John von Neumann Institute for Computing



Ultra-Thin Magnetic Films and Magnetic Nanostructures on Surfaces

Gustav Bihlmayer, Paolo Ferriani, Stephanie Baud, Marjana Ležaić, Stefan Heinze, and Stefan Blügel

published in

NIC Symposium 2006 ,
G. Münster, D. Wolf, M. Kremer (Editors),
John von Neumann Institute for Computing, Jülich,
NIC Series, Vol. **32**, ISBN 3-00-017351-X, pp. 151-158, 2006.

© 2006 by John von Neumann Institute for Computing
Permission to make digital or hard copies of portions of this work for personal or classroom use is granted provided that the copies are not made or distributed for profit or commercial advantage and that copies bear this notice and the full citation on the first page. To copy otherwise requires prior specific permission by the publisher mentioned above.

http://www.fz-juelich.de/nic-series/volume32

Ultra-Thin Magnetic Films and Magnetic Nanostructures on Surfaces

Gustav Bihlmayer[1], **Paolo Ferriani**[2], **Stephanie Baud**[3], **Marjana Ležaić**[1], **Stefan Heinze**[2], **and Stefan Blügel**[1]

[1] Institute for Solid State Research, IFF
Research Centre Jülich, 52425 Jülich, Germany
E-mail: {g.bihlmayer, m.lezaic, s.bluegel}@fz-juelich.de

[2] Institute for Applied Physics
University of Hamburg, 20355 Hamburg, Germany
E-mail: {pferrian, sheinze}@physnet.uni-hamburg.de

[3] Laboratoire de Physique Moléculaire, UMR
CNRS 6624, Université de Franche-Comté, F-25030 Besançon Cedex, France
E-mail: stephanie.baud@univ-fcomte.fr

We present *ab initio* calculations of low-dimensional systems with complex magnetic ground states. The computational method and its efficient implementation on massively-parallel supercomputing architectures is outlined and characteristic examples from the field of ultra-thin magnetic films and nanowires on stepped surfaces are given. These calculations allow not only the description of the ground state properties, they may be also exploited for the prediction of finite-temperature properties of this technologically important class of materials.

1 Introduction

The miniaturization of magnetic data storage devices forces modern technology to store a bit of information on increasingly smaller units of magnetic material. In the limit of a few hundred atoms that are supposed to represent this bit on a microscopic level, the stability of the magnetic structure is pushed to its limits. External fields or thermal fluctuations may destroy the magnetic order easily and thus render the storage device unuseful for many applications. The magnetic boundary between individual bits may become larger than the bits themselves. Such technological problems call for the development of new materials that are able to overcome the limitations of conventional magnetic storage materials. The Institute for Solid State Research (IFF) investigates various possible candidates for new device technology including ferroelectric materials, tunneling magnetoresistance structures, and improved magnetic material combinations. In the following examples, we will focus on the latter.

An understanding of the magnetic properties on a microscopic level can only be gained on a quantum-mechanical level. The institute Theory I in the IFF has, therefore, developed computational methods to investigate theoretically these properties based on quantum-mechanics. Such methods that require no experimental input parameters are often referred to as *ab initio* methods. The computational effort of an *ab initio* investigation of "real" materials can be tremendous and it is the combination of high-performance computing and theoretical material science that lies on the basis of success. In this respect, only the close collaboration between the Central Institute for Applied Mathematics (ZAM) and the IFF

in the Research Centre Jülich made it possible to perform leading-edge material science calculations.

2 Method & Computational Scheme

Density functional theory provides the framework of most *ab initio* methods used in solid-state physics. The quantum-mechanical equations at the basis of this theory are differential equations similar to the Schrödinger equation. They determine the wavefunctions, from which all further properties of the studied system are derived, most important of which is the electron density n entering the density functional theory. If these wavefunctions are expanded in basis-functions, the differential equation can be recast in the form of a standard problem of linear algebra, the eigenvalue problem

$$\mathcal{H}[n]\mathbf{c} = \epsilon\mathcal{S}\mathbf{c} \tag{1}$$

where the matrices $\mathcal{H}$ and $\mathcal{S}$ are of the dimension of the number of the used basis-functions. The problem is to determine the eigenvector $\mathbf{c}$, that specifies the wavefunction and the scalar ϵ that is the eigenvalue corresponding to the wavefunction. In general the ground state density n is unknown. Giving a start density, the solution of Eq. (1) determines the density entering again in Eq. (1). Obviously, this defines a selfconsistency problem in which Eq. (1) is solved during each self-consistency step.

