Solid State Communications, Vol. 81, No. 8, pp. 707–710, 1992.
Printed in Great Britain.

0038-1098/92 $5.00 + .00
Pergamon Press plc

ELECTRONIC STRUCTURES OF Mn_2Sb AND MnAlGe: PHOTOEMISSION AND INVERSE PHOTOEMISSION SPECTROSCOPY

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(*Received* 26 *September* 1991 *by A. Okiji*)

Synchrotron radiation photoemission and inverse photoemission spectra are measured for ferrimagnetic Mn_2Sb and ferromagnetic MnAlGe. The different contributions from two inequivalent Mn sites (I and II) in Mn_2Sb 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_2Sb and MnAlGe are known to have a Cu_2Sb type crystal structure. Mn_2Sb 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_2Sb is ferrimagnetic with a Curie temperature of 550 K. According to neutron diffraction studies, there is a spin reorientation transition at $T_{sf} = 240$ 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–antiferro magnetic transition occurs when a small part of Mn is replaced by Cr [2]. In recent years, Co-modified Mn_2Sb ($Mn_{2-x}Co_xSb$) is found to show also the ferri–antiferro magnetic 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 $Mn_{2-x}Co_xSb$, 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_2Sb type compounds [6, 7]. For the paramagnetic phase of Mn_2Sb 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 $h\nu$ = 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 $h\nu$ = 70 eV. The base pressure of the analyzer

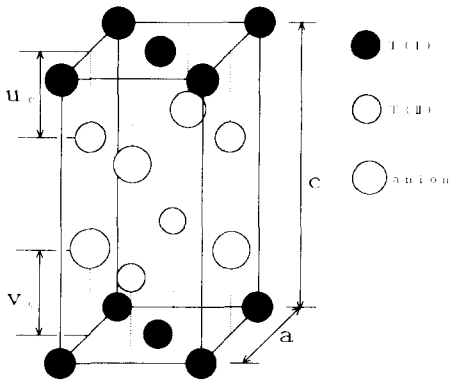

Fig. 1. Cu_2Sb type crystal structure.

chamber was 3×10^{-11} torr which rose up to 6×10^{-11} torr during the measurement. Surface contamination was checked by monitoring an emergence of the oxygen $2p$ photoelectron structure around the binding energy (E_B) of 6 eV.

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 $h\nu = 9.4$ eV with a total resolution of ± 0.3 eV (at half maximum). The pressure of the analyzer chamber was 5×10^{-11} torr.

We have measured the valence band photoemission spectra of Mn_2Sb and MnAlGe with changing the incidence photon energy covering the Mn $3p$ core excitation region ($h\nu$ = 45–61.5 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_2Sb and MnAlGe show clear Fermi energy (E_F) cut off for all $h\nu$, Mn_2Sb shows much higher photoemission intensity around E_B = 3.0 eV as seen above $h\nu$ = 50 eV. The structures indicated by the vertical bars show the energy positions of the structure ascribable to the $M_{23}M_{45}M_{45}$ Auger electron emission.

In order to reveal the difference of the electronic structures between Mn_2Sb 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 eV in Mn_2Sb 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_2Sb. The CIS spectra for E_B larger than 6 eV are much influenced by the overlap of the $M_{23}M_{45}M_{45}$ 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 eV in Mn_2Sb. 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 3.0 eV feature of Mn_2Sb judging from the CIS line shape [9]. The CIS spectrum for E_B = 6.6 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_2Sb 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_2Sb. Secondarily, the half width of the Auger peak is a factor to obscure the Auger structure. Namely, the $M_{23}M_{45}M_{45}$ Auger peak of MnAlGe is broader than that of Mn_2Sb as understood from the result in Fig. 2a, b. It is recalled that the Mn $M_{23}M_{45}M_{45}$ Auger structure is much weaker in the case of MnO or $Cd_{1-x}Mn_xTe$ [11, 12], 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_2Sb is delocalized compared with MnO and $Cd_{1-x}Mn_xTe$. The presence of the appreciable Auger peak in Mn_2Sb 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 μ_B, whereas Mn(I) and Mn(II) in Mn_2Sb have moments of 2.1 μ_B and 3.9 μ_B at 4.2 K. Assuming that the Mn $3d$ partial DOS ascribable to the Mn(I) site is not much different between Mn_2Sb and MnAlGe, we have evaluated the Mn(II) $3d$ partial DOS in Fig. 2c by subtracting the spectrum of MnAlGe from that of Mn_2Sb at $h\nu$ = 61.5 eV. The difference spectrum shows a prominent peak around E_B = 3.0 eV, and a weak hump around E_B = 5.5 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

