ABOUT THE HEXAGON ON THE TITLE PAGE

Color rendition of the Raman D peak intensity measured across a graphene flake modified by incident laser light. Graphene, a single plane of carbon atoms arranged in a honeycomb lattice, was prepared by micromechanical exfoliation of highly oriented pyrolytic graphite on top of a silicon substrate covered with 300 nm silicon dioxide. The six corners of a hexagon were ‘written’ with a diffraction limited laser beam spot (400 nm). Laser exposure initially removes dopants locally. For longer exposure times, $sp^2$ carbon-carbon bonds are disrupted. These defects enhance the electron scattering and can be detected as an increase in the intensity of the Raman D peak (see also p. 19).

Corresponding articles:

Laser-induced disassembly of a graphene single crystal into a nanocrystalline network.

Graphene: Dim the lights.
In this report that you hold in your hands we intend to give an impression of the manifold scientific activities at the Max-Planck-Institut für Festkörperforschung during the year 2008. In the first part, we present a selection of highlights of the scientific accomplishments in our Departments, Junior Research Groups, and Scientific Service Groups. The second part contains a complete list of publications as well as other useful information on our Institute. More details can be found on our web page ‘www.fkf.mpg.de’.

This year another Independent Junior Research Group, led by Peter Wahl, was established at the Institute. The new group performs spectroscopic mapping of correlated electron materials, complementing nicely the other research activities of the Institute.

We thank all the members of the Institute for their hard work and dedication. It is thanks to their efforts and performance that the Institute has been able to maintain its high standard of research.

Stuttgart

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Contents

General information on Abteilungen,
Junior Research Groups, and Scientific Service Groups . . . 1

Selected research reports ................................. 13

Publications ............................................. 105

Habilitation, PhD, Master, and Diploma theses ............ 131

Invention reports & patent applications .................... 133

Organization & budget ..................................... 135

Colloquia ..................................................... 143

Guest scientists ............................................ 147

PhD, Master, and Diploma students ....................... 153

Staff scientists ............................................. 159
SELECTED RESEARCH REPORTS

Graphene

The chemical route to graphene
M. Burghard, C. Gómez-Navarro, R.S. Sundaram and K. Kern ........................................... 13

Structural and electronic properties of epitaxial graphene on SiC(0001)
C. Riedl and U. Starke .................................................................. 16

Laser-induced disassembly of a graphene single crystal

Doping by metal contacts in graphene devices
K. Balasubramanian, E.J.H. Lee, R.T. Weitz, M. Burghard and K. Kern ............................. 23

Quasiparticle chirality in epitaxial graphene probed at the nanometer scale
I. Brihuega, S. Bose, C.H. Michaelis, L. Vitali and K. Kern;
P. Mallet, F. Varchon, L. Magaud, C. Bena and J.Y. Veuillen ................................... 26

Superconducting materials

Energy gaps and Kohn anomalies in elemental superconductors
P. Aynajian, L. Boeri, T. Keller and B. Keimer; K. Habicht; S.M. Shapiro ................................. 31

Evidence for gap anisotropy in CaC$_6$ from far-infrared and point-contact spectroscopy
J.S. Kim and R.K. Kremer; U. Nagel, D. Hüvonen, E. Joon and T. Rööm; R.S. Gonnelli, D. Daghero,
D. Delaude, M. Tortello and G.A. Ummarino; V.A. Stepanov; A. Sanna; G. Profeta; S. Massidda ...... 35

Controversies in superconductivity
S. Deng, A. Bussmann-Holder, J. Köhler and A. Simon ..................................................... 38

Magnetic properties of BaFe$_2$As$_2$ from spin-spiral calculations
A.N. Yaresko, G.-Q. Liu, V.N. Antonov and O.K. Andersen .............................................. 40

Incommensurate spin density modulation in a copper-oxide chain compound with
commensurate charge order
M. Raichle, M. Reehuis, M. Sofin, M. Jansen and B. Keimer; G. André; L. Capogna ................. 43

Iron pnictides: Single crystal growth and effect of doping on superconducting properties
G.L. Sun, D.L. Sun and C.T. Lin .................................................................................... 47
Structure and bonding

Investigations of the three-dimensional random network of SiBNC ceramic by solid-state NMR
Y.H. Sehlleier, A. Verhoeven and M. Jansen ................................................ 52

The N3− anion in alkali metal nitrides: Structural evolution of sodium nitride Na3N at high pressure
G.V. Vajenine, X. Wang, I. Efthimiopoulos, S. Karmakar and K. Syassen; M. Hanfland ............. 55

The high-pressure crystal structure of the NLO compound BiB3O6 from 2D powder diffraction data
R.E. Dinnebier, B. Hinrichsen and M. Jansen; A. Lennie ................................................ 58

Unusual short intermolecular halogen-halogen contacts in chlorinated derivatives of fullerenes

Discrete and extended metal-metal bonding

Interfaces and surfaces

Conversion from ionic to electronic conduction in CeO2 when approaching the SiO2 interface
X.X. Guo, G. Gregori, Y.Q. Zhang and J. Maier .................................................. 68

Interplay of catalysis and defect chemistry: CO and CH4 oxidation by Sr(FeₓTi₁−ₓ)O₃−δ
M. Vracař, R. Merkle and J. Maier .......................................................... 70

Novel electronic and magnetic properties of La₀.₅Ca₀.₅MnO₃ films deposited on (111) SrTiO₃ substrates
G. Aydogdu-Kuru, Y. Kuru and H.-U. Habermeier .............................................. 72

Transport

Nanoscale transistors for large-area electronics

Role of ohmic contacts for the current distribution in quantum Hall samples
J. Weis, F. Dahlem and K. v. Klitzing .......................................................... 80

Kondo effect in single atom contacts: The importance of the atomic geometry
L. Vitali, R. Ohmann, S. Stepanow and K. Kern; P. Gambardella;
K. Tao, R. Huang, V.S. Stepanyuk and P. Bruno ............................................. 84

Hopping transport far from equilibrium: A generalized current equation
I. Riess and J. Maier ................................................................. 88
Electronic properties

A novel type of Peierls instability in spin chains
J. Sirker, A. Herzog, A.M. Oleś and P. Horsch .................................................. 90

Critical temperature near quantum critical points
P. Jakubczyk, P. Strack, A. Katanin and W. Metzner .......................................... 93

Atomistic modeling of semiconductor nanostructures
G. Bester, R. Singh and J. Peng ........................................................................ 95

Coupling of self-assembled quantum dots to plasmonic nanoantennas
M. Pfeiffer and M. Lippitz; H. Giessen; L. Wang, A. Rastelli and O.G. Schmidt ............... 98

Coulomb-enhanced spin-orbit splitting: The missing piece in the Sr$_2$RhO$_4$ puzzle
Chemistry

JANSEN’s department puts its main emphasis on basic research in the field of preparative solid state chemistry with the goal of developing modern materials. Classes of materials currently, under investigation include oxides and nitrides of metals and non-metals as well as fullerenes, e.g., new binary and ternary oxides synthesized under high oxygen pressure, ionic conductors, structural oxide ceramics and pigments, amorphous inorganic nitridic covalent networks, or endohedral fullerenes and fullerides.

Besides employing traditional solid state synthesis methods, a large number of alternative techniques is used, e.g., the sol-gel process, synthesis under high pressure, via an rf-furnace, at low temperatures in liquid ammonia, by electrochemical methods, or by low-temperature atomic beam deposition. Optimizing the syntheses of these materials is only a first, though crucial step, however. In addition, their chemical and physical properties, in particular optical, electrical and magnetic behavior, are analyzed both at high and low temperatures, with particular emphasis on X-ray diffraction and spectroscopic methods. This provides the basis for placing the results in the proper context regarding structure-property relationships and modern concepts of bond theory.

A long-term goal of the department is to increase the predictability of solid state chemistry, e.g., to predict the existence of not-yet synthesized compounds, calculate their properties, and finally provide prescriptions for their synthesis. This work involves both theoretical and synthetic aspects. On the theoretical side, structure candidates are determined by studying the energy landscapes of chemical systems using global exploration techniques, while on the preparative side kinetically controlled types of reactions that allow low-temperature synthesis of (possibly metastable) compounds are being developed. [52,62]

LHS: When simultaneously evaporating graphite and a metal in an rf-furnace (shown), endohedral fullerenes can be synthesized in relatively high yields. RHS: Synthesis at high oxygen pressures produces novel materials with interesting electronic, chemical and physical properties. Compounds such as Ag₁₃OSO₆ (shown) are characterized using various spectroscopic, physical and diffractive methods.

MAIER’s department is concerned with physical chemistry of the solid state, more specifically with chemical thermodynamics and transport properties. Emphasis is laid on ion conductors (such as inorganic or organic proton, metal ion and oxygen ion conductors) and mixed conductors (typically perovskites). As local chemical excitations (point defects) are responsible for ion transport and simultaneously represent the decisive acid-base active centers, a major theme of the department is the understanding of mass and charge transport, chemical reactivities and catalytic activities in relation to defect chemistry. This includes experiments (in particular electrochemical studies) as well as theory (in particular phenomenological modeling), and comprises investigations of elementary processes but also of overall system properties. In this context, interfaces and nanosystems are to the fore.

Since electrochemical investigation immediately affects the coupling of chemical and electrical phenomena, the research is directed towards both basic solid state problems and the technology of energy and information conversion or storage (fuel cells, lithium-batteries, chemical sensors).
General information on Abteilungen, Junior Research Groups, and Scientific Service Groups

Conceptually speaking, we want to address the following questions: Can we – given the materials, the control parameters and the driving force – understand or even predict concentrations, mobilities and reactivities of ionic charge carriers? How do these properties change at interfaces and in confined systems? What are the basic mechanisms of ion transport and ion transfer? How can we use this fundamental knowledge to develop at will materials for given (or novel) applications? [68,70,88]

Ionic and electronic charge carriers (e.g., vacancies) are the relevant particles as far as chemical kinetics and mass transport is concerned. They are establishing the interaction with the neighboring phases and act on electrical and chemical driving forces.

SIMON’s department emphasizes the investigation of metal-metal bonding with main group, d- and f-metals. The purpose of the work is on one side the development of structural concepts (e.g., condensed cluster concept) and on the other side the search for new materials, their phase relationships and connections between structure, chemical bonding and properties.

Targets are metal-rich compounds of transition metals, particularly oxides and halides, reduced rare earth metal halides, hydride, carbide, boride, boride carbide, aluminide and silicide halides of the rare earth metals, alkali and alkaline earth metal suboxides and subnitrides. Electron microscopy is used to characterize microcrystalline phases up to full structure refinement as well as analysis of real structure. Superconductivity is of special interest following a chemical view of the phenomenon in terms of a tendency towards pairwise localization of conduction electrons in a flat band–steep band scenario. New colossal magnetoresistance materials result from an interplay of d- and f-electrons.

Other fields of interest are structures of molecular crystals, in particular, in situ grown crystals of gases and liquids. Experimental techniques like diffractometry with X-rays and neutrons, high-resolution transmission electron microscopy, electron crystallography and measurements of magnetic susceptibility as well as electrical transport properties are used. [38,65]

Ba$_{14}$CaN$_6$Na$_{14}$ – subnanodispersed salt in a metal.
Physics

KEIMER’s department studies the structure and dynamics of highly correlated electronic materials by spectroscopic and scattering techniques. Topics of particular current interest include the interplay between charge, orbital and spin degrees of freedom in transition metal oxides and the mechanism of high-temperature superconductivity. Experimental techniques being used include elastic and inelastic neutron scattering, normal and anomalous X-ray scattering, Raman scattering off and in resonance, spectral ellipsometry (including synchrotron radiation as a source), and infrared, Raman, and X-ray measurements under high magnetic fields. Experiments at external neutron sources are carried out on a regular basis, and a spectrometer at the new research reactor FRM-II in Munich has recently been completed. The latter instrument uses a novel combination of triple-axis and neutron spin echo techniques to optimize the energy resolution and allow the determination of lifetimes of magnetic and lattice vibrational excitations throughout the Brillouin zone.

The group operates a high-magnetic field facility for X-ray scattering at the National Synchrotron Light Source (NSLS) at Brookhaven National Lab (USA). At the ANKA synchrotron in Karlsruhe, the group also operates Fourier ellipsometers for the far infrared spectral range. Close collaborations also exist with the theory and chemistry departments at the MPI-FKF; with the Crystal Growth Service Group where large, high-quality single crystals of oxide compounds are prepared with optical furnaces, and with the Technology Service Group that prepares state-of-the-art oxide heterostructures and superlattices. [31,43]

Investigation of a mosaic of crystals of a high-temperature superconductor with neutron beams (yellow). Neutrons are elementary particles that generate a magnetic field through their internal rotation (‘spin’), similar to a tiny bar magnet. When a neutron beam falls onto a magnetic material, the neutron spin is flipped and the beam is deflected. In experiments with neutron beams, Max Planck scientists are studying an unusual, fluctuating magnetic order in high-temperature superconductors that could be of central importance for an explanation of this phenomenon.

Research efforts in KERN’s department are centered on nanometer-scale science and technology, primarily focusing on solid state phenomena that are determined by small dimensions and interfaces. Materials with controlled size, shape and dimension ranging from clusters of a few atoms to nanostructures with several hundred or thousand atoms, to ultrathin films with nanometer thickness are studied.

A central scientific goal is the detailed understanding of interactions and processes on the atomic and molecular scale. Novel methods for the characterization and control of processes on the atomic scale as well as tools to manipulate and assemble nanoobjects are developed. Of particular interest are: Self-organization phenomena, atomic scale fabrication and characterization of metal, semiconductor and molecular nanostructures, quantum electronic transport in nanostructures, atomic scale electron spectroscopy and optics on the nanometer-scale. As surface phenomena play a key role in the understanding of nanosystems, the structure, dynamics and reactivity of surfaces in contact with gaseous or liquid phases are also in the focus of interest. [13,23,26,84]

The scanning tunneling microscope image shows a silver dendrite grown at 130 K on a platinum (111) surface.
The electronic properties of heterostructures, quantum wells, superlattices and carbon based quantum structures (graphene, nanotubes), in particular the influence of quantum phenomena on the transport and optical response are the main topics in von Klitzing’s department. Optical and transport measurements in magnetic fields up to $B = 21.5$ Tesla and temperatures down to $10$ mK combined with TEM/scanning probe techniques are used to characterize the systems. Picosecond sampling techniques are developed for ultrafast time-resolved measurements on nanodevices. The quantum Hall effect is studied by analyzing time-resolved transport, edge channels, the behavior of composite fermions and the response on microwave radiation and surface acoustic waves. Time-resolved photoconductivity, luminescence, and Raman measurements in magnetic fields are methods of characterizing the low-dimensional electronic systems. Coupled two- and zero-dimensional electronic systems are produced by highly specialized molecular beam epitaxy growth and by electron beam lithography. Phenomena like electron drag, exciton condensation, Kondo resonance, Coulomb blockade, ballistic transport, commensurability phenomena in periodically modulated two-dimensional systems and the interaction between electron and nuclear spins are investigated. The detection and generation of terahertz radiation using low-dimensional electron systems is one of the new research activities. [19,80]

Demanding technologies are needed for the preparation of devices used in quantum transport experiments. The figure shows a typical example where the combination of interrupted epitaxial growth, special etching processes, focused ion beam writing, contact diffusion, and gate evaporation leads to two electron layers with a distance of only $10$ nm and separate contacts.
Theory

The electronic structure plays a key role in determining transport, magnetic, optical, and bonding properties of solids. The members of Abteilung Andersen study the electronic structure of both weakly and strongly correlated materials, where the dominating energy of the electrons is the kinetic and Coulomb energy, respectively.

The work on weakly correlated systems is based on the density functional theory (DFT). For strongly correlated $d$-electron systems, an essential aim is to introduce chemical realism into the description by developing realistic Hubbard Hamiltonians, e.g., by using basis sets of Wannier functions derived from NMTO DFT calculations. The Hubbard Hamiltonians have been solved in the static and dynamical mean-field approximations, often together with Karsten Held and collaborators from Metzner’s department (now TU Vienna), as well as in dynamical cluster approximations. Another focus is the calculation of phonon spectra and the electron phonon interaction, using DFT and attempting to include electronic correlations. Properties of particular interest has been metal-insulator transitions in transition metal oxides, as well as superconducting, magnetic, optical, and dynamical properties studied experimentally and theoretically (Giniyat Khaliullin) in Keimer’s department. Materials of particular interest have been the layered iron-pnictide and chalcogenide superconductors, high-$T_c$ cuprates, and orbital engineering of nickelate heterostructures. [40,101]

Electronic properties of solids are analyzed and computed in Metzner’s department with a main emphasis on systems where electronic correlations play a crucial role, such as cuprates, manganites and other transition metal oxides. Besides symmetry-breaking phase transitions leading to magnetism, orbital and charge order, or superconductivity, correlations can also cause electron localization and many other striking many-body effects not described by the generally very successful independent electron approximation.

Our present research focuses in particular on high-temperature superconductors with their complex interplay of magnetic, superconducting and charge correlations, and also on manganites, titanates, and vanadates, whose electronic properties are determined by the interplay of orbital, spin and charge degrees of freedom. Another topic is the influence of lattice degrees of freedom on electronic properties, via Jahn-Teller distortion and electron-phonon interaction. Besides bulk properties of one-, two- and three-dimensional systems also problems with a mesoscopic length scale such as quantum dots, quantum wires, and quantum Hall systems are being studied. The correlation problem is attacked with various numerical and field-theoretical techniques: exact diagonalization, density matrix renormalization group, dynamical mean-field theory, functional renormalization group and (1/N)-expansion. Modern many-body methods are not only being applied, but also further developed within our group. [90,93]

Orbital order in a single layer of undoped LaMnO$_3$. The study of electronic properties of doped manganites, which show such remarkable phenomena like the colossal magnetoresistance, is an active research field because of the subtle interplay of charge, orbital, spin and lattice degrees of freedom.

One of the three congruent $t_{2g}$ NMTO Wannier-like orbitals for V$_2$O$_3$. Lobes of opposite signs are respectively red and blue.
Junior Research Groups

Research in the **Organic Electronics Group** (Klauk) focuses on novel functional organic materials and on the manufacturing and characterization of organic and nanoscale electronic devices, such as high performance organic thin-film transistors, carbon nanotube field-effect transistors, inorganic semiconductor nanowire field-effect transistors, and organic/inorganic hybrid radial superlattices. Of particular interest is the use of organic self-assembled monolayers in functional electronic devices. We are developing materials and manufacturing techniques that allow the use of high-quality self-assembled monolayers as the gate dielectric in low voltage organic and inorganic field-effect transistors and low power integrated circuits on flexible substrates. We are also studying the use of self-assembled monolayers for the preparation of nanoscale organic/inorganic superlattices that exhibit unique electrical, optical, and mechanical properties. Scientific work in organic electronics is highly interdisciplinary and involves the design, synthesis and processing of functional organic and inorganic materials, the development of advanced micro- and nanofabrication techniques, device and circuit design, and materials and device characterization. [76]

- n-Octadecylphosphonic acid $\text{C}_{18}\text{H}_{37}\text{PO(OH)}_2$ forms dense, insulating monolayers on natively oxidized metal substrates, such as aluminum. As a high-capacitance gate dielectric, these monolayers allow organic transistors and large-scale digital circuits (background) to operate with low voltage (1.5 V) and low power (1 nW per gate).

The **Junior Research Group Tunneling Spectroscopy of Strongly Correlated Electron Materials** (Wahl), established in October 2008, is focused on mapping the excitations in correlated electron materials with high spatial and spectral resolution with spectroscopic imaging STM. In correlated electron materials, electronic states have both, localized and delocalized character. This duality of electron behavior makes the difference to conventional materials, but also renders both their theoretical description and experimental detection difficult. The aim of this research group is to enhance the understanding of the low-energy excitations in these materials and get a clearer picture of the electronic structure. To this end new instrumentation will be developed optimized for the retrieval of spectroscopic maps at low temperatures and in high magnetic fields.

- The logo depicts at the same time the measurement geometry implemented to perform tunneling spectroscopy with the tip shown as a ‘v’ and the surface as a dash. At the same time, it schematically depicts the ‘v’- (or ‘u’-) shaped tunneling spectrum of a $d$-wave superconductor close to the Fermi energy as found e.g., in cuprate superconductors, probably the most famous class of correlated-electron materials.
The Independent Junior Research Group THEORY OF SEMICONDUCTOR NANOSTRUCTURES (Bester) was established in October 2007. The research will focus on the theory of semiconductor nanostructures. The special interest resides in quantum mechanical effects that become apparent when the carriers of charge and magnetic moment, e.g., electrons or holes, are confined into space regions with dimensions in the nanometer range. The aim is to develop theoretical concepts and implement them into computational methods where the atomistic nature of the problem is retained. At one end of the size scale, when the confining region encompasses only dozens of atoms, we are in direct contact with the chemical world of molecules. At the other side of the length scale we enter the fast growing and expanding world of artificially structured solids, such as quantum wells, quantum wires and quantum dots. We work in close collaboration with experimentalists to benchmark our theory and to provide understanding and insight into the quantum states probed experimentally. [95]

☐ State density of the bonding electron state of two vertically stacked self-assembled InGaAs quantum dots (quantum dot molecule) calculated with the atomistic empirical pseudopotential method. The dots have the shape of a truncated cone with 25 nm diameter and a vertical separation of 5 nm. The two translucent red isosurfaces enclose 75% and 40% of the total state density. The physical dot dimensions are shown in blue.

The ULTRAFAST NANOOPTICS GROUP (Lippitz) is a joint junior research group of the Max Planck Institute for Solid State Research and the Department of Physics at the University of Stuttgart. The research interest is ultrafast spectroscopy at and beyond the optical resolution limit. The group combines nonlinear optical methods such as pump-probe spectroscopy and higher harmonics generation with high-resolution optical microscopy to investigate ultrafast dynamics on the nanoscale. One focus is on single nanoobjects such as metal nanoparticles, semiconductor quantum dots or molecules. Traditional ultrafast spectroscopy averages over large ensembles of these systems, thereby removing all the details of the variation between individual objects. Only the spectroscopy of a single particle can yield the full picture of a nanoobject’s ultrafast dynamics. We use for example single-particle pump-probe spectroscopy to investigate elastic properties at the nanoscale. A second focus is on nanostructured materials like metallic photonic crystals. The periodic arrangement of metallic structures leads to new optical properties of the combined medium. We make use of interactions between metal stripes or layers to, e.g., increase the lifetime of particle plasmons or produce ultrafast transmission changes. [98]

☐ Optical parametric amplifier generating tunable femtosecond pulses for coherent spectroscopy.
Scientific Service Groups

The Chemical Service Group (Kremer) develops techniques and maintains experimental facilities in order to support all experimental groups of the Institute with the characterization of electrical, thermal and magnetic properties of new compounds and samples. Our mission targets at a great versatility and flexibility of the experimental methods including the development and cultivation, e.g., of experimental techniques to perform measurements, e.g., on chemically highly sensitive and reactive small samples under inert gas conditions.

Presently available are two commercial SQUID magnetometers, home-built ac-susceptometers, dc- and ac-electrical resistivity setups and calorimeters in a broad range of temperature and magnetic fields. Materials currently under investigation are novel superconductors (rare earth carbides and carbide halides, intercalated graphite, magnesium diboride), new or unusual magnetoresistive materials (rare earth halides and hydride halides), low-dimensional and frustrated magnetic systems and systems with unusual magnetic ground states (frustrated quantum chain systems, multiferroic materials). [35]

\[ Y_2C_2X_2 \] – A halide superconductor. The white solid lines symbolize the electrical resistivity, the heat capacity and the magnetic susceptibility proving \( Y_2C_2I_2 \) to be a superconductor with a \( T_c \) of 10 K.

The Computer Service Group (Burkhardt) runs the Institute’s central mail, print, software, backup and web servers, as well as the ten servers providing department specific services. All servers use the Linux operating system. The central Fibre-Channel based Storage Area Network (SAN) hardware has been modernized and all data was smoothly migrated to the new SAN hardware. Backup remains based on Tivoli Storage Manager (TSM); currently the total backup data volume is 70 TB. The backup server hardware and the tape robot were moved to 3D3 far away from the institute’s server rooms 2E2 and 6B13.

In 2008 the group integrated 123 new PCs and 45 laptops into the network, bringing the estimated total number to about 1200 PCs used as desktops and for data acquisition purposes. Of these about 70% run Windows and 30% run Linux. Due to the high load of 1.25 million pages per year and increasing maintenance problems all centrally maintained printers were replaced in 2008.

The IBM Bladecenter System was extended to 180 Intel architecture blades with 1000 cores, making the x86/x86-64 based systems the new computational backbone for the Andersen, Bester, Jansen, Maier and Metzner groups. All existing codes were ported by the group to the new set of compilers (Intel, Portland) and libraries (Intel mkl, gsl). The number of PowerBlades remained constant at 128 CPUs (258 cores), while three rack-mounted Linux clusters with a total of 208 Intel Xeon cores (IBM xSeries 335, x3550) are expected to be shut down in 2009 due to low energy efficiency. The last POWER4 system consisting of eight p655 nodes with eight cores each was shut down for the same reason.

Energy efficiency and improved climatization were at the focus of the group in 2008 and will remain a ‘hot’ topic for the years ahead. Less efficient hardware (old architectures, many low efficiency power supplies) are subsequently replaced by modern blade technology with modern architectures and shared high-efficiency power supplies.
These blade installations with their high-energy density, however, are a challenge to the existing air cooling infrastructure. To overcome the problem, water-cooled backdoors were installed in 6B13 to cool the racks directly. These backdoors lowered the temperature behind the blade installations from 45°C to 25°C. The backup hardware in 3D3 was sealed in a closed water-cooled rack, since this room had no other means of climatization.

View inside the Tape library of the DV-FKF. Every night the data of 100 computers in the Institute is backed up. At the moment the total TSM backup and archive volume amounts to 70 Terabytes.

The Crystal Growth Service Group (Lin) applies, modifies and develops techniques, such as traveling solvent floating zone with infrared image furnace, Bridgman, top seeded solution growth and Czochralski methods to grow single crystals from the melt or solution. These range from isotopically pure semiconductors to fullerenes and transition metal oxides. Three floating zone furnaces, including Xenon lamps heating up to 3000°C, are fully operational. They are used predominantly to grow large single crystals of transition metal oxides for neutron and optical spectroscopy. Vapor transport methods are modified to grow crystals of II-VI and III-V compounds with defined isotopic components from low amounts of source materials. Accurate characterization is done with the aim of obtaining high-quality single crystals, for instance, superconductivity and magnetism performed using SQUID, crystal compositions determined by SEM/EDX, structure and phase identified by X-ray diffraction method, polling of twin domains, differential thermal and thermal gravimetric analysis. Thermal behavior of investigated compounds can be direct in situ observed under high temperature optical microscope. [47]

A view of the inside chamber of the four ellipsoidal infrared image (TSFZ) furnace.

Research within the High Pressure Service Group (Syassen) is concerned with the effects of hydrostatic pressure on structural, lattice dynamical, and electronic properties of crystalline solids and their high-pressure phases. Advantage is taken of recent developments in diamond anvil cell techniques, including progress in analytical methods that utilize synchrotron X-ray radiation (diffraction as well as inelastic scattering), synchrotron infrared radiation, and laboratory-based low-temperature optical spectroscopy. Subjects of interest range from improving the understanding of chemical bonding and phase formation at high densities to illuminating the interplay between subtle changes in crystal structure, electron delocalization, magnetism, and superconductivity in correlated electron systems of different dimensionality. In terms of materials, the interest in covalently bonded semiconductors and nanostructures continues, while the ‘simple’ alkali metals have attracted attention due to their surprisingly complex structural and electronic behavior at high density.

The main focus, though, is on the physics of transition metal compounds with metal ions in high oxidation states, e.g., systems being located close to the insulator-metal borderline and undergoing pressure-driven Mott-like delocalization transitions. [55]
The Central Information Service (Marx/Schier) for the institutes of the Chemical Physical Technical (CPT) Section of the Max Planck Society is located at the Max Planck Institute for Solid State Research in Stuttgart. The CPT Information Service is accessible for all scientists within the entire society and provides support in all demands of scientific information. The service has access to many commercial databases and patent files not included in the range of end user databases and should be contacted, if searches in the available databases are not sufficient. Professional searches in chemistry, materials science, and physics are performed in the various files offered by STN International. In particular, the files of the Chemical Abstracts Service in conjunction with the STN search system enable sophisticated searches regarding compounds, reactions, and spectra. New analyze tools allow establishing research field statistics. Beside the databases, covering general disciplines like chemistry and physics, there are many databases for specific research fields like materials science, engineering, and environmental sciences. In addition, factual databases enable searching numerical data like chemical and physical properties of compounds and various national and international patent files are available. Furthermore, the service offers citation data, including citation statistics with respect to scientists or research institutes for the demands of research evaluation. Finally, the service offers help and training for searching end user databases like SciFinder, INSPEC, and Web of Science.

The archives of science are rapidly growing: One of the about 30 million substances registered in the compound file of the American Chemical Abstracts Service. Powerful databases and search systems have become indispensable tools in processing the actual information flood in science.

The Interface Analysis Service Group (Starke) investigates the atomic and electronic structure of solid-solid and gas-solid interfaces. Using electron spectroscopy techniques, quantitative low-energy electron diffraction, scanning probe microscopy and secondary ion mass spectrometry (SIMS), the atomic geometry and morphology as well as the chemical composition and bond coordination are determined for the sample surface and its immediate vicinity. Thin films and buried interfaces are accessible by sputtering techniques or sample cleavage methods. Experimental facilities available include a time-of-flight SIMS machine to quantify the chemical composition at the surface, within the film and at interfaces. Chemical and electronic properties are investigated in a multicomponent chamber containing high-resolution electron spectroscopy for chemical analysis. A scanning Auger microscope yields spectroscopic images with high lateral resolution. Sample morphology can be studied using an atomic force microscope and a white-light interferometer. The research activities of the group are directed towards growth and analysis of surfaces and ultrathin films of novel materials for semiconductor technology, e.g., wide bandgap semiconductors (SiC), metal silicides, as well as epitaxial metal films. Material growth, heterojunctions, metallization and ferromagnetic layers are investigated on an atomic level for a detailed understanding of the fundamental interactions involved in the growth process. In particular, graphene layers grown epitaxially on SiC surfaces are investigated. In addition, molecular adsorbates are studied on these surfaces as model systems for a variety of applications. [16]
The MBE SERVICE GROUP (Dietsche) provides semiconductor heterostructures based on the GaAs/AlGaAs system by using molecular beam epitaxy (MBE). By appropriate doping, two-dimensional charge carrier systems form at the interfaces between different semiconductors. A low impurity level is required for the high mobility of the charge carrier systems which are needed to study electron correlation phenomena like the fractional quantum Hall effect. Also important are 2d electron gases located closely to the surface. In these structures, lithographically defined quantum dot systems with dimensions of a few nanometers can be electrically manipulated via surface gate contacts.

