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Surface Science 513 (2002) L451–L457



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Surface Science Letters

Spin-resolved photoelectron spectroscopy of Fe_3O_4 [☆]

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Received 13 December 2001; accepted for publication 5 April 2002

Abstract

Spin-polarized photoelectron spectroscopy has been used to study the candidate half metal Fe_3O_4 . By using higher photon energies we can study polarization in “as received” samples, essentially “looking through” the disrupted surface. Our data agree with theoretical calculations for Fe_3O_4 but exhibit a lowered polarization.

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Keywords: Electron density, excitation spectra calculations; Visible and ultraviolet photoelectron spectroscopy; Synchrotron radiation photoelectron spectroscopy; Surface structure, morphology, roughness, and topography; Iron oxide; Low index single crystal surfaces; Magnetic films; Magnetic surfaces

1. Introduction

The existence of a new class of magnetic materials displaying metallic character for one electron spin population and insulating character for the other was first postulated by DeGroot et al. [1] in 1983 based on theoretical band structure calculations of the ferromagnetic Heusler alloy NiMnSb. Since then such half metallic materials, which by definition possess 100% electron polarization at

the Fermi energy (E_f), have attracted considerable theoretical, experimental, and technological interest as potential pure spin sources for use in spintronic devices [2]. In addition to Heusler alloys (e.g. NiMnSb, PtMnSb [3]), half metallic character has also been predicted to occur in a wide range of manganites (e.g. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [4,5], $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ [5]), metallic oxides (e.g. Fe_3O_4 [6], CrO_2 [7]) and CMR systems [8]. However, such predictions have proven to be extremely difficult to confirm experimentally [9]. Possible reasons for this include the theoretical limitations arising from the complex crystallographic structure of many such materials and limitations in applying the single electron picture to materials where strong electron correlation may be present; this is compounded by experimental difficulties posed by their

[☆] Previously entitled: “Evidence for a possible source of fully spin-polarized electrons.”

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structural complexity and issues such as surface contamination, segregation, [10] and reconstruction [11]. To date, the most noteworthy results have been for CrO_2 with Andreev reflection [12] and for LaSrMnO_3 with lower energy photoelectron spectroscopy [13], although questions have been raised about this study, including issues such as the impact of surface segregation [14]. These results have spurred considerable interest in other half metallic candidates, and in particular the metallic oxides such as Fe_3O_4 [15–17]. Such oxides possess relatively simple crystallographic structures in comparison to other candidate materials, making them significantly easier both to prepare experimentally and to model theoretically. Hence metallic oxides provide ample scope for the further exploration and development of device physics applications. Moreover, an important reason to use spin-polarized photoelectron spectroscopy (SPES) with Fe_3O_4 is the presence of the Verwey transition, which effectively precludes the utilization of Andreev reflection measurements.

2. Offsite sample preparation and quality determination

Magnetite, Fe_3O_4 , is the earliest known magnetic material, having been studied since antiquity. However, despite much research, many of its electronic and magnetic properties are still poorly understood. Fe_3O_4 has an inverse spinel structure: the larger O atoms form a close packed fcc structure whilst the smaller Fe atoms occupy two distinct interstitial sites. The tetrahedrally coordinated A sites consist solely of Fe_3^+ ions. The octahedrally coordinated B sites contain a mixture of 2^+ and 3^+ states. The magnetic moments within each sublattice are ferromagnetically aligned, but the two sublattices are antiferromagnetically coupled with respect to each other, leading to an overall ferrimagnetic character with a net magnetic moment of $4.1 \mu\text{B}$ per formula unit [18] and a Néel temperature of 858 K. Upon cooling through $T_v = 120 \text{ K}$, bulk Fe_3O_4 displays a sharp Verwey transition characterized by a structural transition from a cubic to monoclinic lattice together with an abrupt drop in the electrical conductivity of two

orders of magnitude. This is associated with a “freezing out” of the electron hopping between the 2^+ and 3^+ ions of the B sublattice, which is the primary mechanism involved in conduction at temperatures above T_v . Differences in the sharpness, magnitude, or onset temperature of this transition between thin film and bulk samples are strongly indicative of the presence of strain, small deviations from perfect stoichiometry, or sample inhomogeneity in the films. Hence precise characterization of the Verwey transition is crucial for successful preparation of high quality thin film samples.

