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Electronic Structure of Transition Metal Disilicides

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Abstract

Selfconsistent Augmented Plane Wave (APW) calculations have been performed on transition metal disilicides $TMSi_2$ (with $TM = Fe, Co, Ni$ and Y) in the high symmetry fluorite structure. For each compound a set of tight binding parameters is deduced from a Slater and Koster fit on the APW bands structures. The basis used is orthogonal and includes d states for transition metal and sp states for silicon, interactions are taken up to third neighbours. We show that these tight binding parameters are very accurate as the DOS of $CoSi_2$ calculated through a decimation technique is in good agreement with the APW one. $CoSi_2$ set of parameters is then compared to data deduced from Harrison scheme and Papaconstantopoulos handbook.

1. Introduction

Because of their nearly perfect interface with Silicon, Cobalt, Nickel and Yttrium disilicides are compounds of choice to investigate phenomena ruling interfaces and especially mechanisms bound to Schottky Barrier Height (SBH). Many *ab initio* calculations are available on $CoSi_2$ and $NiSi_2$ electronic structure [1–8] but problems appear when going to interface with silicon. In fact, in this kind of method, supercells have to be used to recover the 3 dimensional periodicity and this implies the use of rather big cells to minimize interface–interface interaction. The other point comes from the use of local density approximation which gives Silicon with a gap of nearly half the experimental one and by the way to determine the Schottky Barrier Height [9–11]. These problems are avoided in semi-empirical methods which do not require 3 dimensional periodicity. For instance, tight binding approximation coupled with a decimation technique [19] has been successfully applied to heterojunctions study. The main point of this approach lies in the determination of a good set of parameters. Our aim is first to do an *ab initio* calculation on the bulk compound, then with a Slater and Koster fit we get the tight binding Hamiltonian and so, we will go on more complex problems such as low symmetry structures or interface with silicon which would be rather difficult and heavy to study with *ab initio* methods.

In the second Section of this paper, we present APW calculations on $FeSi_2$, $CoSi_2$, $NiSi_2$ and YSi_2 in the fluorite structure. Only $CoSi_2$ and $NiSi_2$ crystallize in this structure, $FeSi_2$ is orthorhombic and YSi_2 hexagonal but here we are interested in the evolution of bonding mechanisms with the atomic number of the transition metal. A detailed APW computation of YSi_2 in its hexagonal phase will be published elsewhere. The densities of states (DOS) split in two groups: $FeSi_2$, $CoSi_2$, $NiSi_2$ on one hand and YSi_2 on the other one. In Section 3, the APW results are used to determine tight binding parameters with a Slater and Koster fit. The bulk DOS of $CoSi_2$ is then recalculated with a decimation technique [19] to check the fitting procedure. $CoSi_2$ parameters

are compared to the ones deduced from Harrison law [12] or Papaconstantopoulos handbook [13] in Section 4. These general laws and tables give a qualitative view of the main physical aspects.

2. APW calculations

Ab initio calculations have been performed in the high symmetry CaF_2 (Fig. 1(a)) structure with a self consistent and scalar relativistic Augmented Plane Wave Method [14]. The