Of particular scientific interest is the growth of electronic double layers, which are electrically isolated from each other but have separate electric contacts. Strong evidence of exciton superfluidity has already been observed in these structures. Much lower impurity levels are required to produce structures, which are suitable for topological quantum computing utilizing the fractional state at 5/2. The MBE growth of materials with a slight misfit in their lattice constants leads to the formation of quantum dots. An example is InGaAs on GaAs. The position of these dots can be pre-determined by lithographic patterning of the substrate. This work is done in collaboration with the group of O. Schmidt (IFW Dresden).

Atoms impinge, diffuse and nucleate on the surface of a heated crystalline substrate under ultrahigh vacuum conditions. This process is called molecular beam epitaxy.

The TECHNOLOGY SERVICE GROUP (Habermeier) offers service work in the fields of thin film preparation, microlithography and fabrication of bonded contacts to semiconductors and ceramic materials. The experimental facilities include high-vacuum evaporation and sputtering (dc, rf and reactive) techniques. Additionally, pulsed laser deposition systems are installed to prepare thin films of materials with complex chemical composition such as high-temperature superconductors (HTS), perovskites with colossal magnetoresistance (CMR) and other related functional oxide ceramics. Dry etching techniques complement the spectrum of experimental techniques available. The research activities are closely related to the service tasks. Thin film deposition of doped Mott insulators such as HTS and CMR materials play a central role. The main focus of interest is the study of interface related phenomena in complex oxides such as epitaxial strain in functional ceramics, mesoscopic phase separation and electronic and magnetic interactions at HTS–CMR interfaces as well. This research activities are performed in close scientific cooperation with the departments Maier and Keimer. Additionally, the preparation and investigation of magnetic and superconducting oxide superlattices (manganites, ruthenates and cuprates) and their mutual electronic interaction, as well as the study of special oxide heterostructures are designed for polarized spin injection, exchange bias effects and magnetic flux-line pinning phenomena are of central interest. [72]

Pulsed laser deposition has become a widespread technique for the fabrication of epitaxial thin films of multicomponent materials like doped lanthanum manganites and superconducting materials.
The X-ray Diffraction Service Group (Dinnebier) provides X-ray diffraction measurements of single crystals and powders in the laboratory at room and low temperature. Research within the group is mainly concerned with the determination of crystal structures and microstructural properties (strain, domain size) of condensed matter from powder diffraction data. In addition, methodological development within this area is pursued. Special expertise in the field of solution and refinement of crystal structures from powder diffraction data can be provided. Scientific cooperation in the field of non-routine structure determination (phase transitions, disorder, anisotropic peak broadening, etc.) from powders is offered. This includes the performance of experiments at synchrotron and neutron sources at ambient and non-ambient conditions. Materials currently under investigation include organometallic precursors, binary and ternary oxides, ionic conductors, electronic and magnetic materials, and rotator phases.

[58]

Quasispherical molecule of tetrakistrimethylstannylsilane with underlying two-dimensional image plate powder diffraction pattern. The superimposed Bragg reflections demonstrate the difference in resolution between laboratory and synchrotron data.
Graphene

Graphene, a flat hexagonal network of carbon atoms, is one of the most studied systems ever since researchers were first able to prepare it in 2004. Although the simple arrangement of carbon atoms in graphene is long known from the three-dimensional equivalent graphite, it was quickly discovered that the atomically thin layer analogue exhibits special physical properties like a high carrier mobility and an unusual electronic band structure with a linear dispersion relation at the Fermi level. These properties are fascinating from a fundamental research point of view and might be exploitable in applications like sensors or Qubits. One focus of the Institute’s research is the fabrication of high-quality graphene samples. Besides the classical route of extracting graphene from graphite, fabrication processes include epitaxial growth and chemical synthesis with the goal to control both size of the graphene flakes and its defect density, the latter strongly affecting their electronic properties. Moreover, post-fabrication methods are developed to modulate the electronic properties of existing flakes by laser-induced changes in the structure or by metal contacting. A second focus is to contribute to the understanding of the fundamental physics of graphene. Local techniques like scanning tunneling microscopy are used to detect pseudospin and chirality of quasi-particles in single graphene flakes. These degrees of freedom are a result of the two-atom unit cell of graphene which results in a spinor structure of the carrier wave functions.

The chemical route to graphene

M. Burghard, C. Gómez-Navarro, R.S. Sundaram and K. Kern

Graphene, which is a monolayer of carbon atoms arranged into a two-dimensional honeycomb lattice, constitutes a semi-metal material without bandgap. Through application of a gate voltage, the charge carriers in graphene can be continuously tuned between electrons and holes. Moreover, the very high mobility and carrier velocity promises graphene-based ballistic devices with high switching speeds. In addition to applications in nanoscale electronics, graphene has proven to be useful for the reinforcement of polymers, thereby opening access to electrically conductive composite materials, or as a transparent electrode in photovoltaic cells.

Numerous investigations have been performed on graphene sheets obtained via mechanical exfoliation of highly oriented pyrolytic graphite (HOPG). An alternative approach comprises epitaxial growth of graphene on metal surfaces or silicon carbide substrates. However, all these fabrication methods face serious drawbacks. Specifically, the exfoliation method is restricted by the very low yield and limited size of the resulting graphene sheets. The epitaxial methods, on the other hand, do not readily provide access to sheets in a gate-tunable contact configuration. It is hence not surprising that increasing efforts are currently directed towards the controlled chemical synthesis of graphene. As one possibility, chemical vapor deposition (CVD) based strategies have been explored, which so far afforded mainly multilayered graphene nanosheets. An alternative route starts from graphite oxide, which can be obtained in large amounts via strong oxidation of graphite [1].
The oxygenated functional groups in graphite oxide substantially weaken the interlayer binding force, thus facilitating exfoliation of this material into individual graphene oxide (GO) sheets upon gentle sonication in water. From such dispersions, GO monolayers with sizes of up to several tens of micrometers be deposited in high density onto a wide range of surfaces, as exemplified in Fig. 1(a) for a HOPG substrate.

![Graphene oxide (GO) sheets on a HOPG substrate.](image)

Figure 1: (a) Atomic force microscopy (AFM) image of graphene oxide (GO) sheets on a HOPG substrate. From AFM cross-sections, it is concluded that ≈50% of the objects are monolayers. (b) I-V traces of an individual GO monolayer, recorded at room temperature, after chemical reduction under the indicated conditions.

Atomic force microscopy investigation under ambient reveals a GO monolayer height of ≈1.1 nm, which includes a water adsorbate layer on top of the sheets. Chemical reduction by hydrazine or hydrogen plasma to remove the oxygen-containing functional groups then yields chemically-derived graphene sheets. This conversion is accompanied by a pronounced decrease in electrical resistance by about three orders of magnitude (Fig. 1(b)). The electrical conductivity of the resulting graphene is of the order of a few S/cm at room temperature [2]. Although this range may be sufficient for some applications, it is still two to three orders of magnitude below the conductivity of mechanically exfoliated, pristine graphene. This difference originates from defects that remain after the chemical reduction of the sheets. The presence of these defects is manifested in a strong D-band (at ≈1350 cm⁻¹) in the Raman spectra of the sheets, as well as in scanning tunneling spectroscopy (STM) images, wherein well-ordered regions interspersed with disordered regions can be discerned (Fig. 2) [2].

![Scanning tunneling microscopy (STM) image taken under ambient from a chemically reduced GO monolayer.](image)

Figure 2: Scanning tunneling microscopy (STM) image taken under ambient from a chemically reduced GO monolayer. The bright regions encircled in green are assigned to the presence of remaining oxygenated functional groups and point defects. These regions are separated by areas of intact hexagonal lattice structure.

Analysis of the Raman data based upon the Tuinstra-Koenig expression provides an estimated size of the order of 6 nm for the intact regions, in good agreement with the STM results. The defects likely include residual oxygen-containing groups, point defects and...
holes, however, their detailed chemical nature and distribution is currently under investigation. Consistent with the model of intact graphene areas surrounded by defective regions, the temperature-dependence of conductance of the reduced GO sheets indicates variable range hopping as the dominant conduction mechanism.

Besides their electrical properties, the mechanical performance of the sheets is of interest. We have used AFM indentation to explore the mechanical properties of free-standing monolayers of reduced GO (Fig. 3(a)) [3]. The evaluation of the elastic regime of force vs. displacement curves (Fig. 3(b)), as acquired from a range of differently sized sheets, yielded a mean elastic modulus of $E = 0.25$ TPa. This value is remarkably high for a two-dimensional membrane, and approaches that of pristine graphene ($\approx 1$ TPa).

At the same time, the suspended sheets display only small built-in tensions of just a few nN, about two orders of magnitude below the values previously detected for mechanically exfoliated graphene attached on top of pre-formed trenches. The smaller tensions in the present samples can be attributed to the fact that the sheets are first deposited on the substrate and then rendered free-standing by under-etching the SiO$_2$.

Another interesting feature of the chemically derived graphene monolayers is that their elastic modulus scales inversely with their electrical conductivity (Fig. 1(c)). This finding reveals that the covalent linkage of atoms to graphene can have only a weak influence on the inter-carbon bond strength, whereas the electrical conduction is principally deteriorated upon covalent modification, independent of the bonding configuration of the added atoms or functional groups. For not too high degrees of functionalization, the mechanical performance can be expected to be largely preserved if, for instance, oxygen (epoxide) bridges are formed between the graphene carbons.
In view of the impressive recent advancements in the synthesis of graphene-like materials, it appears well-feasible to further improve the structural integrity of the chemically reduced GO sheets, such that their electrical and mechanical performance could approach that of pristine graphene in the near future. One intriguing application of the GO-based approach comprises the implementation of electronic devices into a single graphene sheet. For this purpose, regions not subjected to reduction could serve as well-defined charge transport barriers which separate electrically active channels composed of high-quality graphene areas.


Structural and electronic properties of epitaxial graphene on SiC(0001)
C. Riedl and U. Starke

Graphene, a mono-atomic layer of graphite, shows a linear dispersion of its π-bands at the Dirac point. Accordingly, electron transport in graphene is governed by Dirac’s (relativistic) equation which leads to unconventional two-dimensional electron gas properties. Micrometer sized graphene flakes can be obtained by micromechanical exfoliation of graphite. However, for a possible application in carbon based electronic devices, the preparation of larger graphene layers on a solid substrate would be desirable. This can be achieved by the controlled graphitization of SiC surfaces by high temperature annealing in ultrahigh vacuum (UHV). The dispersion curves of the π-bands as measured at synchrotron light sources can be used for the determination of the number of graphene layers. However, it would be preferable to precisely count the number of layers continuously during the preparation procedure without being dependent on a synchrotron facility. Here we show that angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) from He II excitation and low energy electron diffraction (LEED) give a solution to this problem [1]. We discuss a possible dependence on the doping level of the substrate as well as the influence of the polytype.

4H- and 6H-SiC(0001) on-axis oriented samples with different levels of nitrogen doping (from semi-insulating to a doping density of \( \approx 10^{19} \text{ cm}^{-3} \)) were hydrogen etched in order to remove polishing damage, to chemically passivate the surface and to generate a regular array of atomically flat terraces of approximately 0.5 \( \mu \text{m} \) width. After loading into the UHV chamber, the samples were prepared by Si deposition (1 monolayer/min) and annealing in order to reach the Si-rich (3 \( \times \) 3) reconstruction as the starting point for the graphitization process [2]. The (6\( \sqrt{3} \times 6\sqrt{3})\text{R}30^\circ \) reconstructed buffer layer was obtained by further annealing to about 1150°C (without Si). One to three layers of graphene were then prepared by heating the sample to 1200–1350°C. The ARUPS experiments were conducted in the same UHV system at a temperature of 100 K using He II radiation from a monochromatized UV source.
The sample manipulator allows for an accurate alignment of both the azimuthal and polar surface orientation to about 0.1°. A hemispherical analyzer equipped with a 2D detector and a video camera was used to map the band structure.

Figure 4 displays ARUPS data revealing the electronic structure in the vicinity of the $K$-point of the Brillouin zone of graphene for annealing temperatures of 1200°C, 1275°C, and 1350°C. The sketch in panel (a) defines the $k_{∥}$-mapping direction. The detailed dispersion of the different π-bands is well resolved as shown in the 2D plots in panel (a). By counting the number of π-bands one, two and three graphene layers can clearly be distinguished [1]. We note that in the data shown here for monolayer graphene the beginning of a bilayer contribution can be detected. For a quantitative evaluation, momentum and energy distribution curves (MDC and EDC) for mono-, bi- and trilayer graphene are displayed in Fig. 4 (b) and (c). The Dirac point is shifted below the Fermi energy by 430 meV for monolayer, 320 meV for bilayer and 300 meV for trilayer graphene and also an energy gap at the Dirac energy can be observed for bi- and trilayer graphene [1].

Although the determination of the number of graphene layers by means of ARUPS would be a rather convenient method, it cannot be applied during preparation, and a machine with the appropriate precision might not normally be at hand. However, a LEED data acquisition system is available in practically every preparation chamber. We have recently shown that both the LEED pattern of the $(6\sqrt{3}\times6\sqrt{3})R30^\circ$ reconstruction as well as the intensity spectra of the first-order diffraction spot of graphene (marked in green in Fig. 5) display characteristic variations with increasing temperature [2].

The calibration of these fingerprints with the ARUPS data shown in Fig. 4 allows for an unambiguous assignment of the LEED intensities to the number of graphene layers, as shown in Fig. 5. Thus, specific features in the intensity spectra, which are highlighted in the figure and which are generated by the complex multiple scattering processes in LEED, allow for an accurate determination of the number of graphene layers using LEED alone [1].

Not every LEED system may permit one to record such intensity spectra, but already the LEED pattern at 126 eV allows for an approximate determination of the number of lay-
Select research reports Graphene

ers by comparing the relative intensity of the ‘graphene’ spot to that of the surrounding spots in the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) pattern as shown in Fig. 5.

Figure 5: LEED spot intensity spectra for different numbers of epitaxial graphene layers grown (at the indicated temperatures) on 4H-SiC(0001). As indicated in the inset, the spectra were obtained for the green marked spot of the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) reconstruction, which corresponds to the unit cell of graphene. The first-order diffraction spot for the SiC substrate is indicated in the LEED pattern in yellow, the position of the \((2/3,2/3)\) spot of the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) reconstruction in the inset. Yellow patches indicate fingerprint like features in the spectra that allow the unambiguous determination of the number of graphene layers. LEED patterns at 126 eV are shown on the right, also allowing for a discrimination.

It should be emphasized that the graphene related diffraction spot is the only one in the LEED pattern of the \((6\sqrt{3} \times 6\sqrt{3})R30^\circ\) reconstruction that can be used for an assignment of the number of layers. All other spots do not show this distinct dependence on the preparation temperature in their intensity spectra. This is demonstrated in Fig. 6(a) for the first-order diffraction spot of the 4H-SiC-substrate. To have a good comparison the spectra for higher annealing temperatures are amplified with respect to the ones at lower annealing temperatures in order to compensate the attenuation of the signal of the SiC-substrate by the graphene layers above. The graphene growth barely influences the position of the maxima and minima in the I(E) spectra.

Figure 6: (a) LEED intensity spectra of the integer order 4H-SiC-substrate spots for different stages of graphitization. In contrast to the graphene related diffraction spot no changes can be observed. (b) LEED Intensity spectra of the graphene related diffraction spot for mono- and bilayer graphene for the two polytypes 4H- and 6H-SiC(0001).
Epitaxial graphene on SiC(0001) can either be grown on a 4H- or a 6H-SiC-substrate. The number of equally oriented bilayers at the surface of 4H- and 6H-SiC corresponds to two (‘S2 termination’) and three (‘S3-termination’), respectively. As the surface termination is different a possible polytype dependence of the graphene growth could therefore be expected. However, the band structure of graphene around the K-point is identical for epitaxial graphene grown on 4H-SiC(0001) and 6H-SiC(0001) (not shown). Figure 6(b) demonstrates that also the LEED intensity spectra for the graphene related diffraction spot equally do not show any polytype dependence. So obviously, with the same preparation procedure, the polytype has no influence on the structural and electronic properties of epitaxial graphene on SiC. In addition it could be verified that both the band structure data and the LEED intensity spectra do not show any dependence on the doping density of the SiC substrate.

In summary, we have shown that LEED together with ARUPS are effective and practicable methods to get deep insight into the structural and electronic properties of epitaxial graphene on SiC(0001) without depending on synchrotron radiation facilities. LEED fingerprints can be used continuously during the preparation procedure in order to count the number of layers. The methods presented here pave the way for a large variety of simple and precise in situ experiments with few layer graphene. A crucial issue towards device applications is to shift the Dirac energy back towards the Fermi energy. Experiments in this direction by depositing metals or functional molecules on top of the graphene surface are currently under way in our group.


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**Laser-induced disassembly of a graphene single crystal**


The successful isolation of graphene has triggered a tremendous research effort. To distinguish graphene monolayers from multilayers, Raman spectroscopy has been considered a convenient, non-invasive technique. Raman spectroscopy has historically played an important role in carbon based systems as it allows to distinguish the different hybridization of bonds ($sp$, $sp^2$, $sp^3$) and extract information about disorder. In layered graphite related systems with $sp^2$-bonding, Raman data can in addition reveal the crystallite size, the presence of doping and defects. It even enables studies of the phase breaking length and the distinction between various local arrangements of carbon atoms at the edge such as the zigzag or armchair configurations. In the following we will show, that laser exposure as used for Raman spectroscopy is not necessarily benign and should be dosed cautiously as it may induce structural modifications. The time evolution of the Raman spectrum points to a laser induced gradual local decomposition of single crystal graphene into a network of interconnected nano-crystallites with a characteristic length scale down to 10 nm due to bond-breaking. The broken bonds offer additional docking sites for doping adsorbates as confirmed in transport and AFM height studies. Conversely, laser irradiation may be exploited to enhance the local reactivity of graphene on purpose, to trim graphene based sensors and to generate patterns with spatially varying doping levels.
Figure 7 shows a typical Raman spectrum obtained on a freshly prepared flake with a diffraction-limited 1 mW laser spot of 488 nm wavelength. The following Raman features can be distinguished: The first observable peak appears at 1590 cm\(^{-1}\) and is associated with the zone center in-plane longitudinal optical phonons (middle inset in Fig. 7). This well-known G peak is characteristic for \(sp^2\)-hybridized carbon-carbon bonds. The second prominent peak is located at 2700 cm\(^{-1}\). This \(D^*\) peak originates from a double resonance process: The incoming laser light creates an electron-hole pair and after two inelastic scattering events involving phonons with opposite momenta Raman light is emitted during recombination (right inset in Fig. 7). If defects are present, one of the two scattering events can occur elastically (left inset in Fig. 7). This yields the defect or D peak. This peak competes with the \(D^*\) peak and exhibits only half the Raman-shift. The D peak is not observable in our pristine flake, which attests the good crystalline quality.

A shape analysis of the \(D^*\) peak has been successfully used in the literature to distinguish single layers from bilayers or multilayers. For monolayer graphene the \(D^*\) peak can be fitted to a single Lorentzian while the multiple bands in multilayer graphene give rise to a more complex peak structure that requires for instance fitting to 4 Lorentzians for bilayers. Here, the \(D^*\) peak clearly indicates that the flake is a monolayer. Figure 7 also plots the Raman spectrum (blue line) after the graphene flake has been exposed for 18 hours to the laser spot. The Raman spectrum has drastically changed. A strong D peak at 1350 cm\(^{-1}\) has emerged. It indicates a large increase in the number of defects. Concomitantly a peak has appeared at approximately 2950 cm\(^{-1}\), a Raman shift equal to the sum of the G and D peak Raman shifts. This combined D + G peak is in general only observed in the vicinity of defects. We note that the increase of the D peak is accompanied by a drop in intensity of the \(D^*\) peak as both are associated with competing scattering processes. The \(D^*\) peak of the treated flake remains composed of a single Lorentzian despite the apparent local structural modifications of the flake. Note that this Raman spectrum after long term laser exposure is distinct from that of amorphous carbon, \(sp^3\)-bonded diamond as well as graphite oxide.

In order to gain more insight into these laser induced modifications, we have performed time-resolved Raman measurements. The results are displayed in Fig. 8. It plots the G, D and \(D^*\) Raman peak intensity (left hand side) as well as their position (right hand side). The time evolution of the G peak position (Fig. 8(b)) for instance can be divided into three regimes. We assert that regime I is dominated by the removal of dopants due to laser induced heating. While dopants continue to be removed, the longer term behavior (regime II) is mainly attributed to \(sp^2\)-carbon-carbon bond breaking and the gradual disassembly of the macroscopic single graphene crystal at the laser spot. Finally, in regime III bond disruption slows down and the curve saturates.
Graphene

Selected research reports

Figure 8: Time evolution of the G, D and D* Raman peaks. Panels (a), (e) and (g) show the intensity of these peaks as a function of time during laser exposure with 1 mW of power and a wavelength of 488 nm. For each data point on these curves a Raman spectrum was acquired in the range from 1024 cm$^{-1}$ to 3770 cm$^{-1}$ with a 30 s integration time. In panel (e) also the intensity ratio between the D and G peaks has been included. Panels (b), (f) and (h) display the time development of the position of each of these Raman peaks. The FWHM of the G peak is given in (d). The observed changes with time suggest a structural modification of a single crystal of graphene into a network of graphene nano-crystallites as illustrate in a cartoon like fashion in panel (c).

We first consider regime I and the influence of removing doping adsorbates on the Raman spectrum. In graphene, the adiabatic Born-Oppenheimer approximation is not valid. The charge carrier density $n$ enters the electron phonon coupling and causes a softening of the G phonon when $n$ decreases. Raman experiments combined with field-effect measurements indeed confirm this behavior. They additionally revealed, that also the D* peak is red shifted when $n$ is lowered. Additional evidence for dopant removal comes from the full width at half maximum (FWHM) of the G peak. At high doping levels, the energy of the G phonon ($\approx 200$ meV) is insufficient to create an electron-hole pair as there are no occupied states available (left inset of Fig. 8). Consequently, phonons have a long life time and the Raman peak is narrow. At low doping levels (right cone in Fig. 8(d)), this is no longer true and phonons can decay rapidly by creating electron-hole pairs. The FWHM will grow as the charge carrier density drops. Without special treatment, our as prepared flakes are doped at the level of about $5 \times 10^{12}$ holes/cm$^2$. This number is obtained from field-effect measurements. Under laser exposure, all the above signatures for dopant removal are present in the experimental data in Fig. 8(b), (d) and (h). The charge carrier density $n$ indeed decreases. If we remove the dopants with a heat treatment prior to laser exposure, regime I is absent. This corroborates further the assertion of dopant removal as the dominant mechanism for the Raman changes in regime I.

Regime II is heralded by a blue-shift of the G peak. The previous exposition would suggest that it reflects an increase of the carrier density. However, this is not correct since the blue shift of the G peak is not accompanied by a blue shift of the D* peak. Moreover, the FWHM of the G peak does not decrease. Hence, another mechanism must be responsible for this time dependent Raman behavior in regime II. The most striking feature in this regime is no doubt the strong enhancement of the D peak intensity (Fig. 8(e)). It indicates that a substantial number of $sp^2$-carbon-carbon bonds get cracked. Previous studies on powders of graphite crystallites with different sizes have demonstrated that the intensity ratio between the G and D peak is a measure for the percentage of ‘boundary’ in the sample.

21
Based on these studies reported in the literature, we conclude from the ratio observed in Fig. 8(e) that the laser induced structural modification of our graphene single crystal is equivalent to disassembling the crystal into a network of graphene nano-crystallites with a characteristic size down to 10 nm. The increase of the D peak intensity is also accompanied by a blue shift of the G peak position. If due to carbon-carbon bond disruption the graphene flake locally disintegrates into nano-crystalline graphene patches, it is natural to attribute the shift of the G peak to phonon confinement. In the pristine graphene flake, the incident photons only interact with phonons that have essentially zero momentum \( q \approx 0 \) in order to fulfill momentum conservation. For nano-crystallites of size \( d \), the Heisenberg uncertainty principle relaxes this momentum selection rule and also phonon modes with a non-zero momentum up to \( \Delta q = 2\pi/d \) contribute to the Raman intensity. For an average crystallite size of 10 nm, we obtain a maximum momentum transfer of 0.6 nm\(^{-1}\). The Raman active zone center phonon mode exhibits a positive dispersion when moving away from the zone center. Due to the lack of experimental phonon dispersion data for graphene, we resort to reported inelastic X-ray scattering data of graphite to estimate this energy dispersion. A linear approximation yields a slope of 13 nm/cm. For 10 nm crystallites, phonon modes with an energy larger by at most 8 cm\(^{-1}\) compared with the zone center phonon energy will contribute to the Raman
G peak. Since all phonons with $q$ between 0 and 0.6 nm$^{-1}$ take part, the G peak will broaden. The estimated maximum blue shift is compatible with our experimental data.

Figure 9 displays spatial Raman maps of the D, G and D\* peak (a)–(f) as well as tapping mode atomic force microscopy images (g),(h) of the pristine flake (upper panel) and the flake after laser exposure (lower panel). Here, the laser spot was defocused in order to enlarge the spatial extent of the modified area. The modifications are spatially confined to the spot size. We attribute the increased height in the AFM image (Fig. 9(h)) to the absorption of molecules from ambient air when the laser is switched off, because the disruption of carbon-carbon bonds offers additional docking sites. This assertion is proved in transport experiments (not shown here). Hence, laser irradiation may locally enhance the reactivity of the graphene flake, a property which may be exploited in graphene based sensors.

In summary, we have demonstrated that laser irradiation of graphene can be invasive and may remove dopants as well as induce structural modifications. Laser exposure locally disassembles a single crystalline layer of graphene into a network of interconnected graphene nanocrystallites. The additional ‘boundaries’ provide docking sites for molecular adsorbates, so that the reactivity can be locally enhanced.

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**Doping by metal contacts in graphene devices**

K. Balasubramanian, E.J.H. Lee, R.T. Weitz, M. Burghard and K. Kern

Graphene is a single layer of carbon atoms covalently $sp^2$-bonded together in a honeycomb lattice, constituting an ideal two-dimensional system. It is emerging to be an important material due to a number of interesting physical properties – such as high carrier mobility and peculiar band structure showing linear energy dispersion around the Fermi level – making it highly promising for a variety of applications. Towards this goal, it is important to have a clear understanding of the electronic properties of graphene. Especially, knowledge about the effect of metal deposition is vital for the successful realization of graphene devices. We observe that there is significant charge transfer to graphene from the deposited metal, leading to a change in the local electronic structure. We have utilized a local photocurrent technique to study the effect of metallic contacts on the band structure of exfoliated graphene devices. The experiment delivers us information about the tunability of the electronic properties of graphene by a right choice of the metal.

In graphene, the conduction and valence bands meet at the Dirac point, enabling the electrical transport to be tuned between hole and electron conduction by varying the Fermi level through an external electrical field. Ambipolar transport behavior is hence observed in graphene devices fabricated in a field-effect transistor configuration. In contrast to typical semiconductor devices, where the contacts are optimized to avoid scattering, the metal-graphene contact might have a strong influence on the charge transport through graphene devices. Another important aspect is the influence of graphene edges, which are expected to have a considerable impact on device operation, analogous to surface states in bulk semiconductors. Here we report on the use of scanning photocurrent microscopy (SPCM) to explore these issues in graphene monolayer devices under different operating conditions.
SPCM is a well-established tool for studying the interface characteristics and mapping the local electrostatic potential of nanostructures such as carbon nanotubes [1].

The graphene monolayers prepared by mechanical exfoliation were contacted by Ti (0.3 nm)/Au (20 nm) electrodes on Si/SiO₂ substrates. The Si-substrate was used as a backgate, with a 300 nm thermally grown oxide layer serving as the gate dielectric. Fig. 10(a) shows an atomic force microscopy (AFM) image of a typical device for four-probe measurements. AFM height measurements and Raman spectroscopy were used to confirm that the samples comprised a single layer. SPCM was performed under ambient conditions by scanning the device through a diffraction-limited laser spot and the reflected light and photocurrent recorded simultaneously [1]. A representative photocurrent image taken at zero bias and zero gate voltage is shown in Fig. 10(b). The image displays several weak photocurrent lobes within the sheet, indicating the presence of local built-in electric fields or local potential variations. This observation is consistent with other experiments reporting the formation of electron-hole puddles leading to such potential fluctuations.

Figure 10: Photocurrent response of a graphene device. (a) Atomic Force microscope (AFM) height image of a graphene monolayer contacted by four gold electrodes. (b) Zero-bias photocurrent image (V₁s = V₂ = 0 V) taken simultaneously along with a reflection image. λ exc = 514.5 nm, spot size ≈ 0.4 μm, power ≈ 100 kW/cm², S: source, D: drain.

In addition to the relatively weak photocurrent signals along the flake, significant photocurrents occur at the two metal contacts. The power dependence of this photocurrent and its magnitude suggest the presence of potential steps at the contacts [2].

As shown in Fig. 11(a), a difference in the work functions of the metal and graphene leads to charge transfer at the contact interface [3]. Owing to the low density of states in the vicinity of
the Dirac point, this results in the formation of pronounced interface dipole layers, resulting in a potential step. The magnitude of this potential step including the effect of the gate voltage can be expressed as

\[ \Delta V = \Phi_M - \Phi_G - \Delta E_F + \text{sgn}(V_g)h\nu_F \sqrt{\pi\alpha}V_g, \]

where \( V_g = V_{gs} - V_{gs}^{\text{Dirac}} \), \( \alpha = 7.2 \cdot 10^{10} \text{ cm}^{-2} \text{V}^{-1} \), \( \Phi \) denotes work-function of the metal (M) or graphene (G), \( V_{gs} \) is the applied gate voltage and \( V_{gs}^{\text{Dirac}} \) is the gate voltage at which the Dirac point is seen. \( \Delta E_F \) is the shift in Fermi-level arising due to doping from the metal contact. Since the potential step (\( \Delta V \)) is directly proportional to the photocurrent at the contacts, a plot of the photocurrent against the gate voltage enables the estimation of \( \Delta E_F \) and thereby the doping effect. Figure 11(b) and 11(c) shows the gate dependence of the photocurrent at the source contact for two different metals namely Au and Ti. Applying the above equation to the curves in these two figures and using appropriate values for the metal work-functions [2], the Fermi-level shift is estimated to be \( \Delta E_F = -0.23 \text{ eV} \) and +0.25 eV for the Ti- and Au-contacted devices respectively. Consistent with theoretical calculations [3], these values confirm that Ti contacts result in n-type doping and Au contacts in p-type doping of graphene, with carrier densities of \( 5.5 \cdot 10^{12} \text{ electrons/cm}^2 \) and \( 6.5 \cdot 10^{12} \text{ holes/cm}^2 \), respectively. Furthermore, the potential step at the Dirac point for Ti/graphene and Au/graphene contacts could be deduced as 30 meV and -50 meV, respectively.

