Probing the Ground State Electronic Structure of a Correlated Electron System by Quantum Well States: Ag/Ni(111)

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(Received 17 April 2005; published 5 December 2005)

The ground state electronic properties of the strongly correlated transition metal Ni are usually not accessible from the excitation spectra measured in photoelectron spectroscopy. We show that the bottom of the Ni d band along [111] can be probed through the energy dependence of the phase of quantum-well states in Ag/Ni(111). Our model description of the quantum-well energies measured by angle-resolved photoemission determines the bottom of the Λ_1 d band of Ni as 2.6 eV, in full agreement with standard local density theory and at variance with the values of 1.7–1.8 eV from direct angle-resolved photoemission experiments of Ni.

DOI: 10.1103/PhysRevLett.95.247601 PACS numbers: 73.21.Fg, 71.20.Be, 71.27.+a, 79.60.Jv

A thorough understanding of the electronic structure of solids is prerequisite for predicting physical properties such as electrical conductivity, optical response, and lattice and magnetic structure. Density functional theory and the local density approximation (LDA) represent a most successful approach to the electronic structure. Via the total energy, LDA predicts ground state properties such as the equilibrium lattice or the type of magnetic order for direct comparison to the experiment, and it delivers $E(\mathbf{k})$ band dispersions, revealing the role of individual electronic states for these properties. While there is no experimental method available to probe $E(\mathbf{k})$ dispersions in the ground state, the excitation spectra obtained by electron removal in an angle-resolved photoemission experiment provide detailed quasiparticle dispersions [1].

One of the first metals where angle-resolved photoemission was systematically measured against $E(\mathbf{k})$ dispersions from LDA is Cu, and the comparison revealed excellent quantitative agreement between the dispersions obtained from the excitation spectra and the predictions for the ground state [2,3]. For other metals, the relation resulted in at least fair agreement, but Ni represents an exception to the rule in several respects: It shows features not described by LDA calculations as there are photoemission satellites in core-level spectra [4] and the valence band [5,6]. The width of the occupied d band was found to be significantly smaller than predicted by LDA calculations [7], an observation fully confirmed by detailed measurements using angle-resolved photoemission [8–10].

The generally accepted reason for these observations is strong electron correlation which becomes significant when the on-site repulsion due to the Coulomb interaction U equals or exceeds the width of the conduction band W. The on-site repulsion as well as the long-range tail of the Coulomb interaction are missed in the LDA, and a number of methods have been developed to include strong correlation into the LDA. Electron correlation in the $3d$ band is important for the magnetic ground state of transition metals, and inclusion of U has led to improvements in several ways [11,12], e.g., towards realistic Curie temperatures for Ni [11]. A different strategy is pursued by quasiparticle calculations [13,14], which predict the excitation spectrum of Ni and its $\mathbf{k}$ dependence for direct relation to the angle-resolved photoemission experiment. It has, e.g., been shown that assuming the presence of a stationary hole takes the $E(\mathbf{k})$ dispersion much closer to the photoemission experiment and reproduces the satellite peak [13].

In this situation, it is unclear whether the effect of the Coulomb interaction U predominates on the ground state or on the excitation. The same question surrounds the screening of U by other electrons. Much theoretical effort is being invested in improving the LDA treatment of Ni and its band structure, but, in view of the strong final state effects present [13], detailed comparison to $E(\mathbf{k})$ dispersions from the LDA is discouraged unless the ground state can be measured.

It has, to our knowledge, never been attempted to determine the occupied Ni electronic structure in the ground state by experiment. It is, in principle, possible to probe the Ni electronic structure and not excite the Ni electrons. To this end, Ni shall form the boundary of a metallic quantum well where coherent scattering at the surface and the Ni interface lead to the formation of standing electron waves. The electronic structure of Ni determines the phase shift of the electrons scattered at the interface. The energy dependence of the phase shift determines, in turn, the quantum-well energies. The electrons occupying quantum-well states are probed by angle-resolved photoemission, ensuring the necessary resolution in $\mathbf{k}$ and E.

