Ultrafast Optical Spin Injection into Image-Potential States of Cu(001)

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(Received 22 February 2007; published 31 May 2007)

We report the observation of a net spin polarization in the $n = 1$ image-potential state at the Cu(001) surface. The spin polarization is achieved by spin-selective multiphoton excitation of electrons from the spin-orbit split Cu d bands to the image-potential state using circularly polarized ultrafast light pulses. We show that by tuning the exciting photon energy, we can adjust the resonant coupling of the image-potential state to d bands of different double-group symmetry. This allows us to tune the spin polarization injected into the image-potential state.

DOI: 10.1103/PhysRevLett.98.226601 PACS numbers: 72.25.Fe, 73.20.−r, 79.60.−i, 82.50.Pt

Optical manipulation of spins in magnetic [1–3] and nonmagnetic solids [4,5] and their surfaces is of great interest for ultrafast magnetism, spintronics, and quantum information processing. The observation that magnetization dynamics can be traced to single-electron spin-flip processes [6] underscores the importance of addressing elementary spin scattering processes to understand macroscopic phenomena like laser-induced demagnetization [7]. To this end, spin and time-resolved multiphoton photoemission [1,6,8,9] provides one of the most specific and sensitive probes of electron-spin phenomena on the femtosecond time scale.

The strong coupling of spins in ferromagnetic materials, however, can make the measurement and analysis of the spin dynamics of excited electrons intrinsically difficult. Spin dynamics can in fact occur through a superposition of both magnetism-induced as well as magnetism-independent processes, whose separate contributions are sometimes difficult to address selectively. In this respect, the investigation of spin dynamics by nonlinear photoemission would surely benefit from the availability of a source of spin-polarized excited electrons at nonmagnetic surfaces. Spin-dependent transport and scattering at interfaces, relevant to the operation of spintronic devices, could also be studied in more detail.

It is well known that photoexcited spin-polarized electrons can be produced at unpolarized targets, provided that the incident light has circular polarization. Spin-orbit coupling (SOC) in combination with optical selection rules provides the mechanism by which electrons can be spin-selectively excited. This forms the basis of various effects related to optical spin orientation [10,11]. For one-photon photoemission from metals, it has been demonstrated that significant spin-orbit coupling leads to strong spin-polarization effects of the photoelectrons even in a relatively low-Z material like copper [12]. The extension of the optical spin orientation effect to multiphoton transitions in solids would allow one to transiently spin polarize excited intermediate states below the photoemission threshold which in principle cannot be sensed by one-photon photoemission. Such a multiphoton excitation scheme can then be directly exploited to study spin-dependent scattering of excited electrons in solids.

In this Letter, we report the observation of large (40%) spin polarization of the $n = 1$ image-potential (IP) state on the Cu(001) surface by means of spin-resolved multiphoton photoemission. The spin polarization is achieved by resonantly coupling the spin-orbit split Cu d bands with the IP state via a multiphoton transition excited by circularly polarized light. We observe that both the sign and the magnitude of the IP-state spin polarization can be selected by balancing the resonant coupling to different spin-orbit split d bands. Our observation provides the basis for the coherent manipulation and probing of the spin dynamics of excited electrons at nonmagnetic surfaces.

The photoemission experiments were carried out in an ultrahigh vacuum system (pressure $<5 \times 10^{-11}$ mbar). The ultrashort excitation pulses were provided by the frequency-doubled output of a self-built Ti:sapphire oscillator. The pulse central energy could be continuously varied in the range of $h\nu = 3.00$–3.14 eV by tuning the phase-matching angle of the frequency-doubling 80 μm-thick β-BaB$_2$O$_4$ (BBO) crystal. At the energy of $h\nu = 3.07$ eV, the pulse length at the surface was ≤ 20 fs, and the pulse energy $\sim$1 nJ. Right- and left-circular (RCP, LCP) and linear polarization were set by a combination of achromatic $\lambda/4$ and $\lambda/2$ wave plates. The laser beam was focused to a spot of ≈ 40 μm in diameter on the surface. The angle between the incident beam and the axis of the analyzer was fixed at 42° (Fig. 1). A clean and ordered Cu(001) surface was prepared by standard sputtering and annealing procedures. The optical plane was aligned parallel to the [100] direction. All the experiments were carried out at 300 K.