The two-dimensional potential landscape of the graphene device at different carrier densities can be effectively studied using SPCM in different transport regimes by acquiring images at various gate voltages. Figure 12 displays such a sequence of zero-bias photocurrent images covering the n- to p-type transition of the graphene device. At high carrier densities corresponding to the n- and p-type regimes (top left and bottom right) the contacts dominate the photocurrent responses suggesting that the local electric fields associated with the potential steps at the contacts become substantially larger than the potential landscape within the graphene sheet. By contrast, at lower carrier densities, potential fluctuations associated with charged impurities within the flake gain importance, because the screening promoted by the charge carriers in the flake is reduced. Furthermore the n- to p-type transition occurs inhomogeneously along the graphene sheet, leading to a transversal p-n-p profile in the vicinity of the Dirac point [2].

Figure 12: Spatially resolved photocurrent maps at various transport regimes of a graphene device. The sequence of images display the n- to p-type transition, as the gate voltage is swept from +30 V to -30 V. The dashed lines in the top left image indicate the position of the drain (D) and source (S) electrodes.

In conclusion, the spatially resolved photocurrent responses have given quantitative estimates of the amount of doping from metal electrodes on to graphene. These findings highlight the relevance of both material boundaries and contact interfaces in the operation of graphene-based devices. For the future, SPCM will serve as an ideal tool to provide valuable information regarding the effect of chemical doping and the behavior of multi-terminal devices.

Graphene has recently spurred a tremendous scientific interest, stimulated by experimental evidences of its tantalizing electronic properties. Such properties stem from a particular symmetry in the wavefunctions of graphene’s quasiparticles, which leads to the concepts of pseudospin and electronic chirality, two entities that have no equivalency in any other two-dimensional system. Our work [1] shows how pseudospin and quasiparticle chirality can be experimentally detected at the nanoscale by means of STM, since they are reflected in the quasiparticle interference processes that take place in graphene. Our STM data, complemented by theoretical calculations, demonstrate that the quasiparticles in epitaxial graphene on SiC(0001) have the chirality predicted for ideal (free standing) graphene, which proves the Dirac character of the quasiparticles in this system.

From the atomic point of view graphene is one single layer of carbon atoms packed in a honeycomb structure, it has two identical C atoms in each unit cell and thus two equivalent atom sublattices. The first consequence of the honeycomb structure is that the low energy quasiparticles of graphene are described by a Dirac-like Hamiltonian. The energy spectrum is thus linear, and consists of two Dirac cones centered at the opposite corners K and K’ of the Brillouin zone. This is, however, insufficient to understand properly the specific electronic properties of graphene. Due to the presence of the two atoms per unit cell in the honeycomb lattice, the quasiparticles have to be described by two-component wavefunctions, each component specifying the (complex) amplitude on the corresponding atomic sublattice. This results in an additional degree of freedom known as pseudospin. The projection of the pseudospin on the direction of the momentum defines the chirality of the quasiparticles; in graphene the direction of the quasiparticle pseudospin is parallel (positive chirality) or antiparallel (negative chirality) to their momentum. Within one single Dirac cone (one valley), electrons (or equivalently holes) of opposite direction have opposite pseudospin, but the same chirality. In graphene bilayer with Bernal stacking the C–C symmetry is broken, chiral Dirac fermions are also found, but they are massive and their chirality differs from the one found in graphene monolayer.

In order to integrate graphene in future electronic devices it is of primary importance to be able to assess the pseudospin and chirality of the graphene quasiparticles, because many of the unconventional electronic properties of graphene can be rationalized as due to the conservation of these two. They are responsible, for example, of the new ‘chiral’ quantum Hall effects (QHE) observed for monolayer and bilayer exfoliated graphene, which are the most direct evidence for Dirac fermions in graphene. Paradoxically, the QHE has not been yet observed in epitaxial graphene, which leaves open the question about the Dirac nature of the quasiparticles in this system. Therefore, a direct measure of the electronic chirality and pseudospin in a single epitaxial graphene layer is really appealing in order to prove the Dirac nature of the quasiparticles in this system.

Epitaxial graphene was grown on a 6H-SiC(0001) substrate by thermal desorption of silicon at high temperatures, in ultrahigh vacuum. Parameters were chosen to obtain a mixed surface with a similar coverage of monolayer and bilayer terraces, with typical width of
50 nm. Recent angle-resolved photoemission spectroscopy (ARPES) measurements on epitaxial graphene layers on SiC(0001) demonstrate that the graphene layers are electron doped and are arranged in the Bernal stacking, the stacking found in graphite. For a graphene monolayer, ARPES shows a low energy linear dispersion, a fingerprint of Dirac like fermions. However, different results were obtained by two groups concerning the crossing of the bands: An energy gap of 0.25 eV was found at the Dirac point by only one of the groups [2]. It was proposed by the authors that the gap arises from a substrate-induced breaking of the sublattice symmetry of graphene, suggesting that the quasiparticles in epitaxial graphene monolayer may not have the chirality expected for ideal graphene.

Our experiments were done using a home-made STM operating at 4 K in ultrahigh vacuum. At high sample bias, the interface contribution in the constant current images is larger for the monolayer than for the bilayer, which results in an enhanced corrugation for the monolayer (Fig. 13(a)). This identification of monolayer terraces is confirmed by images with atomic resolution exhibiting honeycomb patterns.

At low sample bias (a few mVs), the constant current STM images reflect essentially the maps of the surface local density of states (LDOS) at $E_F$. For several surfaces, it has been shown that the 2D Fourier Transform (FT) of low bias STM images was closely related to a map of the Fermi surface (FS) of the surface states. However, it was recently reported that the correspondence between FT-STM maps and the FS is not always systematic. For example, on low index surfaces of heavy elements, the spin degeneracy of the surface electron states is lifted by the spin-orbit coupling. Accordingly, most of the elastic scattering events expected for the case of spin independent states are suppressed and the experiments have shown that only the quantum interference (QI) patterns corresponding to spin conserving scattering processes are observed.

As mentioned above, to properly describe the electronic properties of graphene it is necessary to introduce a pseudospin. In the following we show how this pseudospin affects the QIs generated by the static defects and how this can be used to determine the quasiparticle chirality of graphene at the nanometer scale. From ARPES, it appears that the FSs of epitaxial monolayer and bilayer graphene on SiC(0001) are essentially identical. As illustrated in Fig. 13(b), they consist of two tiny circular pockets, of radius $q_F$, surrounding the K and K’ points. Due to the
structure of graphene’s FS, we may expect elastic electron scattering processes between the two non-equivalent Dirac cones at K and K’, as depicted in Fig. 13(c) (e.g., intervalley scattering), together with elastic scattering processes between two electron states located on the same Dirac cone (e.g., intravalley scattering).

Figure 13(d) presents a constant current STM image taken at +2 mV that includes two adjacent graphene monolayer and bilayer terraces. A striking difference is measured in the LDOS patterns between the left and right terraces. A clear long-range modulation, of wavelength $5.2 \pm 0.3$ nm, is found for the graphene bilayer terrace. This modulation is attributed to quantum interferences of wavevector $2q_F$ due to intravalley backscattering (Fig. 13(f)). Surprisingly, we do not find any equivalent modulation on the monolayer, which is puzzling if we keep in mind that the two systems have almost the same FS.

The lack of LDOS modulation for the monolayer implies that QIs associated with intravalley backscattering are virtually absent. Intuitively, this can be understood considering that in monolayer graphene the pseudospin of the backscattered wave is opposite to that of the incident wave and their overlap should be zero (Fig. 13(e)). Recent theoretical works show that for a general impurity potential, LDOS modulations with wavevector $2q_F$ (associated with intravalley backscattering) should be strongly attenuated. In reference [3] one of us proposed that this strong attenuation should have a clear impact on the 2D-FT of the LDOS modulations: while on bilayer graphene the efficiency of intravalley backscattering should give rise to a central ring of radius $2q_F$ in the FT map similar to the one observed for conventional 2D systems, the strong attenuation of intravalley backscattering on monolayer graphene should generate a FT image with no central ring.

In the following, we present high-resolution Fast Fourier Transform (FFT) of STM images recorded at low sample bias on 50 nm wide graphene terraces. We first show real-space STM images of such terraces, in the case of graphene monolayer (Fig. 14(a)) and graphene bilayer (Fig. 14(b)). Note that both images exhibit a triangular pattern with a $6 \times 6$ periodicity with respect to the SiC(0001) surface. This periodicity originates from the underlying reconstruction of the buffer layer, and appears as a sextuplet of bright spots in the corresponding FFT images (Fig. 14(c) and (d)).

The low frequency central region of the FFT in Figs. 14(c) and 14(d) is related to intravalley scattering: a clear ring-like feature of average radius $1.2$ nm$^{-1}$ is found for the bilayer (Figs. 14(d) and 14(g)). On the monolayer terrace, no central ring is found (Figs. 14(c) and 14(e)).
14(e)), despite the unprecedented momentum resolution obtained here. This has been checked on many different monolayer terraces, which allows us to conclude that the result is robust and systematic. As discussed above, pseudospin and electronic chirality are the key parameters for the absence (presence) of the central ring in the FFT image of mono (bilayer) graphene.

In the high-frequency regions of the FFTs of Figs. 14(c) and 14(d), we find six outer pockets with ring-like shapes surrounding the K(K') points. These pockets result from intervalley scattering, associated to real space LDOS modulations with a \((\sqrt{3}\times\sqrt{3})\) R30° periodicity with respect to the graphene lattice. As shown in Figs. 14(f) and 14(h), the intensity of the high-frequency rings in the FFT is not isotropic. The anisotropy is much more pronounced for graphene monolayer, for which a splitting of the ring into two arcs is found (Fig. 14(f)).

The experimental results are compared with theoretical predictions made along the lines of Ref. [3], using a T-matrix calculation. Figure 15(a) corresponds to the FT of a LDOS map for a monolayer graphene at \(E_F\), with \(E_D = E_F - 0.45\) eV, in the presence of a single localized impurity. It is clear from the calculation that no central circular ring is generated in the FT images in this case. This is the signature of LDOS modulations resulting from inefficient intravalley backscattering, and it is the most direct fingerprint of graphene’s chirality. This is in very good agreement with the experimental absence of the central ring and proves that for a single epitaxial graphene layer on SiC(0001), the quasiparticles at the Fermi energy have the chirality expected for ideal graphene. Also, the high-frequency rings, resulting from the LDOS oscillations generated by the intervalley scattering, are nicely reproduced by the theoretical calculation. The splitting of the latter ring structure, which is also a consequence of the quasiparticle chirality, is similar to that seen in the experimental data.

Figure 15: Theoretical calculation of the Fourier Transform (FT) of the local density of states at the Fermi energy (\(E_F\)) for different graphene layers with a single delta-function impurity. (a) FT map for an electron-doped graphene monolayer. The calculation predicts no central ring related to intravalley scattering. (b) FT map for a bilayer, showing a clear central ring. (c) FT map for an asymmetric monolayer. The symmetry breaking between the two carbon sublattices restores the efficiency of intravalley backscattering as shown by the reappearance of a central ring in the FT map.

Figure 15(b) is an equivalent map as Fig. 15(a) but for a graphene bilayer, with \(E_D = E_F - 0.3\) eV. Note the appearance of the inner circle of radius 2\(q_F\), as well as the presence of outer circles which have not obvious splitting. The agreement with the experimental FFT is excellent.

Finally, we propose the use of STM to check any possible breaking of graphene’s sublattice symmetry. To this end, we have calculated the FT of the LDOS map for a monolayer with the same parameters as in Fig. 15(a), including an arbitrary asymmetry between the two carbon atoms of each unit cell. For the results shown in Fig. 15(c), the site energy difference is 250 mV, which is the gap value measured by Zhou et al. using ARPES. The calculation shows a clear inner ring in the FT, corresponding to efficient QIs due to intravalley backscattering. Indeed, if the two carbon sublattices of the graphene layer are not equivalent, the chirality of the quasiparticles is modified. Accordingly, efficient QIs related to intravalley backscattering become allowed, and a central ring is recovered in the FT. The absence of the central ring in the experimental FFT image (Fig. 14(c)) demonstrates that epitaxial graphene monolayer on SiC(0001) has
the electronic chirality predicted for ideal (symmetric) graphene. This questions the scenario of the substrate-induced carbon-carbon asymmetry proposed by Zhou et al. to explain the gap at $E_D$.

In summary, by analyzing the Fourier transform of low bias STM images, we have demonstrated that the pseudospin and chirality of epitaxial graphene quasiparticles can be probed directly at the nanometer scale [1]. We show that graphene monolayer on SiC(0001) exhibits the chirality of an ideal graphene sheet. Together with the previous ARPES findings of the linear dispersion of the quasiparticles, a complete description of the Dirac nature of the low energy electronic states of this system is obtained.


Superconducting materials

The study of superconductors and related materials has been one of the main topics of the Institute for many years. In particular, high-temperature superconductors, fullerides, MgB$_2$ and related compounds, cobaltates, iron pnictides and conventional superconductors have been studied. Due to the availability of new neutron scattering facilities with extremely high resolution, the conventional superconductors Pb and Nb have been re-examined, and unexpected results for the energy gaps are presented below. Anisotropic energy gaps and multi-band superconductivity has attracted much interest. This has been studied here for CaC$_6$, which was found to have a substantial anisotropy. CaC$_6$ has also been used as a test case for a general theory of superconductivity. For unconventional superconductors, magnetism often plays an important role. Magnetic properties have therefore been studied for iron pnictides and a copper-oxide chain compound. Finally, very large, high-quality iron-arsenic single crystals have been grown, and their transport and magnetic properties have been measured.

Energy gaps and Kohn anomalies in elemental superconductors

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Over the past half-century, a comprehensive framework based on the Bardeen-Cooper-Schrieffer (BCS) formulation has been developed for the interpretation of experimental data on superconductors. Although this framework has been challenged by the discovery of high-temperature superconductivity, it provides a remarkably successful description of the physical properties of conventional low-temperature superconductors. Even today, however, the prediction of two of the most important quantities characterizing a superconductor – the transition temperature and the energy gap at the Fermi level – from first principles presents a formidable challenge to theory, because they depend exponentially on material-specific parameters such as the phononic and electronic densities of states and the electron-phonon coupling. We have obtained neutron scattering data on the lifetimes of acoustic phonons in Pb and Nb (the two elements with the highest superconducting transition temperatures, $T_c = 7.2$ K and 9.3 K, respectively) that shed new light on the energy gap in conventional superconductors.

The energy gap can be directly determined in phonon lifetime measurements, because electron-phonon scattering is suppressed (and the phonon lifetimes are thus enhanced) for energies below the gap. Our data indicate a surprising relationship between the superconducting gap and the geometry of the Fermi surface, which also leaves an imprint on the phonon lifetimes: For phonon wavevectors connecting nearly parallel segments of the Fermi surface, the electron-phonon scattering probability is enhanced, and lifetime extrema (termed Kohn anomalies) are generally expected. We have discovered hitherto unknown Kohn anomalies in both Pb and Nb, and found that the low-temperature energy gap coincides with such an
anomaly in both materials. This phenomenon has not been anticipated by the standard theoretical framework for conventional superconductors.

Both Kohn anomalies and superconductivity-induced phonon renormalization have been observed by inelastic neutron scattering. However, as the requisite energy resolution is difficult to obtain, these investigations have been limited to a few selected materials, and both effects have thus far not been studied accurately in the same material. The systematic investigation reported here was made possible by recent advances in resonant spin-echo spectroscopy with neutrons [1,2], which have enabled the determination of the lifetimes of dispersive excitations with $μ$eV energy resolution over the entire Brillouin zone. Briefly, the spin echo is generated on a triple-axis spectrometer by using radio-frequency magnetic fields to manipulate the spin polarization of neutrons scattered from a crystal before and after the scattering event. The excitation lifetime is then extracted from the spin-echo decay profile.

The measurements were taken on high-purity Pb and Nb single crystals [3]. Figure 16 shows the intrinsic wavevector dependent linewidths $Γ$ of the lowest-energy, transverse acoustic phonon mode $T_1$ of Pb along $q=(ξ,ξ,0)$. At all temperatures, sharp anomalies in the phonon linewidths are seen at $ξ ≈ 0.25$, $ξ ≈ 0.35$, and $ξ ≈ 0.50$ reciprocal lattice units (r.l.u.). Although the phonon spectrum of Pb has been studied extensively by conventional neutron spectroscopy, these particular features have not been recognized because of insufficient energy resolution. Figure 16(b) shows that the same features also appear in the phonon dispersion relation: maxima in the phonon linewidth coincide with characteristic S-shaped deviations from the $q$-linear dispersion, as stipulated by the Kramers-Kronig relation that holds for all excitations in solids. Artifacts associated with the new measurement method would generally not be Kramers-Kronig consistent and can thus be ruled out. This implies that phonons with the anomalous wavevectors shown in Fig. 16(a) are intrinsically unstable towards decay into other elementary excitations. In principle, the decay products can be either other phonons (generated, for instance, by anharmonic terms in the lattice potential) or electron-hole pairs (originating from Kohn anomalies).

The features at $ξ ≈ 0.35$ and 0.5 can be associated with Kohn anomalies, because these wavevectors are known as nesting vectors of the Fermi surface. Indeed, Kohn anomalies have been observed at these wavevectors in the longitudinal phonon branch of Pb. The origin of the feature at $ξ ≈ 0.25$ is more subtle, because this
wavevector does not match any known spanning vector of the Fermi surface. A possible origin is a three-phonon decay process previously observed in the spectrum of phonons in liquid helium, which are unstable because their phase velocity exceeds the velocity of sound. Anharmonic terms in the lattice potential may also contribute to the anomaly.

Figure 17: Contribution of the electron-phonon interaction to the linewidth of the transverse acoustic phonon along \( q = (\xi, \xi, 0) \) in Pb. The corresponding phonon energy \( E \) is provided by the scale at the top; note the nonlinear \( E \) versus \( q \) relationship. The lines are results of least-squares fits to the BCS excitation spectrum function. The inset shows the temperature dependence of the superconducting energy gap (filled squares) and Kohn anomaly (open triangles) extracted from the fits. The line in the inset shows the BCS expression for the superconducting gap, which was experimentally confirmed by tunneling spectroscopy.

We will focus on the influence of superconductivity on the phonon linewidths below \( T_c = 7.2 \) K. As the superconductor is cooled below \( T_c \), the electron-hole decay channel is closed (and \( \Gamma \) is reduced) below the energy gap \( 2\Delta(T) \). This effect is observed at low wavevectors \( \xi \) in Fig. 16(a). In particular, \( \Gamma \to 0 \) for \( T \ll T_c \) around \( \xi = 0.32 \) (corresponding to a phonon energy of 2.47 meV, below the low-temperature limit of \( 2\Delta \approx 2.7 \) meV known from tunneling measurements). For lower energies around \( \xi \approx 0.25 \), however, \( \Gamma \) remains nonzero even at the lowest temperatures, supporting the notion that the linewidth anomaly at this wavevector originates from the three-phonon down-conversion process discussed above and/or lattice anharmonicity, and not from electron-hole pair production. We have removed the contribution of this process for clarity and show only the phonon linewidth \( \Gamma_{e-p} \) directly attributable to the electron-phonon interaction (Fig. 17). As expected, \( \Gamma_{e-p} \) exhibits a maximum due to the pileup of electronic density of states above \( 2\Delta(T) \), which moves to progressively higher energies upon cooling and closely tracks the energy gap determined in prior tunneling measurements (inset in Fig. 17).

Surprisingly, however, the superconductivity-induced maximum of \( \Gamma_{e-p} \) merges with the Kohn anomaly as \( T \to 0 \). At \( T = 0.5 \) K, both anomalies are indistinguishable within the measurement error.

In order to explore whether the coincidence of \( 2\Delta(T \to 0) \) and the Kohn anomaly in Pb is accidental, we have performed similar experiments on phonons in Nb, an elemental superconductor with a different Fermi surface and phonon spectrum. Figure 18(a) shows the momentum-dependent linewidths of the transverse acoustic phonon branch along \( (\xi, 0, 0) \) in Nb at temperatures above and below \( T_c = 9.3 \) K. The data above \( T_c \) are in fair agreement with prior work, but they reveal several sharp features that have not been identified before. Based in part on ab initio lattice dynamical calculations, they can be identified as Kohn anomalies (see below). The existence of a Kohn anomaly at \( \xi \approx 0.17 \) persisting up to room temperature has been suggested based on prior experimental work. As described above for Pb, the linewidths are reduced below and enhanced above the gap for quasiparticle-pair production, \( 2\Delta(T) \), in the superconducting state, and the low-temperature electron-phonon linewidth shows the expected dependence on wavevector (or energy). Similar to the observation in Pb, the \( 2\Delta(T \to 0) \) extracted from the low-temperature \( \Gamma_{e-p} \) of Nb again coincides with the lowest-energy Kohn anomaly within the experimental
error (Fig. 18). To help interpret these observations, we have calculated the phonon dispersions and linewidths in the framework of ab initio density functional perturbation theory in the local-density approximation (LDA), on a very fine mesh of \( \mathbf{q} \)-points in reciprocal space. The results are in reasonable overall agreement with the experimental data (Figs. 17 and 18). In particular, both the phonon frequencies and the linewidths associated with Kohn anomalies in the high-energy transverse acoustic phonons of Nb (Fig. 18(a)) and in the longitudinal phonon of Pb (not shown) are well described, indicating that the resolution of the calculations is sufficient to reproduce subtle structures in \( \mathbf{q} \)-space.

The lowest-lying Kohn anomalies in the transverse-acoustic phonon branches of both Pb and Nb are, however, not reproduced by the calculations. These anomalies therefore originate in factors not included in the calculations, such as the relativistic spin-orbit coupling, phonon non-adiabaticity, or many-body correlations beyond the LDA. As the Kohn anomalies in Pb and Nb are of comparable strength, the spin-orbit coupling (which is much stronger in Pb than in Nb) cannot be responsible. Because of the large Fermi energies of both materials, non-adiabatic electron-phonon coupling effects should also be extremely weak.

This leaves electron correlation effects beyond the LDA as the most likely mechanism responsible for the low-energy Kohn anomalies. It seems reasonable to assume that the same correlations are also responsible for the observed coincidence of \( 2\Delta(T \rightarrow 0) \) with the same anomalies. As the anomalies persist to temperatures above 100 K, superconducting fluctuations are unlikely to be directly responsible. We note, however, that the formation of spin or charge density waves driven by electron correlations has been predicted for Pb and other elemental metals.

Although extensive searches for static density waves in simple metals have been unsuccessful, it is conceivable that fluctuations characteristic of such states dynamically enhance the nesting properties of the Fermi surface, and hence the propensity for Kohn anomalies in the phonon spectrum. It is interesting to point out a possible analogy to research on high-temperature superconductors, where an anomalous coincidence of the superconducting gap with a weakly temperature-dependent ‘pseudo-gap’ has recently been reported in some regions of momentum space.

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**Figure 18:** (a) Linewidths of transverse acoustic phonons along \( q = (\xi,0,0) \) in Nb at two different temperatures. The grey symbols are the results of lattice-dynamical calculations, as described in the text. (b) Blowup of the low-\( q \) segment of panel (a). The lines are guides-to-the-eye.

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Evidence for gap anisotropy in CaC₆ from far-infrared and point-contact spectroscopy

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About three years ago Weller et al. reported superconductivity in alkaline earth intercalated graphite AEC₆ (AE = divalent alkaline earth) with Tc’s up to 11.5 K for CaC₆, significantly higher than that of of the alkali metal intercalated graphite phases studied before. This discovery stimulated much research on the investigation of their properties as well as the search for new superconducting graphite intercalated compounds (GICs). In this effort our group has successfully prepared samples of these new AE GICs and investigated experimentally and theoretically (in close collaboration with Abt. Andersen of our Institute) their superconducting properties. Also we discovered SrC₆ as a new superconductor (Tc = 1.65 K) in this series [1,2].

One of the most important parameters of a superconductor is the superconducting gap Δ(T), especially its magnitude and temperature dependence. Several early experiments on CaC₆ evidenced a single, isotropic, s-wave gap with a ratio 2Δ/kBTc close to that expected from weak-coupling BCS theory. Tunneling spectroscopy investigations, on the other hand, pointed to an isotropic gap with a magnitude more than 40% higher than that found before, establishing an unsatisfying rather large uncertainty for the superconducting gap Δ(0) ranging from 2Δ(0) = 3.2 to 4.6 meV. However, all techniques employed to measure the gap so far, were either bulk techniques and could not distinguish between in-plane and out-of-plane gap or probed the gap along the c-axis direction.

On the other hand, recent first-principles density functional calculations of the superconducting properties of CaC₆ have predicted the presence of a moderately anisotropic gap which varies between 2Δ(0) = 2.2 meV and 4.6 meV, depending on the position in the Brillouin zone and which part of the Fermi surface (π or interlayer sheets) mediate the Cooper pairing. Another aspect of the gap properties of CaC₆ which was also widely debated and never conclusively ruled out was the possibility of two or multi-band superconductivity.

To investigate the superconducting gap in CaC₆, especially with respect to a non-isotropic and multi-band character, we have carried out detailed far-infrared terahertz spectroscopy as well as point-contact Andreev reflection spectroscopy parallel and perpendicular to the c-axis direction on high-quality samples of CaC₆.

In superconductors infrared photons with energy larger than 2Δ break Cooper pairs in a process of scattering off impurities and create pairs of quasiparticles. This scattering leads to a step-like feature in the reflectance spectra. This step as the characteristic signature of the opening of the superconducting gap increases along with increasing scattering rate of the quasiparticles.

In the superconducting state the infrared zero-angle reflectance spectra of CaC₆ show such step-like features below ≈4 meV. The amplitude of the step is largest at ≈3 K. The onset shifts to lower energies and the amplitude
decreases as the temperature approaches $T_c$. Figure 19 shows the reflectance at 6 K normalized to the reflectance in the normal state at 15 K. In order to obtain information about the superconducting gap and its temperature dependence, the zero-angle reflectance spectra were fitted by using well-known relations between the complex dielectric constant $\varepsilon(\omega)$ and the complex conductivity $\sigma(\omega)$ assuming a Drude-type conductivity in the normal state and results for a BCS (Bardeen-Cooper-Schrieffer) superconductor using $\Delta(0)$, $T_c$ and the scattering rate $\gamma$ as fitting parameters. As additional input parameters for the fit a dc-conductivity $\sigma_{dc} \approx 1 \mu S/cm$, consistent with the dc-resistivity measurements and a dielectric constant $\varepsilon_\infty$, were used. The resulting fit with a single BCS gap with $2\Delta(0) = 2.8$ meV shown as a dotted line in Fig. 19 reveals some deviations which can be markedly reduced if an anisotropic gap is used.

For this the formalism was extended by assuming that the conductivity in the superconducting state results from a superposition of conductivities according to

$$\sigma_{sc}(\omega) = \sum_i f(2\Delta_i)\sigma_{sc}(\omega, 2\Delta_i) / \sum_i f(2\Delta_i),$$

where $f(2\Delta_i)$ is the distribution function of the gaps according to Sanna et al. [3] scaled by a factor $0 \leq s(T) \leq 1$ which transforms each gap value according to $\Delta(T) = s(T)\Delta(0)$ (see Fig. 19(b)) and details in [4]). Using the gap distribution suggested by Sanna et al. the fits improved significantly (solid line in Fig. 19(a)). A similarly, good fit, however, can also be achieved if a Gaussian distribution of gaps with peak value $2\Delta(0) = 3.1$ meV and 1 meV FWHM (full width at half maximum) is used. The fitted temperature dependence of the IR spectra resulted in gaps which are in good agreement with the BCS temperature dependence confirming that $\text{CaC}_6$ is an $s$-wave superconductor. The occurrence of the gap signature in the far-infrared spectra indicates that $\text{CaC}_6$ is a superconductor in the dirty limit. The infrared data are in accordance with the predicted gap distribution based on a moderately anisotropic gap.

Final confirmation of the anisotropic superconducting order parameter in $\text{CaC}_6$ came from point-contact Andreev reflection spectroscopy (PCAR) [5]. In order to measure the PCAR, instead of the standard metal tip, point contacts in our experiments were made by using a very small drop of Ag conductive paint (diameter $\approx 50\mu m$), attached on an etched or freshly cleaved surfaces of the sample. Such ‘soft’ point contacts were found particularly stable both in time and towards temperature variation and they provide current injection mainly perpendicular to the contact plane [6]. The size of the samples allowed us to apply contacts either on the flat surface (|| $c$) or on the edges (|| $ab$).

Figure 20 shows the temperature dependence of a typical set of normalized conductances versus bias voltage measured with current injection either || $c$ or || $ab$. A total of 35 contacts with resistances ranging between 0.5 $\Omega$ and 6.4 $\Omega$ were investigated.
The conductance traces show typical Andreev-reflection characteristics with an almost flat conductance at $|V| \geq 8\text{ meV}$ and no dips indicating a violation of pure ballistic conduction in the contacts. The conductances were fitted to a modified single-band 3-dim Blonder-Tinkham-Klapwijk (BTK) model using the order parameter $\Delta(T)$, the barrier-height parameter $Z$ and a broadening parameter $\Gamma$ to account for finite quasiparticle lifetime and extrinsic broadening effects. Figure 21 displays a fit of the temperature dependence of the order parameter $\Delta(T)$ with the BCS-type temperature dependence. A difference of $\Delta(0)$ between the gaps measured $\parallel c$ and $\parallel ab$ is clearly revealed. The critical temperatures $T_c$ (Andreev critical temperatures of the junctions) averaged over the investigated set of different samples amounted to $11.3(1)\text{ K}$, in very good agreement with the bulk critical temperature of the samples. The fitted gaps showed a Gaussian distribution with values of $2\Delta_{ab}(0) = 2.70(28)\text{ meV}$ and $2\Delta_c(0) = 3.42(16)\text{ meV}$. A fit of a two-band BTK model did not show any improvement of the fits.

