The electronic structure of YSi$_2$

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Abstract. We present here the first study of the electronic structure of YSi_2. The density of states is calculated within a tight-binding scheme and charge transfer is treated in a self-consistent way. The results show that hybridisation between silicon and yttrium is mainly due to Si p_z and Y d coupling and that YSi_2 is a metal. The densities of states compare well with those from the ultraviolet photo-emission and ion photo-emission spectra.

Rare-earth disilicides ($RESi_2$) are of interest for their technological applications because of their small mismatch with the silicon (111) lattice and their small Schottky barrier height on n-type silicon (Knapp 1986). Silicon atoms in these compounds form two-dimensional layers. The s and p orbitals give sp^2 hybrids in contrast with the three-dimensional bonds exhibited by transition-metal disilicides. This could account for their unusually small Schottky barrier height (0.35 eV compared with 0.6–0.75 eV for transition-metal disilicides on n-type silicon). On the experimental side, very few ultra-violet photo-emission and ion photo-emission spectra are available. However, no theoretical electronic structure studies of these systems exist, to our knowledge. It is thus worth studying the bulk properties before considering the interface with silicon.

The aim of this paper is to focus on the problem of the electronic structure of YSi_2. Although yttrium has no f electron, it has the chemical properties of rare earths and is representative of these elements. $RESi_2$ compounds, RE varying from Gd to Lu and Y, crystallise in a hexagonal structure of the AlB_2 type (figure 1) characterised by alternate silicon and rare-earth planes in the (0001) direction. In reality, the actual compound is not stoichiometric since one silicon atom out of every six is missing. These vacancies are randomly distributed. In this work, we assume the vacancies to play only a minor role; the geometrical configuration of the system is then represented by the AlB_2 structure.

The densities of states (DOSS) are calculated within the tight-binding approximation and by the decimation technique. The determination of a good set of parameters is the main problem of this approximation. At the moment, no calculation of the YSi_2 band structure is available and very few experimental results exist; so we use the values obtained by Papaconstantopoulos (1986) for yttrium and silicon parameters and adapt them to YSi_2 inter-atomic distances with a scaling law in $1/d^2$ for s and p orbitals and $1/d^5$ for d orbitals. Y–Si interactions are obtained from the geometrical mean of Si–Si and Y–Y interactions:

$$t_{\text{Si-Y}\sigma} = (t_{\text{Si-Si}\sigma} t_{\text{Y-Y}\sigma})^{1/2}. \tag{1}$$

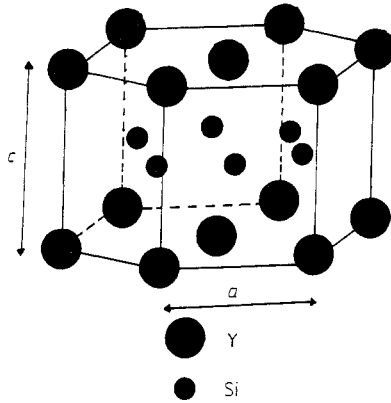The Hamiltonian is built up according to the Slater and Koster relations. Interactions

Figure 1. Structure of YSi_2: $a = 3.842$ Å; $c = 4.14$ Å.

are introduced up to first neighbours for yttrium and up to second neighbours for silicon. The calculation includes s and p orbitals for silicon and d orbitals for yttrium. Charge transfer is treated in a self-consistent way; each program iteration changes on-site energy values according to

$$\varepsilon_d = \varepsilon_d^0 + \Delta n_d \, U_d$$
$$\varepsilon_{sp} = \varepsilon_{sp}^0 + \Delta n_{sp} \, U_{sp}. \tag{2}$$

Δn_d and Δn_{sp} are the charge transfer values and ε_d^0, ε_s^0 and ε_p^0 the on-site energies. The values of these parameters were taken from Hermann and Skillmann tables and ε_d^0 is modified so that YSi_2 is in the $5s^1 4d^2$ configuration (Froyen 1980). A set $(\varepsilon_d, \varepsilon_s, \varepsilon_p)$ corresponds to one charge transfer $(\Delta n_d, \Delta n_{sp})$. Self-consistency is reached when the charge transfer no longer changes with further iterations. For the parameters U_d and U_{sp}, we use the values of 1.6 eV and 0.5 eV, respectively, according to Friedel (1969). All the parameters are shown in Table 1.

The decimation method (Guinea 1983) works in $k_\parallel$-space and gives a Green function $G(E, k_\parallel)$. A special point technique (Cunningham 1974) is used to avoid summation over the whole first irreducible Brillouin zone. We then obtain the DOS as a set of delta peaks which can be broadened by calculating G just above the real axis, i.e. at $E + i\varepsilon$. Then DOSs can be deduced from the Green function according to

$$n(E + i\varepsilon) = -\frac{1}{\pi} \text{Im} \left(\sum_{\kappa_\parallel} G(E + i\varepsilon, \kappa_\parallel) \right). \tag{3}$$

Table 1. LCAO parameters for Si–Si and Y–Si interactions in YSi_2.

