Unexpected Negative Exchange Splitting of the Fe(001) Image State

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We have observed a surprising *negative* exchange splitting of the $n = 1$ image-potential surface state at Fe(001) using spin resolved inverse photoemission, indicating that the minority-spin level has a lower energy than the majority-spin level. Calculations show the negative sign results from two superimposing effects. A true reverse polarization of the image state, which hybridizes with bulk bands, which is then enhanced by matrix element effects in inverse photoemission. [S0031-9007(96)00790-9]

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The long-ranged Coulombic attraction between an electron in front of a metal surface and the induced image charge gives rise to a hydrogeniclike infinite series of states loosely bound to the crystal at energies just below the vacuum level. These so-called image states have been extensively studied in recent years [1], and have been exploited in applications as diverse as monitoring the growth and morphology of ultrathin metal films [2], as a source of elemental contrast in the scanning tunneling microscope [3], and in the study of electron localization in insulators and at the metal/dielectric interface [4]. Image states have been experimentally identified primarily through inverse photoemission (IPE) [5–7] and two-photon photoemission [8]. When the crystal lacks a suitable projected band gap to prevent penetration of the image state into the metal, hybridization with bulk states gives rise to image *resonances*. These are less pronounced but still visible in IPE spectra [9,10].

In the case of a ferromagnetic surface the exchange interaction between the image state and the electrons in the crystal depends upon the spin of the electron. Hence the possibility of a spin splitting (a different energy for majority- and minority-spin levels) which is expected to be a useful probe of surface magnetism. Himpsel [10] has used a simple phase-shift model coupled with the two-band approximation to predict splittings for various ferromagnetic surfaces, and subsequently a number have been recorded experimentally [11–15]. There has also been a detailed theoretical calculation [16] for the Fe(110) surface which has predicted a splitting of 55 meV at $\bar{\Gamma}$ (the center of the surface Brillouin zone) for the $n = 1$ image state, twice that given by the two-band model [10] but in excellent agreement with the recently measured value [15] of 57 ± 5 meV. We report here the first result (both theoretical and experimental) concerning the spin splitting of an image resonance, that which is found at the Fe(001) surface. Remarkably, we find a *negative* splitting, corresponding to the minority level having lower energy than the majority level. Of all the electronic states in bcc Fe this is the first (either occupied or unoccupied) to be found to have a negative exchange splitting, and points to a complicated relationship between substrate and image-state magnetism.

Our experiments are spin resolved inverse photoemission [17] in which we collect photons emitted during the radiative decay of spin-polarized incident electrons into empty metal states. We work in isochromat mode, selecting photons at a fixed energy of $h\nu = 9.6 \pm 0.3$ eV while varying the energy of the collimated and transversely polarized incident beam produced by a negative electron affinity photocathode [18]. For this we use a thin (100 nm) GaAs layer deposited on a *p*-doped AlGaAs substrate in good lattice matching conditions. This source has a higher polarization [$P_0 = (42 \pm 2)\%$ [19]] than bulk GaAs crystals, as electrons excited in the thin layer are less effectively depolarized than in the bulk [20]. The acquisition time is consequently reduced by a factor of ~ 2 when compared with usual sources with $P_0 \simeq 30\%$, the figure of merit of the source being proportional to the square of the polarization [21]. Spin-polarized spectra are then normalized to a hypothetical 100% electron beam polarization through a standard procedure [22]. All IPE data are recorded at room temperature. We report results for electrons incident normal to the surface, probing electron states at $\bar{\Gamma}$.