Using recent results of the electronic structure for CaC$_6$ [3] detailed *ab initio* model calculations of the Andreev conductance for the two injection directions were performed. Especially $Z$ and $\Gamma$ were varied to cover the relevant parameter range found from the fits to the experiment.
These calculations showed excellent agreement of the theoretical with the experimental conductance curves. Even though characteristic dips or shoulders in the Andreev conductance curves were smeared out by the finite quasiparticle lifetime \( \Gamma \neq 0 \), the conductance traces still contain the anisotropy information which can be revealed by the fitting procedures.

In conclusion, the first directional point-contact Andreev reflection measurements in CaC\(_6\) carried out down to \( \approx 400 \) mK both along the \( ab\)-plane and the \( c\)-axis direction give strong and reproducible evidence of the predicted anisotropic nature of the superconducting gap in this GIC. New first-principles calculations of the expected anisotropy in the PCAR curves give further support for our findings and indicate that the actual gap anisotropy in CaC\(_6\) could be even slightly larger.

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**Controversies in superconductivity**

S. Deng, A. Bussmann-Holder, J. Köhler and A. Simon

Graphite intercalation compound CaC\(_6\)

In the last years, we have proposed a ‘flat/steep’ band model for the origin of superconductivity [1]. The recent discoveries of superconductivity at unexpectedly high temperatures for graphite intercalation compounds (GIC’s) such as CaC\(_6\) provided a new test case for our model. As the first step, we have studied the low energy electronic structure of CaC\(_6\) on the basis of different theoretical approaches. Ca has usually been considered as an \( s\)-metal by chemists which becomes metallic by \( s/p\) hybridization. However, the significant occupation of \( d\)-states is essential for the understanding of the chemical bonding of elemental Ca [2] and also CaC\(_6\) [3].

We have demonstrated that the Ca-3\( d\) state in CaC\(_6\) is a necessary and sufficient condition to produce an interlayer band which is fundamental for many of its important properties [4]. Through constructing a new tight-binding model and first-principle studies, it has been shown that this interlayer band has dominantly a tight-binding character instead of a quasi-free-electron one as frequently stated in literature. By using new computational techniques developed by the authors, the C nuclear field and the exchange-correlation effect are shown to be responsible for the stability of Ca-3\( d\) states. Furthermore, the deep involvement of the Ca-3\( d\) states in the chemical bonding of the \( sd\)- and \( pd\)-band is also revealed (Fig. 22).
The established facts do not only provide an explanation for the observed unusual Ca isotope effect in CaC$_6$, but also help to resolve the controversy about the nature of the interlayer band and the mechanism for superconductivity.

**Mixed $s$-$d$ order parameter in high-$T_c$ oxocuprates**

Cuprate high-temperature superconductors are frequently described in terms of a $d$-wave order parameter only. However, the deviations from a strictly square symmetry of the CuO$_2$ planes, which is present in all these compounds, suggest that the superconducting order parameter is more complex and has to have an additional $s$-wave component. These considerations are supported by muon spin rotation measurements, where an inflection point in the superfluid density at low temperatures has been observed which is a clear signature of the coexistence of a small and a large gap. From the magnetic field dependence of the individual components it must be concluded that $s$+$d$-wave symmetry of the order parameter are realized here [5], see Fig. 23.

An additional support for this scenario is obtained from extended X-ray absorption fine structure measurements where a divergence of the mean square Cu–O displacement at the pseudogap temperature and at the superconducting transition temperature can only occur, if the order parameter is composed from an $s$-wave and a $d$-wave admixture [6] (Fig. 24).

Figure 22: Band structure for CaC$_6$ calculated with the FP-LMTO method. The broken curve indicates the tight-binding band from our TB model. The red dotted line shows the energy dispersion of quasi-free electrons along two different directions. The three bands crossing the Fermi level are named $pp$, $sd$ and $pd$, respectively.

Figure 23: Temperature dependence of the $\mu$SR relaxation rate of single crystals of La$_{1.85}$Sr$_{0.15}$CuO$_4$ where green and blue lines show the individual contributions from the $d$- and $s$-wave gap.

Figure 24: The mean square displacement $\sigma^2(T)$ as a function of temperature. The open red squares (full grey squares) refer to an $s$-wave (a $d$-wave) order parameter, respectively. For comparison the bare unrenormalized mean square displacement is added (dashed line). The inset shows the experimental data for La$_{1.85}$Sr$_{0.15}$CuO$_4$. 
The observed divergences have been shown to originate from polaron formation, coherence and coupling to superconductivity. Both experiments thus provide clear evidence that polarons play a crucial role in the physics of cuprates and are also the origin of all mostly unconventional isotope effects observed there.


The discovery of superconductivity in F-doped LaFeAsO1−xFx ($T_c = 27$ K) by Kamihara and co-workers [1] initiated an avalanche of experimental and theoretical works on iron pnictides. The interest in these compounds heated up even more when superconductivity below $T_c = 38$ K was reported in completely oxygen free Ba1−2yK2yFe2As2 doped with potassium, for which good quality single crystals were synthesized. Both families of the iron pnictides have a quasi 2D tetragonal crystal structure, in which FeAs layers are separated by either LaO or Ba layers. Fe ions form a square lattice sandwiched between two As sheets shifted so that each Fe is surrounded by a distorted As tetrahedron. Both stoichiometric parent compounds undergo a structural transition, at which the symmetry of the lattice lowers to orthorhombic. At the same (BaFe2As2) or slightly lower (LaFeAsO) temperature the so-called stripe AFM order sets in, with Fe magnetic moments ordered ferromagnetically (FM) along the shorter b-axis and antiferromagnetically (AFM) along the a- and c-axes. Electron doping of the FeAs layers in LaFeAsO1−xFx suppresses the structural and magnetic transitions in favor of superconductivity already at $x = 0.03$ [2]. In Ba1−2yK2yFe2As2, the transition is also suppressed but at much higher level ($2y \approx 0.3$) of K doping [3], which corresponds to the doping of the FeAs layers with 0.15 holes per Fe ion. Since the superconducting transition occurs already at $y \approx 0.1$, the superconducting and magnetically ordered phases seem to coexist in a wide range of K contents.

Although it is not clear yet whether superconductivity in the iron pnictides is mediated by AFM fluctuations or superconductivity and magnetism compete, it is difficult to overestimate the importance of understanding the magnetic properties of these compounds.

In this work the magnetic interactions between Fe moments are studied by performing self-consistent calculations for co-planar spin-spiral structures in Ba1−2yK2yFe2As2 with $y = 0, 0.1, 0.2, 0.3$. The calculations were carried out within the local-spin-density approximation on the base of the generalized Bloch theorem using the linear muffin-tin orbital method. For all doping levels the experimental room temperature crystal structure of BaFe2As2 was used. The effect of doping was simulated by using the virtual crystal approximation.
The total energies were calculated for the wavevector $q$ of a spin spiral varying along the edges of the irreducible triangle of the 2D Brillouin zone (BZ) formed by $\Gamma$-, $\Xi$-, and $M$-points, which in the $\pi/d$ units have the coordinates (0,0), (1,0), and (1,1), with $d$ being the nearest Fe–Fe distance. The spin spirals with $q = (1,0)$ ($\Xi$) and (1,1) ($M$) correspond to the stripe and checkerboard AFM orders, respectively. The total energy and Fe magnetic moment are plotted as functions of $q$ in Fig. 25. In agreement with the experimental data the total energy minimum for the undoped BaFe$_2$As$_2$ is found at the $\Xi$-point, e.g., for the stripe AFM order. Additionally, a local minimum of $E(q)$ appears at $q_{\text{min}} = (0.75, 0.75)$ along the $M-\Gamma$ line. The calculated Fe magnetic moment varies weakly along the $\Xi-M$ line (Fig. 25) but rapidly decreases to zero as $q$ approaches the $\Gamma$-point.

In the range of $q$, for which a magnetic solution exists, the calculated $E(q)$ curve can be surprisingly well approximated by the classical Heisenberg model on the square lattice with AFM nearest neighbor $j_1$ and next-nearest neighbor $j_2 > j_1/2$ interactions. The position of the local minimum at $q_{\text{min}}$ determines the $j_2/j_1$ ratio of 0.77. Then, $j_1 = 95$ meV and $j_2 = 73$ meV can be estimated from the energy difference $E(q_{\text{min}}) - E(\Xi)$, using the value of the Fe spin $S = 0.67$ calculated at the $\Xi$-point. These values of $j_1$ and $j_2$ are comparable to the values calculated for the undoped LaFeAsO [4]. The energy of the $j_1-j_2$ Heisenberg model is compared to the calculated total energy in Fig. 25.

The hole doping of the FeAs layer due to K substitution results in strong reduction of the stabilization energy of the magnetic solution. The Fe moment calculated for the stripe AFM order decreases from 1.34$\mu_B$ in the undoped compound to 0.99$\mu_B$ for $y = 0.3$. Nevertheless, the stripe AFM order remains stable in a wide doping range. Only at $y = 0.3$ the total energy minimum finally shifts away from the $\Xi$-point. The calculations show that the stripe AFM order in Ba$_{1-2y}$K$_2$Fe$_2$As$_2$ is more resistant to doping as compared to LaFeAsO$_{1-x}$F$_x$, in which the minimum shifts to incommensurate $q$ at much smaller level of F doping [4]. This conclusion is supported by experimental observations of the traces of the spin density wave phase at K concentration as high as 40%, i.e., well into the superconducting region.

The effective exchange coupling constants estimated for different levels of K doping are summarized in Tab. 1. The strong doping dependence of $j_1$ and $j_2$ indicates that the magnetic properties of Ba$_{1-2y}$K$_2$Fe$_2$As$_2$ cannot be adequately described by the simple $j_1-j_2$ Heisenberg model.

The strength of the interlayer exchange coupling in BaFe$_2$As$_2$ was evaluated by adding a nonzero $q_z$ component to the wavevector of the spin spiral at the $\Xi$-point. As $q_z$ increases, the
relative orientation of the Fe moments in adjacent FeAs layers changes from ferro- to antiferromagnetic one, whereas the stripe AFM order within each layer is not affected. The calculated $q_z$ dependence of the total energy indicates that the AFM interlayer coupling in BaFe$_2$As$_2$ is significantly stronger than in LaFeAsO, in which the magnetic interactions are much more 2D-like [4].

Table 1: Doping dependence of the exchange coupling constants $j_1$ and $j_2$ in Ba$_{1-2y}$K$_{2y}$Fe$_2$As$_2$.

<table>
<thead>
<tr>
<th>y</th>
<th>$j_1$ [meV]</th>
<th>$j_2$ [meV]</th>
<th>$j_2 / j_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>95.0</td>
<td>73.1</td>
<td>0.77</td>
</tr>
<tr>
<td>0.1</td>
<td>76.7</td>
<td>65.2</td>
<td>0.85</td>
</tr>
<tr>
<td>0.2</td>
<td>39.1</td>
<td>43.1</td>
<td>1.10</td>
</tr>
<tr>
<td>0.3</td>
<td>19.4</td>
<td>21.3</td>
<td>1.10</td>
</tr>
</tbody>
</table>

Both the imaginary $\text{Im} \chi_0(q, \omega \rightarrow 0) / \omega$ and real $\text{Re} \chi_0(q,0)$ parts of the susceptibility of undoped BaFe$_2$As$_2$ show sharp peaks at $q=(1,0)$ (Fig. 26), which appear as a result of the nesting of quasi-two-dimensional Fermi surface (FS) sheets. Indeed, as shown in Fig. 27 corrugated hole-like cylinders around $\Gamma$ match elliptical electron-like sheets centered at the $X$-point, when shifted by the vector $(\pi/a, \pi/a, 0)$ which corresponds to $q = (1,0)$ in the 2D BZ.

With the increase of K content the FeAs layer is doped with holes. As a result the hole-like cylinders around $\Gamma$ expand, whereas the electron-like sheets around $X$ shrink. They are no longer connected by the nesting vector $q = (1,0)$ and the susceptibility at the $X$-point decreases rapidly with doping. Instead, a peak develops in both the imaginary and real parts of $\chi_0(q,0)$ at those wavevectors, at which the electron- and hole-like cylinders cross each other.

In conclusion, the self-consistent total energy calculations performed for spin spirals in Ba$_{1-2y}$K$_{2y}$Fe$_2$As$_2$ confirm that in the undoped compounds the minimum of the total energy is reached at the wavevector $q = (1,0)$, which...
The interplay between the magnetic and electric properties of copper oxides has recently been the subject of intense research activity. For instance, states with collinear and non-collinear magnetic order are currently under discussion in the contexts of ferroelectricity in undoped copper-oxide chain compounds and of the anomalous transport properties of underdoped high-temperature superconductors. Since theoretical methods are well established in one dimension (1D), compounds with quasi-1D electronic structure are particularly suitable as model systems to obtain a detailed understanding of this interplay. However, research on the effect of doping in copper-oxide chain compounds has been limited by the scarcity of materials that support a significant density of holes on the chains. Most of the attention has been focused on the ‘telephone number compounds’ \((\text{La, Sr})_{14-x}\text{Ca}_{x}\text{Cu}_{24}\text{O}_{41}\) (LSCO), which contain chain and ladder systems based on edge-sharing \(\text{CuO}_4\) square plaquettes. However, complications originating from the presence of two distinct electronically active subsystems with different hole concentrations and from the random potential of substituents (for \(x \neq 0\)) partially mask the intrinsic behavior of the copper-oxide chains. Moreover, recent work has shown that the magnetic properties of this material are strongly influenced by an incommensurate structural modulation arising from a mismatch of different units constituting the crystal lattice. \(\text{Ca}_{2-x}\text{Y}_{2-x}\text{Cu}_5\text{O}_{10}\) (CYCO), a class of materials containing only copper-oxide chains, also exhibits a complicated structural modulation unrelated to charge ordering. In addition, the magnetic properties of doped chains in this material appear to be influenced to a large extent by substitutional disorder and/or oxygen non-stoichiometry.

\(\text{Na}_x\text{CuO}_2\), a recently synthesized family of compounds with very low chemical disorder, offers new perspectives in this regard [1]. This material consists entirely of electronically inert \(\text{Na}^+\) ions and chains built of edge-sharing
CuO₄ plaquettes similar to those in LSCO and CYCO (Fig. 28). Holes donated to the chains by the Na ions form long-range ordered superstructures that are generally incommensurate with the Na sublattice. However, in contrast to other copper oxides with dopable chains, incommensurate structural modulations due to purely steric constraints are not present, so that incommensurate charge order can be established if $x$ is a rational number. By carefully adjusting the chemical synthesis conditions, a state with $x = 1.60$, corresponding to a hole filling factor of $2/5$ on the chains, has recently been stabilized. The stoichiometric compound created in this way, Na₈Cu₅O₁₀, is a unique testing ground for theories of magnetism in doped copper oxides, without complications arising from substitutional disorder and/or incommensurate lattice distortions.

We have determined the magnetic structure of Na₈Cu₅O₁₀ below its Néel temperature $T_N = 23$ K by neutron powder diffraction. We find that the spins are collinear and exhibit an incommensurate spin density modulation that is unusual for magnetic insulators. A possible origin is a network of competing interchain exchange interactions [2]. An investigation of the mechanisms stabilizing this state compared to the helicoidal states found in the undoped analogues (Na, Li)Cu₂O₂ may provide important insights into the competition between collinear and non-collinear magnetism in other copper oxides of topical interest.

Figure 28: (a) Nuclear unit cell and spin structure of Na₈Cu₅O₁₀. (b) Cut of the lattice structure along the $ab$-plane, showing inequivalent copper sites and superexchange parameters, as explained in the text.

Powder samples of Na₈Cu₅O₁₀ were synthesized in a single batch as described previously [1]. Their magnetic susceptibility was found to be in good agreement with prior reports [1]. In particular, a magnetic transition temperature $T_N = 23$ K was obtained by analyzing the derivative of the magnetization as a function of temperature. As Na₈Cu₅O₁₀ is sensitive to air, the samples were sealed in air-tight vanadium cans, which were loaded into a helium flow cryostat. The neutron diffraction data were taken at the Laboratoire Léon Brillouin in Saclay, France. Figure 29 shows a high-resolution powder diffraction pattern obtained at room temperature. The nuclear intensities for our sample were refined with the program Fullprof on the basis of the monoclinic space group $Cm$ [2]. The unit cell parameters and atomic positions obtained from the refinement agree with the results of earlier X-ray diffraction studies [1]. The resulting diffraction pattern yields an excellent description of the experimental data (Fig. 29), as indicated by the goodness-of-fit-parameter $R_F = 0.0854$. This confirms that the sample is chemically homogeneous, and that the lattice structure is commensurate.
Figure 29: High-resolution neutron powder diffraction pattern of Na₈Cu₅O₁₀ at room temperature. The black line shows the result of the Rietveld refinement discussed in the text. The positions of nuclear Bragg reflections are indicated by green marks. The blue curve gives the difference between the calculated and measured intensities.

The atomic positions within the unit cell are displayed in Fig. 28. The unit cell comprises ten copper ions, which are organized in two parallel CuO₂ chains pointing along the b-axis. The chains are separated by Na ions. Four of the copper ions in each unit cell (Cu3 in Fig. 28(b)) were found to exhibit bonding patterns characteristic of spinless Zhang-Rice singlet states with formal valence 3⁺ [1]. The Cu–O bond lengths of the remaining six copper ions indicate a valence state of Cu²⁺ with spin 1/2. The Cu²⁺ ions are located in two inequivalent sites, which are surrounded by two Cu³⁺ ions (Cu1), and one Cu¹⁺ ion and one Cu²⁺ ion (Cu2), respectively. Nominally di- and trivalent copper ions are ordered in the sequence 2-2-3-2-3-2-3-... along the chains (Fig. 28). The charge order is stable up to temperatures well above room temperature [1].

Figure 30 shows the low-angle segment of the high-flux powder pattern measured at 1.4 K (red points). The black line shows the results of the Rietveld refinement discussed in the text. The upper (lower) green marks indicate the positions of nuclear (magnetic) Bragg reflections. The blue curve gives the difference between the calculated and measured intensities. The inset shows the result of a refinement based on a commensurate spin structure.

The positions of the magnetic Bragg peaks indicate an approximate doubling of the unit cell along a and c, whereas the magnetic and nuclear unit cells coincide along the spin-chain axis b. A systematic shift away from scattering angles corresponding to commensurate Bragg reflections (inset in Fig. 30) reveals that the magnetic structure is incommensurate. Note that this shift can be extracted with high confidence, because the reference lattice parameters are determined by many Bragg reflections over a wide range of scattering angles (Fig. 29). The propagation vector resulting from the refinement is (−0.5 + α, 0, 0.5 − β) with α = 0.089(3) and β = −0.030(1) (at 1.4 K). The Miller indices

\[ T_N, \] which indicates homogeneous magnetic long-range order in the low-temperature phase [2]. This conclusion is supported by our refinement (Fig. 30), which shows that the widths of the magnetic Bragg reflections are limited by the instrumental resolution. This refinement of the magnetic structure was obtained using the software package Fullprof.
of the magnetic Bragg reflections are shown in Fig. 30. The asymmetric lineshape of the magnetic peak at higher scattering angle is well-explained as a consequence of the superposition of two resolution-limited, nearly coincident incommensurate Bragg reflections.

Although only three inequivalent magnetic Bragg reflections are visible, the diffraction pattern imposes strong constraints on the magnetic structure. Because of the large unit cell and the incommensurate magnetic modulation, most possible spin arrangements generate additional Bragg reflections with intensities well outside the experimental error bars, where none are observed (especially at the position indicated by the black arrow in Fig. 30). By far the best agreement with the data (Bragg $R = 0.049$, magnetic $R = 0.114$) was obtained based on a collinear spin structure in which the two Cu$^{2+}$ moments on Cu2-sites directly adjacent along the chains are parallel, whereas Cu1 and Cu2 moments separated by Cu3 ions are antiparallel. The magnetic moment on the Cu3-site was refined to zero, consistent with the Zhang-Rice singlet state. The incommensurate propagation vector perpendicular to the chains modulates the magnitude of the Cu$^{2+}$ moments. The modulation amplitude was refined as $0.84 \pm 0.10 \mu_B$ on both Cu1- and Cu2-sites, consistent with a spin-1/2 state. The spin direction resulting from the refinement is $(0.86 \pm 0.39, 0, 0.92 \pm 0.07)$. An additional refinable parameter is the phase difference $\Psi_{12} = 44.6 \pm 4.5^\circ$ of the modulation on Cu1- and Cu2-sites. The spin arrangement within the nuclear unit cell is displayed in Fig. 28. The corresponding diffraction pattern is in excellent agreement with the data (Fig. 30) [2].

The observed spin amplitude modulation is formally analogous to spin density waves in metallic systems, but the insulating nature and robust charge order of Na$_8$Cu$_5$O$_{10}$ imply that it cannot arise from a Fermi surface instability. We therefore discuss our data in terms of superexchange interactions between local magnetic moments, focusing first on the commensurate spin structure along the chain axis $b$. The spin alignment along this axis indicates a ferromagnetic nearest neighbor (nn) exchange interaction $J_{\parallel 1}$ and an antiferromagnetic next-nearest neighbor (nnn) interaction $J_{\parallel 2}$ (Fig. 28(b)), in agreement with undoped chains with similar bond lengths and angles as the ones in Na$_8$Cu$_5$O$_{10}$. Since the Cu–O–Cu bond angle in the edge-sharing chain geometry is close to 90°, $J_{\parallel 1}$ is anomalously small, and the competing nnn coupling $J_{\parallel 2}$ is comparable or larger in magnitude. The undoped spin systems of (Li,Na)Cu$_2$O$_2$ respond to the resulting frustration by forming incommensurate, helical magnetic order propagating along the chains [3]. In Na$_8$Cu$_5$O$_{10}$, charge ordering lifts this frustration and gives rise to a commensurate spin structure along the chains, as predicted by model calculations.

The situation is different for interactions between different chains. For simplicity, we first ignore the small incommensurability along $c$ and consider the magnetic bonding pattern in the $ab$-plane (Fig. 28(b)), including both interactions between directly adjacent chains within the same unit cell ($J_{\perp 1}$, $J_{\perp 2}$) and interactions between nnn chains ($J_{\perp 3}$). The simplest explanation for the approximate doubling of the unit cell along $a$ is that $J_{\perp 3}$ is dominant and antiferromagnetic, leaving the interactions between nn chains frustrated. In principle, the spin system can respond to the frustration by establishing either non-collinear magnetic order, as observed in (Na,Li)Cu$_2$O$_2$ [3], or periodic spin-singlet correlations, as found in models of frustrated and/or doped 1D and 2D quantum antiferromagnets. An admixture of such correlations is a possible mechanism underlying the observed spin density modulation in Na$_8$Cu$_5$O$_{10}$. Considering collinear classical spins coupled by sinusoidally modulated exchange bonds with amplitudes shown in Fig. 28(b), we obtain a crude estimate of the magnitude of the interchain interactions in the framework of this scenario [2]. While a full quantum-mechanical calculation
is required to assess the viability of this scenario, this simple estimate indicates that the exchange interactions between CuO$_2$ chains along $a$ are comparable to those within the chains, as observed for other copper-oxide chain compounds. The smaller incommensurability along $c$ suggests weaker exchange interactions in this direction.

In view of the helicoidal states observed in (Li,Na)Cu$_2$O$_2$, the collinear spin density modulation in Na$_8$Cu$_5$O$_{10}$ may seem surprising. However, as other cuprates with undoped edge-sharing chains exhibit collinear spins, the energy balance between both types of order appears to be quite subtle. This is confirmed by ab initio calculations. Anisotropic exchange and/or order-from-disorder mechanisms may be responsible for tipping the balance towards collinear order in Na$_8$Cu$_5$O$_{10}$.

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Iron pnictides: Single crystal growth and effect of doping on superconducting properties

G.L. Sun, D.L. Sun and C.T. Lin

A new class of high-temperature superconductors has been discovered in layered iron arsenic compounds [1,2]. Results in this rapidly moving field may shed light on the still unsolved problem of high-temperature cuprate superconductivity. Among the newly discovered compounds, F-doped LaFeAsO$_{1-x}$F$_x$ (1111) shows the superconducting transition temperature $T_c \approx 26$ K [1] and SmFeAsO reaches as high as 55 K under pressure [3]. Moreover, a simpler class of materials based on the BaFe$_2$As$_2$ (112) parent compound that does not contain oxygen also superconducts with $T_c \approx 38$ K when potassium is doped [4]. All of these iron arsenides are considered as the second class of high-$T_c$ superconductors since the discovery of the cuprates two decades ago.

The growth of 112 crystals was reported using Sn-flux method, however, Sn could incorporate into the crystal and resulted in the change of physical and chemical properties. Self-flux growth using extra Fe–As could avoid the contamination, but the high vapor pressure of arsenic and doping element of potassium as well as the poisoning of the compound gave rise to an extremely difficult to grow single crystal. Therefore, the growth of single crystals, particularly the superconducting doping variants and large size, is a challenge.

We present a method using a specially designed furnace for either Sn-flux or self-flux growth and obtained centimeter-large crystals. The source material was used from pure elements of Ba/Sr, K, Fe, As and Sn in a mol ratio of $\frac{(Ba/Sr)_{1-x}K_xFe_2As_2}{Sn} = 1 : 45–50$ or in $1 ((Ba/Sr)_{1-x}K_x) : 5 Fe : 5 As$ for the self-flux. Usually 90 g of the mixtures with Sn or 15 g with self-flux were loaded in a zirconia crucible. A crucible with lid was used to minimize the evaporation loss of K as well as As during growth. The crucible was sealed in a quartz ampoule filled with Ar and loaded into a box furnace. Free-standing crystals were obtained by decanting the residual flux, which was
poured to flow out the holes drilled through the crucible-lid. The schematic drawing of the apparatus used for growth is shown in Fig. 31.

![Figure 31](image)

Figure 31: A schematic drawing of the apparatus used to grow single crystals of $A_{1-x}K_xFe_2As_2$ ($A = Ba, Sr$). Free standing crystals are observed to dominantly grow on the bottom of crucible after flux decanted.

Large and high-quality crystals could be obtained in a homogeneous melt by slow cooling. To achieve a homogeneous melt the maximum heating temperatures of 980°C and 850°C were applied for soaking the pure and doped compounds with Sn flux, respectively. For the self-flux growth the heating temperatures of 1190°C and 1080°C were used for pure and doped crystals, respectively. The soaking temperatures were then maintained for 2–4 hours. Subsequently, the temperatures were decreased at a low cooling rate of $\approx 3^\circ C/h$ down to $\approx 550^\circ C$ for the Sn-flux and $\approx 890^\circ C$ for the self-flux. As-grown crystals were then decanted from the flux. The free-standing crystals were observed to grow dominantly at the bottom of the crucible. It is noticed that to obtain crystals entirely free from flux the decanting temperature had to maintain for 2 h and then cooling to room temperature. This allows the residual flux flowing out completely to leave free-standing crystals inside of the crucible. It is emphasized that the decanting device is designed with a movable nickel wire for tilting the crucible to drop the residual flux at high decanting temperature on the top of outside the furnace. This can avoid any poisoning from As in case of a crack of quartz tube. As-grown single crystals obtained are shown in Fig. 32(a). Figure 32(b) shows the typical crystals with surface layer seen partly ‘opened’ from the $c$-plane, which was underwent by a sharp change of high decanting temperature and then suddenly cooling to room temperature. Besides, the layered structure with weak bonding along the $c$-direction may cause crystal layers readily cracked by the thermal shock.

![Figure 32](image)

Figure 32: (a) The harvest single crystals of $BaFe_2As_2$ obtained at the bottom of $ZrO_2$ crucible. The small division is 1 mm. (b) The typical separated single crystals showing a partly opened top layer $(001)$ and the well-developed crystallographic faces.
Owing to the layered structure, the iron arsenic crystals exhibit platelet-like morphology and the c-axis is normal to the (001) face. The crystal facets can well develop according to the crystallographic orientation. The Miller index faces of the as-grown crystals were identified using a two-circle optical goniometer. The typical crystallization facets are shown in Fig. 32(b). The crystal exhibits the tetragonal structure comprised the main index faces of (001), (013) and (010) around the crystallization axis of [010]. According to the developed facets, the crystals show an anisotropic growth behavior. The growth rate along the (010)/[100] direction is faster than the (001), because the atomic bonding energy is higher for the \( a \) than the \( c \). Along the \( a \)-direction the total number of bonds is 16, i.e., Ba–As (8), Fe–As (4) and Fe–Fe (4), while along the \( c \) there is only Ba–As (8), for the case of BaFe\(_2\)As\(_2\). The doping of K\(^+\) (1.51 Å) causes a decrease of As–Fe–As bond angle and an increase of the bond length, leading to a weakening the bonding energy. This can result in a lower growth rate in the \( c \) direction and formation of thinner platelets.

There is an interesting crystal habit for all such pnictide compounds that exhibit multilayer stacks, macrosteps, step bunches and inclusions in the (001) face. These typical features are shown in Figs. 33(a)–(f). Figure 33(a) shows an edge of crystal exposing multiple layers for each thickness of \( \approx 5 \mu m \). These crystal layers are readily cleaved mechanically. Figure 33(b) is a wined sheet of the cleaved layer due to its metallic-like behavior. The macrosteps are observed on the (001) plane, as shown in Fig. 33(c). The step terraces were formed at an uncompleted growth state. The frontier of the steps has a tetragonal structure with the well developed facets of [100]/[010], as shown in Fig. 33(d). These macrosteps spread laterally along the [100]/[010] direction, and then a new growth center occurred on the grown layer of (001). No growth spirals were observed in the (001) faces. It is indicated that the crystal growth on the (001) face occurs at a relatively high supersaturation according to two-dimensional nucleation, i.e., layer-by-layer growth mechanism. The precipitates of Sn give rise to step bunches in the (001) face. These bunches can cause curved shapes at the crystal growth fronts and finally stop developing crystal facets. The typical punches are indicated by arrows in Fig. 33(e). The Sn precipitates could be trapped as inclusions and lead to form secondary phases in crystals. Figure 33(f) shows the Sn inclusion lines as impurities formed in the (001) face of the SrFe\(_2\)As\(_2\) crystal grown from the melt in supercooling state.

