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First-principles theory of tetrahedral bonding and crystal structure of lead

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From linear muffin-tin-orbital calculations using suitable basis sets we derive, from first principles, sp^3 bonding characteristics for group-IV elements. Particular attention is paid to lead, for which the importance of relativistic effects in determining the most stable structure is examined. The mass-velocity shift of the Pb 6s state is so large that the s-p hybridization in a hypothetical diamond structure is too weak to allow the formation of sufficiently strong sp^3 bonding. Omission of relativistic effects would make the diamond structure of Pb more stable than the observed (fcc).

I. INTRODUCTION

The elements in the fourth group of the periodic table are characterized by their tendency to crystallize in structures stabilized by strong covalent bonds. Carbon is apparently most stable in the graphite structure. The free energy, however, of graphite is only slightly lower ($\simeq 1$ mRy difference) than that of diamond.[1] The metastable diamond, which energetically is separated from graphite by a large barrier, is characterized by strong tetrahedral bonds. This, and the occurrence of the diamond structure for Si, Ge, and α-Sn is due to the fact that the outer electronic s and p states are sufficiently close in energy to allow an $s^2p^2 \rightarrow sp^3$ transfer favoring a strong tetrahedral bonding. The covalency of the bond, however, decreases with increasing row number, and simultaneously the metallicity increases. Tin (α-Sn) is almost unstable in the diamond structure, and it easily transforms to the β-Sn structure. Lead, at the bottom of group IV, assumes at ambient conditions the fcc structure. The reason for this is usually ascribed to relativistic effects.[2] In Pb these lower the 6s states so much below the 6p states that the sp^3 hybridization in the diamond structure is too weak to cause the formation of sufficiently strong bonds. In the present work we show, by quantitative first-principles calculations, that this picture is correct. We show that a *nonrelativistic* theory predicts that Pb is more stable in the diamond structure than in the fcc structure. The bonding in the diamond structure is examined by nonrelativistic as well as fully relativistic calculations of sp^3 character and "metallicity." Further, we calculate the total energy versus volume for Pb in the diamond β-Sn, hcp, bcc, and fcc structure. In the case of hcp we optimize the c/a ratio, and examine the fcc → hcp pressure-induced phase transition.

II. CALCULATED sp^3-CHARACTER AND METALLICITY

An estimate of the relativistic shifts of the s-p separation in the band structure of Pb may be obtained from atomic calculations.[3] The mass-velocity correction causes downshifts of the 6s and 6p states by 0.68 and 0.08 Ry, respectively. The Darwin shift of the 6s level is 0.37 Ry (towards higher energies). Thus, the relativistic effects increase the 6s-6p separation E_{sp} in the atom by 0.23 Ry ($\sim$3.13 eV). The nonrelativistic value of E_{sp} is $\simeq$0.46 Ry which is very close to the 5s-5p separation, 0.47 Ry, in Sn. The bonding properties of lead would therefore be similar to those of Sn if relativistic effects could be neglected.

In order to study the bond more quantitatively, we calculate the sp^3 character. The self-consistent band structure is calculated within the local-density approximation[4] by means of the linear-muffin-tin-orbital (LMTO) method,[5] and we use a basis consisting of orthogonal orbitals.[6,7] These (i.e., the s and p states) are then used in construction of atom-centered sp^3 hybrids,[8] and the bonding (B) and antibonding (AB) portions are projected out, and we use the bond order $b \equiv$B-AB to characterize the "strength" of the sp^3 bonding in diamondlike crystals. Chemical trends of the bonding properties of the semiconductors are conveniently examined in a simple tight-binding (TB) model.[9] It is possible to transform the LMTO exactly to a TB scheme by using[6,7] the most localized orbitals as basis functions. This would lead[8] to a 36×36 Hamiltonian, but for the purposes of the present work, where the band structures need not be very accurate in detail, the basis set can be reduced to four on each atomic site (one s and three p states). Thus our TB scheme is formally equivalent to Harrison's model with an 8×8 Hamiltonian. The difference between our TB and that of Ref. 9 is that we express the matrix elements in terms of the band-center ($\bar{C}$) and bandwidth ($\bar{\Delta}$) potential parameters[6,7] derived from the first-principles LMTO calculations, whereas Harrison's scheme uses atomic energy levels and semiempirical scaling laws.