The electrons photoemitted along the surface normal were analyzed by a cylindrical sector analyzer (set to

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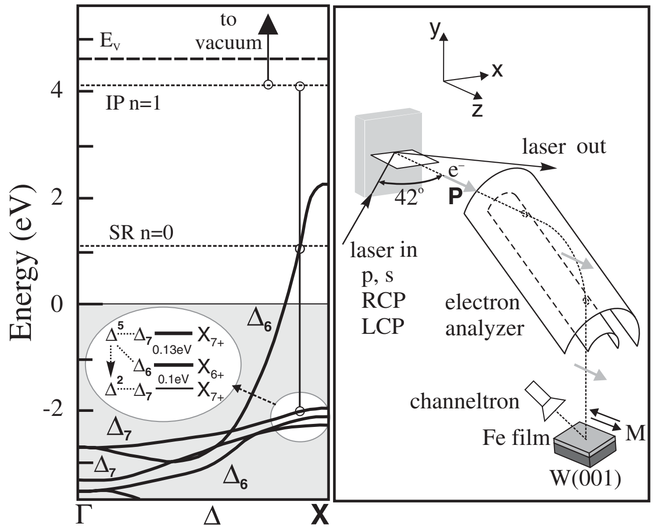

FIG. 1. Left: Relativistic band structure of Cu(001) along the Δ line (after Ref. [15]). The energy position of the $n = 0$ SR and $n = 1$ IP state at $\bar{\Gamma}$ is shown. Vertical lines represent photo-induced electronic transitions at typical energies employed in our experiment. The open circles at line termini represent the spectral width of the excitation pulses. The inset shows a magnified view of the spin-orbit split d-band region near the X point. Right: Experimental setup in the normal-emission geometry.

150 meV energy resolution) coupled with a newly developed spin detector, based on very low energy electron scattering on a magnetized ultrathin Fe/W(001) film [13,14] (Fig. 1). The spin detector included facilities for W(001) crystal flashing, Fe film growth, magnetization reversal of the Fe film, additionally allowing a non-spin-resolved mode. The detector Sherman function was $S = (0.23 \pm 0.02)$, with excellent long-term stability as characterized by constant reference measurements over typically two weeks without repreparation of the Fe film.

The basic principle underlying the multiphoton optical orientation process for the Cu(001) IP state is shown in Fig. 1. There we show the calculated relativistic band structure of Cu(001) along the Δ line (after Ref. [15]), pertinent to the normal-emission geometry, along with the $\bar{\Gamma}$ energy positions of the $n = 0$ surface resonance (SR) and the $n = 1$ IP state [16]. One-photon transitions at energies representative of the ones employed in our experiment are depicted as the vertical lines. The spatial single-group and the double-group symmetry character of the states involved is denoted by superscripts and subscripts, respectively. It can be clearly seen that the IP state can be populated from initial states located in the d bands in the proximity of the X point by a resonant excitation pathway proceeding via the unoccupied sp band or the $n = 0$ SR [17]. The magnification of the band structure in the region near the X point (inset of Fig. 1) shows that the Δ^5 band is spin-orbit split in two bands with strong Δ^5 spatial symmetry and Δ_7 and Δ_6 double-group symmetry, with reported binding energy differences between 100 meV [12] and 130 meV [18], while a Δ_7 band with strong hybridization of Δ^5 and Δ^2 spatial symmetry is present at about 100 meV larger binding energy.