In an infinite periodic system the number of basis-functions, that have to be used, is of course infinite. But the translational symmetry of the periodic crystal allows to block-diagonalize the matrices $\mathcal{H}$ and $\mathcal{S}$ into an infinite number of finite matrices that are labeled by a vector, the $\mathbf{k}$-point. The size of one such matrix is determined by the chemical and structural complexity of the system at study, i.e. the larger the unit-cell of the crystal, the larger the size of the matrix. Of this infinite number of matrices, only a subset is actually calculated and then an interpolation is done, to account for the remainder. Here, a small unit-cell (or periodicity) requires a larger set of samples that have to be taken for the interpolation.

In summary, the (main) computational problem consists of either the solution of a few large eigenvalue problems or the solution of many small ones. Both tasks can be parallelized, the latter one very simple and efficiently by distributing the small eigenvalue problems over individual nodes of a parallel-computer. Distribution of a single, large eigenvalue problem over many nodes can be handled by optimized libraries like ScaLAPACK. This kind of parallelization requires more communication than the previous one, but reduces the memory requirements on a singe node, thus enabling calculations of systems with very large unit cells. Our parallelization scheme, employed in the FLEUR-code[1] relies on a combination of both strategies to optimize the performance for all types of problems (cf. Fig. 1)

Compared to non-magnetic problems, the accurate treatment of magnetic systems in density functional theory is a computationally much more demanding task: non-collinearity (i.e. if the magnetic order is not simply ferro-, ferri- or antiferromagnetic) and/or spin-orbit coupling effects increase the dimension of the eigenvalue problem by a factor of two. The magnetic unit cell is usually larger than the chemical one, and its size is generally not known in advance. The symmetry, that can be exploited in these calculations is normally reduced (e.g. changing a real symmetric eigenvalueproblem into a

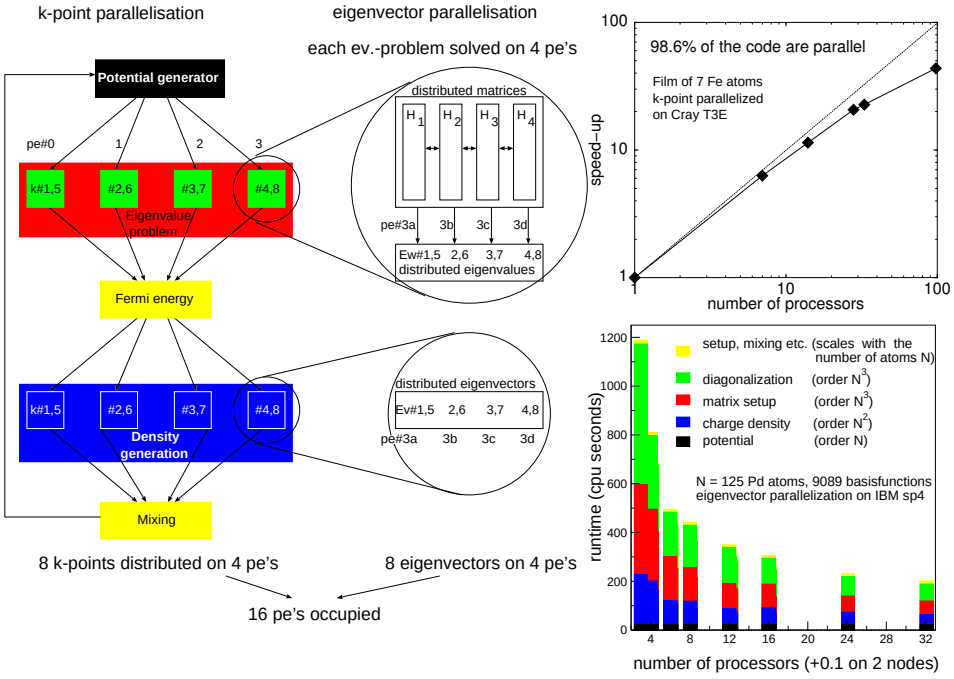


Figure 1. Combined parallelization used in the Fleur-code: depending on the problem, either a large number of small matrices or a small number of large matrices have to be diagonalized. In the former case, the "k-point parallelization" is most efficient, the latter case calls for "eigenvector parallelization". Both schemes can be combined as indicated on the left. Performance tests (right) allow to find optimized ways, how both parallelizations should be combined for specific problems.

complex hermitian one) and the involved energy scales are very small. Not many *ab initio* methods worldwide are suited for such complex calculations. The full-potential linearized plane wave method, as implemented in the FLEUR-code, provides a powerful tool for the computational investigation of general, non-collinear magnetic structures[2].

