PHYSICAL REVIEW B VOLUME 57, NUMBER 2 1 JANUARY 1998-II

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

Oliver Rader*
Department of Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Akio Kimura, Nozomu Kamakura, Ki-Seok An, and Akito Kakizaki
Institute for Solid State Physics (ISSP), University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan

Shintaro Miyanishi and Hiroyuki Akinaga
Joint Research Center for Atom Technology, National Institute for Advanced Interdisciplinary Research (JRCAT-NAIR), 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

Masafumi Shirai
Department of Physical Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama-cho, Toyonaka 560, Japan

Kenya Shimada and Atsushi Fujimori
Department of Physics, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

(Received 8 October 1997)

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.[4] 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 μm 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 spectros-

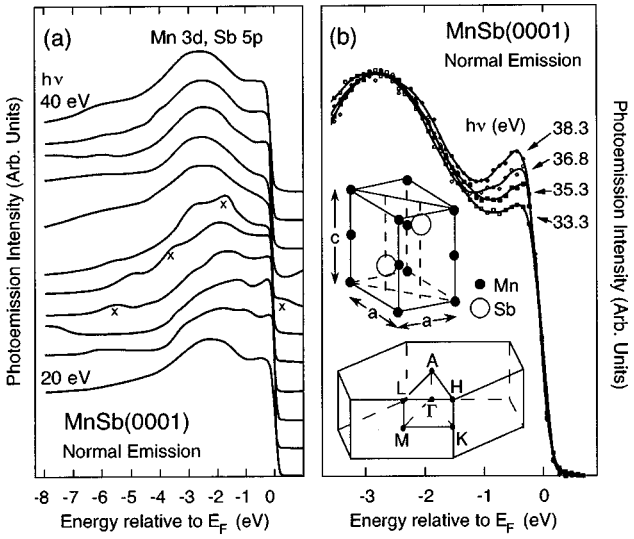

FIG. 1. (a) Angle-resolved photoemission spectra between 20 eV and 40 eV photon energy in steps of 2 eV. Light polarization is mixed $s+p$. Intensity induced by second-order light is marked. (b) Selected spectra for mainly s-polarized light near Γ. The spectra are consistent with a minority-spin band crossing E_F on the way from A to Γ. Crystal structure (NiAs type) of MnSb and bulk Brillouin zone are also given.

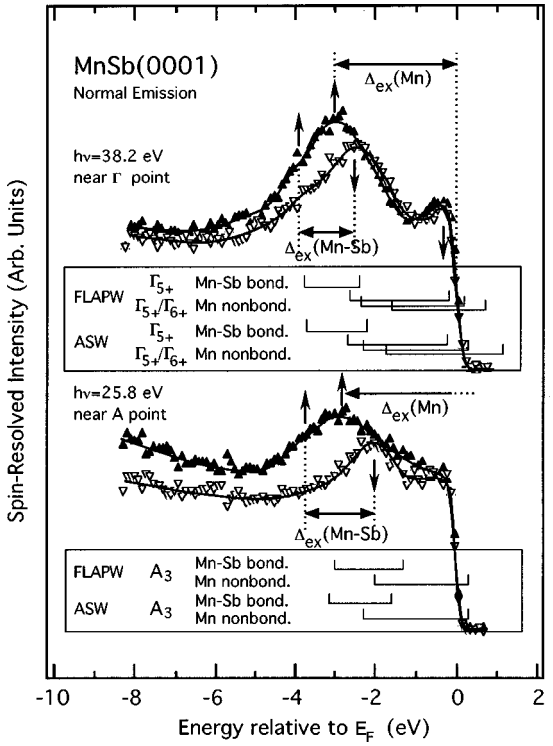

FIG. 2. Spin- and angle-resolved photoemission spectra of MnSb(0001). Upward triangles denote majority spin, downward triangles minority spin. Spectral features corresponding to exchange-split pairs of states are indicated. In addition, predictions for energy positions of exchange split states from this work (FLAPW) and Ref. 3 (ASW) are given.

