

Magnetization-induced symmetry breaking at the surface of ferromagnetic Ni(111)

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Abstract – The exchange-split *sp* states of Ni(111) are investigated for different magnetization conditions by means of angle-resolved photoelectron spectroscopy with polarized synchrotron radiation. Significant shifts of intensity maxima in both energy and wave vector are found upon reversal of the magnetization. The shifts, not present in demagnetized samples, are unequivocally related to the direction of the magnetization vector and, hence, attributed to the spin-orbit interaction. Symmetry considerations corroborate that the experimental findings are related to magnetization-induced explicit symmetry breaking at fcc(111) surfaces.

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Introduction. – Symmetry is a fundamental concept and powerful tool in physics, commonly meaning invariance with respect to specific operations. For ferromagnetic materials these operations are spatial rotations, and the associated order parameter is the magnetization vector. Above the Curie temperature, the order parameter is zero and there is no symmetry breaking. Below the Curie temperature, however, the magnetization vector acquires a nonzero magnitude and a specific direction. The residual rotational symmetries that leave the orientation of this vector invariant remain unbroken but the other rotations become spontaneously broken. In this letter, we report on the experimental evidence of a magnetization-induced symmetry breaking at the (111) surface of ferromagnetic Ni, as obtained by high-resolution angle-resolved photoelectron spectroscopy (ARPES). This experimental technique probes the orbital degrees of freedom of the electronic states of a sample, which is obvious from the fact that the transition matrix elements include only the spatial parts of the wavefunctions (note that spin is conserved in the transition). Since a change of the photoemission intensity is observed upon magnetization reversal, the orbital degrees of freedom have to be coupled to the magnetization direction, *i.e.* to the spin degrees

of freedom of the electronic states. Therefore, the effect reported here has to rely on the spin-orbit interaction. As will be shown, it is neither a (conventional) magnetic dichroism nor a Rashba effect at a magnetic surface.

In a ferromagnetic solid, the local magnetic moments attached to each lattice site typically lower the symmetry (with respect to the nonmagnetic lattice), depending on their direction \mathbf{M} . Hence, observables can depend on the orientation of the magnetization ($\pm\mathbf{M}$). Magnetic dichroism in photoelectron spectroscopy [1,2], in which the photocurrent I changes upon reversal of \mathbf{M} , *i.e.* $I(+\mathbf{M}) \neq I(-\mathbf{M})$, is an example. Besides core level photoemission, it was also found in valence band photoemission [3–5], allowing to map intensity maxima to the electronic structure resolved with respect to the point-group representations [6,7]. Evidently, the orbital degrees of freedom of the electrons have to be coupled to the spin degree of freedom which is mediated by the spin-orbit interaction [8]. *Nota bene*, investigations performed so far addressed mainly the dependence of the photocurrent I on the magnetization orientation [5,9].

The presence of a surface breaks the three-dimensional translational invariance of the bulk crystal, leading to a further reduction of the symmetry. In this letter we report experimental evidence that at surfaces of magnetic solids also the band structure can depend on the magnetization

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direction, *i.e.* $E(\mathbf{k}_{\parallel}, +\mathbf{M}) \neq E(\mathbf{k}_{\parallel}, -\mathbf{M})$, whereas the bulk electronic structure is not affected. Here, \mathbf{k}_{\parallel} is the in-plane wave vector that characterizes the electronic states. As system we choose Ni(111) and focus in particular on the dispersion of the sp states (photoemission intensities were already studied in detail in ref. [10]). The effect shows up as shifts of intensity maxima in both energy and wave vector upon reversal of \mathbf{M} , thereby indicating band structure changes, and is accompanied by changes of the photocurrent, as expected for magnetic dichroism. It is phenomenologically understood by symmetry considerations involving the point group of the fcc(111) surface. The reported effect is ‘more than’ magnetic dichroism (which is mainly related to hybridization regions in the band structure, *i.e.* band gaps induced by spin-orbit coupling [11,12] and leads to intensity variations). Hence, it is observed also in sp states which are considerably less influenced by spin-orbit coupling than d states. It is further not attributed to Rashba-Bychkov spin-orbit coupling because the observed shifts of the photoemission maxima are not compatible with those expected for surface states with Rashba-Bychkov splitting. The latter was investigated in detail for the majority surface state on Gd(0001) [13]. In contrast to ref. [13], this letter does not deal with surface states but with the electronic structure of magnetic surfaces in general.

