Spin Polarization and Temperature Effects in Reflection Diffraction from W(001)

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Simultaneous low-energy electron diffraction (LEED) and electron-spin polarization measurements have been made on clean W(001) for the first time at a high angle of incidence (47.5°) with a surface azimuth of 50°. Polarization peaks ranging from +15% to −27% have been observed and occur at energies where the LEED intensities are close to a minimum. After a cleaning flash, effects ascribed to specimen cooling caused changes with time in LEED intensities but not in spin polarization. Reasons are discussed.

We report measurements of spin polarization as well as intensities in low-energy electron diffraction (LEED) from tungsten (001) surfaces. These results are compared with theoretical calculations based on a 5% surface contraction. The angle of incidence θ was 47.5° and the azimuthal angle φ was 50° (measured with respect to the 01 direction in the surface) for the (00) beam in the energy range from 30 to 190 eV. These are the second such measurements reported and the first at a high angle of incidence. A previous Letter[1] gave results for W(001) at $\theta = 11°$ and 14° and $\varphi = 0°$. In this work we have paid particular attention to surface cleanliness and time effects. All intensity and spin-polarization results were reproducible and were obtained with a system pressure of $< 1\times 10^{-9}$ Torr.

The experimental apparatus, a schematic of which is shown in Fig. 1, consisted of a normal LEED system modified to incorporate a Mott detector for polarization analysis at ultrahigh vacuum (UHV).[2] The unpolarized incident beam was scattered from the W(001) crystal placed at the center of curvature of the LEED optics. Electron spin polarization is induced by the spin-orbit interaction during atomic scattering. Electrons scattered in the (00) beam passed through a side arm in the LEED chamber and were energy analyzed before being accelerated to 90 keV and scattered from thin targets of gold in the Mott detector. This second scattering of a polarized electron beam at ± 120° to the incident direction results in a difference between the currents scattered to left and right and the magnitude of this scattering asymmetry is a measure of the degree of spin polarization once the system or geometric asymmetry has been subtracted. The count rate in the Mott detector provided a convenient measure of LEED intensity and consequently LEED spin-polarization and intensity data could be obtained simultaneously.

For measurements of electron spin polarization it is essential to have a reliable estimate of the geometric asymmetry. This was attempted in three ways: (1) by using thin aluminum films for which the asymmetry due to polarization is approximately 0.1 that for gold; (2) by using an unpolarized straight-through beam from an additional electron gun (Fig. 1); (3) by comparing results obtained from a clean and a grossly contaminated surface. In the latter case the polarization is approximately zero.[3] This method was found to be the most reliable. Polarization measurements were first obtained from the clean crystal relative to specific LEED energies (190 eV, 100 eV) and were then repeated using a deliberately contaminated crystal (by leaking in air at 10^{-2} Torr after which no spots were visible.) All spin-polarization results here have been corrected for the geometric asymmetry measured in this way (generally around 5%).

Prior to any measurements the crystal was cleaned using established procedures that remove carbon and oxygen. As monitored by Auger-electron spectroscopy (AES), carbon was successfully removed for up to 0.5 min after flashing. In contrast to Ref. 1, the LEED spots re-

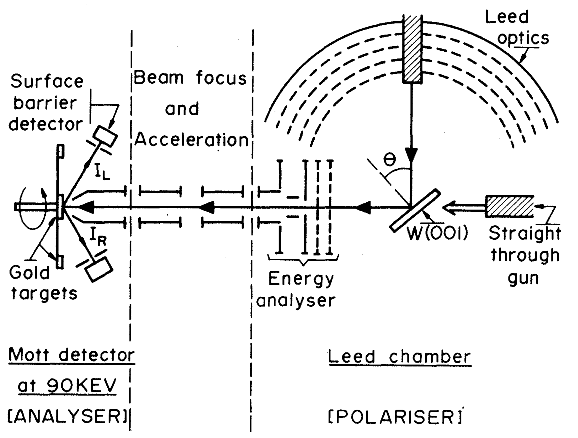

FIG. 1. Schematic of the experimental apparatus.