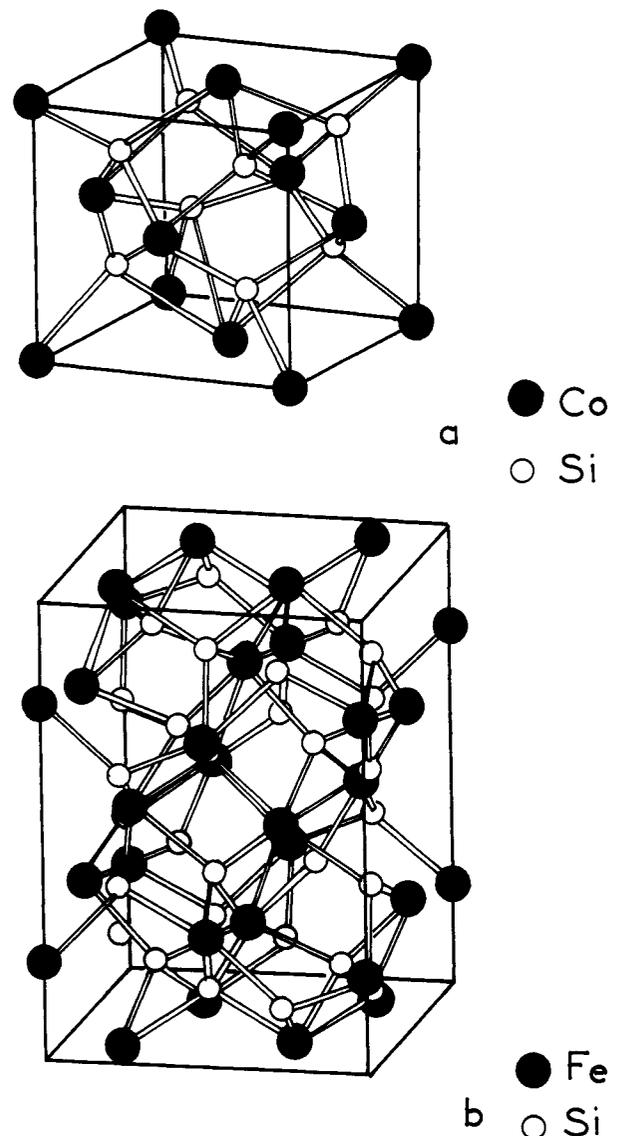


Fig. 1. Crystallographic structures: (a) fluorite (CaF_2), (b) orthorhombic $\beta FeSi_2$.

Local Density Approximation (LDA) is used with the Hedin Lundqvist formulation for the exchange and correlation potential [15]. Radii of muffin tin spheres are chosen to get them in touch. Calculation involves 19 k points in the irreducible Brillouin Zone, that is 256 points in the whole zone. Consistency is reached up to more than 0.001 Rydberg, then DOS are evaluated on the same mesh of 19 k points by the tetrahedron method [16].

Figure 2 shows the total densities of states of FeSi_2 , CoSi_2 , NiSi_2 and YSi_2 . The first three results (FeSi_2 , CoSi_2 , NiSi_2) are very similar and completely different from the last one (YSi_2). In the first case, the DOS can be divided into four parts: the first one A, comes from silicon s states, peak B is due to silicon p-metal d bonding states, peak C to metal d non bonding states and part D to silicon p-metal d anti-bonding states. Going from Iron to Nickel disilicide can be explained by a rigid band shift. The Fermi level goes up in the band, it falls in the rather high antibonding peak in FeSi_2 , just before the pseudo gap in CoSi_2 and after it in NiSi_2 . Partial densities of states of the three compounds are very similar. The sp^3 character of silicon bonds in FeSi_2 , CoSi_2 , NiSi_2 , is kept, as shown in Fig. 2(e). The results are similar to LMTO calculation of Lambrecht [2] and LAPW calculations of Tersoff [2] and Mattheiss [3]. CoSi_2 total and partial DOS are found in good agreement with UPS and SXES measurements [18]. There is a big density of states at the Fermi level in FeSi_2 consistent with the fact that this compound is not stable in the fluorite but crystallizes in an orthorhombic structure at low temperature.