Single crystal epitaxial thin films of $\text{Fe}_3\text{O}_4(001)$ were prepared by the University of California—San Diego and Pacific Northwest National Laboratory. UCSD samples were grown by reactive d.c. sputtering of Fe onto $\text{MgO}(001)$ substrates. Deposition was conducted in a partial pressure of O_2 ($2\% \pm 0.2\%$) at a substrate temperature of $400 \text{ }^\circ\text{C}$. The existence of many stable iron oxide phases necessitates precise control of gas composition and substrate temperature if the correct stoichiometry and crystal structure are to be achieved. Direct growth of Fe_3O_4 on $\text{MgO}(001)$ is pseudomorphic, with a lattice mismatch of $\sim 0.3\%$, leading to significant in-plane tensile strain. Such samples would exhibit both anomalous magnetic behavior [19] and a suppressed Verwey transition [20] that occurs at a somewhat lower temperature than that observed in bulk single crystals. In-plane strain was, however, alleviated by growth of a 300 \AA buffer layer of epitaxial $\text{Fe}(001)$ between the MgO and the 1000 \AA Fe_3O_4 layer. These multilayer films display negligible interfacial strain or roughness when characterized by X-ray diffraction or reflection high energy electron diffraction (RHEED), and exhibit a pronounced Verwey transition at 120 K that is characteristic of that seen in bulk single crystals. Thus, ex situ preparation of these high quality samples avoids the problems associated with in vacuo oxidation of Fe surfaces [15].

Samples grown at PNNL were prepared by evaporation of Fe at a rate of $0.5 \pm 0.1 \text{ \AA s}^{-1}$ in an oxygen plasma ($1.0 \times 10^{-5} \text{ Torr}$) activated by an electron cyclotron resonance source [11]; deposition was again onto $\text{MgO}(001)$ substrates. Substrate temperature was maintained at $450 \text{ }^\circ\text{C}$ for

the first 1000 Å, before being lowered to 250 °C between 1000 and 1200 Å. This temperature was then maintained for the remaining 800 Å of deposition. Initiation of growth at 450 °C results in outdiffusion of Mg from the substrate into the lower levels of the Fe₃O₄ film resulting in step flow growth which relieves strain, removes defects and produces atomically smooth Fe₃O₄ surfaces. Samples were characterized in situ by X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED), and RHEED, as well as ex situ by scanning tunneling microscopy and Auger electron spectroscopy (AES).

3. Onsite characterization at the ALS

Samples were transferred ex situ to the Beamline 7.0 Spectromicroscopy Facility [21,22] of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory, for study by SPES. The undulator provides a tunable high brightness source of photons over an 80–1300 eV energy range. Peak flux from first harmonic radiation, which provides optimal conditions for SPES, is obtained from 80–190 eV. It should be noted that this energy range, and hence both the kinetic energy of the emitted photoelectrons and the resulting experimental sampling depth, is significantly higher than that commonly used for SPES at most other facilities. Emitted photoelectrons are collected by a PHI 10–360 SCA hemispherical analyzer modified to be capable of operating in both spin integrated (conventional XPS) and spin resolved modes. In spin resolved mode the analyzer has an energy resolution of approximately 0.5 eV and an angular resolution of $\pm 7^\circ$ resulting in parallel and perpendicular reciprocal space momentum (k) resolutions of 1.56 and 0.1 Å⁻¹ respectively. When combined with the relatively large unit cell of Fe₃O₄ ($a = 8.3962$ Å, and $G = 0.75$ Å⁻¹), this means that the SPES measurements are largely free of k -dependent angular effects. Furthermore, photoelectron diffraction effects have previously been demonstrated to have a negligible impact on electron spin polarization [23] so the results presented can be considered to be fully angle integrated in character. Angular inte-

gration is important so as to measure the entire density of states (DOS), not merely a small slice as in angle resolved experiments. An extensive series of measurements, including angular, temperature and photon energy variations, has been performed and reported elsewhere [24].

