Magnetic Dichroism from Optically Excited Quantum Well States

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(Received 16 March 2009; published 11 August 2009)

We demonstrate magnetic dichroism from optically excited states in two-photon photoemission. Using ultrathin cobalt films grown on Cu(001), we observe unoccupied quantum well states which give rise to a sizable intensity change in photoemission under magnetization reversal. The simultaneous comparison of both circular and linear magnetic dichroism in the same system permits us to check fundamental symmetry requirements and allows us to explicitly elucidate the common origin of both effects. Based on our observations we argue that the observed effect is related to spin-orbit coupling in the intermediate quantum well states.

DOI: 10.1103/PhysRevLett.103.077601 PACS numbers: 79.60.−i, 73.21.Fg, 75.70.Rf

The relativistic coupling between spin and orbital angular momentum of electrons is an essential mechanism in the physics of ultrafast magnetism [1], spintronics, and quantum information processing [2]. Besides its fundamental role in the interplay of spin, electronic and lattice degrees of freedom, a unique capability of spin-orbit coupling is to provide an access to the electron spin via purely optical excitation. In a magnetic system, the optical transition rates can be strongly influenced by spin-orbit interaction, leading to element-specific dichroism in optical absorption [3] and photoemission [4,5]. When combined with ultrashort laser pulses, magnetic dichroism allows us to analyze the dynamics of spin and orbital angular momentum down to the femtosecond time scale [6,7], providing key insights into long-standing issues of nonequilibrium magnetism triggered by the optical excitation [8]. Since excited states play a central role in optically driven processes, it is of great interest to characterize their intrinsic spin-orbit coupling strength, with potential implications for optical control of spin and magnetism on ultrashort time scales.

In order to probe the spin-orbit interaction in excited states, decisive spectroscopic measurements are required, which can be obtained when the excited electronic states act as intermediate levels in a two-photon-photoemission (2PPE) process [9,10]. In combination with magnetic dichroism, 2PPE thus can offer a direct grasp on spin-orbit coupling in the optically excited, initially unoccupied electronic states. Recently, magnetic linear [11] and circular [12] dichroism were indeed observed in 2PPE experiments. Nevertheless, in both cases the dichroic signal could not be correlated to specific excited states: In the first case, Pickel *et al.* [11] observed dichroic signals of up to 20% which were associated with intensively spin-orbit influenced regions in the occupied band structure of cobalt. In the second case, Hild *et al.* [12] carried out nonspectroscopic 2PPE total yield measurements from Heusler alloys, not allowing identification of the intermediate states, and accompanied with a maximum signal of 0.35%.

In this Letter, we demonstrate the effect of magnetic dichroism by specific intermediate optically excited states. Well-characterized unoccupied quantum well states in ultrathin ferromagnetic cobalt films on Cu(001) [13,14] serve as the intermediate levels in a two-photon-photoemission experiment. By control over the incident polarization of