Experimental. – ARPES data were collected at the APE-LE beamline of INFM at Elettra, delivering photons of tunable energy (from 8 eV to 150 eV) and selectable polarisation (linear s and p as well as circular left- and right-handed). By using a SES-2002 electron spectrometer featuring 6 meV and 0.2° energy and angular resolution, a 14° degrees angular range was detected simultaneously. The data were acquired at room temperature on atomically clean Ni(111) surfaces of a picture-frame single crystal, as described thoroughly in ref. [10]. The magnetization was applied by injecting the discharge current of a 940 mF capacitor in a filament wound around the back face of the picture-frame crystal (pulse of $I \approx 100\text{A}$, duration $50 \mu\text{s}$). Ni $L_{2,3}$ X-ray magnetic circular dichroism (XMCD) was measured on the APE-HE beamline to determine the remanent magnetization. The latter was about 40% of the saturation magnetization and directed in-plane at 23° off the $[\bar{1}10]$ axis, that is close to a projection onto equivalent $[111]$ axes. The XMCD data reflect mainly the bulk magnetization: its slight misalignment with respect to the exact projection of the bulk easy magnetization direction can be attributed to the shape anisotropy of the disk-shaped sample. The actual magnetization direction at the surface might also deviate slightly from that in the bulk¹.

Results. – The symmetry of a ferromagnetic crystal above and below the Curie temperature was investigated

¹From spin-resolved measurements [14,15] on the same crystal, with higher surface sensitivity than XMCD, it was concluded that the remanent magnetization was about 15% of the saturation value.

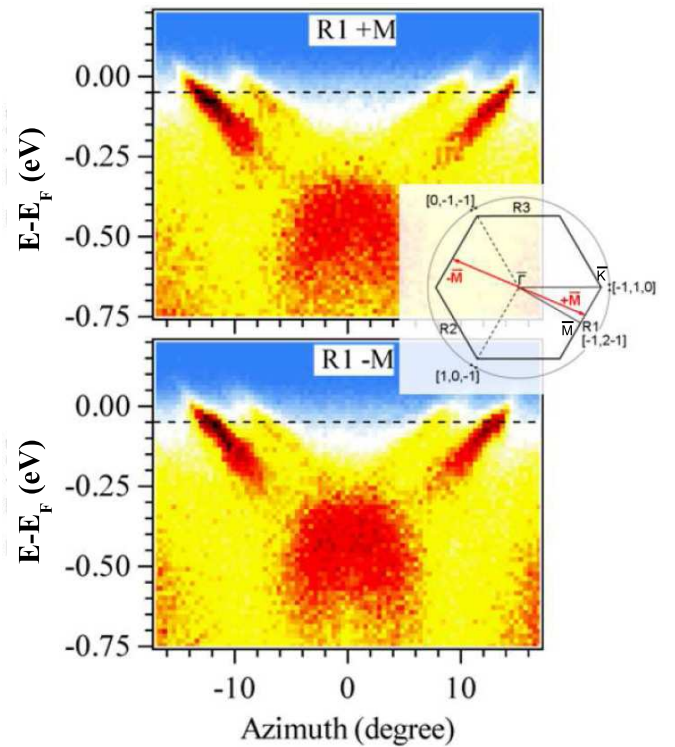


Fig. 1: (Color online) Maps of the photoemission intensity of the sp -states at 30 eV photon energy, p -polarised light, and 56° polar angle (*i.e.* $|\mathbf{k}_{\parallel}| = 1.14a_0^{-1}$) calculated for a kinetic energy of 25.6 eV for region R1 with (a) “positive” ($+\mathbf{M}$) and (b) “negative” ($-\mathbf{M}$) magnetization orientation. The zero of the azimuthal angle coincides with the $[2\bar{1}\bar{1}]$ axis. The dashed lines indicate binding energy and azimuthal angle at which the MDCs of fig. 2 are extracted. Regions, crystal axes and magnetization orientations are drawn in the inset. Red arrows indicate the ($+\mathbf{M}$) and ($-\mathbf{M}$) orientations of the magnetization which is tilted by 7° off the $[\bar{1}2, \bar{1}]$ axis.

