Is there an interlayer band in α- and β-$ThSi_2$? An *N*MTO analysis

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Since the discovery of superconductivity in MgB_2 much effort has been spent on studies of sp^2-bonded intercalated graphites and structurally related compounds (Fig. 1). With 4 electrons per boron, MgB_2 is isoelectronic with graphite, but is unique in having intercalated doubly-charged ions (Mg^{2+}) which lower the energy of the boron p_z-bands to the extent that holes occur at the top of the sp^2-bonding σ-bands. As first suggested by density-functional calculations, it is the strong coupling between these holes via the optical bond stretching modes which causes superconductivity with $T_c = 40$ K [1]. Whereas MgB_2 may thus be viewed as heavily hole-doped graphite, CaC_6, YbC_6, and Ca(AlSi), with respectively $4\frac{1}{3}$ and 5 electrons per C or Al/Si, are heavily electron-doped graphites with carriers in the ubiquitous interlayer band, which lies well above the σ-bands and crosses the p_z-antibonding π*-band. The interlayer band and the π*-band couple via buckling modes of the graphite sublattice and via in-plane modes of the intercalant sublattice, and this causes superconductivity with $T_c = 11$ K, 6 K, and 8 K, respectively [2]. The interlayer band has intercalant *s* and some d_{3z^2-1} character, but it exists also without intercalation. For the electron-phonon interaction it is important that the Wannier function of the interlayer band, chosen to be centered on the intercalant site, does not change sign upon 6-fold rotation, while the Wannier function of the π*-band has nodes between the C-atoms [2]. In this contribution we investigate whether a metallic interlayer band exists in the structurally related 6-electron compound $ThSi_2$ [3].

$ThSi_2$ can exist in one of two structures, depending upon the temperature of preparation. The hexagonal form, β-$ThSi_2$ shown at the top of Fig. 1, has the same AlB_2 structure as MgB_2: The silicon sublattice is cubic graphite (honeycomb) and the thorium atoms are located between two parallel hexagons thus forming triangular layers. The tetragonal form, α-$ThSi_2$, is a twisted version of this, and is shown at the bottom of Fig. 1: Starting out from a σ-bond in the *z*-direction (Si_1-Si_2 or Si_3-Si_4), the two remaining sp^2-directed orbitals at one end of the bond (Si_1 or Si_3) form σ-bonds lying in the *xz*-plane, while those at the other end (Si_2 or Si_4) form σ-bonds lying in the *yz*-plane. The silicon hexagons are thus cut and twisted to form intersecting honeycomb-stacks running in the *y*- and *x*-directions. At the intersections are the thorium atoms, which have 12 nearest silicon neighbors, like in β-$ThSi_2$. The α-form has two formula units per cell and the thorium sublattice is that of a high-pressure form of cesium (Cs IV). $ThSi_2$ is superconducting with the relatively low $T_c = 2$ K and 3 K for the β- and α-forms, respectively.

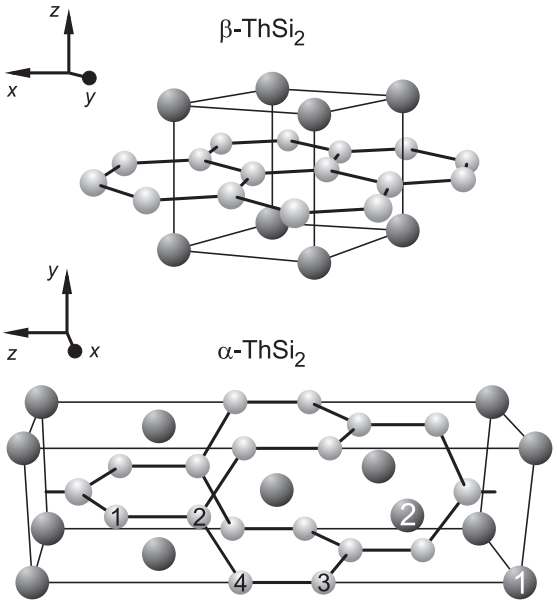

Figure 1: Unit cells of β- and α-$ThSi_2$. Si/Th are the white/grey atoms.

The upper parts of Figs. 2 and 3 show the LDA bands of β- and α-$ThSi_2$, respectively, with red and blue fatness (line thickness) proportional to the Si sp^2 and p_z partial-wave characters, respectively, and pink fatness proportional to the sum of the Th *s*- and d_{3z^2-1}-characters.