After introduction into the vacuum system, samples were maintained at a pressure of $\sim 5 \times 10^{-10}$ Torr throughout subsequent analysis. As a result of exposure to atmosphere during the ex situ transfer, the samples displayed initial “as-received” surface contamination levels of ~ 0.5 –1 nm, as measured by AES and XPS ($h\nu = 1250$ eV), which consisted entirely of C and O species [24]. Despite this initial surface contamination, SPES conducted on the “as received” samples at a photon energy of 160 eV (Fig. 1a) revealed strong

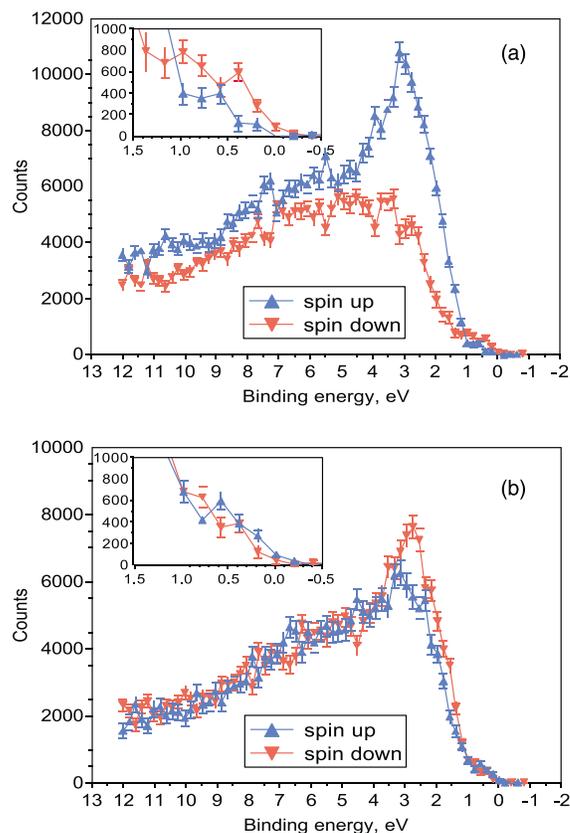


Fig. 1. Spin-resolved valence band spectra of Fe₃O₄ (a) before and (b) after 5 min sputtering with Ne⁺.