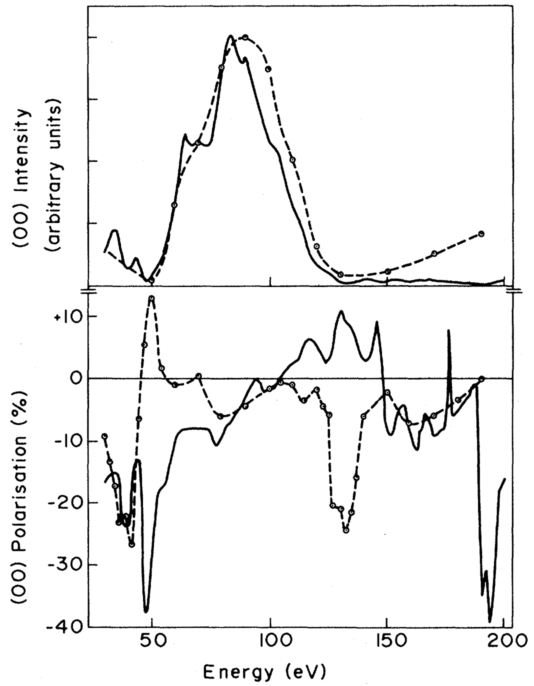

FIG. 2. Intensity and polarization profiles. Solid line, theoretical results (Ref. 4) for $\theta=47.5°$, $\varphi=45°$, $T=300$°K and a 5% surface contraction. Dashed line, experimental measurements for $\theta=47.5°$, $\varphi=50°$. The intensity profile corresponds to $T=400$°K. The ordinates of the experimental points are subject to ± 3% error. The theoretical polarization has been divided by 2, and has assumed an exponential surface barrier.

mained sharp and bright, with no extra spots, for more than 24 h after the crystal had been flashed. This would indicate that any carbon was providing either an amorphous or an "in-step" layer on the W(001) surface. Since the ratio of (00) spot intensity to background intensity, checked at several energies, increased by only a factor of 4 (in the worst case) during the 24 h following a flash, the carbon residing on the crystal during the 20 min required to obtain full measurements must be slight. Nevertheless, as a precaution the crystal was flashed to >2300°K at each energy before measurement.

The intensities and spin polarizations obtained in this way are shown in Fig. 2. The polarization curve is characterized by peaks ranging from +15% to −27%. Also included are the theoretical results obtained by Feder[4] for the same θ but a slightly different φ assuming a 5% surface contraction. Agreement between the intensity profiles is very good up to 150 eV. However, for the polarization curves the agreement between theory and experiment is not good. Both curves show very little polarization in the energy range corresponding to the intensity maximum and have peaks close to those energies (50 eV, 130 eV) for which the intensity is a minimum. This is consistent with the results obtained from free-atom scattering and indicates that for tungsten, for which the core scattering is strong, the spin-orbit single-core effects are noticeable despite the multiple scattering. However, theoretical and experimental polarization peaks below 150 eV, while occurring at similar energies, appear to be of opposite polarity. These differences cannot all be because the theoretical curve was calculated for a slightly different φ. However, the shape of the theoretical curve is sometimes very sensitive to the amount of surface contraction assumed, and the optimum parameters may not have been taken. Clearly spin polarization provides a very sensitive test of the parameters and assumptions used in the theory, since the LEED intensities matched theory whereas spin polarizations do not at this stage. It is worth noting that the fit between theory and experiment[1,5] for previously published polarization results is not good. There is also a poor fit between the quoted experimental LEED intensity curve and previous intensity measurements at the same diffraction conditions.[6]

Polarization and LEED intensity data at each energy were obtained in 0.5-min intervals for up to 21 min after a cleaning flash to >2300°K. The LEED intensity shown in Fig. 2 corresponds to 19.5–20 min after a flash. The polarization measurements were normally averages over 5 min, the first period being 1–6 min after the flash. Time variations were found to be significant for the LEED intensity at some energies. At all energies the intensity change was small between 1 and 3 min after a flash but, as is shown in Fig. 3(a), there is a difference between the overall curve and a curve taken after 20 min. Similar behavior was found using a spot photometer for θ in the range 3°–10° with $\varphi=50°$ but the variations were not so dramatic as for $\theta=47.5°$. They were found to be θ as well as energy dependent.