Temperature-dependence of the in-plane resistivity for BaFe\(_2\)As\(_2\) single crystals was measured between 4 K and 300 K under zero field. The results are plotted in Fig. 34(a). Weak temperature dependence is seen from 138 K to 300 K for the sample obtained by self-flux and 85 K to 300 K by Sn-flux growth. It is indicative of both crystals having metallic behavior at higher temperatures.
A pronounced different spin density wave $T_s$ anomaly is observed between the two crystals, which might be attributed to the tiny amount of Sn incorporated into the crystals and correlated with a reduction in $T_c$ temperature. Upon cooling below 85 K the resistivity increases rapidly to 50 K and then decreases again to 4 K. The resistivity is approximately 30% (at 50 K) and 20% (at 4 K) higher than it is at 85 K. A very sharp superconducting transition temperature $T_c$ occurred at 38.5 K for the doped Ba$_{0.68}$K$_{0.32}$Fe$_2$As$_2$, while above $T_s$ there is a near linear temperature dependence up to room temperature. The in-plane resistivity is smaller for doped than undoped single crystals at $T > 85$ K and a sharp superconducting temperature transition occurs at $\approx 38.5$ K, as shown in the inset of Fig. 34(a).

The magnetic susceptibility data in Fig. 34(b) show a clear transition at 85 K on the $H \parallel c$ curve. The data below and above $T \approx 85$ K are reproduced by two separate Curie-Weiss fits for both temperature regions. This behaviour is seen for the crystals grown using Sn-flux but not self-flux or polycrystalline samples, which exhibit a spin density wave transition associated with a structure transition from tetragonal to orthorhombic at $\approx 138$ K. This pronounced discrepancy may be an effect associated with the basal plane of FeAs that Fe sites were partly replaced by Sn. The tiny amount of Sn was likely to incorporate into Fe sites during crystal formed in Sn solvent, since the ionic radius of Fe$^{2+}$ (0.78 Å) is closer to Sn$^{2+}$ (0.93 Å).

The sharp transition temperature $T_c \approx 38.5$ K measured by magnetic susceptibility for the Ba$_{0.68}$K$_{0.32}$Fe$_2$As$_2$ crystal, as shown in the inset of Fig. 34. The shielding fraction close to 1 demonstrates a bulk nature of the superconductivity. The shielding fraction close to 1 demonstrates the bulk nature of superconductivity. The onset transition temperature of $T_s \approx 38.5$ K defined by a 10% decrease from the normal state magnetic susceptibility is the highest ever reported. The superconducting transition width $\Delta T_c = T_c (10%) - T_c (90%) = 0.3$ K is the smallest ever reported.
In conclusion, very large $A_{1-x}K_xFe_2As_2$ (with $A = \text{Ba, Sr}$) single crystals sized up to centimeters can be obtained in a specially designed furnace. The well developed crystallographic facets of $(001)$, $(013)$ and $(010)$, $(001)$ are observed and exhibit the anisotropic growth behavior. The discrepant spin density wave abnormal $T_s \approx 138 \text{ K}$ and $\approx 85 \text{ K}$ occurred in the pure $\text{BaFe}_2\text{As}_2$ crystals grown using self- and Sn-flux, lightly substituted for Fe site in the FeAs basal plane. The doping of K suppresses the spin density wave and induces superconductivity in the iron arsenic crystals.

Investigations of the close and complex relationships between bonding interactions and structures are one of the Institute's long standing traditions. Special challenges are associated with the investigation of metastable structures and structures missing periodicity. This section presents examples for both, a nuclear magnetic resonance investigation of the bonding between N and C in SiBNC random networks, which are known for their outstanding thermal and chemical stability, and metastable Na₃N, which is accessible by the reaction of a Na/K alloy with plasma activated nitrogen. As a consequence of very weak electrostatic stabilization, the ambient structure is very open, and the application of high pressure induces several phase transitions, which are investigated in detail. Pressure has also been applied to change structure and bonding of BiB₃O₆, a compound containing lone pair electrons, which progressively become involved into covalent bonding with increasing pressure. Sometimes, structures of building units are only accessible by derivatization. Higher fullerenes (C₇₆, C₇₈, C₈₀) have been isolated as chlorides and crystallized as such. A special case are metal–metal bonds, e.g., in the Hg rich amalgam Cs₂Hg₂7, for which structural details of a Hg₁₀₅ cluster are described.

The development of ceramic materials based on Si/B/N/C ceramics has been intensively studied in recent years due to their combination of mechanical and chemical stability and low weight. These ceramic materials are promising candidates for industrial applications that require high thermal stability and strong resistance against oxidative attack. Especially the Si/B/N/C quaternary ceramic synthesized from the single-source precursor TADB (BCl₂-NH-SiCl₃) and methylamine and its subsequent pyrolysis retains a dense and amorphous form at temperatures as high as 1900°C [1]. The exceptional properties of this precursor-derived ceramic may originate from the homogeneity of the network associated with its high degree of connectivity and the strength of the covalent bonds between the constituent elements of silicon, boron, nitrogen and carbon [2]. Solid-state NMR (nuclear magnetic resonance) is one of the most powerful methods for the structure analysis of this and similar materials. However, full information about the coordinations of carbon and nitrogen could not be achieved up to now because of low natural abundances of carbon and nitrogen nuclei with a nuclear spin of 1/2.

Therefore, we employed a novel isotope labeling synthesis method of the SiBNC ceramic, introducing the stable isotopes ¹³C and ¹⁵N by performing the polymerization with ¹³C, ¹⁵N-labeled methylamine [3]. This facilitates the study of carbon and nitrogen environments by solid-state NMR, and makes it possible to apply modern double resonance NMR techniques such as REDOR (Rotational Echo Double Resonance) to derive the strength of...
dipolar coupling between spins, which is directly related to the internuclear distance. This technique is based on the Hahn-echo NMR pulse sequence. By applying this sequence to the first spin species (in our case carbon) without radio-frequency (rf) pulses on the second spin species (nitrogen), the maximum echo amplitude, $S_0$, is obtained. When the experiment is repeated with rf pulses on the second spin species the magnetic dipoles associated with the nuclear spins interact, resulting in a decreased echo amplitude. This decreased signal amplitude is designated $S$. The analysis of the experiment is done by drawing the so-called REDOR curve. This curve can be obtained from a plot of the normalized difference of the two experiments ($\Delta S/S_0 = (S_0 - S)/S_0$) as a function of the echo time. By comparing the experimental REDOR curve with REDOR curves obtained from computer simulation, a dipolar coupling constant and the corresponding internuclear distance can be derived.

The result of a $^{13}$C{$^{15}$N} REDOR with our ceramic sample pyrolyzed at 1400°C is shown in Fig. 35. Since several different arrangements of carbon and nitrogen nuclei are possible in the investigated materials, the experimental REDOR curve is compared with simulated REDOR curves based on several different spin systems. Surprisingly, the experiment reveals the presence of direct carbon-nitrogen bonds in the amorphous network even after the pyrolysis at 1400°C. Based on the limiting value of the REDOR dephasing curve, roughly 80% of the carbon nuclei seem to have a directly bonded nitrogen neighbor. The best match with the experimental REDOR curve is found for the simulated curve of a carbon-nitrogen bond with some double bond character. However, it should be noted that the experimental REDOR curve can also be the result of the superposition of different configurations.

To confirm that the described analysis of the REDOR curve is correct, an alternative method of analyzing the curve was performed. The so-called second moment ($M_2$) is associated with the second derivative of the REDOR curve at time zero. The comparison of $M_2$ from the REDOR experiment with a theoretical $M_2$ based on chemically possible coordinations of carbon and nitrogen atoms is shown in Fig. 36. The advantage of the use of $M_2$ is that one can easily check whether a large number of nitrogen atoms without a direct bond to carbon may account for the shape of the experimental REDOR curve. The observed $M_2$ (bar k in Fig. 36) is significantly larger than that of any chemically relevant case of multi-spin interactions with no direct bonds (bars i and j in Fig. 36). The possibility of van-der-Waals contacts can also be excluded (see also bars g and h in Fig. 36). The experimental $M_2$ agrees with those of systems with a carbon atom bonded to one or two nitrogen atoms with a bond order larger than 1 (bars c, d and e in Fig. 36).
must be limited because of the high abundance of carbon-nitrogen bonds. An example of how the structure could look like on an atomic scale is given in Fig. 37. It includes all topologies identified in these and earlier experiments.

To summarize, we observed that a large number of carbon-nitrogen bonds is present in the final ceramic after the pyrolysis at 1400°C. These bonds had been thought to be unstable above 600°C. As carbon forms small polycyclic aromatic segments and is bonded to the rest of the network by bridging nitrogen atoms, a nearly homogeneous distribution of the elements is maintained and no large carbon-rich domains seem to be present. The participation of nitrogen atoms in the π-system of the aromatic segment shortens the length of the carbon-nitrogen bond, and this carbon-nitrogen bond is possibly stabilized at high temperature by connecting the carbon atoms with strong BN₃ and SiN₄ units in their vicinity. The combination of this work with previous solid-state NMR studies and computational structural modeling in our group gives a detailed picture of the first and second coordination spheres of all the elements in the final ceramic. Furthermore, the observed strong covalently bonded networks between all constituting elements in this material provide an explanation for the superb properties of this material.

Some unsaturated carbon-carbon bonds were also observed by ¹³C-2D RFDR experiments. The number of interconnected carbon atoms...
In contrast to alkali fluorides and oxides, the nitrides of the heavier alkalis Na to Cs have been elusive until recently, with only lithium forming a stable binary nitride Li$_3$N. A first structural characterization of sodium nitride was carried out on films of Na$_3$N formed by depositing atomized elements on a cooled substrate [1]. Recently, a practical route to produce larger amounts of sodium nitride was developed [2]. It is based on the reaction between a liquid Na–K alloy with plasma-activated nitrogen at room temperature. The initially proposed cubic anti-ReO$_3$-type ($Pm\bar{3}m$, $Z=1$) structure was confirmed for Na$_3$N based on X-ray diffraction data collected on powder and single crystals, and the accessibility of the nitride on a laboratory scale allows for further investigations of this unusual compound.

Sodium nitride is metastable because the coordination of the N$^3$– anion by only six singly charged and relatively large Na$^+$ cations leads to weak electrostatic stabilization. The same argument can be used to explain the fact that in contrast to alkali oxides and fluorides, Na$_3$N is a dark-blue semiconductor; the valence-band N 2$p$ states lie relatively high in energy, which results in a narrow band gap.

Not less intriguing is the very open crystal structure of Na$_3$N, featuring rare two-fold linear coordination of the sodium cations (Fig. 38, topmost structure). The lattice constant of cubic sodium nitride (4.73 Å) is significantly larger than that of isostructural ReO$_3$ and Cu$_3$N ($\approx 3.8$ Å). The resulting open network of Na$_3$N possesses low mass density of only 1.3 g/cm$^3$ and it might even be able to host small atoms and molecules.

Figure 38: Crystal structures of phases I to V of Na$_3$N (left column) with the corresponding coordination polyhedra (right column) of sodium atoms (yellow spheres) around the nitrogen atoms (blue spheres). For the sake of clarity, the phase Na$_3$N-IV is represented by an undistorted Li$_3$P-type structure (see text).
As such a very open structure is prone to collapse under pressure, structural transformations are likely. So, lithium nitride Li$_3$N, which also has a rather unique open crystal structure \[3\], is known to transform from the ambient-pressure $\alpha$-modification ($P6/mmm$, $Z = 1$) to a more compact Li$_3$P-type $\beta$-phase ($P63/mmc$, $Z = 2$) at 0.6 GPa, followed by an even denser cubic Li$_3$Bi-type ($Fm\bar{3}m$, $Z = 4$) $\gamma$-modification [4,5] above 40 GPa. A number of potential structural candidates for sodium nitride have already been identified theoretically using the Hartree-Fock method, see [6]. Two of them, the hexagonal $\alpha$-Li$_3$N- and Li$_3$P-type phases, were suggested to be more stable than the experimentally observed open cubic anti-ReO$_3$-type structure even at ambient pressure [1].

The earlier studies of alkali nitrides motivated us to investigate the structural phase stability of Na$_3$N at high pressure in the range up to 36 GPa. By using angle-dispersive synchrotron X-ray diffraction in combination with diamond anvil cell techniques, four high-pressure modifications have been identified, c.f. Fig. 38. Their structural parameters have been determined with the help of Rietveld refinements.

At 1.1 GPa sodium nitride transforms to the hexagonal Na$_3$N-II phase which is isostructural to $\alpha$-Li$_3$N. Upon further pressure increase two new modifications, denoted Na$_3$N-III and Na$_3$N-IV, appear simultaneously at 3.4 GPa. The phase Na$_3$N-III is orthorhombic and of the anti-YF$_3$ structure type; it is observed only up to 5.2 GPa. The phase Na$_3$N-IV is hexagonal; it is structurally related to Li$_3$P and Cu$_3$P-type Na$_3$As. This fourth modification is followed by the cubic Li$_3$Bi-type Na$_3$N-V phase above 22.2 GPa, the last high-pressure modification observed up to the highest pressure of 36 GPa employed in this investigation.

Figure 39 shows the experimental volume per formula unit as a function of pressure for all five modifications of Na$_3$N. The rather open ambient-pressure Na$_3$N-I phase undergoes a large overall volume change under pressure on the way to the most dense modification Na$_3$N-V. At the highest pressure of 36 GPa, Na$_3$N is compressed to $\approx 38\%$ of its ambient-pressure volume. The volume discontinuities at the phase transitions reflect changes in coordination numbers, as briefly addressed in the following.

![Experimental volume versus pressure data for five modifications of Na$_3$N. Solid curves represent results of least squares fits of an empirical finite-strain equation of state.](image)
The high-pressure modification Na$_3$N-III was always accompanied by the Na$_3$N-IV phase and the maximum fraction of Na$_3$N-III was about 60%. Orthorhombic Na$_3$N-III is an anti-type of the YF$_3$ structure with space group $Pnma$, it contains nitrogen atoms surrounded by a triply capped trigonal prism of sodium atoms, a polyhedron frequently observed in halides of rare-earth metals. All sodium atoms are three-coordinated by a nearly planar arrangement of the neighboring nitrogen atoms.

Most diffraction maxima of the third high-pressure phase of Na$_3$N-IV can be described in a satisfactory manner by the hexagonal Li$_3$P structure type which is also realized in $\beta$-Li$_3$N stable between 0.6 GPa and 40 GPa. The coordination number of the nitrogen atoms is further increased to 11. The coordination polyhedron can be described as a five-fold capped trigonal prism.

The similarity between the high-pressure structural chemistry of Na$_3$N and Li$_3$N is completed by the most dense fifth modification of sodium nitride. Similar to $\gamma$-Li$_3$N, Na$_3$N-V crystallizes in the cubic Li$_3$Bi-type structure type with alkali-metal atoms occupying all octahedral and tetrahedral voids of a cubic close-packed arrangement of nitrogen atoms. This also leads to the maximum coordination number of 14 for the nitrogen atoms.

The experimental observations are compared to results of total energy calculations for the identified phases based on density functional theory (DFT). The calculated energies (Wien2k, APW+lo) as a function of volume are shown in Fig. 40. The computed equations of state for the five phases of Na$_3$N agree quite well with the experimentally observed behavior. This applies to the volume differences between phases, elastic parameters (values of bulk moduli), and the phase stability ranges. Only Na$_3$N-III lies slightly higher in energy (by $\approx 0.15$ eV per formula unit) than expected based on the experimental findings. This is, however, partly consistent with the narrow pressure range in which the phase is observed and with the fact that it was not observed in pure form, possibly due to a kinetic stabilization of this phase.

Figure 40: Calculated total energies of the Na$_3$N modifications I to V. Solid curves represent fitted results using a finite strain expression.

The DFT calculations reveal details about pressure-induced changes in chemical bonding which will be addressed elsewhere. It should be mentioned that the calculated band structures are not in conflict with a semiconducting behavior of all high-pressure modifications of Na$_3$N.

In summary, the observed evolution of the sodium nitride crystal structure under pressure represents an example for the potential richness of pressure-induced phase transformations in ionic AB$_3$ compounds. At pressures up to 36 GPa, four high-pressure modifications have been identified for Na$_3$N and three of the phase transitions are reversible.

In the direction of increasing pressure, the sequence of phases can be easily rationalized by the steady increase in the coordination number of the nitrogen atoms from six over eight, nine, and eleven to finally fourteen, along with an increase of sodium coordination numbers as well.
Increasing electrostatic stabilization of the nitride anion in high-pressure modifications of Li$_3$N and Na$_3$N due to coordination changes might indicate a route to stabilize even more labile nitrides of K, Rb, and Cs by preparing them under high-pressure conditions.


The high-pressure crystal structure of the NLO compound BiB$_3$O$_6$ from 2D powder diffraction data

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As part of a long term project on the effect of stereochemically active lone pairs on crystal structures at high pressure, α-bismuth borate was studied in the pressure range from ambient pressure to 11.6 GPa. In general, lone pairs can be viewed as pseudo-ligands in compounds exhibiting increasingly covalent bonding contributions, significantly changing the space requirements and bonding situation in the affected solids. As these crystal structures are rather open, it can be expected that such compounds undergo pressure induced phase transitions. In general, high-pressure powder diffraction data from DAC’s (diamond anvil cell) are often difficult to interpret due to the fact that usually very few extremely intense spikes, originating from grains in an ideal diffraction position tend to dominate the diffraction pattern. Therefore, we developed a phenomenological model for the description of such intensity distributions which we applied here to extract normally distributed intensities using well-known fractile filters.

The crystal structure of the lone pair bearing compound α-BiB$_3$O$_6$ has recently attracted considerable interest as a polar, non-ferroelectric compound with exceptional non-linear optical (NLO) properties. A technical application is possible, since single crystals of sufficient size and quality could be synthesized. The crystal structure of α-BiB$_3$O$_6$ at ambient conditions can be described as a phylloborate layer structure consisting of alternating layers of borate anions and bismuth cations perpendicular to c-axis. The borate groups consisting of BO$_3$ triangles and BO$_4$ tetrahedra in a 2:1 ratio form a 2-dimensional net linked by corners. The coordination of the BiO$_6$ polyhedron is highly irregular, due to the non-bonding lone pair electrons of the sp$^3$ hybridized Bi$^{3+}$ orbitals. The NLO properties were attributed to the bonds in the triangular [BO$_3$] units and to the lone pair at the Bi$^{3+}$ cation. α-BiB$_3$O$_6$ exhibits one of the largest anisotropies in the elastic constants and the thermal expansion observed in ionic crystals, anisotropy which is attributed to the preferential orientation of the lone electron pair of Bi$^{3+}$. In the temperature range from 8 K to 999 K, no structural phase transition was found for α-BiB$_3$O$_6$. Preliminary investigations using Raman spectroscopy at room temperature and elevated pressure did not show any evidence for structural changes up to a pressure of $p = 18$ GPa.
Figure 41: Powder diffraction data of ε-BiB₂O₄ at \( P = 8.35 \) GPa, collected by a two-dimensional image plate detector. The raw image (a) and the filtered image (b) are shown. The green mask represents the pixels which belong to the top 48% of the intensities per integration bin. The blue mask shows the pixels which belong to the bottom 2% of the intensities per integration bin. The yellow mask is the beam stop mask filtering the first 2° 2\( \theta \) of the diffraction image. Only the uncolored region of the image is used for the integration to a 1D diffractogram. The intensity distribution of an unfiltered (c) and filtered (d) bin is displayed showing fits to the expected normal and the proposed normal-Pareto distribution. The effect of filtering is further visualized on the final integrated and background corrected pattern (e) and on the standard deviations (f) (In red the integrated pattern of the unfiltered image, in blue the diffractogram of the filtered image).
Because of the high compressibility due to the lone pair of the Bi$^{3+}$ cation and the extreme anisotropy of the thermal expansion, we decided to investigate the pressure dependence of the crystal structure of α-BiB$_3$O$_6$, a study which we consider a prerequisite for future investigations of additional possibly quenchable high-pressure modifications. For this purpose, in situ high-pressure powder diffraction experiments using a diamond anvil cell (DAC) were performed at the high-flux powder diffraction Station 9.5HPT of Daresbury Laboratory, U.K., equipped with a MAR345 image plate detector. The image plate orientation and sample to plate distance were determined using a silicon powder standard (NIST 640b). Initially, a traditional calibration routine was run using the Powder3D IP software. The results were later refined using the whole image refinement (WIR) procedure. To do this successfully the background had to be determined and the outlier intensities had to be extensively filtered prior to the refinement.

The image plate recordings of α-BiB$_3$O$_6$ at high pressure were quite spotty (Fig.41(a)) and needed effective filtering before integration to extract the underlying information correctly. A fractile filter removing a fraction of the highest and lowest intensities from each bin was used. The fraction to be removed was determined using the relation of the normal to the normal-Pareto distributed intensities of a strong peak. This resulted in 58% of the highest intensity being removed from each bin before integration (Fig. 41(b)).

This filtering method led to approximately normally distributed intensities, ideally suited for least squares refinement (Figs. 41(c) and(d)). Integration of all data sets was then performed with Powder3D IP, resulting in 19 diagrams of corrected intensities versus the scattering angle 2θ. The crystal structure of ambient α-BiB$_3$O$_6$ is highly compressible (bulk modulus of 38(1) GPa) and stable to a pressure of at least $P = 6.09$ GPa. The positional parameters of α-BiB$_3$O$_6$ at elevated pressure vary only slightly from the published values at ambient conditions. α-BiB$_3$O$_6$ crystallizes in the acen
centric polar space group C2. The crystal structure of α-BiB$_3$O$_6$ is built of alternating layers of bismuth atoms and networks of borate groups networks. Two thirds of the borate atoms are trigonally coordinated and one third of the boron atoms are tetrahedrally coordinated, with all four corners of each [BO$_4$]$^{5−}$ tetrahedron connected to a separate [BO$_3$]$^{3−}$ triangle. All [BO$_3$]$^{3−}$ triangles share two corners with neighboring [BO$_4$]$^{5−}$ tetrahedra with the remaining oxygen atom bonded exclusively to two bismuth atoms. The trivalent bismuth cations are irregularly coordinated by 4 + 2 oxygen atoms, formally forming [BiO$_6$] units sharing six edges with neighboring [BiO$_6$] units. The effect of the lone pair electrons on the crystal structure is quite visible through open channels down the c-axis. The largest convexity of the channels is along the b-axis, which is exactly the direction in which the soft lone-pair electrons of Bi$^{3+}$ point (Fig. 42). The channels are reminiscent of those in the AB$_2$O$_4$ type structures in which the lone-pairs of B-atoms cause large channels running through the structure.

The main effect of increasing external pressure on the crystal structure of α-BiB$_3$O$_6$ is a strong anisotropic compression of the unit cell (Fig. 43) with the maximum compression along the b-axis due to the soft lone pairs of Bi$^{3+}$ (Fig. 42). Interestingly, the a-axis expands with increasing pressure over the entire range of existence of α-BiB$_3$O$_6$. It can be shown that mainly the preferential orientation of the lone electron pair of Bi$^{3+}$ is responsible for this so called ‘Nuremberg scissor’ effect within the ab-plane.

Between a pressure of $P = 6.09$ GPa and $P = 6.86$ GPa, α-BiB$_3$O$_6$ exhibits a first-order phase transition into a considerably stiffer (bulk modulus $B = 114(10)$ GPa) high-pressure phase, called ε-BiB$_3$O$_6$ (Fig. 43), whose crystal crystal structure was solved by simulated annealing and energy minimization.
On a first view, the crystal structure of the high-pressure $\alpha$-phase of BiB$_3$O$_6$ is quite similar to that of $\alpha$-BiB$_3$O$_6$. On a closer look, differences can be seen in the small reorientations of the $[\text{BO}_3]^{3-}$ triangles and $[\text{BO}_4]^{5-}$ tetrahedra, and in the higher coordination of the Bi$^{3+}$ cation.

The trivalent bismuth cations are now irregularly coordinated by 2 + 6 oxygen atoms, formally forming $[\text{BiO}_8]$ polyhedra. The Bi–O separation in two short and four ($\alpha$-BiB$_3$O$_6$) or six ($\epsilon$-BiB$_3$O$_6$) longer bonds suggest the existence of $[\text{O} - \text{Bi} - \text{O}]^{-1}$ groups and thus the presence of the lone pair for the entire pressure range under investigation.

From the observation, that the direction of highest compressibility is along the two-fold axis ($b$-direction) for $\alpha$-BiB$_3$O$_6$, the mechanism of the phase transition at high pressure can be understood. If the pressure is high enough, the space requirement of the electron lone pair can no longer be satisfied. The lone pair can either be forced to adopt spherical $s$-character or evade the pressure by changing its orientation. The latter is responsible for the $\alpha$- to $\epsilon$-phase transition of BiB$_3$O$_6$ (Fig. 42).
This study shows in particular the supreme importance of high-quality data and data reduction methods to extract Rietveld quality powder diffraction patterns from two-dimensional data with extreme intensity distributions. The accuracy to determine and Rietveld-refine such a crystal structure allowing for the interpretation of minor structural changes was made possible by employing a newly developed sophisticated algorithm for the determination of optimized intensity filters of noisy and spotty 2D powder diffraction images.

Unusual short intermolecular halogen-halogen contacts in chlorinated derivatives of fullerenes


Shortly after the accessibility of C_60 and C_70 fullerenes and progress in separation techniques, a number of particular properties of fullerene containing compounds such as superconductivity and ferromagnetism have been discovered. Beside the two members of the fullerene family mentioned above, which are formed almost exclusively during the evaporation of graphite, the fullerene soot contains about 1% of higher fullerenes. However, as it is very difficult to separate individual species in pure form, the chemistry of the higher fullerenes is still poorly explored and the investigation of their properties remained illusive. Moreover, the study of the higher fullerenes is drastically complicated by the existence of several structural isomers. The isomeric diversity, their virtually spherical shape and the rotational mobility cause a very poor quality of fullerene crystals and hamper the structural analysis by X-ray diffraction. Therefor, no ordered crystal structures of pristine fullerenes have been so far reported, except for C_60 and C_70, and most recently, for C_84(14) in a cocrystal with silver tetraphenylporphyrin [1].

A feasible way to overcome these problems is the derivatization of the fullerenes. In particular, halogenation has proven to be a versatile and efficient approach for obtaining well crystallized fullerene species. The use of Br_2 in TiCl_4 as a highly selective chlorinating agent, allowed us to synthesize a number of high-quality crystals of chlorinated higher fullerenes. Among those are two chiral fullerenes, C_76Cl_18 [2] and C_80Cl_12 [3], and three individual isomers of C_78: C_78(2)Cl_18, C_78(3)Cl_18 [4] and C_78(5)Cl_18 [5]. Besides the precise determination of the cage structure of the above mentioned species, detailed analyses of the crystals have clearly demonstrated the presence of numerous short Cl···Cl intermolecular contacts (Fig. 44) which are remarkably shorter than the sum of the van-der-Waals radii of two chlorine atoms (3.6 Å).

The formation of short Cl···Cl contacts is regarded to be typical for chlorinated aromatic hydrocarbons which are characterized by low C–Cl bond polarity (C–Cl distance of about 1.70–1.73 Å) and rather rare in the case of highly polar C–Cl bonds with C–Cl distances of 1.79–1.81 Å. A proportional relation between C–Cl bond length and bond polarity, however, is not consistent with the observed structures of the chlorinated fullerenes, where the C–Cl bonds are enormously elongated (1.82–1.87 Å). The participation of these Cl atoms in short Cl···Cl contacts is highly unexpected, if a significant negative charge is assumed.
A closer look to the molecular packing of C$_{78}$(5) Cl$_{18}$ (Fig. 44(b)) even shows, that the shorter three-centered contacts (3.34 Å) involve larger C–Cl bonds (1.86 Å) as compared to the two-centered contacts (Cl···Cl: 3.45 Å; C–Cl: 1.82 Å).

The large variety of arrangements found in the chlorinated fullerenes as well as the observed relation between short Cl···Cl contacts and elongated C–Cl bonds do not agree with the present view of halogen bonding. Of course, the packing of molecules in crystals is governed by all the possible intermolecular interactions. A short Cl···Cl contact in a crystal itself is not a proof for a specific attraction. However, in the halogenated C$_{78}$ (2, 3 and 5) fullerenes, no other intermolecular contacts are present which may influence the molecular packing. In this case, the ordered crystallization of the fullerenes and the short Cl···Cl distances can only be explained by attractive interactions which are presumably different from those of the halogen bonding described previously.
Table 2: Dimerization energies DE (kJ/mole) and Cl···Cl and C–Cl distances (Å) of R3CCl (R = –H, –CH=CH2), computed with various methods and basis sets.

<table>
<thead>
<tr>
<th>method</th>
<th>R = H; aug-cc-pVTZ basis set*</th>
<th>R = vinyl; aug-cc-pVDZ basis set*</th>
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<tr>
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<td>DE (0) RCl = 1.80</td>
<td>DE (0) RCl = 1.90</td>
</tr>
<tr>
<td>hybrid (B3LYP)</td>
<td>(0) – 1.80</td>
<td>(0) – 1.90</td>
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<tr>
<td>MP2</td>
<td>–2.4 3.49 1.78</td>
<td>–5.6 3.39 1.85</td>
</tr>
<tr>
<td>CCSD</td>
<td>–2.7 3.56 1.87</td>
<td></td>
</tr>
<tr>
<td>CCSD(T)</td>
<td>–1.7 3.59 1.79</td>
<td></td>
</tr>
</tbody>
</table>

* basis set for the hydrogen atoms: cc-pVTZ (R = H) and cc-pVDZ (R = –CH=CH2)

In order to comprehend the intermolecular attraction between two halogen atoms, quantum chemical calculations were performed, focusing on four aspects: 1) computational method, 2) quality of the basis set, 3) chemical environment of the chlorinated carbon atom, and 4) geometrical constraints being enforced by the cage structure of the fullerene. In Tab. 2 we summarize results for the dimers of two model compounds, chloromethane and trivinylchloromethane, the latter mimicking the sp2 carbon atoms surrounding the chlorinated carbon in the fullerenes.

With the DFT methods applied here, no binding is obtained for the dimers, neither with the gradient-corrected functional PBE, nor with the hybrid functional B3LYP. With coupled cluster methods, the chloromethane dimer is computed to be stable only with a basis set of at least valence triple zeta quality with additional diffuse functions (aug-cc-pVTZ). Applying perturbation theory of second-order (MP2) leads to an overestimation of the dimerization energy.

The different chemical environment in trivinylchloromethane leads to an enhancement of the binding energy, to an elongation of the Cl–C bond and to a shortening of the Cl···Cl contact. The values given in Tab. 2 are for a linear arrangement of the dimers. A slightly larger binding energy is obtained for a bent configuration. This is also the case if the Cl–C–R angle is enlarged to a value similar to the one observed in the fullerenes.

