m_{\mathrm{opt}}^{\mathrm{f}}$	0.109	0.13,[g]0.15[h]
$m_{\parallel}^{\mathrm{HE}}$	1.478	
$m_{\perp}^{\mathrm{HE}}$	0.075	
Holes		
Γ_8^+		
$m_{(100)}^{\mathrm{HH}}$	0.2102	
$m_{(110)}^{\mathrm{HH}}$	0.3996	0.195,[h]0.26[g]
$m_{(111)}^{\mathrm{HH}}$	0.5974	
Γ_7^-		
$m_{(100)}^{\Gamma_7^-}, m_{(110)}^{\Gamma_7^-}, m_{(111)}^{\Gamma_7^-}$	0.087	0.058[b]
Γ_7^+		
$m_{(100)}^{\mathrm{SO}}, m_{(110)}^{\mathrm{SO}}, m_{(111)}^{\mathrm{SO}}$	0.051	0.041[b]
Valence bands at L		
Longitudinal masses, $m_{\parallel}$ (111)		
$L_{4,5v}^{-}$	0.5361	
L_{6v}^{-}	0.5361	
Transverse masses, $m_{\perp}$		
$L_{4,5v}^{-}$	0.1149	
L_{6v}^{-}	0.1688	

[a]From Ref. 27.

[b]An average value from Ref. 16.

[c]L_{6c}^{+} refers here to the L_{6c}^{+} level 0.175 eV above Γ_{8vc}^{+}.

[d]$m_{\mathrm{DOS}} = \sqrt[3]{m_{\parallel}^{\mathrm{HE}} m_{\perp}^{\mathrm{HE}} m_{\perp}^{\mathrm{HE}}}$.

[e]From Ref. 30.

[f]$m_{\mathrm{opt}} = 3\left(\frac{2}{m_{\perp}^{\mathrm{HE}}} + \frac{1}{m_{\parallel}^{\mathrm{HE}}}\right)^{-1}$.

[g]Directional average from Ref. 28.

[h]Directional average from Ref. 16.

TABLE VI. Luttinger parameters, momentum matrix elements, and $\mathbf{k}\cdot\mathbf{p}$ parameters (in atomic units) obtained from the energy levels and effective masses of Tables II and V, respectively, compared with published values.

	This work	Other work[a]
γ_1	-12.00	-14.97
γ_2	-8.45	-10.61
γ_3	-6.84	-8.52
F	+46.366,+41.23[b]	
M	-5.48	
q	0.279	0.30
κ	-9.77	-11.84
G	-0.992	
P	+0.588,+0.555[b]	
Q	+0.494	

[a]From Ref. 13.
[b]From the split-off band.

empirical-pseudopotential method. Preliminary calculations of hydrostatic deformation potentials for Ge using the present method of correcting the band structure indicate that the calculated deformation potentials are more accurate than those having a V_1-like potential also in the empty spheres.[9]

TABLE VII. Selected deformation potentials in eV for α-Sn under hydrostatic strain. The values in the column labeled "This work" include V_{ext} as determined from the corrected band structure. 5.9 eV must be added to the absolute deformation potentials in order to obtain them within the DME model (Ref. 19).

