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Spin-polarized surface state of MnSb(0 0 0 1)

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Abstract. Knowledge of the spin-dependent electronic structure at surfaces and interfaces plays an increasingly important role when assessing possible use of novel magnetic materials for spintronic applications. It is shown that spin- and angle-resolved photoelectron spectroscopy together with *ab initio* electronic structure methods provides a full characterization of the surface electronic structure of ferromagnetic MnSb(0 0 0 1). Two different surface reconstructions have been compared in spin- and angle-resolved valence-band photoemission. For annealing at elevated temperatures, the (1×1)-structure transforms into 2×2 and a majority-spin peak appears at -1.7 eV inside a majority-spin bulk band gap at the surface Brillouin zone centre. Its sensitivity to oxygen supports an interpretation as magnetic compound surface state. Local spin density calculations predict at the same energy (-1.75 eV) a prominent d_{z^2} surface state of majority

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spin for (1 × 1)-Mn terminated MnSb(0 0 0 1) but no such feature for (1 × 1)-Sb termination. The calculation shows that neither the bulk nor the surface is half-metallic, in agreement with the expectation for the hexagonal NiAs structure.

Contents

1. Introduction

Ferromagnetic materials envisioned for spintronic applications are typically of complex structure. This holds in particular for the so-called half-metallic compounds with 100% predicted spin polarization at the Fermi energy. In recent years, the method of spin- and angle-resolved photoemission [1] has been used to probe the spin-dependent electronic structure of some of these materials and to prove the half-metallicity in $La_{0.7}Sr_{0.3}MnO_3$ [2]. Subsequently, half-metallicity or at least a high-spin polarization in the vicinity of E_F have been reported for various systems [3]–[5]. Photoemission and inverse photoemission are sensitive to the atomic layers at the surface when performed at kinetic energies between 10 and 100 eV which means that spectra will be affected if the spin-dependent electronic structure is strongly altered at the surface. This holds for an ideal bulk-truncated surface and will be particularly important in the case of surface segregation and/or surface reconstruction.

We have chosen the comparatively simple system MnSb(0 0 0 1) to demonstrate the capability of spin-resolved photoemission for assessing the spin-dependent bulk and surface electronic properties of a ferromagnetic compound. The transition-metal pnictides of NiAs-type crystal structure have interesting physical properties connected to their long-range magnetic order [6]. One reason why manganese monopnictides MnAs, MnSb, and MnBi, which are ferromagnetic metals, are considered candidates for future magnetic storage devices is the large magneto-optical effects and favourable Curie temperatures of MnSb and MnBi [7]. Multilayers of MnSb/Sb have shown perpendicular magnetic anisotropy [8]. The idea to apply these materials for magnetic storage has received renewed attention since growth of MnAs and MnSb epitaxially on semiconductor substrates has been achieved [9]–[11], enabling in this way the implementation of magnetic storage into integrated electronic circuits. Recently, with spin-dependent transport effects, an additional field of interest has been opened up for the application of manganese monopnictides: In granular MnSb films grown by molecular-beam epitaxy on sulfur-passivated GaAs(1 0 0) a magnetoresistive effect has been observed which leads to a ten-fold change in the electric current [12].