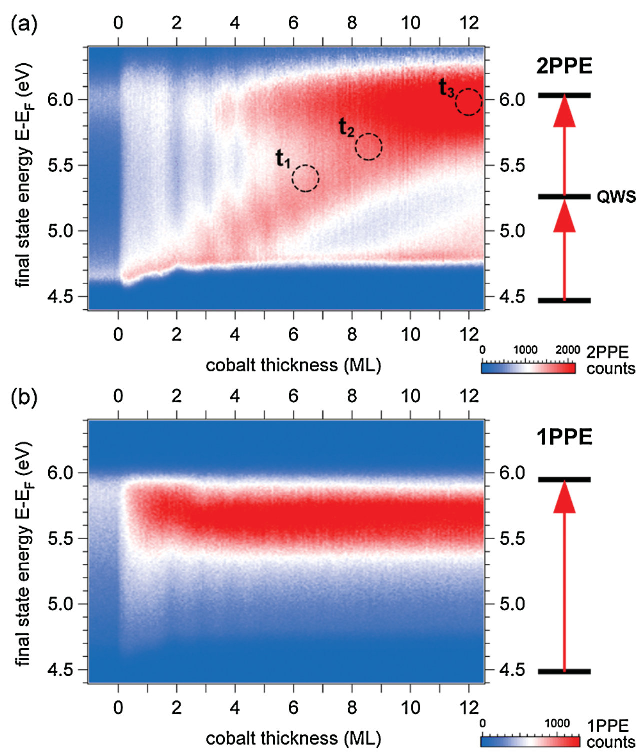

FIG. 1 (color). (a) Thickness dependent 2PPE spectra ($h\nu = 3.1$ eV) measured in normal emission during the deposition of a Co film on Cu(001). Three selected positions of the quantum well state are marked by $t_{1...3}$ (see text). (b) Equivalent experiment as in (a) but with one-photon photoemission (1PPE, $h\nu = 6.0$ eV). The excitation light is p polarized in both cases. General energy level schemes for 2PPE and 1PPE are shown on the side.

light, we experimentally demonstrate the common principle that governs both magnetic circular and linear dichroism: the interference between optical transitions coupled by mutually orthogonal electric field components. Taking into account the available experimental and theoretical data on the initial, intermediate, and final state electronic structure relevant to our system, we attribute the observed dichroism to spin-orbit coupling in the intermediate quantum well states.

The experimental setup has been described before [15]. Deposition and photoemission measurements are performed at 300 K in an ultrahigh vacuum chamber with base pressure lower than 1×10^{-10} mbar. The ultrathin films were grown by electron-beam evaporation from a Co rod. Simultaneously with the Co film growth, we measured thickness dependent normal-emission 2PPE and one-photon photoemission (1PPE) spectra which are shown in Fig. 1. Beginning with initial double layer growth [16], both 2PPE and 1PPE show intensity oscillations with monolayer (ML) periodicity, which we ascribe to additional scattering centers in incomplete layers. Comparison of the 2PPE and 1PPE spectra allows us to immediately identify a contribution from an intermediate state in the 2PPE data, as shown in Fig. 1. The final state energy of this feature disperses characteristically as a function of cobalt thickness and is compatible with unoccupied quantum well (QW) states derived from the sp band of the cobalt film [13,14]. The increased intensity at around 6.0 and 5.8 eV in 2PPE and 1PPE is attributed to the occupied Co d band near the Fermi level.

To examine a possible magnetic dichroism in 2PPE, we employed the experimental geometry shown in Figs. 2(a) and 2(b) for measurements with circularly and linearly polarized light. The sample magnetization M is in the optical plane, with $\pm M$ parallel and antiparallel to the Co [110] magnetic easy-axis. We note that the geometry of Fig. 2(b) is not the standard magnetic linear dichroism setup, where M is usually taken perpendicular to the optical plane [17]. Our setup instead allows us to systematically investigate the effects of light polarization on dichroism with the magnetization in the optical plane. The plane of linear polarization can be continuously rotated by an angle α relative to the optical plane OP [Fig. 2(b), $p: \alpha = 0°$, $s: \alpha = 90°$]. The photoelectrons are detected in normal emission. Photoemission through the quantum well state and from the Fermi level is indicated by $E_{\mathrm{QW}} + h\nu$ and $E_F + 2h\nu$, respectively. The normalized intensity change under magnetization reversal A (dichroic asymmetry) is determined from the magnetization dependent 2PPE intensities $I_{\pm M}$ for circularly (A_{MCD}) and linearly polarized light (A_{MLD}) according to $A_{\mathrm{MCD,MLD}} = (I_{+M} - I_{-M})/(I_{+M} + I_{-M})$.

The 2PPE spectra observed using circularly polarized light are shown in the upper panel of Fig. 2(c), and the derived A_{MCD} curves for right- as well as for left-circularly polarized light (σ^-, σ^+) are shown in the lower panel.

