ELECTRONIC STRUCTURES OF Mn$_2$Sb AND MnAlGe: PHOTOEMISSION AND INVERSE PHOTOEMISSION SPECTROSCOPY

A. Kimura, S. Suga, H. Matsubara, T. Matsushita, Y. Saitoh, T. Daimon, T. Kaneko* and T. Kanomata*
Department of Material Physics, Osaka University, Machikaneyama, Toyonaka, Osaka 560, Japan
and
* The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan
† Department of Applied Physics, Faculty of Technology, Tohoku Gakuin University, Tagajo, Miyagi 985, Japan.

(Received 26 September 1991 by A. Okiji)

Synchrotron radiation photoemission and inverse photoemission spectra are measured for ferrimagnetic Mn$_2$Sb and ferromagnetic MnAlGe. The different contributions from two inequivalent Mn sites (I and II) in Mn$_2$Sb are experimentally revealed by taking the difference of the photoemission spectra of two materials as well as by the resonance photoemission technique. It is found that the Mn(II) site has less itinerant character than the Mn(I) site. The results are consistent with the difference of the magnetic moments associated with both sites.

THE INTERMETALLIC compounds, Mn$_2$Sb and MnAlGe are known to have a Cu$_2$Sb type crystal structure. Mn$_2$Sb has two different magnetic sites I and II, where Mn(I) atoms are situated at the tetrahedral sites in regard to the surrounding Sb atoms and Mn(II) atoms are situated at the octahedral sites as shown in Fig. 1. From the structural point of view, the Mn(I)-Sb distance is shorter than the Mn(II)-Sb distance. Mn$_2$Sb is ferrimagnetic with a Curie temperature of 550 K. According to neutron diffraction studies, there is a spin reorientation transition at $T_d = 240$ K [1]. The atomic spins are aligned parallel and perpendicular to the c-axis above and below this temperature. In addition, a first order ferri-antiferromagnetic transition occurs when a small part of Mn is replaced by Cr [2]. In recent years, Co-modified Mn$_2$Sb (Mn$_{2-x}$Co$_x$Sb) is found to show also the ferri–antiferromagnetic transition at lower temperatures [3]. This phenomenon was interpreted on the basis of “Kittel’s exchange inversion theory” [4] which was introduced by using a molecular field approximation. This model, however, could not explain various other magnetic properties. For example, the transition temperature of Mn$_{1.9}$Co$_{0.1}$Sb decreases with increasing pressure, contrarily to the prediction given by Kittel’s theory.

In the case of Mn$_{1.8}$Co$_{0.2}$Sb, Co atoms are found to occupy only the I site. In contrast to this, Al atoms occupy only the II site in the case of MnAlGe, whereas Mn atoms occupy the I site. Since Al is a non-magnetic atom, MnAlGe is a simple ferromagnet and shows strong magnetic anisotropy along the c-axis [5].

In order to understand these complex behaviors, it is very important to know the electronic structures of these compounds. A self-consistent APW calculation was recently carried out on various Cu$_2$Sb type compounds [6, 7]. For the paramagnetic phase of Mn$_2$Sb the calculated band width of the Mn(I) 3d state is much broader than that of the Mn(II) 3d state. For MnAlGe, the calculation was performed on both non-magnetic and ferromagnetic phases. It is predicted that the hybridizations between the Mn–3d and Al–3p or Ge–4p states are not strong and the Fermi surface has a strong two-dimensional character. The calculated magnetic moment in the ferromagnetic state is in good agreement with the observed one [7].

For getting experimental information on the occupied electronic states of these materials, we have carried out the first photoemission measurement by using synchrotron radiation. An inverse photoemission spectrum is also measured for probing the unoccupied conduction bands.

The photoemission measurement was performed at room temperature on clean surfaces obtained by in situ scraping by use of a diamond file. The measurement was done over the photon energy range of $hv = 32$–120 eV at BL-2 of SOR-RING (an electron storage ring operated at 380 MeV) of the University of Tokyo. A combination of a double stage cylindrical mirror analyzer and a modified Rowland type monochromator was used to obtain angle integrated photoemission spectra. The total resolution was set to about 0.3 eV at $hv = 70$ eV. The base pressure of the analyzer
The inverse photoemission spectrum was measured in a separate chamber by use of a home-made BaO electron gun and a band pass filter at $h\nu = 9.4\text{eV}$ with a total resolution of $\pm 0.3\text{eV}$ (at half maximum). The pressure of the analyzer chamber was $5 \times 10^{-8}\text{torr}$.