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[9] 19A of ISSP at Photon Factory, Tsukuba, for excitation and a 100-keV Mott detector[10] 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 2×10^{-10} Torr, and the sample was cooled to LN_2 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 $h\nu=20$ eV and 40 eV [Fig. 1(a)]. Emission was found to extend from E_F 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 Mn$3d$- and Sb$5p$-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)].[11] 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 Mn$3d$ over Sb$5p$ at this photon energy.[12] 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 Mn$3d$ states in view of the large measured Mn moment of $3.5\mu_B$, and they are for this reason assigned as exchange-split states with substantial Sb$5p$ character. The maximum of the intense peak centered around -2.8 eV is, on the other hand, assigned to Mn$3d$. 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.[13]

This interpretation is corroborated by our electronic structure calculations from first principles using the full-potential linearized augmented plane wave (FLAPW) method:[14] In Fig. 3 we have highlighted Mn-Sb bonding states (dashed) and Mn nonbonding states (solid). For symmetry reasons[15] we expect in the present setup along [0001] (Γ-Λ-A direction) emission from Λ_5 and Λ_6 initial states. The band structure shows that the A point is fortunate for determining the exchange splitting since Λ_5 and Λ_6 states are degenerate here and, for minority spin, emission from only one initial state (A_3 symmetry) is expected.

Towards Γ, the Λ_5 bands disperse to lower energies. This

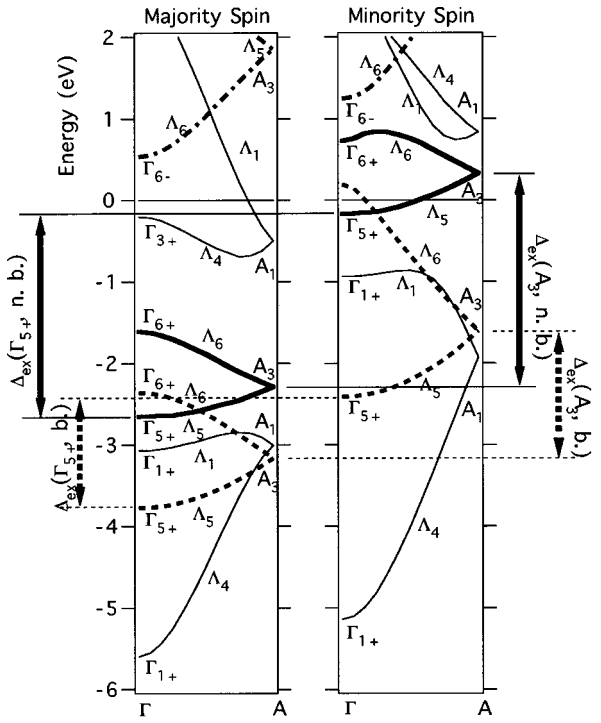

FIG. 3. MnSb band structure along Γ-Λ-*A* calculated from first principles. Exchange splittings of Mn-Sb bonding (b, thick dashed line) and Mn nonbonding (nb, thick solid line) states are indicated. Sb5*s*-derived bands at lower energy are not shown. Energies are referred to E_F.

can also be seen from the spectra in Fig. 2. The position of the minority-spin peak assigned to Sb changes from −2.0 eV at $h\nu=25.8$ eV to −2.5 eV at 38.2 eV. In our calculation, the Mn nonbonding minority-spin Λ_5 band follows this dispersion, and it is predicted that this band becomes occupied halfway between *A* and Γ. 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 eV) because the calculations predict, in agreement with our spectra, a smaller exchange splitting of Mn-Sb bonding states at Γ than at *A*, the main cause for a reduced polarization at $h\nu=38.2$ 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 Γ. The only crossing of E_F predicted is the Mn nonbonding Λ_5 minority-spin band, and we suggest therefore that the exchange splitting of Mn 3*d* 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 eV.

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

TABLE I. Measured exchange splittings of Mn-Sb bonding (b) and Mn nonbonding (nb) states compared to theory (in eV). The total magnetic moment is also given (in μ_B).