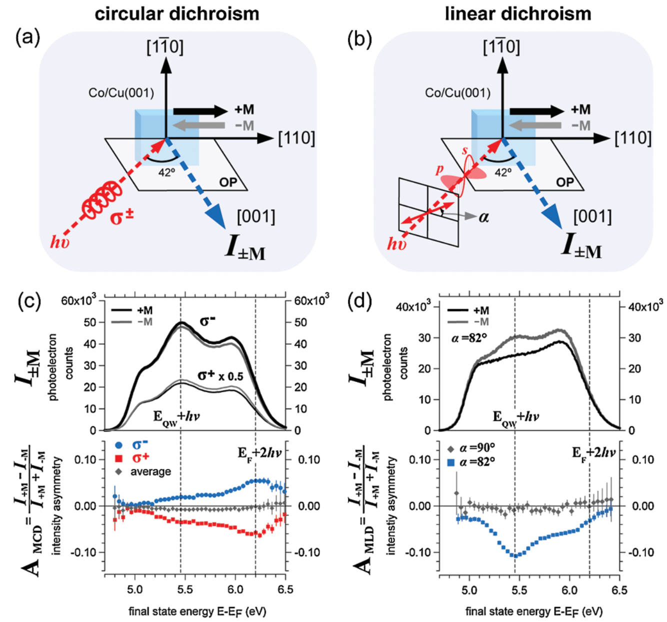

FIG. 2 (color). (a) and (b) Experimental geometry. OP denotes the optical plane, and the angle of the linear polarization plane is α. (c) upper panel: 2PPE spectra measured for opposite sample magnetizations $\pm M$ using right- (σ^-) and left-circularly polarized light (σ^+); lower panel: dichroic asymmetry A_{MCD} for σ^- (blue circles) and σ^+ (red squares), and their average (gray diamonds). (d) upper panel: 2PPE spectra measured for $\pm M$ using linear polarized light at $\alpha = 82°$; lower panel: dichroic asymmetry A_{MLD} for s-polarized light ($\alpha = 90°$, gray diamonds) and for $\alpha = 82°$ (blue squares). The Co film thickness was 6 ML.

Looking at A_{MCD}, we observe a large dichroism of 5% originating from the occupied states near the Fermi level [11,18]. More importantly, a signal of about 3% is observed at the position $E_{\mathrm{QW}} + h\nu$ of the unoccupied QW state.

While we cannot observe any dichroic asymmetry within our detection limit for nominally p- and s-polarized light, magnetic dichroism appears for a tilted polarization plane ($\alpha \neq 0°$, $\pm 90°$, $180°$), in agreement with symmetry requirements [17]. For $\alpha = 82°$, we observe a very large dichroic signal of 10% at $E_{\mathrm{QW}} + h\nu$, and a small signal of 2% at $E_F + 2h\nu$, as is shown in Fig. 2(d). In order to verify the intrinsic connection of the dichroic feature at $E_{\mathrm{QW}} + h\nu$ to the QW state, we measured the thickness dependence of the dichroism as shown in Fig. 3 for films of 6, 8, and 12 ML thickness. There we see in the lower panel that the maximum dichroic signal in A_{MLD} moves consistently with the dispersion of the QW state feature in the thickness dependent 2PPE spectra shown in Fig. 1(a). The behavior of the circular dichroism A_{MCD} in the upper panel of Fig. 3 is less obvious due to the overlap of the relatively small contribution from the QW state at $E_{\mathrm{QW}} + h\nu$ with a larger signal from $E_F + 2h\nu$, but a consistent shift of the partial contribution from the QW state can still be identified.

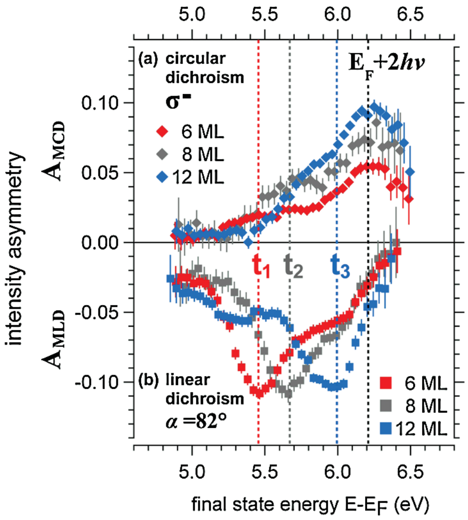

FIG. 3 (color). Thickness dependence of magnetic circular and linear dichroism (MCD and MLD) from Co/Cu(001). MCD obtained with σ^- light and MLD with $\alpha = 82°$ are shown in the upper and lower panel, respectively. The positions of the QW state $E_{QW} + h\nu$ for three different thicknesses are marked by $t_{1\ldots3}$ (see also Fig. 1). 2PPE from near the Fermi level is indicated at $E_F + 2h\nu$.

