10-24-1994

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41st American Vacuum Society National Symposium, Denver, CO, October 24-28, 1994, to be published in Jour. Vacuum Science and Technology

*Work supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract #W-31-109-ENG-38 (Argonne), by the National Science Foundation through grant #DMR-92-21655 and the Center for Materials Research and Analysis at the University of Nebraska, and is carried out at the Synchrotron Radiation Center in Stroughton, WI, which is funded by the NSF.

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Ultrathin Gd films have been studied with constant initial-state spectroscopy (CIS) of photoemission utilizing linearly polarized light of synchrotron radiation. The photoemission cross-section of the 5d surface state near E_F shows strong photon energy dependence, i.e., sharp peaks in CIS spectra near the Gd $5p_{1/2}$ adsorption edge. These peaks originate from resonant photoemission processes involving the occupied 5p and unoccupied 5d levels of the surface atoms. The symmetry of the unoccupied states were determined experimentally by changing the polarization of light, where p-polarized light excites only to the unoccupied d_{z2} or $d_{xz,yz}$ states and s-polarized light to all the d states including d_{x2-y2} and d_{xy} states. Based on the symmetry assignments, the lower bound of the exchange splitting of the Gd $5d_{z2}$ surface state can be abstracted, which increases when the thickness of Gd film decreases and reach maximum at the monolayer limit.

I. INTRODUCTION

Extensive studies on the electronic structure of the Gd surfaces have been conducted because of the needs to understand the unusual surface magnetic properties of Gd(0001),[1-18] i. e., enhanced Curie temperature of the surface compare to the bulk.[19-23] Such a dramatic effect in surface magnetism is by now known to be connected with the surface electronic structure of Gd, namely, a highly localized surface state at the Fermi Level (E_F).[8-15] Magnetism in ultrathin Gd layers is also very interesting particularly at near the monolayer limit.[24-28] Calculations show an increase in exchange splitting due to further localization of the electrons at low dimensions[10] based upon some preliminary experimental evidence.[4-6] Farle et al., on the other hand, demonstrated that the flat Gd layers epitaxially grown onto W(110) exhibit a scaling of T_C vs. thickness.[27] It is therefore necessary to explore how the electronic structure of Gd changes with film thickness down to the monolayer regime, and relate the electronic structure to magnetism. While there are some film thickness dependent studies with photoemission,[4-6,9,12] no thickness dependence information is available for the unoccupied bands. Only for the thicker films is there inverse photoemission data.[7,17] The investigation of the empty states are especially important to assess the surface 5d exchange splitting since the counter part with minority spin character of the occupied surface state with majority spin is above E_F, at least for the ground state.[10,11,13-15]

While inverse photoemission is well-accepted technique for measurement of band structure above E_F, adsorption and resonant photoemission can also probe those unoccupied states under some circumstances.[4-6] One can also change light polarization to detect the symmetry character of the unoccupied states.[4,29-32] This symmetry is often difficult to determine in many inverse photoemission setups, making resonant photoemission a valuable tool. In this paper, we will present our resonant photoemission studies of Gd ultrathin films down to monolayer regime. Based upon dipole selection rules in the resonant photoemission process and resulting symmetry assignment of the unoccupied states, we suggest the possible evidence of enhanced exchange splitting of Gd at monolayer.

II. EXPERIMENTAL

The experiments are carried out at Synchrotron Radiation Center in Stoughton, Wisconsin on a 6-meter toroidal grating monochromator. Angle-resolved photoemission in both energy dispersion curve (EDC) and constant initial state (CIS) mode were conducted in an UHV chamber equipped with a hemispherical electron energy analyzer and a low-energy electron diffraction (LEED) system.[4] The CIS spectra were taken by scanning the photon energy and electron kinetic energy simultaneously to record the intensity changes of the same initial state, the surface state at E_F in this case.[8-12] The features in CIS are representative of the resonant photoemission processes, where the total photoemission intensity is enhanced by the additional channel of the Gd 5p-5d resonance. All the spectra in this work were taken at normal emission, with the linearly polarized incident light from the storage ring 38 or 66 degrees off normal to provide larger portion of light as s- or p-polarized respectively. The combined energy resolution of photoemission was 0.15-0.2 eV and angular resolution $\pm 1.5^{o}$.

