Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

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Contents

1 Editorial

In the **General News** section there is some information on distributing the *Psi-k Newsletters* and on the Psi-k 2000 Conference. In the section **News from the TMR1 Network** readers will find scientific highlights of the TMR1 Network summarizing the past two years of its activity. In the section **News from the TMR2 Network** there is an annual review of the first year activity of the TMR2 Network. Also, in this *Newsletter* we have a new section devoted to the UK's CCP9 programme, where a report and abstracts of contributed talks of a **"One day KKR meeting"** at Daresbury are presented. After the **Abstracts** section we have an annoncement of a special issue of the *Computational Materials Science* journal on **"Tight-Binding Molecular Dynamics Simulations in Materials Science"**. Please check the table of content for details on reports and variety of announcements.

The scientific highlight by *E. Hernández* (Sussex) and *A. Rubio* (Valladolid) is on **"Nanotubes: Mechanical and Spectroscopic Properties"**.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resour ce Locator* (URL) is:

http://www.dl.ac.uk/TCSC/HCM/PSIK/main.html

The above contains pointers to home pages of some of the members of our electronic structure community. If you maintain a home page on your activities we will be happy to include a pointer from the *Networks'* home page to your home page.

Please note that the home page of the Psi-k Networks has recently been updated. It contains useful information regarding funding of workshops and collaborative visits within the ESF Programme. Its major new feature is a separate highlight section which contains all highlight articles of the Newsletters published so far.

Please submit all material for the next newsletters to the email address below.

The following email addresses, which remain in operation, are repeated for your convenience, and are the easiest way to contact us.

	function
psik-coord@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

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2 General News

2.1 Distribution of Psi-k Newsletters

It has been suggested to us that many recipients of the Psi-k Newsletter may prefer to download the newsletters from WWW instead of processing the distributed electronically latex or postscript files. It has also been indicated that for some of our readers pdf-file would be a preferred option.

Readers may not have been aware that the latex- and postscript files have always been available at:

`http://www.dl.ac.uk/TCSC/HCM/PSIK/newsletters.html`

From now on also the pdf-files will be available at the above address. However, as usually, we shall keep on distributing the newletters electronically. The reason being, that the spectrum of our readers is very broad and the facilities at their disposal are not always of the same standard.

Please note that the information on the above URL locator is given at the very beginning of the latex document of the newsletter, in the percentaged area, containing details on the length of the newsletter, issue, etc.

We would appreciate any comments and suggestions for improvements from all our readers. Thank you.

2.2 Psi-k 2000 Conference

Schwäbisch Gmünd, 22-26 August, 2000

"Ab initio Electronic Calculations for Elucidating the Complex Processes in Materials"

The organization of the conference is firmly on its way. We have a first circular on the web. It contains a preliminary timetable which we also print below.

There was a mistake in the previous newsletter, stating that the date of the conference was September 2000. Apologies for that. Of course the conference will take place in August 2000. We shall be distributing posters announcing the conference within next two months or so.

Please do keep on checking for an updated information on the **Psi-k 2000 Conference** at:

`http://www.dl.ac.uk/TCSC/HCM/PSIK/psi-k2000.html`.

PROVISIONAL TIMETABLE

March	1999	First circular on the WWW
October	1999	Second circular, suggestions for symposia and invited speakers
December	1999	Deadline for suggestions
March	2000	Third circular, details on symposia and speakers
May	2000	Deadline for submission of abstracts and registration
June	2000	Final programme
August	2000	The Conference

3 News from the TMR1 Network

TMR-Network on "Interface Magnetism"

3.1 Midterm Review: Scientific Highlights

A Series of New, Highly Accurate and Efficient KKR-Codes

The tight-binding KKR-Green's function method represents an original and unique product of our Network, which has led to a series of new, highly accurate and efficient KKR codes which are not matched by any other program worldwide. The project was started with a joint publication of the Vienna and Juelich team, who showed that the well-known Korringa-Kohn-Rostoker (KKR) theory can be exactly transformed into a "screened" representation with structure constants decaying exponentially in space. This concept has proved to be extremely powerful for layered systems since the numerical effort scales linearly with the number of monolayers and since it allows for an exact solution of the halfspace problem. Thus, the project has lead to exciting activities in three nodes of the network. The Austrian team has performed with this method extensive fully-relativistic calculations for the magnetic anisotropy of layered systems and for the Giant Magnetoresistance which are reported elsewhere. Their scheme was recently extended to include the layer relaxations. The Juelich-Dresden teams have developed TB-codes for the slab-, halfspace- and multilayer-geometry and applied them in very accurate calculations for interlayer coupling and quantum well states. Based on the Green's functions of these reference systems codes for the calculations of impurities at surfaces and interfaces have been developed. In parallel to this a full-potential code for ideal surfaces and defects on surfaces has been constructed by the Juelich group. The Munich-Juelich teams have started a large effort to extend practically all existing scalar relativistic KKR programs into a fully relativistic Dirac scheme with spin polarisation. At present fully relativistic codes exist already for the bulk, for impurities in the bulk, for surfaces and for impurities on surfaces. Finally, the Daresbury group is working on a flexible real space code using sparse matrix techniques for applications to photoemmission and other spectroscopies. All these coherent and complementary program developments open up a bright perspective for the application of the KKR-Green's function method, which is not restricted to typical ground state calculations, but just allows as well applications to problems connected to spectroscopy, transport and linear response. Most of the above activities would not have happened without the existence of this Network.

GMR: Spindependent Propagation versus Spindependent Scattering

Although the phenomenon of Giant MagnetoResistance (GMR) was discovered only ten years ago, a technology based on the effect was developed very rapidly and is now available in high-end

products. The explanation of GMR has been the subject of some controversy with early phenomenological theories concentrating on spin-dependent scattering to explain the effect. The early discussions were almost entirely focussed on the issue of the importance of bulk versus interface scattering; the origin of the spin-dependent scattering and the influence of the complex transition metal bandstructure were almost completely neglected. A scientific highlight of our Network is the insight gained into the origin of GMR by the German and Dutch groups. Both have demonstrated that bandstructure effects make a major contribution to GMR. The German team has used calculated Fermi surface velocities and wavefunctions to analyse the effect of impurity scattering at different sites in Co/Cu (001) multilayers in the current-in-plane (CIP) and the current-perpendicular-to-plane (CPP) configurations. They conclude that the CIP transport is particularly sensitive to the presence of impurities at the interface. The Dutch team studied the origin of the interface resistance which occurs in the very successful "resistor model" used to describe the dependence of multilayer resistances on the thickness of the layers in the CPP configuration. They first derived an expression for the interface resistance in terms of a phenomenological model for the diffuse bulk scattering and of the transmission and reflection matrices used to describe specular interface scattering. The resulting expressions were evaluated for Co/Cu multilayers by calculating the specular scattering for single interfaces using the Green's function embedding method. Values of the interface resistances in very good agreement with the experimental values were found. The same methodology of transmission and reflection matrices has been used to study ballistic transport through magnetic domain walls, a subject of considerable current interest. The Austrian Group has recently started an ambitious project to evaluate the CIP resistance of disordered magnetic multilayers and spinvalves based on the Kubo formula. The method uses the TB-KKR Green's function method, with the disorder being described by the CPA for layered systems, in this way allowing a realistic description of both the band propagation as well as the disorder scattering. As a special highlight recently the Motorola Spin Valve has been simulated by these ab-initio techniques, yielding a GMR value in excellent agreement with experiment. For the next years we expect an even stronger effort of the network in the field of spindependent transport, which, as a response to the changing activities of our industrial partner Philips, will also include calculations of the Tunneling Magnetoresistance (TMR). Concluding from these highlights we note that also in the field of spindependent transport the members of our network belong to the leading international contenders.

News from Perpendicular Magnetism

The spin-orbit induced Magnetic Anisotropy is of vital importance for the fundamental understanding of magnetism as well as for practically all technological applications. For these reasons four Network nodes have concentrated their efforts towards an understanding of the magnetic anisotropy in layered systems. Of special interest is the Ni_n/Cu(001) system, since it is the only known system in which the orientation of the magnetisation switches with increasing thickness from in-plane to perpendicular. As the Austrian team found, the secret for this peculiar behaviour turned out to be a tetragonal distortion in the Ni-film, namely a contraction of the interlayer distance as compared to the one in the Cu substrate. The Swedish team complemented these thin film results with calculations for bulk Ni, being tetragonally distorted as to

resemble the geometry of epitaxial films. Both calculations basically came to the same conclusions, and the calculated anisotropy constants of the Ni film are in excellent agreements with experimental values. The Austrian team also studied the reorientation transition in the alloy system $(Fe_xCo_{(1-x)})_n/Cu(001)$, which with increasing thickness and varying composition shows a very rich reorientation phasediagram. The calculations show that the driving force for the reorientation is closely related to the occurrence of antiferromagnetic ordering between the layers which naturally depends strongly on the concentration of Fe. Thus, the theory gives an astonishingly simple explanation of the complicated thickness and composition dependence observed experimentally. An exciting highlight concerns the manipulation of the magnetic anisotropy of Fe, Co and Ni layers by applying an electric field. Extensive calculations by the Juelich group show that it is possible to switch the magnetisation direction by applying an electric field to the layers. This might e.g. be realised by applying a voltage on an STM tip. The effect represents a completely new discovery and could be of interest for technical applications, e.g. magnetic writing with an STM tip. Another technologically interesting system is (CoPt) layers on Pt substrates which are used in most magneto-optical devices. Here it could be shown by the Austrian team that - as compared to Co films on Pt(001) and Pt(111) - only for (CoPt) superstructures with tetragonal symmetry the magnetisation is strongly oriented perpendicular to plane, whereas interdiffusion reduces this effect very strongly. Complimentary calculations were performed by the UK team for disordered CoPt bulk alloys, showing that the inclusion of short-range order of the (CoPt) superstructure type increased the anisotropy by orders of magnitude, in qualitative agreement with the film results of the Austrian team. In summary the large number of highly interesting results on perpendicular magnetism shows that our Network has internationally the leading position in this important field.

Interlayer Coupling: Seeing the Fermi Surface in Real Space

The phenomen of interlayer exchange coupling of two magnetic layers by a non-magnetic metallic spacer was discovered by Gruenberg more than 10 years ago. In a now classic paper our Network member P. Bruno showed that the oscillations of the interlayer coupling in real space are attributed to stationary calipers of the spacer Fermi surface. Due to the establishment of our network a substantial increase of the theoretical activities on interlayer coupling occured to which all six network nodes contributed. A particular strong effort came from the combined Austrian, German and French teams. Among the highlights are a careful study of the alloying effects on interlayer coupling due to interdiffusion at the interface, due to alloying of the magnetic layer and of the spacer material. An off-spring was e.g. the vertex cancellation theorem, which proves that in disordered systems the coupling can be calculated by the ensemble averaged Green's function. Other highlights are the direct relation of interlayer coupling to the spin-dependent reflectivity at the interface as well as to the occurance of quantum well states in the spacer material. Excellent agreement was obtained between the calculated quantum well states of Co/Cu(001) and the experimental results of our collegues at Juelich. In detail and in parallel to experimental studies of the industrial partner Philips the oscillatory dependence of the coupling with magnetic layer thickness were studied, and in addition an oscillatory dependence with the thickness of caplayers was predicted. A recent interesting study concerns the

temperature dependence of the interlayer coupling, where considerable progress in the understanding was achieved. The Swedish group made among others some important contributions to quantum well states. In addition to mediating the coupling of the magnetic layer these can lead e.g. to the on-set of magnetism in an otherwise non-magnetic layer. They also showed that quantum well states can lead to an oscillatory dependence of the magnetic anisotropy on the thickness of the magnetic caplayer. The UK node focussed on the ab-initio calculation of the asymtotic expression for the interlayer coupling, i.e of the period, amplitude and phase of the oscillation and their relation to the Fermi surface. In particular they showed, that the periods in the Fe/Cr and Fe/$Cr_{1-x}V_x$ system are directly related to the hole pocket at the N-point of the Brillouin zone. Moreover they point out that the oscillatory coupling is an important new technique for probing the Fermi surfaces of random alloys. In total the contributions of our Network have greatly improved the understanding of interlayer coupling. It is an exemplary case that complementary contributions from six different nodes lead to a large synergetic effect, so that one can now say that interlayer coupling is well understood. As a consequence two of our members are writing review papers on this project.

Spectroscopic Studies of Interface Magnetism

Spectroscopies play a crucial role in studying the magnetic properties of magnetism at interfaces. The discovery of the sum rules in the dichroism spectra has lead to the 'experimental' determination of site-dependent orbital moments and magneto-crystalline anisotropy energy. One of the discoverers of these sum rules, G. van der Laan of Daresbury Laboratory, is part of the Network. The Network has devoted considerable resources to this project. Two Network post-docs, the Austrian and English ones, are specifically working on this project. Moreover, the Swedish Network post-doc is a photoemission expert, the French node has re-directed its flagship project towards dichroism studies with the FP-LMTO and finally, a substantial German effort is centered around the work of the Muenchen group. In particular, the Muenchen group is looking at dichroism in the EXAFS regime, which allows for the study of magnetic SRO. Whilst there is an excellent through-put of new code developments of these five groups together with applications to the systems of current interest, such as the above mentioned Ni/Cu(001), it might be more exciting for this highlight to select some of the more speculative findings of the theoretical calculations. Firstly, the Austrian node has studied the possibility of using spin-resolved Auger spectroscopy as a possible tool for magnetic domain mapping. Secondly, the Swedish node found that magnetic dichroism in threshold photoemission provides a contrast mechanism for imaging of magnetic domains. Thus, photo-electron emission microscopy could become feasible with laboratory light sources, in addition to synchrotron facilities.

Quantum size effects can be studied in electronic quantum-well states which considerably affect the magneto-anisotropy of ultra-thin films and manifest in distinct effects in photoemission. For example, intensity oscillations in constant-initial-state spectroscopy allow for the identification of quantum well states and provide information on film thickness and film quality, as has been investigated for the prototypical system Cu/fcc-Co(001) by the Swedish team. Moreover this team also found in spin-polarized LEED from Co/W(110) - in both experiment and theory - intensity oscillations due to electron confinement. The UK team has just completed a set

of new codes to study photoemission in real space and will apply them to the study of these quantum-well systems. Moreover, the breadth of the spectroscopies since the inception of the Network has increased. A promising new project on STM is taking place in a German/ Austrian collaboration focussing on the understanding of STS spectra and the chemical identification of surface atoms. In the UK node a project on magnetisation-induced second harmonic generation has been started.