Si–Si interaction ($d = 2.218$ Å)	
ssσ	−2.652
spσ	2.092
ppσ	3.209
ppπ	−1.063
Y–Si interaction ($d = 3.034$ Å)	
sdσ	−1.749
pdσ	−1.924
pdπ	0.772
On-site energies	
Silicon, E_s	−13.52 eV
Silicon, E_p	−6.49 eV
Yttrium, E_d	−4.138 eV

To ensure that we used enough k-points, we compared the integrated DOSs obtained at the first iteration with nine and 18 points. We found a difference of less than 0.01 electron; so we used a set of nine k-points.

Table 2. First inter-atomic distances in YSi$_2$.

	Distance (Å)
Si–Si	2.218
Y–Si	3.034
Si–Si	3.842
Y–Y	3.842

Table 2 shows the first inter-atomic distances in YSi$_2$. In the stoichiometric phase studied here, each silicon atom has three silicon first neighbours and six yttrium second neighbours. Yttrium has 12 surrounding silicon atoms and six yttrium atoms. The distance between two silicon atoms in the same (0001) plane is 1.35 times smaller than that between silicon and yttrium; so we first calculate the DOS of the silicon sublattice with no silicon–yttrium interaction. The corresponding total and partial (sp^2 and p$_z$) DOSs are shown as broken lines in figures 2(c)–2(e). The p$_z$ orbitals are orthogonal to the (0001) plane and only couple together; they give bonding and anti-bonding states and thus the symmetrical DOS in figure 2(e). Figure 2(d) shows the sp^2 DOS; the peak located at -5.5 eV is due to Si s states.

Figure 2 shows YSi$_2$ total and partial DOSs. The total DOS can be divided into four parts: the first part extends from -22.5 to -10 eV and is from Si sp^2 states; next is peak
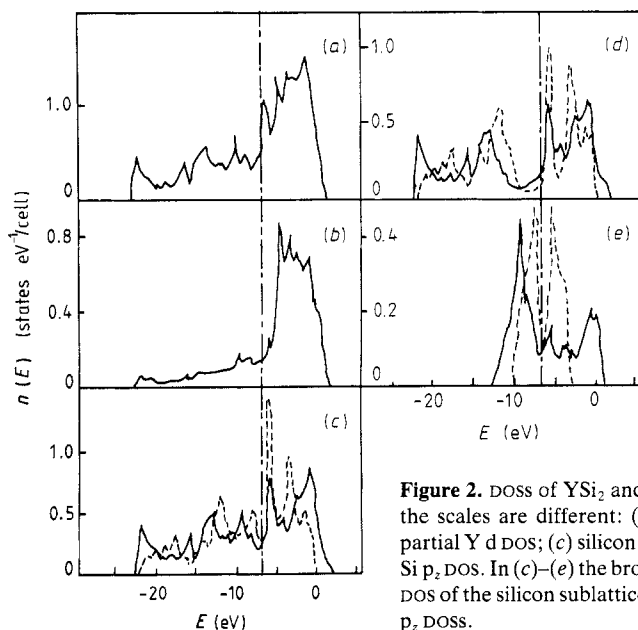

Figure 2. DOSs of YSi$_2$ and the silicon sublattice; the scales are different: (a) YSi$_2$ total DOS; (b) partial Y d DOS; (c) silicon DOS; (d) Si sp^2 DOS; (e) Si p$_z$ DOS. In (c)–(e) the broken lines represent the DOS of the silicon sublattice and its partial sp^2 and p$_z$ DOSs.

A, which is located at -9.4 eV and is due to Si p_z orbitals; then we have peak B which occurs at -5.62 eV and is due to Si s orbitals; the last part, from -5 to 1.5 eV has a pronounced d character with peak C from non-bonding d states. The Y–Si interaction is mainly due to coupling between Si p_z and Y d orbitals. This can be explained by the geometry of the system; p_z orbitals are orthogonal to (0001) planes and thus point to yttrium atoms much more than sp^2 do. Furthermore, the energy difference $E_{sp^2} - E_d$ ($= 4.7$ eV) is larger than $E_{p_z} - E_d$ ($= 2.35$ eV); so hybridisation between sp^2 and d orbitals has a small effect, as shown in figure 2(d). The sp^2 structures are pushed away from the d level. The d states spread all over the band but the d character is more pronounced above the Fermi level. This one falls at -6.2 eV, at the beginning of the sharp Si s peak; we find a small charge transfer of about 0.12 electrons from each yttrium atom to silicon.

Our results can be compared with the ultraviolet photo-emission and ion photo-emission spectra obtained by Baptist *et al* (1988). The following main characteristics are reproduced: the position of the Fermi level E_F in a sharp peak, the position of the Si p_z peaks at around 3 and 1.2 eV below E_F and the position of the Y d peak above E_F. Baptist *et al* also noticed a small charge transfer from yttrium to silicon.

As a conclusion, let us point out that the Fermi level falls in a zone of rather high DOS, in agreement with the metallic character of YSi_2. Up to now, we have studied only perfect YSi_2 but, as is well known, this compound is not stoichiometric. The importance of vacancies should not be crucial. The lack of one silicon atom out of every six will destroy some sp^2 hybrids and push the position of the Fermi level downwards. Charge transfer will be thus increased by a small amount. We are currently studying the YSi_2–Si(111) interface in order to calculate the Schottky barrier height.

Acknowledgments

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