The feasibility of this method has already been demonstrated for sp electrons in Ag and Al films probing the interfaces Ag/Cu(111) [15], Al/Si(111) [16], and Ag/Si(100) [17]. In this Letter, we report quantum-well states of ultrathin Ag layers on Ni(111) with thicknesses from 0 to

15 monoatomic layers (ML) in normal emission (Figs. 1). Alternatively, we studied how the emission-angle dependence is affected by the Ni substrate and arrived at the same conclusions [18]. The electronic structure of Ag is perfectly suited for the formation of quantum-well states [19,20], because it is of simple Bloch-type with only sp electrons dispersing along [111] from 0.3 eV binding energy down to 4 eV (where, in addition, Ag d states contribute) [Fig. 2(b)]. This energy range fully covers the Ni d states along [111] (notation Γ-L or Λ). The bottom of the Ni d states is marked by the minimum of the Λ_1 band $\Lambda_1^{\min}$, which defines the upper border of the band gap [Fig. 2(c)]. The dispersion of the Λ_1 band in Ni is known with high accuracy from several independent photoemission experiments and LDA calculations. Λ_1 originates at Γ_{25}', which is at 2.14 eV (Korringa-Kohn-Rostoker method [21,22]) and 2.15 eV (linear combination of Gaussian orbitals [LCGO] [23]) in LDA and at 1.1–1.2 eV [8,10] in angle-resolved photoemission. For $\Lambda_1^{\min}$ this means 2.69 and 2.70 eV from theory and 1.7 and 1.8 eV from experiment. This deviation by almost 1 eV is typical of the strongly correlated electronic structure of Ni and allows for a clear statement to be expected from the present experiment: Is the ground state of Ni appropriately described by conventional local (spin) density theory and the typical functionals for exchange and correlation and the shift by 1 eV fully due to photoemission, or does strong electron correlation need to be explicitly incorporated to describe the ground state?

Photoemission experiments were done at the VUV beam line at Elettra and the Russian-German beam line at BESSY using mixed s- and p-polarized light. Base pressure was below 2×10^{-10} mbar. Hemispherical electron energy analyzers were used in normal-electron-emission geometry at 100 meV energy and 1° angle resolution. The Ni(111) surface was prepared by multiple cycles of sputtering with 1.2 keV Ar^+ followed by annealing at 550 °C. Cleanliness and structural quality of the surface have been verified by the presence of a sharp $p(1 \times 1)$ pattern in low energy electron diffraction as well as by photoemission from the Ni valence band. Ag has been evaporated from a resistively heated drop on a tungsten filament.

Spectra of the clean Ni(111) and of 14 ML Ag grown on top are given in Fig. 1(b) and the intermediate thicknesses in Fig. 1(a). Discrete quantum-well states derived from the Ag $sp(\Lambda_6)$ band are clearly visible [for details of the band structure of Ag and Ni, we refer to Figs. 2(b) and 2(c),

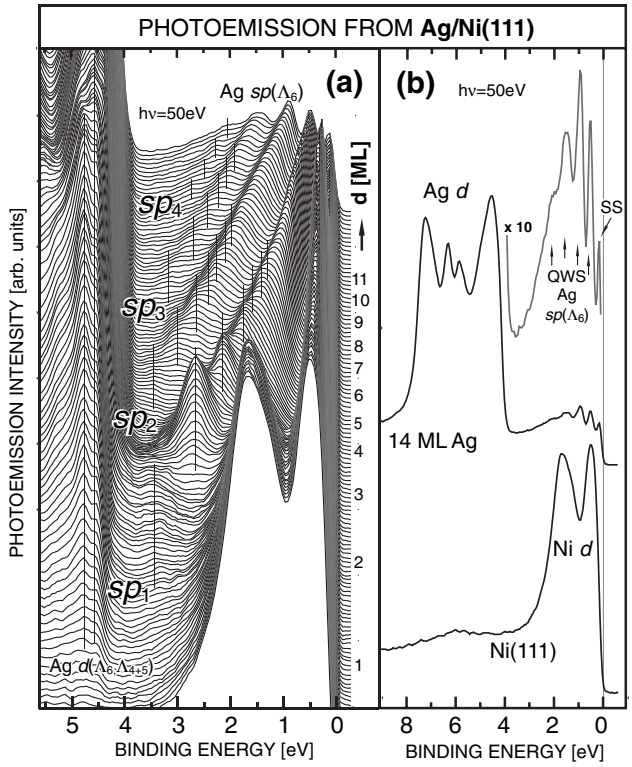

FIG. 1. (a) Development of sp- and d-quantum-well states in Ag overlayers on Ni(111) measured by photoemission upon increasing the thickness of the Ag film up to 14 ML (normal emission). (b) Full range reference photoelectron spectra of clean Ni(111) and of a 14 ML-thick Ag film grown on top.