by Tinkham using group theory [16]. The electronic structure of a ferromagnetic solid above the Curie temperature is identical in all irreducible parts of the two-dimensional Brillouin zone (2BZ) and, therefore, measuring in one of them is sufficient. The irreducible parts of the 2BZ of a fcc(111) surface are triangles delimited by lines connecting the Γ , \bar{K} and \bar{M} points. Their sizes are $1/12$ of that of the entire 2BZ because of the three mirror planes. Hence, for demagnetized Ni(111), the regions R1, R2 and R3 defined in the inset of fig. 1 are equivalent. This is, however, not the case for an in-plane magnetized sample.

In the present photoemission experiment, light incidence direction ω , surface normal, and electron detection direction \mathbf{k} are coplanar and span the scattering plane. Thus, the in-plane magnetization \mathbf{M} results in a chiral set-up, its degree being defined as $\mathbf{M} \cdot (\omega \times \mathbf{k})$. Therefore, R1, R2, and R3 differ in their degree of chirality. Note further that the angle between the scattering plane and the magnetization direction changes with the detection azimuth ϕ . The crystal axes and the definition of three regions in reciprocal space are comprised in fig. 1.

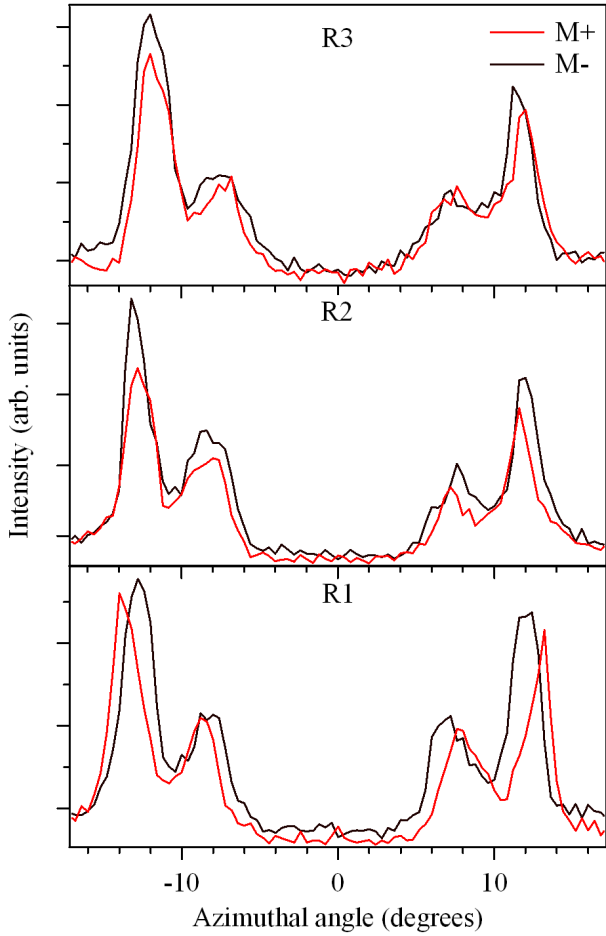


Fig. 2: (Color online) Momentum distribution curves extracted from fig. 1 at 50 meV binding energy and integrated over a 15 meV range measured in regions R1–R3 (as indicated). Black (red) spectra are for $+M$ ($-M$) orientation of the magnetization (inset in fig. 1). The azimuth is relative to the crystallographic axis associated with each region (cf. the inset in fig. 1).