The Fe(001) single crystal was cleaned by extensive heat treatment in H_2 atmosphere and subsequent sputter-annealing cycles in ultrahigh vacuum (base pressure 3×10^{-11} Torr). As described elsewhere [23] the best quality surface, important in image state spectroscopy, is achieved by annealing a thin (~ 30 Å) Fe film homoepitaxially grown on the clean Fe(001) substrate. For cleanliness reasons we refresh the surface every 2 h by sputter annealing and re-evaporation, although no evidence of contamination (in x-ray photoemission spectroscopy, low-energy electron diffraction spectroscopy, or IPE) is detected before 3 h. Samples were magnetized in plane along the [010] direction of the Fe lattice by means of a current pulse through a coil surrounding the sample, then

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IPE spectra taken in magnetic remanence so as to provide a definite incident electron momentum. In order to evidence only true spin effects, series of spectra have been recorded for each of the four possible relative vector orientations of sample magnetization and beam polarization. However, the spin asymmetries were identical (opposite in sign), removing any possibility of spurious effects. The spectra from each of the clean surfaces were accurately checked and then summed to obtain the requested statistic ($>50 \times 10^3$ counts per point, 50 points/eV).

The inset in Fig. 1 shows IPE data for Fe(001). Besides the bulk derived spectral features B_1 and B_2, already reported and discussed elsewhere [22,24], there appears a smooth peak at about 3.8 eV above the Fermi energy (E_F) originating from transitions into the $n = 1$ image resonance. This feature is shown with enlarged scale in Fig. 1. The peaks corresponding to the image resonance are superimposed upon a steplike increase at the high energy side representing the unresolved higher-order members of the Rydberg series and the continuum of states above the vacuum level [13,25]. In order to determine a magnetic splitting we have performed a least-squares fit with a Lorentzian representing transitions to the image resonance superimposed upon a steplike and linear background. The resulting curves, broadened with a Gaussian 0.7 eV wide (full width at half maximum) representing the experimental response function, are shown in Fig. 1 as lines through the data points. We have repeated the fitting procedure using various different background shapes and energy interval and the relative difference between spin-up and spin-down peaks was found to be within the values given below.

The analysis reveals a *negative* magnetic exchange splitting, with the IPE feature due to the image resonance in

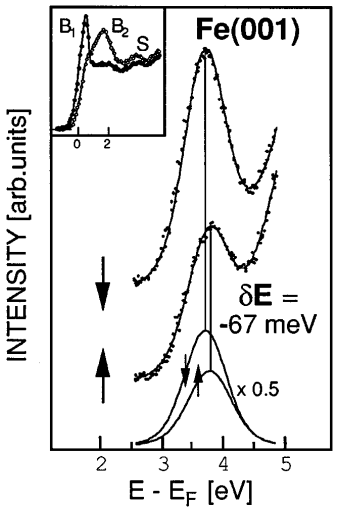

FIG. 1. Measured spin resolved IPE data (dots) at normal incidence of the image potential induced state in Fe(001): majority ↑ and minority ↓. The spectra are offset for the sake of clarity. The broadened Lorentzians best fitting the data (see text) and the resulting fitting curve are also shown. The inset displays IPE data in a wider energy range above E_F.

the minority-spin channel lying lower in energy than in the majority-spin channel, as well as different intensities in the two spin channels. The splitting is determined as -67 ± 17 meV. Apart from the anomalous sign, the magnitude is comparable to splittings observed for image states at the surfaces of other ferromagnets [13 ± 13 meV for Ni(001) [12], 18 ± 3 meV for Ni(111) [13], and 57 ± 5 meV for Fe(110) [15], all at $\bar{\Gamma}$, and 125 ± 24 and 96 ± 30 meV at $\bar{Y}$ for Co($10\bar{1}0$) [14]]. However, it is not possible to immediately conclude that the Fe(001) image resonance actually has a negative exchange splitting. This is because the IPE signal is not strictly a direct measure of the electron states at the surface but is generated over an ill-defined depth at the surface, depends upon the availability of (high energy) initial states, and also depends upon the coupling to the photon field. These matrix element effects can influence the IPE spectra and have been studied in detail by Schaich [26] using model one-dimensional calculations of IPE. He has shown that whereas the energies of features in IPE spectra coincide with the positions of true surface states, shifts of several tenths of an eV are possible in the case of resonance states. If matrix element effects in the case of Fe(001) were to cause different shifts in the two spin channels, this itself might explain the unusual spin splitting.

