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Minority-spin states for V and Mn on Ag(111) by inverse photoemission

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Unoccupied states have been observed with momentum-resolved inverse photoemission for thin layers of V and Mn on Ag(111) ranging from 0.2 monolayer to thick bulklike films. An assignment in terms of exchange- and crystal-field-split $3d$ states is given by comparison with similar data from the Mn-in-Ag spin glass and with first-principles calculations. The states are located at 0.9 and 1.8 eV above E_F for Mn and at 0.5 and 1.7 eV above E_F for V. The data are consistent with large magnetic moments for V and Mn films up to a monolayer, in contrast to the absence of ferromagnetism in the bulk materials.

The prospects for changing magnetic properties at the surface or near an interface has stimulated a large amount of theoretical[1-10] and experimental[11-20] work. A substantial enhancement of the magnetic moment and even ferromagnetic order of a paramagnetic substrate[11,12] have been observed. For elements near the middle of the transition metal series (e.g., V, Cr, Mn) such an enhancement can be made plausible by the following simple idea: The free atom has a large moment because all spins are lined up due to Hund's rule. In the solid this coupling is partially destroyed by interaction with neighbors (band formation), but part of the large atomic moment can be recovered by diluting the atoms at a surface, interface, or in a noble metal matrix. For dilute Mn-in-Ag spin glasses,[21-24] for example, the magnetic moment comes close to the atomic value of $5\mu_B$.

For understanding enhanced magnetism at surfaces and interfaces it is essential to know the electronic states near the Fermi level that are driving the magnetic phase transition. Occupied states have been probed by photoemission[15-19] but there is no experimental information about unoccupied states. For spin glasses, unoccupied minority-spin states have been observed using inverse photoemission.[23-25] The energy of these states agrees qualitatively with first-principles local density calculations.[21,22] The exchange splitting between majority and minority spin states can be as large as 4.7 eV for Mn in a Ag matrix.[24] Empirically, there exists a linear relationship between exchange splitting and magnetic moment in itinerant ferromagnets with about 1-eV splitting per μ_B. Therefore, an energy resolution of 0.3 eV achievable in inverse photoemission[25,26] allows for a fairly sensitive probe of magnetism.

In this work we have used our experience in the mapping of unoccupied minority-spin states of bulk ferromagnets[27] and, in particular, of the Mn-in-Ag spin glass.[24] These results are used as a reference for studying thin overlayers of V and Mn on Ag(111) ranging in thickness from 0.2 monolayer to bulklike films. In the low-coverage limit we find unoccupied Mn states at 0.9 and 1.8 eV above E_F similar to the minority-spin states in the Mn-in-Ag spin glass. At about monolayer coverage, the density of states increases near E_F indicating the formation of a bulklike band structure with reduced (or zero) exchange splitting.

The experiments were performed with a momentum-resolving, tunable spectrometer which has been described previously.[26] The Ag(111) surface was chosen as a substrate because it exhibits a large band gap at $k_{\parallel}=0$ in the region where the minority-spin states of Mn and V are expected. The crystals were mechanically and chemically polished and cleaned by sputter annealing before each

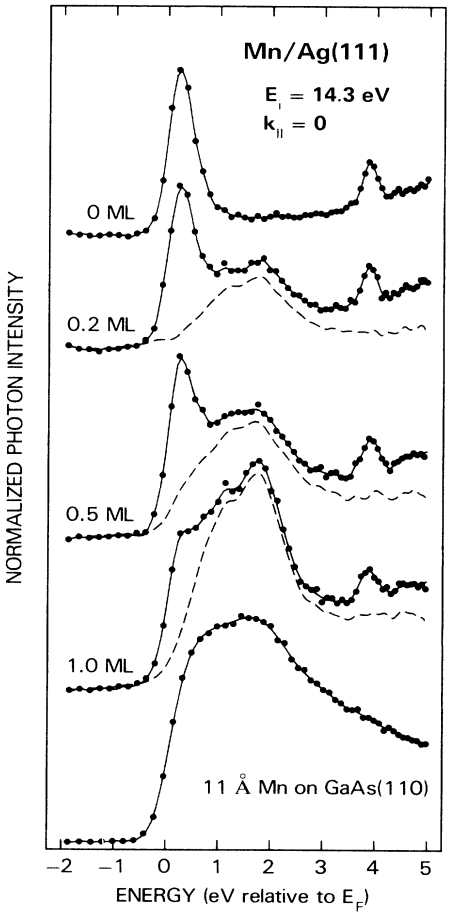

FIG. 1. Inverse photoemission spectra for clean and Mn covered Ag(111) (dots and solid lines). The Mn contribution to the unoccupied states can be seen from the difference spectra (dashed lines). The bottom spectrum was recorded from a thick bulklike Mn layer on cleaved GaAs(110).

evaporation in a vacuum in the low 10^{-10}-Torr range. Mn and V were evaporated from a miniature electron beam evaporator, which was carefully outgassed such that the pressure at the sample remained below 6×10^{-10} Torr during evaporation.