In contrast with the time behavior of the LEED intensities the spin polarization, at those energies (40, 50, 60, 70, 80, 100 eV) investigated in detail, were found to be time independent. This is illustrated in Fig. 3(b) by the behavior of the polarization with time at 40 eV, an energy at which the polarization is close to a peak. In fact, measurements extended up to 1 h after a flash at this energy gave no indication of a change of the

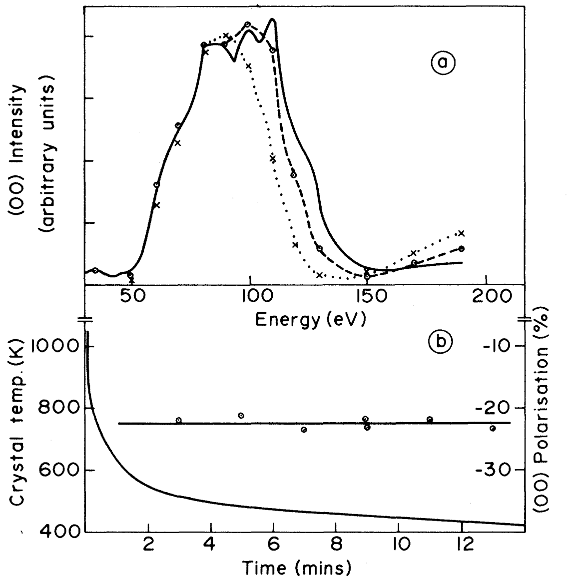

FIG. 3. (a) Intensity curves as a function of temperature. Solid line, 625°K; dashed line, 500°K; dotted line, 400°K. (b) Dashed line, crystal-cooling curve. Solid line, polarization at 40 eV vs time. Each experimental point is an average of data obtained in the 2 min prior to that time.

polarization with time.

Contamination is an obvious explanation of the time effects that occur in the intensity curves. However, since the crystal is flashed to >2300°K prior to data acquisition, another time effect, namely the cooling of the crystal, is introduced. The cooling curve in Fig. 3(b), obtained with an infrared pyrometer, indicates that the crystal is rapidly cooling during the first minute. No intensity or spin-polarization measurements are made during this time. Subsequently the temperature variation becomes more gradual and room temperature is reached after about 30 min. Since the contamination on the crystal immediately following a flash is negligible (see earlier discussion) we conclude that the major cause of the rapid LEED intensity variation is the cooling of the crystal.

We now discuss the finding that the spin polarization is independent of time in this experiment. Qualitatively the time independence can be simply explained by the temperature independence of the spin-orbit coupling responsible for the production of polarized electrons. More exactly, in the current relativistic dynamical theory of LEED, both intensity and spin-polarization calculations include temperature effects in the phase shifts of the electrons scattered by the crystal. Unfortunately this is analytically very complex to solve with respect to deriving a temperature dependence. However, we present a very simplified method of considering the temperature dependence. Strictly speaking, the effect of temperature is to modify atom core positions during vibrations. Hence we adopt the procedure of taking the effect into account approximately by introducing a factor modifying the wave vector $\vec{k}$. Now, neglecting multiple-scattering effects, the spin polarization is given by[7]

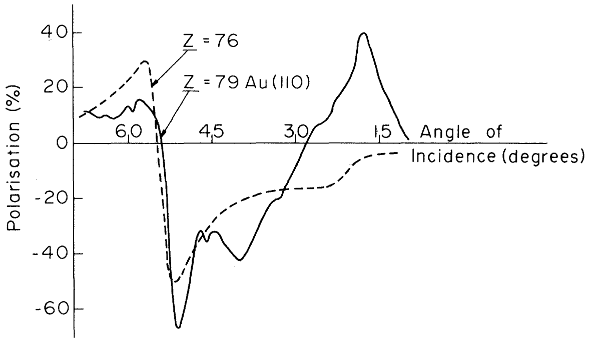

FIG. 4. Experimental (00) LEED spin polarization as a function of θ from Au(110) at 50 eV (Feder, Müller, and Wolf, Ref. 8) compared with the atomic spin polarization from osmium ($Z=76$) at the same energy (Gregory and Fink, Ref. 9).