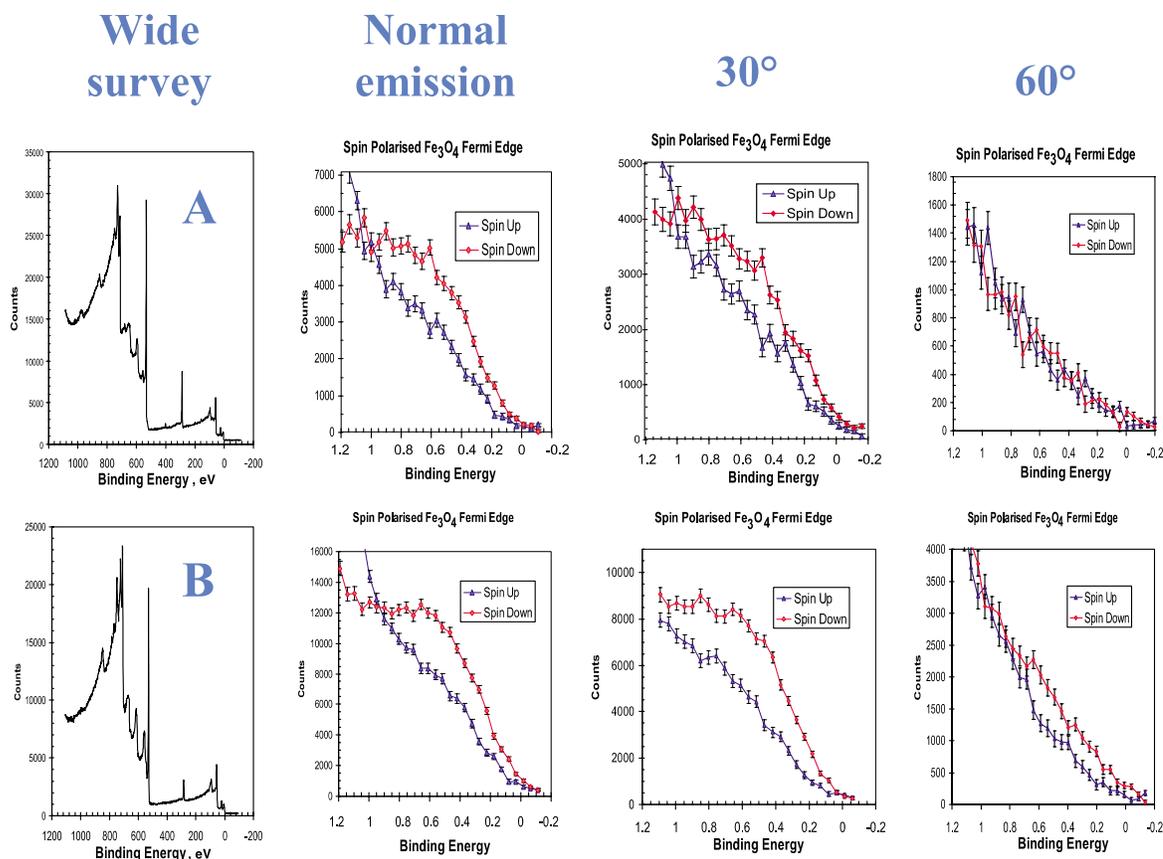


Fig. 2. Here are shown a series of spectra for two samples, A and B. Leftmost are wide, spin integrated scans, which exhibit the core level and Auger peaks of each sample. The vast majority of each of these scans is composed of spectral features associated with Fe and O. The contaminant C peak at a binding energy of 285 eV is the C 1s, which can be used as a measure of surface corruption. Sample A exhibits a significantly greater degree of surface contamination. The other three panels for each sample show spin resolved emission as a function of takeoff angle, measured versus the surface normal. Sample A exhibits the classical signature of a smooth, contiguous and homogenous overlayer: the underlayer effect, in this case the polarization, decreases with larger takeoff angle. For lower levels of contamination, e.g. sample B, the angular dependence is lost, due to the effect of the discreteness of the constituent atoms of the contaminant overlayer.

positive polarization ($\sim 40\%$) of the valence band that decreases to a crossover in the sign of the polarization at approximately 1 eV binding energy. Extensive studies were performed, relating surface contamination or corruption to the degree of spin polarization. This included spin-dependent depth profiling measurements based upon emission angle variation (Fig. 2) and photon energy, which will be described in more detail in a future publication [24]. The strong negative polarization of the Fermi edge region ($\sim -30\%$ to -40%) is comparable to that previously observed at the

photoelectron threshold of in situ cleaved bulk Fe_3O_4 crystals in spin-polarized secondary electron spectroscopy [25]. The spin polarized spectra are also essentially identical to those taken using in situ prepared samples [17].

Initial attempts at in situ cleaning included limited (5 min) Ne^+ bombardment, designed to minimize surface damage, or annealing in vacuum at 500 °C. Either method resulted in immediate total loss of the previously strong valence band and near E_f spin polarization (Fig. 1b), and indeed even some evidence of a reversal of that polarization

[26]. Despite the dramatic change in polarization observed in Fig. 1, XPS, ultra-violet photoelectron spectroscopy and AES spectra, which were also conducted before and after this brief sputtering period, remained indistinguishable. Thus, these techniques provide no indication of such a significant modification of the surface magnetic properties. In contrast, SPES evidently provides a powerful probe of the magnetic quality of the surface and near surface region of the sample. Subsequent attempts at sample cleaning by annealing at 500 °C in O₂ at 1×10^{-5} Torr for 15–30 min proved more successful, leading to complete removal of all adventitious C and O and increasing the absolute value of the valence band polarization by almost 10%. However, high temperature O₂ annealing carries significant risk of surface modification, particularly by rapid migration of Mg from the substrate to the surface. Hence subsequent discussion will focus on the “as received” samples.

4. Spin analysis

A crucial issue of the SPES measurements is how they compare to calculations of the Fe₃O₄ spin specific DOS. The bulk spin-resolved bands structure of Fe₃O₄ has been modeled by Zhang and Satpathy [6] using a local spin density approximation approach. These calculations predict the presence of a band gap in the majority spin states at E_f and a band gap in the minority states at a binding energy of 3 eV. Thus no majority states are present at binding energies lower than approximately 0.5 eV and the majority spin population is predicted to be insulating in character. In contrast, the minority carriers possess a metallic character with states derived predominantly from the Fe 3d bands of the B lattice sites present at the Fermi level. Hence this model predicts –100% electron polarization at E_f (and thus half metallicity) as well as +100% polarization at a binding energy of 3 eV. It should be noted that the calculations are performed at an effective temperature of 0 K and the measurements primarily at temperatures near 130 K. Nevertheless, a comparison of experiment and theory would be useful. Before a direct comparison can be made between these

theoretical calculations and the experimental data reported here, a number of additional external factors must be considered. The effects of finite analyzer resolution, surface imperfections, and differing photoelectron cross-sections must be introduced into the calculations in order to produce “simulated” spin-resolved spectra that facilitate comparison with the experimental data. The effects of analyzer broadening can be reproduced simply by convoluting the calculated spin populations with a 0.5 eV Gaussian. From these broadened spin spectra (I_{Th}^+ and I_{Th}^-), we can generate a theoretical polarization, following Kessler [27] and Johnson [28] and using Eq. (1) below.