Non-Collinear Magnetism at the Fe/Cr Interface

The Fe/Cr interface is an extremely complicated system due to amongst others topological defects caused by the steps at the interface. Not so long ago, a full conference on the Fe/Cr interface was organized in Strasbourg. Non-collinear magnetism has been largely investigated by the Strasbourg TMR node using a semi-empirical tight-binding method. It has been shown experimentally that magnetic frustrations will induce non-collinear magnetism. For instance imperfect interfaces with single steps in Fe/Cr lead to complicated topological defects with non-collinear spin arrangements. The large number of inequivalent atoms in these systems inhibits ab-initio computations and makes the empirical tight-binding approach the method of choice for the study of physical properties.The French team showed that the phenomenological variation law, proposed for the change of the total energy as a function of the misalignment of the two ferromagnetic layers coupled through a non-magnetic or antiferromagnetic spacer, can well be applied to FeCo/Mn systems and less to the Fe/Cr one within the framework of the semi-empirical method. The so called "perpendicular" coupling, observed experimentally, has been described in details for Fe/Cr and FeCo/Mn systems. In fact, the magnetic behavior of each individual atom can be quite complex but the general trend of the spin magnetic moments near the interface is simple and is now well understood.

3.2 Workshop Announcements

3.2.1 Riksgränsen Workshop

Interface anisotropy, spin and orbital magnetism

May 5-9, 1999

We—Lars Nordström, Jürgen Henk, and Olle Eriksson—are organizing a workshop on 'Interface anisotropy, spin and orbital magnetism' scheduled for May 5–9, 1999. We would like to invite all those who are interested to register as well as to send in scientific contributions (oral or poster). Oral contributions will be 20 minutes, including questions. This is the first and final call for registration and scientific contributions. The deadline for the registration is April 7, 1999.

The focus of the workshop is to present a more fundamental description of interface anisotropy, spin and orbital magnetism with respect to traditional conferences. Hence, invited lectures will be given in a more 'educational' form with a thorough introduction to the field and with a detailed description of experimental and theoretical methods. The scope of the talks will primarily be aimed towards younger researchers—such as students and post-docs—in the audience. A tentative program is enclosed.

The conference will take place in one of the more exotic parts of Europe, Riksgränsen, a ski resort on the border between Sweden and Norway, some 1000 kilometers from Stockholm. In May, the weather is spring-like, but there will still be snow on the slopes and we encourage people to bring clothes for skiing and possibly also ski equipment, although one can rent skis and boots at the resort. Once in Kiruna, you will be picked up by a bus (we will possibly solve this part of the transportation by train) which takes you to Riksgränsen in one hour. The travel from Stockholm to Riksgränsen is thus not expected to take more than 3 hours. A schedule of flights to and from Riksgränsen can be found on our home page (www.fysik4.fysik.uu.se/∼maw).

The registration fee for the conference is 500 SEK for students and 1500 SEK for senior researchers. All further communication concerning the conference, such as registration, booking of hotel rooms, questions concerning flights, requests for special meals, submission of scientific contribution (oral or poster) etc. should be made to the conference secretary. The persons to communicate with are Petra, Malin, and Madeleine. They can be reached via e-mail (malin.strombom@utkab.uu.se and madde@utkab.se) and telephone (+46 18-274807). For travel schedule and details for the registration see the WWW page www.fysik4.fysik.uu.se/∼maw.

The workshop is sponsored by the European Science Foundation (ESF) and is a part of the TMR network 'Magnetism of Surfaces and Interfaces'.

With hope to see you in Riksgränsen in May.

Tentative program

May 5

14.00-14.45	Registration and Coffee
14.45-15.00	L. Nordström, General information and welcoming
15.00-17.00	K. Baberschke, Experimental aspects of thin film magnetism I
17.00-18.15	*Dinner*
18.15-20.15	M. Brooks, Theoretical aspects of thin film magnetism I

May 6

08.15-10.00	N. N.
10.15-12.00	N. N.
12.00-18.00	*Lunch and break for discussions/Poster session*
18.00-19.15	*Dinner*
19.15-21.00	P. Jensen, Theoretical aspects of thin film magnetism III

May 7

08.15-10.00	R. Wu, Theoretical aspects of thin film magnetism IV
10.15-12.00	A. Shick, Theoretical aspects of thin film magnetism V
12.00-18.00	*Lunch and break for discussions*
18.00-19.15	*Dinner*
19.15-21.00	B. Hjörvarson, Experimental aspects of thin film magnetism III

May 8

08.15-10.00	H. Eschrig, Theoretical aspects of thin film magnetism VI
10.15-12.00	S. Blügel, Theoretical aspects of thin film magnetism VII
12.00-18.00	*Lunch and break for discussions*
18.00-19.15	*Dinner*
19.15-21.00	H. Ebert, Theoretical aspects of thin film magnetism VIII

May 9

08.15-10.00	L. Szunyogh, Theoretical aspects of thin film magnetism IX
10.15-12.00	C.-M. Schneider, Experimental aspects of thin film magnetism IV

4 News from the TMR2 Network

'Electronic Structure calculations of materials properties and processes for industry and basic science'

4.1 Annual Review

The TMR2 Network has now been in operation for one year. In the following a short status of the scientific and other networking activities in the past year is presented.

The TMR2 Network is concerned with atomic scale computer simulation methodology to understand complex properties and processes in solids and at solid surfaces. The Network is structured around 8 subprojects with 8 international teams. Initially we encountered difficulties in recruiting sufficiently well qualified PostDocs, but at the end of the first year 7 young researchers are funded by the network, one more is appointed but has not started yet, and one position is still vacant (in Belfast).

The network homepage is

http://www.dfi.aau.dk/~svane/tmr-psik.htm

Status of the scientific subprojects:

Surfaces

The **Surfaces** subproject has a PostDoc associated with MSI, Paris (P. Gavril, **IE**, since June 98). Significant progress has been made in the study of catalytic processes on Fe_2O_3. The calculational accuracy of various ab-initio schemes have been tested on the clean Fe_2O_3 surfaces and on isolated molecules, such as H_2, O_2, styrene and ethylbenzene. It has been found that a localized basis set constructed out of numerical atomic functions provides an accurate description of the atomic and electronic structure of both surface and molecular systems. For accurate geometries the gradient corrected functionals are used. Next step to be pursued is the combination of molecule and surface, which is currently being done.

In a collaboration between Belfast, Grenoble and MPI-FKF Stuttgart the mechanism of catalysis of CO oxidation on a Pt surface was studied and published (see Newsletter, June 98).

f-electrons

This subproject had problems hiring a PostDoc, as the first person appointed declined to take up the position. After a second advertisement a well qualified person has been found (L. Petit, **LU**, starting September 99, based in Århus).

The relativistic LMTO code with self-interaction corrections included has nonetheless been developed and is running extremely efficient on test systems. Applications of this methodology to 5f systems beyond the testing level awaits the PostDoc. A strong collaboration between Århus, Karlsruhe and Daresbury on investigations of 4f systems (without spin-orbit coupling) has resulted in several publications. This work is ongoing and has been extended with collaborations in Uppsala and Keele. Also a collaboration between Uppsala and Darmstadt on the magnetic structures of Gd and U compounds has been initiated.

Interfaces

A major difficulty for managing the **Interface** Programme has been the recruitement of two suitably qualified PostDocs, as foreseen in the workplan. In the second round of advertisement a well qualified person was hired (B. Montenari, **IT**, starting January 99 in Belfast), while a third announcement is being initiated for the second position.

Quite some progress has been made on the study of metal overlayers on Al_2O_3, where extensive studies of Nb have been finalised and published. The technical improvements to our methodology include the calculation of bond orders and Mulliken populations, which helps the understanding of the largely ionic nature of the interface bonding. Investigations of approximate methods have been initiated and first results for zirconia published, while the work intensifies with the newly started PostDoc.

Magnetism

The **Magnetism** subproject has a PostDoc associated with TU-Wien (D. Hobbs, **IE**, from October 98). In accordance with the workplan the implementation of a non-collinear magnetic moment capability in the LMTO, TB-LMTO and RS-TB-LMTO codes has started, allowing for a varying quantization axis on different atomic sites, as well as spin-orbit coupling effects.

First applications of these techniques included: a) Calculation of the magnetic anisotropy in thin layers of Ni on Cu(100) substrates using a magnetic torque-force approach. b) Calculations of the magnetic structure and of the interlayer exchange- interactions in $Fe_n/Cr_m/Fe_n$ trilayers and $(Fe_n/Cr_m)_\infty$ multilayers, accounting for the possibility of a noncollinear magnetic structure in systems with frustrated exchange interactions. c) Calculations of the non-collinear magnetic structure of α-manganese have been started.

The main lines of the implementation of a non-collinear–moment capability in the spin-polarized version of the plane-wave (PW) and projector-augmented-wave (PAW) program packages of the Vienna group (the VASP program) were discussed in a collaboration between the TU-Wien and Uppsala groups.

LAPW

This subproject has two PostDocs employed at the FZ-Jülich (G. Bihlmayer, **AT**, who started September 98, and S. Clarke, **GB**, who started October 98).

The research activity of the **LAPW** subproject has focussed, as planned, on the development of efficient FLAPW codes for the dynamics and the application to problems related to the spin-polarized relativistic effects, such as the magnetic anisotropy and magneto-optics. Two codes are

currently being developed, the WIEN97 and the FLEUR98. In order to improve the efficiency of the codes and to learn from the different performances of the codes, we have set up a couple of benchmark problems (i.e. the (4x2)Cu(110) surface) which are treated by both codes. These tests continue into the second year. Performances of the codes are prepared to be published.

The spin-polarization of the codes have been extended to treat non-collinear structures in real space (Jülich) and in reciprocal space (spin spiral, Uppsala group). In the real space version, the magnetic moments within the sphere around an atom takes one particular direction and can take any direction with respect to neighboring atoms. The magnetization density in the interstitial region is treated in terms of a vector magnetization density.

The spin-orbit interaction has been implemented into both codes (TU-Wien and Jülich groups) exploring various approximations such as the second variation. Furthermore several versions of the force theorem were tested to calculate the magnetic anisotropy. Matrix elements for the magnetooptic such as the Kerr-angle have been implemented and are in the test phase. (Graz and Uppsala groups).

The parallelization of the codes are on course. At present 2 parallelization strategies are persued. First is the k-point parallelization (Jülich and Berlin). This is very important for the calculation of the magnetic anisotropy of magnetic systems, since here a huge number of k-points are needed. Second is the parallelization of the eigenvalue problem. This has been started by the TUWIEN and FZJ partners, and will be continued in the second year.

In the course of this work it was realized that the efficiency of the FLAPW-method may be improved by choosing a more efficient basis-set, a FLAPW basis-set complimented with local orbitals. This approach has a considerable potential and will be further explored in the future.

A collaboration between TU-Wien and Berlin has been initiated on the quantum dynamics of H_2 dissociation on Rh, Pd, and Ag (111) surfaces.

Excitations

This subproject has a PostDoc based in Helsinki (J.-L. Mozos, **ES**, since May 98). The focus of the research is on the description of electronic excitations, dynamics and associated phenomena in extended systems in the framework of ab-initio total energy calculations.

The strong collaboration between Helsinki and Würzburg on time-dependent density functional theory has resulted in first test results for atoms and Silicon. It has been found necessary for the application of this methodology to solids to represent the excited states by Wannier states, since the straightforward application of the formalism to extended states gives vanishing results. This development is still in the technical stage. The Wannier functions are believed to give better descriptions of the initial hole states. As for the final states, issues of convergence with respect to conduction bands are currently being tested. Other tests include alkali halides, where the localized picture is valid both for initial and final states.

Several other schemes aiming at improving the description of excitations have been tested, notably the screened-exchange method, the local-mass approximation and generalized density functional theory. The dynamics of the silicon self-interstitial has been studied and published.

A collaboration has been initiated between Helsinki and TU-Wien aiming at the application of

the PW- and PAW-code VASP for calculations of defects in semiconductors and of the adsorption of atoms on surfaces. Furthermore the intention is to implement a new procedure for the calculation of excited states in the PW-code.

Superconductivity

The **Superconductivity** subproject has a PostDoc based in Würzburg (L. Fast, **SE**, started October 98).

The high point of the year was an invited talk at the Second Polish-American Symposium on High Temperature Superconductivity. It summarized the work of the Bristol-Daresbury-Stuttgart collaboration on the quasi-particle spectra of various High-T_c materials. Most of these spectra have been published. During the last part of the funding period we extended these results by calculating the temperature dependence of the penetration depths. This will be presented at the centennial meeting of the American Physical Society in March 99 as part of an invited talk. The theme that runs through the above work is the role of the Van Hove singularities in the electronic structure of YBCO. The question then arises whether or not the effect survives the introduction of disorder into the problem. We have investigated this phenomenon by developing a Coherent Potential Approximation(CPA) description of disordered d-wave superconductors. These calculations indicate that the degradation of the T_c-enhancement effect due to the Van Hove singularity is gradual, and our quantitative calculations agree well with the experiments.

Training and Dissemination

This subproject is concerned with the training and dissemination activities of the network. Daresbury is coordinating these activities, which strongly involve all network partners. This encompasses the publication of the Psi-k Newsletter every two months and organization of topical workshops and hands-on courses to train young researchers in the methodology of electronic structure calculations for materials properties.

During the reporting period, 6 Newsletters were published. Part of the newsletter is a scientific highlight section to which the **Excitations** subproject (Helsinki group) contributed an article on 'Nanowires: electronic and ionic structures, cohesive and transport properties' (November 98) and the **Interfaces** subproject (Belfast group) contributed an article on 'Reaction Pathway of CO oxidation on Pt(111)' (June 98).

