Exchange splittings of Mn- and Sb-derived states by spin-resolved valence-band photoemission of MnSb

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We have grown epitaxial (0001)-oriented films of the ferromagnetic intermetallic compound MnSb on GaAs(111) substrates. The ex situ grown samples can be reprepared in such a way that clean, ordered, and magnetically saturated surfaces are obtained. Using spin-resolved photoemission, Sb5p- and Mn3d-derived spectral features are identified, and large exchange splittings (1.4 and 1.7 eV for Mn-Sb bonding states and about 3.0 eV for Mn nonbonding states) are measured. Our ab initio band-structure calculation agrees rather well with the experiment, reproducing the exchange splittings of Mn-Sb states but slightly underestimating that of Mn states. [S0163-1829(98)50802-8]

Progress in various research areas has in the past years rendered the ferromagnetic manganese monopnictides MnAs, MnSb, and MnBi prime candidates for materials of novel electronic devices: Large Kerr rotation angles, needed in magneto-optical recording, have been measured for MnBi (Ref. 1) and MnSb5%Pt. 2 Both MnSb and MnBi have a large magnetic moment and a Curie temperature well above room temperature (e.g., MnSb: $\mu = 3.5 \mu_B$ and $T_C = 585$ K; see Ref. 3). The hexagonal crystal structure [NiAs type, Fig. 1(b)] is favorable for obtaining uniaxial magnetocrystalline anisotropies, and it has already been achieved to induce perpendicular magnetic anisotropy, which is desired in recording devices, in films of MnSb$_{1-x}$Bi$_x$. 2 MnSb has been studied by magnetic circular x-ray dichroism, and a substantial orbital magnetic moment was found. 3 Very recently, epitaxial growth of MnAs (Ref. 5) and MnSb (Ref. 6) films on GaAs crystals has become possible, thus enabling the integration of ferromagnetic storage into semiconductor devices.

The various theoretical approaches to the electronic structure of MnSb have been reviewed in Ref. 3. In brief, ionic-like models and alloylike models for different degrees of hybridization between Mn and Sb electronic states have been proposed. Recently, several calculations employing a band-structure model were conducted. 3,7 However, these predictions have never been tested by angle-resolved photoemission, and comparison to experimental data was limited to magnetic-moment and specific-heat measurements. Valence band x-ray photoemission 8 was only of limited benefit as it was found to be in agreement both with a simple superposition of spectra of pure Mn and Sb in Ref. 8 and with a band calculation predicting a large Mn moment and strong Mn3d-Sb5p hybridization in Ref. 3.

Using spin- and angle-resolved photoemission, we want to verify experimentally which model of the electronic structure is appropriate. The experiment on MnSb is particularly challenging from the preparative point of view because of the limited probing depth of the experiment (a few atomic layers) and the possibility of losing the large Mn magnetic moment and the ferromagnetic coupling of these moments in the probed surface area if that should deviate from the ideal MnSb crystal structure. It will be seen that it is possible to obtain well-ordered and magnetically saturated surfaces and that analysis of the spin is indeed essential in order to assign spectral features and to verify in this way the complicated electronic structure of MnSb.

MnSb(0001) films in the $\mu$m thickness range were grown onto GaAs(111) in a molecular beam epitaxy chamber at JRCAT. Characterization during the growth was done using reflection high-energy electron diffraction and Auger electron spectroscopy. Growth parameters were similar to the ones published in Ref. 6. The samples were capped with Sb and exposed to air during transport to the beamline. Sample surfaces were reprepared by Ne$^+$ ion bombardment and annealing cycles until an intense and sharp hexagonal low-energy electron diffraction pattern became visible indicating a well-ordered surface. It was verified by Auger specros-
copy and photoemission at low photon energies that carbon and oxygen contaminations had completely been removed. Samples were remanently magnetized by applying a magnetic pulse in the film plane. We verified with magneto-optical Kerr effect that the remanent magnetization was almost 100% of the saturation magnetization. Spin- and angle-resolved photoemission measurements have been performed using linearly polarized light from the revolver undulator beamline 19A of ISSP at Photon Factory, Tsukuba, for excitation and a 100-keV Mott detector for spin analysis. The light was predominantly s polarized (18° off-normal incidence). Angle-resolved photoemission spectra were also taken at beamline 18A with mixed (s and p) polarization (45° incidence). The vacuum was between 1 and 2 x 10^{-10} Torr, and the sample was cooled to LN2 temperature during spin-resolved measurements.