There are further characters which are not indicated, e.g., Th *d*. Six bands are full in the β-form and 12 in the α-form. Since the latter are bewilderingly complicated, we first explain those of the β-form (Fig. 2). At Γ, the three lowest states have σ-, the 4th Th-, the 5th π-, and the 6–8th sp^2-antibonding σ*-character.

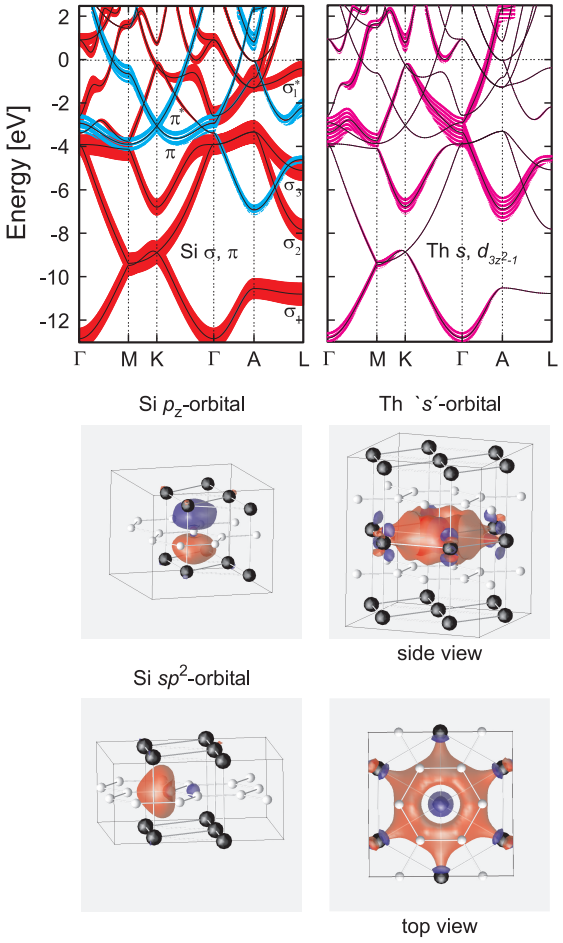

Figure 2: Top: Band structure of β-$ThSi_2$. The red/blue fatness is proportional to the Si sp^2/p_z character, and the pink fatness to Th *s*- and d_{3z^2-1}-character. Bottom: The Si sp^2- and p_z- and the Th *s*- (side and top view) *N*MTO Wannier-like functions which span the 2(3+1)+1 = 9 lowest bands, 6 of which are filled.

The π*-level is above the frame. Compared with the corresponding σ-levels in CaC_6 and YbC_6, the Si π-level is relatively higher and the Th level relatively lower, the latter being due to the relativistic mass-velocity and Darwin effects, as well as the higher filling of the Th-band. The three σ-bands are full, and so is essentially the lowest σ*-band, although in a region around M, it splits due to hybridization with the Th-band. The π- and π*-bands are also full, except near Γ, where the π*-band is empty and the Th-band full. Near ΓA, the lowest π- and π*-like bands are more Th- than Si-like. At the Fermi level, there are well-defined σ*-, π*-, and Th-bands.

In order to decide whether the – somewhat fractured – Th-band can be viewed as the ubiquitous interlayer band, which by coupling to the σ*- and π*-bands via Si-buckling and Th-displacive modes, is the likely cause of the observed superconductivity, we consider its Wannier-like function. This we take as the Th *s*-like orbital of a complete, minimal basis set containing also the Si sp^2- and p_z-like orbitals generated by the *N*MTO downfolding-plus-*N*ization procedure [2-4]. The set of $1+2\times4=9$ *N*MTOs spans the occupied part of the 9 lowest bands exactly, and its orbitals are shown in the bottom part of Fig. 2. The Th *s*-*N*MTO has the property that it has *no* Th *s*-character on any *other* Th site and *no* Si *s*- or *p*-character. Similarly for the Si sp^2- and p_z-*N*MTOs. Other partial-wave characters are present in the amounts needed to make the basis set complete. We see that the Th *s*-orbital *is* invariant to the 6-fold rotations, is shaped like a torus with a hole in the middle caused by the 7*s*- and $6d_{3z^2-1}$ characters, and bonds to 7*p*- and 6*d*-characters of the thorium neighbors in the plane. Since this orbital is very similar to the calcium-centered Wannier function for the interlayer band in CaC_6 and also for the vacancy $\boxdot C_6$ [2], we conclude that the Th-band in β-$ThSi_2$ *is* the interlayer band.