We have therefore sought to confirm the experimental observation by studying the Fe(001) image resonances theoretically, using multiple-scattering calculations of both the surface electronic structure and of the IPE spectra. For the former we use the layer KKR method [27], which enables us to study a semi-infinite substrate. This is vital in the present context in order to correctly describe the continuum of bulk states at the surface, to which the image states couple. We characterize the image-derived surface electronic structure by evaluating the spin resolved local density of states (LDOS, the number of states per unit energy at a given energy) integrated through a near-surface region [25] which extends 10 a.u. into vacuum from the jellium edge (half an interlayer spacing beyond the outermost atomic layer). This is the same volume that previous studies of image states and resonances [16,25] have focused on.

For the IPE calculations we have used Pendry's one-step theory [28], a quantitative single-particle theory which treats IPE as the time-reversed photoemission (PE) process. Within geometrical and phase-space factors the differential IPE yield is proportional to $\Im\langle\psi|\Delta G^+\Delta^\dagger|\psi\rangle$, where $\langle\mathbf{r}|\psi\rangle$ is the wave function of the emitted photoelectron and $\langle\mathbf{r}|G^+|\mathbf{r}'\rangle$ the propagator of the low-energy hole state in the corresponding PE event. Both are sensitive to the surface barrier potential but G^+ especially, giving rise to the image-derived structure in the IPE spectra. Δ is the photon field operator, for which we ignore poorly known dielectric effects and assume a uniform field.

The IPE calculations [29] evaluate ψ and G^+ using the same scattering methods that are used in the electronic structure calculations. By using the same crystal and

vacuum barrier potentials for both sets of calculations it is possible to make a direct comparison of image-derived features, and therefore we are able to quantify matrix-element effects. We use an atomic sphere representation of the crystal potential [27], taken from self-consistent layer KKR calculations for the Fe(001) surface [30] in which the potential within the three topmost atomic layers was determined self-consistently (we actually find a bulk-terminated Fe substrate gives comparable results). For the vacuum barrier we have considered various saturated image potential profiles [7], differing in how the long-range image tail is modified upon approaching the crystal. As noted by Smith [7] in regard to the binding energies of image states, we find the various parametrizations give rise to similar results, although for differing positions of the image plane. Applying our scheme to the Fe(110) surface we obtain a splitting of the (true) image state of 55 meV ignoring the barrier polarization, compared with 63 meV previously reported using a more sophisticated approach [16]. Calculations using perturbation theory indicate that polarization of the barrier, whose omission increases the splitting at Fe(110) by 8 meV [16], has a negligible effect on the Fe(001) image resonance.

In Figs. 2 and 3 we show the results of our IPE and electronic structure calculations for Fe(001). Figure 2 shows the spin resolved normal incidence IPE spectra calculated for final-state energies in the vicinity of the vacuum level and a photon energy of $h\nu = 9.6$ eV. We find oscillatory features in both spin channels which can be attributed to the image potential, as they are absent in IPE spectra calculated using short-ranged barrier potentials. The structure between -0.25 eV and the vacuum level is rather sensitive to the final state lifetime, which in the calculations is simply modeled through a constant optical potential. By reducing the value of this potential and so increasing the lifetime it is possible to resolve more peaks in the spectra, which form a Rydberg-like series converging on the vacuum level. However, we find the major peak near -0.5 eV changes little with variations in the optical potential. This feature corresponds to the $n = 1$ image resonance, which lies closest to the crystal surface where the IPE signal is generated and consequently gives rise to the strongest signal. It also has the greatest overlap with the continuum of crystal states, and it is this coupling which dominates the width of the peak.

The most notable feature in the calculated IPE spectra is the spin splitting which is -45 ± 5 meV for the $n = 1$ derived peak, lying higher in the majority spin channel than the minority spin. This is in good agreement with the experimental measurement. The peaks at -0.2 eV corresponding to the $n = 2$ image state also exhibit a negative spin splitting, but considerably smaller as the $n = 2$ wave function is located significantly further away from the surface and the coupling to the polarized crystal is much weaker. For true image states the splitting obeys a $1/n^3$ scaling [16].