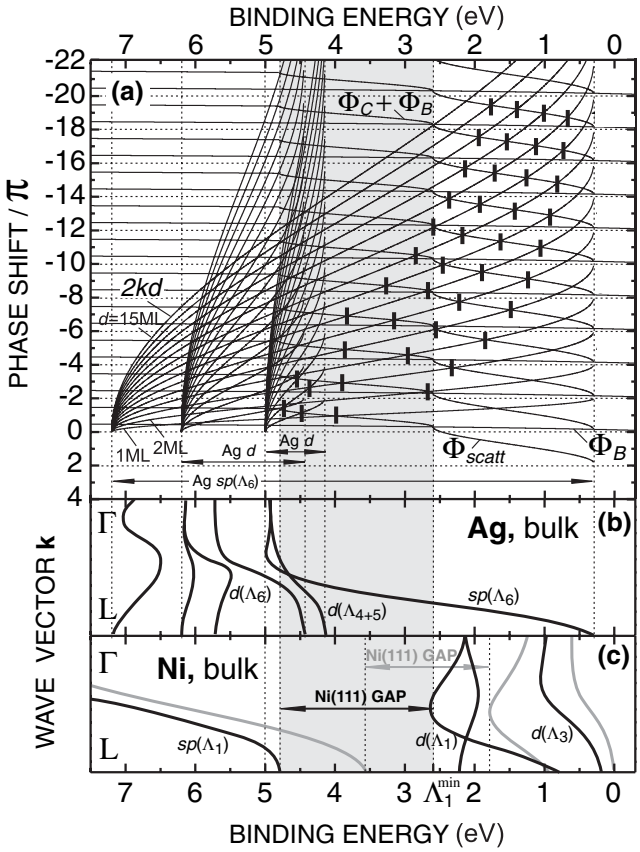

FIG. 2. (a) Graphical solution of the extended phase equation (1). Intersections of phase shift due to propagation $2kd$ for increasing thickness d (in ML) with interface phase shifts (shifted by multiples of 2π). (b) and (c): Band structures of Ag and Ni given along Γ-L on the same energy scale in double- and single-group notation, respectively. Gray in (c): experiment [8–10]; black: local density theory [23]. The Ni(111) surface projected gap for which quantum-well energies are derived is represented by the gray bar.

where bulk dispersions are shown in the Γ-L direction [111] of the bulk Brillouin zone]. The first quantum-well peak labeled sp_1 in Fig. 1(a) appears at 3.5 eV and corresponds to the completion of the first Ag monolayer. Upon development of the second monolayer, this peak is replaced by one at 2.7 eV. The intensities of these peaks allow us to count integer monolayer thicknesses up to 10 ML and obtain an absolute scale for the thickness. In Fig. 3, experimentally measured energies of the quantum-well states (open circles, diameters scale with photoemission intensity for each peak, the layer thickness is evaluated at maximum intensity) are plotted versus Ag thickness. At 4 ML thickness, there appears a new branch of quantum-well states (sp_2), again nearly at 3.5 eV, which corresponds to a standing electron wave with a wavelength half of the one of sp_1. In total, we can resolve four branches sp_{1-4} plus distinct quantum-well states of d-type at binding energies 4.0–5.0 eV.