	Expt.	ASW (Ref. 3)	FLAPW
$\Delta_{ex}(\Gamma_{5+},b)$	1.4±0.3	1.51	1.36
$\Delta_{ex}(A_3,b)$	1.7±0.3	1.72	1.56
$\Delta_{ex}(\Gamma_{5+},nb)$	≈3.0	2.51	2.48
$\Delta_{ex}(A_3,nb)$	>2.8	2.66	2.62
μ	3.5 (Ref. 3)	3.24	3.21

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 eV FWHM) agrees with the one determined in Ref. 16 for Fe, neighboring Mn in the periodic system (1.2 eV at 2 eV below E_F). The energy position measured at 25.8 eV cannot directly be compared to the calculation because $\mathbf{k}_\perp$ is uncertain, but the position measured for $h\nu=38.2$ eV (−2.5 eV) is equal or lower than the calculated bottom of the Λ_5 minority-spin band (−2.41 eV here; −2.16 eV in Ref. 3). We also see that the measured exchange splitting of Mn nonbonding states of about 3.0 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 underestimation 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 $c(2\times2)$ CuMn/Cu(100),[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.[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.

O.R. acknowledges financial support by the Japan Society for the Promotion of Science and a Grant-in-Aid by the Ministry of Education, Science and Culture, Japan, as well as support by Alexander von Humboldt-Stiftung. This work was partly supported by the New Energy and Industrial Technology Development Organization (NEDO).

*Electronic address: rader@exp.bessy.de

[1] K. Egashira and T. Yamada, J. Appl. Phys. **45**, 3643 (1974).

[2] M. Takahashi, H. Shoji, Y. Hozumi, and T. Wakiyama, J. Magn. Magn. Mater. **131**, 67 (1994).

[3] R. Coehoorn, C. Haas, and R. A. de Groot, Phys. Rev. B **31**, 1990 (1985). Eigenvalues quoted here were taken from Fig. 4.

[4] A. Kimura, S. Suga, S. Imada, T. Muro, T. Shishidou, S. Y. Park, T. Miyahara, T. Kaneko, and T. Kanomata, J. Electron Spectrosc. Relat. Phenom. **78**, 287 (1996); Phys. Rev. B **56**, 6021 (1997).

[5] M. Tanaka, J. P. Harbison, M. C. Park, Y. S. Park, T. Shin, and G. M. Rothberg, Appl. Phys. Lett. **65**, 1964 (1994).

[6] H. Akinaga, Y. Suzuki, K. Tanaka, K. Ando, and T. Katayama, Appl. Phys. Lett. **67**, 141 (1995); H. Akinaga, K. Tanaka, K. Ando, and T. Katayama, J. Cryst. Growth **150**, 1144 (1995).

[7] K. Motizuki, J. Magn. Magn. Mater. **70**, 1 (1987).

[8] K. S. Liang and T. Chen, Solid State Commun. **23**, 975 (1977).

[9] A. Kakizaki, H. Ohkuma, T. Kinoshita, A. Harasawa, and T. Ishii, Rev. Sci. Instrum. **63**, 367 (1992).

[10] J. Fujii, T. Kinoshita, K. Shimada, T. Ikoma, A. Kakizaki, T. Ishii, H. Fukutani, A. Fujimori, K. Soda, H. Sugawara, in *Proceedings of the International Symposium on High Energy Spin Physics*, edited by T. Hasegawa, N. Horikawa, A. Masaike, and S. Sawada (Universal Academy Press, Tokyo, 1992), p. 885.

[11] Critical-point energies could not ambiguously be extracted from angle-resolved photoemission spectra. Therefore, $\mathbf{k}_\perp$ 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, A and Γ 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 Mn3d vs Sb5p 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)].

[13] 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.

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

[15] F. J. Himpsel and D. E. Eastman, Phys. Rev. B **21**, 3207 (1980).

[16] A. Santoni and F. J. Himpsel, Phys. Rev. B **43**, 1305 (1991).

[17] K. Mimura, H. Sato, S. Senba, H. Namatame, and M. Taniguchi, Physica B **237-238**, 392 (1997).

[18] O. Rader, W. Gudat, C. Carbone, E. Vescovo, S. Blügel, R. Kläsges, W. Eberhardt, M. Wuttig, J. Redinger, and F. J. Himpsel, Phys. Rev. B **55**, 5405 (1997).

[19] R. A. de Groot, F. M. Mueller, P. G. van Engen, and K. H. J. Buschow, Phys. Rev. Lett. **50**, 2024 (1983).