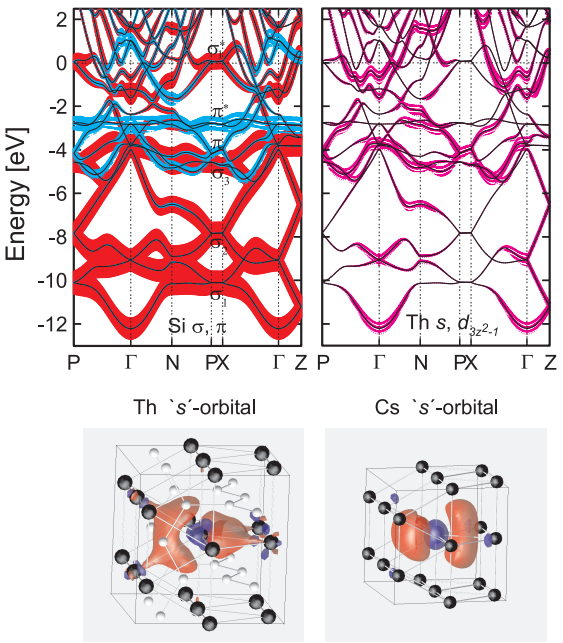

Figure 3: The same as in Fig. 2, for α-$ThSi_2$. The Si sp^2- and p_z-*N*MTOs are not shown since they are nearly identical to those calculated for β-$ThSi_2$. The Th-related orbital is strikingly different (seen here from the side). Also shown is the *N*MTO obtained for Cs-IV.

The bandstructure of α-$ThSi_2$, shown at the top of Fig. 3, may now be analyzed and found to be similar to that of β-$ThSi_2$, provided that the relation between the two structures (Fig. 1) is rec-

ognized. This result comes out much simpler if we construct the same minimal basis set as for the β-form. We then find that the Si sp^2- and p_z-*N*MTOs are so similar to those obtained for β-$ThSi_2$, that there is no point in showing them. At first, the Th *s*-*N*MTO in the bottom left panel of Fig. 3 appears to differ greatly from the interlayer orbital in β-$ThSi_2$ (Fig. 2), until one realizes that it *is* this torus-shaped orbital, but cut in two and twisted exactly like the Si-sublattice in Fig. 1.

Thus, for both allotropes of $ThSi_2$, the Th *s*-*N*MTO is strikingly similar to the previously calculated interlayer Wannier functions in graphites [2]. This suggests that the electron-phonon mechanism of superconductivity in $ThSi_2$ is similar to the one in the heavily electron-doped intercalated graphites where there are interlayer and π^*-bands at the Fermi level. In $ThSi_2$, also the σ^*-band is metallic. Since thorium is a heavy metal, one might fear that spin-orbit coupling between the several 6*d*-characters in α-$ThSi_2$ would remove the interlayer band from the Fermi level. But as fully relativistic calculations show, the Fermi surface is very little affected; there *is* in effect only one *d*-character.

A final remark: In elemental Cs IV, high pressure has transformed the cesium 6*s*-electron into a 5*d*-electron whose orbital is the one shown in the bottom right part of Fig. 3. Its shape is seen to be that of the Th-orbital in α-$ThSi_2$, but turned 90° in order to make up for the lack of silicon backbone, as conjectured by von Schnering and Nesper [3-5].

[1] *Kortus, J., I.I. Mazin, K.D. Belashchenko, V.P. Antropov, and L.L. Boyer.* Physical Review Letters **86**, 4656–4659 (2001); *An, J.M. and W.E. Pickett.* Physical Review Letters **86**, 4366–4369 (2001); *Kong, Y., O.V. Dolgov, O. Jepsen and O.K. Andersen.* Physical Review B **64**, 020501 (2001).

[2] *Giantomassi, M., L. Boeri and G.B. Bachelet.* Physical Review B **72**, 224512 (2005); *Boeri, L., G.B. Bachelet, M. Giantomassi and O.K. Andersen.* Physical Review B **76**, 064510 (2007); *Andersen, O.K., E. Zurek, L. Boeri, O. Jepsen, G.B. Bachelet and M. Giantomassi.* MPI-FKF Wissenschaftlicher Tätigkeitsbericht 2006, 60–62 (2007); the front-page logo is the interlayer Wannier function of CaC_6.

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[5] *von Schnering, H.G. and R. Nesper.* Angewandte Chemie International Edition **26**, 1059–1080 (1987).