ELSEVIER Journal of Electron Spectroscopy and Related Phenomena 101–103 (1999) 657–660

JOURNAL OF ELECTRON SPECTROSCOPY and Related Phenomena

Electronic structure of MnSb and MnP

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Abstract

We have investigated the valence-band and conduction-band electronic structure of MnSb and MnP by means of ultraviolet photoemission and inverse-photoemission spectroscopies. The photoemission and inverse-photoemission spectra are qualitatively consistent with the results of band-structure calculations. The spectral shapes are substantially different between MnSb and MnP, which indicates that the Mn 3d electrons in MnP are more itinerant than those in MnSb.

Keywords: MnSb; MnP; Electronic structure; Photoemission; Exchange splitting

1. Introduction

Manganese pnictides MnX (X=P, As, Sb, Bi) have attracted considerable interest because of their various physical properties associated with their ferromagnetism, such as strong magneto-optical effects, uniaxial magnetic anisotropy and structural phase transition. MnSb with a NiAs-type crystal structure is ferromagnetic below T_c=587 K [1]. On the other hand, MnP has a crystal structure, so called MnP-type, which slightly distorts from the NiAs-type. The compound is antiferromagnetic with a helical spin structure below T_α=47 K, ferromagnetic between T_α and T_c=291.5 K and paramagnetic above T_c [2,3].

In order to understand the physical properties of these compounds, knowledge of the electronic structure, in particular, hybridization between Mn 3d and anion p states is indispensable. Coehoorn et al. [4], Motizuki [5], and Shirai and Tokioka [6] have done first-principle band-structure calculations on MnSb and discussed its physical properties from the itinerant electron point of view. These calculations have revealed a large magnetic moment on Mn atoms and strong p–d hybridization. Rader et al. [7]performed spin- and angle-resolved photoemission studies for MnSb, and discussed the Sb 5p and Mn 3d contributions to the valence-bands and larger exchange energies than those given by the band-structure calculations. Yanase and Hasegawa [8] reported the density of state (DOS) of MnP and revealed that the Mn 3d minority-spin states mainly contribute to the DOS near the Fermi level. Kakizaki et al. [9] carried out photoemission measurements for MnP and pointed out the strong itinerant nature of Mn 3d electrons.

To our knowledge, however, there has been no direct information on the conduction bands. In this paper, we report the valence-band and conduction-band electronic structures of MnSb and MnP by

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0368-2048/99/$ – see front matter
PII: S0368-2048(98)00331-4

means of ultraviolet photoemission and inverse-photoemission spectroscopies (UPS and IPES). We discuss the electronic structures of MnSb and MnP comparing the UPS and IPES spectra with the DOSs given by the band-structure calculations.

2. Experimental

Polycrystals of MnSb and MnP were grown by the Bridgman method. Equal amounts of pure Mn and Sb in quartz ampoule was heated to a maximum temperature of 950°C, kept at this temperature for a few days, and slowly cooled down to a lower temperature. In the case of MnP, the same procedure was employed, except that a maximum temperature of 1150°C was used. We confirmed homogeneous crystal phases of NiAs- and MnP-type structures by X-ray powder diffraction analysis. The compositions of the crystals were evaluated by electron-probe micro-analysis.

The apparatus used for the present experiments is composed of three ultrahigh vacuum chambers for sample preparation, UPS and IPES measurements. The UPS spectrometer is equipped with a He discharge lamp ($h\nu$=21.2 and 40.8 eV) and a double-stage cylindrical-mirror analyzer. The energy resolution was set to be 0.2 eV. The IPES spectrometer consists of a low-energy electron gun of the Erdman-Zipf type and a bandpass photon detector centered at 9.43 eV. The overall energy resolution was 0.56 eV [10,11]. Clean surfaces of samples were prepared by scraping them with a diamond file in the preparation chamber, and transferring them in situ into the UPS and IPES chamber. The base pressures for sample preparation, UPS and IPES chambers are 5×10^{-11}, 4×10^{-10} and 7×10^{-11} Torr, respectively. All experiments were performed at room temperature.

3. Results and discussion

Fig. 1 shows valence-band UPS spectra measured at photon energies of $h\nu$=21.2 and 40.8 eV and the conduction-band IPES spectrum of MnSb. Energy refers to the Fermi level. The UPS spectrum taken at $h\nu$=21.2 eV exhibits a main peak at −3.0 eV and a small structure at around −5.7 eV. In the UPS spectrum taken at $h\nu$=40.8 eV, the main peak becomes dominant, and a broad structure due to Sb 5s states appears at around −10.1 eV. The difference between the UPS spectra taken at $h\nu$=21.2 and 40.8 eV is due to the energy-dependent photoionization cross-sections of Mn 3d and Sb 5p states. The cross-section of Mn 3d states is nearly equal to that of the Sb 5p states at $h\nu$=21.2 eV, while it is much larger at $h\nu$=40.8 eV [12]. The basic features in the valence bands agree well with the results of synchrotron radiation photoemission experiments for MnSb (0001) film grown ex situ by molecular beam epitaxy [7]. The IPES spectrum shows a main peak at 1.2 eV and a broad structure at around 4.3 eV.