3 Applications

Low-dimensional magnetic systems differ in many respects from what is known from bulk structures: the magnetic order, the ordering temperature, the magnetization direction, the magnetic domains and their separating walls are not only different in a thin film or a wire, they can also depend on different physical parameters than in a three-dimensional solid. While in bcc Fe, hcp Co, or fcc Ni the magnetic properties are mainly determined by the elements interaction with its 8 or 12 nearest neighbor atoms, in low dimensions the coordination is reduced (2 – 6 nearest neighbors) and a more "atomic like" behavior can be observed: the magnetic moment is higher, orbital magnetism becomes important, the ordering temperatures (in the ferromagnetic case the Curie temperature) is lowered. Since the thin film or wire has usually to be stabilized on a supporting surface, interactions with this substrate can further influence the magnetic properties.

3.1 Thin Magnetic Films

Thin films of iron or manganese on a transition-metal substrate illustrate the peculiarities met in low-dimensional systems: the spin moment of Fe, which is $2.2\mu_{\mathrm{B}}$ in bcc Fe, increases to $2.7\mu_{\mathrm{B}}$ for a Fe monolayer on Cu(111) and even $3.2\mu_{\mathrm{B}}$ on Ag(111). On the weakly interacting close-packed surfaces of the coinage metals Cu and Ag, that only provide a template on which the Fe atoms are grown, the magnetic (spin) moment increases to almost atomic-like values ($4\mu_{\mathrm{B}}$). Also on the (001) surface of Cu, Fe has a large magnetic moment, and in all these examples Fe forms a ferromagnetic film. Unfortunately, this ferromagnetic order, which is technologically desirable, is not very stable against temperature fluctuations. The weak interaction with the substrate, which on the one hand increases the magnetic moment, on the other hand does nothing to increase the Curie temperature, which is – in these systems – determined both by the (exchange) interactions to the neighboring atoms and by the magnetic anisotropy, a relativistic effect. The latter effect is strong for heavy atoms, but the atoms at the bottom of the periodic table do not easily form magnetic moments in the condensed state. Therefore, combinations of light magnetic species and heavy substrate atoms become technologically more and more important.

If one tries to increase the interaction with the substrate and the magnetic anisotropy by e.g. replacing copper by the heavier element tungsten, surprisingly also the magnetic order is changed: a monolayer of Fe on W(001) is no longer ferromagnetic, but shows instead a checkerboard like magnetic structure (cf. Fig. 2). This unexpected change of magnetic order was not only predicted by our calculations, it was also confirmed experimentally[3]. But further calculations revealed more surprises: many magnetic elements change their magnetic ground state on the W(001) substrate, Co becomes antiferromagnetic, but Cr and Mn, normally antiferromagnetic, turn into ferromagnets with large spin moments[4]. Using different substrates, it is possible to tune the magnetic interactions to form a variety of magnetic structures in a way unknown in bulk systems.

Beautiful examples of complex magnetic structures are formed, when the magnetic interactions are on the border between antiferromagnetic and ferromagnetic and for certain topologies of the crystal lattice: e.g. we have predicted a complex, three-dimensional magnetic structure for Mn on Cu(111), which is formed from four chemical unit cells[5]. Recently, a magnetic structure consisting of at least 15 chemical unit cells was found experimentally for Fe/Ir(111)[6]. Theoretical considerations have shown, that such a magnetic structure can arise from an even more complex non-collinear state, which is currently under investigation. The unit cells required for such a study contain 150 atoms and the matrices, that have to be diagonalized numerically require not only more than 10 GB of memory, but also computing time that is only available on massively parallel supercomputers.