Ultrathin Gd films were prepared *in situ* by depositing Gd thermally onto room temperature W(110)[12] or Cu(100)[4] substrates at a rate of ~1Å/min. as described elsewhere. The pressure during growth was lower than $1x10^{-10}$ torr, while the base pressure was ~$4\text{-}5x10^{-11}$ torr. While it is known that subsequent annealing can improve the magnetic properties substantially for Gd/W(110),[26] the effect is relatively insignificant for photoemission possibly because of the relatively local nature of the photoemission technique. All the results of this work are on "as-deposited" films to ensure the uniformity and purity of the films. The cleanliness of the substrate and films were checked with valence band photoemission, and the ordering was confirmed with LEED. Gd/W(110) was ordered, with diffused LEED spots, while Gd/Cu(100) films were disordered. All the films grow on W(110) with a Gd(0001) surface. The thickness of the films were measured with a quartz-crystal thickness monitor, which is most accurate in terms of the

relative thickness changes rather than the absolute thickness. The sample holder could be cooled with liquid nitrogen, and the temperature was measured with a W5%Re/W25%Re thermocouple which was calibrated with a type-K thermocouple at low temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the constant initial state spectra of Gd for two film thicknesses using the Gd(0001) surface state at E_F, as indicated in the inset, as the initial state. As indicated by the photon energy range, these CIS spectra were taken around the Gd 5p threshold. It is clear that the CIS spectra exhibit well-defined structures. The p-polarized spectra show two peaks separated by ~2eV. The similar structures are observed in p-polarized spectra if the bulk band at binding energy at 1-2 eV is chosen as the initial state, but which do *not* exist if the initial state energy is chosen at background.

The CIS spectra are strongly dependent on the light polarization. The onset of the s- and p-polarized spectra do not match with each other, but instead are shifted by from several hundred meV to 1.7eV depending on film thickness. As shown in Fig. 2, the energy differences of the onset of the p- and s-polarized spectra has a strong thickness-dependence. The shift between the two has a maximum at around 1-2ML. The measurements were done for ordered and disordered Gd films, which show similar trend. At low temperature, such a shift remains even at thicker regions, while at room temperature they decrease to almost zero above 10Å.

In order to understand these data, we first review the resonant photoemission process. In a resonant photoemission process one electron is first excited from the 5p shallow core level to the unoccupied 5d bands. When those unoccupied states are localized enough, the electron can later decay back via an Auger process, i.e., the super Coster-Kronig transition. It can be written as following:

$$5p^6 4f^7 5d^1 6s^2 \rightarrow 5p^5 4f^7 5d^2 6s^2 \rightarrow 5p^6 4f^7 5d^0 6s^2 + e^-$$

This provides an additional channel of photoemission with the same initial and final energy states as the direct process. This additional channel exists only when a resonance between the 5p and empty 5d levels occurs, and should result in an increase in intensity of the surface state at those photon energies. The direct photoemission process, on the other hand, should have a weak, structure-less photon energy dependence. The structure in the CIS intensity is therefore mainly from the resonant photoemission process and indicate the relative energy positions of the flat portions of unoccupied 5d states. In addition, the above process is mainly an intra-atomic process. Since the surface state is chosen as the initial state, our measurements mainly probe the electronic structure localized at surface. As pointed out in previous work, this surface state is highly localized with d_{3z2-r2} (d_{z2}) character.[8,9,12]

The light polarization dependence of the CIS spectra can be understood from the dipole selection rule of the resonant photoemission process. The second Auger process involves two electrons, instead of one, and has little symmetry selection. The first process is photon adsorption which determines, with the dipole selection rules, the symmetry characters of the unoccupied states that can be reached. For the bands along Γ of the Gd(0001), the point group is C_{6v}.. With p-polarized light,

$$A_1\ (p_z) \rightarrow A_1\ (d_{z2});$$

$$E_1(p_{x,y}) \rightarrow E_1\ (d_{xz,\ yz}).$$

Only the unoccupied 5d states with d_{z2} and $d_{xz,\ yz}$ characters can be reached. With s-polarized light,

$$A_1\ (p_z) \rightarrow E_1\ (d_{xz,\ yz});$$

$$E_1(p_{x,y}) \rightarrow A_1\ (d_{z2});$$

$$E_1(p_{x,y}) \rightarrow E_2(d_{x2-y2,\ xy}).$$

In this case, all the 5d states can be reached. A detailed analysis of the transition matrix, in atomic limit,[32] suggests that pure p-polarized light excites 5p electrons into unoccupied $5d_{z2}$ states 4 times more and into $5d_{xz,yz}$ states 2 times more than pure s-polarized light does. S-polarized light, on the

other hand, has a larger cross section for the $d_{x2-y2,xy}$ states. It is therefore clear that the structures in the p-polarized spectra correspond to the empty states with d_{z2} or $d_{xz,yz}$ character.

