Spin-Polarized Photoelectrons from Nickel Single Crystals

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Photoelectrons emitted from nickel single-crystal surfaces defined by low-energy-electron diffraction and Auger-electron-spectroscopy analysis exhibit negative electron-spin polarization at threshold. The abrupt change from negative to positive polarization occurs at $\hbar\omega \simeq \Phi + 0.05$ eV, where Φ is the work function. This excludes an interpretation based on a simple band theory of magnetism and also explains why the negative electron-spin polarization has not been observed in earlier experiments on polycrystalline films.

Photoemission studies on thin films of Ni revealed neither the temperature-dependent splitting of spin-up and spin-down states postulated by the Stoner-Wohlfarth-Slater (SWS) band theory nor the resulting negative electron-spin polarization (ESP) near threshold.[1,2] In agreement with these photoemission experiments, positive spin polarization, i.e., magnetic moment parallel to the magnetization, has been observed for electrons tunneling from states even within 1 meV of the Fermi energy E_F in thin films of Ni.[3] In field-emission experiments the sign of ESP has been found to depend on the crystal face.[4,5] These results have aroused a widespread interest since a large correction seemed to be necessary either to the theory of band magnetism or to the interpretation of photoemission and tunneling.[6-9]

It is interesting that a negative ESP at E_F is postulated in both a naive band limit *and* the atomic limit, since Ni has a more than half-full $3d$ shell from which the minority spins should be emitted with minimum photon energy $\hbar\omega$. Also the screening of the hole left behind which might be different for up- and down-spin holes as proposed by Doniach[10] cannot account for the observations since these effects are zero for states at E_F.[11]

The difficulty in understanding the positive ESP at threshold has motivated us to perform new experiments on clean single-crystal faces of Ni. We believe that these experiments have resolved the puzzle in that a negative ESP is indeed observed right at threshold, at least for (100) and (111) faces. But the rise from negative to positive ESP is so sharp that it cannot be detected in samples with inhomogeneous work function Φ as in the case of polycrystalline films, and it also indicates clearly that the Stoner splitting observed in photoemission experiments cannot be as large as 0.3 eV. Hence the new results do not contradict the former experiments. The present data might be the basis for a quantitative understanding of $3d$ magnetism (and photoemission).

The measurements were performed on the Ni(100) face and preliminary results have also been obtained from the (111). The surfaces are prepared by repeated sputter cleaning with Ar^+ and annealing to 900°C by electron bombardment following the procedure described by Demuth and Rhodin.[12] The surface was then examined by low-energy-electron diffraction (LEED) for crystal structure and by Auger-electron spectroscopy (AES) for contaminations, with a standard Varian spectrometer. For the (100) face the LEED pattern showed the $p(1\times 1)$ structure. In the Auger spectrum we found some traces of C (< 5% of a monolayer). Since the escape depth of photoelectrons with a kinetic energy less than 6 eV is 5 to 10 Å,[13] which is somewhat larger than the mean free path of the Auger electrons, one can state that AES is a good tool to define a clean surface for photoemission. The cleaned crystal was then transferred *in situ* to the main chamber, where the measurement of photothreshold and ESP was performed at a temperature $T = 273$ K and a pressure of 4×10^{-10} Torr in the chamber. The pressure at the measuring position should be lower since the sample is surrounded by walls cooled to liquid He temperature. In order to remove the Weiss domains a magnetic field of 3.4 kOe was applied perpendicular to the photoemitting surface. On increasing the field, the ESP remained constant indicating that magnetic saturation was reached. The principle of the measurements of spin polarization has been described elsewhere.[11,14]

Figure 1 shows the spectrum of spin polarization from Ni(100) obtained by averaging over four different measurements in order to decrease the statistical uncertainty. The work function Φ of the clean crystal as determined from Fowler plots was between 5.15 ± 0.05 and 5.20 ± 0.05 eV. After the measurement, which typically took

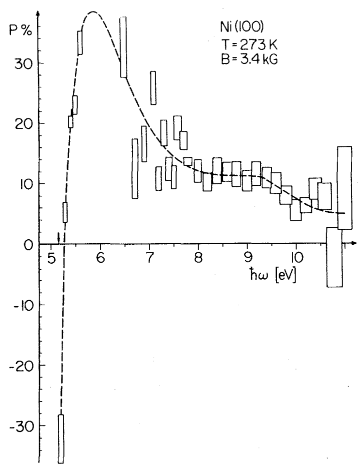

FIG. 1. Dependence of photoelectron spin polarization in percent on photon energy in eV. Vertical extension of measured points indicates statistical uncertainty; horizontal extension, resolution of monochromator. Photothreshold is indicated by arrow.

about 17 h, Φ increased slightly to 5.22 and 5.33 eV, respectively, as a result of contamination during the measurement. Subsequent LEED and AES analysis showed that this contamination was not severe.[8] The averaged spectrum of ESP shown in Fig. 1 was obtained by shifting the spectra observed on four different surfaces in energy to the common average $\Phi = 5.20$ eV.

The spectrum in Fig. 1 shows three essential features: (1) A sharp drop of the ESP on approaching the threshold. The zero intercept is reached at only $h\omega - \Phi \cong 0.05$ eV. (2) A rapid decrease of the ESP for 6.5 eV $\leqslant h\omega \leqslant$ 8.4 eV. (3) A further decrease to about 5% at $h\omega \cong 10$ eV.

