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A comparison of experimental and theoretical densities of states in CoSi_2

E Belin[†], C Senemaud[†], L Martinage[‡], J Y Veuillen[‡],
D A Papaconstantopoulos^{‡§}, A Pasturel[‡] and F Cyrot-Lackmann[‡]

[†] Laboratoire de Chimie Physique, 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France

[‡] Laboratoire d'Etudes des Propriétés Electroniques des Solides—CNRS, Associated with Université Joseph Fourier, Grenoble, BP 166, 38042 Grenoble Cédex, France

[§] Naval Research Laboratory, Code 4690, Washington, DC 20375-500, USA

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Abstract. A comparison between experimental and theoretical densities of states (DOS) is performed for CoSi_2 . Partial DOS of CoSi_2 are studied by soft x-ray spectroscopy (sxs) through Si $\text{K}\beta$ ($3p \rightarrow 1s$) and Co $\text{L}\alpha$ ($3d \rightarrow 2p_{3/2}$) emission bands. In addition, x-ray photoemission spectroscopy (XPS) measurements of the valence band are presented. On the theoretical side, a scalar relativistic self-consistent augmented plane wave calculation is performed from which the partial DOS are obtained. The theoretical DOS, with a Lorentzian broadening, are compared with the experimental results and found to be in good agreement.

1. Introduction

The electronic structure and electronic properties of metal silicides have attracted considerable attention in recent years because of their practical importance in Si device applications. This is particularly true for the cubic silicides NiSi_2 and CoSi_2 , which can be grown epitaxially on Si (111) and (100) surfaces. This had led to many studies of bulk electronic structure of these compounds, both theoretical and experimental. However, very few of them are devoted to partial densities of states. In this paper, we present the first comparison between experimental and theoretical DOS of CoSi_2 and especially silicon p and cobalt d partial densities. The valence band electronic distribution of CoSi_2 was investigated by both soft x-ray spectroscopy and x-ray photoemission spectroscopy. These two methods provide complementary information. Indeed, sxs allows us to probe partial local densities of states since x-ray transitions involve an inner level of a given symmetry, whereas XPS gives the total valence band distribution modulated by the photoionisation cross sections. From the theoretical point of view, a scalar relativistic, self-consistent APW calculation is performed on CoSi_2 in its real fluorite structure. The DOS, calculated by the tetrahedron method, are broadened and compared with the experimental spectra.

The paper is organised as follows. Details of the experimental determination of the DOS are given in section 2. In section 3 we recall briefly the calculational methods. In section 4 we compare the theoretical results with the experimental ones.

2. Experimental techniques

The Si $K\beta$ ($3p \rightarrow 1s$) and Co $L\alpha$ ($3d \rightarrow 2p_{3/2}$) spectra were recorded step by step using Johann-type vacuum bent-crystal spectrometers equipped respectively with gypsum (020) and mica (001) crystals. The detection was achieved via proportional A-CH₄ counters. The experimental resolution was 0.2 eV for Si $K\beta$ and 0.3 eV for Co $L\alpha$.

The emissive target was crystalline CoSi₂ affixed to the cooled metallic anode of the x-ray tube.

Incoming electrons of 5000 eV for Si $K\beta$ and 1500 eV for Co $L\alpha$ were used; in the latter case, the influence of satellite emissions, which could affect the full width at half maximum (FWHM) of the band, is avoided. The sample depths were respectively 1800 Å for Si and about 150 Å for Co, so we can consider that the spectra are characteristic of the bulk material.

The spectra were obtained as a function of the x-ray transition energy. They are observed in different spectral ranges. In order to compare the data on a binding energy scale, it is necessary to locate the Fermi level on each x-ray transition energy scale. This is possible from the determination of the binding energies of Si 1s and Co 2p_{3/2} levels involved in the x-ray transitions. Notice that the energy of inner levels in CoSi₂ may differ significantly from the values of the pure elements.

In CoSi₂, the Si 1s energy was obtained as already detailed (Senemaud *et al* 1987) by combining XPS measurement of the Si 2p_{3/2} binding energy level with respect to the Fermi one, and that of the 2p_{3/2} → 1s x-ray line. The precision was thus ±0.3 eV. The Co 2p_{3/2} binding energy in CoSi₂ is directly deduced from XPS measurements with a precision of ±0.2 eV.

By the dipole selection rules, the Si $K\beta$ and Co $L\alpha$ emission bands correspond respectively to the convolution product of the Si 3p or Co 3d DOS and the Lorentzian distribution of the inner levels Si 1s (0.45 wide) or Co 2p_{3/2} (0.6 wide).