The latter refer to azimuthal angles around the $[\bar{1}2\bar{1}]$ (R1), the $[2\bar{1}\bar{1}]$ (R2), and the $[\bar{1}\bar{1}2]$ (R3) directions. We stress that photoemission intensities from magnetic samples depend on the chirality, even for core levels [17–21]. In particular for Ni(111), the intensities depend strongly on the light polarization due to matrix element effects, as is discussed in refs. [10] and [22]. In order to detect unequivocally the new electronic-structure effect, it is important to disentangle it from all other possible experimental artifacts.

In the following we consider in particular the sp states at energies close to the Fermi level. Exchange split by about 200 meV, they show up clearly in regions R1, R2, and R3 (as seen in fig. 1). Their dispersion was determined by ARPES with 30 eV photon energy and various light polarizations². Azimuthal scans of the photoemission

²The details of the data acquisition can be found in refs. [14] and [15]. The difference with to those works is in the detector angular resolution, 0.2° in our case.

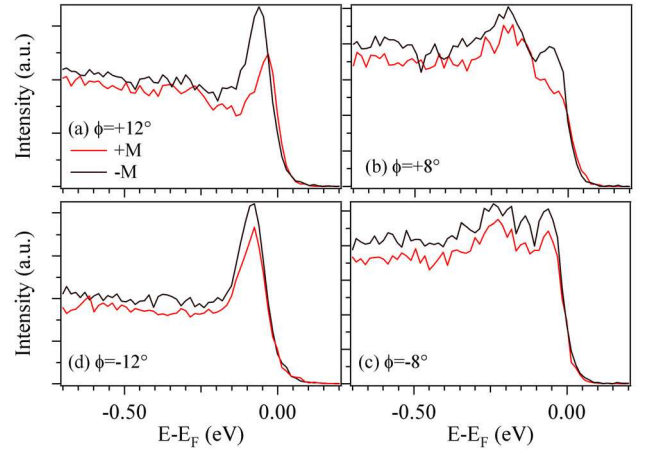


Fig. 3: (Color online) EDCs extracted from the ARPES maps of fig. 1 at the angles (a) $\phi = +12^\circ$, (b) $\phi = +8^\circ$, (c) $\phi = -8^\circ$, (d) $\phi = -12^\circ$, as indicated in the labels of each panel for the “positive” (red) and “negative” (black) magnetization directions. The difference in the binding energies in the four images is another way of representing the azimuthal shifts reported in fig. 2. The order of the images is such to show the effect of the magnetization reversal on the position of equivalent peaks (in the non-magnetic case) lying on opposite sides of the mirror plane.

intensity in R1 show that the four exchange-split sp states disperse towards the Fermi level with increasing ϕ (in absolute value; fig. 1). The maps for $+M$ (top) and $-M$ (bottom) show that the band dispersion depends indeed slightly on the magnetization orientation, as it is better seen by extracting momentum distribution curves (MDCs, fig. 2) and energy distribution curves (EDCs, fig. 3).

The momentum distributions show the azimuthal variation of the intensities of the spin-split sp band at 50 meV binding energy (fig. 1). The “inner” peaks are attributed to the spin-down, the “outer” peaks to the spin-up sp band. The four peaks in each region appear shifted in azimuth between -1.2° and $+1.6^\circ$ upon reversal of M . These azimuthal shifts of the intensity maxima, $I(\phi, +M) \neq I(\phi, -M)$, are a clear indication of the electronic-structure effect, $E(\mathbf{k}_\parallel, +M) \neq E(\mathbf{k}_\parallel, -M)$. The angular shifts are one way to visualize the electronic structure effect also present in the EDCs, but identified in binding energy shifts taken at identical azimuthal angles.