Based on these symmetry assignments, the relative position of lowest unoccupied d_{z2} state can be identified. The onset of the CIS peaks is the threshold of Gd 5p-5d resonance, that is, the electrons in the 5p core levels are excited to the first dipole-allowed state above E_F. The fact that the onset of p-polarized spectra occurs at higher photon energy than that of s-polarized ones suggests that the density of states near E_F is mainly contributed by the states with $d_{x2-y2,xy}$ states, while the d_{z2} and/or $d_{xz,yz}$ states mainly exist at about several hundred meV to 1.7 eV above E_F.

Realizing that the occupied surface state just below E_F has d_{z2} character, the energy difference between the onset of $d_{x2-y2,xy}$ states and d_{z2}, $d_{xz,yz}$ ones defines the lower bound of the exchange splitting of the surface state, which can be further illustrated with a schematic energy level diagram in Fig. 3. We take the energy shift of the onset values for different light polarization as minimum exchange splitting which is less or equal to the actual exchange splitting. It is therefore possible, as shown in Fig. 2, that the exchange splitting of the surface state changes with Gd thickness and is enhanced at monolayer limit.

The shift approaches zero for the thicker films at room temperature. This is consistent with our inverse photoemission measurements where an empty state near E_F is evident at room temperature. At lower temperature, however, the minimum exchange splitting is clearly non-zero.

Our results are qualitatively consistent with the theoretical predictions that magnetic systems with lower coordination numbers have larger magnetic moments, and therefore larger exchange splitting.[33] As a comparison, we plot the theoretical values[10] of the exchange splitting for the Gd slabs into Fig. 2, which shows a similar trend that enhances at monolayer limit.

It should be noted that exchange splitting is mainly the indication of local moment which tends to increase when the electrons become more localized, as evidenced by their enhancements at surfaces. The maximum of exchange splitting and magnetic moment is reached at atomic limit. While the increase of magnetic moment *could* lead to enhancement of magnetism, it is not a sufficient condition. The Curie temperature is mainly determined by the strength of exchange

interaction, which may or may not scale with the local magnetic moment. Our results on the enhanced exchange splitting therefore do *not* contradict with the scaling of T_C with thickness, where T_C decrease instead of increase at monolayer limit.

IV. CONCLUSIONS

We present our CIS studies of Gd ultrathin films, which clearly show strong light polarization and thickness dependence. We discuss the resonance photoemission process and the dipole selection rules to govern it and therefore made symmetry assignments for the CIS features as resonance from 5p into the 5d states above E_F with different symmetry characters. We postulate that the exchange splitting of the surface state changes with thickness and is enhanced at monolayer limit.

ACKNOWLEDGMENTS

The work at Argonne was supported by the US DOE BES Materials Sciences under contract # W-31-109-ENG-38. Funding was also provided by the National Sciences Foundation through grant # DMR-92-21655 and the Center for Materials Research and Analysis at the University of Nebraska. This work was carried out at the Synchrotron Radiation Center in Stoughton, Wisconsin which is funded by the NSF.