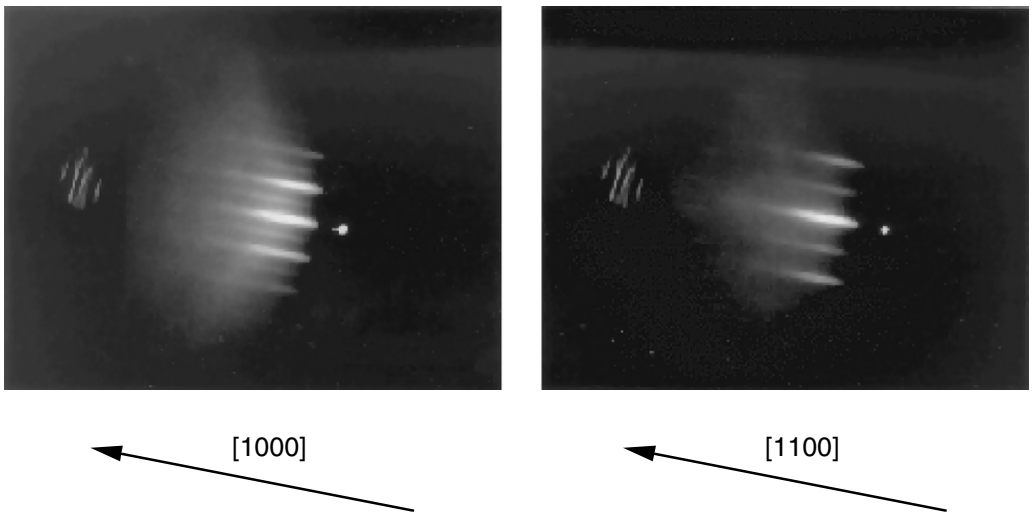

Figure 1. Reflection high-energy electron diffraction patterns showing a (2 × 2)-structure measured during film growth.

We have studied the spin-dependent electronic structure, geometry and composition of the MnSb surface in greater detail. We tested the behaviour of thick MnSb(0 0 0 1)/GaAs(1 1 1) upon annealing to different temperatures and upon oxygen dosage. It is observed that the spin-dependent electronic structure at the surface changes substantially. Our results indicate the formation of a magnetic surface state of an intermetallic compound.

2. Experiment

The MnSb(0 0 0 1) films in the μm thickness range have been grown onto GaAs(1 1 1) by molecular beam epitaxy using growth parameters like the ones given in [11]. Reflection high-energy electron diffraction has been performed during growth and is shown in figure 1. The angle of 30° between the two primary beam directions of [1 0 0 0] and [1 1 0 0] in figure 1 allows us to conclude on the surface structure. Both directions show intense additional streaks midway between the main streaks and are consistent with a (2 × 2)-superstructure. This superstructure was present after growth before capping with Sb and transfer to the spin-resolved photoemission setup. Sample surfaces were then reprepared by Ne^+ ion bombardment and annealing as has been described in a previous report [13], where the surface reconstruction was 1 × 1 and the MnSb bulk electronic structure has been explored. Similar to the previous study [13], the revolver undulator beamline [14] 19 A at Photon Factory, an angle-resolving electrostatic analyser, and a 100 keV Mott-type spin detector have been used. The light was predominantly s-polarized (18° off-normal incidence). The vacuum was between 1 and 2 × 10^{-10} Torr.

Figure 2(a) shows low-energy electron diffraction (LEED) patterns of (1 × 1)-type obtained after sputtering and annealing to 180 °C. When the sample is heated higher (≈250 °C for 10 min), the sharp and intense (2 × 2)-superstructure of figure 2(b) becomes visible.

Figure 3(a) shows the spin-resolved photoemission spectrum in normal emission geometry from the (1 × 1)-surface, which has already been interpreted previously [13]. In normal emission, photoemission transitions occur along the Γ–A line of the bulk Brillouin zone, and at 25.8 eV

