Brief Reports

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Fully relativistic self-consistent energy bands of WSi_2

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We compare the energy bands, binding and cohesive energies, projected densities of states, and Fermi surface of WSi_2 calculated with the spin-orbit interaction included *ab initio* with an earlier semirelativistic calculation. The Fermi surface consists of two (one electron and one hole) large simply connected sheets.

We have recently performed the first fully relativistic self-consistent calculation of the electronic structure of a crystal[1] in which the spin-orbit interaction was included *ab initio* on an equal footing with the other terms in the Hamiltonian. This was computationally feasible because of the relativistic pseudopotential[1-3] which reduces the Dirac equation (to order of the fine-structure constant squared) to a Schrödinger equation containing a weak pseudopotential and spin-orbit pseudopotential. In this paper we present the results of the first such calculation for a compound, by adding the spin-orbit pseudopotential to our previous semirelativistic calculation[4] of WSi_2 (hereafter called I). We constructed the Si spin-orbit pseudopotential in the same manner as the W; the latter is displayed in Fig. 1 of Ref. 1.

Aside from the fact that spin doubles the 88 Gaussian Bloch-basis-function set and makes the secular determinant complex, the calculation here is identical to that in I. We sample the same 56 independent points equivalent to 784 points in the Brillouin zone (BZ) to obtain the charge density and Wigner correlation plus relativistic Kohn-Sham exchange potentials at the same 1600 independent points in the unit cell. These are fit with the same sets of plane-wave and Gaussian functions. The various contributions to the binding energy which are listed in Table I are also calculated as in I. The spin-orbit contribution is implicitly contained in the sum of one-electron eigenvalues. Because our tungsten calculations[1,5] indicate that spin-orbit effects on the equilibrium bond lengths are less than the uncertainties in the calculation, this calculation was performed only for that W–Si bond length, $u = 0.337c$, which gave the maximum semirelativistic cohesive energy with the experimental values of c and a used in I. Comparing the binding energy in Table I in I with that of Table I here, we see that the spin-orbit interaction increases it by only 0.08 eV whereas the cohesive energy is reduced by 0.12 eV to its fully relativistic value of 20.21 eV, slightly improving agreement with the experimental value of 19.13 eV. The atomic energies were calculated as in Ref. 1 using the broken symmetry method[6] which maximizes the sum of the spin-orbit and exchange-correlation contributions. For W metal[1] the crystal spin-orbit energy was larger than the atomic, resulting in an increase of cohesive energy.

The energy bands are displayed in Fig. 1. (The BZ with symmetry labels is displayed in Fig. 2 of I.) All states have the twofold degeneracy required by time reversal in a crystal with inversion symmetry, but none have greater degeneracy. Except along the Λ line and at high symmetry points, only one irreducible representation of the double group exists for odd half-integer spin states. Thus all band crossings that existed in Fig. 3 of I vanish except along the Λ line. The only twofold degenerate levels without spin lay along Λ and at its end points, Z and Γ. These are split into twofold levels with the inclusion of spin. Note especially the splitting of the Λ_5 level crossing E_F. The spin-orbit splitting here is much smaller than in W metal. For example, the Γ_5^+ level at -2.72 eV splits by 0.168 eV into a Γ_7^+, Γ_6^+ pair. This can be compared with the Γ_5^+ splitting in W of[1] 0.52 eV. The reduced splitting can in part be attributed to the fact that the WSi_2 Γ_5^+ is only twofold degenerate whereas in W it is

TABLE I. Various contributions to the binding and cohesive energy of WSi_2 as described in I. Note $E_{\text{atom}} = E_W + 2E_{Si}$ where $E_W = 7.662\,046$ hartree and $E_{Si} = 3.811\,970$ hartree.

$\sum_{n,\mathbf{K}} \epsilon_{n\mathbf{K}}$	0.955 943 hartree
$-\sum_{\mathbf{K}} V(\mathbf{K})\rho(\mathbf{K})$	10.073 086 hartree
$\frac{1}{2}4\pi\Omega \sum_{\mathbf{K}} \rho^2(\mathbf{K})/K^2$	0.205 488 hartree
$\int [\epsilon_{xc}(\rho_T)\rho_T - \epsilon_{xc}(\rho_c)\rho_c]$	−5.923 397 hartree
E_{Ewald}	−21.340 383 hartree
$-E_{\text{binding}}$	−16.029 263 hartree
E_{atom}	15.286 486 hartree
E_{cohesive}	20.210 96 eV

