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SPIN POLARIZED INVERSE PHOTOEMISSION STUDIES OF SURFACE MAGNETISM AND ELECTRONIC STRUCTURE

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Spin polarized inverse photoelectron spectroscopy (SPIPES) is shown to be a powerful new technique to study surface and near-surface electronic structure and magnetism. The process, the information obtained, and the apparatus required in a spin polarized inverse photoemission measurement are compared to the complementary spin polarized photoemission measurement. In SPIPES spectra of a clean Ni(110) surface, transitions to the minority spin 3d holes that give rise to ferromagnetism in Ni can be directly observed, as can sp states which are spin slit as an indirect consequence (via s-d hybridization) of the exchange splitting of the d bands. The adsorption of oxygen or carbon monoxide on Ni(110) causes a dramatic decrease in the number of minority 3d holes, that is, in the magnetic moment of the Ni atoms. The data allow us to severely limit the possible models of how chemisorption induces changes in surface magnetism. Other SPIPES studies, such as the temperature dependent behavior of empty bands in ferromagnetic Fe, and future directions and applications of SPIPES will be reviewed.

1. Introduction

Inverse photoemission spectroscopy (IPES), also known as bremsstrahlung isochromat spectroscopy, is a powerful technique to study the unoccupied energy levels of surfaces [1,2]. An electron which is incident on the sample surface may first couple into an unoccupied level and then make a transition to a lower-lying unoccupied level with the emission of a photon – hence, the name inverse photoemission. If the incident electron wave vector is well-defined, then we have *k*-resolved inverse photoemission [3] analogous to angle resolved photoemission. If, in addition, the incident electron beam is spin-polarized, electrons couple into an initial state of that particular spin and orientation. With this spin polarized IPES, or SPIPES, the spin-dependent electronic structure of ferromagnets can be determined.

In an ordinary photoemission spectroscopy (PES) measurement, electrons are excited from occupied states below the Fermi level to unoccupied states above the vacuum level (~ 5 eV above E_F). It is those states between the Fermi level and vacuum level, which are inaccessible in PES, that are of particular interest in IPES. Exchange-split d and f states frequently lie in this energy range, making it of special interest in SPIPES studies of ferromagnets. For investigations of ferromagnets, SPIPES and spin polarized PES are clearly complementary techniques that determine the spin dependence of unoccupied and occupied states, respectively.

In both spin-polarized photoemission and inverse photoemission, a macroscopic area of the surface a few atomic layers thick is probed so that typically a uniformly magnetized, or single domain, sample is used. Changes in the surface and near-surface magnetization as a function of chemisorption on the surface or as a function of temperature can be monitored by SPIPES and spin polarized PES. These techniques can also determine which electronic states are actively involved in changes of the surface magnetization.

2. Experimental apparatus

2.1. Spin polarized inverse photoemission

The first SPIPES measurements [4] were made of a Ni(110) surface using a spin polarized electron beam from a GaAs photocathode [5] and a Geiger–Müller (GM) counter for the photon detector [6], arranged as depicted in fig. 1. The peak sensitivity at $\hbar\omega = 9.7$ eV and the bandpass of 0.7 eV of the GM counter are determined by the combined effects of the iodine photoionization threshold and the ultraviolet transmission cut off of the CaF_2 window. Advantages of this detector are its simplicity and large solid angle of photon acceptance. Its major disadvantage is that it is limited to a fixed photon energy.

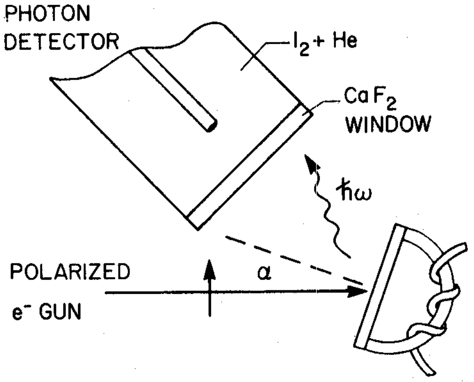

Fig. 1. Schematic of the SPIPES apparatus of this work showing the spin polarized electron beam incident at an angle α with respect to the normal of a uniformly magnetized crystal, and the Geiger-Müller counter to detect the radiated photons.