To calculate energy levels of confined sp and d states, we used the phase accumulation model [24], which predicts standing electron waves for the case that the sum over all phase changes experienced during one round trip equal 2π times a quantum number n. The extended phase

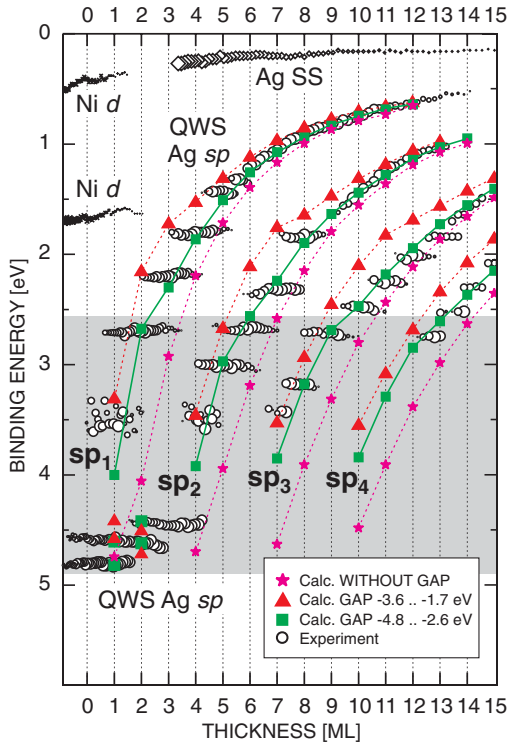

FIG. 3 (color online). Thickness-dependent electronic structure of quantum-well states in Ag on Ni(111). Measured binding energies are given as open circles. Squares denote optimal quantum-well state energy levels obtained for the gap 4.8–2.6 eV. Red triangles represent the quantum-well state energies calculated for the experimentally measured gap taken from Refs. [8–10], which deviate by one monolayer for most of the energy range. A similarly large deviation occurs when the band gap is completely absent (magenta stars).

equation

$$\Phi_B + \Phi_C + 2kd - \Phi_{\text{scatt}} = 2\pi n \qquad (1)$$

has been described in detail in Ref. [25]. In brief, the terms Φ_B and Φ_C denote the phase shifts of the wave function upon electron reflection at the surface barrier and at the interface, respectively [24]. $k(E)$ is the wave vector of the electron propagating in the Ag overlayer and is given by the upper and lower borders of the Ag sp band ($E_U^* = 0.3$ eV and $E_L^* = 7.2$ eV binding energy, respectively) in the form $k(E)d = N\arccos(1 - 2E/(E_U^* - E_L^*))$ and *mutatis mutandis* two d bands. d denotes the overlayer thickness, N the thickness in ML. Φ_{scatt} describes electron scattering at the interface for energies outside of the energy gap. Both Φ_C and Φ_{scatt} are expressed in terms of the gap border $E_{U,\text{gap}} = \Lambda_1^{\text{min}}$ as $\Phi_C = 2\arcsin[(E - E_{L,\text{gap}})/(E_{U,\text{gap}} - E_{L,\text{gap}})] - \pi$ and $\Phi_{\text{scatt}} = 2\arccos(1 - 2E/(\Lambda_6^{\text{max}} - \Lambda_1^{\text{min}}))$, and this will be used to determine Λ_1^{min}.

In Fig. 2(c), two alternative band structures of Ni are shown. One (black lines, gap from 2.7 to 4.8 eV) is the LCGO calculation from Ref. [23]. The other band structure (gray lines, gap from 1.7 to 3.6 eV) was measured by angle-resolved photoemission [8,9]. The diagram in Fig. 2(a) illustrates the solution of the phase equation, Eq. (1). We involve in the analysis three bands of Ag—$sp(\Lambda_6)$ for the calculation of sp quantum-well branches below 4 eV, and two d bands (Λ_6 and Λ_{4+5}) to describe quantum-well states of d-type between 4 and 5 eV. We developed a fit procedure to determine the edges of the Ni gap. In this method, the top of the Ni gap $E_{U,\text{gap}} = \Lambda_1^{\text{min}}$ as well as the bottom $E_{L,\text{gap}}$ are varied independently, seeking the best agreement between calculated and measured quantum-well energies. Results of the variational fit analysis are reported in Fig. 3. The best correlation (green squares) is achieved for the gap from 2.6 to 4.8 eV (gray area in Fig. 3). This is very close to the LCGO calculation [23] [Fig. 2(c)]. Red triangles correspond to the solution with the Ni gap from photoemission [8,9]. It is seen that these predictions are strongly shifted away from experiment for energies $\geq$1.7 eV due to a kink in each quantum-well branch at this energy. For the result of the fit analysis, this kink appears at 2.6 eV and closely follows the experimental data. Note also that the green squares provide a description for *all* observed quantum-well states, as opposed to the red triangles, where some energies are missing, in particular, in the sp_2 branch. How sensitive the energies of quantum-well states are to the choice of Λ_1^{min} becomes clearer from Fig. 4. For the branch with quantum number $n = 1$, the energy difference $(E_N - E_{N-1}) \cdot E_N$ of subsequent quantum-well states with thicknesses $N - 1$ and N ML is plotted. The Ni band gap reveals itself as a kink in this plot. The present experiment (○) agrees with a band gap boundary at 2.6 eV as calculated by LDA [21–23] and not with the value from Ni photoemission of 1.7–1.8 eV [8–10]. It is seen in Fig. 3 that in this energy range quantum-well state energies given by the model deviate by up to 0.15 eV from