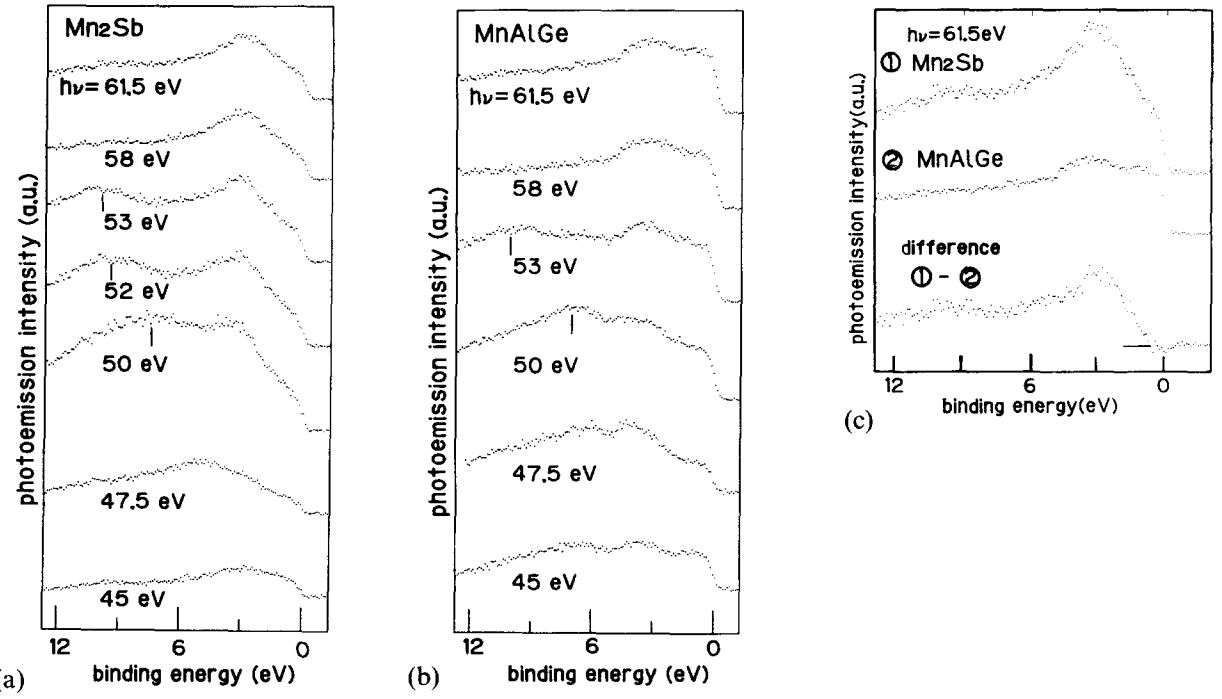

Fig. 2. Valence band UPS spectra of (a) Mn_2Sb and (b) MnAlGe for photon energies in the Mn $3p \rightarrow 3d$ core absorption region. The vertical bars indicate the energy positions of the Mn $M_{23}M_{45}M_{45}$ Auger peak. (c) Difference spectrum between Mn_2Sb and MnAlGe at $h\nu = 61.5$ eV.

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_2Sb is very small at E_F.

We have measured an inverse photoemission spectrum of Mn_2Sb 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_2Sb. We compare the photoemission and inverse photoemission spectra with the result of band calculation of Mn_2Sb 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_2Sb 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.

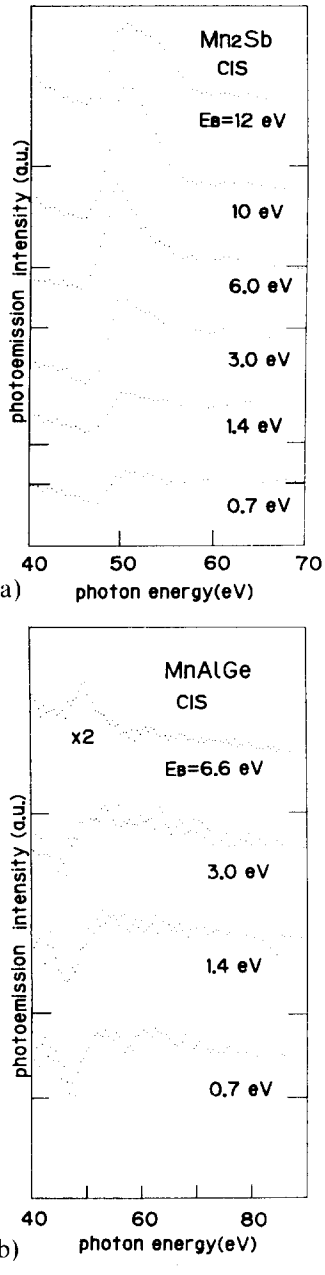

Fig. 3. CIS spectra of (a) Mn_2Sb and (b) MnAlGe in the Mn $3p \rightarrow 3d$ core absorption region.

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 SRL, 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.

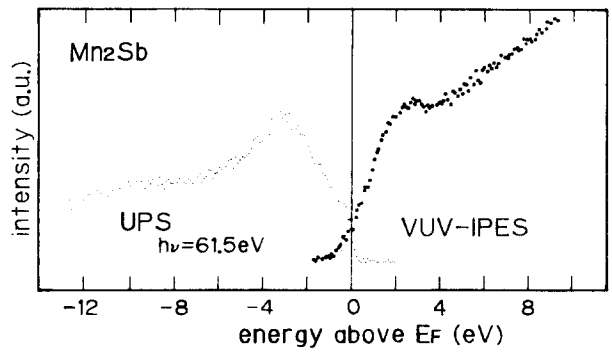

Fig. 4. UPS ($h\nu$ = 61.5 eV) and VUV-inverse photoemission spectra of Mn_2Sb.

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