REFERENCES

[1] S.D. Barrett, Surf. Sci. Repts, 14, 271 (1992); A.J. Freeman, and Ruqian Wu, J. Magn. Magn. Mat., 100, 497 (1991)

[2] E. Vescovo, O. Rader, U. Alkemper and C. Carbone, Phys. Rev. B47, 13899 (1993)

[3] R.G. Jordan, Phys. Script. T13, 22 (1986)

[4] P.A. Dowben, D. LaGraffe, and M. Onellion, J. Phys. Cond. Matt. 1, 6571 (1989)

[5] D. LaGraffe, P.A. Dowben and M. Onellion, Phys. Rev. B40, 3348 (1989)

[6] D. LaGraffe, P.A. Dowben and M. Onellion, Mat. Res. Soc. Symp. Proc. 151, 71 (1989)

[7] Dongqi Li, P.A. Dowben, J.E. Ortega, F.J. Himpsel, Phys. Rev. B47, 12895 (1993)

[8] Dongqi Li, C.W. Hutchings, P.A. Dowben, C. Hwang, Rong-Tzong Wu, M. Onellion, A.B. Andrews and J.L. Erskine, J. Magn. Magn. Mater. 99, 85 (1991)

[9] Dongqi Li, C.W. Hutchings, P.A. Dowben, Ron-Tzong Wu, C. Hwang, M. Onellion, A.B. Andrews and J.L. Erskine, J. Appl. Phys. 70, 6565 (1991)

[10] Ruqian Wu, Chun Li, A.J. Freeman and C.L. Fu, Phys. Rev. B44, 9400 (1991)

[11] Ruqian Wu and A.J. Freeman, J. Mang. Magn. Mater. 99, 81 (1991)

[12] Dongqi Li, Jiandi Zhang, P.A. Dowben and M. Onellion, Phys. Rev. B45, 7272 (1992)

[13] W. Nolting, T. Dambeck, and G. Borstel, Z. Phys. B94, 409 (1994)

[14] Dongqi Li, Jiandi Zhang, P.A. Dowben, and K. Garrison, J. Phys. Cond. Matt. 5, L73 (1993)

[15] Dongqi Li, Jiandi Zhang, P.A. Dowben, K. Garrison, P.D. Johnson, H. Tang, T.G. Walker, H. Hopster, J.C. Scott, D. Weller and D.P. Pappas, 313, 451 (1993)

[16] H. Tang, D. Weller, T. G. Walker, J. C. Scott, C. Chappert, H. Hopster, A. W. Pang, D. S. Dessau, and D. P. Pappas, Phys. Rev. Lett. 71, 444 (1993).

[17] A. V. Fedorov, K. Starke, and G. Kaindl, Phys. Rev. B 50, 2739 (1994).

[18] G. A. Mulhollan, K. Garrison, and J. L. Erskine, Phys. Rev. Lett. 69, 3240 (1992).

[19] C. Rau and S. Eichner, Phys. Rev. B34, 6347 (1986)

[20] C. Rau and M. Robert, Phys. Rev. Lett, 58, 2714 (1987)

[21] D. Weller, S.F. Alvarado, W. Gudat, K. Schroder and M. Campagna, Phys. Rev. Lett. 54, 1555 (1985)

[22] D. Weller and S.F. Alvarado, Phys. Rev. B 37, 9911 (1988).

[23] C. Rau, J. Magn. Magn. Mater. 30, 141 (1982)

[24] M. Farle, and K. Baberschke, Phys. Rev. Lett., 58, 511 (1987)

[25] K. Baberschke, M. Farle, and M. Zomack, Appl. Phys A44, 13 (1987)

[26] U. Setter, M. Farle, K. Baberschke and W.G. Clark, Phys. Rev B 45, 503 (1992)

[27] M. Farle, K. Baberschke, U. Stetter, A. Aspelmeier, and F. Gerhardter, Phys. Rev. B 47, 11571 (1993).

[28] P.A. Dowben, D. LaGraffe, Dongqi Li, A. Miller, Ling Zhang, L. Dottl, and M. Onellion, Phys. Rev. B43, 3171 (1991).

[29] G.J. Lapeyre and J. Anderson, Phys. Rev. Lett., 35, 117 (1975)

[30] C.T. Chen, L.H. Tjeng, J. Kwo, H.L. Kao, P. Rudolf, F. Sette and R.M. Fleming, Phys. Rev. Lett., 68, 2543 (1992)

[31] H. Ueba, Surface Science, 242, 266 (1991)

[32] A. Bianconi et al., Phys. Rev. B 44, 10126 (1991)

[33] A. J. Freeman and Ru-qian Wu, J. Magn. Magn. Mater. 100, 497 (1991).

FIGURES

Figure 1. Constant initial state spectra of Gd films at normal emission with the initial state chosen as the surface state near E_F as indicated in the inset. The circles and the triangles are the spectra taken with more s- and p-polarized light respectively. Inset: Photoemission spectrum of Gd film at EDC mode taken at normal emission with photon energy of 33 eV. The Gd 4f, Δ_1 bulk band and surface state are indicated.