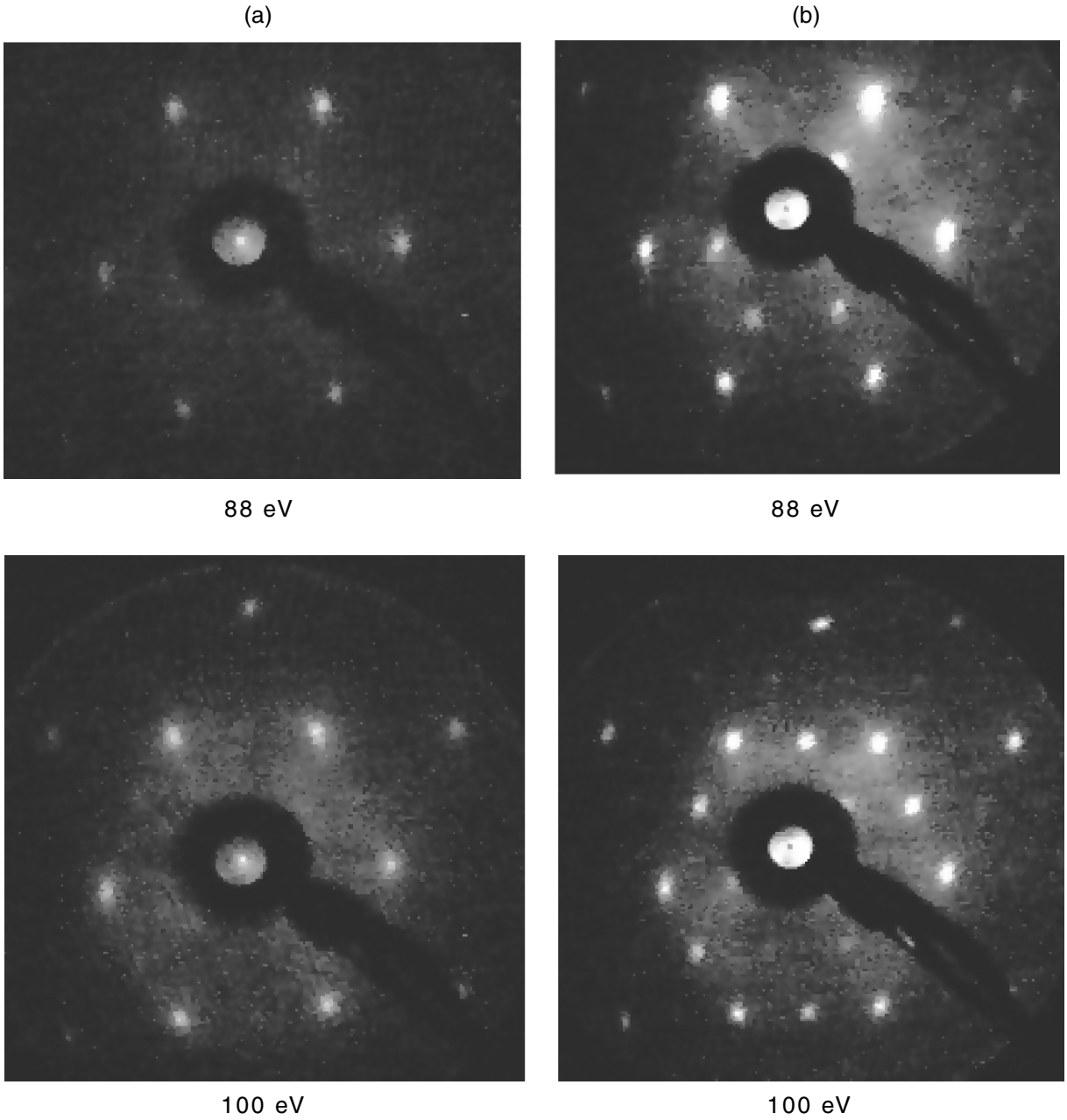

Figure 2. LEED patterns after annealing to 180 °C. A (1 × 1)-structure appears (a). The (2 × 2)-structure (b) occurs after annealing to ≈250 °C.

photon energy the A-point is reached. The assignment of peaks and shoulders to two kinds of bulk-derived states at the A-point, namely Mn 3d non-bonding states with large exchange splitting (about 3 eV) and Mn 3d–Sb 5p bonding states with smaller exchange splitting (1.7 eV), has been adopted for figure 3(a). Figure 3(b) shows the spectrum after annealing to ≈250 °C and (2 × 2)-formation. The spin polarization is generally smaller than in figure 3(a), and the bulk-derived peaks appear less sharp. The intensity at the Fermi energy has increased; the spin-polarization at E_F, however is still zero (equal intensities in the majority-spin and minority-spin spectra).