The **Training and Dissemination** team coordinated the Industry Workshop (Vienna June 3-4, 98) which was attended by more than 60 participants. This Workshop succeeded in its aim of establishing a dialogue between industrial scientists and academics. An increasing number of industrially relevant problems can now be solved using advanced electronic structure calculations. Therefore, industrial scientists show a growing interest in this methodology, they start to apply these approaches, and notice aspects which need to be improved. Developers of electronic structure methods, who are working predominantly in academic or government research organisations, are keen to see their methods applied to industrial problems and are eager to receive feedback in order to orient their new developments. The success of this workshop was a clear testimony of the timeliness of this dialogue between industrial researchers and developers of electronic structure methods.

A workshop on new developments in the LAPW methodology was organized in Jülich, **DE**, November 6-7, 98. The team members of the **LAPW** subproject convened for a 2 days mini-workshop in order to exchange information on the recent progress of the individual members, to investigate and evaluate new approaches to further develop the FLAPW method, and to discuss and coordinate future activity. At first, a few talks were presented on the realization and capabilities of the existing FLAPW-codes, followed by a discussion of coordinated action on improving our codes. A second set of talks focussed on new algorithmic developments either making the FLAPW method more efficient or branching into new fields and areas. Alternatives of present solutions were discussed. A third set of talks focussed on applications. The workshop was attended by about 22 participants.

A workshop on Superconductivity was organized in Bristol, **GB**, November 20-22, 98. This workshop brought together researchers in superconductivity for an exchange of ideas and new developments. The workshop was attended by 35 people.

A topical workshop on 'Materials Under Pressure: From Ices to Metals' (Daresbury, **GB** December 17-18, 98) was also organised. This workshop was attended by more than 30 scientists. The range of materials covered by the workshop was truely breathtaking, ranging from studies of elemental metals and intermetallics, to minerals and molecular systems such as ices. The purpose of the workshop was to review the recent experimental developments on synchrotrons and neutron facilities which have led to much improved structural studies of materials under pressure. Simultaneously, more accuracy in the band structure studies of materials have allowed to explore the crystal structure under pressure in greater detail. The workshop aimed to increase the dialogue between experimentalists and theoreticians. This succeeded beyond expectations and a new theoretical (Uppsala, **SE**) and experimental (Edinburgh, **GB**) collaboration was established and is seeking funding in **SE** and **GB**. This workshop replaced the LMTO Workshop of the workplan. The LMTO Workshop will now take place at a later stage.

Finally, good progress has been made in the organisation of the Psi-k Conference. This Conference, **Psi-k2000**, will take place in Schwäbisch Gmünd, **DE**, on August 22-26, 2000. This we are already advertising on the web and in the physics and material sciences conferences lists.

4.2 Workshop Announcements

4.2.1 IWOSMA Workshop

International Workshop on
Orbital and Spin Magnetism of Actinides (IWOSMA)

Friday 4 and Saturday 5 June 1999
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom

Organisers: *Gerrit van der Laan and Walter Temmerman, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

Sponsored by: TMR1, TMR2 and ESF

A two-day workshop at Daresbury Laboratory to bring together experimentalists and theorists on the theme of orbital and spin polarization in actinides. At this workshop we hope to emphasise the things that are not understood, rather than those that are understood. There will be ample time for discussion. The workshop is open to everybody. Registration fee GBP 50 - including two buffet lunches and conference dinner. Participants are encouraged bring to posters.

For information and registration:
`http://srs.dl.ac.uk/msg/MSG_Events_IWOSMA.html`

or contact:

Ms Alison Mutch
Synchrotron Radiation Department
Daresbury Laboratory
Warrington WA4 4AD, UK
tel: +44 - 1925 - 603363
fax: +44 - 1925 - 603124
email: a.m.mutch@dl.ac.uk

Invited speakers:

L. Havela (*Prague*)
Electronic structure and magnetism of actinide systems

P. Carra (*ESRF Grenoble*)
Resonant x-ray scattering in actinides (UO2, USb, and heavy fermions)

G.H. Lander (*KFA Karlsruhe*)
Spin and orbital moments as seen by neutrons in actinide systems

Ch. Vettier (*ESRF Grenoble*)

Magnetic resonant effects in U and Np compounds (M and L edges)

A. Yaouanc (*CEA-Grenoble*)
Spin and orbital magnetic moments in U compounds from x-ray dichroism and magnetic Compton measurements

G. Kaindl (*Berlin*)
X-ray absorption near-edge structure studies of actinide compounds

G. van der Laan (*Daresbury*)
Are the sum rules letting US down?

R.J. Cernik (*Daresbury*)
DIAMOND, a source for the new millennium

P. Weinberger (*Vienna*)
Actinides in the next millennium

B. Johansson (*Uppsala*)
Electronic structure of actinides

H. Ebert (*Munich*)
X-ray magneto-optical effects

M.S.S. Brookes (*Karlsruhe*)
Theory of itinerant magnetism

P.M. Oppeneer (*Dresden*)
An understanding of orbital magnetism from magneto-optical spectra

J.G. Tobin (*Livermore*)
Photoemission of actinides

5 News from the ESF Programme

"Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

5.1 Reports on Collaborative Visits

Report on a visit of Diemo Ködderitzsch (Halle/Saale, Germany) to Professor Walter Temmermans's group (Daresbury Laboratory, Great Britain) January 12 - February 5, 1999

Within the STRUC-Ψ_k ESF Programme, I have spent four weeks (12.1.99–5.2.99) at Daresbury Laboratory, in the group of Professor Walter Temmerman to start a collaboration on the electronic structure of transition metal oxide surfaces.

During my stay at Daresbury Laboratory I have become familiar with the computer code already developed in the group of Professor Temmerman for calculating the electronic structure of strongly correlated systems within the framework of density functional theory. This code includes the self–interaction correction (SIC) to the local density approximation and uses the LMTO formalism with a tight–binding representation of structure constants to solve the electronic structure problem in an efficient manner [Z. Szotek, W. M. Temmerman, H. Winter, Phys. Rev. B **47**, 4029, 1992].

We intend to use this computer code to calculate the electronic structure of transition metal monoxide surfaces for simulating STM images. A supercell approach will be used to perform the electronic structure calculation for a surface. Since computing time increases rapidly when going from bulk to a supercell the use of a parallel implementation is essential.

However, when adapting the code to an HP–computer in Halle (SPP2000, parallel) some problems have occured, concerning both the sequential and parallel versions of the code, mainly due to different Fortran compilers. These have been solved and the code has been applied succesfully to study different magnetic structures of bulk NiO, i. e., AF1, AF2 and ferromagnetic orderings.

To summarize, the stay at Daresbury Laboratory has provided me with the knowledge on performing SIC–LSDA calculations for bulk materials. Hopefully this experience will enable me to set up calculations for transition metal oxide surfaces, which I will start upon my return to Halle.

Diemo Ködderitzsch

Daresbury Laboratory, February 6, 1999

Report on a visit of Elisabeth Sjöstedt (Uppsala University) to the Fritz-Haber-Institut (Berlin)

3–7 February, 1999

The motivation for visiting the Fritz-Haber-Institut was to give a talk on the newly developed APW+lo method (an alternative way of linearizing the APW method), and for the group in Berlin to judge whether this would be a useful implementation in their LAPW code. The aim was also for me to learn more about the FHI-version of the WIEN-FP-LAPW, and how it is applied to surface calculations. As the group is also working with pseudo potential methods, I wanted to learn more about those codes as well.

All this was achieved within the 2 1/2 days of the visit. After my talk on the APW+lo method, we discussed why, and for what particular systems the APW basis set, complemented by local orbitals, is more efficient compared to the closely related LAPW basis set.

Through discussions I got to know how surface energies are calculated using multilayers, and how those surface energies can be used to look at the growth of a surface, or to study atoms on a surface. This will be very useful, and atoms on surfaces will serve as an excellent trial system for the APW+lo method, completing the tests already made for bulk and molecules. We also discussed more code specific matters, like the speeding-up of the LAPW code (some routines by a factor larger than 18) performed by Max Petersen (FHI). Finally I learnt the basics about pseudo potential methods and the construction of pseudo potentials. There were also time for a short demonstration of the interface to the pseudo potential program fhi98md, developed by the group.

Although the visit was very short, a lot of different topics were discussed, and those discussions will continue over e-mail and hopefully through future visits between the two groups.

Elisabeth Sjöstedt

5.2 Workshop Announcements

5.2.1 Workshop on Computational Materials Science

Dipartimento di Fisica, Universita‘ di Cagliari Istituto Nazionale per la Fisica della Materia, Unita‘ di Cagliari

IX WORKSHOP ON COMPUTATIONAL MATERIALS SCIENCE

10 - 13 September 1999

Tanka Village, Villasimius (CA)

web page: **http://www.dsf.unica.it/CMS99**

under the patronage of UNESCO

with the sponsorship of ESF Psi-k Programme, Regione Autonoma Sardegna, Comune di Villasimius, Agrosarda

See PROGRAM and REGISTRATION INFO below.

FORMAT: About 20 invited lectures plus POSTER contributed session.

VENUE: Tanka Village at Villasimius (CA), an attractive sea resort on the south-eastern coast of Sardinia, providing comforts and an informal atmosphere.

CONTACT: For scientific queries:
vincenzo.fiorentini@dsf.unica.it
paolo.ruggerone@dsf.unica.it

For logistics: Corsi&Congressi, Cagliari, corsieco@tin.it

CONTRIBUTIONS AND PROCEEDINGS:
Contributions in poster format are invited. ALL contributions will be probably published in a special issue of the journal Computational Materials Science. Deadline for abstract submission: July 31, 1999.

Contact:
V. Fiorentini at +39 070 6754912 or P. Ruggerone at +39 070 6754847 or at vincenzo.fiorentini@dsf.unica.it or paolo.ruggerone@dsf.unica.it for further details.

Manuscripts will be due at the Workshop.

PROGRAM

SATURDAY SEPTEMBER 10

Morning: working session 1: THEORY OF MATERIALS: DENSITY FUNCTIONAL AND BEYOND

8.30 E. K. U. Gross (Universitaet Wuerzburg)
9.30 R. Resta (Universita‘ di Trieste)
11.00 R. Godby (University of York)

Afternoon: working session 2: SOFT AND GRANULAR MATTER

17.30 V. Marinari (Universita‘ di Cagliari)
18.30 D. Wolf (Universitaet Duisburg)

SUNDAY SEPTEMBER 11

Morning: working session 3: GROWTH AND REACTIVITY

8.30 D. Wolf (Universitaet Duisburg)
9.30 B. Smit (Amsterdam Universitet)

Afternoon: excursion

21.00 Poster session with refreshments

MONDAY SEPTEMBER 12

Morning: working session 4: ORGANIC AND BIO-SYSTEMS

8.30 C. Molteni (Cavendish Lab, Cambridge)
9.30 B. Smit (Amsterdam University)
11.00 F. Seno (Universita‘ di Padova)

Afternoon: working session 5: SOLID-STATE APPLICATIONS

17.30 J. Kohanoff (Abdus Salam Center for Theoretical Physics, Trieste)
18.30 R. Godby (University of York)

TUESDAY SEPTEMBER 13

Morning: working session 6: NEW COMPUTATIONAL METHODS

8.30 R. Resta (Universita‘ di Trieste)
9.30 J. Kohanoff (Abdus Salam Center for Theoretical Physics, Trieste)
11.00 S. Baroni (International School for Advanced Studies, Trieste)

Afternoon: working session 7: THEORY AND PRACTICE OF NANOSTRUCTURES: A PERSPECTIVE

17.30 E. Molinari (Universita‘ di Modena)
18.30 R. Cingolani (Universita‘ di Lecce)

REGISTRATION

Please send the REGISTRATION form by fax or e-mail, STRICLY before July 1, 1999 to

Corsi&Congressi
via Ghibli 8, I-09126 Cagliari
tel +39 070 383373
fax +39 070 3837102
e-mail: corsieco@tin.it

The registration MUST BE ACCOMPANIED BY PAYMENT RECEIPT OF THE CONFERENCE FEE. The fee includes full-board lodging at Tanka Village from 9/9 dinner to 14/9 breakfast, coffee breaks, and excursion, and it amounts to:

Double room lodging: Italian Lire 850000 (∼US $475)/person
Single room lodging: Italian Lire 950000 (∼US $535)/person

PAYMENT should be effected by bank money transfer on the bank account # 27660 of Corsi&Congressi, at Credito Italiano, via Scirocco 46/A, 09126 Cagliari, Codice ABI 02008 - CAB 04804.

No fee is requested from the invited speakers.

The Organizing Committee hopes to be able to offer partial support to a limited number of young scientists, preferrably PhD students. Since this possibility depends on funds availability, support will be decided upon only shortly before the workshop.

REGISTRATION FORM

Name .....
Institution .....
e-mail address .....
Arrival date: / /99 - Departure date: / /99
Accomodation: Single room [_] Double room [_]
Plan to present a poster entitled:

Series Chairman : prof. A. Baldereschi - EPFL Lausanne
Workshop Chairman : prof. F. Meloni - INFM and Universita‘ di Cagliari
Scientific Secretariat: dr. V. Fiorentini - dr. P. Ruggerone
INFM and Universita‘ di Cagliari

6 News from CCP9

UK's Collaborative Computational Project 9 on "Computational Studies of the Electronic Structure of Solids"

6.1 Report on 'One day KKR meeting'

Daresbury Laboratory, UK
Wednesday 17th February 1999 Supported by UK's CCP9

This one day meeting was attended by more than 20 representatives from groups across the UK, including Bath, Bristol, Cambridge, Daresbury, Keele and Sheffield. The purpose of this meeting was to primarily review current developments in KKR-methods – however, as there are several members of the UK KKR-community leaving and 'new blood' arriving, it was an excellent opportunity for the dissemination of recent ideas and the start of new collaborations. Topics of discussion focused on the exploitation of the sparsity of the KKR-matrix (Petit), the influence of symmetry and compositional order on the magnetoanisoptropy energy (Razee), the various developments in the KKR method for the study of layered systems (Ernst, Woods, Arola) and the use of screened KKR-methods in the description of oscillatory exchange coupling (Lathiotakis). Work was also presented concerning the comparison of a first principles KKR-study of Bloch wall properties with a model which used a Heisenberg description (Schwitalla) and the use of a simple classical 1D spin model in the description of nanowires (Eisenbach).