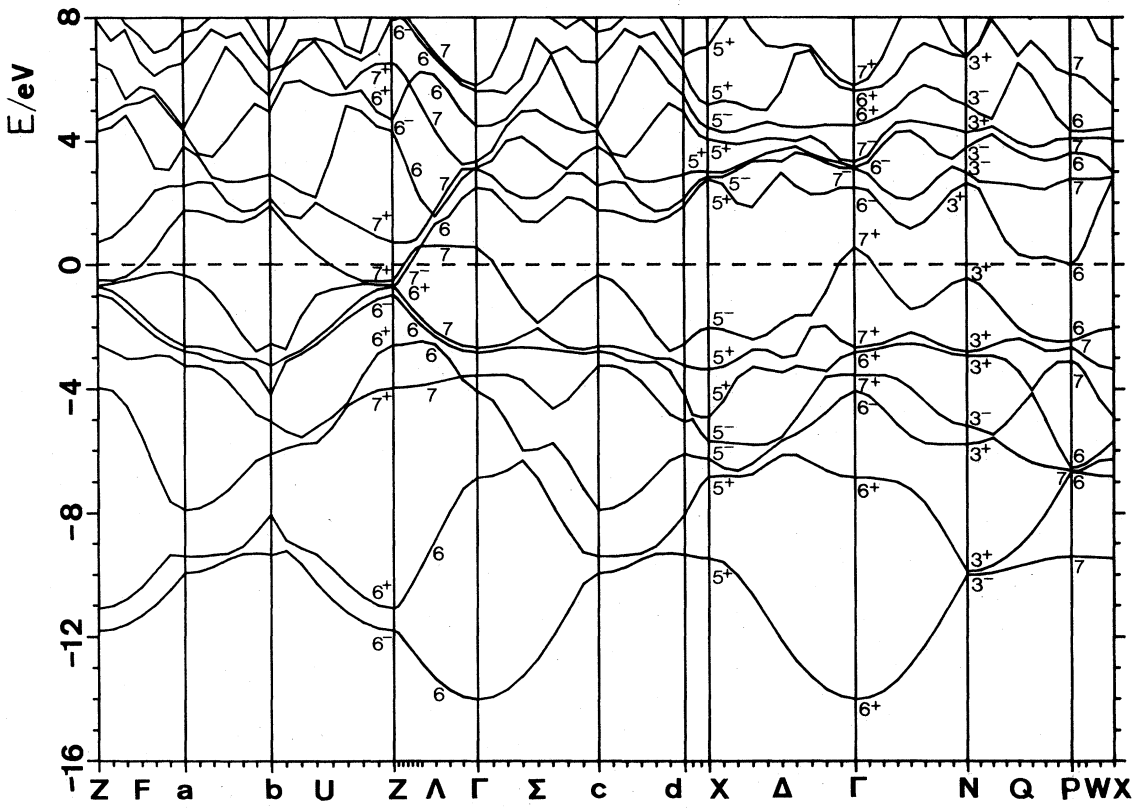

FIG. 1. Fully relativistic energy bands of WSi_2 (in eV measured from E_F). The irreducible representations are labeled at all points in the Brillouin zone where more than one odd half-integer spin IR exists.

threefold and to the fact that a Löwdin[7] projection (see Table III in I) shows it to be only 56.7% W d orbitals with the remainder being Si p and d. The largest spin-orbit splitting in WSi_2 is the 0.29-eV splitting of Z_5^- at -0.77 eV into Z_6^- and Z_7^-. This W p-orbital splitting can be compared with the H_6^-, H_8^- splitting of 2.54 eV in W.

We have calculated projected densities of states[7] and charge density contour plots but these are indistinguishable from Figs. 4–7 in I calculated without spin orbit. Finally, in Fig. 2 we display the Fermi surface of WSi_2 which consists of two large simply connected sheets. This was calculated by fitting each energy band at 136 independent points (including the 56 point mesh used to achieve self-consistency, the points calculated in order to draw the bands in Fig. 1, and a few other points) with 80 symmetrized combinations of plane waves. The intersection of the Fermi surface with two planes intersecting at 45° along the $\Gamma\Lambda Z$ line together with its intersection with perpendicular planes at Γ and Z is drawn. The piece labeled 7 (8) consists of holes (electrons) in the seventh (eighth) band. Were it not for the spin-orbit splitting of the Λ_5 band previously mentioned, the two pieces would touch at the points labeled 3 and 4. The magnitude of the Fermi wave vector measured from Z to the points labeled 1, 2, and 3 is (in inverse Bohr radii) $k_1 = 0.2193$, $k_2 = 0.3161$, $k_3 = 0.0635$ and from Γ to 4, 5, and 6 is $k_4 = 0.3420$, $k_5 = 0.0889$, $k_6 = 0.0814$. Note the P_6 state in Fig. 1 which lies only 0.020 eV above E_F. This point is a local minimum in the eighth band and were it to actually lie below E_F, it would result in two additional small hole pieces. If sufficiently good samples could be made, de Haas–van Alphen experiments should easily be able to measure the cross-sectional areas of the large pieces of Fermi surface we have predicted.

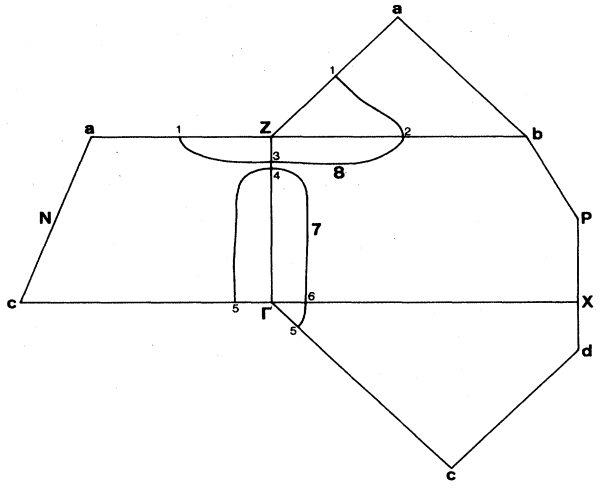

FIG. 2. Intersection of the seventh-band hole and eighth-band electron pieces of Fermi surface with principal planes of the Brillouin zone. The magnitude of k_F measured from Z to the points 1, 2, and 3, and from Γ to 4, 5, and 6 is given in the text.

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[1]D. M. Bylander and L. Kleinman, Phys. Rev. B **29**, 1534 (1984).
[2]L. Kleinman, Phys. Rev. B **21**, 2630 (1980).
[3]L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1452 (1982).
[4]B. K. Bhattacharyya, D. M. Bylander, and L. Kleinman, Phys. Rev. B **31**, 2049 (1985).
[5]D. M. Bylander and L. Kleinman, Phys. Rev. B **27** 3152 (1983).
[6]D. M. Bylander and L. Kleinman, Phys. Rev. Lett. **51**, 889 (1983).
[7]P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).