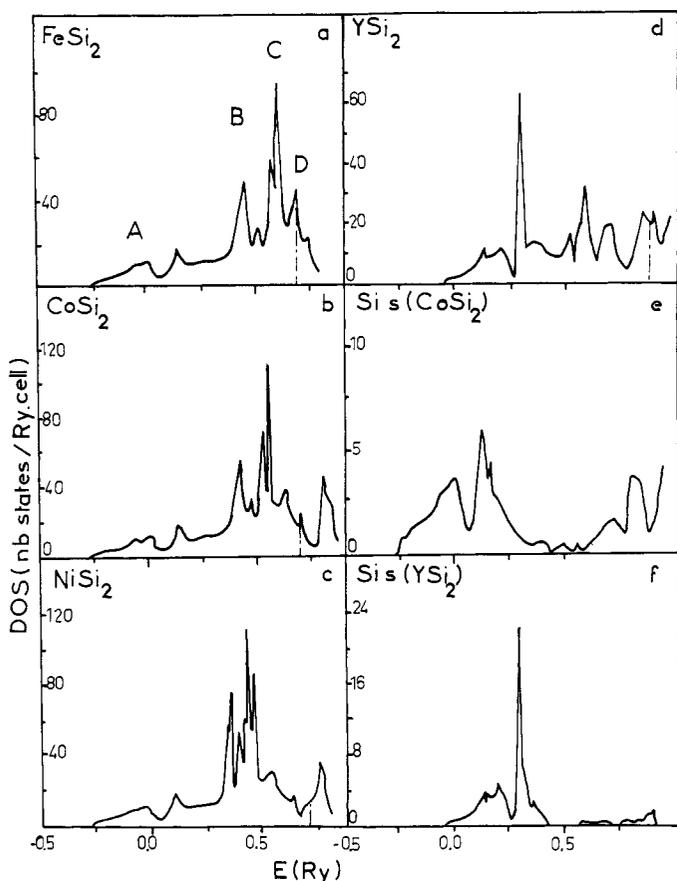


Fig. 2. APW densities of states: (a) total DOS of FeSi_2 , (b) total DOS of CoSi_2 , (c) total DOS of NiSi_2 , (d) total DOS of YSi_2 , (e) partial Si s DOS in CoSi_2 , (f) partial Si s DOS in YSi_2 .

The case of YSi_2 is completely different, the density of states looks like a nearly free electron band with a sharp peak due to Silicon s-Yttrium d e_g hybridisation. Partial DOS no more show the sp^3 character (Fig. 1(f)) and Yttrium d band is large, more than 10 eV. A previous calculation had been performed on YSi_2 in the hexagonal structure and exhibited a completely different behaviour [17]. In this calculation density of states at the Fermi level was not so important, showing that YSi_2 is not stable in the fluorite.

3. Slater and Koster fit

For each compound, a set of 14 two centers orthogonal Slater and Koster parameters are obtained from a fit to 7, 8 or 10 (YSi_2 and FeSi_2 , CoSi_2 , NiSi_2) APW bands. Metal d and silicon sp states are introduced leading to a 13×13 hamiltonian with interactions up to third neighbors. Due to the large number of parameters, this procedure requires an important computational work and must be carefully followed to keep a physical meaning. Fitting errors are around 20 mRy, Table I gathers all the parameters.

The large difference between the two kinds of densities of states can be explained by the values of on site energies. Yttrium d levels (e_g , t_{2g}) are very close to silicon p while they are between Si s and p for the three other compounds. This leads to completely different hybridisation involving Si sp^3 and d orbitals in Fe, Co, Ni disilicides and Si p-Y d states for YSi_2 .

To check the accuracy of the fit, we recalculate the density of states of CoSi_2 with the obtained parameters set and by a decimation technique [19]. This method works in k_{\parallel} space, we use a set of 9 special k points in the irreducible part of the hexagonal (surface 111) Brillouin Zone to build up the DOS. Due to this rather small number of k points, the density of states should be made of a juxtaposition of peaks. So we broaden them with a gaussian to get a soft DOS. A comparison of APW and tight binding (TB) results is shown in Fig. 3. They are very similar but with a shift of d peaks toward lower energies in the tight binding results. Differences come from the fitting errors and the restriction to silicon sp and metal d states in the hamiltonian. An important point to go on disilicide-silicon interfaces is that densities of states at the Fermi level are the same.