We have measured the valence band photoemission spectra of Mn$_2$Sb and MnAlGe with changing the incidence photon energy covering the Mn 3p core excitation region ($h\nu = 45-61.5\text{eV}$) as shown in Fig. 2a and b after normalization by photon flux. The photoionization cross section of the Mn 3d states is known to be much larger than those of the Sb 5s5p, Ge 4s4p and Al 3s3p states in this photon energy range [8].

Although both Mn$_2$Sb and MnAlGe show clear Fermi energy ($E_F$) cut off for all $h\nu$, Mn$_2$Sb shows much higher photoemission intensity around $E_b = 3.0\text{eV}$ as seen above $h\nu = 50\text{eV}$. The structures indicated by the vertical bars show the energy positions of the structure ascribable to the Mn$_{23}\text{M}_{45}\text{M}_{45}$ Auger electron emission.

In order to reveal the difference of the electronic structures between Mn$_2$Sb and MnAlGe, we have measured the constant initial state spectra (CIS) at various $E_b$ as functions of $h\nu$. The spectra normalized by the photon flux are shown in Fig. 3a, b. Most CIS curves have shown resonance behavior near the Mn 3p core excitation threshold. Such a resonance behavior is due to an interference between (1) the direct Mn 3d photoelectron emission and (2) the electron emission associated with the direct recombination following the $3p \rightarrow 3d$ core excitation [9]. Thus the strength of the interference represents the atomic nature or the localized nature of the involved Mn 3d electronic states.

The CIS spectrum for the structure at $E_b = 3.0\text{eV}$ in Mn$_2$Sb shows a clear dip and a peak below and above the 3p core absorption threshold, respectively [10]. The relative magnitude of the resonance oscillation is much weaker for smaller $E_b$ in Mn$_2$Sb. The CIS spectra for $E_b$ larger than 6eV are much influenced by the overlap of the $\text{M}_{23}\text{M}_{45}\text{M}_{45}$ Auger peak whose intensity may become maximum at the absorption maximum. One thus notices that the localized character of the Mn 3d state is remarkable around $E_b = 3.0\text{eV}$ in Mn$_2$Sb. On the other hand, the CIS spectra of MnAlGe show a common feature with a clear dip below the 3p core absorption threshold for $E_b$ smaller than 3 eV. This result indicates that the Mn 3d character is uniformly spread in a wide energy range of the valence band in MnAlGe and that the Mn 3d state is more itinerant than the 3.0eV feature of Mn$_2$Sb judging from the CIS line shape [9]. The CIS spectrum for $E_b = 6.6\text{eV}$ in MnAlGe is again strongly influenced by the Auger peak.

The contribution of the normal Auger peak seems to be much weaker for MnAlGe than Mn$_2$Sb in both photoemission and CIS spectra. This is primarily due to the Mn occupancy of only the I site in MnAlGe compared with the occupancy of both I and II sites in Mn$_2$Sb. Secondarily, the half width of the Auger peak is a factor to obscure the Auger structure. Namely, the $\text{M}_{23}\text{M}_{45}\text{M}_{45}$ Auger peak of MnAlGe is broader than that of Mn$_2$Sb as understood from the result in Fig. 2a, b. It is recalled that the Mn $\text{M}_{23}\text{M}_{45}\text{M}_{45}$ Auger structure is much weaker in the case of MnO or Cd$_{1-x}\text{Mn}_x\text{Te}$, in which the direct recombination seems to be a predominant decay channel for the Mn 3p core excited state near the 3p core absorption threshold. This fact suggests that the Mn 3d state in both MnAlGe and Mn$_2$Sb is delocalized compared with MnO and Cd$_{1-x}\text{Mn}_x\text{Te}$. The presence of the appreciable Auger peak in Mn$_2$Sb and MnAlGe hinders the evaluation of the Mn 3d partial density of states (DOS) from the difference of the photoemission spectra for $h\nu$ at resonance maximum and minimum.

