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High-resolution inverse-photoemission study of a clean and an oxidized Ag-Mn(111) random substitutional alloy

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We have studied the unoccupied electronic band structure in Ag—15 at. % Mn(111). Minority-spin Mn states appear at 1.7±0.1 eV above the Fermi level E_F with a full width at half maximum of 1.7 eV. They show no dispersion. An image-potential state is resolved at 0.74±0.08 eV below E_{vac}. On exposure to oxygen, new empty states appear at $\simeq$2.9 eV above E_F.

The recent development of **k**-resolved inverse photoemission spectroscopy provides many new opportunities for the investigation of the unoccupied region of the electronic band structure in a wide range of materials. One area where it will likely play an important role is with studies of random substitutional alloys. Various physical properties (e.g., strength, structure and stability, the occurrence of magnetism, superconductivity) are related to the underlying electronic structure and in order to understand such properties we need to establish a realistic description of the electronic spectrum. Currently, the electronic structure in a large number of pure (ordered) metallic systems can be calculated with a high degree of precision using modern *ab initio* band-theory techniques. The impurity limit has been treated in a similar fashion (for Mn in Ag, see Ref. 1). In the case of random alloys, however, the subject is not so well developed, although there has been much progress in the past 10 years following the development of calculational schemes based on the Korringa-Kohn-Rostoker coherent-potential approximation (KKR-CPA).[2] The first calculations were done for Cu-Ni alloys[3] and many of the features have been confirmed quantitatively by uv photoemission measurements.[4,5] Since then the KKR-CPA method has been applied to other alloy systems such as (fcc) Ag-Mn.[6]

A crucial component in the development of electronic structures is the use of experimental techniques which probe the occupied and unoccupied bands in **k**-point detail, thus confronting theory in a most profound way. As alluded to above, angle-resolved uv photoemission is the most useful method of investigating the occupied bands in alloys. In this paper we describe the first **k**-resolved inverse photoemission measurements on a random substitutional alloy [Ag—15 at. % Mn(111)] and we show that it is a powerful tool for studying the unoccupied regions for both the bulk and surface electronic structure in such systems.

Ag-Mn alloys containing <20 at. % Mn are spin glasses. In an attempt to understand the magnetic forces responsible for this behavior, Munõz *et al.*[6] developed a theory [based on a three-component KKR-CPA scheme using spin-density-functional theory in the local-spin-density (LSD) approximation] which allowed them to calculate the electronic structures. They find that the Mn states are exchange-split by 3.3 eV into (occupied) spin-up and (unoccupied) spin-down bands. Some dispersion and changes in shape of the majority-spin feature are seen in the Bloch spectral function away from the Γ point but little (if any) modification of the minority-spin feature. The occupied Mn band has been observed in various photoemission studies, but the presence of the unoccupied band—originally inferred from uv photoemission studies of surface states[7]—was confirmed recently by van der Marel *et al.*[8] using low-resolution bremsstrahlung-isochromat spectroscopy on polycrystalline specimens. They identified the feature in difference spectra and by analyzing their data with model calculations they deduced the local Mn d—band density of states. Our measurements are obtained at considerably higher resolution and since we obtain **k**-specific information we can compare our data with the results of Munõz *et al.* more directly. Although the conceptual simplicity of their approach relies on some important assumptions,[6] theirs are the only detailed first-principles calculations of the electronic structure in Ag-Mn alloys. One result which has been confirmed experimentally is the concentration dependence of the neck radius on the Fermi surface at the L point. By studying the dispersion of the Shockley-type surface state in Ag-Mn(111) alloys, Jordan and Sohal showed that the neck radius increased with Mn content.[7] It was suggested that this observation was indirect evidence for the presence of a Mn minority-spin band above E_F.

In fact, the nature of surface states in random alloys [e.g., those on the (111) faces of noble-metal-based alloys around the $\bar{\Gamma}$ point in the two-dimensional Brillouin zone] (Ref. 7) is itself an interesting and important area for study. In pure metals these states are located in the band gap near E_F and they are derived from bulk states; their complex wave vectors ensure that they are localized at the surface. In alloys, however, the situation is rather different since the bulk states themselves have complex wave vectors. Calculations for Cu-Ni show that the behavior of surface states can be correlated with features in the bulk spectral density[9] and, furthermore, when a (s-p—type) surface-state band crosses an impurity d band at finite $k_{\parallel}$, strong hybridization will occur which modifies substantially the normally free-electron-like dispersion.[10] We have investigated, therefore, the dispersion of the Shockley-type surface state in the alloy as we expect it to move into the Mn minority d band above E_F.