While these magnetic superstructures are probably only stable at low temperatures, other complex magnetic patterns are formed when the temperature is above zero. A snapshot of an (e.g. ferro-) magnetic material at finite temperatures will show a superposition of various elementary magnetic excitations, or magnons, which form a non-collinear magnetic state. *Ab initio* calculations of these snapshots allow – in conjunction with statistical methods – to access important material properties like the Curie temperature[7]. As we pointed already out, the ordering temperature of two-dimensional systems depends not only on the interactions between the neighboring spins in the lattice, but also on the interaction of the spin with the field of the crystal lattice itself. This arises from spin-orbit interaction and our method allows us to investigate this tiny relativistic effect (which be-

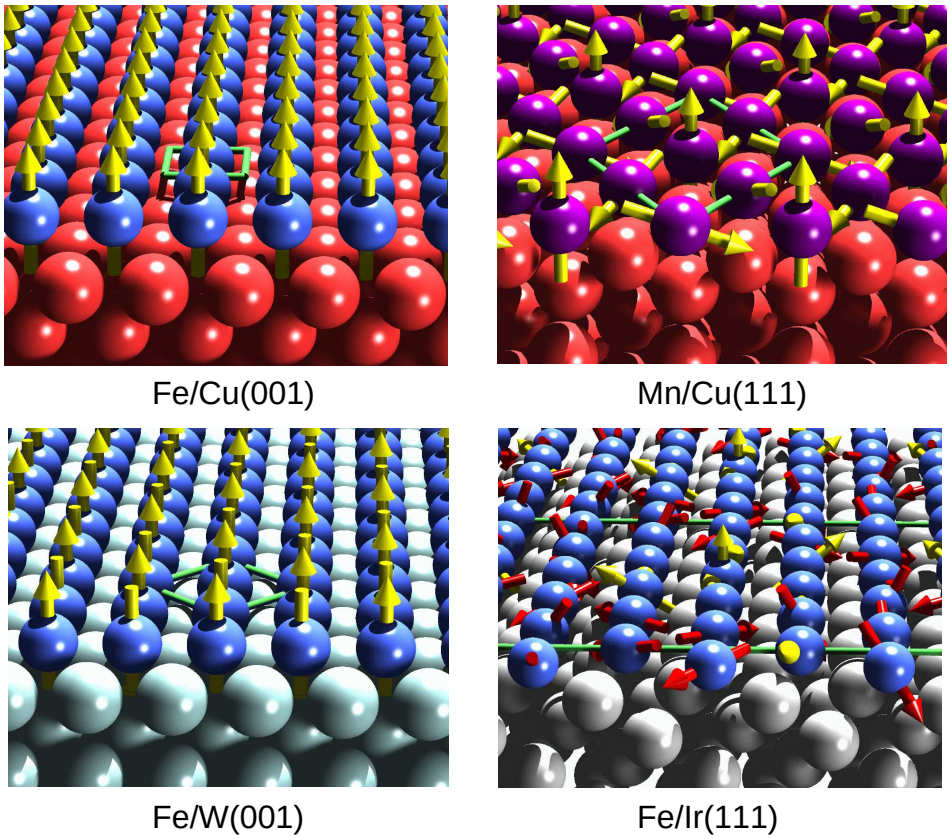


Figure 2. Magnetic structures of thin Fe and Mn films on different substrates: on a square lattice, like Cu(001), collinear magnetic order is common, on triangular lattices, like Cu(111), more complex, non-collinear magnetic ground states can be obtained. The magnetic ground-state of Fe on Ir(111) (lower right) is currently under investigation.

comes important on a large scale) from first principles. To determine this effect accurately, a large number of **k**-points has to be sampled, requiring that many eigenvalue-problems have to be solved.

3.2 Magnetic Nanostructures

Even more exotic properties can be encountered in magnetic materials, when the dimensionality is lowered further to one or zero dimensions. Of course, in practice these wires or clusters have to be supported on some substrate again, so that strictly speaking only quasi-lowdimensional structures are obtained. But experimental techniques have been refined in the last years, to produce well-defined magnetic nanostructures and to characterize their magnetic properties in some detail.