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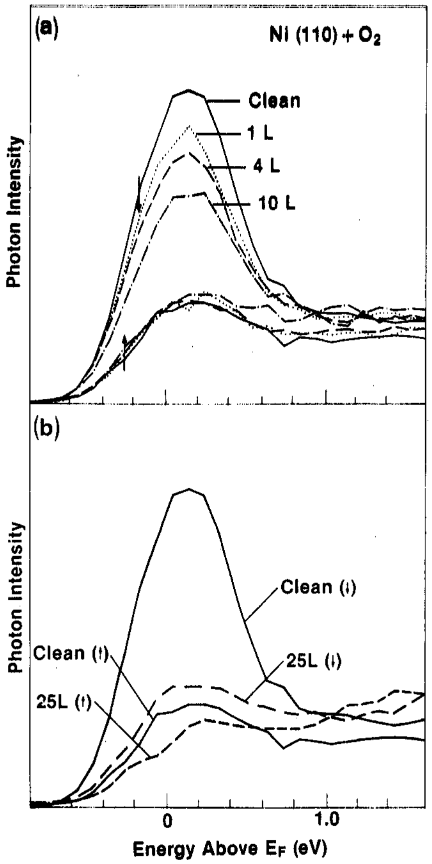

Fig. 3. Spin-resolved photon intensity spectra as a function of final state energy, at room temperature and 25° angle of incidence of the spin polarized electron beam. The measurements are at a constant photon energy, $\hbar\omega = 9.7$ eV, as the incident electron energy is varied. The spectrum of the clean Ni(110) surface is compared to surfaces with oxygen exposure of (a) 1, 4, 10 L and (b) 25 L.

how the chemisorption induces a coupling between different 3d orbitals; this coupling could provide a mechanism by which the minority spin band may be drawn below the Fermi level.

Returning to fig. 3, the majority spin peak which derives from the Ni s, p levels remains unchanged for exposures up to 10 L, which corresponds to a coverage of 0.6 ML. It is at approximately this coverage where the nucleation and growth regime begins [13]. At the higher exposure of 25 L there is finally a decrease in the majority spin s, p peak which we believe is correlated with the onset of oxidation and reduction of the magnetization in subsurface layers. At still higher exposures, the structure within 1 eV above E_F disappears and there is a broad NiO peak about 3 eV above E_F. This peak is the same for majority and minority spins as is expected for an antiferromagnetic oxide.

When CO is chemisorbed on Ni(110) the minority spin d peak decreases as in the case of oxygen in fig. 3(a). At the same time a large $2\pi^*$ antibonding peak, which has no measurable spin dependence, builds up at 3.5 eV above E_F. The details of the CO SPIPES spectra, which will be published elsewhere [17], are summarized in fig. 4. In the upper part of the figure the intensity of the CO $2\pi^*$ peak is plotted as a function of coverage expressed in units of the Auger C_{KLL}/Ni_{LMM} peak ratio. The top axis of the figure shows the corresponding exposure. The increase in the CO $2\pi^*$ intensity shows that the CO coverage on the surface is continuously increasing. The bottom half of the figure shows decreases in the spin integrated d band peak intensity and the minority spin peak intensity as a function of coverage. Both decrease nearly linearly up to a coverage corresponding to 0.5 ML (Auger peak ratio 0.033) and then remain approximately constant in marked contrast to the CO $2\pi^*$ peak intensity. Because no further decrease is observed above 0.5 ML coverage, one is led to the conclusion that each chemisorbed CO molecule destroys the magnetic moment of two Ni atoms. It is interesting to note that in the ferromagnetic resonance studies of thin Ni films, Göpel [18] found that per adsorbed CO molecule, two Ni surface atoms ceased to participate in the thin film ferromagnetism.