The inverse photoemission measurements were made in a spectrometer incorporating a spherical grating monochromator with a large acceptance angle ($f/4$).[11] Detection of the entire photon spectrum between 8 and 30 eV is accomplished by the use of two microchannel plate detectors. The electron source is a Pierce-type gun with a low-temperature BaO cathode. The energy and momentum resolution are typically 0.3 eV and 0.1 Å^{-1}, respectively. The Ag(111) and Ag—15 at.% Mn(111) specimens were cleaned in an attached preparation chamber by a series of Ar^+ bombardment-annealing cycles. Since the alloy specimen had been used in previous photoemission studies, the recipe adopted was the same as before,[7] i.e., Ar^+ bombardment at 1 keV for 30 min followed by an anneal at 450—500 °C for 30 min *in vacuo*—this procedure produces stable and reproducible surfaces. The measurement chamber has a base pressure of 5×10^{-11} Torr, and the surfaces remained clean for about 6 h. The work function was measured *in situ* using a piezoelectrically driven Kelvin probe.[12] The energies of the photons, $h\nu$, are measured for a series of initial electron energies, E_i. Our spectra show the photon intensity (corrected for monochromator and detector efficiencies) as a function of the final-state energy E_f, where $E_f=E_i-h\nu$, and they are the sum of several (typically 3 or 4) separate measurements, each taking 1000 s. The values plotted along the abscissa are all normalized to the same incident-electron current so that direct comparisons with different initial energies are possible.

Inverse photoemission spectra ($k_{\parallel}=0$) for Ag—15 at.% Mn(111) are shown in Fig. 1 for various incident electron energies E_i corresponding to momenta along the ΓL line. In Fig. 2 we show data for pure Ag(111), the alloy, and the oxygen-exposed alloy at $E_i=14.25$ eV. There are three main features in the alloy spectra corresponding to emission from (i) the unoccupied part of the (Shockley-type) surface state near E_F, (ii) an image-potential state near 4 eV, and (iii) the Mn minority-spin states at about 1.7 eV. There are numerous reports in the recent literature of a Rydberg-like series of image-potential states on the low-index faces of a variety of pure metals (see, for example, Straub and Himpsel,[13,14] Hulbert *et al.*,[15] Goldmann *et al.*,[16] and Reihl *et al.*[17]). However, we believe our observation (of an $n=1$ state) is the first ever reported for random alloy. The peak position remains fixed in energy at 0.74±0.08 eV below the vacuum level ($\Phi=4.81$ eV) which compares with a value of 0.77 eV obtained for pure Ag in a recent high-resolution two-photon experiment.[18] Our observation supports the contention that the binding energy of image states (referred to E_{vac}) is material independent.

The position of the Mn feature is 1.7±0.1 eV above E_F and does not change with E_i. This value is slightly lower than that measured by van der Marel *et al.*,[8] but somewhat larger than that obtained by Muñoz *et al.*[6] If we assume that the initial states in the alloy are similar to those calculated by Eckardt *et al.*[19] for Ag, then at our lowest energy $|\mathbf{k}|$ is roughly halfway along ΓL. As E_i increases, $|\mathbf{k}|$ decreases until at $E_i=17$ eV the Γ point is reached. Thus, the minority-spin Mn d states show no dispersion along ΓL, in agreement with the calculations.[6] The width of the feature remains constant [$\simeq$1.7 eV full width at half-maximum (FWHM)] and is substantially smaller than that measured by van der Marel *et al.* but slightly greater than that estimated from the Bloch spectral function along ΓL.[6] For convenience all the relevant data are shown in Table I.