Figure 2. Minimum exchange splitting as discussed in the text. Filled diamond: Gd/W(110) at 210K; open square: Gd/W(110) at 295K; filled square: Gd/Cu(100) at 230K. The calculated exchange splitting for ferromagnetic surface layers[10] are indicated with crosses in the figure for comparison.

Figure 3. Schematic of energy levels of Gd. The actual exchange splitting and the minimum exchange splitting are indicated in the figure.

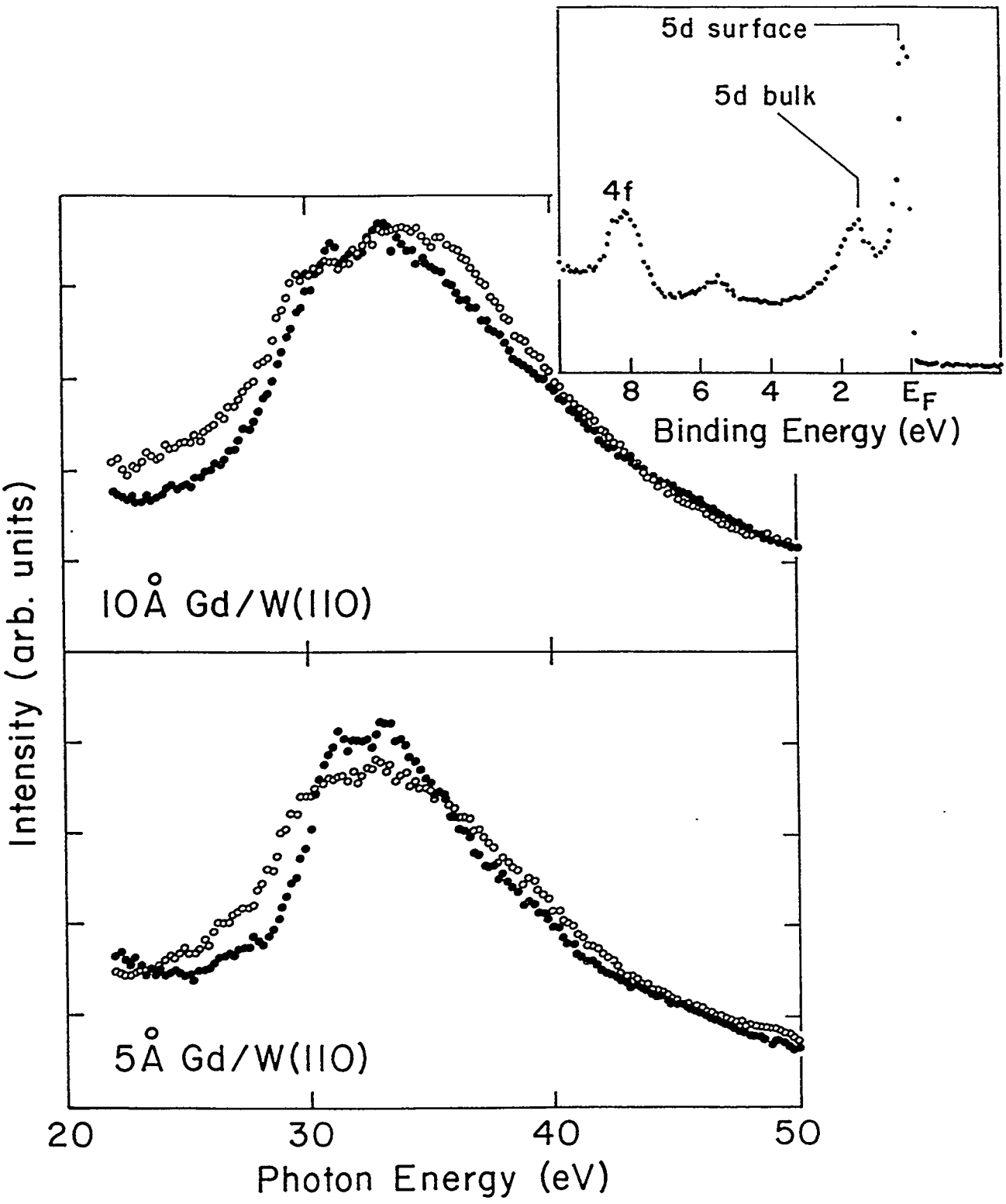

Fig. 1 SS1 - We A9

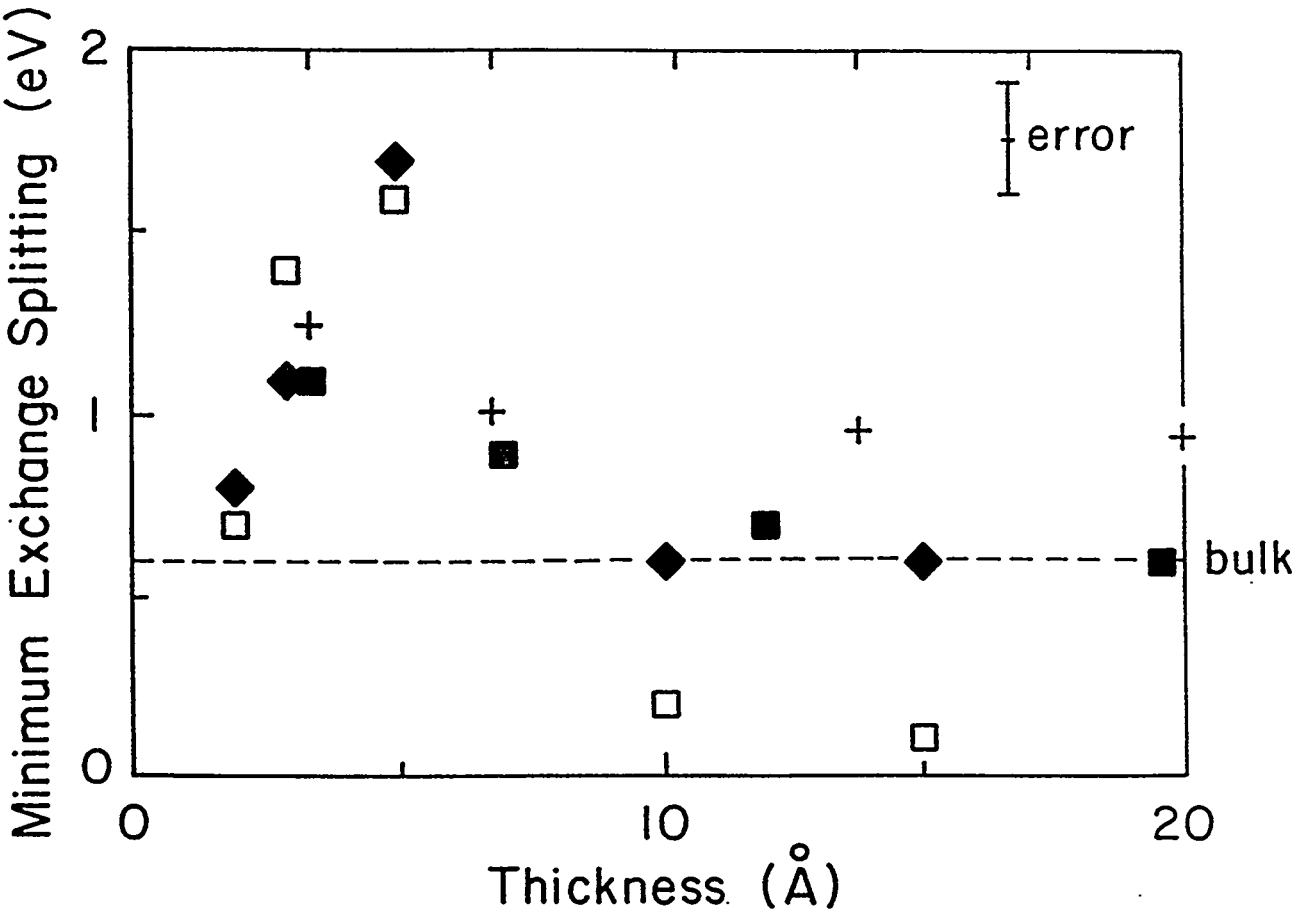
Minimum Exchange Splitting (eV)
2
1
0
0
10
20
Thickness (Å)
error
bulk