The approximate 8×8 TB Hamiltonian has the diagonal matrix elements E_p and E_s (corresponding to ε_p and ε_s in Ref. 9):

$$E_{s(p)} = \bar{C}_{s(p)} + \bar{\Delta}_{s(p)} \bar{S}^{\mathrm{on}}_{s(p)} , \tag{1}$$

and the off-diagonal elements are of the form

$$\begin{aligned} V_{ss} &= 4\sqrt{\bar{\Delta}_s}\,\bar{S}_{ss}\sqrt{\bar{\Delta}_s} , \\ V_{xx} &= 4\sqrt{\bar{\Delta}_p}\,\bar{S}_{xx}\sqrt{\bar{\Delta}_p} , \end{aligned} \tag{2}$$

and similar sx, xy, xz, yz elements. In (1) $\bar{S}^{\mathrm{on}}$ are the on-

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TABLE I. Calculated values of the *s*-*p* separation, bond-formation/promotion-energy ratio [δ, Eq. (3)], metallicity (α_m), and sp^3 bond order (b) [α_m (WAH) is from Ref. 9].

	E_p-E_s (eV)	δ	α_m	α_m(WAH)	b
C	8.73	2.60	0.37	0.34	0.760
Si	8.59	1.39	0.76	0.66	0.687
Ge	10.17	1.10	0.99	0.81	0.670
Sn	8.88	1.03	1.06	0.87	0.660
Pb	10.32	0.65	1.95	···	0.548
NR-Pb	7.14	0.99	1.14	···	0.639

site screened structure constants, and $\bar{S}_{ss}$, $\bar{S}_{xx}$, $\bar{S}_{sx}$, etc. are the screened nearest-neighbor *s*-*s*, *p*-*p*, and *s*-*p* structure constants. These, and the potential parameters ($\bar{\Delta}$ and $\bar{C}$) are described in detail in Ref. 7. Once the connection from the standard LMTO scheme to the formal 8×8 TB has been established, we can derive first-principles values of the metallicity, α_m, as defined in Ref. 9, the ionicity of compounds,[8] or to polarities.[8,9] Apart from α_m, we shall here examine trends in the ratio between the *bond-formation energy* and the $s^2p^2 \rightarrow sp^3$ promotion energy.

For the homopolar semiconductors this ratio is calculated as

$$\delta \equiv \frac{-4h}{E_p-E_s}\ , \tag{3}$$

where E_p and E_s are given by (1), and h is the sp^3 hopping integral of the TB Hamiltonian $\bar{H}^{(1)}$

$$h=\tfrac{1}{4}\langle s+p_x+p_y+p_z\,|\,\bar{H}^{(1)}\,|\,s-p_x-p_y-p_z\rangle\ . \tag{4}$$

In Table I we list the calculated values of these quantities together with the sp^3 bond order b. Also, we include the metallicity values α_m (WAH) given in Ref. 9. Our α_m values are slightly larger than α_m (WAH), reflecting the well-known fact that the local-density scheme gives gap values[8] too small for the semiconductors. Except for the last row [NR(nonrelativistic)-Pb], where all relativistic effects are omitted, the calculations are derived from the relativistic LMTO method. It is clearly seen that the relativistic effects dramatically increase the promotion energy in lead, making the formation of sp^3 bonds unfavorable in that case. The previously mentioned similarity with the sp^3 character in NR-Pb and Sn also follows from the b values given in Table I.

III. TOTAL ENERGY CALCULATIONS

The large relativistic effects found in the bonding parameters of Pb in the previous section also appear in the total-energy curves. In Fig. 1 we show the volume variation of the total energy of NR-Pb in the fcc, β-Sn, and diamond structures. It is interesting to note that the minimum of the diamond curve is the lowest; i.e., without relativistic correction Pb is more stable in the diamond structure than in fcc. This again agrees with the great similarity between NR-Pb and α-Sn. In contrast to Sn, however, the β-Sn structure for NR-Pb has a large energy, i.e., NR-Pb under pressure would not go from $B3$ to the