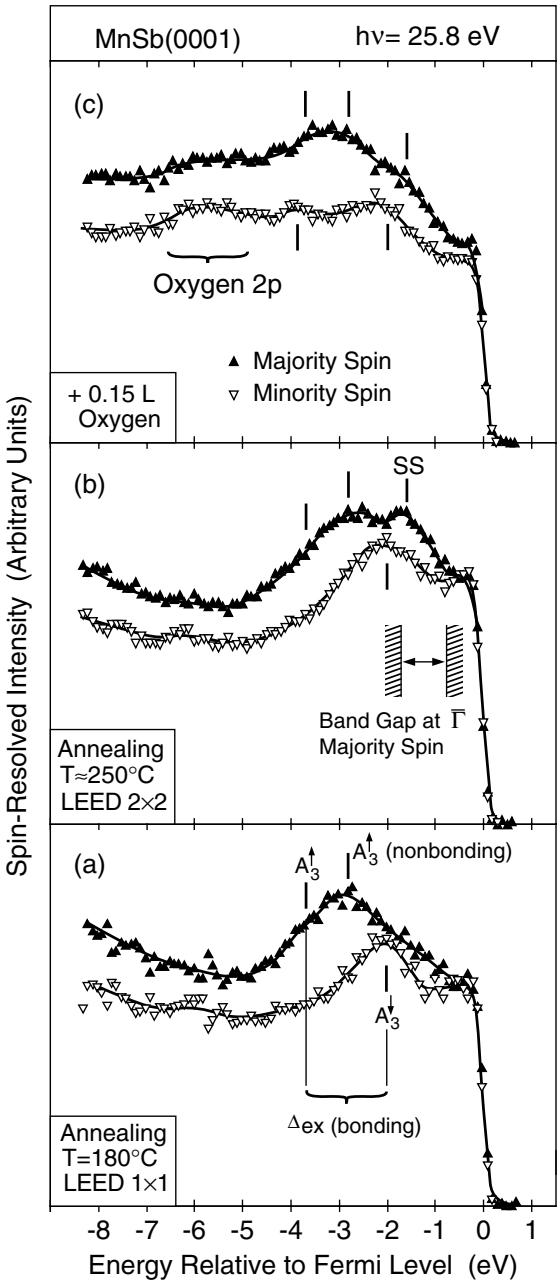

Figure 3. Spin-resolved photoemission spectra for both reconstructions (a, b). Upward (downward) triangles denote majority (minority) spin. Test of surface sensitivity by *in situ* dosage of 0.15 Langmuir oxygen (c). The peak SS is identified as magnetic surface state.

We noted previously that the intensity at E_F is higher and the spin polarization lower than what is expected from the bulk band structure [13]. The other apparent change in figure 3(b) is the appearance of an intensive extra peak 1.7 eV below E_F, which has been labelled SS. Analysis of the band structure [7, 13, 15, 16] reveals the existence of a bulk band gap. It appears along Γ–A and is thus effective at $\overline{\Gamma}$, the centre of the surface Brillouin zone. The gap exists only for majority spin and is marked in figure 3(b). The peak labelled SS at −1.7 eV appears inside but