Using systematic measurements of linear and circular dichroism, we can check general symmetry relations that are expected to hold in the experimental geometry. For circular dichroism, reversal of the light helicity combined with a reversal of the sample magnetization should not change the photoemission intensity in our setup [17,19]. The average of A_{MCD} from σ^- and σ^+ light, shown in Fig. 2(c) (lower panel, gray diamonds), would thus give zero in the ideal case. We ascribe the remaining experimental average of below 1% to the apparatus asymmetry. Furthermore, since the photoemission intensity is a current in the optical plane OP, it must be invariant under the mirror operation (m_{OP}), whereas the magnetization M, the helicity of circularly polarized light σ and the angle α of linearly polarized light are reversed by m_{OP}. This implies the relations [17,19,20]: $I_{\pm M}(\sigma^+) \overset{m_{OP}}{=} I_{\mp M}(\sigma^-)$ and $I_{\pm M}(\alpha) \overset{m_{OP}}{=} I_{\mp M}(-\alpha)$. From these relations we can trace the cause of circular and linear dichroism back to the difference in photoexcitation between the σ^+/σ^- and $+\alpha/-\alpha$ settings, respectively. For both cases, it is the sign of the s-polarized component that is reversed when applying the mirror operation. This can be followed by looking at Fig. 2(b) where we explicitly indicate the p- and s-polarized components of the incident electric field. The difference between circular and linear dichroism is only the switch in phase difference between s and p components, which is $+90°/-90°$ between σ^+ and σ^-, and $0°/180°$ between α and $-\alpha$. We checked these expectations experimentally by measuring the 2PPE intensities I_{+M} and I_{-M} at $E_{QW} + h\nu$ as a function of the polarization plane angle α. In the upper panel of Fig. 4, the experimental data are fitted under the assumption of a constant contribution I_s plus a contribution varying with angle and sign of magnetization as $I_p \cos^2(\alpha \pm \Delta\alpha/2)$. Very good agreement can be reached assuming a constant shift angle $\Delta\alpha = 5°$ (solid lines). In the lower panel, we show the experimental dichroic asymmetry $A_{MLD}(\alpha)$ together with a curve resulting from the fit in the upper panel. As one can clearly see, the predicted symmetry property $A_{MLD}(\alpha) = -A_{MLD}(-\alpha)$ is convincingly fulfilled by the experimental data. The assumptions of the model fit in Fig. 4 are derived from the common interpretation of linear dichroism in terms of interference of photoemission pathways where $\Delta\alpha$ is related to the product of transition matrix elements coupled to the components of the electric field which are perpendicular and parallel to the surface [19,20]. Such interference is provided by states of mixed spatial symmetries in the presence of spin-orbit coupling. The good agreement of the model with the experimental data strongly supports the interference mechanism behind the observed magnetic dichroism.