The changes in the magnetic moments on CO chemisorption have been discussed theoretically by Raatz and Salahub [19] based on calculations of CO bonded to 13 atom Ni clusters. They emphasize the importance of the hybridization of filled Ni d levels with 5σ levels of the CO to form Ni-5σ bonding and antibonding levels in such a way that there is shift of the Ni d states and the minority spin hole states are pulled below E_F. In another cluster calculation, Kao and Messmer [20] also find that the bonding is predominantly local with the CO promoting the Ni atom from a $3d^9$ to a $3d^{10}$ configuration. This mechanism is also expected to take place on extended Ni surfaces and is consistent with the SPIPES data discussed here.

3.3. *Temperature dependence of ferromagnetic electronic structure*

The temperature-dependent behavior of the empty bands in Fe have been investigated by Kirschner et al. [21] using SPIPES. The experiments showed no change in the energetic positions of the rather flat minority spin band which generates most of the empty density of states in Fe. However, the unoccupied spin-slit dispersive bands near the H point, were found to "collapse" together with increasing temperature.

While there is general agreement in current theories that local moments exist at temperatures in the vicinity of the Curie temperature, there is considerable controversy about the degree of short range order. Disordered local moment theory predicts [22] zero short range order whereas a fluctuating band model predicts [23] substantial short range order. Haines et al. [24] discuss how the range of the short range order can be

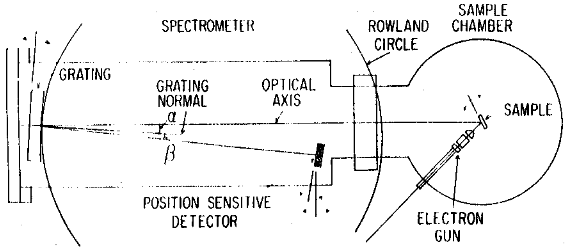

Fig. 2. Schematic of a variable photon energy IPES spectrometer which becomes spin resolved by using a spin-polarized electron gun (from ref. [7]).

A variable photon energy IPES spectrometer [7] is shown in fig. 2. Compared to the GM detector, a smaller solid angle of photon flux is accepted and there are losses at the grating. However, the losses are compensated by using position sensitive detection which allows the measurement of several photon energies simultaneously. Excellent IPES spectra have been obtained [7] with electron gun currents of 5–10 μA. This apparatus is readily converted to a SPIPES apparatus by replacing the conventional electron gun with a GaAs type spin-polarized electron gun which easily delivers similar currents [8,9]. The high currents and narrow energy spread of such electron guns make them attractive even for IPES measurements where spin resolution is not a requirement.

2.2. Spin polarized photoemission

The analog of the inverse photoemission apparatus with the GM detector (Fig. 1) is the photoemission apparatus with a fixed photon energy resonance lamp. The equivalent comparison to the inverse photoemission spectrometer is spin-polarized photoemission using the variable photon energy of synchrotron radiation from a storage ring [10].

Although IPES and PES are frequently considered to be the time reverse of each other, the extent to which this is true depends on the localization of the states. In the localized limit PES removes an electron leaving behind an ion whereas IPES adds an electron to the previously neutral atom, two obviously different situations. In the other limit of delocalized band states in the solid, the system is changed negligibly by the addition or removal of an electron and the time reverse picture holds. In this case, it can be shown [11] that the ratio R of the IPES to the PES cross section is

$$R = \frac{q^2}{k^2} = \left(\frac{\lambda_{\text{elec}}}{\lambda_{\text{phot}}}\right)^2$$

where q is the photon momentum, k the electron momentum, and λ_{elec} and λ_{phot} the electron and photon wavelengths respectively. The photon momentum is much smaller than the electron momentum at ultraviolet photon energies; for energies of order 10 eV, R is of order 10^{-5}. Nevertheless, the availability of intense electron beams make IPES measurements as convenient as PES measurements. In a spin resolved PES measurement, the spin polarization of the electrons is measured by a scattering process which requires count rates at least 10^4 higher than in the non-spin resolved photoemission measurement for equivalent statistics. By contrast in the SPIPES measurement, spin-polarized electron beams are available with the same intensity as unpolarized ones. For this reason, SPIPES measurements are much easier than their spin-polarized PES counterpart.