Si $K\beta$ and Co $L\alpha$ curves are given in figures 1(a) and 2(a) with the Fermi level taken as the origin. Each one is arbitrarily normalised on the intensity scale.

The Si $K\beta$ curve shows a main peak at $E_F - 4.2$ eV and a shoulder at about $E_F - 1$ eV which broadens the band up to 6 eV at half maximum. It noticeably differs from that of pure crystalline silicon which shows a peak at $E_F - 2.8$ eV and a faint shoulder at $E_F - 7.2$ eV (Senemaud and Costa-Lima 1979).

The general shape of Co $L\alpha$ from CoSi₂ is very close to that of pure cobalt. It presents a structureless asymmetrical line whose maximum is situated at $E_F - 1.6$ eV and the FWHM is 3.0 ± 0.2 eV, i.e. slightly narrower than in pure Co.

Photoemission experiments were carried out in an ultra-high-vacuum multitechnique system with a base pressure in the region of 10^{-10} mbar. The apparatus has been described previously (Veuillen *et al* 1989). The CoSi₂ sample (70 Å thick) has been grown epitaxially *in situ* on a clean Si (111) -7×7 substrate by solid-phase epitaxy: 20 Å of Co and 40 Å of Si were deposited successively by electron bombardment on the substrate held at room temperature. The film was then annealed at 580 °C for 10 min. This procedure is known to give a uniform CoSi₂ layer with a high percentage (almost 100%) of type B orientation and a low density of pinholes (Hunt *et al* 1987, Fisher *et al* 1988, Hellman and Tung 1988).

The LEED diagrams of the annealed layer were sharp and showed a threefold symmetry in the 75–80 eV range characteristic of a Si-rich silicide surface (Hellman and Tung 1988). XPS spectra were recorded using the unmonochromatised Mg $K\alpha$ line. The overall resolution was about 1 eV. The cleanliness of the surface was checked by core-level XPS before each measurement.

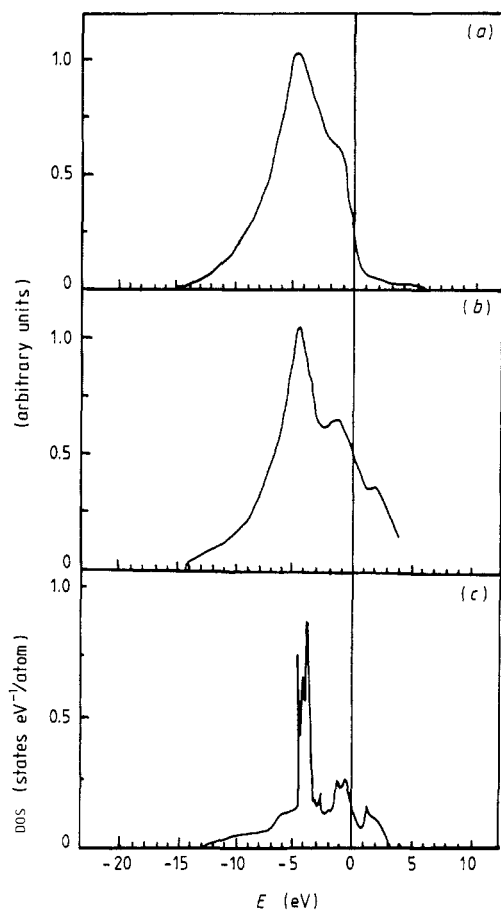


Figure 1. Experimental and theoretical partial Si p DOS in CoSi_2 . (a) Experimental SXS spectra. (b) Theoretical DOS broadened by a Lorentzian of FWHM equal to 0.6 eV. (c) APW DOS.