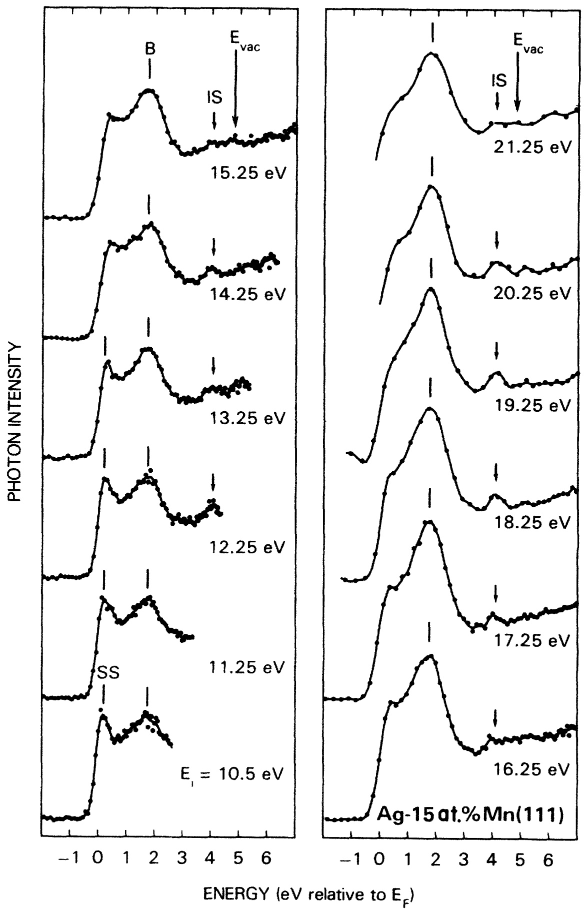

FIG. 1. Inverse photoemission spectra for Ag—15 at.% Mn(111) with $k_{\parallel}=0$. SS, B, and IS indicate emission from the surface state, the Mn minority-spin bulk states, and the image-potential state, respectively.

The height of the Mn-related feature shows some variation with electron energy, having a maximum at 17±1 eV. In a simple picture the photon intensity will be related to the joint (one dimensional) density of states, and since the Mn feature shows no dispersion (nor any substantial changes in width) we can suppose, to a first approximation, that the observed intensity variation reflects changes in the density of initial states. The maximum at 17 eV, therefore, can be identified with the (Ag-related) Γ_{7-} critical point, which is in agreement with the value for pure

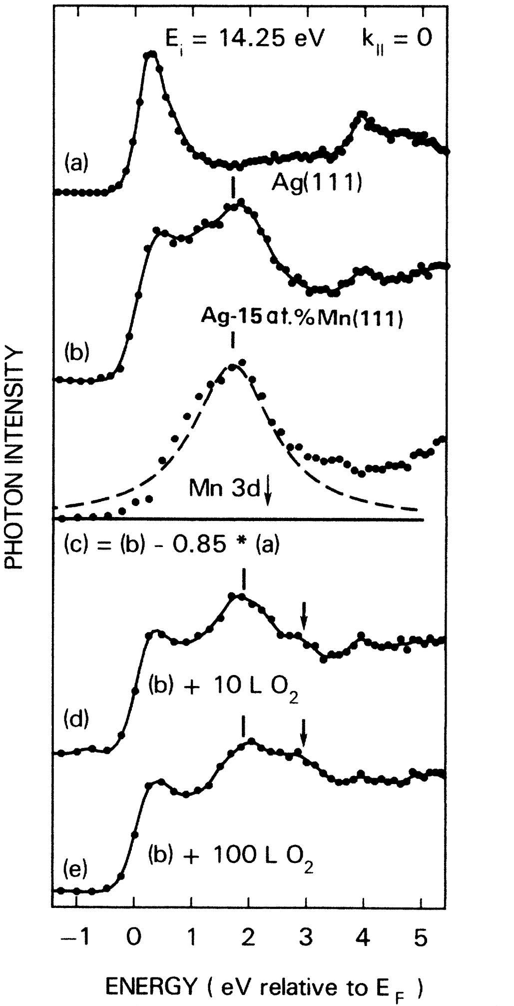

FIG. 2. Inverse photoemission spectra with $k_{||}=0$ for (a) Ag(111), (b) Ag—15 at.% Mn(111), and (d) and (e) Ag—15 at.% Mn(111) exposed to 10 and 100 L of oxygen, respectively. The initial energy is 14.25 eV in all cases. The difference spectrum (c) isolates the Mn 3d minority-spin states. For comparison, a Lorentzian centered at 1.7 eV with 1.7 eV FWHM is shown (dashed).

for pure Ag calculated by Eckardt *et al.*[19]

With oxygen exposure a new state appears at 2.9 eV above E_F. There are two possible assignments: (i) as a minority spin 3d state of oxydized manganese and (ii) as O 2p state of chemisorbed oxygen. We tend to factor assignment (i) since oxygen generally reacts with the early transition metals to form an oxide. In a rigid-band model the bands of the oxide are shifted upward relative to the metal because electrons are extracted by the oxygen. There exist several more detailed models[20] of the band structure of transition-metal oxides. If interpretation (ii) is assumed the electron transfer from the metal to the oxygen would be much smaller. Therefore the metal bands should be unaffected and unoccupied O 2p states should exist like those observed for oxygen chemisorbed on Ni.[21]