Table I. Tight bonding parameters of FeSi_2 , CoSi_2 , NiSi_2 and YSi_2 obtained from a fit on APW band structures, a is the lattice constant and d the interatomic distance

		FeSi_2 (eV)	CoSi_2 (eV)	NiSi_2 (eV)	YSi_2 (eV)
M-Si	$d = a\sqrt{3}/4$	$sd\sigma$ -1.075	-1.023	-1.899	-1.671
		$pd\sigma$ -0.478	-0.391	-0.313	-1.627
		$pd\pi$ 0.634	0.641	0.596	1.158
Si-Si	$d = a/2$	E_s 4.803	5.009	4.139	6.84
		E_p 10.035	10.269	9.834	12.424
		$ss\sigma$ -1.375	-1.431	-1.342	-1.261
		$sp\sigma$ 1.818	1.917	1.792	1.361
		$pp\sigma$ 2.0815	2.336	2.365	1.419
		$pp\pi$ -0.976	-1.044	-1.015	-1.076
M-M	$d = a\sqrt{2}/2$	$E_{t_{2g}}$ 7.170	6.497	5.408	11.550
		E_{deg} 7.693	7.104	5.881	12.253
		$dd\sigma$ -0.361	-0.232	-0.148	-0.676
		$dd\pi$ 0.119	0.093	0.065	0.300

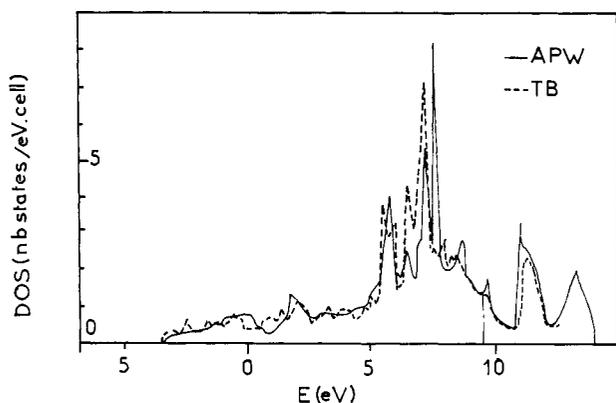


Fig. 3. Comparison of APW and TB total DOS of CoSi_2 .

4. Comparison with other sets of parameters

Parameters determination is the main problem of tight binding approximation. This can be solved using the Harrison scheme [12] or handbook such as Papaconstantopoulos one [13]. On site energies are often deduced from atomic values (Herman and Skillman tables). For transition metals, they are modified to go from the atomic configuration ($s^2 d^n$) to the crystal one ($s^1 d^{n+1}$). The main effect is to move d energies from a quantity U which has been calculated for each element [20]. In the handbook, hopping integrals have been calculated for a given distance. They are then adapted to the compound with laws such as Harrison's prescription in $1/d^n$, n equals 1 for sp integrals, $7/2$ for sp-d interactions and 5 for d ones. Another problem occurs when dealing with alloys since these tables or laws only provide parameters for pure elements. Further approximations are introduced to calculate interatomic hopping integrals with for example, Shiba's formula:

$$t't'm = \sqrt{ttm \cdot t't'm}$$

where t and t' are the orbital types and m is the symmetry. Alloy effect on on site energies can be treated with charge transfer, this requires another parameter U the Coulomb term [21].

The main difficulty lies in parameters transferability. The use of the same set of parameters in two completely different structures is very questionable. The solution should be to determine directly the parameters for the real structure.

We want here to compare our adjusted parameters set (A) to the ones given by Harrison (H) and Papaconstantopoulos

Table II. Papaconstantopoulos and Harrison sets of parameters for CoSi_2

		Papaconstantopoulos	Harrison
M-Si	$sd\sigma$	-1.288	-1.267
	$pd\sigma$	-1.417	-1.928
	$pd\pi$	0.686	0.714
Si-Si	Es	-13.55	-13.55
	Ep	-6.52	-6.52
	$ss\sigma$	-1.82	-1.48
	$sp\sigma$	1.44	1.95
	$pp\sigma$	2.20	3.44
	$pp\pi$	-0.72	-0.86
	Ed	-8.74	-8.74