It is known that the magnetic moment of Mn(I) in MnAlGe is 1.7$\mu_B$, whereas Mn(I) and Mn(II) in Mn$_2$Sb have moments of 2.1$\mu_B$ and 3.9$\mu_B$ at 4.2K. Assuming that the Mn 3d partial DOS ascribable to the Mn(I) site is not much different between Mn$_2$Sb and MnAlGe, we have evaluated the Mn(II) 3d partial DOS in Fig. 2c by subtracting the spectrum of Mn$_2$Sb from that of Mn$_2$Sb at $h\nu = 61.5\text{eV}$. The difference spectrum shows a prominent peak around $E_b = 3.0\text{eV}$, and a weak hump around $E_b = 5.5\text{eV}$. Remembering that photoionization cross section of the Al and Ge states is much weaker than that of the Mn 3d state, the off resonance valence band spectrum
of MnAlGe is thought to be representingly the Mn(I) 3d partial DOS. The Mn(I) 3d partial DOS thus grows up from 4.5 eV below $E_F$ and crosses $E_F$ with high intensity. The large dispersion responsible for such a large band width of the Mn(I) 3d state represents the itinerant character of the involved electronic states and is consistent with the reduced magnetic moment compared with the Mn(II) 3d state. The clear Fermi energy cut off of the partial DOS of the Mn(I) 3d state is also its natural consequence. Such a remarkable dispersion is also confirmed by the band calculation of MnAlGe [7]. On the other hand, the partial DOS of the Mn(II) 3d state in Mn$_2$Sb is very small at $E_F$.

We have measured an inverse photoemission spectrum of Mn$_2$Sb as shown in Fig. 4, where a clear peak is observed around 3 eV above $E_F$. Such a peak is not observed in MnAlGe, so we can assign the structure to unoccupied Mn(II) 3d states in Mn$_2$Sb. We compare the photoemission and inverse photoemission spectra with the result of band calculation of Mn$_2$Sb in the ferrimagnetic phase. The calculation has predicted that the Mn(II) 3d partial DOS with majority spin is located about 2.5 eV below $E_F$, few eV deeper than the center of gravity of the partial DOS of the opposite spin Mn(I) 3d state in this ferrimagnet [13]. The prediction is in a qualitative agreement with our experimental result. The calculation also shows that the partial DOS of Mn(II) is very low near $E_F$ and the partial DOS of Mn(II) with minority spin is located about 1.5 eV above $E_F$. The large energy splitting between the minority and majority spin Mn(II) 3d state is due to the large spin exchange splitting associated with the large magnetic moment. The center of gravity of the minority spin Mn(II) 3d DOS is, however, slightly lower than the experimental result. Such a deviation may be due to the electron correlation effect which should be studied in more detail in future.

Partial density of states of the Mn(I) and Mn(II) 3d states in ferrimagnetic Mn$_2$Sb and ferromagnetic MnAlGe has been derived by synchrotron radiation photoemission spectroscopy. From the Fermi level crossing and the large band width, the itinerant character of the Mn(I) 3d state is confirmed experimentally. Combined with the inverse photoemission spectrum, a weak itinerant character is revealed for the Mn(II) 3d state. The present interpretation is consistent with the recent band calculation.

In future, angle resolved and spin polarized photoemission as well as inverse photoemission spectroscopy is required to resolve the detailed band structures.
ELECTRONIC STRUCTURES OF Mn$_2$Sb AND MnAlGe

Fig. 3. CIS spectra of (a) Mn$_2$Sb and (b) MnAlGe in the Mn 3$p$ → 3$d$ core absorption region.

Acknowledgements — The authors are much obliged to Professor K. Motizuki and Dr M. Shirai for useful discussion and showing us results of band calculation prior to publication. The discussion with Professor A. Fujimori and Professor S. Shin is deeply acknowledged. The authors are grateful to the staff of ISSP for technical support. The work is partly supported by the Grant in Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan and by the Shimadzu Science Foundation.

REFERENCES
4. C. Kittel, Phys. Rev. 120, 335 (1960).