$$P_{Th} = (I_{Th}^+ - I_{Th}^-)/(I_{Th}^+ + I_{Th}^-). \quad (1)$$

The overall effect of surface imperfections will be to reduce the observed polarization. By assuming that this reduction is largely independent of electron energy, a rough estimate of its magnitude can be determined by comparison of the average of the observed polarization at the valence band intensity maximum (at a binding energy of 3 eV) with that predicted from the model and applying this correction over the full binding energy range. This approach suggests that surface imperfection reduces the overall polarization by approximately 60%, so the calculated polarization must be multiplied by 0.4 across the whole binding energy range to facilitate direct comparison with the experimental data. Finally, the effects of photoelectron cross-sections can be accounted for by combining the derived theoretical polarization with the experimental spin integrated spectrum (I_{exp}). (See Eq. (2a) and (2b), following Refs. [27,28]). This enables us to produce simulated spin up (I_{Sim}^{\uparrow}) and spin down (I_{Sim}^{\downarrow}) spectra derived from theoretical predictions which can be compared directly to experimental data.

$$I_{Sim}^{\uparrow} = I_{exp}[1 + P_{Th}] \quad (2a)$$

$$I_{Sim}^{\downarrow} = I_{exp}[1 - P_{Th}] \quad (2b)$$

The result of this process can be seen in Fig. 3. There is strong agreement between the experimental data and the simulated spectra derived from first principles. The overall envelopes agree closely in terms of peak position and relative

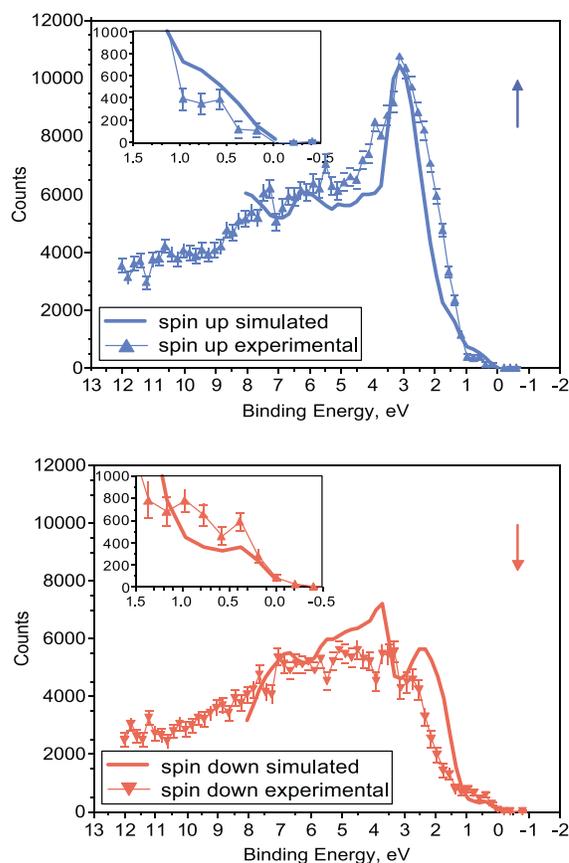


Fig. 3. Comparison between simulated and experimental spin-resolved valence band spectra of Fe_3O_4 , for spin up and spin down populations.

magnitude of spectral structure, with strong positive polarization around the valence band peak at ~ 3 eV and strong negative polarization of some -40% at E_f . Peak position and magnitude in valence band photoelectron spectroscopy are representative of, although not identical to, the DOS. Hence, the overall nature of the experimental bandstructure is in close agreement with theoretical models which predict half metallic character once the effects of finite analyzer energy resolution, surface imperfections, and photoelectron cross-sections are taken into account. (The lower polarization may also reflect the higher temperature of the experiment relative to theory [29].) This result and interpretation are consistent with the spin-polarized study of the Fermi level of Fe_3O_4 [16].