The relativistic selection rules for normal emission from an fcc(001) surface dictate the final state symmetry to be Δ_6^1. Furthermore, RCP light couples spin-down (spin-up) electrons from a Δ_6^5 (Δ_7^5) symmetry initial state to a Δ_6^1 symmetry final state (and vice versa for LCP excitation) [19]. This provides the basic mechanism by which oppositely spin-polarized photoelectrons are excited selectively from the two spin-orbit split bands of different symmetry to the unoccupied IP state. In our experimental geometry, no asymmetry in photoelectron intensity (dichroism) is expected for excitation with reversed helicity [20], and the spin-polarization vector points in a direction very close to the surface normal [21]. We will henceforth discuss the z component of the spin polarization only.

The experimental observation of spin injection from spin-orbit split d bands into the IP state is demonstrated in Fig. 2. There, in the upper panel, we show two typical spin-up and spin-down photoelectron spectra $I_\uparrow$ and $I_\downarrow$, measured with RCP incident light at $h\nu = 3.02$ eV photon energy (dashed lines and solid lines, respectively). The spin-resolved spectra are calculated from the measured intensity asymmetry under reversal of the magnetization direction of the Fe/W(001) spin detector. The spin polarization along the z direction for RCP (LCP) incident ra-

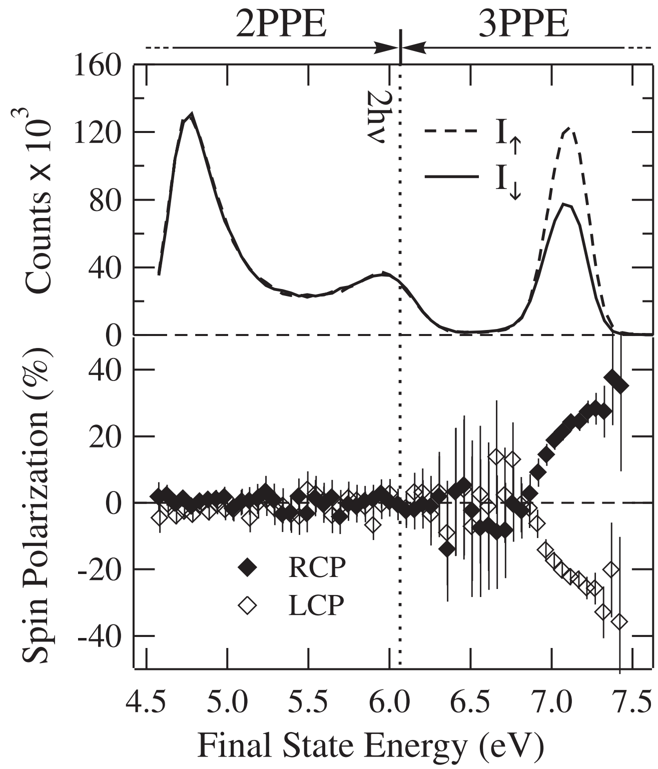

FIG. 2. Top panel: Spin-up (dashed line) and spin-down spectra (solid line) for RCP incident radiation at $h\nu = 3.02$ eV. Bottom panel: Spin polarization for RCP (solid diamonds) and LCP (open diamonds) incident radiation.

diation is reported in the lower panel as solid (open) diamonds. No detectable spin polarization was observed for excitation with p-polarized light (not reported). In the spectra, the two-photon photoemission (2PPE) Fermi edge is clearly observable at $2h\nu = 6.04$ eV, whereas the prominent peak near 7.0 eV corresponds to three-photon photoemission (3PPE) via the IP state [17]. A significant spin polarization of up to 30% appears in the 3PPE region at final state energies roughly between 6.5 and 7.5 eV, including the IP-state photoemission peak. This demonstrates the successful injection of a spin-polarized electron population into the IP state. The observation that the helicity reversal of the exciting light causes a sign change of the spin polarization further confirms that the spin polarization appears due to the multiphoton optical spin orientation effect described above. We also notice that the photoelectrons in the 2PPE part of the measured spectra originate from the sp band just below the Fermi energy. As can be seen from the relativistic band structure, these states are not split by SOC, and accordingly, spin-selective excitation is not observed.