The results are shown in Fig. 1 [Mn/Ag(111)] and Fig. 2 [V/Ag(111)]. For clean Ag(111) we observe only low-intensity emission due to surface states.[24] The peak near the Fermi level is due to an intrinsic s-,p-like surface state, which disperses through the Fermi level close to $k_{\parallel}=0$. The peak at 3.9 eV above E_F is due to an image potential surface state. Already at a coverage as low as 0.2 monolayer a clear signal from unoccupied transition metal d states can be picked up. In order to get the proper line shape we subtract the emission from the substrate after taking the attenuation by the overlayer into account (dashed lines in Figs. 1 and 2). Thereby, an electron mean free path of 5 Å has been assumed, which minimizes residual emission from surface states in the difference spectra.

From Mn on Ag(111) the interpretation of the Mn-induced states is straightforward when using the analogy with the Mn-in-Ag spin glass (Fig. 3). The similarity of the spectra (taken at the same $k_{\parallel}$ and same initial electron energy) suggests that the Mn states are mainly minority spin as calculated for the spin glass [Fig. 3(c)]. The energy position of the Mn states [obtained by a least-squares fit of Gaussians to the spectra after background subtraction, dashed and full lines in Figs. 3(a) and 3(b)] has not changed significantly from the spin glass to the submonolayer film. Therefore, the exchange splitting must be similar in both cases and, likewise, the local magnetic moment which is $4\mu_B$ for the spin glass. The splitting of the minority-spin peak into two structures at 0.9 and 1.8 eV could be caused by the crystal field, which splits d states into $e_g(\Gamma_{12})$ and $t_{2g}(\Gamma'_{25})$ symmetry in the bulk [Λ_3 and $\Lambda_3+\Lambda_1$ for a hexagonal (111) overlayer]. Calculations[5] for a monolayer of V on Ag(100) (see below) give a comparable, although somewhat larger crystal field splitting of 1.4 eV.

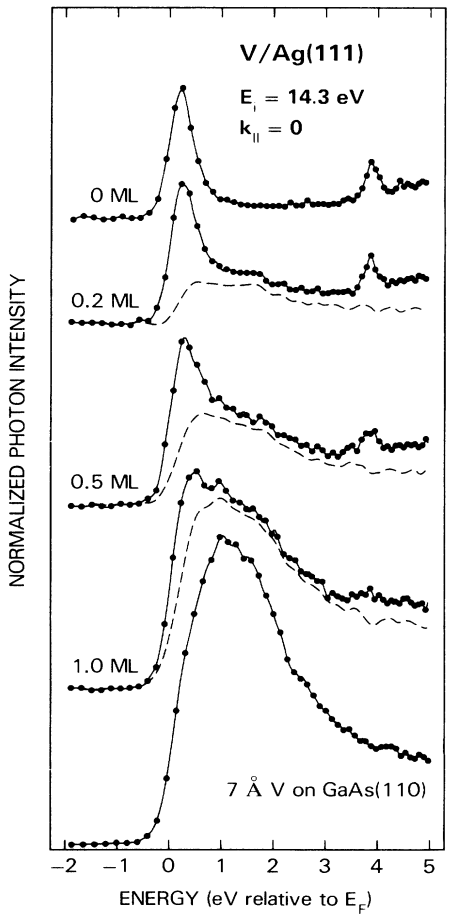

FIG. 2. Similar to Fig. 1 for V on Ag(111).