3. Results and discussion

3.1. Chemisorption-induced changes in surface magnetism

The effect of chemisorption on surface magnetism has traditionally been investigated by making bulk magnetic measurements on high surface area samples [13]. With SPIPES we have a surface sensitive spectroscopy that probes the electronic states or orbitals actually involved in the chemisorption induced changes. Measurements have been made of two quite different chemisorption systems, oxygen and carbon monoxide, on the Ni(110) surface. Oxygen chemisorbs dissociatively onto the long bridge site of the Ni(110) and introduces extensive reconstruction of this surface. Beyond the initial rapid chemisorption at coverages $\theta \leqslant 0.5$ monolayer, there is nucleation and growth of NiO islands which are two to three layers thick, and at higher coverages a slow in-depth growth of the oxide [13]. In contrast, CO resides purely on the surface, adsorbs molecularly, and bonds primarily in terminal sites [14].

The chemisorption of oxygen causes a reduction in the Ni minority spin d hole peak as illustrated in fig. 3 [15]. The experimental resolution of 0.7 eV precludes detailed measurements of the exchange splitting (~ 0.3 eV). However, if the oxygen were causing a reduction of the exchange splitting in the form of a rigid shift of the d bands, one would expect majority spin holes to be pushed above E_F with a corresponding growth in the majority-spin SPIPES peak. This expectation is clearly not observed. Likewise, if the effect of the oxygen were to destroy the coupling between neighboring moments, i.e., randomizing the orientation of the magnetic moments, we would observe a decrease in the minority spin-peak and a growth of the majority-spin peak until they were equal in size. There is also no evidence for the transfer of Ni d electrons to the oxygen which would create holes that would be observed in the spectrum. With the assumption that to a first approximation the d state count is constant, the data point to a decrease in the magnetic moment of the Ni surface atoms. Calculations suggest that the Ni3d–O2p interaction causes a redistribution of the electronic states. Liebsch [16] shows

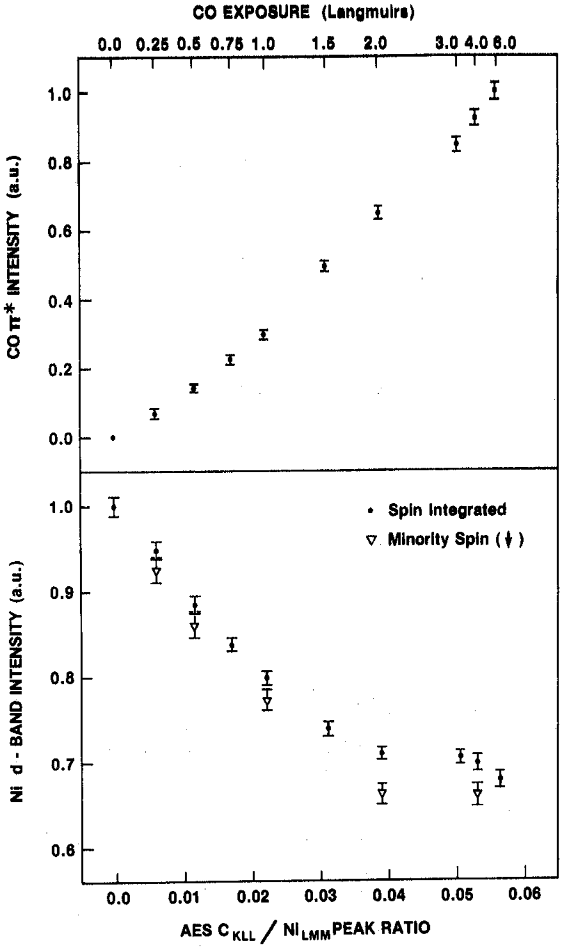

Fig. 4. Summary of SPIPES measurements as a function of CO exposure on Ni(110). The continuous increase of the π^* peak intensity at the top of the figure is to be compared to the leveling off of the minority spin d band intensity and the spin integrated d band intensity plotted in the lower part.