close to the border of this gap. This border is, however, defined by Γ_{6+}, which is far away in k-space, so that the next expected majority-spin emission is indeed the one marked in figure 3(a) at −3.0 eV. From this argument it becomes obvious that the peak SS cannot be explained from the band structure of stoichiometric bulk MnSb leaving a non-stoichiometric bulk state and a surface state of the compound as possible interpretations. We have tested the dependence of the spectra on gas adsorption. A freshly prepared sample has been exposed to a small amount of oxygen (0.15 Langmuir) at lower temperature (≈130 K). The changes due to oxygen adsorption (figure 3(c)) are the following: (i) O-2p-derived emission appears between −5 and −6 eV in the spectra. (ii) The features assigned to bulk MnSb become broadened. (iii) The intensity at E_F is reduced and, again, the spin polarization at E_F is not very different from zero. This indicates that the surface is probably not responsible for the low spin polarization at E_F. (iv) A small peak appears for minority spin (and possibly also for majority spin) around −3.8 eV. It can be assigned to oxide formation as we observe extra intensity around −4 eV typically during the entire cleaning procedure. (v) The peak SS at −1.7 eV is reduced in intensity. The attenuation of SS is in fact stronger than that of the majority-spin peak at −3.0 eV which we have assigned to a bulk initial state. This is interpreted in favour of an assignment of SS as a compound surface state. The bulk-derived minority-spin peak at −2.0 eV ($A_3^{\downarrow}$, bonding) appears to be reduced in intensity as well. However, it is likely that rather than a reduction of this peak, it is growing in intensity at the higher-binding-energy shoulder of $A_3^{\downarrow}$ which wipes the slope of the peak out. A similar observation is made for the majority-spin spectrum.

3. Calculation

We have performed first-principles calculations of the electronic structure of MnSb(0 0 0 1). In the calculations, we employed the full-potential linearized augmented plane-wave method (FLAPW) [17, 18] in the FLEUR implementation [19]. We have modelled the MnSb(0 0 0 1) in a film geometry in two alternative ways: by a 15-layer Sb-terminated film and by a 17-layer Mn-terminated film. The band structures are displayed in figures 4(a) and (b) for the range +1 eV to −2 eV around the Fermi energy. The (0 0 0 1)-projection of the bulk band structure (grey) shows that for minority spin (figure 4(a)), there is no gap at $\overline{\Gamma}$, whereas for majority spin (figure 4(b)), a large gap opens from −0.75 to −1.75 eV. (Apparent gaps of smaller size, e.g., around the Fermi energy, are not considered because they are an effect of the finite layer thickness.) In this gap, a majority-spin surface state, non-degenerate with the bulk, is predicted for the Mn-terminated surface (blue). Such a state does not appear for Sb-termination (red). From this most simple model of the MnSb(0 0 0 1) surface, we conclude that the observed spin-polarized surface state is of Mn 3d character and that the surface atomic layer is either completely of Mn or Mn constitutes at least a large portion of the stochiometry of the (2 × 2)-MnSb(0 0 0 1) surface. The possible effects of an enlarged surface unit cell on spin-polarized surface states have recently been discussed for the NiMnSb(1 0 0) surface [20]. By comparison to the (1 × 1)-terminated calculation, it appears that there is no significant influence of the (2 × 2)-reconstruction in the present case and its origin remains unclear. There are several ways in which a hexagonal compound surface can form a (2 × 2)-reconstruction, and we recall the long controversy surrounding the $(\overline{1}, \overline{1}, \overline{1})$-surface of GaAs which was finally solved by scanning tunnelling microscopy [21, 22].

In our previous report [13], we noted that the intensity near E_F depends on the annealing conditions. The spin polarization at E_F for normal electron emission is almost zero whereas the bulk band structure predicts minority spin for emission near the A-point of the bulk Brillouin