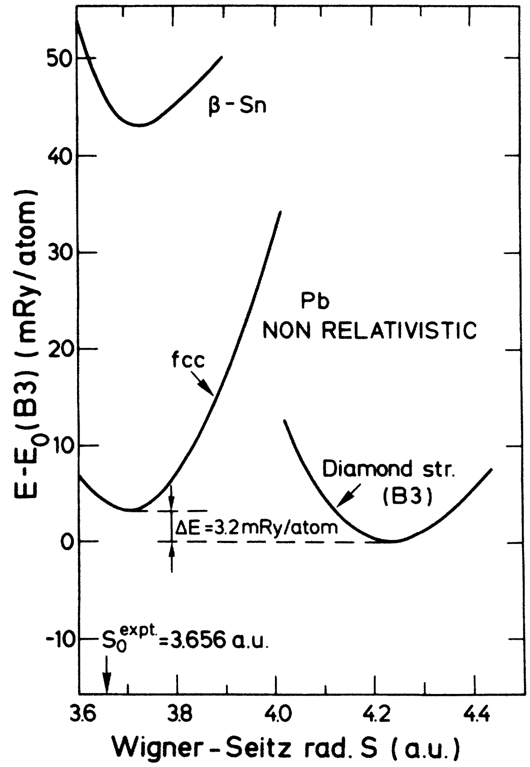

FIG. 1. Total-energy variations (local-density approximation) calculated nonrelativistically for Pb in the fcc, diamond, and the β-Sn structures.

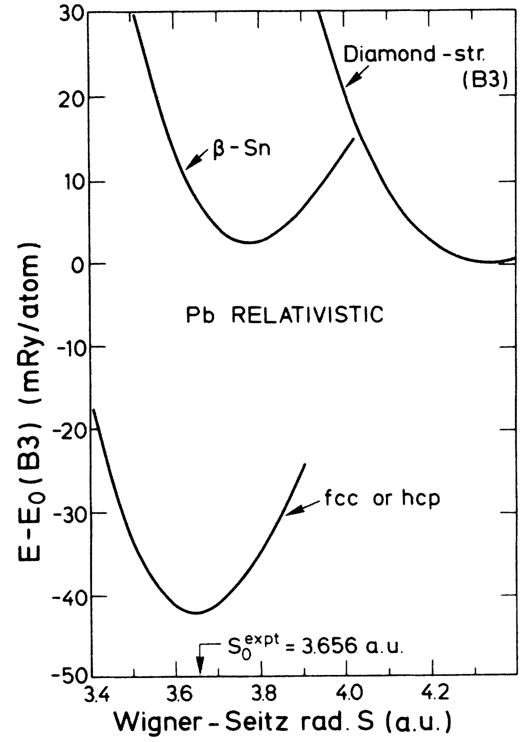

FIG. 2. Relativistic (scalar) calculations of total energy for Pb in diamond, β-Sn (c/a =0.5164), hexagonal (hcp with c/a =1.63), and fcc structures.

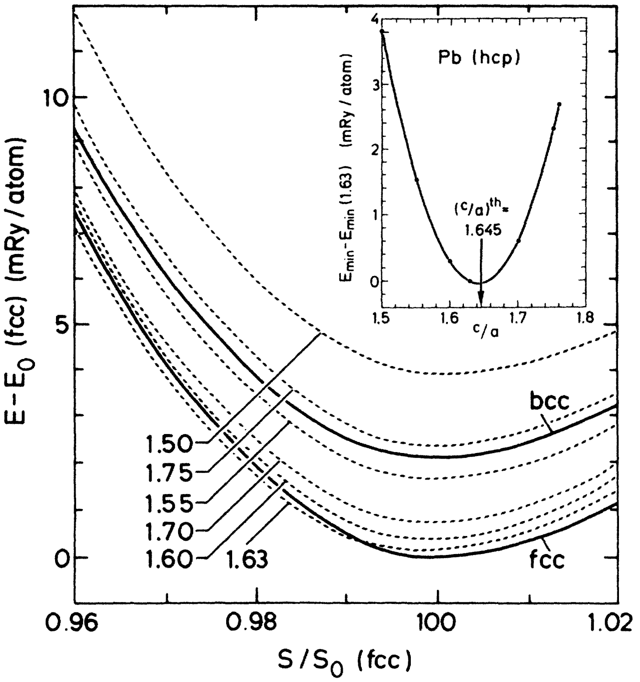

FIG. 3. Total energy variations (scalar relativistic) for Pb in the fcc, bcc, and hcp structures (dashed). The numbers indicate the *c/a* ratio in the hexagonal structure. The inset shows the minimum hcp energy vs *c/a*.