For 5.6 eV $\leqslant h\omega \leqslant$ 6.5 eV it was not possible to take data because both light sources used in this experiment, the high-pressure Hg-Xe arc lamp and the hydrogen discharge in the Hinteregger-Eastman design,[15] are very weak in this range. The ESP of -30% at the threshold energy should be taken with reserve. Photocurrents at $\hbar\omega$ only 50 meV higher than Φ are extremely small and absolute errors introduced by the apparatus become more important. Additionally, photoemission will mainly occur from special points or areas with a lower local Φ. Yet every measured surface consistently showed negative ESP and we want to put the main emphasis on this fact and not on the numerical value.

A straightforward application of the SWS theory with a Stoner splitting of 0.3 eV predicts negative ESP for $h\omega \leqslant 0.4$ eV $+ \Phi$, in contrast to the observation (1). Considerations given by Anderson,[6] Doniach,[10] Wohlfarth,[8] Hertz and Edwards,[16] and Sokoloff, Finashkin, and Turov,[17] can account for the observed sharp drop. The results on polycrystalline samples[1] as well as new angle-resolved photoemission studies[18] of Ni(100) for temperatures below and above the Curie temperature confirm the observation that the Stoner splitting appearing in photoemission experiments is considerable smaller than 0.3 eV. The preliminary results obtained on the (111) surface are quite similar to those from (100) shown in Fig. 1; in particular there is the same sharp drop at threshold.

This indicates that it is not the crystal orientation but the effect of the density of states which is responsible for the main features. It should be noted that an atomic model in which the Ni atom is thought to be simultaneously in a $3d^8$ and $3d^9$ state with a spin moment fluctuating in magnitude and direction, to account for the broken Bohr magneton number, also leads to the observed polarization spectrum. The reason for this is the fast timescale of the photoemission process. The two configurations $3d^8$ and $3d^9$ appear separately and the multiplet structure of the ion core left behind after photoemission leads to a negative polarization near E_F. The ESP spectrum obtained from Fe^{2+} and Fe^{3+} in Fe_3O_4, in which a mixture of $3d^5$ and $3d^6$ configurations coexists at the same cubic lattice site, is actually very similar to the one observed on Ni.[19] By means of the temperature dependence of the ESP it should be possible to distinguish between the atomic picture and the modified band model. The width of the dominant structure e.g., observation (2) in the spectrum of Fig. 1, indicates that the total emission from the Ni d states extends over a region of 2–3 eV in accordance with the energy distribution curves of photoelectrons taken with x rays.[20]

The asymptotic value of 5% for $h\omega \approx 11$ eV agrees with the saturation magnetization of $n_B = 0.5\mu_B$ per Ni atom. Per definition, the ESP is given by n_B/n, where n is the total number of electrons per Ni atom. With $n = 10$ one obtains 5% which means that all the electrons are emitted with equal probability on increasing $\hbar\omega$. Since $n_B = 0.5$ is the bulk magnetization, observation (3) shows that one tests bulk properties in this experiment. Further measurements are in progress.

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Photoionization Line Shape of the Surface State on W(100)

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Surface-state photoemission from W(100) is observed for photon energies up to 40.8 eV, contrary to previous measurements. The linewidth of this feature shows an excitation-energy dependence, which extrapolates to the field-emission value. Asymmetric broadening occurs at higher photon energies and is interpreted in terms of many-body effects associated with a heavy-hole state, implying a relaxation shift of the energetic position of the surface state.

A strongly surface-sensitive feature is observed in photoemission[1-3] and field-emission[4,5] spectra from tungsten and molybdenum (100) crystal faces at an energetic position 0.4 eV below the Fermi level, E_F. This feature has been attributed[6] to a surface state located in the uppermost d-band spin-orbit gap, based on the prediction of similar states in the sp-d hybridization gap[7] at much lower energies. Recent calculations[8] support this view. However, subsequent studies[9-11] raised doubts as to the detailed nature of the origin of the observed peak. The intensity of this peak has been found to be substantial for photon energies from 7.7 to 16.8 eV,[12] in agreement with the assignment to a surface state. However, Waclawski and Plummer[1] (WP) reported a sharp decrease in intensity at a photon energy of 21.2 eV, extrapolating to zero surface-state emission at around 23 eV. In a subsequent paper, Egelhoff, Linnett, and Perry[13] (ELP) interpreted their results at 16.8- and 26.8-eV photon energy as indicative of surface-state photoemission occurring only at photon energies below the bulk plasmon frequency of about 23 eV for tungsten. This leads to the conclusion that the intensity of surface-state excitation is critically dependent upon the degree to which the dynamic polarization screening of the local photon field at the surface allows photoionization to occur via the $\vec{p}\cdot\vec{A}$ term of the operator in the photoexcitation matrix element.

In this Letter we report the result of a study of the photoexcitation-energy dependence of the *intensity* of the surface-state feature on W(100) and show that emission continues to be observed for photon energies up to 40 eV. In addition the *width* of the peak is observed to increase asymmetrically with photon energy, extrapolating smoothly to the field-emission value for energies below E_F. The excitation-energy dependence of the line-shape asymmetry is interpreted as arising from many-body effects associated with the creation of a heavy-surface-state hole in the pho-