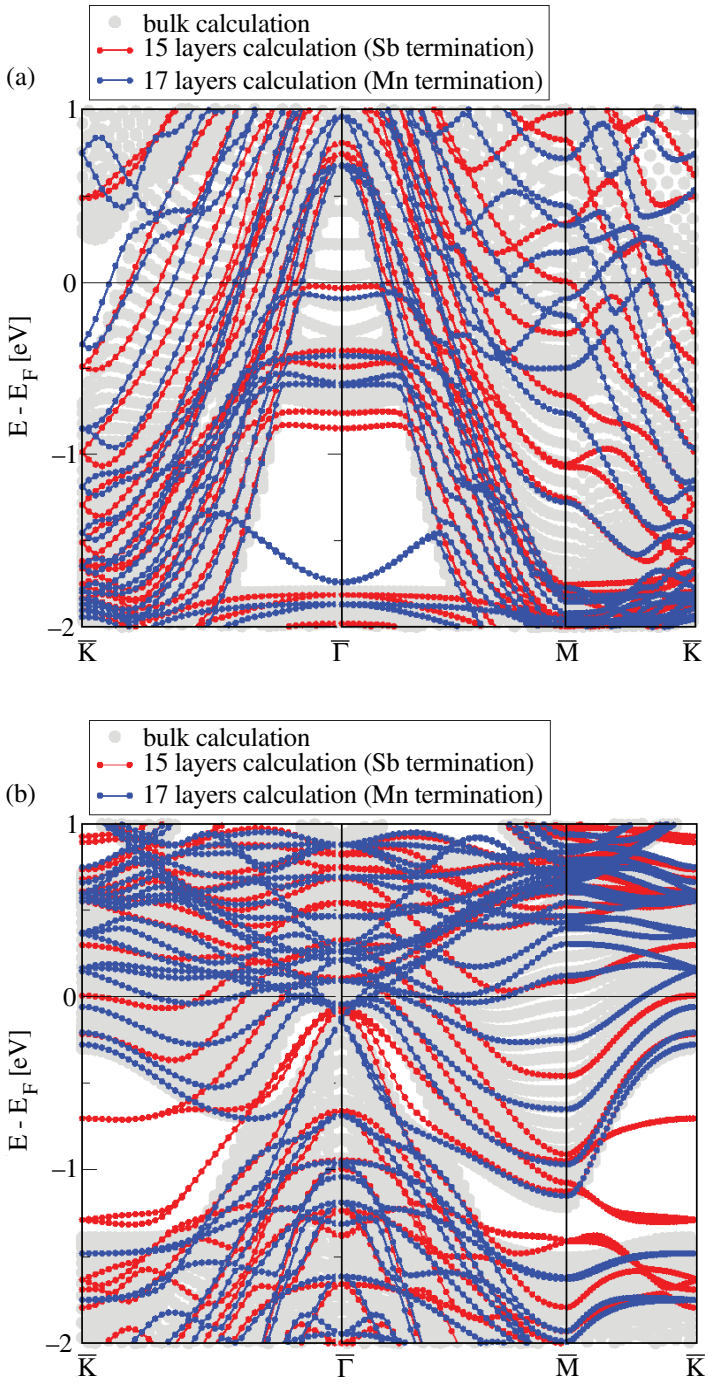

Figure 4. Surface band structure of majority spin (a) and minority spin (b) for a 15-layer MnSb(0 0 0 1) film with Sb-termination (red) and a 17-layer film with Mn-termination (blue). Surface-projected bulk bands are shown in grey. The Mn-terminated surface shows a majority-spin surface state at -1.75 eV at $\overline{\Gamma}$.

zone. The solution may be found in figure 4 which suggests that for Mn-termination (blue) a majority spin surface state at about -0.1 eV compensates for the spin polarization from the bulk photoemission transition.