Program and Abstracts

10:30 - 11:00		Coffee
11:00 - 11:30	Leon Petit	Screened Real-Space study of the magnetic properties of the transition metals
11:30 - 12:00	Arthur Ernst	Self-consistent KKR-method for layered systems

12:00 - 12:30	Matthew Woods	Relativistic Photoemission for magnetic and non-magnetic metallic surfaces
12:30 - 13:00	Eero Arola	Relativistic scattering theory of magnetic second harmonic generation from magnetic metals
13:00 - 14:00		Lunch
14:00 - 14:30	Jurgen Schwitalla	Bloch Wall properties from First Principles Calculations
14:30 - 15:00	Nektarios Lathiotakis	Oscillatory Exchange Coupling across a Cu spacer : A screened KKR study using asymptotic analysis
15:00 - 15:30	Sayed Razee	Effect of Symmetry and Compositional order on magnetocrystalline anisotropy
15:30 - 16:00	Markus Eisenbach	States of orientation along a magnetically inhomogeneous nanowire
16:00 - 16:30		Coffee and Discussion

Abstracts

Screened real-space study of the magnetic properties of the transition metals

L. Petit
Physics Department, University of Shefield

We have implemented screening in the fully relativistic spin-polarised version of the Korringa-Kohn-Rostoker (KKR) band-structure method. Exploiting the resulting sparsity of the KKR matrix we were able to accelerate the matrix inversions, and to study the convergence of the magnetic moment and the magnetic anisotropy energy (MAE), on the central site of a local interaction zone, as a function of atoms in this zone. We show results obtained for the magnetic moment and MAE of Fe, Co and Ni.

Self-consistent KKR-method for layered systems

A. Ernst
Daresbury Laboratory, Daresbury

This code has been developed for the ab-initio study of photoemission spectra of layered transition metal systems. The two-dimensional structure constants are calculated using two different approaches. In the first approach direct Fourier transformations of the screened real-space structure constants are used. This method is very fast, but not very accurate. In the second approach

the two-dimensional structure constants are obtained using Kambe's method. We show some tests for the convergence of the total energy and photoemission spectra of transition metals.

Relativistic photoemission for magnetic and non-magnetic metallic surfaces

M. Woods
Physics Department, Keele University

An outline of the theory of relativistic photoemission will be presented and a cluster code will be described. Ongoing calculations (based on real-space KKR) for Cu(100) and Cu(111) will be compared with experimental results and non-relativistic calculations.

Relativistic scattering theory of magnetic second harmonic generation from magnetic metals

E. Arola
Physics Department, University of Bath

We describe the outline of our first-principles theory on magnetic second harmonic generation (MSHG) of lase light from magnetic materials including surface, interface and multilayer features. The theory has been constructed in terms of the time-dependent second order perturbation theory in connection with the fully relativistic, spin-polarised layer-KKR method (R-SP-LKKR). A remarkable benefit of our MSHG theory is that it allows a realistic treatment of the electron potential, and that the interband transitions are included. Therefore, our theory goes beyond the conventionally formulated SHG approach where the simple jellium model has been use to account for the electron structure of a semi-infinite system, and where interband transitions are not present. Secondly, the advantage of the present theory is that being fully relativistic it treats spin-orbit coupling and spin-polarisation effects on an equal footing.

Bloch Wall properties from first principles calculations

J. Schwitalla
H.H. Wills Physics Laboratory, University of Bristol

In this talk I will present the status of our work on first principles calculations of Bolch wall properties.

We model a Bloch wall by a half infinite bulk system on the left hand side with magnetisation in one easy direction, a half infinite bulk system on the right hand side with magnetisation in another easy direction and N layers in between with the magnetisation linearly turning around between the two limiting directions.

The energy difference between such a configuration and the pure bulk system can then be calculation as a function of the thickness N. The minimum of the resulting curve E(N) provides

an estimate for the Bloch wall thickness and the Bloch wall energy.

Within the Heisenberg model $E(N)$ is given by $E(N) = \frac{\alpha}{N} + \beta N$ where α is proportional to the exchange coupling parameter J and β is proportional to the anisotropy constant K.

Comparing the curve $E(N)$ obtained from the first principles calculation with the prediction from the Heisenberg model provides a test on the applicability of the latter and furthermore yields a value for J which can be compared with other independent theoretical predictions e.g. from spin wave calculations.

I will present results for bcc iron.

Oscillatory Exchange coupling across a Cu spacer : A screened KKR study using asymptotic analysis

N. Lathiotakis
H.H. Wills Physics Laboratory, University of Bristol

A model based on the screened KKR-CPA method has been developed for studying the Oscillatory Exchange Coupling across binary alloy spacers. The stationary phase method is employed and an analytic asymptotic form of the coupling energy is derived. The model is used to calculate the Oscillatory Exchange coupling for all the (100), (110) and (111) growth directions of the Co/Cu/Co trilayer and the results compare well with both full integration calculations over $\mathbf{k}$ and the experiment.

Effect of symmetry and compositional order on magnetocrystalline anisotropy

S. Razee
Physics Department, University of Warwick

Symmetry (including dimensionality) and compositional order play an important role in the determination of the magnetocrystalline anisotropy (MCA) of a system. I will describe a first principles theory of the MCA based on the spin-polarised relativistic KKR-CPA scheme. I will present results for the disordered CoPt alloys (both bulk and films) as well as the ordered and layered CoPt alloys. I would also report on our ongoing works on the effects of lattice distortions on the MCA as well as some new results on the magnetic annealing effects in permalloy.

States of orientation along a magnetically inhomogeneous nano wire

M. Eisenbach
H.H. Wills Physics Laboratory, University of Bristol

We investigate the magnetic states of nano wires (diameter 50 – 500 Å) which consist of disc shaped magnetic segments separated by non-magnetic spacers. To describe this system we propose a simple classical one dimensional spin model and study its consequences. In particular

we examine the ground state and thermal behaviour as function of both anisotropy of the ferromagnetic discs and thickness of the non magnetic spacer. We find a rich structure of possible ground states and a temperature driven reorientations of the magnetic moments in various regions of the parameter space.

We shall also report on our preliminary investigation of the above system in terms of an itinerant model based on mobile electrons and their spins. The Hubbard like model investigated here incorporates the dipolar interaction between the magnetic moments at different sites, and we are able to calculate the shape anisotropy of a disc in the Hartree-Fock approximation of our itinerant model.

7 General Job Announcements

Postdoctoral Positions in Solid State Theory Group

National Renewable Energy Laboratory

http://www.sst.nrel.gov

The Solid State Theory Group at the National Renewable Energy Laboratory invites applications for a few postdoctoral research positions to start in the summer or fall of 1999. Applications are accepted now. The position is for two years, renewable upon mutual agreement to a third year, and is in the area of development of electronic structure theory, algorithms and applications to nanostructures and alloys. The starting salary is US$ 42-52 K/year depending on qualification. The Solid State Theory Group currently consists of ten Ph.D.'s in condensed matter theory and interacts with a broad range of experimentalists at NREL. The group has outstanding computational facilities, an excellent basic-research atmosphere, and is located near the beautiful Rocky Mountains. For more information about the group research activities, publications and personel, see http://www.sst.nrel.gov. Interested candidates should immediately send in writing (no e-mail submission) a curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and should arrange for 2-3 reference letters to be sent directly to:

Dr. Alex Zunger
Solid State Theory Group
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado, 80401

NREL is an equal opportunity/affirmative action employer.

Post-doctoral Position in Electronic Structure of Magnetic Systems

Andrew Zangwill (Georgia Institute of Technology) and Mark Stiles (National Institute for Standards & Technology) seek a dedicated and creative person to join a team as a post-doctoral scientist to develop, implement, and exploit an electronic structure methodology that combines current-density functional theory with exact exchange and correlation. The immediate goal is to study orbital magnetism in solids but the interests of the successful candidate will help determine future directions. He/she will be an employee of Georgia Tech (Atlanta) but resident in the Electron Physics Group at NIST (Gaithersburg). The position is for one year plus a second year with mutual agreement. The salary is $45,000 per year with health benefits. Demonstrated expertise with large-scale electronic structure calculations is essential; previous experience with magnetism is helpful but not required.

E-mail a resume and at least two letters of recommendation to andrew.zangwill@physics.gatech.edu AND mark.stiles@nist.gov as soon as possible. Georgia Tech is an equal opportunity employer.

Position for Ph. D. Student in Computational Materials Science

At the Science College "Computational Materials Science" operated jointly by the University of Vienna and the Technical University of Vienna a position for a doctoral student is immediately available. The salary is 2/3 of that of an university assistant. The activities of the Science College are concentrated on the investigation of materials properties and on the simulation of processes in materials using ab-initio quantum-mechanical methods. The research topics cover a wide area including alloys, structural materials, magnetic materials (including thin-film magnetism), surfaces and interfaces, and catalysis. Candidates should have a diploma in physics, chemistry, materials science or applied mathematics and sound expertise in numerical computing and programming. Applications with the usual supporting material (diploma, curriculum vitae, letters of recommendation and eventual publications) should be adressed to the speaker of the Science College, Professor Juergen Hafner (Institut fuer Materialphysik and Center for Computational Materials Science, Universitaet Wien, A-1090 Wien. Email: jhafner at tph.tuwien.ac.at).

8 Abstracts

Magnetic Circular Dichroism in Resonant Raman Scattering in Perpendicular Geometry at the L edge of 3d Transition Metal Systems

L. Braicovich[1,2], G. van der Laan[3], G. Ghiringhelli[4], A. Tagliaferri[1,2],
M.A. van Veendendaal[5], N.B. Brookes[4], M.M. Chervinskii[6], C. Dallera[1],
B. De Michelis[1,2] and H.A. Dürr[3] [1]*INFM Instituto Nazionale di Fisica della Materia, Italy*
[2]*Dip. di Fisica Politecnico, P.L. da Vinci 32, 20133 Milano, Italy*
[3]*Magnetic Spectroscopy Group, Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*
[4]*European Synchrotron Radiation Facility, BP 220, 38043 Grenoble, France*
[5]*Materials Science Center Division, Argon National Laboratory, IL 60439*
[6]*Mendeleyev institute for Metrology, Skt. Petersburg, Russia*

Abstract

We measured circular dichroism in resonant x-ray scattering $3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 3s^1 3d^{n+1}$ with incidence perpendicular to the magnetization where the absorption dichroism vanishes. The advantages of photon scattering over other techniques make it possible to study a wide range of materials. The Ni L_3 dichroism in $NiFe_2O_4$ is $28 \pm 5\%$, in agreement with a localized model. In Co metal the dichroism is reduced to $10.4 \pm 1\%$ (L_3) and $6.8 \pm 1.5\%$ (7.5 eV above L_3) indicating a large sensitivity to the nature of the valence states despite the fact that this spectroscopy is based on inner shell transitions.

(Physical Review Letters, accepted)
Manuscripts available from: g.vanderlaan@dl.ac.uk

A theoretical study of the magnetism within Gd/Mo and Gd/W multilayers

A.C. Jenkins and W. M. Temmerman
CLRC, Daresbury Laboratory, Daresbury, Warrington, Cheshire, UK, WA4 4AD

Abstract

The local-spin-density-approximation (LSDA) and generalised-gradient-approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) are implemented within the framework of the semi-relativistic self-consistent TB-LMTO-ASA scheme. Energy-volume and magneto-volume studies of bulk Gd, Mo and W are presented. Use of the LSDA in the study of Gd indicates that the antiferromagnetic structure is energetically favourable at the equilibrium lattice parameter which is 3% smaller than the experimental value. Application of the PBE functional predicts the experimentally observed ferromagnetic ground state at an equilibrium lattice parameter close to (+0.5%) the experimental value. Magnetovolume studies of Mo and W predict that, although both these metal possess a non-magnetic *bcc* ground state , they will exhibit antiferromagnetic behaviour at large volumes regardless of whether the structure of the idealised unit cell is *bcc*, fcc or *hcp*. Magnetic behaviour as a consequence of volume expansion is also predicted to occur on the Mo or W sites within Gd/X (X=Mo,W) bilayers. Moreover for the case of a 5Gd/3Mo multilayer, constructed using the volume parameters of bulk Gd, the magnetic behaviour of the Gd and Mo layers is nearly identical to that of the constituent bulk elements at the same volume. We have thus demonstrated that any possible occurrence of a magnetic moment on a Mo or W site within such a multilayer is a direct consequence of volume effects only.

(submitted to Phys. Rev. B)
Manuscripts available from: a.c.jenkins@dl.ac.uk

Local Density Approximation for Superconductors

S. Kurth
Department of Physics and Quantum Theory Group, Tulane University, New Orleans, LA 70118, USA
M. Marques and E.K.U. Gross
Institut für Theoretische Physik, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Abstract

A universal LDA-type density functional describing the electronic correlations in superconductors is developed from first principles. The functional is constructed from the exchange-correlation free-energy density, f_{xc}^{hom}, of a homogeneous electron gas, exposed to an external translationally invariant pairing field. The quantity f_{xc}^{hom}, which is a function of the density and a functional of the induced order parameter, is calculated by many-body perturbation theory.

(submitted to Phys. Rev. Lett.)
Manuscripts available from: marques@physik.uni-wuerzburg.de

Cuprate core level line shapes for different Cu-O networks

K. Karlsson
Inst. för Naturvetenskap, Högskolan Skövde, S-541 28 Skövde, Sweden
O. Gunnarsson and O. Jepsen
Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany

Abstract

We have studied the Cu core level photoemission spectra in the Anderson impurity model for cuprates with different Cu-O networks, dimensionalities (zero, one, two and three) and Cu valencies (two and three). We focus on the shape of the leading peak and obtain very good agreement with the experimental data. We show how the shape of the spectrum is related to the valence electronic structure and the Cu-O network but also that other atoms can play a role.

(Phys. Rev. Lett., accepted for publication)
Latex-file available from `cond-mat/9903138`
(Contact person: gunnar@and.mpi-stuttgart.mpg.de)

Growth, electronic, magnetic and spectroscopic properties of transition metals on graphite

C. Binns, S. H. Baker
Department of Physics, University of Leicester, Leicester LEI 7RH, GB
C. Demangeat and J. C. Parlebas
Institut de Physique et Chimie des Matériaux (IPCMS-GEMME)
UMR 7504 du CNRS-Université Louis Pasteur,
23 rue du Loess, 67037 Strasbourg Cedex, France

Abstract

This report presents a combined theoretical and experimental study of the electronic structure of nanostructures of transition-metals on graphite. In the last few years a variety of techniques has been used to prepare mesoscopic metal islands on this substrate and novel effects associated with the electronic structure in nanoscale systems have been reported. These include magnetism in the bulk paramagnetic metals V and Ru.