We can strongly influence the multiphoton optical orientation process by changing the excitation photon energy and tuning the two-photon resonance between the d bands and the IP state. In Fig. 3 we show the IP state spectral region of spin-up and spin-down spectra (dashed lines and solid lines, respectively) and corresponding spin polarizations (solid symbols) measured at three different incident photon energies with RCP light. The spectra are plotted normalized to the IP-state intensity, whereas the spin-polarization data are plotted with equal vertical scales. When decreasing the photon energy from $h\nu = 3.14$ eV (top curves) to $h\nu = 3.00$ eV (bottom curves), we observe a systematic change of the IP-state spin polarization, whose value swings from approximately -25% at $h\nu = 3.14$ eV to $+40\%$ at $h\nu = 3.00$ eV, passing through zero at the intermediate energy of $h\nu = 3.07$ eV.

For a better understanding of the strong photon-energy dependence of the IP-state polarization, we summarize in Fig. 4 the results of a larger set of measurements, performed at different photon energies with RCP incident light. Defining the final state energy of the IP-state peak as E_{IP}, the initial state energy E_d of the d band electrons populating the IP state is given by $E_d = E_{\mathrm{IP}} - 3h\nu$. In Fig. 4 we report the photon-energy dependence of E_{IP} (top panel, open circles), E_d (middle panel, open squares), and the corresponding spin polarization at the IP-state peak (bottom panel, solid diamonds). The solid black lines are linear fits to the photon-energy dependence of E_{IP} and E_d. The energies E_{IP} and E_d exhibit a linear dependence on the photon energy, with respective slopes of 1.1 ± 0.1 and

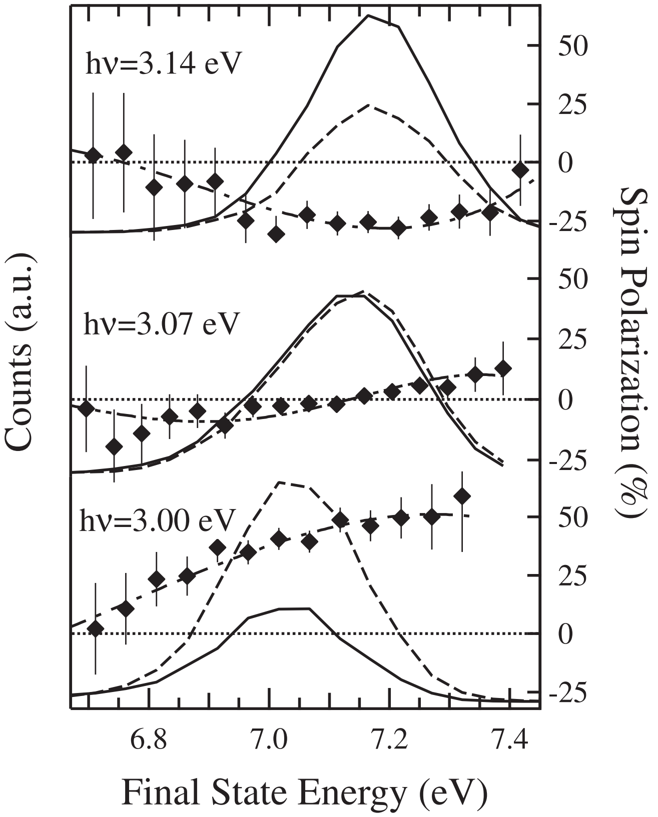

FIG. 3. Spin-up (dashed line) and spin-down (solid line) spectra, respectively, measured with RCP light for three different exciting photon energies (top to bottom: 3.14, 3.07, and 3.00 eV). Symbols: Corresponding spin polarizations obtained from the experimental spectra. Dash-dotted lines are guides to the eye.