We investigated the dispersion of the surface state along $\bar{K}\bar{\Gamma}\bar{K}$ by fixing the angle of incidence at ±10° and varying E_i. The results are shown in Fig. 3. The dispersion of the alloy surface state is expected to distort when it reaches the Mn minority-spin states at 1.7 eV above E_F. Similar behavior has been predicted for the corresponding surface states in Cu-Ni(111) alloys.[10] Indeed, the surface-state dispersion that we observe in the alloy is greater than previously reported for pure Ag. However, a variation in **k** resolution from one experiment to the other may account for the effect. An approximation of the surface-state dispersion is given by a parabola obtained by a fit to our data points with effective mass $m^*=0.43m_e$ starting at $E_F-0.15$ eV. These results are close to the values of $(0.7\pm0.2)m_e$ and $E_F-0.05$ eV as recently reported[18] for the occupied surface states on pure Ag(111).

We have shown that high-resolution inverse photoemission measurements can provide detailed **k**-specific information about the bulk and surface electron structure in random alloys. We have confirmed how the moment is formed in Ag-Mn (spin-glass) alloys, although our (bulk) observations do not agree in all respects with the calculations of Munoz̃ *et al.*[6] In particular, the calculated exchange splitting of 3.3 eV is significantly smaller than our

TABLE I. Experimental and theoretical values of the majority- and minority-spin peak positions and widths. Energies are given relative to the Fermi level E_F.

Sample	Clean surface $E_\uparrow$ (eV)	 $E_\downarrow$ (eV)	$\Delta E_\downarrow$ (eV) (FWHM)	Oxidized surface $E_\downarrow$ (eV) (10 L)	 $E_\downarrow$ (eV) (100 L)
Ag—15 at.% Mn(111)[a]	−3.0±0.1[d] (≃0.7 ΓL)	1.7±0.1 (≃0.3 ΓL)	1.7	1.9±0.2 2.9±0.3	1.9±0.2 2.9±0.3
Ag—15 at.%, 10 at.% Mn (polycrystalline)[b]	−3.1±0.2	2.1±0.2	2.4		
Ag—10 at.% Mn (theory, alloy)[c]	−2.65	0.65	1.2		
Ag-Mn (theory, impurity)[e]	−2.4	0.6	1.0		

[a] This work.
[b] Reference 8.
[c] Reference 6.
[d] Reference 7.
[e] Reference 1.

experimental value of 4.7 eV. One possible explanation is that the calculations are not fully electronically self-consistent. However, the differences could also be a consequence of excited-state effects in photoemission and inverse photoemission.[22] Our data suggest that the self-energy is different for the two Mn features; the shift is small in the case of the filled majority-spin band (-0.4 eV) but somewhat larger for the partially filled minority-spin band ($+1$ eV). Another argument points to a possible upward shift of the minority-spin band in the excited state. In order to obtain the correct value for the total moment the appropriate occupancy of the minority-spin states is 0.8–1.0 electrons, assuming a fully occupied majority-spin band. The emission observed near the Fermi level in our difference spectra [see Fig. 2(c)] is too small to give such an occupancy. Using a Lorentzian line shape (dashed line in Fig. 2) one can get an occupancy close to the required value but the tail of the Lorentzian lies above our data points near the Fermi level. The Lorentzian line shape is only appropriate in the impurity limit. At 15 at. % concentration there are significant changes in the line shape, as indicated by calculations.[6]

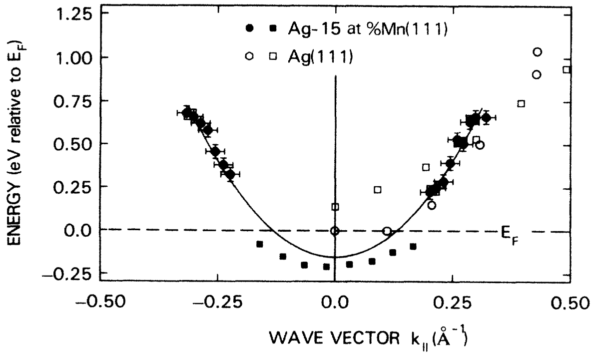

FIG. 3. Dispersion of the surface state in Ag–15 at. % Mn(111) along $\bar{K}\bar{\Gamma}\bar{K}$. The solid squares are photoemission data (Ref. 7); the solid circles the result of this work. The results for Ag(111) are from Refs. 15 (open circles) and 16 (open squares). The parabola with an effective mass $m^* = 0.43 m_e$ starting at 0.15 eV below E_F is shown as a line.

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