The calculations on the model compounds show, that a proper quantum chemical description of the attractive intermolecular interactions in the chlorinated fullerenes is very demanding, both concerning the method and the quality of the basis set. Moreover, the specific chemical and geometrical environment as it is found in the chlorinated fullerenes has to be considered as well. None of the models used so far for the description of halogen bonding is adequate to describe the particular packing of chlorinated fullerenes in crystals. The present investigations will provide new insight on the role of halogen bonding in the field of crystal engineering.

The mercury-richest amalgam: \( \text{Cs}_2\text{Hg}_{27} \)

The synthesis of the mercury richest of all structurally known amalgams \([1]\) and the elucidation of its crystal structure was enabled by an electrolysis technique developed for the growth of ammonium amalgam crystals \([2]\). \( \text{Cs}_2\text{Hg}_{27} \) crystallizes in an own structure type \([3]\). The cubic unit cell (space group \( \text{Im}-3 \), No. 204, \( a = 16.557(4) \) \( \text{Å} \)) contains six formula units. The interatomic distances (\( d_{\text{Hg-Hg}} = 298 \) pm to \( 427 \) pm, \( d_{\text{Cs-Hg}} = 368 \) pm to \( 409 \) pm) and the coordination numbers (CNCs = 20) are very similar to those in known mercury-rich alkali metal amalgams.

The structure can best be described by a system of concentric polyhedra, as shown in Fig. 46 for the asymmetric unit. The central \( \text{Hg}(7) \) atom is surrounded by 12 \( \text{Hg}(3) \) atoms, forming an icosahedron. It is enclosed by 20 \( \text{Hg} \) atoms (12 \( \text{Hg}(5) + 8 \text{Hg}(6) \)) which form a pentagon-dodecahedron, surrounded by a cuboctahedron built from 12 \( \text{Hg}(4) \) atoms. The outermost \( \text{Hg} \) polyhedron is a strongly distorted truncated icosahedron of 60 atoms (12 \( \text{Hg}(1) + 48 \text{Hg}(2) \)). This cluster of 105 mercury atoms is enclosed by a slightly distorted sodalith cage of 24 cesium atoms. The entire crystal can be assembled from those sodalith cages via sharing of all faces. Each \( \text{Cs} \) atom belongs to four sodalith cages, and the \( \text{Hg}_{105} \) clusters are condensed via the puckered six-membered outermost rings beneath the hexagons of the sodalith cages. The sum formula of the structure therefore is \( \text{Cs}_{24/4}\text{Hg}(7)_{1}\text{Hg}(3)_{12}\text{Hg}(5)_{12}\text{Hg}(6)_{8}\text{Hg}(4)_{12}\text{Hg}(1)_{12}\text{Hg}(2)_{48/2} = \text{Cs}_6\text{Hg}_{81} \). The structure of \( \text{Cs}_2\text{Hg}_{27} \) is closely related to the atomic arrangement in Bergman phases, well-known 1/1 approximants of quasi-crystalline ternary intermetallic structures. Deviations of the atomic coordinates of the atoms \( \text{Hg}(1) \), \( \text{Hg}(2) \) and \( \text{Hg}(4) \) with respect to the Bergman structure leads to a different polyhedral system and hence to a regular crystalline structure.

The formal reduction of all \( \text{Hg} \) atoms inside the \( \text{Cs} \) sodalith cage to one big sphere reveals the topological similarity of the structures of \( \text{Cs}_2\text{Hg}_{27} \) and \( \alpha \)-\( \text{AgI} \). In the \( \alpha \)-\( \text{AgI} \) structure the \( \text{I} \) atoms have bcc type packing, and the partially occupied \( \text{Ag} \)-sites form undistorted sodalith cages.

**Figure 46:** ‘Aufbau principle’ of the structure of \( \text{Cs}_2\text{Hg}_{27} \) (see text).

\( \text{La}_9\text{Br}_{10}\text{Fe} \): Cluster with \( M_6X_{12}/M_6X_8 \) type environment

\( M_6X_8 \) and \( M_6X_{12} \) units are textbook examples of transition metal clusters. In the \( M_6X_{12} \) cluster, all edges of the \( M_6 \) octahedron are bridged by non-metal atoms \( X \). In the \( M_6X_8 \) cluster, all faces are capped by \( X \) atoms. These clusters can be linked or condensed to chains, sheets or three dimensional frameworks. In the case of \( M = \) rare earth metal the \( M_6X_{12} \) type arrangement is generally chosen, and the cluster is stabilized by endohedral atoms, e.g., \( \text{C} \) up to \( \text{Au} \).
The structure of La₆Br₁₀Fe is a first example of a mixed M₆X₈/M₆X₁₂ type cluster [4]. It contains the familiar octahedral La₆Fe unit, however, only nine Br atoms lie above edges and three above faces of the octahedron as shown in Fig. 47(a). Out of the 12 Br atoms above the octahedron apices, 4 also bridge the edge or cap the face of an adjacent La₆Fe octahedron, and 8 are shared with two other La₆ octahedra, linking one corner and bridging one edge or capping one face of these two octahedra as shown in Fig. 47(b).

Figure 47: (a) La₆Fe octahedron coordinated by Br atoms in the La₆Br₁₀Fe structure, (b) Interconnection of the La₆Fe units.

Neglecting the Br atoms above the apex atoms the discrete cluster has the composition La₆Brₑ¹⁰⁻Brₙ³Fe where e and f denote positions above the edges and faces of the octahedron, respectively. As the e-type atoms Brₙ₁ and Br₁₀ are shared between adjacent clusters in the same functionality, the formula La₆Brₑ²¹/₂Brₙ³Fe = La₆Br₁₀Fe results.

The pronounced asymmetry of the Br coordination polyhedron around the La₆Fe octahedron has two important consequences. First, the La octahedron is heavily distorted, in first approximation squeezed along a four-fold axis. Second, the rock salt type arrangement, i.e., the common close-packing of Br atoms and La₆Fe units as normal with the M₆X₁₂ type cluster is disrupted. The distortion could be of electronic origin. A formal electron partition of (La³⁺)₄(Br⁻)₁₀Fe²⁻·6e⁻ shows that there are 16 cluster electrons in the La₆Fe octahedron including those of Fe²⁻, and 6 electrons form metal-metal bonds in the La₆ cage. As four electrons would occupy the degenerate t₁u orbitals in a regular cluster the Jahn-Teller effect clearly favors a distortion of the cluster as observed in La₆Br₁₀Fe.

Undulated and planar sheets of La₆(C₂) units

In the system of lanthanum ethanide chlorides we found a series of new compounds with the chemical formulae La₆(C₂)₃Cl₄, La₆(C₂)₄Cl₅, La₁₄(C₂)₇Cl₆, La₂₀(C₂)₁₀Cl₁₇, La₂₂(C₂)₁₁Cl₁₄, La₃₆(C₂)₁₈Cl₂₃ and La₂(C₂)Cl [5]. The crystal structures are composed of distorted C₂ (‘ethanide’) centered La₆ octahedra which are condensed into chains via common edges. Three (3) and/or (4) such chains join into ribbons. Finally, the 3-, 4-ribbons are
condensed into undulated (up: (+), down: (−)) sheets with the Cl atoms between them, as denoted in Fig. 48.

The compounds are members of the series \((La_6(C_2)_3Cl_4)_m\) \((La_8(C_2)_4Cl_5)_n\) with \(m = 1, n = 0\) (Fig. 48(a)), \(m = 0, n = 1\) (Fig. 48(b)), \(m = 2, n = 2\) (Fig. 48(c), 46(d)), \(m = 4, n = 2\) (Fig. 48(e)), \(m = 2, n = 4\) (Fig. 48(f)), \(m = 4, n = 6\) (Fig. 48(g)). HRTEM investigations confirm the X-ray results. For \(La_{14}(C_2)_7Cl_9\) a second modification is found (Fig. 46(c)). Arrangements of greater complexity so far have not been observed. The examination of the number of combinations with two different ribbon sizes in alternating orientations, +, −, using a combinatorial approach including redundancy based on symmetry resulted in 110 possible structural variants for a sequence of up to 10 ribbons. In the meantime we found compounds of a new series based on 4- and 5-ribbons, namely \(Ce_{18}(C_2)_9Cl_{11}\) with the sequence \(\cdots 4_-5_+4_-5_-\cdots\) and \(Ce_{26}(C_2)_{13}Cl_{16}\cdots\) with \(\cdots 5_-4_+5_-4_-4_+5_-\cdots\). Obviously, we face the tip of an iceberg with these phases.

Interfaces and surfaces

The properties of solids may heavily change when approaching interfaces or surfaces. Deviations from electroneutrality near charged surfaces modify the population of point defects, lattice mismatches may induce strain. Both can change properties as in the three examples presented in this section. Close to ceria/silica interfaces, ceria turns from an ionic to a predominant electronic conductor. In the case of Fe doped SrTiO$_3$ surfaces, interactions with the surrounding gases modify the near surface defect chemistry, which, in turn, is crucial for its catalytic activity. For epitaxial layers of lanthanum manganates on SrTiO$_3$, it is the strain within the manganate which modifies its electronic and magnetic properties.

Conversion from ionic to electronic conduction in CeO$_2$ when approaching the SiO$_2$ interface

X.X. Guo, G. Gregori, Y.Q. Zhang and J. Maier

A growing number of examples underlines the importance of ionically dominated space charge zones in solids. Some examples include the enhancement of ionic conductivity achieved by the introduction of insulating second phase particles or ionic redistribution phenomena at the contact of two ionic conductors. In some cases, the space charge zones lead to a switch-over of the ionic conduction mechanism (vacancy-interstitial junction). In all these cases, the concept of ‘heterogeneous doping’ provides an adequate basis of explanation [1].

More recently, there have also been evidences of a variation in the mixed electronic/ionic conductivity in ceria nanocrystals [2,3]. It is assumed that the overall conductivity of doped oxide ceramics (in the case of weak acceptor doping) turns from ionic into electronic upon grain size reduction in the nanometric range. This again could be fully explained in the framework of the above mentioned model [3].

Here, we report on the investigation of Gd-doped CeO$_2$ (with various doping contents) thin films on quartz substrates. The conductivity along the interface is measured by impedance spectroscopy as a function of temperature, oxygen partial pressure and film thickness (L). The dependence on the latter parameter allows for a safe separation of the parallel interfacial contribution from the bulk contributions. As for the perpendicular grain boundaries effects, their contribution can be separated through the analysis of the frequency dependence.

Figure 49: Schematic drawing of the parallel conductance as a function of layer thickness. $\Delta Y_{\text{acc}}$, $\Delta Y_{\text{dep}}$, $\sigma_{\infty}$ denote the contribution from interfacial accumulation, the contribution from interfacial depletion and the bulk contribution, respectively.
Figure 49 shows that, for film thicknesses large enough to avoid space charge layer overlap, a linear dependence of the normalized conductance $Y_{\parallel}$ with $L$ is expected. The slope corresponds to the bulk conductivity while the extrapolated intercept yields the interfacial contribution.

Figure 50 shows the expected space charge profiles for weakly and heavily doped CeO$_2$. In the latter case, the Gd concentration is compensated by oxygen vacancies making this material a good oxygen ion conductor. Simultaneously, for defect-chemical reasons, the conduction electron concentration is at a very low level unlike undoped ceria. Here, a positive space charge potential then leads to a depletion of the conductivity (which is ionic).

Figure 50: Carrier concentrations in the heavily acceptor-doped CeO$_2$ (red) and in the lightly doped CeO$_2$ (blue).

A positive electronic potential has been demonstrated for various oxide boundaries, and this might be attributed to a deficiency of O$^{2-}$ at the boundaries for structural/energetic reasons. The second profile in Fig. 50 shows the situation for weakly doped CeO$_2$. As conduction electrons have to be enriched according to $c_n(x)/c_n(\text{bulk}) = (c_v(x)/c_v(\text{bulk}))^{-1/2}$ for electrostatic reasons, and as the bulk level is not negligible here, the result is a predominant electronic conductivity at the interface. This leads to the striking phenomenon of a local conversion of the conduction mechanism from ionic into electronic. In view of Fig. 49, we predict a slightly negative intercept in the first case and a positive intercept in the second. Figure 51 shows that this is indeed fulfilled.

The partial pressure dependence of both boundary and bulk conductivity provides further confirmation of electronic conductivity close to the interface and ionic conductivity in the bulk. Quantitative calculation reveals an astonishingly high space charge potential at the CeO$_2$/SiO$_2$ interface (700 mV), which is distinctly larger than the typical values at the free surface and at the grain boundaries (300 mV). The reason of such high potential might consist in the oxygen termination of the quartz substrate inducing the O$^{2-}$ removal in the formation of equilibrated interface.

It is expected that such interfacial effects at heterostructured oxides can lead to amazing variations in the ionic and ionic/electronic transport behavior. This is particularly important if we manage to control the conduction properties at interfaces with a specific sign and magnitude.

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In spite of the paramount significance of catalysis, the role of catalyst’s defect chemistry has not been adequately appreciated [1]. Ionic and electronic defects are excited states of higher energy than the environment and typically exhibit a higher acid-base or redox activity than the environment. The concentrations of these point defects are functions of the component partial pressures, temperature and doping contents; the decisive thermodynamic control parameter in the case of oxides is the oxygen partial pressure. But the local effective oxygen partial pressure determining the defect concentration is also governed by the kinetics of the reaction to be analyzed.

Irrespective of mechanistic details [2] the reaction scheme of $O_2$ with CO (yielding $CO_2$) or $CH_4$ (eventually yielding $CO_2$ and $H_2O$) can be decomposed into different branches as shown in Fig. 53. Note that on the conceptual level of this brief report we do not have to distinguish between the more reactive CO and the less reactive $CH_4$ (see Fig. 52). $O^*$ stands for the oxygen species at which the branching occurs, it may be the adsorbate $O^*_ad$ or the surface lattice oxygen $O^*O$ ($\epsilon$ and $\eta$ smaller than 2). The two possibilities lead to different kinetic models and different expressions of the rate equations but exhibit the following common feature: If the specific rate of the ‘oxygen branch’ is the quickest, then lattice oxygen is in equilibrium with the outer partial pressure of oxygen $pO_2$ (for simplicity we call this ‘A-case’), and at fixed $pO_2$ the defect concentrations are time invariant. They follow the typical curves that are well established for $Sr(Fe_xTi_{1-x})O_{3-\delta}$ in equilibrium (see the blue curves in Fig. 54).

To highlight this interplay – importance of defect chemistry for catalysis and importance of catalytic reaction for the defect chemistry – we choose well-studied reactions, namely oxidation of CO and $CH_4$, as well as an oxide whose defect chemistry is understood in detail, namely $Sr(Fe_xTi_{1-x})O_{3-\delta}$. In this oxide Ti can be continuously replaced by Fe in 3+ or 4+ oxidation state offering a particularly well-suited toolbox as regards doping. That this oxide is catalytically active and how important the $x$-parameter is, can be seen in Fig. 52.
If, however, the CO/CH₄ branch is the quickest, the O⁺ concentration will be lowered, therefore the defect concentrations all through the catalyst become themselves sensitively dependent on the reaction kinetics (‘B-case’). They can be related to an effective oxygen partial pressure which may be much lower than the outer p_O₂ (red curves in Fig. 54 in low-T range).

Figure 54: Thermogravimetry under in situ CO and CH₄ oxidation conditions for an iron-rich catalyst (Sr(FexTi1−x)O₃−δ). The deviation in low-temperature range of the red curves from the solid blue curve can be expressed in terms of an effective oxygen partial pressure.

Table 3: Summarized results of thermogravimetry and optical absorption measurements.

<table>
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<tr>
<td>x &gt; 0.03</td>
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<tr>
<td></td>
<td>CH₄ oxidation</td>
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Thermogravimetry on high-x powder catalysts and optical absorbance measurements on low-x single crystals under in situ CO/CH₄ oxidation conditions allow us to determine the oxygen non-stoichiometry δ (as diffusion is fast under the experimental conditions, the catalysts have homogeneous oxygen stoichiometry). We can thus answer the question whether and in which regimes the interesting B-case occurs. The results of these measurements are summarized in Tab. 3, and the thermogravimetry measurements are depicted in Fig. 54 for illustration.

The quantitative analysis [2] is not given here, rather we may concentrate on Tab. 3. An important separation line is the x value at which the appearance of an Fe-impurity band changes the electronic structure of the Sr(FexTi1−x)O₃−δ catalyst significantly. The different colors indicate whether we find A-case kinetics (blue) or B-case kinetics (red). At high temperature we find both reactions in A-case regime for x > 0.03 and in B-case regimes for x < 0.03. At high x values we find CH₄ oxidation for all T to follow A-type kinetics, whereas a switch-over from A- to B-type kinetics occurs in the case of CO oxidation on lowering T. This is clearly seen in Fig. 54. This figure gives in situ thermogravimetry curves for both reactions on the x = 0.5 catalyst. The solid blue curve for 1.5% O₂ displays the intrinsic oxygen non-stoichiometry of the catalyst (no CO nor CH₄ present and only the oxygen branch important). The dashed blue curve for CH₄ oxidation is qualitatively similar to the solid blue curve which proves that the system is in the A-case for the whole temperature range in spite of the ongoing CH₄ oxidation (regimes (3) and (4) in Tab. 3). The three red curves which refer to CO oxidation clearly show a decrease of the oxygen content at temperatures lower than approximately 500°C (regime (3)) which depends both on p_CO and p_O₂. This over-reduction (as compared to the nominal p_O₂) is a direct evidence of B-case kinetics. In such cases, the interplay of catalytic reaction and defect chemistry is very striking. Not only is it the significance of the point defects for the reaction kinetics that is obvious, also the defect chemistry becomes a sensitive function of the kinetics itself, it even varies the partial reaction orders. In such cases clearly gas phase, surface and solid form a common system, and the variable defect chemistry of the solid has to be self-consistently brought into play.

Novel electronic and magnetic properties of La$_{0.5}$Ca$_{0.5}$MnO$_3$ films deposited on (111) SrTiO$_3$ substrates

G. Aydogdu-Kuru, Y. Kuru and H.-U. Habermeier

The doped rare earth manganites have attracted considerable attention in both, bulk and thin film form, due to their potential use as colossal magnetoresistance (CMR) materials suitable for device applications. Taking La$_{1-x}$Ca$_x$MnO$_3$ as an example, the (coexistence and/or) competition of several phases with different charge-, orbital-, spin-ordering states, results in the well-known complex phase diagram [1]. The underlying physics is based on a complexity of interactions (including electron-lattice interactions) of comparable energy scales. This can give rise to local inhomogeneities in the electronic phases commonly described as nanoscale phase separation.

It has recently been shown that it is possible to tune the properties of manganites by external perturbations without changing their chemical composition [2]. One way of achieving this is to employ strain as a tool for controlling the phase separation. For instance, it has been demonstrated that an applied compressive hydrostatic stress enhances the conductivity and increases the Curie temperature ($T_C$). In the case of epitaxial films, lattice parameter mismatch between the film and the substrate can be used in order to impose strain on the film.

Previously it has been shown that a tensile epitaxial strain induces a decrease in the saturation magnetization of the La$_{0.7}$Sr$_{0.3}$MnO$_3$ thin films accompanied by an increase in their resistivity [3]. In contrast, compressive strain causes an increase in conductivity for La$_{0.5}$Sr$_{0.5}$MnO$_3$ and La$_{0.5}$Ca$_{0.5}$MnO$_3$ films on (001) LaAlO$_3$ (LAO) substrates [4]. This effect is presumably related to the promotion or obstruction of the formation of the charge-ordered phase according to the distortion caused by the applied strain. For the (001) SrTiO$_3$ (STO) substrate, a distortion similar to the one caused by the formation of the charge-ordered antiferromagnetic phase occurs; in-plane lattice parameters increase while the out-of-plane lattice parameter shrinks, which promotes the formation of the charge-ordered phase. On the other hand, for the (001) LAO substrate, a distortion contrary to the one caused by the formation of the charge-ordered antiferromagnetic phase is created; in-plane lattice parameters shrink while the out-of-plane lattice parameter increases, which can obstruct the formation of the charge-ordered phase.

In this study, La$_{0.5}$Ca$_{0.5}$MnO$_3$ (LCMO), thin films of various thicknesses were deposited on (111) STO substrates for the first time. This composition is at the boundary between the charge ordered antiferromagnetic (CO-AFM) and the ferromagnetic (FM) phase and strain related phase transitions or modifications of the phase separation are expected. Novel electronic and magnetic properties, such as metal to insulator transition for thicker films and absence of an antiferromagnetic transition for all thicknesses, due to structural constraints imposed by the substrate, were observed.

The LCMO films were deposited on (111) planar STO single crystal substrates by pulsed laser deposition (PLD) technique at 1073 K and with an oxygen pressure of 0.4 mbar. After deposition, films were annealed at 1173 K for 30 minutes in ambient oxygen pressure. Determination of epitaxial relationship between the film and the substrate and phase analysis were carried out by X-ray diffraction (XRD) using Cu Kα radiation. Pole figures were taken in a Philips X’Pert MRD diffractometer equipped with an Eulerian cradle. The 2θ–ω scans at various inclination angles ψ; (2θ is the angle between the incident and the diffracted
X-ray beams; $\omega$ is the angle between the incident beam and the specimen surface; $\psi$ is the angle between the diffraction vector and the surface normal) were performed with a four-circle Bruker D8 Discover diffractometer, which were used to calculate the lattice parameters of the films via the Nelson-Riley equation. The temperature dependence of magnetization was investigated by a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The magnetic field (0.01 T) was oriented parallel to the film surface and samples were cooled from 300 K to 5 K. Resistivities of the films were measured by four-point probe method within the temperature range between 300 K and 5 K. Evaporated chromium-gold pads and silver epoxy were used to attach the gold wires to the specimen. The DC current was kept at $10^{-7}$ A during the transport measurements.

Lattice parameters of the bulk LCMO were obtained from the XRD data using the Fullprof software. LCMO belongs to the Pnma space group (FeGdO$_3$ type structure). The refined lattice parameters for the orthorhombic cell are $a = 0.54093$ nm, $b = 0.76493$ nm, $c = 0.54101$ nm and $\alpha = \beta = \gamma = 90^\circ$. The 2$\theta$–$\omega$ scans at $\psi = 0^\circ$ and $\{121\}$ pole figures indicate that single phase and epitaxial LCMO thin films with orthorhombic crystal structure were successfully grown on (111) STO substrates. Representative for all films, 2$\theta$–$\omega$ scan and $\{121\}$ pole figure of the 290 nm thick LCMO film are shown in Fig. 55. (022)-planes of the films are oriented parallel to the (111)-planes of the STO substrate (Fig. 55(a)). According to the pole figures, three-fold symmetry is observed. Inclination angles of the peaks in the pole figures ($\psi = 34.7^\circ$) are consistent with the angle between (121)- and (022)-planes of LCMO. Two points should be noted: (i) Epitaxial strain is tensile as in the case of (001) STO substrate, (ii) all three lattice parameters are directly affected by the adherence of the film to the substrate. The epitaxial relationship of the LCMO films and the (111) STO substrate is such that $a$-edge and the diagonal of the $b$-$c$ plane of the LCMO unit cell are oriented parallel to the (111) STO substrate surface. That is different for the other films deposited on (001) STO or (LAO) substrates where out-of-plane lattice parameter $b$ of LCMO films is oriented perpendicular to the substrate surface.

Figure 56 represents the magnetization versus temperature graphs for bulk LCMO (a) and various thicknesses of LCMO films (b). There are two magnetic transitions for the bulk LCMO; the first one is a paramagnetic to ferromagnetic transition at around 270 K and the second is a ferromagnetic to antiferromagnetic transition when 150 K is reached. The saturation magnetization is approximately $0.18 \mu_\text{B}/\text{Mn ion}$ on the other hand, a ferromagnetic to antiferromagnetic transition is absent and saturation magnetization is considerably higher (approximately $1.3 \mu_\text{B}/\text{Mn ion}$; Fig. 56) for the 290 nm thick LCMO film.
Transport measurements for the LCMO films with various thicknesses are given in Fig. 57. Resistivities of the films thinner than 145 nm steeply increase with decreasing temperature, associated with the insulating behavior. However, an insulator to metal transition exists for the films thicker than 145 nm when the temperature is gradually decreased below a certain threshold value, so-called metal to insulator transition temperature ($T_{MI}$). Furthermore, it is found out that $T_{MI}$ is positively correlated with the film thickness.

In order to elucidate the reason of the thickness-dependent electronic properties of LCMO films (Fig. 57), apical and equatorial Mn–O distances ($d_{Mn–O}$) were determined from the lattice parameters measured by XRD and the crystal structure and atomic positions of LCMO obtained from the literature using the software EnClFer.

The results are summarized in Fig. 58 showing that the two equatorial $d_{Mn–O}$ distances indicate an increase with increasing film thickness whereas the apical $d_{Mn–O}$ distance remains

![Figure 56: Magnetization versus $T$ graphs of (a) bulk LCMO and (b) various thicknesses of LCMO films on (111) STO.](image1)

![Figure 57: Resistivity versus $T$ graphs of various thicknesses of the LCMO films on (111) STO.](image2)

![Figure 58: Mn–O distances for the LCMO films on (111) STO.](image3)
nearly constant. That means the distortion of MnO$_6$ octahedra becomes smaller when the film thickness increases. The enhancement of metallic behavior for the thicker LCMO films can be caused by their low room temperature Jahn-Teller distortions.

In conclusion, formation of the charge-ordered antiferromagnetic phase at low temperature is suppressed and metallic behavior is favored for the LCMO films deposited on (111) STO substrates as epitaxial relationship between the film and the substrate confines the LCMO unit cell. Thereby, the structural distortion caused by the charge-ordered antiferromagnetic phase cannot take place straightforwardly as in the case of bulk. Moreover, these films exhibit a systematic enhancement of the metallic behavior with increasing film thickness which can be ascribed to the low room temperature distortion for the relatively thick films; the possibility is now given to tune the electronic and magnetic properties of LCMO thin films by altering the thickness.

Electronic and ionic charge transport in systems of varying dimensions are key research areas in the Institute. Nanoscale transistors based on carbon nanotubes, nanowires, and organic thin films are being developed for emerging large-area electronic applications. Since a decade the quantum Hall effect in two-dimensional electron systems has been studied not only in electrical transport measurements but also locally by scanning force microscopy, which detects the local Hall potential and current distributions in the Hall devices. Recently the direct comparison between transport and scanning probe data reveals the impact of a partial charge carrier depletion at the Ohmic Contacts on the magnetoresistance measured on quantum Hall samples. Using a scanning tunneling microscope at low temperature, the Kondo physics of single magnetic cobalt atoms on metal surfaces is studied. Here, the influence of the local atomic geometry on the transport properties through a single atomic junction has been addressed as a function of tip-sample distance. On the theoretical side ionic charge transport is modeled in the regime far away from equilibrium. Non-equilibrium transport conditions are met, e.g., for large applied potential differences or transport over small distances. A generalized current equation is derived for these cases that can help to treat for example space charge effects in nanosized matter.

Nanoscale transistors for large-area electronics


Reducing the lateral dimensions of field-effect transistors is motivated by two distinct advantages: an increase in the maximum frequency of operation, and a reduction in the foot print of the transistor. The latter is the main reason for the continued scaling in silicon technology, as described by Moore’s Law, because on a silicon chip smaller transistors translate into more transistors per area and therefore lower cost per chip. As a result, it is now cheaper to manufacture 1000 silicon transistors on a memory chip than to print a single letter in a newspaper.

In contrast, reducing the foot print of the transistors inside the pixels of a flat-panel display has no effect on the cost, because the transistor density is tied to the pixel density. However, making the transistors inside each pixel smaller increases the area available for light emission, and this has a positive effect on the image quality. Similar considerations apply to flat-panel sensors and detectors.

The maximum frequency of operation of a field-effect transistor is determined by the transconductance $g_m$ and the gate capacitance $C_{\text{gate}}$:

$$f_T = \frac{g_m}{2\pi C_{\text{gate}}}.$$  \hspace{1cm} (1)

The transconductance $g_m$ is defined as the change in drain current $I_D$ with respect to the corresponding change in gate-source voltage $V_{GS}$, so in the linear regime $g_m$ is given as:

$$g_m = \frac{\partial I_D}{\partial V_{GS}} = \frac{\mu C_{\text{dielectric}} W}{L} V_{DS},$$  \hspace{1cm} (2)

where $\mu$ is the charge carrier mobility, $C_{\text{dielectric}}$ is the gate dielectric capacitance per unit area, $W$ is the channel width, $L$ is the channel length,
and $V_{DS}$ is the drain-source voltage. The gate capacitance $C_{gate}$ is the sum of the intrinsic gate capacitance (representing the interaction between the gate and the channel charge) and the parasitic gate capacitance:

$$C_{gate} = C_{die} W (L + 2\Delta L),$$

where $\Delta L$ is the length of the gate-to-source and the gate-to-drain overlap that determine the parasitic gate capacitance.

In state-of-the-art silicon transistors, $L \approx 35 \text{ nm}$, $\Delta L \approx 15 \text{ nm}$, $\mu \approx 200 \text{ cm}^2/\text{Vs}$, and $V_{DS} \approx 1 \text{ V}$, so $f_T > 1 \text{ THz}$. In reality, the frequency is limited to a few Gigahertz by the signal delay within the metal interconnects. This is the reason why in silicon technology further scaling does not provide faster circuits; scaling is continued solely to reduce cost. In contrast, state-of-the-art thin-film transistors employed in flat-panel displays have dimensions of a few microns and cutoff frequencies well below 1 MHz, so reductions in lateral dimensions will allow transistors to switch faster and thus provide better display resolution and higher refresh rates, in addition to increasing the area available for light emission.

**High resolution inkjet printing for organic thin film transistors**

Regular inkjet printers dispense droplets with a volume of about 1 pL to 10 pL, creating dots with a diameter of 20 $\mu$m to 50 $\mu$m. This resolution is adequate for artwork, but insufficient for high-performance transistors. To increase resolution, Kazuhiro Murata (AIST, SIJ Technology Inc., Japan) has recently developed an inkjet system that dispenses droplets with a volume of 0.7 fL. The system utilizes a nozzle made from a capillary glass tube with a tip diameter of 1 $\mu$m. The tube is hydrophilic on the inside and hydrophobic on the outside. The hydrodynamic pressure inside the tube is controlled by a pressure controller. A wire located inside the nozzle charges the ink, and electric pulses are applied to eject droplets with a volume of about 0.7 fL that travel straight through the electric flux line and create dots with a diameter of 1 to 2 $\mu$m. By dispensing gold or silver nanoparticle inks, the source and drain contacts of organic transistors can be printed directly on the surface of the organic semiconductor layer.