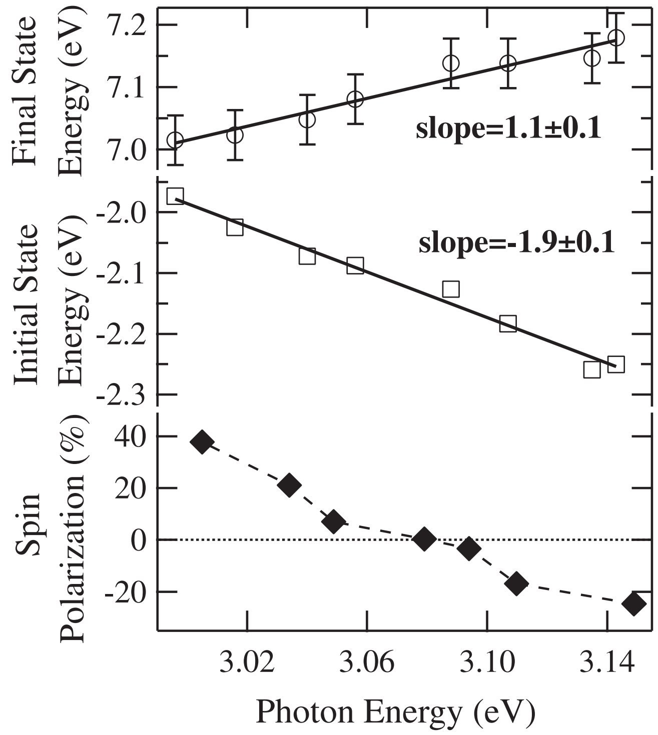

FIG. 4. Photon-energy dependence of the photoemission peak corresponding to IP-state electrons (open circles), of the d-electron initial energy E_d (open squares), and of the IP-state peak spin polarization (RCP excitation, solid diamonds). Solid lines are linear fits to the $h\nu$ dependence of E_{IP} and E_d.

-1.9 ± 0.1. This is expected, since the IP state acts as the penultimate state in a three-photon process (see Fig. 1). The energy of the IP state, which defines the resonance condition for a particular photon energy, is fixed relative to the vacuum level and does not disperse with perpendicular momentum. Therefore, increasing the photon energy by $\Delta h\nu$ near resonance also increases the final state energy E_{IP} by $\Delta h\nu$, whereas the initial state energy E_d has to decrease by $-2\Delta h\nu$. Accordingly, increasing the photon energy from $h\nu \approx 3.00$ eV to $h\nu \approx 3.14$ eV tunes the initial state binding energy from approximately 1.95 to 2.25 eV. This tuning range covers the region of spin-orbit split d bands shown in the inset of Fig. 1.

The evolution of the IP-state peak spin polarization in Fig. 4 from +40% to −25% with increasing photon energy can therefore be ascribed to the tuning of the resonance conditions between each of the individual spin-orbit split d bands and the IP state. At lower photon energies, the Δ_7^5 band lies closer to resonance with the IP state than the Δ_6^5 band, and a positive spin polarization of +40% is accordingly observed. With larger photon energy, the Δ_6^5 band increasingly contributes in the two-photon resonance with an opposite spin polarization. This lowers the net spin polarization at the IP-state peak, which reaches zero for $h\nu \approx 3.07$ eV. Increasing the photon energy further to $h\nu \approx 3.14$ eV, the Δ_6^5 band resonance finally dominates and the sign of the IP-state spin polarization is accordingly reversed. The lower observed value of spin polarization for excitation from the Δ_6^5 band can be ascribed to the contribution arising from the Δ_7 band at higher binding energy, which shows partial Δ^5 character due to hybridization [12].

The values of spin polarization that we observe in our multiphoton experiment are in close agreement with the ones observed in one-photon experiments from Cu(001), where a +45% and −25% spin-polarized signal originating from d bands, respectively, at 1.9 and at 2.3 eV binding energy was measured with $h\nu = 11$ eV photons [12]. Such close agreement suggests that in our experiment the spin polarization is generated within the $\Delta_{6(7)}^5 \rightarrow \Delta_6^1$ one-photon transition that couples the initial spin-orbit split d bands to either the unoccupied sp bands or the $n = 0$ SR, whereas the subsequent transitions, coupling states all of Δ_6^1 symmetry, transfer spin polarization into the image-potential state and, finally, to the photoemitted states. Although very similar spin polarizations are observed in the two experiments, we have to point to characteristic differences. Off-normal light incidence will cause a deterioration of the pure circular polarization inside the metal, and it also will allow unpolarized contributions from Δ_6^1 initial states [21]. The close agreement of our spin-polarization values with respect to Ref. [12] suggests that these influences are effectively small. A quantitative description of the observed spin polarizations requires the calculation of transition matrix elements using realistic wave functions and taking into account the dynamics of the spin-dependent multiphoton photoemission process, which is clearly beyond the scope of this Letter.