Fig. 2 SS-We A9

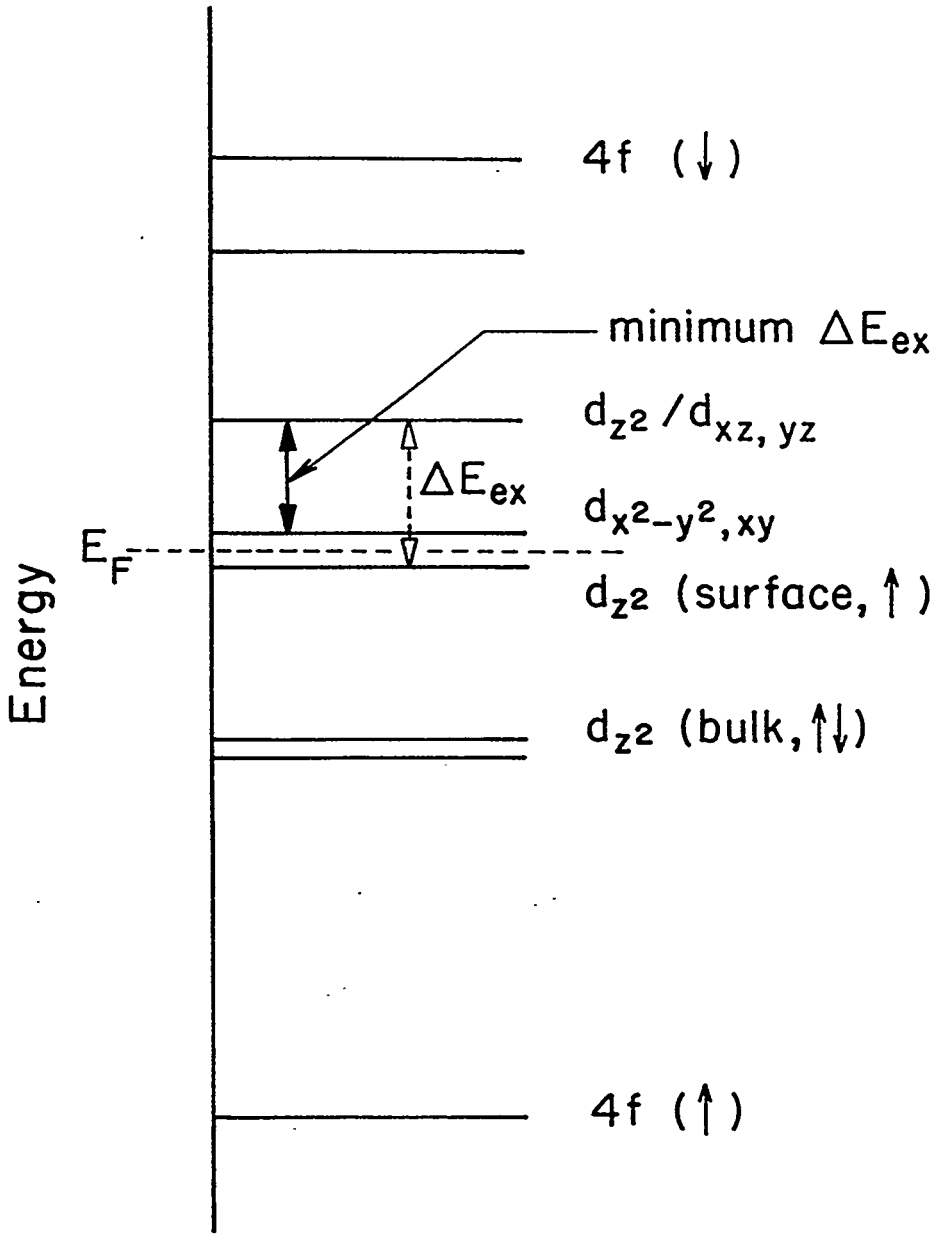
4f (↓)
minimum ΔE_{ex}
d_{z^2} / $d_{xz, yz}$
ΔE_{ex}
$d_{x^2-y^2, xy}$
E_F
Energy
d_{z^2} (surface, ↑)
d_{z^2} (bulk, ↑↓)
4f (↑)

Fig. 3 SS-WeA