	This work	Other calc.
$\frac{dE(\Gamma_{7c}^{-}-\Gamma_{8vc}^{+})}{d\ln V}$	-7.04	
$\frac{dE(L_{6c}^{+}-\Gamma_{8vc}^{+})}{d\ln V}$[a]	-2.14	-1.89[b]
$\frac{dE(\Gamma_{6c}^{-}-\Gamma_{8vc}^{+})}{d\ln V}$	-0.514	
$\frac{dE(X_{5c}-\Gamma_{8vc}^{+})}{d\ln V}$	+1.11	
$\frac{dE(L_{6c}^{+}-L_{45v}^{-})}{d\ln V}$[a]	-3.76	
$\frac{dE(X_{5c}-X_{5v})}{d\ln V}$	-2.46	
$\frac{dE(\Gamma_{8vc}^{+})}{d\ln V}$	-7.77	-3.3[c]
$\frac{dE(\Gamma_{7c}^{-})}{d\ln V}$	-14.81	-13.7[c]
$\frac{dE(\Gamma_{8c}^{-})}{d\ln V}$	-8.41	-5.8[c]
$\frac{d\Delta_0(\Gamma_{8vc}^{+}-\Gamma_{7v}^{+})}{d\ln V}$	-0.36	
$\frac{d\Delta_0'(\Gamma_{8c}^{-}-\Gamma_{6c}^{-})}{d\ln V}$	-0.12	
$\frac{d\Delta_1(\Lambda_{45v}-\Lambda_{6v})}{d\ln V}$	-0.24	
$\frac{d\Delta_1'(L_{45c}^{+}-L_{6c}^{+})}{d\ln V}$	+0.08	
$\frac{dE(L_{45c}^{+}-\Gamma_{8vc}^{+})}{d\ln V}$	-0.52	
$\frac{dE(L_{6c}^{-}-\Gamma_{8vc}^{+})}{d\ln V}$	-0.41	

[a]L_{6c}^{+} refers here to the L_{6c}^{+} level 0.175 eV above Γ_{8vc}^{+}.
[b]From Ref. 19.
[c]From Ref. 20.

Insight into the deformation potential for the SO splitting $d\Delta_0(\Gamma_{8vc}^{+}-\Gamma_{7v}^{+})/d\ln V$ for α-Sn can be gained by a comparison with Ge. In Ref. 21 it was found that simple scaling arguments[22] fail to give a good estimate of this quantity and overestimate the deformation potential by a factor ~ 4. The reason for this is that the valence-electron density near the core is not affected by volume changes to the degree implied by the simple scaling arguments. Self-consistent band-structure calculations beginning with free-atomic potentials gave the value -0.17 eV, in reasonable agreement with experiment. One notes, however, that in Ref. 23 this deformation potential was found to be $+0.02$ eV, also starting with free-atomic potentials.

Finally we comment on the deformation potential for the SO splitting $d\Delta_1'(L_{45c}^{+}-L_{6c}^{+})/d\ln V$.[24,25] As a rule of thumb, $d\Delta_{0,1}/d\ln V \approx -0.5$ eV.[25] The agreement with this rule is not bad, except for the case of $d\Delta_1'(L_{45c}^{+}-L_{6c}^{+})/d\ln V = +0.08$ eV which shows strong deviation from that rule, both in sign and magnitude. In Ge the value $+0.067$ eV was obtained.[26] Experimental results for this deformation potential were not available. It is possible that the small value is related to the admixture of higher d orbitals into the conduction-band wave functions.

IV. CONCLUSIONS

We have presented results for the band structure of α-Sn calculated using the LMTO method including corrections for the inadequacies of the LDA. Additional potentials V_2 on the empty spheres were introduced in order to be able to adjust calculated energy gaps possessing significant p-to-p character. After the introduction of this potential, band structures in good agreement with empirical pseudopotential calculations were obtained. The effective masses are overall in agreement with experiment. Having obtained reasonable values of the energy gaps and effective masses, one also expects reasonable values for the optical matrix elements and hence the dielectric function.

Total-energy calculations in the LDA have recently been carried to obtain the structural parameters of Sn under hydrostatic pressure.[34] The introduction of the external potential V_{ext} is not expected to improve the agreement with the experimental data in this regard. A better route to more accurately calculate energetically global properties, such as cohesive parameters, is via the GW approach[8]—not in the average way carried out here. For calculating energetically more local properties, such as optical spectra, the present approach is of considerable utility.

Selected deformation potentials under hydrostatic strain are presented. Due to the sparcity of data with which to make a comparison, it is difficult to evaluate the accuracy of calculated values; however, based on calculations for Ge (Ref. 26) we expect the hydrostatic deformation potentials obtained here to be more accurate than previous LMTO results. The Ge results[26] also supports

the conjecture that the potential V_2 on empty spheres obeys the scaling law of Eq. (1). In addition, because calculations show that C does not depend strongly on material, the potential V_{ext} can be used in the empty spheres at heterojunctions, for both lattice-matched and pseudomorphic structures.