obtained by comparing calculated and experimental spectra. As an example, the predictions of finite temperature SPIPES spectra [25] of Fe(100) at the $H_{25'}$ point for degrees of short range order ranging from $\Lambda = 0$ to $\Lambda = 5.4$ Å are shown in fig. 5. The differences in the theoretical majority spin (solid line) and minority spin (dashed line) spectra are significant at $\Lambda = 3.7$ and 5.4 Å indicating that a SPIPES measurement with adequate resolution at the $H_{25'}$ point could likely resolve this important controversy. Only a longitudinal polarization was available for the above mentioned SPIPES experiment on Fe(100) [21]; at normal incidence the polarization and surface magnetization are orthogonal which precludes spin-resolved measurement right at the H point where comparison to this calculation would be possible. In previous analysis of spin polarized PES at $\Gamma_{25'}$, interference from other peaks only allowed a lower limit of $\Lambda = 4$ Å for the short range order to be extracted from the measurements [10,24]. At $H_{25'}$, both the majority and minority bands are unoccupied, and there are not interfering transitions, making SPIPES measurements to determine Λ of special interest.

4. Future prospects

The above examples illustrate the rich information which can be obtained from SPIPES investigations of surface magnetism and electronic structure. The technique was however first demonstrated only three years ago [4] and must be considered in its infancy. Variable wavelength spectrometers using a spin polarized electron gun will add a new dimension to the experiments. Then the SPIPES experiment will not only have energy resolution, spin resolution, and angle resolution with easy variation of the angle, but also variable photon energy. In many respect such measurements will be less difficult than their spin-polarized PES counterparts but should be considered complementary with the applica-

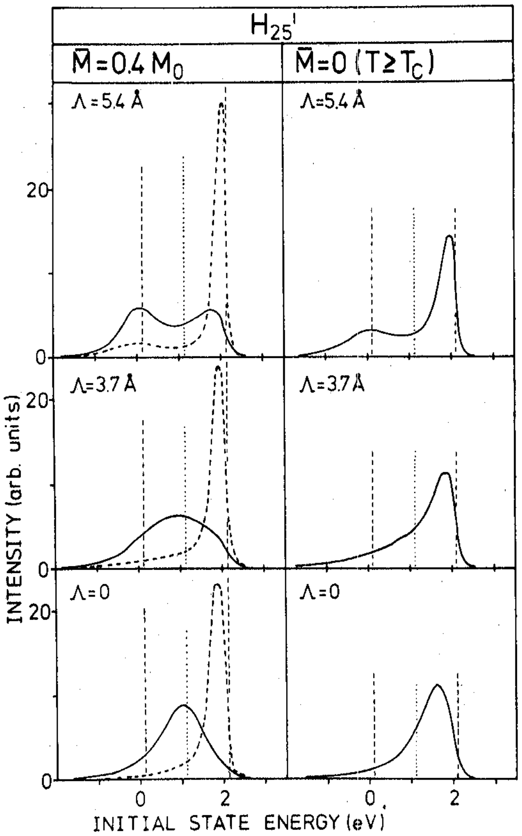

Fig. 5. Theoretical majority spin (solid curves) and minority spins (dashed curves) normal emission spectra for Fe(100) from initial states near $H_{25'}$ shown for $\overline{M} = 0.4M_0$ on the left and above T_c, $M = \overline{O}$, on the right. The assumed values of the short range order length Λ are indicated. Also shown are the low temperature $H_{25'}^{\uparrow}$ and $H_{25'}^{\downarrow}$ energies (vertical dashed lines) and nonmagnetic $H_{25'}$ energy (vertical dotted line) (from ref. [25]).

tion of both techniques to the same system under investigation being the most desirable course.

We expect further studies of ferromagnetic electronic structure. It should be possible to test theories which indicate enhanced moments of thin films of ferromagnetic materials or even predict a ferromagnetic surface on an antiferromagnet like Cr. Further studies of chemisorption induced changes in electronic structure and magnetism will be of particular interest on surfaces with simpler surface unit cells, such as Ni(100), where spin polarized calculations of the adsorbate-ferromagnetic surface system are becoming available. Finally, we hope that SPIPES spectra suitable for comparison to calculations illustrated in fig. 5 will be able to resolve fundamental questions about finite temperature magnetism.

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