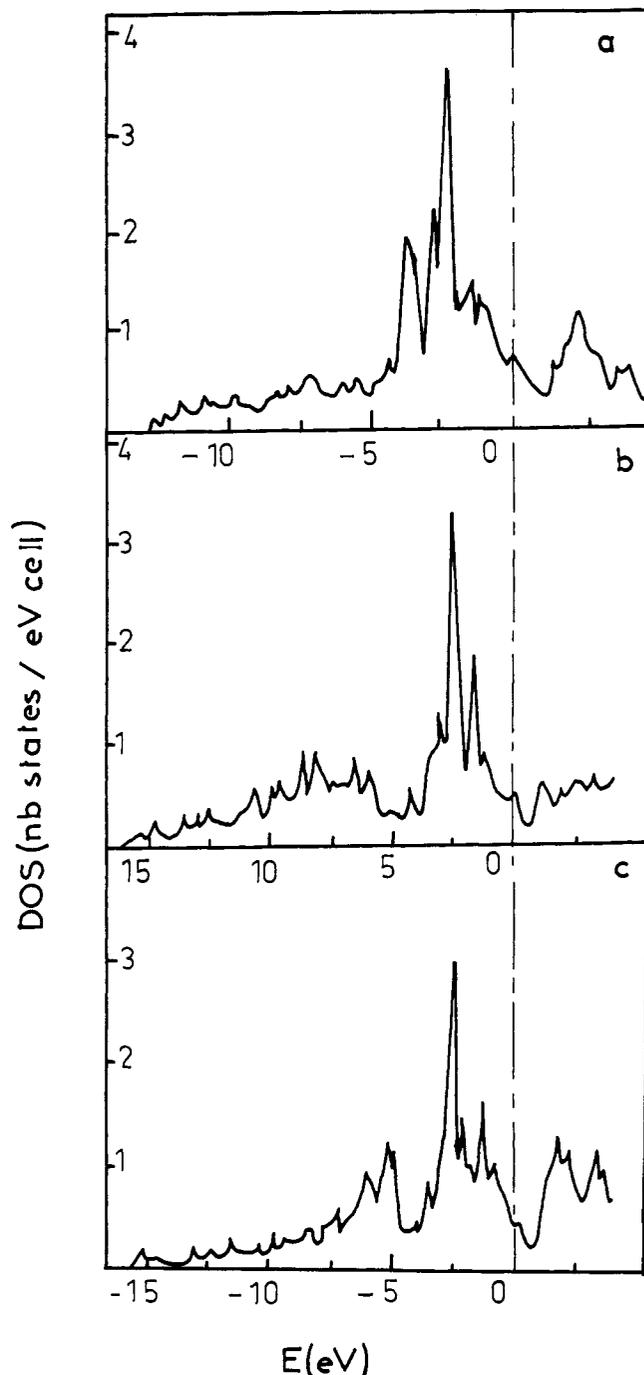


Fig. 4. CoSi_2 total DOS (a) our adjusted set, (b) Harrison's set, (c) Papaconstantopoulos's set.

(P). They are gathered in Table II and the corresponding DOS are shown in Fig. 4. The difference between s and p silicon on site energies and s silicon, d cobalt ones is bigger in sets H and P than for adjusted values, this is found again in band widths of Fig. 4. Densities of states are rather similar and the big non bonding d peaks falls at the same position in the three cases. The main difference occurs in bonding and antibonding Cod-Sip structures. Antibonding states are rather well marked and bonding ones, in set H and P extend more than in the adjusted case. In these two last DOS, full width at mid height of the biggest peak is smaller, exhibiting a more pronounced Si-Co hybridisation due to the importance of $pd\sigma$ parameter.

This comparison shows small differences between DOS deduced from adjusted parameters and obtained with univer-

sal law or tabulation. Anyway these last approaches give a good view of the main physical aspects and they are very helpful when *ab initio* calculations are difficult to perform.

5. Conclusion

The problem of parameters in tight binding approximation can be solved by performing a Slater and Koster fit on *ab initio* band structures. In that case, the parameters are determined all together for interactions up to some chosen distance. This procedure has to be followed carefully to keep the physical meaning of the parameters.

We have shown that the tight binding density of states of CoSi_2 compares well to the APW results and that general schemes such as Harrison's one give the main physical information. We are currently using these sets of parameters to study disilicide/silicon interfaces.

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