In the present report, following the introduction in chapter I, chapter II is devoted to review the growth and spectroscopic properties of $3d$ and $4d$ metals on graphite. A description of the experimental techniques and conditions used by the authors is presented. The morphology of deposited MBE films of Cr, V, Mn and Fe and pre-formed nanoscale clusters of Mn and Fe, determined by XUV reflectivity, SEM and STM is discussed. Results from XPS and other photoemission-based techniques, used to examine the electronic and magnetic properties of the films, are shown and several novel effects expected in nanoscale systems are demonstrated. These include enhanced magnetic moments in Mn nanoclusters, size-dependent screening effects in islanded Mn, Cr and V films and evidence for increased magnetic disorder in Cr and Fe particles.

Chapter III is dedicated to the theoretical investigation of magnetism for hexagonal $3d$ and $4d$ metal monolayers, epitaxially adsorbed on a (0001) graphite surface, by spin-polarized electronic structure calculations using semi-empirical and ab-initio methods. It is shown that, when they exist, the magnetic moments of the adsorbed monolayers are substantially reduced from their unsupported monolayer values. A comparison with one and two adatoms is discussed. Also in this chapter, we present calculations of the 3s-XPS of $3d$ metal atoms chemisorbed on graphite, using a cluster model that takes into account intra-atomic dd and d-core electron exchange and Coulomb interactions as well as hybridization between $3d$ metal orbitals and graphite π states. The ability of the system to undergo a low-to-high spin transition is discussed along the $3d$ series with respect to the metal atom-graphite distance and is clearly evidenced in the evolution of the 3s-core-XPS line shape.

All the transition metal films on graphite presented in this report grow as islands with a thickness of a few nanometers. However the monolayer growth of $3d$ or $4d$ metals on graphite might be achieved in certain cases, even if this corresponds to thermodynamically metastable phases. In this way our report presents interesting and systematic results for new epitaxial systems but still remains a challenge for both experimentalists and theoreticians.

(Surface Science Reports, in press)
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Surface dependence of the magnetic configurations of the ordered B2 FeCr alloy

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Abstract

Tight-binding linear muffin tin orbitals calculations with generalized gradient approximation were carried out for the magnetic configurations at the surface of the ferromagnetic ordered B2 FeCr alloys. For both (001) and (111) crystallographic phases, non ferromagnetic configurations are shown to be more stable than the ferromagnetic configuration of the bulk alloy. For (001) surface we display a c(2x2) ground state for either Cr or Fe at the surface. For Cr top layer the magnetic moments are 700% larger than in the bulk B2 FeCr while they are slightly enhanced for Fe top layer. For (111) surface an antiferromagnetic coupling between surface and subsurface is always obtained i.e. for either Fe or Cr at the surface. This change of coupling between Fe and Cr (from ferromagnetic to antiferromagnetic) is expected to be fundamental to any explanation of the experimental results obtained for the interface alloying at the Fe/Cr interfaces.

(Eur. Phys. Journ. B, in press)
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Induced spin-polarization in V: Fe_nV_m superlattices and thin V films on Fe substrates

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Abstract

The spin polarization at the (100) and (110) Fe/V interfaces is investigated using the tight-binding linear muffin-tin orbital (TB-LMTO) method. For both Fe_nV_m superlattices and thin V_m films on Fe substrates we consider epitaxial growth of V with in-plane inter-atomic distance equal to that of Fe and out-of-plane inter-atomic distance fitted to recover the volume of V bulk. We obtain a short-range induced spin-polarization in V, as well as reduced Fe polarization at the Fe/V interface. In Fe_nV_m superlattices, V couples always antiferromagnetically with Fe. For thin V films grown on Fe(100) the V polarization presents oscillations (layered antiferromagnetic configuration). The magnetic moments of V and Fe depend on the crystallographic orientation of the sample. Our results are compared with the existing experimental observations.

(Phys. Rev. B, in press)
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Non-ferromagnetic solutions for Fe thin films on Co(001)

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Abstract

We have investigated the magnetic configurations of nFe layers on Co(001) substrate within *ab initio* Linear muffin-tin orbitals method in the tight-binding approach. For 1 monolayer (1ML) of Fe we have considered different magnetic configurations. The ferromagnetically ordered monolayer with parallel coupling with Co(001) is found to be the ground state. For 1-2 ML films the ground state is found to be the $p(1 \times 1) \uparrow$ magnetic configuration. For Fe films with more than 2ML, only non-ferromagnetic configurations remain present. This trend is in qualitative agreement with the results deduced from XMCD, MOKE and photoemission experiments.

(J. Magn. Magn. Mat., in press)
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Thermal Contraction and Disordering of the Al(110) Surface

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Abstract

Al(110) has been studied for temperatures up to 900 K via ensemble density-functional molecular dynamics. The strong anharmonicity displayed by this surface results in a negative coefficient of thermal expansion, where the first interlayer distance decreases with increasing temperature. Very shallow channels of oscillation for the second-layer atoms in the direction perpendicular to the surface support this anomalous contraction, and provide a novel mechanism for the formation of adatom-vacancy pairs, preliminary to the disordering and premelting transition. Such characteristic behavior originates in the free-electron-gas bonding at a loosely packed surface.

(To appear, Phys. Rev. Lett.)
Latex-file available from:
`http://www.physics.rutgers.edu/$\sim$marzari/preprints/index.html\#~al110`

Incommensurate and commensurate antiferromagnetic spin fluctuations in Cr and Cr-alloys from ab-initio dynamical spin susceptibility calculations

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Abstract

A scheme for making *ab-initio* calculations of the dynamic paramagnetic spin susceptibilities of solids at finite temperatures is described. It is based on Time-Dependent Density Functional Theory and employs an electronic multiple scattering formalism. Incommensurate and commensurate anti-ferromagnetic spin fluctuations in paramagnetic Cr and compositionally disordered $Cr_{95}V_5$ and $Cr_{95}Re_5$ alloys are studied together with the connection with the nesting of their Fermi surfaces. We find that the spin fluctuations can be described rather simply in terms of an overdamped oscillator model. Good agreement with inelastic neutron scattering data is obtained.

(Phys. Rev. Lett., in press)
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Effective Kohn-Sham Potential for Extended Hubbard Model

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Abstract

Antiferromagnetic and charge ordered Hartree-Fock solutions of the one-band Hubbard model with on-site and nearest-neighbor Coulomb repulsions are exactly mapped onto an auxiliary local Kohn-Sham (KS) problem within a density-functional theory. The mapping provides a new insight into the interpretation of the KS band structure. (i) With an appropriate choice of the basic variable, there is a universal form of the KS potential, which is applicable both for the antiferromagnetic and charge ordered solutions. (ii) The Kohn-Sham and Hartree-Fock eigenvalues are interconnected by a scaling transformation. (iii) The band-gap problem is attributed to the derivative discontinuity of the basic variable as the function of the electron number, rather than a finite discontinuity of the KS potential. (iv) It is explicitly shown how the fundamental conductivity gap and the energies of spin-wave excitations can be entirely described by the parameters of the ground state.

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Zone boundary softening of the spin-wave dispersion in doped ferromagnetic manganites

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Abstract

We argue that the new distinct features observed in doped ferromagnetic manganites $R_{1-x}D_x\mathrm{MnO_3}$ (RD= LaSr, PrSr, NdSr and LaCa), the softening of the spin-wave dispersion at the zone boundary and the increase of the spin-wave stiffness constant with x, have purely magnetic spin origin. They indicate the breakdown of the canonical double-exchange limit, and reflect otherwise natural consequence of the e_g-band filling in the half-metallic regime. Details of the realistic electronic structure are important and significantly modify the analysis based on the minimal tight-binding Hamiltonian for e_g electrons.

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Manuscripts available from: igor@jrcat.or.jp

Ab initio calculation of forces and lattice relaxations in metallic alloys

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Abstract

We present first-principles calculations of forces and lattice relaxations in bcc Fe. In particular, relaxations around 3d, 4d, and 5d transition metal impurities are calculated. The calculations are based on a full-potential Korringa-Kohn-Rostoker Green's function method for defects and employ the local spin density approximation for the exchange and correlation effects. The non-spherical parts of the potential and the charge density are treated correctly, while the forces are calculated by an ionic version of the Hellmann-Feynman theorem. Lattice statics methods are used to describe the longer ranged relaxations. The results are compared with lattice parameter measurements for the volume changes. Because of the correct treatment of the sharp shape of the Wigner-Seitz cell, the angular momentum expansion coefficients of the cell potential have discontinuities in the first derivative, which make some complications when solving the radial equations. An effective method to go around these discontinuities is introduced.

(Phil. Mag. B **78**, 429-433 (1998))
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9 Announcement: Special Issue on Tight-Binding

Computational Materials Science, 12 (1998)
Special Issue on
Tight-Binding Molecular Dynamics Simulations in Materials Science

Luciano Colombo (Guest Editor), Risto Nieminen (Editor)

Starting with the work of Slater and Koster, the tight-binding (TB) theory of electronic structure has played an increasingly important role in computational materials science. It has developed as an effective tool for calculations of atomic and electronic structures, total energies, diffusion barriers, and interatomic forces of large condensed-matter and molecular systems. The benefits of TB theory include ease of implementation, low computational workload, robust transferability as well as relatively good reliability. Yet these features are obtained by maintaining the underlying formulation at the level of the simplest quantum mechanical treatment of condensed-matter systems and within a rather intuitive chemical and physical conceptual framework.

During the years the TB theory has been established as a good compromise beteen ab-initio simulations and model potentials ones, bridging the gap between them. Its simplicity makes it very competitive against fully ab-initio formulations, while its quantum mechanical character makes it much more reliable and transferable than model potentials. The suitability of TB for linear scaling algorithms has boosted the interest in this approach in recent times. Moreover, some fully ab-initio approaches retaining to some extent the features of the TB approach (in the use of localized atomic bases) have been recently proposed, extending the predictive character of the TB formulation.

This topical issue of *Computational Materials Science* is focused on tight-binding molecular dynamics (TBMD) simulations. It covers from formal developements (like linear scaling methods and the first-principles derivation of TB theory) to the application of TB to defects, disordered covalently-bonded materials, and carbon systems (where the TBMD approach has proven to be at its highest level of accuracy and reliability). It also covers the applications of semiempirical quantum chemistry approaches (closely related with TB formulations) to biological systems. Finally, the issue includes a TBMD code which is distributed via Elsevier's website (http://www.elsevier.com/locate/commatsci). The code (written in standard Fortran-77) was developed by L. Colombo and it is primarily intended for training students or researchers with no specific background in molecular dynamics computer simulations.

Contents:

Elsevier's website:

The articles (in `pdf` or `html` formats), as well as the TBMD code, can be downloaded from Elsevier's website: **http://www.elsevier.com/locate/commatsci**

L. Colombo and P. Ordejón

10 SCIENTIFIC HIGHLIGHT OF THE MONTH

April 1999; http://www.dl.ac.uk/TCSC/HCM/PSIK/highlights.html

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Nanotubes: Mechanical and Spectroscopic Properties

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Abstract

Fullerenes, and especially nanotubes, have caused a revolution in chemical physics and materials science in recent years. The unusual structure of these materials results in novel properties that make them interesting not only from a purely scientific perspective; given that these properties are of technological relevance, fullerenes and nanotubes could prove to have wide applicability in nano-technology. In this contribution we provide an overview of this rapidly growing field, focusing mostly on the role played by theoretical electronic structure methods (both semi-empirical and first-principles) in two important aspects of nanotube research: the mechanical and electronic properties of nanotubes, which are of key relevance to practical applications and to our present understanding of low dimensional structures.

10.1 Introduction

The discovery of C_{60} [1], the finding of a way to produce it in large quantities [2] and the subsequent discovery of nanotubes [3], are findings that have opened a completely new field in the science of carbon related materials. Since these discoveries were made, fullerene and nanotube research has become a dynamic and rapidly growing field; ample proof of this fact can be found in a recent survey of publications related to this topic [4]. This survey shows that publications in the field can now be counted in thousands (their number was approaching 15000 at the time the survey was carried out), but perhaps more importantly, the rate of growth of the number of publications relating to fullerenes and nanotubes is increasing every year. This is a clear indication of the fact that more and more research groups are being attracted to this field of research. There are two main reasons for this. On the one hand, fullerenes and nanotubes are novel structures, displaying many interesting properties. The characterisation and understanding of these properties is one aim of research in the field. On the other hand, it is precisely these new properties that make fullerenes, and especially nanotubes, potentially useful in many applications related to nanotechnology. This potential for application is another attractive feature of this field of research.

Nanotubes appear as perfectly graphitized (sp^2 basic structural units), in either single-wall or multi-wall form, with carbon atoms arranged on each shell with various degrees of helicity and capped with pentagons just like the fullerene molecules. Multi-wall nanotubes (MWNT's) are generally in the range of 1-25 nanometers in diameter, while single-wall nanotubes (SWNT's) have diameters in the range 1-2 nm. Both SW and MW nanotubes are usually many microns long and hence they can fit well as components in submicrometer-scale devices and nanocomposite structures that are very important in emerging technologies. Furthermore, SWNT's are mostly arranged in ropes with a close packing stacking [5, 6] forming self-assembled cables that could be the ultimate light-weight high-strength flexible fiber. Recently much progress has been made in the production and purification of SW and MW carbon nanotubes in high yield, as well as in electronic, transport, optical, magnetical and mechanical properties [7, 8, 9, 10, 11, 12], incorporation of foreign atoms in tubeles forming metal wires [13, 14] and in possible technological applications as highly performing nanoscale materials and electronic devices [15] (junctions [16], nanocoils [17], field emitters [18] and pinning material in high T_c superconductors [19], ...) This new field has now grown beyond carbon to encompass other materials as well, such as BN fullerenes [20] and nanotubes [21, 22], BC_3 and BC_2N [17, 23] nanotubes, GaSe [24] nanotubes, WS_2 and MoS_2 [25] nanotubes and fullerenes, etc. A general conclusion can be draw from these experimental/theoretical results: all compounds having layered structures in the bulk phase are likely to form nanotubes and fullerene-like structures.