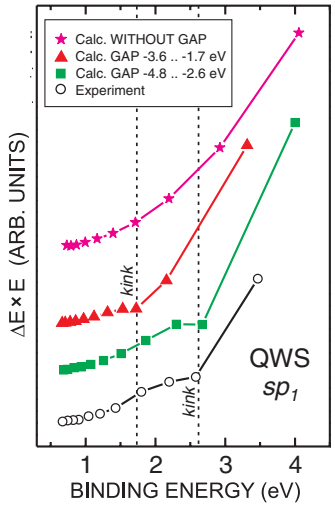

FIG. 4 (color online). Comparison of measured quantum-well energies to model calculations. The plot shows the energy difference between $n = 1$ quantum-well states (QWS) for subsequent thicknesses. The Ni band gap reveals itself as a kink in this plot. The present experiment (○) agrees with a band gap boundary at 2.6 eV as calculated by local density theory [21–23] and not with the value from Ni photoemission of 1.7–1.8 eV [8–10].

experiment, and we take this value as accuracy of our determination of $\Lambda_1^{\min}$.

The bottom of the band gap as calculated by LDA falls into the range of Ag d states, as Fig. 2 shows. They will mask the observation of sp-type quantum-well states and complicate a precise determination of quantum-well energies in their vicinity [the weak sp_1 and sp_2 peaks around 3.5 eV (see Fig. 1) are probably, in addition, affected by the energy dependence of the photoemission cross section]. Also, sp-d hybridization in Ag neglected in our model contributes to the strong deviations seen in Fig. 3 around 3.5 eV. We have, therefore, evaluated d quantum-well states and can, even though few data points exist, report consistency with the LDA value and disagreement with the photoemission value for the bottom of the gap (see Fig. 3).

Before closing, we briefly want to compare our results to the data of Refs. [19,20]. According to these reports, Ag on Ni(111) forms a diffuse boundary where the electron is lost due to incoherent scattering. In this picture, the discrete peaks observed are an effect of quantization only in the final state. While this interpretation may hold for the low photon energies (<15 eV) used in Ref. [20], it is not realistic for high energies such as 50 eV in the present study. The bulk band structures in Fig. 3 suggest that Ag/Ni(111) represents the classical case of a quantum-well system with strong confinement inside of the gap and "leaky" behavior outside. This view is supported by our analysis based on the phase accumulation model.

In summary, we have analyzed the behavior of quantum-well states in Ag/Ni(111) with thickness. Quantum-well energies derived from the phase accumulation model were fitted to the experiment with the Ni bulk band gap as a free parameter. In this way, the minimum of the Λ_1 band is determined as 2.6 ± 0.15 eV, in good agreement with early local density calculations of Ni. Agreement for other values fails, in particular, for those derived from photoemission data. This result lends credit to the simplest possible view on photoemission from Ni: that electron correlation in the ground state is sufficiently described by standard local spin density theory and deviations are predominantly final state effects.

This work was supported by DFG (RA 1041/1-1 and 436RUS113/735/0-1) and a common DFG-RFFI project (03-02-04-024).

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