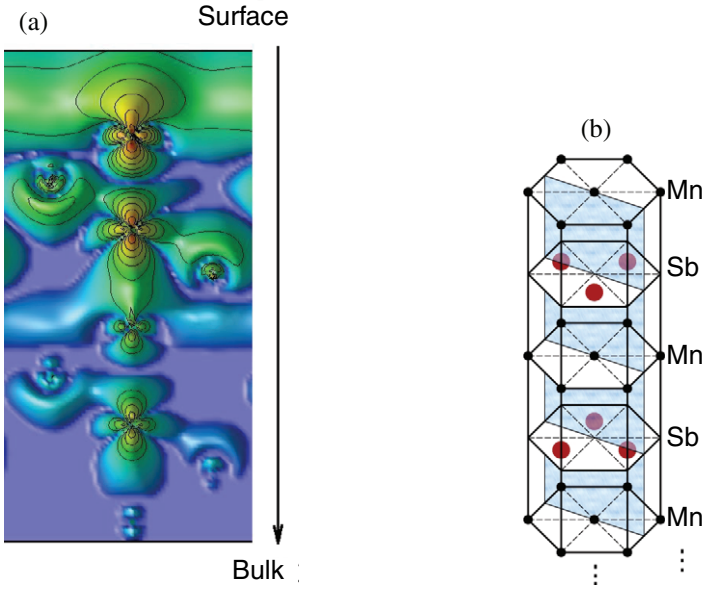

Figure 5. Charge-density map (a) of the surface state identified in figures 3 and 4 for the plane indicated in (b). The charge density is on a logarithmic scale and the surface state is highlighted by black contour lines. It is of d_{z^2}-character and extends down to the third atomic layer.

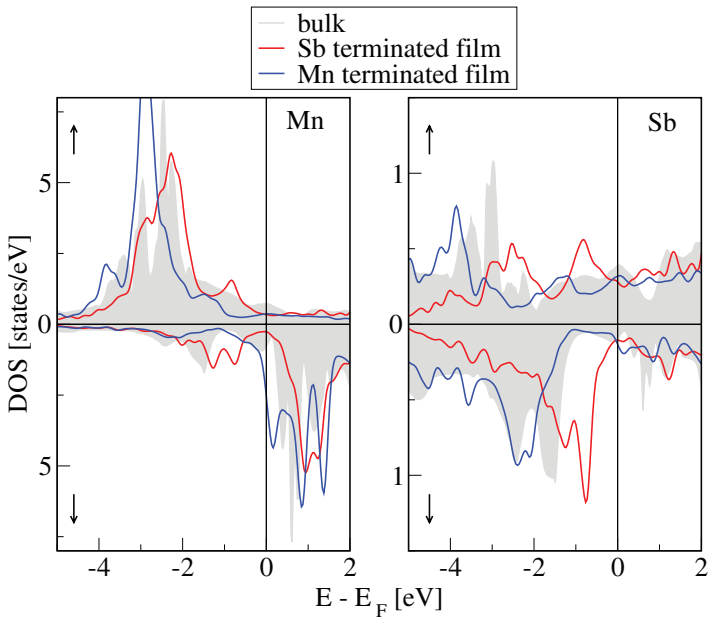

Figure 6. Density of states (DOS) of MnSb(0 0 0 1) at Mn (left) and Sb (right) sites. The surface-layer DOS for Sb-termination (red) and for Mn-termination (blue) is compared to the bulk Sb and Mn DOS (grey), respectively. The surface state identified in figures 3–5 is not distinct in the DOS because of its large dispersion.

Figure 5 shows a charge-density plot of the surface state identified. The surface state is of d_{z^2}-character, and extends into the bulk for about three atomic layers. Note that increasing the thickness of the slab used in the calculation will decouple the surface states coming from the two surfaces. The effect of the surface on the spin-dependent density of states is shown in figure 6. The present surface state does not appear as a sharp peak in the density of states due to its significant dispersion and proximity to the border of the gap. For the Mn-terminated surface, the surface Mn 3d density of states (blue) is shifted downwards with respect to the bulk (grey). This is due to charge that cannot be transferred to Sb neighbours and leads to extra occupation of minority spin states which are not occupied in the bulk. This has been noted for the zincblende MnAs(1 0 0) surface where this effect removes the half-metallicity present in the bulk calculation [23].

4. Conclusion

We have shown with the example of MnSb(0 0 0 1) that spin- and angle-resolved photoemission combined with *ab initio* electronic structure calculations for film geometry can give a detailed account of the surface electronic structure. Identification of a bulk band gap and a surface state as well as its removal by oxygen are all performed with spin resolution and found to be in perfect agreement with theory except for the (2×2)-reconstruction observed. Conversely, the identification of the spin-polarized surface state also means that the topmost surface atomic layer is ferromagnetically ordered in the experiment. These results indicate that it will also be possible to analyse the spin-dependent electronic structure of half-metallic systems like NiMnSb with atomic layer resolution.

Acknowledgments

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