The influence of matrix elements is assessed by comparison with the corresponding LDOS shown in Fig. 3. The LDOS shows a series of image resonances converging on the vacuum level. There is a noticeable difference in the position of the lowest lying peak relative to the corresponding feature in the IPE spectra, which lie about 0.1 eV higher. An upward shift was reported by Schaich in his model calculations [26]. However, the spin polarization of the image resonances remains negative, indicating the shift is comparable for both spin channels. The splitting is -30 meV for the $n = 1$ resonance, confirming the unusual negative exchange splitting for the Fe(001) image resonance seen in the IPE spectra and indicating matrix elements are acting to enhance the splitting. It is interesting to note that the calculated IPE spectra exhibit a greater intensity in the minority-spin channel (integrated intensity of the minority peak 30% greater than majority) as seen in the experiment (40% greater), whereas the LDOS shows only a minor difference. This is another matrix element

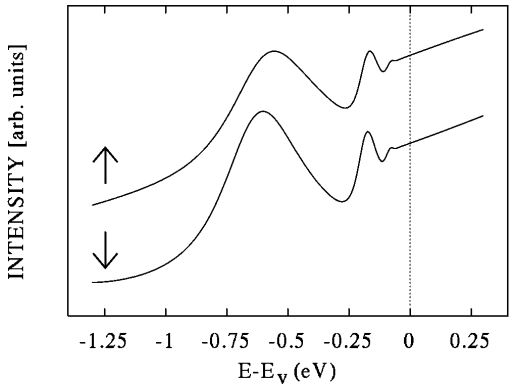

FIG. 2. Calculated spin resolved IPE spectra from Fe(001), for normal incidence majority ↑ and minority ↓ electrons and photon energy $h\nu = 9.6$ eV. E_v is the vacuum level ($E_F + 4.5$ eV).

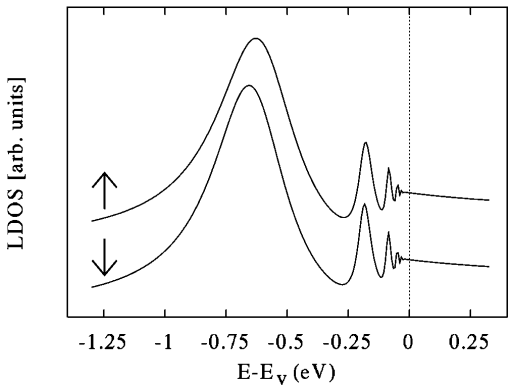

FIG. 3. Calculated spin resolved LDOS from Fe(001), integrated through the near-surface volume described in the text. The calculation includes a small imaginary component in the energy of 0.005 eV which Lorentzian broadens the structure, most noticeably preventing resolution of the infinite Rydberg series of levels approaching the vacuum level E_v. The two curves (majority ↑ and minority ↓) have been offset for clarity—they actually coincide at positive energies.

effect, due to interference with contributions from bulk states, which we reproduced despite our simplistic treatment of the photon field.

The spin splitting of image states results from the interaction with the ferromagnetic substrate. For true image states lying in a substrate band gap the phase-shift model with the two-band approximation relates the splitting to that of the band edges [10], but quantitatively underestimates the Fe(110) splitting by a factor of 2 [10,16]. This indicates the importance of higher Fourier components of the potential, necessary for describing the *d* bands which are fundamental to the magnetism. Outside the band gap the phase-shift model may still be applied if complex phase shifts [31] are used, but even using realistic values for the crystal reflectivity taken directly from the layer KKR calculations we find it incapable of producing a negative spin splitting. The essential missing ingredient is diffraction into other beams by the periodic surface, included in the layer KKR calculations but ignored in the one-dimensional phase-shift model. Again, higher Fourier components of the potential are seen to be vital for a quantitative description of spin-polarized image states.

In conclusion, we have measured the spin splitting of the image resonance at Fe(001) surface with inverse photoemission and find an unexpected negative exchange splitting, with the minority-spin states at lower energy than the majority. Theoretical analysis indicates this arises from two superimposing effects: the local density of states at the surface indicates a true reverse polarization, and this is then enhanced by matrix element effects in the inverse photoemission measurements. Since all other states of the Fe substrate have positive exchange splitting, this observation highlights a complicated relationship between surface and image state magnetism.

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