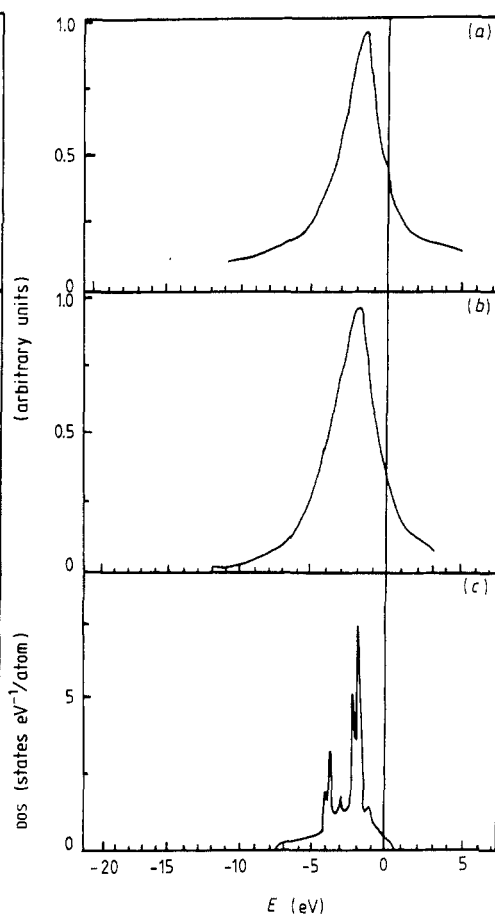


Figure 2. Experimental and theoretical partial Co d DOS in CoSi_2 . (a) Experimental SXS spectra. (b) Theoretical DOS broadened by a Lorentzian of FWHM equal to 0.8 eV. (c) APW DOS.

A typical XPS spectrum is shown in figure 3(a). It is very similar to XPS (Speier *et al* 1989, Veuillen *et al* 1989) and even to ARUPS (Pirri *et al* 1984) measurements found in the literature. Our spectra show a main peak located at 1.5–1.7 eV binding energy (BE), a weaker structure at 3.5–4 eV BE, and a broad one centred at about 9–10 eV BE.

3. Computational procedure

Using the experimental facts that CoSi_2 crystallises in the fluorite structure and has a lattice parameter of 5.36 Å, we have performed a scalar relativistic self-consistent band structure calculation by the APW method (Mattheiss *et al* 1968). This calculation has the following ingredients. It treats exchange and correlation in the local density approximation as prescribed by Hedin and Lundqvist (1971). It makes the muffin-tin approximation in terms of the shape of the crystal potential. This approximation is satisfactory for closed-packed cubic structures as can be seen by comparison with the 'LAPW-no-shape approximation' results of Mattheiss and Hamann (1988).

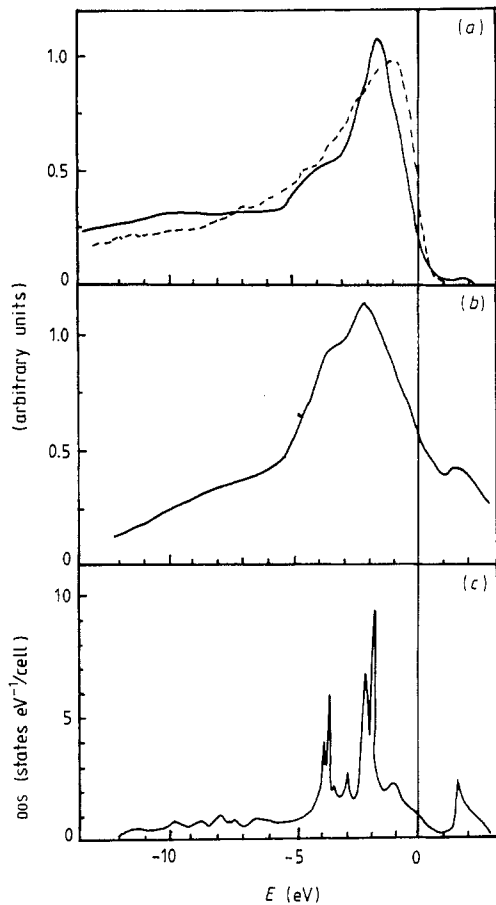


Figure 3. Experimental and theoretical total DOS in CoSi₂. (a) Experimental XPS spectra of CoSi₂ (full trace) and of Co (broken trace). (b) Theoretical DOS broadened by a Lorentzian of FWHM equal to 0.8 eV. (c) APW DOS.

