Electronic structure of epitaxial $\text{Ni}_x\text{Pd}_{1-x}$ alloy films on $\text{Cu}_3\text{Au}(100)$

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We studied epitaxially grown single-crystalline chemically disordered ultrathin $\text{Ni}_x\text{Pd}_{1-x}$ alloy films on $\text{Cu}_3\text{Au}(100)$ by means of photoemission using magnetic circular dichroism in the angular distribution. We clearly observe a well-defined three-dimensional band dispersion in 15 monolayer films. On the basis of relativistic selection rules, this dispersion can be related to specific electronic states. Since the spin-orbit coupling (ΔE_{so}) is smaller for Ni than for Pd, the alloy will assume an average value. We find that this average spin-orbit coupling clearly shows up in the electronic structure and correlates directly to the composition of the NiPd alloy film. The results are discussed in terms of a simple qualitative model. © 2001 American Institute of Physics.
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In order to satisfy future technology demands, it is important to exploit the advantages of new magnetic compounds and alloys in devices for mass storage and magneto-electronics applications. Within recent years numerous studies dealt with binary and ternary bulk systems,¹ whereas only a few investigations focused on ultrathin layers and, particularly, epitaxial films of these materials. This research is mandatory to develop advanced magnetic materials with improved properties. Often details in the electronic structure (hybridization zones, gaps, etc.) are responsible for specific magnetic features, e.g., the magnetic anisotropy. From the electronic structure point of view two spin-dependent interactions are important in magnetic systems, i.e., exchange interaction and spin-orbit coupling. The goal of an experiment is to describe the electronic structure in as much detail as possible. In order to understand and to tailor magnetic properties, both spin-orbit coupling and exchange interaction have to be taken into account on the same level. An established experimental approach to this problem is magnetic circular dichroism in valence band photoemission (MCDAD), enabling one to extract the spin-dependent contributions to a photoemission spectrum on the basis of intensity measurements.² In order to facilitate interpretation of the dichroism spectra, we chose a high symmetry geometry for perpendicularly magnetized films, i.e., normal light incidence and normal electron emission, thus allowing us to exploit relativistic selection rules.³ This way spectral features may be attributed to certain interband transitions, and information about the symmetry character of the bands involved in the photoexcitation process may be gained. Finally, this information may be used to correlate the experimental data to fully relativistic band structure calculations, if available.

Up to now investigations varied the overall magnitude of the exchange interaction in an alloy film within a certain limit by changing the composition. This was previously re-

alized in $\text{Fe}_x\text{Co}_{1-x}$ on $\text{Cu}(100)$,⁴ since Fe and Co exhibit nearly the same magnitude of spin-orbit interaction (~ 0.1 eV), but different strength in exchange coupling, leading to different level splittings of 2.2 and 1.2 eV, respectively. In this article, we have chosen a different approach with $\text{Ni}_x\text{Pd}_{1-x}$ on $\text{Cu}_3\text{Au}(100)$. Both Ni and Pd have comparable exchange correlation integrals,⁵ which in the case of Ni leads to an average experimental exchange splitting of ~ 0.3 eV (Ref. 6) along $\Gamma-X$. We note that neither spin-orbit coupling nor exchange interaction in a solid can be described by a simple number. Both quantities vary throughout the Brillouin zone and depend strongly on the band symmetry, as well as on the degree of hybridization. The following arguments only apply to the d -like bands along the $\Gamma-X$ direction, where the values of the energy splittings ΔE_{so} and ΔE_{ex} are known to vary only marginally with $\vec{k}$. We can thus assume that we directly vary the “spin-orbit coupling” via the alloy composition. The average values for the band splittings along $\Gamma-X$ are $\Delta E_{\text{so}} = 0.1$ eV (Ref. 6) and $\Delta E_{\text{so}} = 0.3$ eV (Ref. 7) for Ni and Pd, respectively. The orientation of the magnetization $\mathbf{M}$ of pristine Ni on $\text{Cu}_3\text{Au}(100)$ depends on the film thickness. It lies in plane up to 5 monolayer (ML) coverage and flips out of plane above. This effect is known as an inverse spin reorientation transition (iSRT).⁸ Pd also has a bigger lattice constant of $3.89 \text{ \AA}$, which is even larger than that of Cu_3Au ($3.75 \text{ \AA}$). As the lattice constant of $\text{Cu}_3\text{Au}(100)$ lies midway between Ni and Pd, it is possible to adjust a certain lattice misfit (ranging from $+6.8\%$ to -3.7%) by choosing a specific NiPd composition. This mismatch changes the film strain, which finally modifies the magnetic properties. This results in the inverse SRT being shifted to higher coverages with increased Pd concentration.⁹ It is known from bulk investigations that NiPd alloys exhibit ferromagnetic behavior up to a Pd concentration of 97% with the magnetic moment and the Curie temperature being concentration dependent.¹⁰ In this work we study the influence of the composition on the electronic structure.