In conclusion, our experiment demonstrates the possibility of injecting spin-polarized electrons into excited states at nonmagnetic surfaces, and it proves that the spin polarization can be adjusted by selecting the appropriate excitation energy. With its straightforward application to pump-probe experiments, this multiphoton optical orientation process opens the way to address directly in the time domain the ultrafast spin dynamics and spin transport in the absence of relaxation processes influenced by magnetism. For the specific case of Cu(001), the relatively long coherence time of the $n = 1$ IP state [22] and d-band holes [18] (>30 fs) could even allow a coherent manipulation of electron spins at metal surfaces by suitable ultrashort laser pulses [23]. Finally, the complete generality of the spin-injection principle here reported suggests that the outlined method could be applied to a large variety of materials other than copper, thereby significantly broadening the field of possible investigations and applications.

F. B. acknowledges support from the Max-Planck-Gesellschaft. M. N. thanks MSM No. 0021620834 for partial support. Technical assistance of F. Helbig is gratefully acknowledged.

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[1] O. Andreyev *et al.*, Phys. Rev. B **74**, 195416 (2006).
[2] A. V. Kimel *et al.*, Nature (London) **429**, 850 (2004).
[3] V. V. Pavlov *et al.*, Phys. Rev. Lett. **98**, 047403 (2007).
[4] M. J. Stevens *et al.*, Phys. Rev. Lett. **90**, 136603 (2003).
[5] J. Hübner *et al.*, Phys. Rev. Lett. **90**, 216601 (2003).
[6] M. Cinchetti *et al.*, Phys. Rev. Lett. **97**, 177201 (2006).
[7] E. Beaurepaire *et al.*, Phys. Rev. Lett. **76**, 4250 (1996).
[8] M. Aeschlimann *et al.*, Phys. Rev. Lett. **79**, 5158 (1997).
[9] A. B. Schmidt *et al.*, Phys. Rev. Lett. **95**, 107402 (2005).
[10] *Optical Orientation*, edited by F. Meier and B. P. Zakharchenya (North-Holland, Amsterdam, 1984).
[11] P. Lambropoulos, Phys. Rev. Lett. **30**, 413 (1973).
[12] C. M. Schneider *et al.*, J. Electron Spectrosc. Relat. Phenom. **51**, 263 (1990).
[13] D. Tillmann, R. Thiel, and E. Kisker, Z. Phys. B **77**, 1 (1989).
[14] R. Bertacco and F. Ciccacci, Phys. Rev. B **59**, 4207 (1999).
[15] H. Eckardt, L. Fritsche, and J. Noffke, J. Phys. F **14**, 97 (1984).
[16] S. L. Hulbert *et al.*, Phys. Rev. B **33**, 760 (1986).
[17] F. Bisio *et al.*, Phys. Rev. Lett. **96**, 087601 (2006).
[18] H. Petek, H. Nagano, and S. Ogawa, Phys. Rev. Lett. **83**, 832 (1999).
[19] W. Kuch and C. M. Schneider, Rep. Prog. Phys. **64**, 147 (2001).
[20] J. Henk and B. Johansson, J. Electron Spectrosc. Relat. Phenom. **94**, 259 (1998).
[21] C. M. Schneider *et al.*, Phys. Rev. B **39**, 1031 (1989).
[22] M. Weinelt, J. Phys. Condens. Matter **14**, R1099 (2002).
[23] A. P. Heberle *et al.*, IEEE J. Sel. Top. Quantum Electron. **2**, 769 (1996).