In the iterative procedure, to reach self-consistency, a regular mesh of 19 k -points in the $\frac{1}{8}$ th of the Brillouin zone was used. This included the 3d and 4s Co states and the 3s and 3p Si states, while the core levels were also recalculated in each iteration using a fully relativistic atomic code (Lieberman *et al* 1971). The 19 k -points self-consistent potential was used to generate eigenvalues for 33 k -points in the irreducible zone, which were then interpolated to a fine grid of k -points by a Fourier series interpolation (Boyer 1979) that takes into account the symmetry of each k -point. These interpolated bands were then used to calculate the DOS by the tetrahedron method (Lehmann and Taut 1972). In the above procedure (Fourier series and tetrahedral interpolation), the integrated charges inside the muffin-tin spheres for each eigenvalue are also interpolated and used as weights in order to obtain the angular momentum components of the DOS. These partial DOS formally enter in the evaluation of $K\beta$ and $L\alpha$ x-ray emission spectra. To a good approximation, one can neglect matrix element effects which have a very weak energy dependence (McCaffrey and Papaconstantopoulos 1974) and assume that the x-ray intensities for $K\beta$ and $L\alpha$ spectra are proportional to the p and d DOS respectively. To facilitate the comparison with our experiments, we have applied to the theoretical partial DOS a Lorentzian broadening that accounts for the spectrometer resolution and the width of the respective core level. In this work we compare the broadened Si p and Co d DOS to our $K\beta$ and $L\alpha$ measured emission spectra and the total CoSi₂ DOS to the XPS spectra.

4. Comparison between experimental and theoretical spectra

APW DOS are presented in figures 1(c), 2(c) and 3(c). The total DOS (figure 3(c)) shows multiple structures and especially a large peak arising from Co d non-bonding states at 2.1 eV under the Fermi level E_F and two smaller peaks on each side of the first one due to silicon p-cobalt d bonding and antibonding states (-4.2 and -1.2 eV). A pseudo-gap follows the non-bonding states and the Fermi level falls below it. The total density of states is very similar to the one obtained by Mattheiss and Hamann (1988) from a linearised augmented plane wave calculation (LAPW) or the LMTO ASA result of Lambrecht *et al* (1987). These calculations stressed the strong silicon p-cobalt d coupling but they do not show the sp^3 character of the silicon bonds which can be seen in figure 1(c). The partial silicon p DOS in CoSi_2 is very similar to that of bulk silicon. This point is evoked in the work of Tersoff and Hamann (1983) in a LAPW calculation of CoSi_2 but their total DOS is less structured than ours.

As discussed above, the theoretical DOS were broadened to be compared with experimental spectra. Densities of states are convoluted with a Lorentzian distribution of FWHM 0.8 eV for total DOS and partial Co d spectra and 0.6 eV for partial Si p spectra. Broadened DOS are shown in figures 1(b), 2(b) and 3(b).

Experimental and theoretical spectra of partial silicon p are given in figures 1(a) and 1(b). The two curves exhibit a similar shape. The positions of the main peak are in very good agreement in the experimental and the theoretical curves. This peak is due to silicon p states which hybridise with Co d ones leading to p-d bonding states. A shoulder is present at $E_F - 1.0$ eV in the experimental spectra and 1.2 eV in the theoretical one. It results from the Si p states involved in the Si p-Co d antibonding states. A very good agreement is found for the energy position of the peaks as well as their relative intensities.

Experimental and calculated Co d curves are also in good agreement. They show one peak located at $E_F - 1.6$ eV in the experiment and $E_F - 2.1$ eV in the theory (figures 2(a) and 2(b)). This peak is related to Co d non-bonding states.

In a one-electron picture XPS spectra reflect the sum of the partial DOS weighted by the photoionisation cross section. Calculations of the XPS matrix elements for CoSi_2 (Speier *et al* 1989) as well as atomic calculations (Yeh and Lindau 1985) indicate that the main contributions to our spectra (figure 3(a)) originate from Co 3d- and Si 3s-derived states. The Si 3s partial DOS is responsible for the broad structure at about $E_F - 9$ eV but it should give only a small contribution near E_F . Our data in the 0-6 eV BE range should then be intermediate between the total DOS and the Co 3d partial DOS after broadening, due to the small cross section of the Si 3p states compared with that of Co 3d states. This can be seen in figures 3(a) and 3(b). The main experimental peak at $E_F - 1.7$ eV is found at -2.1 eV in the theoretical spectra and is due to Co d non-bonding states. The shoulder at $E_F - 3.7$ eV (-3.65 eV in the theory) comes from Co d-Si p bonding states. Note that there is a fair agreement between SXS and XPS data concerning the Co 3d energy position.

5. Conclusion

We have carried out the first experimental determination of CoSi_2 partial densities of states and performed APW calculations to provide a comparison between experimental XPS and SXS spectra and broadened APW densities of states.

A very good agreement is found between the theoretical predictions and the experimental determinations for both the relative position and the overall distribution of the

Co 3d and Si 3p states. This agreement confirms similar successes of the one-electron theory in other materials.

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