$$P=\frac{i(fg^*-gf^*)}{(f^2+g^2)}, \tag{1}$$

where f is the amplitude scattering factor and g is the spin-dependent scattering factor. Here both f and g contain $1/\vec{k}$. We include the effect of a temperature change by modifying $\vec{k}$ by a multiplicative factor $\alpha(T)$. Then, since $\alpha(T)$, like $\vec{k}$, is a factor common to all terms in Eq. (1), P will be independent of temperature, as observed. However, since the intensity scattered from the crystal can be written as $d\sigma/d\Omega=(f^2+g^2)$, where $d\sigma/d\Omega$ is the differential scattering cross section for an unpolarized beam, then use of the factor $\alpha(T)$ would introduce a temperature dependence into the LEED intensity. Hence the latter can be temperature dependent whereas the polarization would be much less so. There is some evidence that at higher angles of incidence, a single-scattering approach as used above may have some applicability. Although there are insufficient theoretical data for tungsten, it is possible to compare the (00) LEED polarization curve from Au(110) ($Z=79$)[8] as a function of θ at 50 eV with the atomic polarization curve calculated for osmium[9] ($Z=76$) at the same energy (see Fig. 4).

Considering that the target atomic numbers are not quite the same, the fit is very good above $\theta \simeq 45°$. Hence single-atom scattering effects can be prominent in this region.

In conclusion, our measurements show that for relatively large angles of incidence the polarizations from W(001) are not very large (maximum 27%). While the match with the theoretical LEED intensity profile is good, the fit with the theoretical polarization is not satisfactory. The reasons for this are not yet established but one factor to be taken into account is that theoretical polarization curves are sometimes much more sensitive than LEED curves to the precise dilation or contraction that has been assumed. LEED, however, appears to be more sensitive to surface temperature than polarization.

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Width of the *d*-Level Final-State Structure Observed in the Photoemission Spectra of Fe_xO

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X-ray photoemission (XPS) measurements of wustite, Fe_xO ($x = 0.90-0.95$), show that the Fe (3*d*) valence-band final states spread ~10 eV below E_F. This is much broader than previous claims based on the analysis of lower-energy (5–90 eV) photoemission spectra. Crystal-field–theory results, based on *ab initio* calculations, are consistent with the broader spectrum. Configuration interaction is found to have important consequences for the position and intensity of the XPS peaks.

Crystal-field–theory (CFT) analyses have been made for the *d*-level final states of Fe_xO by Eastman and Freeouf[1] and by Alvarado, Erbudak, and Munz.[2] The parameters[3] were estimated empirically to obtain agreement with *d*-level structure deduced from UPS (ultraviolet photoelectron spectroscopy) spectra[1,2] In these spectra, metal *d* and ligand *p* levels have comparable intensities making it necessary to deconvolute the spectra.[1,2,4] This led to estimated *d*-level widths of ~5.5 eV[1] and ~6.5 eV.[2] The reported theoretical CFT widths are ~4.5 eV[1] and ~5.5 eV.[2] In XPS (x-ray photoemission spectroscopy), the ligand intensity is reduced and the *d* levels can be observed directly.[5-7] We report the XPS spectrum for Fe_xO. Structure extends ~10 eV below E_F. We have obtained *ab initio* self-consistent-field (SCF) and configuration-interaction (CI) wave functions for an FeO_6 cluster simulating bulk FeO. From these wave functions we have deduced values, appropriate for the photoemission final states, of B and C to represent interactions among the *d* electrons[3] and of $10Dq$ to represent the crystal-field splitting of the +2 and *e* levels.[3] A CFT analysis was then performed where CI wave functions which mix one-electron allowed final states with one-electron forbidden final states are used for the first time. Mixing leads to additional intensity at higher binding energy and to an uncertainty in the relative intensities for some of the states.[8,9]

Previous analysis of Fe_xO involved a separation of the O 2*p* and metal 3*d* contributions utilizing cross-section changes as function of $h\nu$.[1] This yielded an Fe 3*d* final structure spread between E_F and about 5 eV, and an O 2*p* structure centered at ~5.5 eV [Fig. 1(b)]. A subsequent analysis[2] places the O 2*p*-band center at 7.3 eV, and gives slightly broader 3*d* final states [Fig. 1(c)]. This analysis relies on electron-spin-polarization (ESP) measurements on Fe_3O_4 (*not* Fe_xO for determination of the onset of the O 2*p* band. Essentially the argument is that the spin polarization of the photoelectrons, as a function of $h\nu$, will