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FIG. 1. Intensity and asymmetry spectra of 15 ML $\text{Ni}_{83}\text{Pd}_{17}$ films.

The experiments were conducted in a UHV chamber (base pressure 2×10^{-10} mbar) equipped with an Auger electron spectrometer (AES) and a medium energy electron diffraction (MEED) device. After cleaning the $\text{Cu}_3\text{Au}(100)$ single crystal by argon ion bombardment and subsequent annealing, Ni and Pd were co-deposited at room temperature. Photoemission experiments were carried out at the 6.5 m-NIM beamline at BESSY I by taking MCDAD spectra with circularly polarized light in the vacuum UV region. The energy spectrometer provided an angular resolution and an energy resolution of $\pm 3^\circ$ and 250 meV, respectively. In the concentration and coverage range investigated the thin $\text{Ni}_x\text{Pd}_{1-x}$ films were remanently magnetized perpendicular to the surface, so spectra for opposite alignment of the magnetization $\mathbf{M}$ and the helicity σ of the light are compared, $I(\mathbf{M}\uparrow\uparrow\sigma)$ and $I(\mathbf{M}\uparrow\downarrow\sigma)$. As a measure of the magnetic dichroism, we use the dichroic asymmetry.⁶ We have measured NiPd films with concentrations between 100% and 50% Ni for a coverage of 15 ML.

The left part of Fig. 1 shows intensity spectra from 15 ML films with a Ni concentration of 83% for parallel (solid lines) and antiparallel alignment (dashed lines) of magnetization and helicity. The data evaluation procedure with respect to normalization and determination of E_F follows that used in Ref. 6. The resulting intensity asymmetries are shown on the right-hand side of Fig. 1. In general, the spectra in Fig. 1 show similarities to the results reported for Ni/Cu(100).⁶ For example, the spectrum for the lowest photon energy of 11 eV exhibits a clear “minus” asymmetry feature just below E_F . For Ni/Cu(100) one finds a “plus-minus” feature, associated with a specific set of interband

FIG. 2. Influence of ΔE_{so} and ΔE_{ex} on intensity and asymmetry spectra by varying ΔE_{so} in the range of 0.1, 0.15, and 0.22 eV.

transitions starting at Δ_{6-}^5 and Δ_{7-}^5 bands. In our case, the respective “plus” feature in the asymmetry is missing. It shows up weakly at higher photon energies, suggesting that the spectral weight of these transitions correlated to the initial state Δ_{6-}^5 is suppressed. Figure 1 also reveals that by increasing the photon energy the minus asymmetry peak broadens and moves smoothly towards higher binding energies. This is indicative of pronounced band dispersion (as indicated by the solid line) and a well defined three-dimensional electronic structure. The peak broadening could be due to an increase of alloy-related band broadening when moving away from E_F . Obviously this feature is more pronounced in the photon energy range between 17 and 21 eV. Finally, at high photon energies a second plus feature appears at E_F .

Three possible influences, spin-orbit coupling, structural effects (e.g., a rigid band shift), and hybridization effects, must be considered to at least qualitatively explain the results.

The influence of spin-orbit coupling is modeled in Fig. 2, and reflects the interplay between the intensity and asymmetry in order to qualitatively interpret the observed spectra. This is done by comparing the intensity contributions from four transitions, corresponding to the initial states available in the experimental geometry. The splitting of these states is caused by the combination of exchange interaction and spin-orbit coupling (Fig. 2). The initial (Δ_{6-}^5 , Δ_{7-}^5 , Δ_{6+}^5 , Δ_{7+}^5) and final states (Δ_{6-}^1 , Δ_{6+}^1) involved are labeled according to their relativistic symmetry character^{3,6} along the [100] direction. The spectral contributions are added up according to relativistic selection rules, resulting in the partial spectra $I(\mathbf{M}\uparrow\uparrow\sigma)$ and $I(\mathbf{M}\uparrow\downarrow\sigma)$, from which the asymmetry is cal-