One way to stabilize a one-dimensional magnetic structure is to grow magnetic atoms along the step-edges that occur on surfaces. E.g. a Pt(997) surface has rather smooth

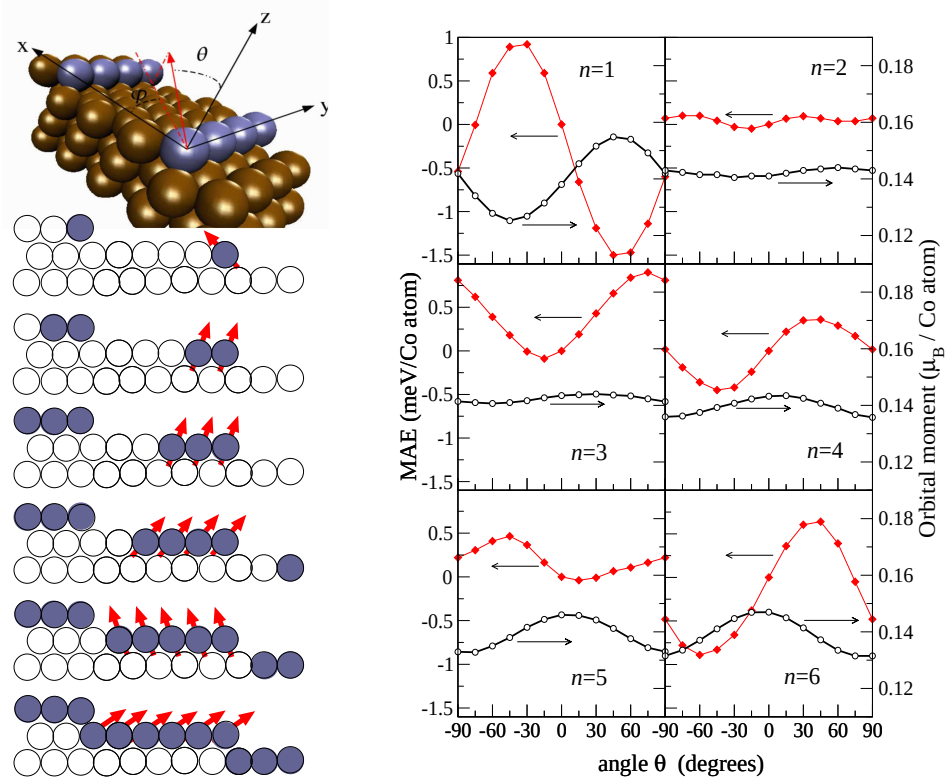


Figure 3. Left: Schematic picture of a single Co chain on a stepped Pt substrate (top) and chains of different width ($n = 1-6$) on a step-edge. The magnetization direction (indicated by red arrows) oscillates as the wires increase in width. Right: Magnetocrystalline anisotropy energy (MAE, full diamonds) and average orbital moment on Co (empty circles) for Co chains of different width (denoted by n) on Pt(664). Note the different scales for MAE (left) and orbital moments (right).

step-edges that are separated by about 2nm and close-packed Pt(111) terraces in between. Experimentally, it was possible to grow not only a singe Co-wire along these edges, but also thicker wires consisting of n strands ($n = 2, 3, 4, ...$). The magnetic measurements of these wires revealed a peculiar behavior[8]: While the magnetization of the single wire is perpendicular to the wire-axis and points towards the upper terrace, for thicker wires the direction of the magnetization changes towards the lower terrace and finally – for a closed Co overlayer – stands perpendicular to the vicinal surface. The magnetic anisotropy also oscillates from large ($n = 1$), to very small ($n = 2$) then rises again for $n = 4$, and finally settles down to the value known for Co layers on Pt(111).

To explain this surprising magnetic behavior, we performed *ab initio* calculations of Co wires on a Pt(664) surface[9,10]. On this surface, the step-edges are a little bit denser packed than on Pt(997), nevertheless the unit-cells required to calculate this surface has to include already 45 atoms. In such a calculation the surface is modeled by a film of finite thickness, so that the innermost layer of this film has already bulk-like properties. In

the present case this thickness corresponds to about 7 Pt(111)-type layers. We studied the effects of relaxation for the case of a single Co wire on this surface[9]. To compensate for the loss of coordination, these relaxations tend to decrease the distance of the step-edge atoms to their nearest neighbors, restoring partially a bulk-like magnetic behavior (e.g. smaller orbital moments and a smaller magnetic anisotropy). But this effect seems to be counteracted by the increasing importance of correlations in low-dimensional materials, so that experimentally the signatures of low-dimensional magnetism are clearly seen.