For R1, which has the least absolute chirality, all four maxima are shifted closer to the mirror plane ($\phi = 0^\circ$) upon reversing $-M$ (red) into $+M$ (black). For regions R2 and R3, the effect is significantly less. Magnetic linear dichroism with p -polarized or unpolarized light is typically strongest if the magnetization M is perpendicular to the scattering plane (largest absolute chirality) [4,7]. Indeed, the intensity changes upon magnetization reversal are sizable for R2 and R3, *i.e.* considerably larger than for R1. This finding provides further support that the electronic-structure effect is not related to magnetic dichroism, in

particular it is not an artifact of intensity changes upon reversal of \mathbf{M} .

Our findings cannot be explained by the Rashba-Bychkov effect at a magnetic surface. The Rashba splitting results in a displacement of the momentum distributions in direction perpendicular to the magnetization (see fig. 3 in ref. [13]). Hence, one would expect the largest effect in R2 and R3, in contrast to our findings (largest effect in R1). Further, the Rashba-Bychkov effect shifts electronic states of the same spin in identical directions, say spin-up to the left and spin-down to the right (see fig. 3f in ref. [13]). However, fig. 2 clearly shows that all maxima shift closer to \mathbf{M} (*i.e.* towards $\phi = 0^\circ$).

It is evident that these findings, especially for R1, are changes of peak positions in MDCs by a few degree in azimuthal scans (fig. 1). The effect shows also up in EDCs as shifts in binding energy and does not depend on the light polarization [22].

Before propagating a new effect possible sources of error have to be discussed and ruled out. i) An imperfect reversal of the magnetization ($\mathbf{M} \not\rightarrow -\mathbf{M}$) is ruled out by the complete XMCD azimuthal dependence. ii) A magnetic stray field, expected to lie in the plane spanned by the surface normal and the in-plane magnetization, would bend the photoelectron trajectories “upwards” or “downwards”, depending on the azimuth (Lorentz force). Hence, the intensity pattern in the MDCs should appear azimuthally rotated and the effect should be very small in R1 (least absolute chirality). Both manifestations of a stray field are not observed in experiment. iii) Misalignment of the surface normal with respect to azimuthal rotation axis is less than 0.5° , as being quantified in before starting the measurements. iv) The stability of both photon beam and detector energy was checked within a 5 meV error, *i.e.* much smaller than the 100 meV total resolution limited by thermal broadening during several days of continuous measurement. v) A temperature drift, giving rise to dispersion and to peak-width changes, is ruled out because the measurements were done at room temperature. vi) Magnetostriction, *i.e.* the difference of the lattice constant of the demagnetized and the magnetized sample, is estimated to be by far too small to be detectable by ARPES.

It is compelling therefore to discuss under what circumstances the electronic structure can be changed by magnetization reversal. Since photoemission in the vacuum-ultraviolet regime is sensitive to the surface electronic structure the effect might be surface specific. The appropriate quantities to consider are thus the spectral densities of the surface, $A_S(E, \mathbf{k}_\parallel; \mathbf{M})$, and of the bulk, $A_B(E, \mathbf{k}_\parallel; \mathbf{M})$.

Symmetry considerations. – It is tempting to explain the experimental changes in band dispersion by the inequivalence of the regions R1–R3 brought about by the magnetization. There are three mirror planes at the fcc(111) surface (point group $3m$ or C_{3v} [23]). If the

Table 1: Effect of point-group operations (left column) of the fcc lattice on the in-plane wave vector $\mathbf{k}_\parallel = (k_x, k_y)$ and the in-plane magnetization $\mathbf{M} = (M_x, M_y)$. 1 is the identity operation whereas m_x and m_z are the reflections at the yz - and the xy -plane, respectively. Note that the fcc(111)-stacking sequence (right column) changes for m_z . At the surface, only the two topmost operations are present.

1	k_x	k_y	M_x	M_y	ABC
m_x	$-k_x$	k_y	M_x	$-M_y$	ABC
m_z	k_x	k_y	$-M_x$	$-M_y$	CBA

magnetization is perpendicular to one of them it lies at $\pm 30^\circ$ with respect to the others. Therefore, a single reflection is maintained (point group m or C_s), while the three-fold rotational symmetry is broken. Consequently, the regions R1–R3 become inequivalent. To support this explanation, the symmetry properties of the spectral densities are discussed in the following.