In collaboration with the group of Professor Takao Someya at the University of Tokyo we have manufactured organic thin film transistors with source and drain contacts prepared by high-resolution inkjet printing, using a prototype system from SIJ Technology.

![Figure 59: Organic thin-film transistors with a channel length of 1 $\mu$m manufactured using sub-femtoliter inkjet printing ((b): pentacene $p$-channel transistor; (c): $F_{16}$CuPc $n$-channel transistor).](image)
Selected research reports

Figure 59 shows a photograph and the electrical characteristics of $p$-channel and $n$-channel organic transistors with inkjet-printed silver contacts [1]. These transistors have a theoretical cutoff frequency of about 1 MHz, which is an improvement of two orders of magnitude over transistors with contacts patterned using shadow masks [2,3].

**Organic transistors with submicron dimensions**

It is expected that the resolution of inkjet printing can be further reduced to perhaps 500 nm or less. In principle, this further reduction in channel length should provide an additional boost in switching frequency, perhaps up to 10 MHz. However, it is unclear if devices with such short channel length will continue to behave as field-effect transistors. To address this issue we have developed a process that utilizes electron-beam lithography to prepare organic transistors with a channel length between 1 μm and 50 nm. Figure 60 shows the schematic manufacturing process, an electron microscopy image, and the electrical characteristics of $p$-channel and $n$-channel organic transistors with a channel length of 200 nm.

![Diagram of organic thin-film transistors with a channel length of 200 nm manufactured using electron-beam lithography.](image)

Figure 60: Organic thin-film transistors with a channel length of 200 nm manufactured using electron-beam lithography ((a) pentacene $p$-channel transistor; (b) F$_{16}$CuPc $n$-channel transistor).
Despite the aggressively reduced channel length, the charge density in the channel is still controlled by the gate field, as evidenced by the very small off-state drain current (<$10^{-13}$ A) and large on/off ratio (>10^5). This high degree of gate-field control over the charge density despite the short channel length is in large part due to the use of a very thin metal oxide/organic monolayer gate dielectric [1–3].

However, as the channel length is reduced below about 1 μm, the transconductance does not scale with 1/L anymore, because the total resistance of the transistor becomes dominated by the contact resistance, rather than the channel resistance. To counter this problem, we have begun to investigate materials and methods to reduce the contact resistance through local molecular doping.

**Nanotube and nanowire transistors**

Organic thin-film transistors are useful for flexible displays, because they can be manufactured at temperatures below 100°C, compatible with plastic substrates. The same is true for field-effect transistors based on semiconducting carbon nanotubes or inorganic semiconductor nanowires, because high temperatures are only required to produce the nanotubes and nanowires, but not to build transistors after the tubes and wires have been dispersed on the flexible substrate. Compared with organic semiconductors, carbon nanotubes and inorganic nanowires provide larger mobility, and by using high-resolution patterning methods, the transistor foot print can be extremely small. This has spurred interest in flat-panel displays that utilize pixel drive transistors based on nanotubes or nanowires [4,5].

![Figure 61: (a) Field-effect transistor based on a semiconducting carbon nanotube. (b) Field-effect transistor based on a ZnO nanowire.](image-url)
To demonstrate high-performance nanotube and nanowire transistors, we utilize carbon nanotubes grown by high-pressure carbon monoxide conversion (HiPCO) as well as zinc oxide nanowires prepared through a hydrothermal growth process on zinc foil. Carbon nanotubes are suspended in a liquid, mixed with a suitable surfactant, and treated by sonication and centrifugation in order to reduce the amount of nanotube bundles. ZnO nanowires are annealed at a temperature of 600°C in order to reduce the density of unintentional dopants incorporated during hydrothermal growth. After dispersing the nanotubes and nanowires on a substrate, field-effect transistors are built using local (patterned) metal gate electrodes, a thin oxide/monolayer gate dielectric [2], and source and drain contacts patterned by electron beam lithography [6,7].

Figure 61 shows the electrical characteristics of a p-channel transistor based on a semiconducting carbon nanotube and of an n-channel transistor based on a ZnO nanowire. Both transistors have an on/off ratio of about $10^7$, a sub-threshold swing of about 80 mV/decade, and a transconductance of about 1 $\mu$S. The gate capacitance of both transistors is about $10^{-14}$ F, so the theoretical cutoff frequency of both transistors is above 10 MHz.


Role of ohmic contacts for the current distribution in quantum Hall samples

J. Weis, F. Dahlem and K. v. Klitzing

Since the discovery of the quantum Hall effect in 1980, several predictions and interpretations of experimental data have been made about the distribution of the current biased externally into the sample. In the last decade we have used a scanning force microscope – sensitive to electrostatics and operated at a temperature of 1.4 K – to investigate the local potential distribution in two-dimensional electron systems (2DESs) under quantum Hall conditions [1]. With the required sensitivity and spatial resolution, such local probe measurements are able to clarify unambiguously the Hall potential and current distribution in quantum Hall samples. Our experimental results and theoretical calculations by Rolf Gerhardts and coworkers [2] have shown that the quantum Hall effect does not necessarily require disorder leading to localization which is the prerequisite usually given in textbooks for the formation of quantum Hall plateaus. In an extensive comparison between magnetoresistance and scanning probe measurements, we have focused in the last years on the role of ohmic contacts and we could visualize the electrical decoupling of bulk and edge of the 2DES even in the presence of contacts.

Our quantum Hall samples are based on a modulation-doped GaAs/Al$_{0.33}$Ga$_{0.67}$As het-
erostructure grown by molecular beam epitaxy. The 2DES is obtained at the GaAs/AlGaAs heterojunction 40 nm below the surface (electron concentration about \( n_e = 5 \times 10^{15} \) m\(^{-2}\), electron mobility between \( \mu_e = 50 \text{m}^2/\text{Vs} \) and 130 m\(^2/\text{Vs}\)). A mesa is formed by wet-etching into the heterostructure and Au/Ge/Ni pads are alloyed in order to contact the 2DES. Over the years, the geometries of the mesa have been varied, as well as the amount and arrangements of the ohmic contacts to the 2DES. In all cases, the width of the mesa was limited by the scan range of our self-made scanning force microscope (20\(\mu\)m \(\times 20\mu\)m). The scanning force microscope probes at 1.4 K and magnetic fields of up to 13 T the local electrostatic potential change which appears in our quantum Hall samples with current flow. Therefore, with scanning over the width of a Hall bar mesa, we directly obtain the Hall potential profile which is caused by the externally biased current through the 2DES.

Self-consistent calculations of the electron density profile at the edges of a 2DES in the 1990’s have predicted the presence of compressible and incompressible strips in the depletion region at the edges of a 2DES. An incompressible strip is characterized by the fact that its local Landau level filling factor has an integer value. As, locally, the Fermi level lies between two Landau levels, the strip behaves electrically insulating, in contrast to compressible regions behaving metal-like. Our results on the Hall potential profiles have proven the existence of incompressible strips and we could interpret the Hall potential profiles in the following way [3]: Close to integer filling factors \( \nu = i \), the current is flowing without dissipation in the mainly incompressible bulk of the 2DES. The local current density \( j_x \) is driven by the local Hall field \( E_y \), e.g., \( j_x(y) = \nu e^2/h E_y(y) \). Due to inhomogeneities, the Hall potential drop could even be non-monotonic, e.g., the current takes snake-like paths through the 2DES bulk. In this regime, the actual Hall potential profile and therefore the current distribution is very sensitive to small magnetic field changes, reflecting the fragile landscape of compressible islands embedded in the mainly incompressible bulk. With reducing the magnetic field (increasing the bulk filling factor to \( \nu > i \)), a connected compressible region appears in the center of the 2DES and the dissipationless current flow is restricted to the innermost incompressible strips which move towards the two edges. The Hall potential drops over these two incompressible strips driving the current without dissipation within these incompressible strips along the Hall bar. The Hall potential profile is flat in the compressible bulk. Since the drop of the Hall voltage occurs only over incompressible strips of same local integer filling factor \( i = \text{int}(\nu) \), a quantized Hall resistance value is still obtained, e.g., the Hall voltage \( V_{fi} \) and the bias current \( I \) are related by \( I = \int j_x(y) \, dy = i e^2/h V_{fi} \). With reducing the magnetic field, these strips are moving further to the edges and get smaller, loosing their insulating property. Scattering of electrons from the compressible edge into the compressible bulk and further to the opposite compressible edge becomes possible, reducing the Hall potential drop over the innermost incompressible strips, and therefore the dissipationless current flow. The Hall resistance is no longer quantized. Before reaching the next Hall plateau at lower magnetic field, the current is distributed homogeneously over the whole width of the Hall bar – a linear Hall voltage drop is observed.

Usually contacts at the edge of a 2DES acting as potential probes are considered as an effective way of equilibrating edge and bulk. This would mean, that, whenever the bulk of the 2DES is compressible, edge and bulk are shortened in their electrochemical potential, and no Hall voltage drop can exist over the incompressible strip present at the etched edges of the 2DES. Our scanning probe measurements have shown that a region of partial depletion (reduced electron concentration) is formed in front of the contact edge within the 2DES (to emphasize, these are good ohmic contacts!). This gives rise to the formation of compressible and incompressible strips in front of the alloyed metal. This partial depletion is not surprising when
taking into account that alloyed contacts and the 2DES do have different workfunctions. We found that the innermost incompressible strip decouples – at least beyond a certain strip width – the bulk from the contact. *Bulk and edge are not shortened in their electrochemical potential.* What does this mean for a Hall measurement? The contact probes the electrochemical potential of the compressible edge at this position. Due to the electrochemical potential drop over the incompressible strip, a current is flowing within the incompressible strip in front of the potential probing contact without dissipation. It is part of the current biased into the sample. It does not pass the contact which would cause dissipation.

In the last years, we made an astonishing observation on the Hall bar geometry depicted in Fig. 62. Depending on the orientation of the Hall bar relatively to the crystal orientation of the underlying GaAs-AlGaAs heterostructure, different magnetoresistance curves are measured for the same measurement configurations. In one case, the Hall plateaus are found at the expected positions whereas in the orientation tilted by 90 degree, the plateaus are shifted to lower magnetic field values. Such features remind on what has been observed on quantum Hall samples where gate electrodes in front of ohmic contacts were used to reflect selectively edge states leading to a non-equilibrium situation between adjacent edge states.

Figure 62: Two-terminal magnetoresistance versus magnetic field on an asymmetrically contacted Hall bar for two different measurement arrangements (a),(b). For the same Hall bar geometry, however tilted by 90 degree, different magnetoresistance curves are measured (c),(d).
Figure 63: Hall potential landscape (right) in front of contact 4 for the Hall bar depicted (left). For filling factor $\nu = 2.2$, the bulk is compressible, separated by an incompressible strip from the compressible edge. Red/blue indicates high/low potential in the 2DES.

Figure 63 shows an example for the Hall potential landscape in front of a contact of a Hall bar with asymmetrically arranged contacts. Striking is the Hall voltage drop from the edge to the bulk along the etched edges and in front of the alloyed contact. The current follows the path perpendicular to this Hall potential drop, e.g., the current follows here the contour of the Hall bar mesa and does not take a direct path between the biased contacts. Such and many other scanning probe measurements reveal that depending on the orientation of the interface line between alloyed metal and 2DES relatively to the underlying crystal orientation of the heterostructure, the incompressible strip decouples bulk and edge more or less well. This anisotropy in decoupling is the origin of the observed anisotropy in the magnetoresistance measurements.

Stimulated by these findings, we have started structural investigations by transmission electron microscopy to get a better insight into the microscopic formation of an ohmic contact between alloyed Au/Ge/Ni and the 2DES. First results have shown that the diffusion of Al out of the AlGaAs heterostructure layer and the formation of a NiGe phase play a crucial role.

Kondo effect in single atom contacts: The importance of the atomic geometry
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It is commonly known that the electron transport properties in a circuit, whose dimensions are reduced to single atom/molecule contact, are strongly influenced by the coupling of the orbitals of the electrodes to the bridging atom or molecule. However, accessing the correct information of the geometrical arrangement of a nanometer scale junction, which is fundamental to the interpretation of the experimental data, is often still challenging. Among other techniques, a junction achieved with the tip of a scanning tunneling microscope (STM) on a metal surface has been proven as a valuable tool to target and select the substrate configuration before and after the contact is formed. Nonetheless, a general picture on the influence of atomistic order on the electron conductance at nanometer scale junctions is, at present, missing.

Co adatoms on copper surfaces constitute an ideal system for studying the electron transport through nanometer scale junctions. The interaction of the unpaired electron spin of single Co atoms and the free electron states on copper surfaces leads to the formation of a narrow electronic resonance at the Fermi level known as the Kondo resonance. This has been extensively characterized in tunneling conditions. One main result of these studies is the evidence that on different supporting surfaces the width of this resonance coincides with a change of the occupation of the d-electron levels of the Co adatom [1]. This inherently reflects a varied coupling of the magnetic impurity to the metal substrate. Indeed, a simple model has been suggested to relate the energy position of the electron d-levels of the impurity and the atomic arrangement in close proximity of the Co adatom. Specifically, a narrower Kondo resonance is observed for Co adatoms on Cu(111) than on the Cu(100) surface in agreement with a shift in energy of the d-levels i.e with an increase in their occupation from the first to the second surface. Due to this dependence, the width of the Kondo resonance is a good reference parameter to characterize the influence of the tip at reduced distances. However, it is a priori not evident if the width of the Kondo resonance will follow a trend similar to the one observed in tunneling configuration on various surfaces also when the tip is approached to the point contact configuration.

In order to address this question we measured the current-voltage characteristics at different tip-sample distances ranging from tunneling to point contact on individual Co adatoms on a Cu(111) surface. As will be shown in the following, the width of the Kondo resonance is practically constant on this surface [2] at all tip-substrate distances in an apparent contradiction with the previously reported results on Cu(100) [3]. Based on ab initio theoretical calculations aimed to determine the electronic and magnetic properties of these two systems, we will show that the opposing results observed on the two copper surfaces are not contradictory but demonstrate nicely the determining influence of the local atomic structure on the transport properties of a nanoscale junction.

The inset in Fig. 64 shows the conductance of a single Co adatom achieved by recording the current while the tip substrate distance is reduced. The current increases smoothly from the tunneling to the point contact regime following the exponential dependence with the tip-substrate distance (z) characteristic of the electron tunneling process $I(z) = I_0 \exp(-Az)$ (where $A$ is proportional to the work function of
tip and substrate). As the point contact regime is reached the current is found to exhibit a characteristic quantization plateau with only a weak dependence on the distance. The plateau is observed to be $G_0$ where $G_0$ is the conductance quantum $G_0 = 2e^2/h$ ($h$ is Planck constant) in agreement with studies on Co/Cu(100). Topographic images acquired before and after the tip was approached and retracted from the point contact configuration confirm that the contact region as well as the tip have not changed during the tip displacements.

Figure 64: Conductance and $dI/dV$ spectra for isolated Co atoms on a Cu(111) surface achieved at different tip-substrate distances $\Delta Z$ from tunneling to point contact. Prior to the point contact measurements the tip was stabilized at a defined sample distance setting the tunneling conditions at 8 meV, 5 nA. In the inset a representative current vs. tip-displacement is shown. $dI/dV$ spectra have been recorded at the position indicated by a circle in the inset. The curves are normalized to the tunneling current at the tip height location and vertical offset has been added for a better visualization. The Kondo temperature $T_K$ given on the right side of the image has been obtained fitting the curves with a Fano line shape (red line).

In Fig. 64, we report also the $dI/dV$ spectra obtained on top of the Co adatom at the tip-substrate separation indicated by the circles in the inset. All the curves obtained in the range from the initial tunneling ($\Delta Z = -2 \AA$) to the point contact ($\Delta Z = 0.2 \AA$) condition show a characteristic dip in the local density of states at an energy close to the Fermi level. This dip, which is due to the Kondo resonance can be characterized according to its width $\Delta E$, which is proportional to the Kondo temperature $T_K$, $\Delta E = 2k_B T_K$, where $k_B$ is the Boltzmann constant. The Kondo temperature can be extracted from these curves by fitting the experimental spectra with a Fano line function according to $dI/dV \propto (q + \varepsilon)^2/(1 + \varepsilon^2)$, with $\varepsilon = (eV - \varepsilon_K)/k_B T_K$ where $q$ and $\varepsilon_K$ define the asymmetry of the Fano curve and the energy position of the resonance with respect to the Fermi energy.

The fitted Kondo temperature $T_K$ is reported in Fig. 64 for each sampled tip position. As can be seen, the Kondo temperature for the Co on Cu(111) system is constant, within the experimental error, from the tunneling to the point contact regime. These results have been reproduced with different tips and different tip treatments which assured a spectroscopic featureless tip in the energy range of the Fermi level.

The observed behavior of the Kondo temperature on the Cu(111) surface contrasts with the behavior previously reported for the Co/Cu(100) system, where a considerable increase of the Kondo temperature (from 70–90 K in tunneling to 150 K in point contact) was observed. As will be shown below this difference can be ascribed to the sensitivity of the Kondo effect to the local atomic geometry.

To obtain a physical understanding of the structural sensitivity, we have modeled at first the atomic relaxation in the single Co atom junction under the influence of the tip proximity and then considered its consequence on the electronic structure.
Figure 65: Atomic relaxation at the single Co atom junction as a function of the tip displacement. The initial tip-adatom distance (H) is the same for Cu(111) and Cu(100) surface. The adatom-substrate (L) distances for Co adatom on the two surfaces is shown in panel (b). The dashed lines show the Co-substrate distance in point contact conditions. A, B and C indicate the position where the LDOS shown in Fig. 66 have been calculated; the values in the brackets are the tip-substrate distances for these three positions.

Indeed, reducing the tip-substrate separation can induce a local perturbation in the atomic ordering at the junction which can affect the coupling between the orbitals of the electrodes and of the Co atom and consequently the electronic and the magnetic properties of the system. Figure 65 shows the variation of the tip-adatom and the adatom-substrate separations during the tip displacement (panel (a) and (b), respectively). On a first glance one can see that beside an initial region, the tip-Co adatom as well as the Co adatom-substrate distances are not linearly proportional to the tip displacement. As the tip-substrate distance is reduced, the atomic order at the junction relaxes: the atoms of the tip, the Co impurity as well as the atoms of the substrate move to new equilibrium positions. The real tip-substrate distance is then a dynamic variable according to the specific location of the tip and to its attractive and repulsive interaction with the surface and the impurity. Specifically, up to the minimum distance of 5.3 Å, the tip Co adatom distance is almost linear with the tip displacement. Approaching further, the distance between the opposite sides of the nanometer scale junction is reduced to a larger extend than the effectively applied tip displacement due to an attractive interaction (up to 4.7 Å). Reducing the tip-substrate distance below 4.7 Å, the interaction becomes repulsive. At this tip proximity, the adatom-substrate distance, defined as the vertical distance between the Co adatom and its first-nearest neighbor, is strongly reduced while the distance between the tip and adatom is only slightly decreased. This implies that the Co adatom shifts towards the substrate. As a consequence when the point contact configuration is reached, the Co–Cu(111) surface distance compares to the equilibrium distance predicted for the tunneling condition (dotted line in panel (b)).

Figure 65 compares also the atomic relaxation process on the two copper surfaces. The general trend of attractive and repulsive interaction of tip-atom and surface can be observed in both cases. However, differences in the atom dynamics under the influence of the tip and in the Co-substrate distance are obvious. Specifically, under the influence of the tip the Co impurity is pushed deeper into the Cu(100) surface in point contact configuration than it is in tunneling conditions (dotted line in panel (b)). This effect is not so strong for Cu(111). Therefore, it can be expected that for Cu(100) substrate the stronger interaction with the surface increases on the the hybridization of the d-levels of the Co adatom with the sp-states of the surface. This and its consequence on the magnetic properties of the junction at various tip proximity, can be understood calculating the local density of states (LDOS) of the Co adatom.

In Fig. 66 the d-levels of Co/Cu(111) are shown for different tip-substrate separations (denoted A, B and C in Fig. 65) with the energies given with respect to the Fermi level. It can be seen that only the occupied density of states of the Co adatom on Cu(111) are slightly affected by the tip substrate distance. Moreover, the energy difference $U$ between the center of the occupied spin-up band (or majority states) and the center of the partially unoccupied spin-down band...
(or minority states) for three tip-substrate separations are nearly the same. Consistently, also the magnetic moment of the Co adatom at these three tip-substrate separations are only slightly affected by the tip proximity. On the contrary a large energy shift of the \( d \)-levels was reported for Co adsorbed on the Cu(100) surface. A comparison of the energy position of the occupied \( d \)-levels is shown in Fig. 66(b). On both surfaces the position of the occupied \( d \)-levels shifts towards higher energies under the influence of the tip proximity.

![Figure 66: Influence of the tip-proximity on the \( d \)-levels of Co atoms on Cu(111). (a) Spin polarized LDOS for the \( d \)-levels. The curves are calculated for tip-substrate displacements as denoted in Fig. 65. (b) Energy position of the occupied \( d \)-band center on Cu(111) and Cu(100) at different tip-substrate positions. The lines connecting the points are a guide to the eye.](image)

On Cu(111) surface this shift is, however, much smaller. On the Cu(100) the substantial change in the occupation of the \( d \)-levels is reflected in the increase of the Kondo temperature in point contact. The difference in the behavior of the Kondo temperature on Cu(111) and Cu(100) is caused by different atomic relaxations which occur on both substrates. For all tip positions the distance between Co adatom and Cu(111) is significantly larger than that on Cu(100) (Fig. 65). Therefore the hybridization of \( d \)-states of Co adatoms with \( sp \)-electrons of the substrate is weaker on Cu(111). As a result, only very small changes in the LDOS of Co adatoms are found on Cu(111). These theoretical predictions and the experimentally observed Kondo temperature in the point contact regime follow the trend described by the model proposed by Wahl et al. for the tunneling regime. The increase of the occupation of the \( d \)-level effects sensibly the Kondo temperature on Cu(100) and almost negligibly on the Cu(111) surface.

In conclusion, the present experimental and theoretical work demonstrates that the local atomic geometry plays a major role in the electron transport properties of nanoscale junctions. The tip proximity in the point contact regime influences the atomic relaxation in the single atom junction and thereby determines the lattice equilibrium position. These structural relaxations induce a modification of the \( sp-d \) hybridization between the electrode surface and the bridging atom. While on the closed packed Cu surface the impurity \( d \)-level is less affected, it shifts substantially in energy on the open (100) surface. This explains the striking difference observed in the behavior of the Kondo temperature of Co adatoms upon point contact formation on Cu(111) and Cu(100). We believe that these results have general validity and might clarify a few of the uncertainties in the electron transport through nanometer scale junctions characterized by break-junction experiments.

Hopping transport far from equilibrium: A generalized current equation
I. Riess and J. Maier

The transport of ions but also of small polarons is viewed as a motion from one position to a neighboring equivalent one through an energetically higher lying transition state with the latter determining the thermal activation. In the following we consider transport of an ion A from a site \( x \) to a site \( x' = x + \Delta x \) and assume for illustration a vacancy mechanism \( (V) \). The process then corresponds to a bimolecular ‘chemical reaction’ (with zero reaction free energy)

\[
A(x) + V(x') \rightleftharpoons V(x) + A(x'),
\]

(4)

a kinetic sketch of which is provided by Fig. 67.

Figure 67: Site exchange of a vacancy and sketch of the local free energy.

In the context of linear irreversible thermodynamics a linear relation between flux \( j \) and driving force holds. As we only consider electrical and compositional variations, the driving force is known to be the electrochemical potential gradient \( (\nabla \tilde{\mu}) \), hence

\[
j \propto -\tilde{\sigma} \nabla \tilde{\mu},
\]

(5)

where \( \tilde{\sigma} \) is the equilibrium conductivity. This equation reduces to Ohm’s law for zero compositional and to Fick’s law for zero electrical effects. Figure 68 displays the validity range which is restricted to a narrow regime on the driving force axis (deviation from equilibrium) but almost unlimited on the concentration axis (interactions).

Figure 68: Validity range of simple chemical kinetics and linear irreversible thermodynamics. The dotted line demarcates the area (gray area) in which local thermal equilibrium and also Eq.(9) is valid.

In many cases, however, one meets situations that are far from equilibrium, e.g., if large potential differences are applied or very small distances have to be covered as in nano-structural materials. If then both electrical and compositional effects need to be considered as in space charge zones, the linear relation does not suffice. One possibility is to expand \( j(\Delta \tilde{\mu}) \) to higher orders. This first of all does not lead very far from equilibrium and introduces additional parameters that are not very straightforward to interpret. Another possibility is to use the above equation but replacing the equilibrium conductivity by the non-equilibrium value \( \sigma = \tilde{\sigma} + \delta \sigma \). This presupposes local thermal equilibrium which is typically a good approximation, but more severely still small local gradients (Fig. 69).
Another approach to such problems is applying chemical kinetics which should deliver an appropriate treatment as long as the processes are Markovian. Then the flux is expressed as

$$j \propto k c_A(x) c_V(x') - k c_V(x) c_A(x'),$$

where the bracketed terms denote concentrations and the pre-factors of forward and backward rate coefficients measuring which fractions of the hopping attempts are successful and hence being proportional to the exponential of the activation free energy. As this is based on simple collision events, no interactions are included and the range of validity is as sketched in Fig. 68. Furthermore it is not seen how the driving force could be simply introduced. It is the non-equilibrium electrical potential difference (conveniently we normalize it with respect to ionic charge per $RT$) between $x$ and $x'$, i.e., $\delta \Delta \Psi$ that superimposes the profile and influences the activation free energy. If no compositional effects occur, Mott’s famous high-field equation

$$j \propto -\sigma \sinh (\delta \Delta \Psi/2)$$

results. (For insiders: This equation can also be interpreted as a Butler-Volmer equation with constant concentrations with the equilibrium exchange flux $j_0$, reducing to the equilibrium conductivity and transfer coefficients being 1/2.) If we also allow for concentration changes we can deduce from hopping kinetics [1]

$$j = j_0 \left( \frac{c_V(x') c_A(x)}{c_V(x) c_A(x')} \exp -\delta \Delta \Psi/2 - \frac{c_V(x) c_A(x')}{c_V(x') c_A(x')} \exp +\delta \Delta \Psi/2 \right) .$$

(8)

As we mentioned, $\delta \Delta \tilde{\mu}$ is the local driving force rather than $\delta \Delta \Psi$ in the general case. It is not straightforward to see how a symmetrical current equation could arise from Eq.(8) given the fact that the pre-factors to the exponential expressions are dissimilar. Yet it can be shown that a generalized current equation can be derived in the form [2]

$$j = -j_0 \sinh (zF \Delta \tilde{\mu}/RT) .$$

(9)

Note that $j_0$ corresponds to a generalized conductivity outside equilibrium. It is important to realize that such a simple equation is arrived at because $\Delta \tilde{\mu}$ has been referred to the difference in the electrochemical potentials of the charge carriers conceived as building units. While vacancies and regular A-ions are structure elements of which the ionic crystal is composed, the building element 'vacancy' refers to the 'difference' V-A expressing that creating a vacancy in a solid implies removing an A-particle and introducing a vacancy instead. While structure elements are the elements on which a kinetic description is built, it is the building elements to which a thermodynamic description has to refer and the consideration of which in the current equation provides a link between flux and thermodynamic driving force. The derived symmetrized current equation does now not only allow us to couple outer driving forces with local fluxes outside equilibrium under both electrical and compositional variations, it also allows one to introduce interactions (local thermal equilibrium presupposed). The range of validity of Eq.(9) is sketched in Figs. 68 and 69. This equation will be definitely helpful in adequately treating space charge effects or stoichiometric polarization effects in solids, in particular in nano-sized matter.


Electronic properties

Phase transitions and structural instabilities are intimately connected to electronic properties. A study of a one-dimensional spin system shows how thermal fluctuations can induce a Peierls instability due to a coupling to purely electronic degrees of freedom. A theory has been developed for the critical temperature close to a quantum critical point, based on a functional renormalization group approach. Nanostructures have attracted an increasing interest due to their fascinating electronic properties. A method has been developed for calculating optical properties and applied to quantum dots and wires. In an experimental contribution, it is shown how a quantum dot and a quantum wire can be combined to emit radiation in the optical frequency range in a well-defined spatial direction. Finally, it has been shown how Coulomb interaction can enhance the spin-orbit splitting, which explains the previously puzzling electronic structure of Sr$_2$RhO$_4$.

A novel type of Peierls instability in spin chains

J. Sirker, A. Herzog, A.M. Oleś and P. Horsch

Structural instabilities of electronic systems can occur due to the coupling of electronic and lattice degrees of freedom (phonons). They are particularly important for quasi one-dimensional (1D) systems where the gain in electronic energy due to a lattice distortion often outweighs the cost in elastic energy. A well-known example is the Peierls instability of the 1D free electron system towards a static lattice distortion determined by the Fermi momentum. For a commensurate distortion, an excitation gap is opened turning a metallic system into a band insulator. A related instability occurs for antiferromagnetic (AFM) spin chains coupled to phonons. The driving mechanism is the gain of magnetic energy by distorting the lattice which leads to the so-called spin-Peierls (SP) transition. Such a transition was discovered in CuGeO$_3$ in 1993 and has led to great interest in related phenomena.

In recent years evidence accumulated, resulting from a collaboration involving experimentalists and theoreticians at the Max Planck Institute for Solid State Research in Stuttgart, for a novel kind of Peierls instability which is not driven by spin-phonon coupling but rather by a coupling of the spins with electronic degrees of freedom (orbitals). This mechanism seems to be responsible for the unusual properties of YVO$_3$ observed in the finite temperature C-type AFM (C-AFM) phase [1], which could be described in the theory [2]. Remarkably, the proposed scenario involves a periodic modulation (dimerization) of a ferromagnetic (FM) spin chain driven by thermal fluctuations, while the ground state is the uniform FM state.