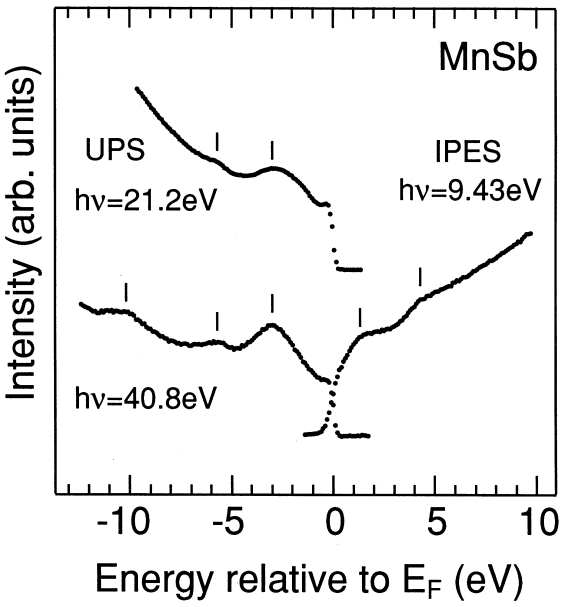

Fig. 1. UPS spectra measured at $h\nu$=21.2 and 40.8 eV, and IPES spectrum of MnSb. Energy refers to the Fermi level. Vertical bars indicate the position of structures.

Fig. 2(a) shows the total DOSs and Mn 3d partial DOSs for the majority (↑)- and minority (↓)-spin states given by the band-structure calculation with a full-potential linearized augmented-plane-wave method [6]. The valence bands and the conduction bands are composed mainly of strongly hybridized Mn 3d and Sb 5p orbitals. The Mn 3d↑ and Mn 3d↓ bands are essentially occupied and unoccupied, respectively. Here, we convolute the theoretical DOSs with the Gaussian and Lorentzian function,

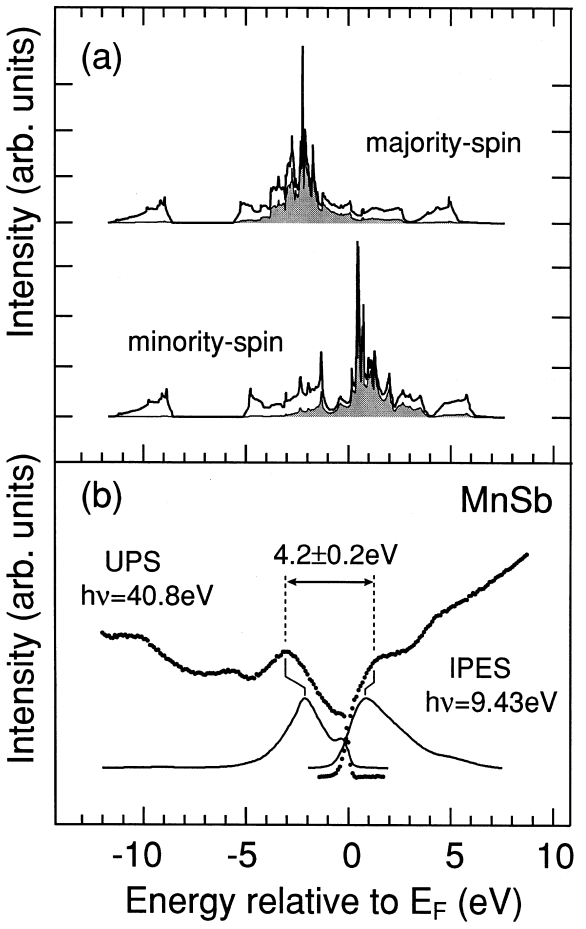

Fig. 2. (a) Theoretical total (solid lines) and Mn 3d partial (shaded area) DOSs for the majority and minority spin of MnSb [6]. (b) The calculated broadened DOS (solid lines) compared with the experimental spectra (dotted lines) of MnSb.

which represent experimental resolution and life time. We also take into account the photoionization cross-section at $h\nu$=40.8 and 9.43 eV. The results are shown in Fig. 2(b) as thin solid curves together with experimental spectra. The overall calculated spectra are consistent with the experimental spectra, although the two calculated peaks are closer than the two UPS and IPES peaks.