Consider a fcc(111) surface with the yz -plane being a mirror plane of the lattice (the z -axis is the surface normal). The magnetization is in-plane, $\mathbf{M} = (M_x, M_y)$. At the surface, the operations given in table 1 imply that for $M_x \equiv 0$ (magnetization in the mirror plane) the surface spectral density obeys

$$A_S(E; k_x, k_y; M_x = 0, M_y) = \\ A_S(E; -k_x, k_y; M_x = 0, -M_y).$$

But there is no operation that leaves the wave vector invariant but reverses the magnetization. Consequently,

$$A_S(E; k_x, k_y; M_x = 0, M_y) \neq \\ A_S(E; k_x, k_y; M_x = 0, -M_y).$$

The effect vanishes for $k_x \equiv 0$, that is for maximum absolute chirality.

In the bulk, there are additional operations. Assuming again $M_x \equiv 0$, m_z (reflection at the xy -plane) is of particular interest because this symmetry is directly broken by the surface. It reverses both the magnetization and the stacking sequence along the [111] direction ($\dots ABCABC \dots \rightarrow \dots CBACBA \dots$). Since the spectral density A_B implies an integration over all k_z , the latter can be compensated by replacing k_z by $-k_z$. Thus,

$$A_B(E; k_x, k_y; M_x = 0, M_y) = \\ A_B(E; k_x, k_y; M_x = 0, -M_y),$$

that is, there is no change of the bulk electronic structure upon reversal of \mathbf{M} , as generally expected.

In an azimuthal scan, the above operations impose the symmetry relations $A(E; \phi; \pm \mathbf{M}) = A(E; -\phi; \pm \mathbf{M})$ and $A(E; \pi/2 - \phi; \pm \mathbf{M}) = A(E; \pi/2 + \phi; \mp \mathbf{M})$ for both A_S and A_B , with the azimuth ϕ measured with respect to the x -axis. By analogous considerations for \mathbf{M} perpendicular to a mirror plane, *e.g.*, $\mathbf{M} \parallel \mathbf{x}$, one deduces that

there is also no effect in the bulk, but a surface effect is maintained. Further, $A(E; \phi; \pm \mathbf{M}) = A(E; \pi - \phi; \pm \mathbf{M})$.

The above symmetry considerations explain qualitatively the experimental findings, namely a change of the electronic structure at the (111) surface but not in the bulk. At cubic (001) and (110) surfaces, the two orthogonal mirror planes should suppress the effect.

Conclusions. – Surface-sensitive photoelectron spectroscopy shows the change of the surface electronic structure of ferromagnetic Ni(111) upon reversal of the in-plane magnetization. Its origin is phenomenologically attributed to a symmetry reduction by the presence of both the surface and of the in-plane magnetization. We expect this effect to be ubiquitous at surfaces, the (magnetic) point group of which contains a single mirror plane, *e.g.* fcc(111) and hcp(0001). For (100) and (110) surface, however, it could be restored on vicinal or artificially patterned surfaces and should show up also in glassy magnetic materials. The presented results and symmetry analysis should be kept in mind as a further source of insight retrievable from ARPES on magnetically oriented surfaces.

Since the effect here reported can be explained by spin-orbit coupling and the symmetry of the surface and the bulk of the fcc(111) lattice, it should also be reproduced by first-principles calculations. However, because of the correlated nature of Ni(111) and of the strong matrix-element effects in photoemission a quantitative analysis has not been attempted, though highly desirable.

We propose both experimental and theoretical investigations of the systems Co(0001) and Gd(0001). These are both hexagonal and ferromagnetic, but differ strongly in the atomic mass. Thus, the symmetry breaking should be present in both cases but strongly enhanced in the latter because of the stronger spin-orbit coupling. One might also consider to study *d*- instead of *sp*-states: due to their larger orbital angular momentum ($l = 2$) the spin-orbit coupling is increased and should result in stronger shifts of the initial states.

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