It would be impossible to give a detailed account of progress in this field in just a few pages. Excellent reviews and monographs [7, 8, 9, 10, 11, 12] exist on this topic, and we refer the interested reader to them for an in-depth discussion. Our aim here is more modest; we will focus on just two aspects of nanotube research, which are nevertheless key aspects in their potential for application: their mechanical properties, which will be discussed in Section 10.4, and their electronic properties, discussed in Section 10.5. Given that the carbon-carbon bond in the graphite basal plane (graphene) is one of the strongest chemical bonds known in nature,

and since carbon nanotubes are nothing but seamless graphene cylinders (see Section 10.3), it is not surprising that nanotubes possess extraordinary mechanical properties, a fact that may lead to their use in the fabrication of light but highly resistant fibers, or for the reinforcement of materials, to cite a few examples. With regard to their electronic properties, single-wall nanotubes can be either conducting or semi-conducting, depending on their structure, a property which could be relevant for applications in nano-electronics.

Nanotube research, and in particular the study of the mechanical and electronic properties of nanotubes, is a clear example of a field of study in which the interplay between theoretical studies and experiment has proved to be extremely fruitful.

10.2 Theoretical models

In this section we present a brief summary of the theoretical methods we have used to study the mechanical and electronic properties of nanotubes.

In the case of carbon materials with mainly sp^2-like bonding the simpler model used is the Tight-Binding (TB) [26] or Hückel model for a π-bonded graphene sheet [7]. In this model we retain only nearest neighbour interaction between p_z-orbitals oriented perpendicularly to the tube axis. The Hamiltonian is $H_{ij}{=}{-}\gamma_0$ for nearest neighbour atoms, and $H_{ij}{=}0$ otherwise and it is known to provide an excellent description of the low energy features for the band structure of isolated armchair nanotubes [27], when $\gamma_0 \sim 2.7$ eV. A brief discussion of how this γ_0-value depends on the structure of the tube is given in Section 10.5. The main advantage of this model is that can be solved analytically. The wavefunctions of the band states crossing the Fermi level ($k_F = 2\pi/3a$) are $\psi_i(x){=}c_i \sin(kx)$, with $c_1{=}c_2{=}{-}c_3{=}{-}c_4$ for the bonding states (descending band), and $c_1{=}{-}c_2{=}{-}c_3{=}c_4$ for the antibonding solutions. This model turns out to be rather useful in describing the STM images of carbon nanotubes [28, 29, 30, 31].

For the extensive calculations on the mechanical properties we have resorted to a non-orthogonal Tight-Binding [26] scheme due to Porezag and coworkers [32], known as the DFTB model (see Section 10.4). This model has been parametrised for C, B, N as well as for other elements, and is thus well suited for the study of nanotubes. We will not go into details of the model here, but suffice it to say that a DFTB parametrisation is constructed on the basis of DFT calculations employing atomic-like orbitals in the basis set. The non-orthogonality of the basis set is retained, in contrast to the usual practice in empirical TB models, but the approximation of disregarding three-centre contributions to the Hamiltonian matrix elements is used in order to simplify the method. As well as the conventional band-structure contribution to the total energy, the model incorporates a short-range pair-repulsive potential, which is constructed in such a way as to reproduce the DFT results obtained with the same basis in a number of reference systems.

We have performed the *ab-initio* calculations using the standard plane-wave pseudopotential total-energy scheme [33, 34] in the local density approximation (LDA) [35] to the exchange correlation potential. *Ab-initio* norm-conserving nonlocal ionic pseudopotentials have been generated by the soft-pseudopotential method of Troullier and Martins [36]. The LDA wave functions were expanded in plane-waves up to a 48-Ry cutoff (see refs. [33, 34] for details of the method). When studying finite length tubes, the large unit cell together with the large number

of atoms involved ($\simeq 1000$) makes the plane-wave calculation prohibitive. In this case we made calculations in a localized atomic-orbital basis set [37] that has been already applied successfully in studying electronic, structural and STM images of carbon-nanotubes [28, 38].

10.3 Nanotube structure

Before discussing in any more detail the mechanical and electronic properties of nanotubes, a brief description of their structure is in order. A nanotube can be regarded as a graphene sheet, i.e. a 2-D array of carbon atoms in a hexagonal pattern, rolled up in such a way as to form a seamless cylinder. This would give the simplest type of nanotube: the single-wall nanotube (SWNT). Often, however, nanotubes are formed by multiple cylindrical shells in a co-axial fashion, with a shell spacing approximately equal to the inter-layer spacing in graphite, namely 3.4 Å. These are known as multi-wall nanotubes (MWNT). Both SW and MWNT share a common feature in that their aspect ratio, that is the ratio of their length to their width, is very large. While the diameter of a SWNT nanotube is usually in the range 1-2 nm, and that of a MWNT nanotube can vary up to 25 nm, their length approaches the μm scale. Thus, nanotubes are essentially 1-D systems.

Consider a flat graphene sheet, and choose a given atom in the lattice as the origin. A vector with its end at the origin and its tip at any other atom of the same type[1] can be written as $\mathbf{c} = n\mathbf{a}_1 + m\mathbf{a}_2$, where n, m are integers and $\mathbf{a}_1$ and $\mathbf{a}_2$ are the lattice vectors. Now, if we take the sheet and cut it along two lines perpendicular to vector $\mathbf{c}$ passing through its tip and its end, and we then fold the graphene band that results in such a way that the tip of vector $\mathbf{c}$ is made to coincide with its end, what results is a nanotube which can be uniquely labeled as (n,m). Nanotubes constructed in this way can be classified into three different kinds: (n,0) nanotubes have atoms arranged in a zig-zag pattern along the circumference of the tube, and are thus called zig-zag nanotubes. (n,n) nanotubes, by contrast, have atoms arranged in an arm-chair pattern. Both zig-zag nanotubes and arm-chair nanotubes are identical to their respective mirror images, and are therefore achiral. General (n,m) (with m$\neq$n$\neq$0) cannot be superimposed on their mirror images, and are therefore chiral nanotubes. From zone-folding symmetry considerations based on the semimetallic band-structure of a single-graphene sheet [27], a tube will be metallic if its values of n and m obey the relation $2n + m = 3q$ where q is an integer; $(n, n + 3i)$ tubes (with i an integer) are small-gap semiconductors with $E_{gap} \propto \frac{1}{R^2}$ and other tubes have larger gaps proportional to $\frac{1}{R}$, being R the radii of the tube. This classification depends critically on the size and location of the graphitic Fermi points.

10.4 Mechanical Properties of Nanotubes: the Young's Modulus

The Young's modulus, Y, quantifies the resistance that a material opposes against deformation in a particular direction. In particular for nanotubes, it is important to determine the Young's

[1] Since the hexagonal graphene sheet is a lattice with a basis of two atoms, type 1 and type 2 atoms, the end and the tip of the vector must connect two atoms of the same type in the basis.

modulus along the axial direction. Y is usually defined by the following expression:

$$Y = \frac{1}{V_0}\left(\frac{\partial^2 E}{\partial \epsilon^2}\right)_{\epsilon=0}, \tag{1}$$

where E is the total energy, ϵ is the strain in the direction of deformation and V_0 is the equilibrium volume[2].

The Young's modulus of conventional materials varies from a few GPa to up to 600 GPa for the hardest materials, such as diamond and SiC. Since the discovery of nanotubes it was speculated that they could have values of Y even larger than this, given that the in-plane C–C bond in graphite is one of the strongest chemical bonds known in nature (the c_{11} elastic constant in graphite is 1.060 TPa [8]). The first hard evidence in this respect was provided by Treacy *et al.* [39], who, by monitoring the amplitude of the thermal oscillations of the free tips of anchored MWNT's at a range of temperatures, were able to obtain an estimation of their Young's modulus. The mean value of Y obtained was 1.8 TPa, but the data for individual nanotubes ranged from 0.4 to 4.15 TPa, evidence of the large statistical errors in their measurement. Although the value first reported by Treacy and coworkers is now generally accepted to be slightly too large, it is nevertheless indicative of the exceptional mechanical properties of carbon nanotubes.

The same experimental technique has been used by Chopra and Zettl [40] to determine the Young's modulus for BN nanotubes. These authors reported a value of 1.22 TPa. More recently, Krishnan *et al.* [41] have also used this technique to determine the value of Y for carbon SWNT's. Their reported value, 1.25 TPa, is much closer to the expected value for graphite along the basal plane, and is probably a more realistic figure than that obtained earlier by Treacy and coworkers [39].

Wong *et al.* [42] have used a different approach to probe the mechanical properties of nanotubes. They have used an Atomic Force Microscope (AFM) to exert a distortion on the free-standing part of an anchored nanotube, while simultaneously recording the force exerted on the tip by the nanotube as this is being pushed out of its equilibrium position. These authors reported a value of 1.28 TPa for MWNT's, in very good agreement with the results of Krishnan *et al.* [41] for SWNT's. That both SW and MWNT's have very similar Young's modulus is indicative of the fact that the stiffness of nanotubes is essentially a consequence of the strength of the C–C bond in the graphene sheets, the interaction between different walls in MWNT's having only a small effect on their mechanical properties. Other groups have also reported experiments aimed at determining the mechanical properties of nanotubes, such as Salvetat *et al.* [43] and Muster *et al.* [44]. All these experiments have contributed to confirming that nanotubes indeed have exceptional stiffness along the axial direction. Also, there are many direct observations of the large bending flexibility [45, 46] of nanotubes, which provide evidence of their capability to sustain large strains without evidence of collapse or failure. This flexibility property stems from the the ability of the sp^2 network to rehybridize when deformed out of plane, the degree of $sp^2 - sp^3$ rehybridization being proportional to the curvature.

[2]For the particular case of a SWNT, V_0 is not well defined, since one cannot unambiguously assign a thickness to a shell which is one-atom thick. The conventional way to bypass this problem is to assume a thickness equal to 3.4 Å, i.e. the inter-layer spacing in graphite. This convention is used by experimentalists and theoreticians alike, although it is not universally followed.

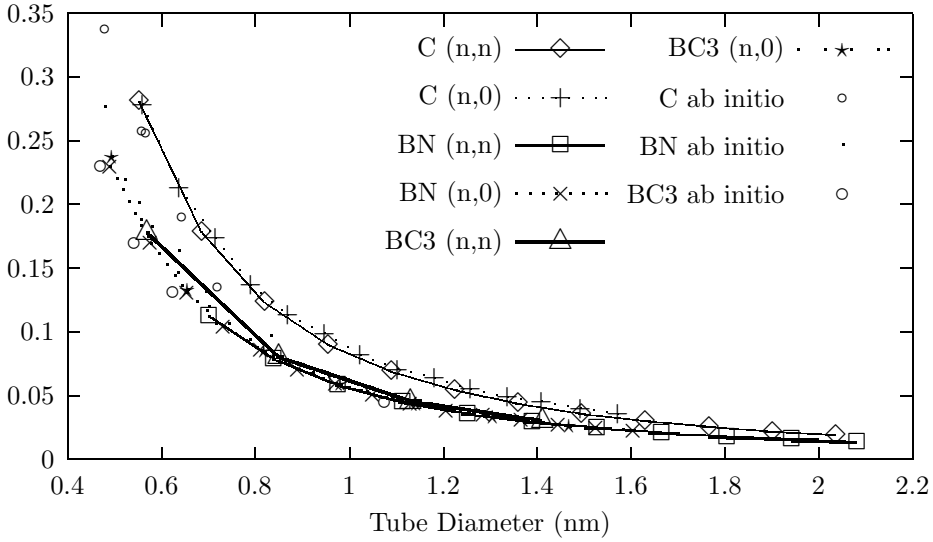

Figure 1: Curvature strain energy as a function of the equilibrium tube diameter, as obtained from the tight-binding calculations, for C, BN and BC_3 nanotubes. The strain energy is given in eV/atom.

The mechanical properties of nanotubes have also been investigated by theoretical means [47, 48, 49, 50, 51, 52, 53]. In the majority of cases these studies have been performed using empirical potential models. Well tested empirical potentials exist for carbon based systems, but no such models are generally available, to our knowledge, for other systems such as BN or BC_3. It would be possible in principle to study composite nanotube systems by means of first-principles Density Functional Theory (DFT) calculations. Indeed we have carried out such calculations for a small number of nanotubes. However, they are extremely costly, and especially for nanotubes, given that these contain large regions of empty space which nevertheless increase the cost of the calculation significantly. Our approach [54] has thus been to perform DFT calculations in a small number of cases only, and to use these results as a benchmark for calculations using a simpler description of the atomic interactions, namely a Tight-Binding (TB) model [26]. The model of our choice has been the non-orthogonal DFTB scheme proposed by Porezag and co-workers [32]. A point worth stressing is the fact that no fitting to mechanical properties of the system under study is carried out during the parametrisation of the model. Nevertheless the parametrisations that result from this scheme are reliable enough as to predict structural, energetic and mechanical properties which are in very good agreement with both empirical data and results from higher levels of theory (first-principles DFT), as will become apparent below.