So far, we have shown that our observations are consistent with general symmetry requirements, independent of the details of the 2PPE process. Now we will discuss where spin-orbit coupling influences 2PPE in our magnetic system, involving initial, intermediate, and final states. In the 2PPE study of Co/Cu(001) by Pickel *et al.* [11], the relativistically calculated band structure of fcc Co shows several spin-orbit hybridization points, one of them located at about 1.3 eV above the Fermi level along the Δ direction, hybridizing unoccupied Co d-band states with the sp band from which the quantum well states are derived. This specific hybridization point is lower in energy than the intermediate quantum well state we measured in Fig. 3 at 2.4 to 2.9 eV above E_F. In this case, the phase difference between spin-orbit coupled bands of different spatial symmetry does not have a sign change in the energy range observed by us. This gives rise to a single-signed magnetic dichroism in both A_{MCD} and A_{MLD} [21]. These qualitative considerations are corroborated by theoretical calculations of photoemission from quantum well states in tetragonally distorted Co films, which indeed show spin-orbit hybridization and corresponding dichroic effects that are consistent with our experimental observations [22]. The Co initial states which are relevant for excitation of the QW state in Fig. 3 show a spin-orbit hybridization point of Δ_5 and Δ_1 majority bands near $E_F - 0.6$ eV [23] and a minority Δ_1 surface resonance is present at $E_F - 0.4$ eV [23]. A significant influence of these initial states on the observed dichroism does not seem compatible with the fact that the dichroic signal of the dispersing QW state feature for linearly polarized light shows almost no variation in Fig. 3 while the relevant initial states move through the strongly variable region of the band structure between $E_F - 0.7$ eV and $E_F - 0.2$ eV. Concerning the final states, which are required to have Δ_1 symmetry for normal emission, we can exclude final state diffraction [24,25] and surface transmission [21,26] effects because they are for-

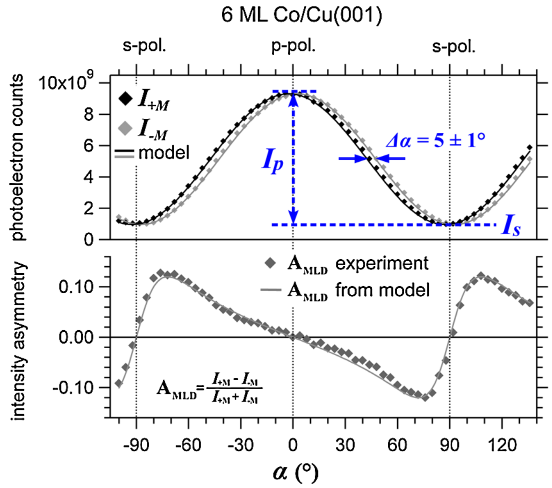

FIG. 4 (color online). Upper panel: Intensity $I_{\pm M}(\alpha)$ as a function of the polarization plane angle, measured at the quantum well state feature on a 6 ML cobalt film ($E_{QW} + h\nu = 5.45 \pm 0.05$ eV). A shift angle $\Delta\alpha = 5 \pm 1°$ is measured. Lower panel: The MLD asymmetry $A_{MLD}(\alpha)$ derived from the experimental data (gray diamonds). Solid curves in both panels are based on the model: $I_{\pm M}(\alpha) = I_s + I_p \cos^2(\alpha \pm \Delta\alpha/2)$ with $\Delta\alpha = 5°$.

bidden in our normal-emission geometry with magnetization and optical plane along a high symmetry crystal direction [25,26]. Additionally, a possible contribution of magneto-optical effects on photoemission [27] is contradicted by the α-independent shift angle $\Delta\alpha$ in A_{MLD} (Fig. 4), which is also much too large for a linear magneto-optical rotation as estimated from known magneto-optical constants ($\theta_{Kerr} \leq 0.5°$ at $h\nu = 3$ eV [28]).

To summarize, we demonstrated both circular and linear magnetic dichroism in two-photon photoemission via optically excited states. Our observations are well explained by the interference between spin-orbit influenced photoemission pathways and indicate the presence of spin-orbit interaction in the unoccupied quantum well states. Our experiments provide a starting point for future pump-probe dichroic studies on femtosecond dynamics of optically excited magnetic systems, allowing extended insights into the relativistic unoccupied band structure at surfaces [17] and spatial imaging of magnetization and spin dynamics [29]. The identification of spin-orbit coupling in intermediate states in a 2PPE process would also be a first step towards the analysis and control of quantum interference effects [30] via multiple spin-dependent excitation pathways at surfaces, enabling for instance the steering of spin-polarized surface currents [31,32] by optical pulses.

We gratefully acknowledge discussions with J. Henk as well as technical assistance by F. Helbig.

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