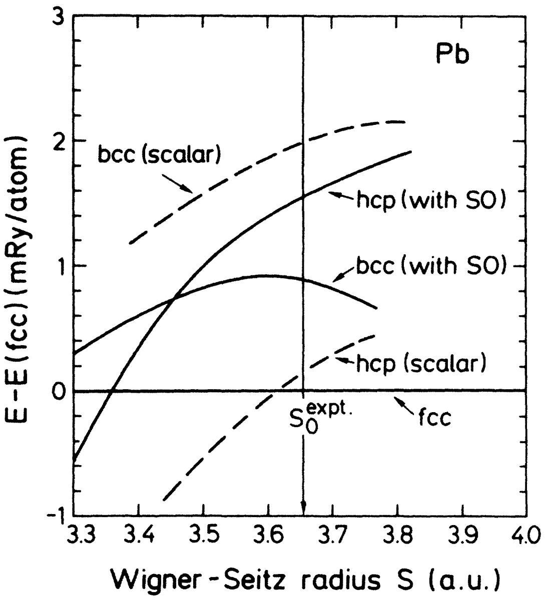

FIG. 4. Total energies with respect to the fcc structure. Dashed curves: scalar relativistic. Full lines: with the inclusion of spin-orbit coupling.

β-Sn structure. Due to their hypothetical nature we did not perform energy minimization calculations for NR-Pb in other crystal structures. In the relativistic case, on the other hand, we investigated the diamond, β-Sn, bcc, fcc, and hcp structures. The energy variations are shown in Figs. 2 and 3. The hcp and fcc structures happen to have almost the same energy (to within 0.1 mRy) in the volume range studied here. Thus, with the present accuracy our method cannot distinguish between these. The most striking difference between Figs. 1 and 2 is that in the relativistic case we find that $E_{\min}(\mathrm{fcc}) \simeq 42.2$ mRy below the minimum of R(relativistic)-Pb in the diamond structure. The theoretical equilibrium lattice constant (fcc) agrees well with experiment; it is only ≈ 0.07% too small. Figure 3 shows the energy variations around the minimum in more detail. In that case we include the bcc and hcp structures with different *c/a* ratios (dashed curves). The inset shows the minimum hcp energy versus *c/a* and it follows that $c/a = 1.645$ optimizes this structure. (The ideal *c/a* ratio is 1.63). Still the fcc structure is predicted to have a lower energy, but only by ~0.2 mRy. According to these calculations a very low external pressure, a few kbar, would provoke a transition from fcc to hcp.

In general it is assumed, and in several cases justified, that the spin-orbit (SO) coupling does not affect the bonding properties since to first order it only splits bands without moving their centers in energy. In lead however, the relativistic effects, including the SO coupling, are so large that this is not true. In Fig. 4 we show the hcp and bcc total energies relative to that of fcc Pb, calculated in the scalar relativistic (i.e., without SO, dashed curves) and with SO coupling (full curves).

It is interesting to note (Fig. 4) that SO lowers the bcc energy with respect to fcc, whereas that of hcp (*c/a* optimized) is increased. Still the calculations predict a pressure-induced fcc→hcp transition, but now the required pressure is considerably higher, 100–150 kbar, than calculated in the scalar relativistic case. Experimentally, such a transition has been observed[10,11] at pressures around 137 kbar.

IV. CONCLUSIONS

The present calculations predict that the fcc structure of Pb is favored with respect to the diamond, bcc, hcp, and β-Sn phases. The role of relativistic corrections has been demonstrated: Without relativistic effects Pb would rather crystallize in the diamond structure than in fcc. Further, in the relativistic case also, the spin-orbit coupling influences the bonding. It increases the fcc→hcp transition pressure by ~100 kbar. By first-principles calculations of metallicities and sp^3 bonding characters, we have quantitatively calculated what Phillips[2] refers to as relativistic (*s-p*) dehybridization effects. Further, the convenience of using the LMTO tight-binding formalism[6,7] for calculations, without empirical adjustment, of chemical bonding properties has been illustrated by application to the elements in group IV.

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