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[1] S. Groves and W. Paul, Phys. Rev. Lett. **11**, 194 (1963).

[2] J. R. Chelikowsky and M. L. Cohen, Phys. Rev. B **14**, 556 (1976).

[3] F. H. Pollak, M. Cardona, C. W. Higginbotham, F. Herman, and J. P. Van Dyke, Phys. Rev. B **2**, 352 (1970).

[4] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).

[5] See, for example, F. Herman in *Proceedings of the International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod, Paris, 1964), pp. 3–22.

[6] N. E. Christensen, Phys. Rev. B **30**, 5753 (1984).

[7] T. Jarlborg and A. J. Freeman, Phys. Lett. **74A**, 349 (1979); D. Glötzel, B. Segall, and O. K. Andersen, Solid State Commun. **36**, 403 (1980); G. B. Bachelet and N. E. Christensen, Phys. Rev. B **31**, 879 (1985).

[8] M. S. Hybertsen and S. G. Louie, Phys. Rev. B **34**, 5390 (1986).

[9] U. Schmid, N. E. Christensen, and M. Cardona, Phys. Rev. B **41**, 5919 (1990).

[10] L. Brey, N. E. Christensen, and M. Cardona, Phys. Rev. B **36**, 2638 (1987).

[11] L. Viña, H. Höchst, and M. Cardona, Phys. Rev. B **31**, 958 (1985).

[12] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[13] P. Lawaetz, Phys. Rev. B **4**, 3460 (1971).

[14] M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988).

[15] M. Cardona, J. Phys. Chem. Solids **24**, 1543 (1963); **26**, 1351 (1965); in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3.

[16] S. H. Groves, C. R. Pidgeon, A. W. Ewald, and R. J. Wagner, J. Phys. Chem. Solids **31**, 2031 (1970).

[17] K. Suzuki and J. C. Hensel, Phys. Rev. B **9**, 4184 (1974).

[18] J. A. Vergés, D. Glötzel, M. Cardona, and O. K. Andersen, Phys. Status Solidi B **113**, 519 (1982).

[19] M. Cardona and N. E. Christensen, Phys. Rev. B **35**, 6182 (1987); N. E. Christensen, I. Gorczyca, O. B. Christensen, U. Schmid, and M. Cardona, J. Cryst. Growth **101**, 318 (1990).

[20] A. Blacha, H. Presting, and M. Cardona, Phys. Status Solidi B **126**, 11 (1984).

[21] P. J. Meltz and I. B. Ortenburger, Phys. Rev. B **3**, 3257 (1971).

[22] D. Brust and L. Liu, Solid State Commun. **4**, 193 (1966).

[23] G. C. Wepfer, T. C. Collins, and R. N. Euwema, Phys. Rev. B **4**, 1296 (1971).

[24] A. Blacha, M. Cardona, N. E. Christensen, and S. Ves, Solid State Commun. **43**, 183 (1982).

[25] F. Cerdeira, J. S. DeWitt, U. Rössler, and M. Cardona, Phys. Status Solidi **41**, 735 (1970).

[26] T. Brudevoll, D. S. Citrin, M. Cardona, and N. E. Christensen (unpublished).

[27] B. L. Booth and A. W. Ewald, Phys. Rev. **168**, 805 (1968).

[28] R. J. Wagner and A. W. Ewald, J. Phys. Chem. Solids **32**, 697 (1971).

[29] G. A. Busch and R. Kern, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1960), Vol. 11, p. 1.

[30] C. F. Lavine and A. W. Ewald, J. Phys. Chem. Solids **32**, 1121 (1971).

[31] T. Hanyu, J. Phys. Soc. Jpn. **31**, 1738 (1971).

[32] M. Cardona and D. L. Greenway, Phys. Rev. **125**, 1291 (1961).

[33] M. Cardona, P. McElroy, F. H. Pollak, and K. L. Shaklee, Solid State Commun. **4**, 319 (1966).

[34] N. E. Christensen and M. Methfessel, Phys. Rev. B **48**, 5797 (1993).