The appropriate photon energies for probing the electronic structure of MnSb lie below the 3p-3d resonant excitation threshold of Mn (50 eV). We measured angle-resolved photoemission spectra between hν = 20 eV and 40 eV [Fig. 1(a)]. Emission was found to extend from EF down to about 6 eV, assigned to Sb 5p and Mn 3d states and 10–11 eV assigned to Sb 5s states (not shown). However, a clear separation of Mn3d- and Sb5p-derived spectral features appears difficult, possibly due to substantial hybridization between these orbitals.

Figure 2 shows spin-resolved photoelectron spectra. For 25.8 eV and 38.2 eV photon energies we expect to probe bulk initial states near the A and Γ points, respectively [see the Brillouin zone in Fig. 1(b)]. The spectrum at the bottom, measured at 25.8 eV photon energy, displays large differences between the majority- (upward triangles) and the minority-spin channel (downward triangles), proving ferromagnetic order in the surface region of the sample. In detail, there appears a single peak in the minority spectrum at −2.0 eV and a broader peak (∼−2.8 eV) with a low-energy shoulder (∼−3.7 eV) in the majority spectrum. We expect Sb-derived emission to be less intense than Mn emission because the photoionization cross section favors Mn3d over Sb5p at this photon energy. The structures in each spin channel with lowest energy, i.e., the majority-spin shoulder at ∼−3.7 eV and the minority-spin peak at ∼−2.0 eV, are of comparable intensity and smaller than the main majority-spin peak. Their energy separation, 1.7 eV, is incompatible with pure Mn3d states in view of the large measured Mn moment of 3.5μB, and they are for this reason assigned as exchange-split states with substantial Sb5p character. The maximum of the intense peak centered around ∼−2.8 eV is, on the other hand, assigned to Mn3d. As a second intense minority spin peak is absent, the spectrum suggests that the Mn exchange splitting is very large (>−2.8 eV), so that the corresponding minority-spin state is unoccupied.

This interpretation is corroborated by our electronic structure calculations from first principles using the full-potential linearized augmented plane wave (FLAPW) method. In Fig. 3 we have highlighted Mn-Sb bonding states (dashed) and Mn nonbonding states (solid). For symmetry reasons we expect in the present setup along [0001] (Γ-A-A direction) emission from Δ5 and Δ6 initial states. The band structure shows that the A point is fortunate for determining the exchange splitting since Δ5 and Δ6 states are degenerate here and, for minority spin, emission from only one initial state (Δ3 symmetry) is expected.

Towards Γ, the Δ5 bands disperse to lower energies. This
FIG. 3. MnSb band structure along $\Gamma$-A-A calculated from first principles. Exchange splittings of Mn-Sb bonding ($b$, thick dashed line) and Mn nonbonding (nb, thick solid line) states are indicated. Sb5s-derived bands at lower energy are not shown. Energies are referred to $E_F$.

can also be seen from the spectra in Fig. 2. The position of the minority-spin peak assigned to Sb changes from $-2.0 \text{ eV}$ at $h\nu=25.8 \text{ eV}$ to $-2.5 \text{ eV}$ at $38.2 \text{ eV}$. In our calculation, the Mn nonbonding minority-spin $\Lambda_5$ band follows this dispersion, and it is predicted that this band becomes occupied halfway between $A$ and $\Gamma$. In the $38.2$-eV spectrum a small peak at $E_F$ is seen but no minority spin polarization. As a whole, this spectrum appears less spin polarized than the $25.8$-eV spectrum. Although a somewhat smaller polarization can be expected (e.g., around $-3 \text{ eV}$) because the calculations predict, in agreement with our spectra, a smaller exchange splitting of Mn-Sb bonding states at $\Gamma$ than at $A$, the main cause for a reduced polarization at $h\nu=38.2 \text{ eV}$ is likely to be the smaller probing depth of photoelectrons and therefore a larger contribution of surface imperfections to the spectrum at this photon energy. We might therefore consider the set of spin-averaged spectra of Fig. 1(b), where we find an indication for a band crossing the Fermi level going from $A$ to $\Gamma$. The only crossing of $E_F$ predicted is the Mn nonbonding $\Lambda_5$ minority-spin band, and we suggest therefore that the exchange splitting of Mn $3d$ states can be measured between the maximum of the majority peak in the $38.2$-eV spectrum and roughly the position of the Fermi energy as $3.0 \text{ eV}$.