Recently, we tried to establish general mechanisms which can drive a Peierls dimerization in FM spin chains [3]. To highlight the differences between AFM and FM chains it is instructive to study first a coupling to lattice degrees of freedom. The phonons are often treated adiabatically which is justified if the phonon frequency is smaller than the Peierls gap. In the adiabatic approximation the Hamiltonian can be written as $H = H_{\text{mag}} + E_{\text{el}}$ with
\[ H_{\text{mag}} = J \sum_{j=1}^{N} \left\{ 1 + (-1)^{j} \delta \right\} \vec{S}_{j} \cdot \vec{S}_{j+1}, \]  

(10)

and \( E_{\text{el}} = NK\delta^2/2 \). Here \( J \) is the exchange constant, \( \vec{S}_j \) a spin \( S \) operator at site \( j \) (and \( \vec{S}_{N+1} = \vec{S}_1 \)), \( N \) is the number of sites, and \( K \) is the effective elastic constant. The dimensionless parameter \( \delta \in [0,1] \) is given by \( \delta = 2g u/(Ja_0) \) where \( g \) is the spin-phonon coupling constant, \( u \) the atomic displacement, and \( a_0 \) the lattice constant. From \( E_{\text{el}} = NKu^2/2 \) we find \( K = K J^2 a_0^2/(4g^2) \). Although the model, Eq.(10), is strictly 1D, the static, mean-field (MF) treatment of the three-dimensional phonons allows for a finite temperature phase transition if \( \delta(T) \) is treated as a thermodynamical degree of freedom determined by minimizing the free energy.

Using field theoretical arguments it is easy to show that the gain in magnetic energy for the AFM case (\( J > 0 \)) is proportional to \( E_{\text{mag}} \sim -\delta^4/3 \) and therefore outweighs the loss of elastic energy. For temperatures \( T < T_{\text{SP}} \), where \( T_{\text{SP}} \) depends on the microscopic constants, the system will therefore dimerize, resulting in \( \delta(T) \neq 0 \). The situation is completely different in the FM case (\( J < 0 \)). For \( \delta \in [0,1] \) the ground state is always the fully polarized FM state and a lattice distortion is therefore not favorable. What we were able to show by a combination of numerical and analytical methods, however, is that thermal fluctuations can activate a Peierls dimerization.

In Fig. 70 the phase diagrams for the \( S = 1/2 \) isotropic AFM and FM Heisenberg models as defined in Eq.(10) are shown. We obtained the phase boundaries and order parameters by minimizing the free energy using a density-matrix renormalization algorithm applied to transfer matrices (TMRG). This numerical method allows it to study the thermodynamic properties of 1D quantum systems directly in the thermodynamic limit. As expected, we find a dimerized phase at low enough temperatures in the AFM case for any value of the elastic constant \( K/|J| \) because the gain in magnetic energy will always win. For the FM, on the other hand, a dimerized phase exists only at finite temperatures and only if \( K/|J| < K_c/|J| \simeq 0.118 \).

Figure 70: Phase diagrams for the dimerized AFM and FM \( S = 1/2 \) Heisenberg chains. The dot-dashed line depicts the second-order SP transition from the uniform (U) to the dimerized (D) phase for the AFM chain. For the FM chain, the D phase exists only at finite \( T \) (in units of \( K_B = 1 \)) and only if \( K < K_c \approx 0.118|J| \) – the transition is either second or first-order, as shown by solid and dashed lines, respectively, and changes its character at the tricritical point (TCP). The insets show the order parameter \( \delta(T) \) for: (a) the FM chain with \( K/|J| = 0.1 \), and (b) the AFM chain with \( K/|J| = 2 \).

To understand why the dimerized phase is stable at all in the FM case, it is instructive to study the entanglement entropy of a weak (w) or a strong (s) bond with the rest of the system. The entanglement entropy is defined by 

\[ S_{\text{ent}}^{(w)} = - Tr \hat{\rho} \ln \hat{\rho}. \]

Here \( \hat{\rho} = Tr(E) \rho \) where \( \rho \) is the density matrix and the partial trace is taken over the environment (E) which consists of all the spins except of the two which form the considered bond. From the TMRG results shown in Fig. 71 it becomes clear that the existence of a dimerized phase in the FM case at finite temperature is related to a gain of entanglement entropy on the weak bonds. Simply speaking, the weakening of a FM bond allows for easier fluctuations and therefore increases the entropy and lowers the free energy. By using a modified spin-wave theory we could further show [3] that the gain in magnetic energy in this case is given by \( E_{\text{mag}} \sim -T^{3/2} \delta^2 \), i.e., it is proportional to \( \delta^2 \) as is the elastic energy. This explains the existence of a critical value \( K_c/|J| \) in Fig. 70.
Let us now come to the case where the Peierls instability of the FM chain is not driven by the lattice but rather by a coupling with orbital degrees of freedom. This mechanism is particularly important for transition metal oxides with perovskite structure where the valence electrons are situated in the \( t_{2g} \) orbitals. Because \( t_{2g} \) orbitals are not bond oriented, the electron-phonon coupling is weak so that we might ignore lattice degrees of freedom to first approximation. We will consider here the case of an effective spin \( S = 1 \) appropriate for systems with a \( 3d^2 \) valence electron configuration, as for example YVO\(_3\), and a twofold orbital degeneracy (as \( n_{xy} = 1 \) at each site) described by an orbital pseudospin \( \tau = 1/2 \). A 1D Hamiltonian reflecting the spin-orbital physics for such a system is given by

\[
H_{\text{Sr}} = J \sum_{<ij>} \left( \vec{S}_i \cdot \vec{S}_j + 1 \right) \left( \vec{\tau}_i \cdot \vec{\tau}_j + \frac{1}{4} - \gamma_H \right),
\]

where \( J > 0 \) is the superexchange energy and \( \gamma_H > 0 \) is proportional to the Hund’s coupling and promotes FM spin correlations. Using a MF decoupling, which is reasonable for FM spin correlations, we write \( H_{\text{Sr}} \approx H_S + H_{\text{c}} \), where \( H_S \) (\( H_c \)) is the Hamiltonian for the spin (orbital) sector, respectively. Note, however, that the two sectors are still strongly coupled to each other, see below.

If we allow for a dimerization in both sectors then \( H_{\text{Sr}} \) is – up to a constant – given by Eq.(10) with \( J \rightarrow J_{S(\tau)} \), \( \delta \rightarrow \delta_{S(\tau)} \), and \( S \) representing the spins \( S = 1 \) or the orbital pseudospins \( \tau = 1/2 \), respectively. The effective exchange constants are given by \( J_S = \Delta_{\tau\tau}/2 + 1/4 - \gamma_H \) and \( J_\tau = \Delta_{SS}/2 + 1 \), with

\[
\Delta_{SS} = \langle \vec{S}_{2j} \cdot \vec{S}_{2j+1} \rangle - \langle \vec{S}_{2j} \cdot \vec{S}_{2j-1} \rangle, \quad \Delta_{\tau\tau} = \langle \vec{\tau}_{2j} \cdot \vec{\tau}_{2j+1} \rangle - \langle \vec{\tau}_{2j} \cdot \vec{\tau}_{2j-1} \rangle,
\]

and \( \Delta_{\tau\tau} \) defined in a similar way. Strong quantum fluctuations for \( \gamma_H > 0 \) will favor AFM coupled orbitals, \( J_\tau > 0 \), and FM coupled spins, \( J_S < 0 \). The dimerization parameters are then given by \( \delta_{S} = \Delta_{\tau\tau} / (2 J_S) \) and \( \delta_{\tau} = \Delta_{SS} / (2 J_\tau) \). This means that the exchange constant and the dimerization for each sector are determined by the nearest neighbor correlations in the other sector and therefore have to be calculated self-consistently. The results we have obtained for \( \gamma_H = 0.1 \) – which is a realistic value for cubic vanadates – are shown in Fig. 72. We find a uniform solution, \( \delta_S = \delta_\tau = 0 \), both at low and at high temperatures, but at intermediate temperatures, \( 0.10 \lesssim T/J \lesssim 0.49 \), the self-consistent MF decoupling leads to finite values for \( \delta_{S(\tau)} \). The phase transitions at finite temperature between a uniform and a dimerized phase are a consequence of the MF decoupling. Such phase transitions would not occur for the strictly 1D
model, Eq.(11). Nevertheless, numerical calculations for this model [2] show that a dimerization is the leading instability at temperatures which support the dimerized phase in the MF decoupling solution.

Figure 72: Phase diagram and dimerization parameters $\delta_S, \delta_\tau$ for the spin-orbital model, Eq.(11) with $\gamma_{11} = 0.1$ in MF decoupling. The uniform and dimerized phases are separated by dashed lines.

To conclude, we have shown that a dimerization can occur in FM spin chains but has to be activated by thermal fluctuations. The gain in magnetic energy at finite temperatures can be related to an increased entanglement entropy on the weak bonds. For a FM chain with spin-phonon coupling we have derived the phase diagram as a function of temperature $T$, and shown that a dimerized phase is only stable in a range of weak effective elastic constant $K$. This type of Peierls instability might therefore, for example, be relevant for monatomic FM chains on surfaces [4], where the elastic coupling is presumably rather weak. For a system of coupled FM spin-1 and AFM orbital pseudospin-1/2 degrees of freedom we found, using a mean-field decoupling, a finite temperature dimerized phase. This shows that a dimerization is a universal instability of FM chains at finite temperatures, and may be triggered by the coupling to purely electronic degrees of freedom. This latter mechanism seems to be relevant for many transition metal oxides with (nearly) degenerate orbital states including the dimerized C-AFM phase of YVO$_3$ [1].


Critical temperature near quantum critical points

P. Jakubczyk, P. Strack, A. Katanin and W. Metzner

Several metallic materials undergo a zero temperature quantum phase transition as a function of a control parameter $\delta$ such as pressure, magnetic field or doping concentration. In various compounds, a line of finite temperature second-order phase transitions in the phase diagram terminates at a quantum critical point at $T = 0$. In such cases, strong quantum fluctuations influence the system also at finite temperatures, leading to anomalous behavior in the so-called quantum critical regime near the quantum critical point. Quantum criticality appears in several heavy fermion compounds and seems to play a role also in cuprate based high-temperature superconductors.

A widely used theoretical framework for the description of quantum criticality in metals is the Hertz-Millis theory [1], where, in the spirit of Landau’s theory of phase transitions, electronic
degrees of freedom are eliminated in favor of a collective order parameter field. Due to the quantum nature of fluctuations near a quantum critical point, the order parameter field fluctuates not only in space, but also in time, which leads to a frequency dependence in Fourier space.

The Hertz-Millis theory was originally formulated for the symmetric phase and does not capture the non-Gaussian classical fluctuations near the transition temperature $T_c$. The latter is estimated by the Ginzburg temperature $T_G$ in the literature, at which fluctuations start to interact strongly. One may ask whether $T_G(\delta)$ provides a good estimate for $T_c(\delta)$ near the quantum critical point at $\delta = \delta_0$. We have extended the Hertz-Millis theory to the symmetry-broken phase, including the regime governed by non-Gaussian fluctuations near $T_c$, and computed both $T_c(\delta)$ and $T_G(\delta)$ for comparison [2]. So far, our analysis is restricted to the case of a discrete broken symmetry, leading to a one-component order parameter $\phi$. This case applies, for example, to Ising type magnetic phase transitions and to orientation symmetry breaking.

The starting point for our calculations is a quantum version of the Landau-Ginzburg-Wilson action for phase transitions

$$S[\phi] = \frac{T}{2} \sum_{\mathbf{p},\omega_n} \int \frac{d^d p}{(2\pi)^d} \phi_{\mathbf{p},\omega_n} \cdot \left[ \frac{1}{|\mathbf{p}|^{z-d}} + \mathbf{p}^2 \right] \phi_{-\mathbf{p},-\omega_n} + U[\phi],$$

where $\phi_{\mathbf{p},\omega_n}$ denotes the order parameter field as a function of momentum $\mathbf{p}$ and frequency $\omega_n$. The dynamical exponent $z$, and also the spatial dimensionality $d$ is either two or three in most cases of interest. The potential $U[\phi]$ has the form

$$U[\phi] = \frac{u}{4!} \int _0 ^{1/T} d\tau \int d^d r [\phi(\mathbf{r},\tau) - \phi_0]^2,$$

where $\phi(\mathbf{r},\tau)$ denotes the order parameter field as a function of space and time, and $u$, $\phi_0$ are positive numbers. The potential is obviously minimal for $\phi = \pm \phi_0$. Expanding $U[\phi]$ around $\phi_0$ yields a quadratic term $\frac{1}{2} \delta \int _0 ^{1/T} d\tau \int d^d r [\phi(\mathbf{r},\tau) - \phi_0]^2$ with $\delta = u\phi_0^2/3$, and higher order terms (cubic and quartic). We will use $\delta$ as control parameter measuring the distance from the phase transition.

The partition function and other physical properties of the model defined by $S[\phi]$ can be written as a functional integral over all order parameter field configurations. Perturbation theory cannot be applied here, since infrared divergences due to critical fluctuations appear. In this situation it is mandatory to integrate over the order parameter configurations successively, proceeding step by step from large to small momenta (or frequencies). This successive integration gives rise to a renormalization group flow as a function of a cutoff scale $\Lambda$. A relatively simple set of approximate flow equations derived from an exact functional renormalization group equation [3] turned out to capture all the relevant features of the flow. The flowing effective action basically maintains the same form as given by Eqs.(13) and (14), but with flowing parameters $u$ and $\phi_0$. In addition, a flowing prefactor $Z$ has to be introduced in front of $\mathbf{p}^2$ in Eq.(13). The latter is important especially near $T_c$, where it captures the anomalous scaling dimension associated with non-Gaussian critical fluctuations.

In the symmetry-broken phase below $T_c$, the order parameter $\phi_0$ remains finite at the end of the flow (for $\Lambda \to 0$). Approaching $T_c$, the final value of $\phi_0$ tends to zero. Since fluctuations reduce $\phi_0$ in the course of the flow, the corresponding initial value of $\phi_0$ in the bare action is positive, and the control parameter $\delta$ corresponding to $T_c$ is thus positive, too. Inverting the results for $\delta(T_c)$ yields the transition temperature $T_c$ as a function of $\delta$. The value $\delta_0$, where $T_c(\delta)$ vanishes, marks the quantum critical point.
In Fig. 73 we show results for $T_c(\delta)$ for a dynamical exponent $z = 3$ in two and three dimensions. We also show the Ginzburg temperature $T_G(\delta)$ for comparison. The latter can be obtained from the scaling behavior of the order parameter as a function of the control parameter. In three dimensions, $T_c$ and $T_G$ almost coincide. Near the quantum critical point, $T_c$ follows the power law $T_c(\delta) \propto (\delta - \delta_0)^\psi$ with $\psi =\frac{3}{4}$, as derived for $T_G(\delta)$ already by Millis [1]. In two dimensions, a sizable window opens between $T_c$ and $T_G$ for $\delta > \delta_0$. However, $T_c$ obeys the same relation $\delta - \delta_0 \propto T_c \log T_c$ derived previously for $T_G$, so that the shape of $T_c(\delta)$ and $T_G(\delta)$ are qualitatively the same. The results for a dynamical exponent $z = 2$ are similar, with an exponent $\psi = 2/3$ in three dimensions.

It will be interesting to extend the analysis to the case of a broken continuous symmetry, where Goldstone modes will affect the critical behavior, and will complicate the theory substantially.


**Atomistic modeling of semiconductor nanostructures**

G. Bester, R. Singh and J. Peng

Semiconductor nanostructures form a new class of materials with a growing number of possible applications. They are used today in biology and medicine as light-emitting markers and can help to resolve structures and processes within the cells. They have a strong potential for providing efficient tunable light sources and light detectors. They are at the heart of the emerging fields of quantum teleportation, quantum cryptography and quantum information, where manipulations of the quantum state is the ultimate goal. These nanostructures, in the focus of nanotechnology, have dimensions of new nanometers to hundreds of nanometers. While they are ‘small’, they do comprise thousands to hundred thousands of atoms.
This state of matter constitutes a difficult challenge for theorists. The most common approach is to resort to a continuum description of the structures, i.e., the atomic resolution is dropped and an effective smooth potential replaces the atomistic crystal potential. However, the structures are often small enough so that the atomic scale (e.g., at interfaces) is important. The alternative is to use an atomistic description and approach the experimental sizes from the bottom-up. In the last few years, numerical and methodological developments [1] have enabled us to treat realistic (e.g., with experimental sizes, compositions and shapes) semiconductor nanostructures atomistically.

In Fig. 74(a) we show the square of the electron and hole wavefunctions of a heterostructure quantum wire and in Fig. 74(c) of a self-assembled lens shaped InAs/GaAs quantum dot. The different atomistic symmetries ($C_{2v}$ for the lens and $D_{2d}$ for the wire) lead to dif-
ferent spatial extent of the wavefunctions. In
the case of the dot, the [110] and [1¯10] di-
rections are inequivalent leading to the elonga-
tion of the electron P states \((e_1, e_2)\) in differ-
et directions, while the wavefunctions in the
wire have a higher symmetry. The optical spec-
trum of these structures can be calculated at the
correlated level using configuration interac-
tion [1]. The results are shown in Fig. 74(b) and
(d). Three groups of peaks can be distinguished,
originating from the optically allowed transi-
tions between electron and hole states with the
same orbital angular momentum S-S, P-P, and
D-D. A hereby important result is that the exci-
tonic line is unsplit (no fine-structure splitting)
in the case of the heterostructure wire on ground
of its symmetry. We suggest this structure as an
ideal candidate for the generation of entangled
photon pairs.

While the study of single nano-objects is still
on the forefront of the field, assemblies are be-
coming available and popular. Laterally cou-
pled quantum dots, with the ability to control
their position on a substrate, seems to be a
promising avenue. They can be used to study
fundamental effects and represent the realiza-
tion of a building block of future devices. We
studied the electronic and optical properties of
such systems with the emphasis on a quantita-
tive estimate of the degree of coupling between
the dots. We find that electrons tunnel between
the dots (with hopping matrix elements in the
range of 1 meV) while holes remain strongly lo-
calized. In Fig. 75(a) we plot the confinement
potential experienced by the electron in the lat-
erally coupled dots. The red line shows the path
connecting the left and the right dot fol-
lowing the floor of the potential valley. We can see that the en-
ergetic barrier between the dots is low, which is
partly due to the existence of a basin connect-
ing the dots. Moreover, the energetic position
of the electron states, drawn as blue line and la-
beled \(e_0, e_1\) in Fig. 75(b) is far above the barrier.

We conclude that the electrons are not tunnel-
coupled, as could be assumed in such a struc-
ture, but rather experience the potential of both
dots as a single contiguous entity. The holes, as
shown in Fig. 75(c), feel a wide potential barrier
that impedes effective tunneling.

023202 (2009).
A single semiconductor quantum dot can act as a model system for a solid-state implementation of an optical two-level system. These atom-like systems have potential applications as single-photon sources or quantum bit for quantum computing. However, the potential applications require efficient coupling of the quantum dot to optical waves that propagate into a well-defined direction. The dipole-like emission of a quantum dot is radiated into almost all directions, making an efficient collection of the light very difficult.

In the radio frequency range, antennas make it possible to direct the emission of an oscillator in a very controlled way towards the receiver. In the optical frequency range we do not have this possibility – up to now. Particle plasmons, e.g., collective resonant oscillations of the electrons in a metal nanoparticle, are a good candidate for antennas in the optical frequency range. Albeit, simple downscaling of concepts from radio waves is not possible, as, for example, losses in metals are much higher in the optical range.

In this project, a single GaAs quantum dot acts as ‘oscillator’, while the ‘antenna’ is a metal nanowire placed in the close vicinity. The antenna increases the local spectral mode density and modifies the emission rate of the quantum dot. Equivalently, one can interpret this effect as enhancement of the electric field around the nanowire due to the particle plasmon resonance of the metal’s free electrons. The top part of Fig. 76 shows the calculated field distribution around a thin gold nanowire on top of a GaAs substrate. The field is polarized perpendicular to the wire and resonant with the plasmon frequency of the wire. The field enhancement is strongly localized and extends some 10 nm away from the wire. Bottom: Angular emission of an optical dipole in different environments.

Only a small part of the radiation is emitted into the air halfspace (towards the top) as the index of refraction of GaAs is around 3.5. This makes it very difficult to couple the dot to a receiver.
which has to be on the air side of the substrate. Already the simple nanowire acts as an antenna and redirects the emission, as the strong lobe away from the wire indicates, and the overall emission rate is increased.

However, a metallic nanostructure close to an emitting dipole does not only modify the emission rate but also dissipates energy. The coherent oscillation of the metal’s free electrons is subject to losses which lead to a reduction of the energy flow into the optical far-field. An uncoupled quantum dot, e.g., without antenna, also possesses these so-called non-radiative channels by which it can dissipate energy without emitting photons. Defects at the surface of the wafer are one source. To quantify these processes, we examine the rates by which an excited quantum dot can revert back to the ground state. All processes that lead to a detectable photon in the optical far-field are called radiative processes and summed up in the rate \( k_{\text{rad}} \), and all processes that do not lead to a photon, the non-radiative processes, are summed up in the rate \( k_{\text{non-rad}} \). The experiment does not allow us to determine these two rates directly. We detect the emission intensity \( I \), e.g., the detection rate of photons from a single quantum dot at a given, fixed excitation rate \( I = I_0 k_{\text{rad}} k_{\text{non-rad}} \),

\[
I = I_0 \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{non-rad}}},
\]

where the constant \( I_0 \) depends on the excitation rate and the detection efficiency. The other quantity that we can detect is the luminescence lifetime \( \tau \), e.g., the average time the quantum dot spends in the excited state

\[
\tau = \frac{1}{k_{\text{rad}} + k_{\text{non-rad}}}. \]

We yield the luminescence lifetime by using time-correlated single photon counting (TC-SPC), e.g., by building histograms of the delay time between excitation of a single dot by a short laser pulse and the consecutive detection of a photon. The temporal resolution of the setup (about 30 ps) is sufficient to determine the luminescence lifetime in the order of 250 ps.

The measurement of single dot luminescence intensity and lifetime would be sufficient to calculate the radiative and non-radiative rates if the constant \( I_0 \) would be known or at least the same for all quantum dots. However, it varies from dot to dot, as both the excitation rate and the detection efficiency vary with the emission wavelength, among others. To circumvent this problem, we perform on each dot a control measurement without the coupling to the nanoantenna. That is possible as the coupling to the nanowire is polarization sensitive (Fig. 77). A nanowire shows a particle plasmon resonance only for polarization perpendicular to the wire. Within our spectral resolution, the two exciton states of a GaAs quantum dot are indistinguishable, but only one has the right polarization to couple to the nanowire. In \( s \)-polarization, we thus can measure the coupled properties \( I_s \) and \( \tau_s \), while the \( p \)-polarization serves as reference. Both polarizations have, however, the same excitation rate and detection efficiency, e.g., a common constant \( I_0 \).

Using the internal reference scheme, we can separate the influence of the antenna on the radiative rate from all other effects. Using

\[
k_{\text{rad},s/p} I_0 = \frac{I_{s/p}}{\tau_{s/p}}
\]

the relative, antenna-induced change \( \Delta k_{\text{rad}} \) in the radiative rate is calculated to

\[
\Delta k_{\text{rad}} = \frac{k_{\text{rad},s} - k_{\text{rad},p}}{k_{\text{rad},s} + k_{\text{rad},p}}.
\]
This quantity does not depend anymore on unknown experimental parameters and can be calculated from a single quantum dot’s photon statistics.

For the experiment, GaAs quantum dots with AlGaAs barriers were used [1]. An only 10 nm thick capping layer was grown to bring the quantum dots as close as possible to the metal nanowire antennas. We lithographically defined thin (about $30 \times 30 \text{nm}^2$) gold wires of $100 \mu\text{m}$ length on the sample’s surface. To increase the probability of coupling between the low-density quantum dots (about $1/\mu\text{m}^2$), the wires were arranged as a grating with a period of 330 nm, e.g., the maximum distance from a dot to the next wire is 165 nm. The quantum dots were excited non-resonantly with 150 fs laser pulses at 3.1 eV. Low-temperature (20 K) luminescence from single dots was collected by a microscope objective and detected by two avalanche photodiodes for the two polarization channels. After acquiring the luminescence map of a patch of the sample surface, we focused on a single dot and measured an excitation-detection delay histogram. That procedure was repeated for about 50 dots. For comparison, similar experiments were performed for slightly different wire geometries where the plasmon resonance of the wire does not coincide with the quantum dots exciton luminescence (1.73 eV).

Figure 78 shows the result for both resonant and non-resonant wires. When the plasmon resonance is not resonant with the quantum dot’s emission, the antenna cannot enhance the radiative rate, e.g., no difference between the rates in $s$- and $p$-polarization should occur. The bottom part of Fig. 78 shows that this is indeed the case, taking into account experimental noise. When the wire is resonant with the dot (top part of Fig. 78) a different behavior is observed. A large percentage of the dots shows a reduced emission rate ($\Delta k_{\text{rad}} < 0$) when being coupled to the antenna, but some dots also show an increased radiative rate. The cases of strong coupling, e.g., large absolute value of $\Delta k_{\text{rad}}$ occur only for an increased radiative rate. Model calculations based on field distributions as shown in Fig. 76 and the reciprocity theorem [2] agree very well with the measured data.

The experiment gives less events with a strong increase in radiative rate when compared to the model. This can be understood by taking into account the quantum dot position. For strong rate enhancement, the dots have to be very close to the metal nanowire. However, in that position also the non-radiative rate will be drastically increased as the metal quenches the dot’s luminescence. Dots in those positions will show a large, positive $\Delta k_{\text{rad}}$, but at the same time their total intensity is very low, as the non-radiative
rate $k_{\text{non-rad}}$ increases even more. Our experiment is biased, as one has to find the dots in the luminescence map to measure them.

In summary, we were able to show that self-assembled semiconductor quantum dots couple reproducibly to the plasmonic nanoantennas. The antenna modifies the radiative rate of the quantum dot exciton that is polarized perpendicularly to the wire. The analysis of the relative change in the radiative rate makes it independent from experimental uncertainties such as the detection efficiency and variations in the non-radiative rate. However, the influence of the latter is found in the clipped distribution of radiative-rate differences. In future experiments, we plan to measure the distance of the dot to the antenna in a direct way, so that we do not have to resort to histograms over many single quantum dots. The coupling of epitaxially grown dots to nanoantennas opens up the way for steering the directed emission of a single photon source towards, e.g., an optical fiber for long distance communication, or for coupling a dot to a plasmonic nanowire for sub-wavelength optics.

Coulomb-enhanced spin-orbit splitting: The missing piece in the Sr$_2$RhO$_4$ puzzle

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Since the discoveries of high-temperature superconductivity and colossal magnetoresistance in Mott insulators made metallic by hole-doping, 3$d$ transition metal oxides have remained at the forefront of research. Their many lattice and electronic (orbital, charge, and spin) degrees of freedom are coupled by effective interactions (electron-phonon, hopping, $t$, Coulomb repulsion, $U$, and Hund’s rule coupling, $J$), and when some of these are of similar magnitude, competing phases may exist in the region of controllable compositions, fields, and temperatures. The interactions tend to remove low-energy degrees of freedom, e.g., to reduce the metallicity. This rarely happens by merely shifting spectral weight from a quasiparticle band into incoherent Hubbard bands, as in the $U/t$-driven metal-insulator transition for the single-band Hubbard model, but is usually assisted by lattice distortions which break the degeneracy of low-energy orbitals and split the corresponding quasiparticle – or partly incoherent – bands away from the chemical potential.

When going from 3$d$ to 4$d$ transition metal oxides, the larger extent of the 4$d$ orbitals cause the hopping, $t$, and the coupling to the lattice to increase, and $U$ and $J$ to decrease. It was therefore hardly surprising that the Fermi surface (FS) of Sr$_2$RuO$_4$ measured by various techniques like dHvA and ARPES was in good agreement with LDA calculations, in which strong electronic correlations are only moderately represented. It was, however, surprising that substituting Rh for Ru, e.g. adding one electron and one nuclear charge and roughly keeping the crystal structure, lead to strong disagreement between experiments and LDA theory [1].


In both the ruthenates and the rhodenates the Fermi level crosses the $t_{2g}$ manifold, but in the latter, the interaction between the $xy$ and the $x^2-y^2$ orbitals due to the rotation of the RhO$_6$ octahedra around the z-axes is such as to gap those two bands at the Fermi level. As a consequence, only the equivalent 1D $xz$-and $yz$-bands, which hardly hybridize with the other $d$-bands nor with each other, remain at the Fermi level, with the single $t_{2g}$ hole distributed equally between them. However, also the LDA FS calculated for the proper structure deviates substantially from the experimental FS [1,2]. This discrepancy clearly seen in Fig. 79 (LDA) is disturbing because there is no experimental indication of any further distortion. Hence, Coulomb-enhanced crystal-field splitting can not be the solution to this puzzle.

We then performed ab initio LDA calculations including the SO coupling [3,4] and later also the on-site Coulomb effects in the LDA+U approximation. The results are shown in Fig. 79. As may be seen in Fig. 79 (LDA+SO), the agreement with ARPES is less good for the ab initio relativistic LDA FS: the SO splitting along $\Gamma M$ is too small. In fact, fitting the LDA+SO FS to our tight-binding model, yields essentially the same values for $t_{\pi}/e_F$ and $t_{\delta}/e_F$, but the SO-parameter $\zeta/e_F$ is smaller than $\zeta_{\text{ARPES}}/e_F$ by the large factor of 2.15. The LDA+SO calculation yields: $\zeta=0.13$ eV, a value which is smaller than the 0.16 eV obtained for elemental fcc Rh due to the $O\,p_z$ tails of the rhodate Wannier orbitals. The TB results in Figs. 80 and 81 are obtained with $\zeta=0$.

In order to enhance the SO splitting we performed relativistic LDA+U calculations with $U-J$ adjusted such as to give the best agreement with the ARPES FS. As is obvious from Fig. 79 (LDA+U+SO), this agreement is even more perfect than for TB+‘SO’.
The LDA+U+SO bands in Fig. 82 are well reproduced in the range from 0.15 eV below to 0.5 eV above the Fermi level by the TB+SO′ bands folded into the BZ/2 with corners at X. Features not reproduced are the tiny splittings due to in-plane $xz$-$xy$ hopping and out-of-plane hoppings neglected in our TB model. The agreement between the TB and the LDA calculation is less satisfactory, first of all because without SO-quenching the in-plane $xz$-$xy$ hopping produces a splitting along ΓM, and secondly because the rotation-induced $xy$-( $x^2-y^2$) gapping is not complete without SO coupling. In fact, it takes the LDA+U+SO to push the lower edges of the $xy$-( $x^2-y^2$) gap to −0.16 eV along ΓM, and even deeper along ΓX, locations close to those observed with ARPES [2]. Note finally, that the LDA+U alone, without SO coupling, brings little improvement compared with the LDA.

In conclusion, resolution of the Sr$_2$RhO$_4$ puzzle has taught us that although usually neglected in 4d-oxides, the spin-orbit coupling belongs to the list of competing interactions which cause the rich physics of these materials.


Figure 82: Band structure of Sr$_2$RhO$_4$ by DFT using different approximations.