We consider the electronic structure of MnSb referring to the schematic energy diagram proposed by Wei and Zunger [13]. MnSb has a NiAs-type structure in which Mn atoms are coordinated by six Sb atoms occupying nearly octahedral (O_h) sites. In O_h symmetry, the Mn 3d states are classified into t_2 and e symmetries. The Mn 3d–e states strongly hybridize with Sb 5p states and their bonding and antibonding states spread over the valence bands and conduction bands. On the other hand, the Mn 3d–t_2 states have an almost nonbonding nature, giving small band dispersions and narrow peak structures in the DOS. Therefore, the main peak at −3.0 eV and the small structure at around −5.7 eV in the UPS spectrum are assumed to reflect the Mn 3d↑ state with t_2 symmetry and p–d hybridized states, respectively. A main peak at 1.2 eV and a broad structure at around 4.3 eV in the IPES spectrum stem from Mn 3d↓ with t_2 symmetry and sp states, respectively. From the energy separation of the two main peaks, the Mn 3d exchange splitting energy (U_{eff}) is estimated to be 4.2±0.2 eV, which is larger than that given by the band-structure calculation (~3 eV) [6].

Fig. 3 shows valence-band UPS spectra measured

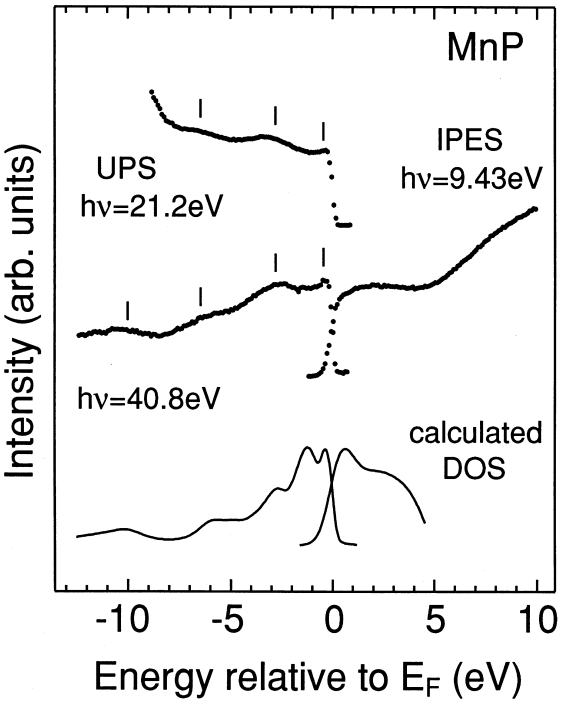

Fig. 3. UPS spectra measured at $h\nu$=21.2 and 40.8 eV, and the IPES spectrum of MnP (dotted lines), and the broadened DOS derived by band-structure calculation (solid lines) [8]. Energy refers to the Fermi level. Vertical bars indicate the position of structures.

at $h\nu$=21.2 and 40.8 eV, and conduction-band IPES spectra of MnP with the DOS calculated by Yanase and Hasegawa [8]. The DOS is broadened as described above. Energy refers to the Fermi level. The UPS spectrum exhibits a small peak at −0.4 eV, just below the Fermi level, and broad structures at −2.6, −6.4 and ~−10 eV, whereas we only recognize a broad structure at around 2 eV in the IPES spectrum. The features of UPS and IPES spectra are in good agreement with the results of the band-structure calculation, which reveal that the Fermi level is located within Mn 3d↓ bands, and all Mn 3d↑ bands are occupied. Therefore, the structures at −2.6 and −0.4 eV in the UPS spectra are attributed to the occupied Mn 3d↑ and Mn 3d↓ states [9], respectively. The U_{eff}-value of MnP is thus estimated to be 2.2±0.2 eV, which is smaller than that of MnSb. The result is consistent with the smaller Curie temperature and magnetic moment of MnP rather than those of MnSb.

The UPS and IPES spectra of MnP are substantially different from those of MnSb, although the differences between their crystal structures are small. Podloucky [14] investigated the spin polarized DOS of NiAs-type MnAs by band-structure calculation. The DOS feature shows prominent peaks due to occupied and unoccupied Mn 3d states and the weight near Fermi level is low. The author also investigated the electronic structure of MnP-type MnAs. In comparison with the results of NiAs-type MnAs, the Mn 3d-derived peaks become broad and Mn 3d states shift towards the Fermi level, which reduces exchange splittings. Therefore, the difference of the electronic structure, in particular, the Mn 3d states between MnSb and MnP would be attributed to the differences in their crystal structures.

The deviation of the experimental U_{eff}-value of MnP from the theoretical value (1.6 eV) [8] is small. The main peak assigned to the occupied Mn 3d↑ states of MnP is fairly weak and broad compared with that of MnSb. The width of the main structure in the IPES spectrum is also broader than that of MnSb. These results indicate that the correlation effect of Mn 3d states in MnP is weaker and that the Mn 3d electrons in MnP have more itinerant character compared with those in MnSb.

Acknowledgements

The authors are grateful to Prof. M. Shirai for providing us with the calculated DOSs of MnSb, to A. Minami for the electron-probe micro-analysis and also to M. Nakatake, K. Takada, Y. Umetani and K. Murakami for their technical assistance. This work is partly supported by the Grant-in Aid for Scientific Research from the Ministry of Education, the Kurata Foundation, the Japan Securities Scholarship Foundation and Izumi Science and Technology Foundation.

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