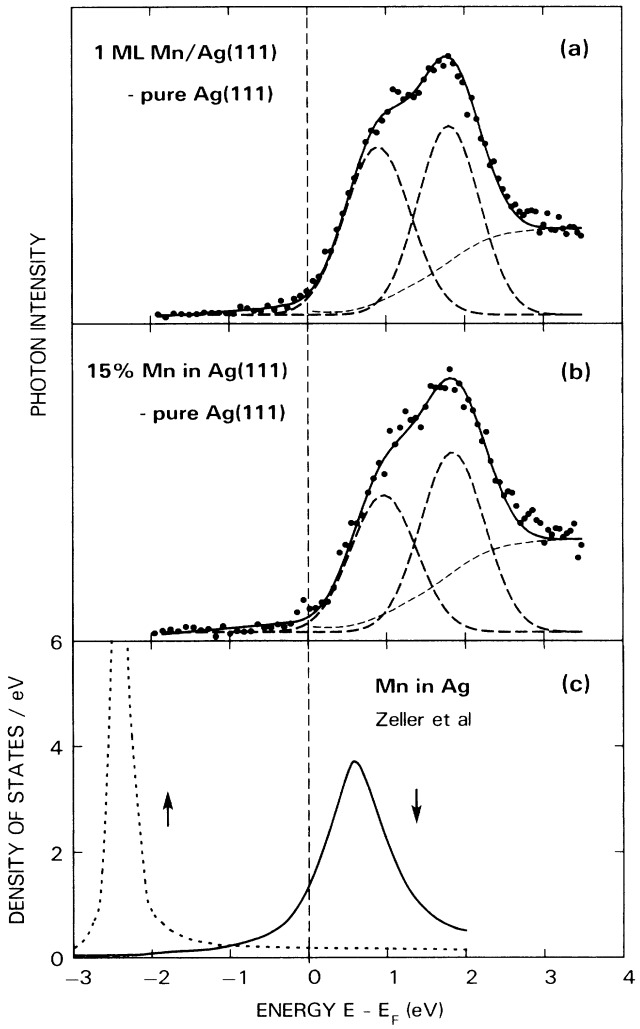

FIG. 3. Comparison of Mn-derived minority-spin states in a thin film to the Mn-in-Ag spin glass. (a) Inverse photoemission results for 1 monolayer of Mn on Ag(111) (see Fig. 1). (b) Inverse photoemission results for Mn in Ag. The spectrum was obtained by subtracting the data for pure Ag(111) from data taken on a Ag–15-at.% Mn(111) alloy (cf. Fig. 2 in Ref. 24). (c) Local density-of-states calculation (Zeller, Podloucky, and Dederichs, Ref. 21) for the majority- (dashed line) and minority-spin (solid line) states for Mn in Ag.

For bulklike Mn films (thicker than two layers) the density of unoccupied states is broader and has substantial emission at the Fermi level. Such a distribution is characteristic of bulk Mn, which is nonferromagnetic. The broadening is caused by three-dimensional band formation. The ferromagnetic exchange splitting collapses and causes high density of states at the Fermi level as expected for a half-filled $3d$ band.

The interpretation of the data for V on Ag(111) is less clear-cut due to the lack of comparable spin-glass data. On the other hand, vanadium has been a prototype for theoretical predictions[1-5] of thin film magnetism. Recent electron-capture experiments[11] demonstrated that the surface of paramagnetic bulk vanadium is ferromagnetic. For submonolayer films of V on Ag(111) there appear to be two structures in the unoccupied density of states (Fig. 2) at 0.5 and 1.7 eV above E_F. For a monolayer of V and above, the maximum in the density of states lies between these two features. Whether or not such a change is due to the collapse of a ferromagnetic exchange splitting or not is difficult to decide from the inverse photoemission data alone. Spin-polarized inverse photoemission[28,29] would be necessary for an unambiguous assignment. Calculations[5] for a ferromagnetic epitaxial V layer on Ag(100) predict peaks in the density of states centered at E_F and 1.2 eV below E_F for the majority spin and at 0.3 and 1.7 eV above E_F for the minority spin, i.e., very close to the inverse photoemission features seen for the submonolayer coverage. The splitting of the spin states is caused by the crystal field.

In summary, we have observed unoccupied $3d$ states of thin films of V and Mn on Ag(111), which change significantly when going from the submonolayer regime to bulklike films. The states can be assigned to minority-spin states by analogy with the Mn-in-Ag spin glass and by comparison with first-principles calculations. These results suggest a large ferromagnetic exchange splitting (about 4–5 eV for Mn, 1–2 eV for V) and a corresponding large magnetic moment. Such observations represent a first step toward the experimental determination of the unoccupied bands in surface-enhanced ferromagnetism.

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