Our calculations of thicker Co wires not only revealed the same oscillatory behavior of the magnetization direction and magnetic anisotropy as was found experimentally (cf. Fig. 3), with the help of our calculations we can also propose a simple physical model that accounts for the experimental observations[10]: If we decompose the overall magnetic properties into contributions of the individual strands of the multi-wires, we can identify four different types of strands, which show a characteristic behavior of the magnetic properties on the magnetization direction (which we can choose freely in the calculation). Since exchange-coupling requires all the magnetic moments of the wires to point in a common direction, this can lead to frustration effects: Properties, like the magnetic anisotropy of the multi-wire can get very small as compared to a single wire, due to a compensation of contributions of different strands. This explains e.g. the tiny anisotropy of the double-wire, but also the increase of the anisotropy in thicker wires.

4 Conclusion

We presented examples of calculations of magnetic monolayers of Fe and Mn on different substrates, as well as Co wires on stepped surfaces. Due to their complexity, these calculations quickly go beyond the limits of conventional computational resources and call for supercomputers as provided by the John von Neumann Institute for Computing (NIC) and the Central Institute for Applied Mathematics (ZAM) in the Research Centre Jülich. The close connection to experimental institutes within and outside the Research Centre in combination with a critical amount of CPU time on supercomputers gives us a cutting edge in responding to the challenging questions in the physics of modern magnetism and on magnetic materials with technological relevance where the investigation by *ab initio* calculations can lead to deeper understanding and the prediction of new promising materials.

Acknowledgments

We are indebted to Dr. Inge Gutheil for her help with the handling of the ScaLAPACK libraries and for the coding of the interface. All calculations were performed with a grant of computer time provided by the VSR of the Research Centre Jülich.

References

1. `http://www.flapw.de`.
2. Ph. Kurz, F. Förster, L. Nordström, G. Bihlmayer, and S. Blügel, *Ab initio treatment of noncollinear magnets with the full-potential linearized augmented plane wave method*, Phys. Rev. B **69**, 024415 (2004).
3. A. Kubetzka, P. Ferriani, M. Bode, S. Heinze, G. Bihlmayer, K. von Bergmann, O. Pietzsch, S. Blügel, and R. Wiesendanger, *Revealing Antiferromagnetic Order of the Fe Monolayer on W(001): Spin-Polarized Scanning Tunneling Microscopy and First-Principles Calculations*, Phys. Rev. Lett. **94**, 087204 (2005).
4. P. Ferriani, S. Heinze, G. Bihlmayer, and S. Blügel, *Unexpected trend of magnetic order of $3d$ transition-metal monolayers on W(001)*, Phys. Rev. B **71**, 024452 (2005).
5. Ph. Kurz, G. Bihlmayer, K. Hirai, and S. Blügel, *Three-Dimensional Spin-Structure on a Two-Dimensional Lattice: Mn/Cu(111)*, Phys. Rev. Lett. **86**, 1106 (2001).
6. K. von Bergmann, S. Heinze, M. Bode, E.Y. Vedmedenko, G. Bihlmayer, S. Blügel, and R. Wiesendanger, *Observation of a complex nanoscale magnetic structure in a hexagonal Fe monolayer*, Phys. Rev. Lett. , submitted (2005).
7. M. Ležaić, Ph. Mavropoulos, J. Enkovaara, G. Bihlmayer, S. Blügel, *Influence of thermal spin fluctuations on the half-metallic band gap*, Phys. Rev. Lett. , submitted (2005).
8. P. Gambardella, A. Dallmeyer, K. Maiti, M. C. Malagoli, S. Rusponi, P. Ohresser, W. Eberhardt, C. Carbone and K. Kern, *Oscillatory Magnetic Anisotropy in One-Dimensional Atomic Wires*, Phys. Rev. Lett. **93**, 077203 (2004).
9. S. Baud, Ch. Ramseyer, G. Bihlmayer, and S. Blügel, *Relaxation effects on the magnetism of decorated step edges: Co/Pt(664)* Phys. Rev. B , submitted (2005).
10. S. Baud, G. Bihlmayer, S. Blügel, and Ch. Ramseyer, *Magnetic anisotropy of Co n-wires ($n = 1 - 6$) on Pt(664)* Surf. Sci. , submitted (2005).