The exchange splittings are summarized in Table I and the boxes in Fig. 2 also show for comparison energy positions of exchange split pairs of states calculated here and in Ref. 3.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>ASW (Ref. 3)</th>
<th>FLAPW</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_{\text{ex}}(\Gamma_{++},b)$</td>
<td>$1.4 \pm 0.3$</td>
<td>$1.51$</td>
</tr>
<tr>
<td>$\Delta_{\text{ex}}(A_1,b)$</td>
<td>$1.7 \pm 0.3$</td>
<td>$1.72$</td>
</tr>
<tr>
<td>$\Delta_{\text{ex}}(\Gamma_{++},\text{nb})$</td>
<td>$\approx 3.0$</td>
<td>$2.51$</td>
</tr>
<tr>
<td>$\Delta_{\text{ex}}(A_1,\text{nb})$</td>
<td>$&gt; 2.8$</td>
<td>$2.66$</td>
</tr>
<tr>
<td>$\mu$</td>
<td>$3.5$ (Ref. 3)</td>
<td>$3.24$</td>
</tr>
</tbody>
</table>

The measured exchange splittings of Mn-Sb bonding states are in very good agreement with the calculation. The energy broadening of the minority peak (about $1.2 \text{ eV}$ FWHM) agrees with the one determined in Ref. 16 for Fe, neighboring Mn in the periodic system ($1.2 \text{ eV}$ at $2 \text{ eV}$ below $E_F$). The energy position measured at $25.8 \text{ eV}$ cannot directly be compared to the calculation because $k_\perp$ is uncertain, but the position measured for $h\nu=38.2 \text{ eV}$ ($-2.5 \text{ eV}$) is equal or lower than the calculated bottom of the $\Delta_5$ minority-spin band ($-2.41 \text{ eV}$ here; $-2.16 \text{ eV}$ in Ref. 3). We also see that the measured exchange splitting of Mn nonbonding states of about $3.0 \text{ eV}$ is slightly larger than that obtained by the calculations.

There is not much experience in probing the band structure of a material with so large ferromagnetic exchange splitting and moment. Fe, Co, and Ni show much smaller splittings (experimentally about 2.2, 1.4, and 0.3 eV, respectively), and a narrowing of the 3$d$ band width (by about $10\%$ for Fe and $30–50 \%$ for Ni) with respect to band theory is found in photoemission, contrasting somewhat the present results, where some peaks are found slightly farther away from $E_F$. On the other hand, deviations reported here for the exchange splitting can already be explained by an understimation of the magnetic moment in the calculation (Table I). The deviations are also much smaller than, e.g., for the strongly correlated systems MnTe($111$) (Ref. 17) and $c(2\times2) \text{ CuMn/Cu}(100)$,\textsuperscript{18} where splittings (in photoemission and inverse photoemission) exceed the ones from band theory by factors of $1.5$ and $2$, respectively. Therefore, we conclude that correlation effects play rather a minor role in the electronic structure of MnSb.

The related, although structurally different, compound NiMnSb has by band theory been predicted to be a half-metallic ferromagnet with the property of full spin polarization at the Fermi level.\textsuperscript{19} The present results lend credit to the band theory approach for the Mn pnictides, and an experimental investigation of this exciting property should be undertaken.

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Critical-point energies could not ambiguously be extracted from angle-resolved photoemission spectra. Therefore, $k_L$ was estimated with free-electron parabolas assuming an inner potential of $-10$ eV and a work function of $4.5$ eV. For initial states of $-3$ eV, $\Delta$ and $\Gamma$ points are predicted at $25.6$ eV and $37.9$ eV photon energy, respectively.

12 Photoionization cross sections vary strongly in the photon energy range studied here. Ratios, calculated for the atom, of Mn$3d$ vs Sb$5p$ cross sections are $5.12$ at $25.8$ eV and $22.70$ at $38.2$ eV [J.-J. Yeh, Atomic Calculation of Photoionization Cross-Sections and Asymmetry Parameters (Gordon and Breach, New York, 1993)].

There is also some intensity closer to the Fermi level (around $-1$ eV for majority spin and around $E_F$ for minority spin). This intensity was found to depend on annealing conditions and is therefore not thought of as representative of stoichiometric bulk MnSb.

For details of the calculations, see M. Shirai and Y. Tokioka, J. Electron Spectrosc. Relat. Phenom. (to be published).