5. Summary and conclusions

The observed polarization at the Fermi energy of Fe_3O_4 has been shown to be extremely sensitive to the morphology of the surface layer to an extent which is significantly greater than that observed in conventional spin-integrated photoelectron spectroscopies. Hence obtaining a surface with a polarization that is truly representative of that of the bulk material is not feasible by conventional sample preparation techniques. However, by probing the spin-resolved band structure of “as received” samples without attempting to further modify the surface in any way, and by using photons of a higher energy than conventionally used for spin-resolved photoemission, we can probe through this disrupted surface layer. The band structure of these “as received” samples has been compared to existing “single-electron” theoretical model which predict half metallic character for Fe_3O_4 and has been shown to be in fairly close agreement once the effects of finite analyzer energy resolution, surface imperfections, and photoelectron cross-sections are considered.

Acknowledgements

This work was performed under the auspices of the US DOE by Lawrence Livermore National Laboratory under contract W-7405-Eng-48. The ALS and the Spectromicroscopy Facility have been built and operated under funding from the Office of Basic Energy Science at DOE. Work at UCSD supported by DOE and the UC Campus-Laboratory Cooperation Program. Work at PNNL supported by the Offices of the Biological and Environmental Research and Basic Energy Sciences at DOE.

References

- [1] R.A. de-Groot et al., Phys. Rev. Lett. 50 (1983) 2024.
- [2] S.A. Wolf, D. Treger, IEEE Trans. Mag. 36 (2000) 2748.
- [3] R.B. Helmholdt et al., J. Magn. Mag. Matter 43 (1984) 249.
- [4] S. Jin et al., Science 264 (1994) 413.
- [5] P.K. de Boer et al., Solid State Commun. 102 (1997) 621.

- [6] Z. Zhang, S. Satpathy, Phys. Rev. B 44 (1991) 13319.
[7] K. Schwarz, J. Phys. F: Met. Phys. 16 (1986) L211.
[8] W.E. Pickett, D.J. Singh, Phys. Rev. B 53 (1996) 1146.
[9] (a) K.P. Kamper et al., Phys. Rev. Lett. 59 (1987) 2788;
(b) D. Orgassa et al., Phys. Rev. B 60 (1999) 13237;
(c) B. Nadgorny et al., Phys. Rev. B 63 (2001) 184433.
[10] G.L. Bona et al., Solid State Commun. 56 (1985) 391.
[11] S.A. Chambers, S.A. Joyce, Surf. Sci. 420 (1999) 111.
[12] Y. Ji et al., Phys. Rev. Lett. 86 (2001) 5585.
[13] J.H. Park et al., Nature 392 (1998) 794.
[14] H. Dulli et al., Phys. Rev. B 62 (2000) R14629.
[15] H.-J. Kim et al., Phys. Rev. B 61 (2000) 15284, 15288.
[16] Y.S. Dedkov et al., Phys. Rev. B 65 (2002) 064417.
[17] D.J. Huang et al., Proceedings of VUV13, Surf. Rev. Lett., 2002.
[18] Z. Kakol, J.M. Honig, Phys. Rev. B 40 (1989) 9090.
[19] D.T. Margulies et al., Phys. Rev. B 53 (1996) 9175;
Phys. Rev. Lett. 79 (1997) 5162.
[20] D.M. Lind et al., Phys. Rev. B 45 (1992) 1838.
[21] J.G. Tobin et al., MRS Symp. Proc. 524 (1998) 185;
Surf. Sci. 478 (2001) 211.
[22] J.D. Denlinger et al., Rev. Sci. Instrum. 66 (1995) 1342.
[23] G.D. Waddill et al., Phys. Rev. B 50 (1994) 6774.
[24] S.A. Morton et al., under preparation;
Bull. Am. Phys. Soc. 45 (2000) 644.
[25] S.F. Alvarado et al., Phys. Rev. Lett. 34 (1975) 319.
[26] M. Aeschlimann et al., Helv. Phys. Acta 60 (1987) 794.
[27] J. Kessler, in: Polarized Electrons, Springer Series on
Atoms and Plasmas, vol. 1, Springer Verlag, Berlin,
1985.
[28] P.D. Johnson, Rep. Prog. Phys. 60 (1997) 1217.
[29] H. Itoh et al., Phys. Rev. Lett. 84 (2000) 2501.