Before describing our theoretical calculations of the Young's modulus let us consider the concept of *strain energy* of nanotubes, i.e. the energy difference between a nanotube and its parent flat graphene structure. Fig. (1) shows the strain energy for tubes of different composition as a function of the tube diameter, calculated by means of the DFTB model and from first-principles DFT calculations [14, 17, 22]. Notice the good agreement that can be observed between the first-principles and the DFTB results, which serves as a first indication that the DFTB model is capable of giving a good description of the energetics of nanotubes of different chemical composition. It can also be seen that carbon nanotubes are predicted to have the highest strain

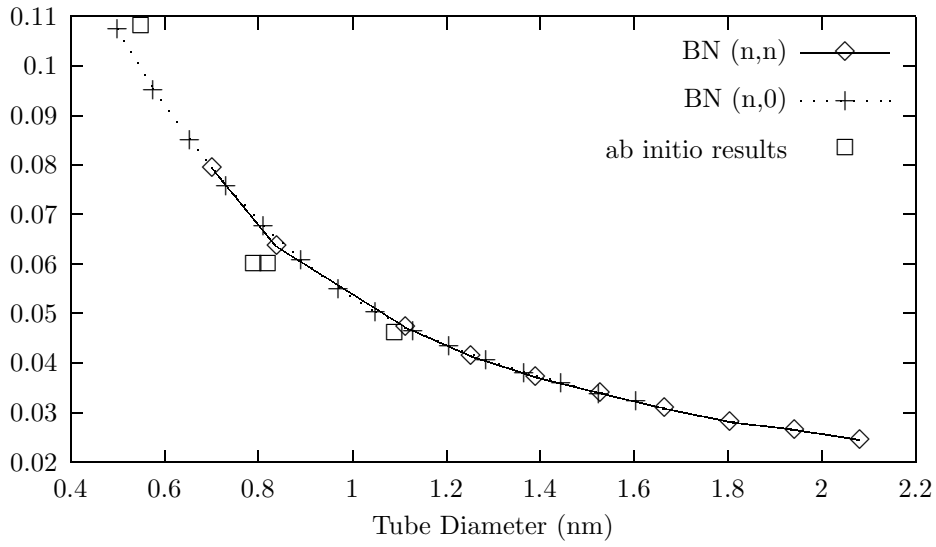

Figure 2: Buckling in the BN nanotube equilibrium structures vs. tube diameter. We define the buckling as the mean radius of the nitrogen atoms minus the mean radius of the boron atoms, and is given in Å.

energy at all tube radii. In fact, this is already an indication that carbon nanotubes have a higher Young's modulus than any of the composite nanotubes considered here. Tibbets [55] has shown that the strain energy in the continuum elasticity theory limit is given by

$$E_s = \frac{Ya^3}{6}\frac{\Omega}{D^2}, \tag{2}$$

where E_s is the strain energy per atom, Y is the Young's modulus, a is a constant of the order of the inter-layer spacing in graphite, Ω is the area per atom and D is the tube diameter. According to this expression, types of nanotubes with higher strain energy should have a higher Young's modulus. Fitting the data of Fig. (1) to an expression of the form $\alpha D^{-\beta}$ shows that the calculated strain energy obtained for the different types of tubes considered here follows very closely the behaviour predicted by Tibbets.

Another indication of the reliability of the DFTB model used in the present study is its ability to reproduce rather fine structural details of these tubular systems predicted from plane-wave DFT pseudopotential calculations [22]. These calculations predict that BN nanotubes are slightly buckled on the surface; the B atoms displace inwards towards the tube axis, while the N atoms displace in the outward direction. The amount of buckling is dependent on the tube diameter, but it is otherwise independent of the tube structure, as can be seen in Fig. (2). This figure also shows the results obtained from the DFT calculations [22], and it can be seen that the agreement between both calculations is rather good.

Finally, let us consider the direct evaluation of the Young's modulus from DFTB calculations. Results for selected nanotubes of the different compositions considered are given in Table. (1). Each tube considered has been simulated as an infinitely long nanotube using periodic boundary conditions along the tube axis. A series of calculations were performed for each tube, varying the length of the repeat cell and relaxing the atomic positions without constraints. From these calculations we obtain the equilibrium configuration as well as stressed configurations, which

$B_xC_yN_z$	(n,m)	D_{eq} (nm)	σ	Y_s (TPa · nm)	Y (TPa)
C	(10,0)	0.791	0.275	0.416	1.22
	(6,6)	0.820	0.247	0.415	1.22
		(0.817)		(0.371)	(1.09)
	(10,5)	1.034	0.265	0.426	1.25
	(10,7)	1.165	0.266	0.422	1.24
	(10,10)	1.360	0.256	0.423	1.24
	(20,0)	1.571	0.270	0.430	1.26
	(15,15)	2.034	0.256	0.425	1.25
BN	(10,0)	0.811	0.232	0.284	0.837
	(6,6)	0.838	0.268	0.296	0.870
		(0.823)		(0.267)	(0.784)
	(15,0)	1.206	0.246	0.298	0.876
	(10,10)	1.390	0.263	0.306	0.901
	(20,0)	1.604	0.254	0.301	0.884
	(15,15)	2.081	0.263	0.310	0.912
BC_3	(5,0)	0.818	0.301	0.308	0.906
	(3,3)	0.850	0.289	0.311	0.914
	(10,0)	1.630	0.282	0.313	0.922
	(6,6)	1.694	0.279	0.315	0.925

Table 1: Structural and elastic properties of selected nanotubes obtained from the tight-binding calculations reported here. Young modulus values given in parenthesis were obtained from first-principles calculations. Also the value of Y with the convention $\delta R = 0.34$ nm is given for comparison. Values given in parenthesis were obtained from plane-wave DFT-pseudopotential calculations, and are given for comparison.

give us the total energy as a function of the imposed axial strain. From this data we are able to obtain the Young's modulus using Eq. (1). The results we obtained, given in Table (1), were obtained using the normal convention of taking the wall-thickness equal to 3.4 Å.

It can be seen from Table (1) that indeed the carbon nanotubes have the highest Young's modulus, as predicted from Tibbet's formula [55] for the strain energy. The BN and BC_3 tubes have similar values of the Young's modulus, around 0.9 TPa, which is less stiff than that of the pure carbon nanotubes, but still considerably stiff. The tubes of BC_2N composition have Young's modulus in between the C and BN/BC_3 nanotubes, having a value around 1 TPa. Although tubes of BC_2N composition have been synthesized, it now appears to be the case that these consist of concentric shells of C and BN, with pure C nanotubes in the inner and outer shells, and BN in the middle; stoichiometrically homogeneous BC_2N tubes have not been yet obtained, to our knowledge.

The value of the Young's modulus obtained for the wider carbon nanotubes is 1.26 TPa, which is in very good agreement with the experimental value reported by Krishnan *et al.* [41] (1.25 TPa) for SWNT's, and also with the value obtained by Wong *et al.* [42] (1.28 TPa) for MWNT's. As we have pointed out earlier, the fact that SW and MWNT's are reported to have very similar

values of Y is not surprising, as we expect Y to be mostly determined by the strength of the C–C bond in the graphene sheets. For the composite nanotubes, the only existing experimental data is that of Chopra and Zettl [40] for BN nanotubes. They quote a value of 1.22 TPa, slightly larger than what we obtain (0.9 TPa for the widest tubes), but still within reasonably good agreement. For the particular case of the (6,6) C and BN nanotubes, plane-wave DFT pseudopotential calculations were also carried out for comparison. The results obtained from these benchmark calculations are also shown in Table (1). Notice the good agreement between these and the DFTB results.

More recently we have also reported results for C_3N_4 nanotubes [56]. Although nanotubes containing C and N have been synthesized [57], it has not yet been possible to obtain structures of C_3N_4 stoichiometry. The presence of N in these structures seems to prevent graphitisation [58], in contrast to what happens when B is present [59]. Nevertheless, since it has been speculated in the past that CN structures could lead to ultra-hard materials [60], we have considered the C_3N_4. Our results indicate that such tubes would be significantly softer than the other tubes considered earlier, having a Young's modulus of the order of 0.6 TPa.

10.5 Density-of-states: STS-spectroscopy

The relation between nanotube chirality and its electrical properties can be complementary explored by theoretical calculations and Scanning Tunneling Microscopy (STM) experiments, since it allows both topographic imaging and Scanning Tunneling Spectroscopy (STS) from which information about the local density of states (LDOS) can be obtained. STM have resolved the atomic structure and confirmed the predicted interplay between geometry and electronic properties [61, 62, 63]. However, the determination of the diameter of the nanotube is not straightforward due to tip-convolution effects and operation mode. The chiral angle can be affected by mechanical distortions [64] and by the geometry of the STM experiment in obtaining the topographic image: the cylindrical geometry of the nanotube produces a geometrical distortion of the image stretched in the direction perpendicular to the tube axis [31]. Interactions stemming from tube-packing or tube/substrate/tip can modify the predicted properties of isolated SWNT and need further study and detailed analysis [28, 29, 30].

The DOS gives a direct information about the metallic/semiconducting behaviour of the nanotubes as well as particular insight into the tube-tube or tube-substrate interactions. Information about structural properties and local environment for a carbon or composite nanotube can be extracted from the computed DOS [30]. In a recent work, the connection between tube-diameter and low-energy features in the DOS has been pointed out[65, 66]. The fact that the electronic DOS for each metallic or semiconducting tube is practically independent of the nanotube chirality, is in qualitative agreement with STS experiments [61]. The simple π-electron TB model was used to get this general correlation between tube-diameter and features in the DOS [65, 66] (see below for more details about this model in comparison with first-principles calculations). We have shown [29] that curvature induced σ-π hybridisation leads to quantitative changes in the DOS in both peak energies and intensities. Therefore, the TB-results are only valid for states a few tenths of an eV above or below the Fermi level, and ab-initio calculations

are needed to address the validity of this simple model and to get a meaningful comparison with experiments.

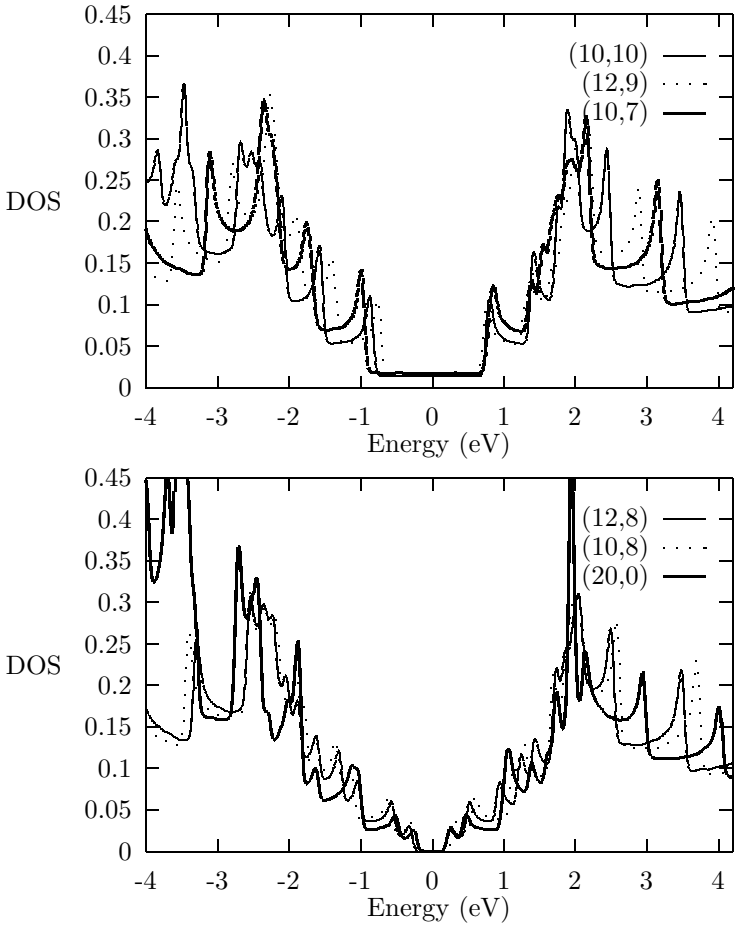

Figure 3: Ab initio DOS for different metallic (top panel) and semiconducting (bottom panel) tubes with diameters in the range of 1-2 nm, namely: 1.17, 1.36, 1.44, 1.23, 1.37 and 1.58 nm for the (10,7), (10,10), (12,9), (10,8), (12,8) and (20,0) nanotubes, respectively. Spikes in the DOS stems from the van Hove singularities of the nanotube 1D-band-structure. All DOS are normalized to the number of atoms in the nanotube unit cell.

In Fig. (3) we plot the computed ab-initio DOS for a set of chiral and non-chiral tubes with diameters around the experimental value of 1.3 nm (between 1.1 and 1.6 nm). The following conclusions can be extracted from the figure:

(i) in metallic tubes the plateau around the Fermi level depends on both tube diameter and, to a lesser extent, on tube-chirality. For almost all tubules with $\sim$1.3 nm diameter the metallic-plateau is about 1.7-2.0 eV. This data is of importance is discriminating metallic and semiconducting tubes in resonant-Raman scattering experiments [67, 68]. The non-armchair tubes belonging to the metallic group are indeed quasimetallic with an extremely small gap introduced at the Fermi level by curvature effects.

(ii) The electron-hole symmetry of the TB-model is no longer valid even for the first spikes in the DOS (see the clear example of the (10,7) metallic tube). This effect gets more clear as the nanotube radius is reduced or/and as we move away from the Fermi level. The

separation between van Hove singularities is also slightly different for both conduction and valence states.

(iii) The direct connection between the diameter and the structure of the spikes in the DOS is not always clear. Note for example that the semiconducting (12,8) and (20,0) nanotubes have very similar DOS close to the Fermi level. However their diameters are 1.37 and 1.58 nm, respectively. The same holds for the metallic (12,9) and (10,10) tubes with very similar "metallic-plateau", but diameters of 1.44 and 1.36 nm, respectively. Then, although the proposal in ref. [65] is very appealing, its practical application to discern the tube-diameter is doubtful in its spatial resolution (not better than 0.15 nm for the diameter).

To get insight into tube-tube interaction in MWNT we plot in Fig. (4) the DOS for a MWNT formed by three concentric armchair tubes such that the inter-tube distance is close to the graphitic value and for a bundle or nanotube-rope constituted by three (8,8) SWNT packed on an equilateral triangle network with 0.345 nm intertube distance. In the MWNT case we see that the low-energy structure seems to give information about the number of layers in the tube, however this identification gets more complicated when non-commensurate metallic or semiconducting tubes participate as main building blocks of the MWNT. As expected, the metallic-plateau of the MWNT is mainly controlled by the outer tube. The interaction among tubes being weak, only shifts a little bit the position of the van Hove singularities in the MWNT with respect to the SWNT. This shift is larger for the conduction states making the electron-hole asymmetry more clear. In the case of the nanotube bundle the interaction clearly modifies the spectra seen in the DOS in the following way:

(i) It opens a "pseudogap" close to the Fermi level as already predicted for random oriented nanotube ropes[69] (pseudogap of ~ 0.1 eV). The bundle remains metallic.

(ii) It makes the electron-hole asymmetry in the DOS more accentuated and the spike structure of the van Hove singularities is smoothed out.

The fact that the position in energy of the peaks is not strongly modified explains the success of using isolated SWNT spectra to describe the experimental data [61]. However the shape of the spectra (relative intensities) is strongly affected by tube-tube interactions.