culated. In Fig. 2, we varied the strength of the spin-orbit coupling from 0.1 to 0.22 eV. This changes the overall appearance of the asymmetry spectrum from “plus-minus-minus-plus” to “plus-minus-plus”-like behavior, where the minus contribution relating to the Δ_{-7}^5 and Δ_{+7}^5 initial states eventually becomes dominant. In addition, in this example the minus peak shifts from -0.9 to -0.84 eV, i.e., it moves closer to or above E_F and it becomes the main feature in the asymmetry spectra. This is qualitatively just the behavior observed in our results, since the minus peak occurs at low photon energies just below E_F and shifts to higher binding energies with increasing photon energy. The missing plus feature (at low photon energies), on the other hand, may be explained by taking into account the band structure calculation for Ni(100).⁶ It suggests that the Δ_{-6}^5 initial state related to the plus feature follows a band dispersion with multiple hybridization points. This might lower its spectral weight. Since our simple spin-orbit coupling model explains our observations reasonably well, we conclude that states of the appropriate double-group symmetry are still available to some extent despite the chemical disorder.

The position of the electronic states and their dispersion may not necessarily be explained only by an increase of spin-orbit coupling. It could also be influenced by structural aspects, e.g., tetragonal distortion and its relaxation to a face-centered-cubic (fcc) film structure for higher film thicknesses. Strange *et al.*¹¹ showed that the lattice ratio c/a affects the energetic position of the d bands. Enhancing c/a shifts the d -like bands closer towards E_F . MEED observations for the NiPd on the Cu₃Au system reveal a persisting fct distortion for 15 ML regardless of the composition,¹² so the vertical lattice parameter stays within a certain range. Therefore we can rule out this as a possible explanation for the shift of the asymmetry features closer to E_F in Fig. 1.

The last issue concerns the influence of electronic hybridization between Ni and Pd states. Focusing on band dispersion, Fig. 1 also shows that with increasing photon energy the asymmetry peaks move smoothly towards higher binding energies as shown by the parabolic line. This behavior also occurs within a similar energy range for the Ni/Cu(100) system. A likely explanation for this similarity can be that the initial state bands have comparable dispersion in the alloy. Although the final states (Δ_{+6}^1 , Δ_{-6}^1) might be split by a small exchange interaction, the energetic position of the photoemission peaks do not differ, since the slope of these final state bands is very steep compared to that of the initial states. Thus the observed features result mainly from the initial states. This is reasonable to assume, because the Pd content is only about 17%. This may also explain why also the average magnitude of the intensity asymmetry (around 8%) approaches the pure Ni values. We conclude that mixing effects for this rather low Pd concentration do not yet play an important role for the electronic band structure.

Films with medium Ni concentrations (52% Ni) show again clear dichroic behavior of the photoemission intensities. The asymmetry dispersion is considerably more complex than in the high Ni concentration regime and in general the minus asymmetry peaks are shifted towards higher energies.

This latter finding is still compatible with our above-mentioned simple model describing spin-orbit coupling. According to this model higher spin-orbit coupling, due to a higher Pd content, will increase and shift the minus asymmetry peak towards E_F , just as observed. On the other hand, we should not overinterpret our model, since it cannot explain the more complex dispersion relation. In this case the influence of hybridization, due to spin-orbit coupling, or mixing effects caused by alloying Ni and Pd in a chemically disordered way, must be considered. As already pointed out, the interpretation of our MCDAD measurements is based on dipole selection rules. Hybridization effects may split states and change the symmetry character of bands, leading to very complex dispersion. For the 50:50 film composition, the band structure is certainly no longer just Ni like. A pronounced mixing between $3d$ Ni and $4d$ Pd states must be expected. Preliminary nonrelativistic band structure calculations by Ebert using a CPA-approximation¹³ give an initial hint as to these mixing and hybridization phenomena. They indicate a strong mixing of the Δ^5 -like states (both spin directions) with Δ^1 and Δ^2 states particularly in the energy region between E_F and 2.5 eV binding energy. Moreover Ebert's studies reveal a pronounced broadening of the spectral weight for the calculated Bloch spectral functions. This feature is caused by chemical disorder in the NiPd alloy, showing a different occupation in adjacent unit cells. The broadening makes it difficult to distinguish individual electronic states. Nevertheless, the pronounced dispersion in the experiment shows that individual states with well-defined relativistic symmetry can be addressed in the photoemission process.

In summary, the comparison between experiment and theory is encouraging, but details of the electronic structure are still masked by disorder-induced broadening. For further investigations, a comparison with the relativistic band structure or photoemission calculations will be needed to fully exploit information contained in the MCDAD data.

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