It is worth discussing these results in terms of the simple π-electron TB model. The hamiltonian in this case has electron-hole symmetry around the Fermi level and the DOS can be expressed in terms of a universal function that depends only on whether the tube is metallic or semiconducting [65]. In terms of the nearest neighbour overlap energy γ_0 we have that, for a semiconducting tube, the band-gap is given by

$$E_g = \frac{2\gamma_0 a_{C-C}}{D} \, , \tag{3}$$

where a_{C-C} is the carbon-carbon bond-length (~ 1.42Å) and D is the nanotube diameter. In the case of metallic tubes, the metallic plateau (E_{met}), given by distance between the two van Hove singularities above and below the Fermi level, is

$$E_{met} = \frac{6\gamma_0 a_{C-C}}{D} \, . \tag{4}$$

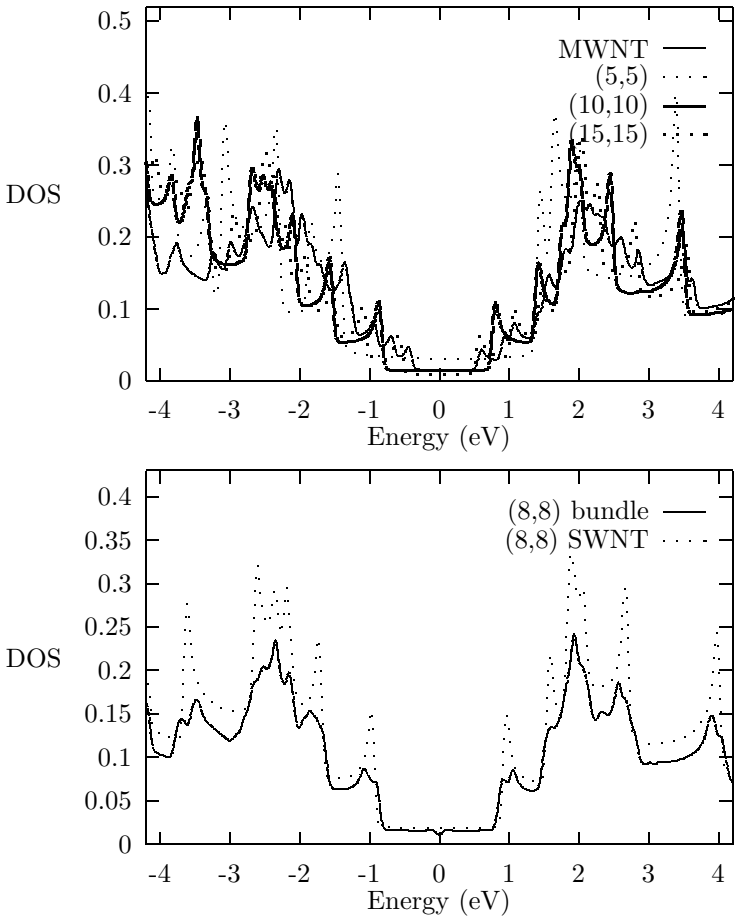

Figure 4: Top panel: DOS for a MWNT formed by three concentric armchair tubes: (5,5)+(10,10)+(15,15). Bottom panel: DOS for a small nanotube-rope (bundle) formed by three (8,8) SWNT (1.09 nm diameter) packed in a triangular lattice with an intertube distance of 0.345 nm. We clearly see the opening of a "pseudogap" of about ∼0.1 eV around the Fermi level. We compare the results for the bundle with the DOS for an isolated (8,8) SWNT (dashed line). Each DOS is normalized to the number of atoms in the unit cell.

In both cases the distance between consecutive conduction or valence van Hove singularities is given by

$$\Delta E = \frac{3\gamma_0 a_{C-C}}{D} \ . \tag{5}$$

This γ_0 parameter plays an important role in the experimental analysis of their electronic structure data. In fact, a fit to STS experiments [61] give a value of γ_0=2.7 eV, whereas the fit to resonant Raman scattering experiments on metallic carbon nanotubes [68] gives γ_0=2.95±0.05 eV. This indirect estimation is in quite good agreement with the direct measurement by STS, and both are smaller than the γ_0=3.16 eV value for graphite [8]. Our results show that the value of γ_0 is not unique due to the anisotropy of the DOS in both peak positions and intensities. Semiconducting tubes are the best candidates to extract experimentally the value of γ_0 from eqn. (3). We got values from 2.77 to 2.95 eV for tubes with diameters of 1.23 and 1.58 nm, respectively. Smaller values are obtained for metallic tubes when fitting the metallic plateau to eqn. (4) (from 2.32 to 2.75 eV for diameters of 0.68 to 2.04 nm, respectively). In general, the value of γ_0 increases with increasing nanotube diameter and the

interaction between tubes also modify this parameter by as much as 10% [29]. In fact, the electron-hole asymmetry in the density of states is a measure of the curvature effects, intertube interactions and anisotropy in the band-structure.

As most STM experiments are performed on supported tubes on substrates [62, 63], therefore it is important to get insight about the role played by the substrate in the experimental images. We have shown [28], in the case of the experimentally supported tubes on Au(111), that the gold substrate modifies the spectrum in several ways.

(i) It opens a small "pseudogap" in the tube states at the Fermi level whenever the symmetries of the tube are not respected by the gold substrate [69]

(ii) It shifts the Fermi level, producing a transfer from the gold to the nanotube and a quite strong tube-substrate bonding that prevents the tube from moving.

However, even if the electronic level structure is very sensitive to external perturbation, we have found [28, 29] that the whole set of STM images of armchair carbon nanotubes can be understood in terms of the isolated SWNT wave-functions that, in the simple TB-model, offers a catalog of just four image patterns [28] (this result is confirmed by ab-initio calculations).

10.6 Finite-size effects

The study of electron standing-wave (SW) in nanostructures is of fundamental interest as one addresses directly theoretical and experimental problems connected with low-dimensional systems (an example are the nanotubes as quasi one-dimensional-molecular wires). Typical aspects of the nanoscale world as Coulomb blockade, localization, oscillations in the conductivity and the quantized conductance (in units of the conductance quantum $G_0 = 2e^2/h$=(12.9 kiloohms)$^{-1}$) of nanotubes have been already observed[15, 70, 71]. In this last case, the nanotubes conduct current ballistically and do not dissipate heat. In fact, conduction electrons in armchair nanotubes have very large electron mean free paths resulting in exceptional ballistic transport and localization lengths of 10μm [72].

The transition from a one-dimensional (1D) to a zero-dimensional (0D quantum-dot) system can be studied by looking at different finite-length carbon nanotubes[28, 62]. More detailed information about the electronic structure of 1D-quantum wires can be directly obtained in STS experiments by mapping the 1D-confinement of electrons in the nanotube structure. This can be achieved by cutting the tube to a finite-length [73], which reduces the periodic band-structure to a discrete set of molecular levels[74] that can now be imaged by STM [62, 75]. In this simple scenario of a 1D particle-in-a-box model, a tube of length L has a set of allowed k's given by $k = n\pi/L$ (n integer). Taking the Fermi level of the tube at the single graphene-sheet value of $k_F = \frac{2\pi}{3a}$, the wavefunctions close to the Fermi level will exhibit a periodic pattern with a wavelength of $\lambda_F = 3a = 0.74$ nm, as observed in STS measurements [62]. Although, this basic standing wave observation can be explained in terms of the simple 1D particle-in-a-box model, further insight is needed to understand their energy and three-dimensional shape [28]. Evidence for 1D quantum confinement was already obtained from transport measurements on single-wall

tubes [70, 76], but the standing-wave states have been observed only recently in 1D scans of scanning tunneling spectroscopy (STS) [62] and described theoretically[28].

In general, the value of the HOMO-LUMO gap decreases with increasing tube length not monotonically but exhibiting a well defined oscillation that is related to the localization and bonding character of the HOMO and LUMO orbitals [3]. By increasing the tube-length we observe a smooth transition from an energy level structure characteristic of a molecular-wire (0D-system) to that of a delocalized one-dimensional system, that seems to be complete for tube-lengths of the order or larger than 5 nm [74].

Furthermore, the geometry of the nanotube-cap give rise to localized states close to the fermi level [63, 77]. The spatial localization and expected coherent electron emission of these states, makes this finite capped nanotubes ideal candidates for the scanning microscopy tip and electron emission materials [18]

10.6.1 STS on Boron-Nitride nanotubes

The electronic properties of BN nanotubes are quite different to carbon, namely: all are stable wide band-gap semiconductors independent of helicity and diameter of the nanotube and of whether the nanotube is single- or multi-walled. The band-gap constancy may be of importance for technological applications because samples containing many different sizes could be grown with predictable electronic properties even in the multiwall case playing an important role in applications involving n-type doping. The existence of NFE-states above E_F is systematically seen in the C-, BC_3-, BC_2N-sheets and tubules but are much higher in energy than for the BN-systems and do not play an important role in their electronic properties as does for BN [22, 78].

In Fig. (5) we present our preliminary data on the spectroscopic properties of BN-nanotubes. The aim is to look for a general behaviour of the van Hove singularities as a function of tube diameter and chirality. In contrast to carbon nanotubes, the first spikes provides us with the semiconducting band-gap that is rather insensitive to tube chirality and diameter. Furthermore, the structure and intensities of the next spikes in the DOS depends clearly not only on the diameter but also on the structural geometry. We are presently working in trying to rationalize this results in terms of a simple parametrised TB model for BN [22] and to describe a general chiral nanotube.

10.7 Conclusions

To summarise our results on the mechanical properties of nanotubes, we have used the non-orthogonal TB scheme of Porezag and coworkers [32] known as DFTB to study the structural, energetic and mechanical properties of nanotubes of $B_xC_yN_z$ composition, obtaining rather good agreement with the available experimental data, as well as with results from DFT calculations. Our results indicate that C nanotubes are very stiff, the stiffest of the different nanotubes

[3]The band-gap behavior can be divided in four classes depending of the tube length, chirality and capping geometry: (i) the gap diminished toward the infinite-tubule value with a period-3 oscillation of amplitude quenched as 1/L; (ii) the gap diminished monotonically as 1/L to the infinite value; (iii) the gap approaches exponentially fast a constant value different than that for the infinite tubule and (iv) the gap is constant [74].

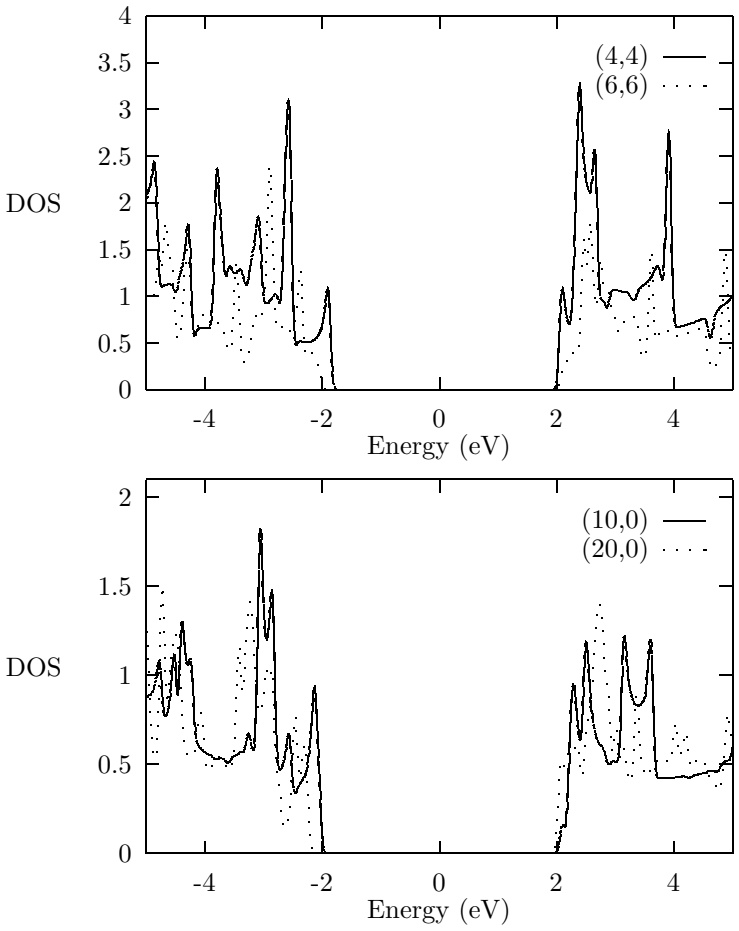

Figure 5: Up: Calculated DOS for SWNT's made of BN. Top panel corresponds to armchair nanotubes and bottom panel to zig-zag nanotubes. The band-gap is less sensitive to chirality and diameter than the peak-structure in the DOS.

considered, having a Young's modulus of approximately 1.26 TPa at the diameter range found in experimental samples of SWNT's (1.3 nm). We indicate that the flexibility of composite nanotubes during bending in a wide range of practical conditions shows substantial promise for structural, fiber applications (the "ultimate" lightweight-high-strength flexible fiber) and nanotube-reinforced materials. This is due to the remarkable flexibility of the hexagonal network, which resist bond breaking and bond switching up to very high strain values. One direct application is related to the atomic-force microscope (AFM). Carbon nanotubes have previously been used as tips in AFM for producing images [79]. Now for the first time nanotube tips have been used as pencils for writing 10-nm-width structures on silicon substrates [80].

The combination of the spectroscopic models developed in the last section for carbon and boron-nitride can be extended to get information about the structural properties of the recent synthesized sandwiches of carbon and boron nitride nanotubes [81]. This structures have is mainly formed by carbon layers at the center and at the periphery, separated by few BN-layers. Further developments of multielement nanotubes forming this type of coaxial "nanocable" structure has been achieved [82]. This new structure resembles a coaxial nanocable with semiconductor-insulator-metal/semiconductor geometry and it is made of silicon carbide at the

core of the nanowire covered by an amorphous layer of silicon oxide. The whole structure is sheathed by graphitic layers of carbon and boron-nitride. This new type of structures could have technological applications.

In summary, more striking advances both in theory and experiments are ready to come in the near future, as can be expected from the tremendous advances in the field in the last years. We have to be ready to discover some "surprises" to stem from the new physical and chemical properties of this whole class of nanocomposite materials.

10.8 Acknowledgments

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