Wissenschaftlicher Tätigkeitsbericht

Max–Planck–Institut für Festkörperforschung

Stuttgart – Grenoble


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About the hexagon on the titlepage

The background shows a false-color 2-dimensional powder diffraction diagram of the high pressure phase rubidium-IV which is stable for pressures between 17 and 20 GPa. The diagram was measured at European Synchrotron Radiation Source with diamond anvil cell pressure techniques. The foreground shows the crystal structure of Rb-IV, which was solved on the basis of the powder diffraction data. The structure is made up of columns of face-sharing square antiprisms formed by one subset of Rb atoms (16 per unit cell). One-dimensional channels in between the columns are occupied by a second subset of Rb atoms. The ordering of atoms within the channels is incommensurate with the framework. The figure illustrates the complex nature of crystal structures adopted by rubidium during the pressure-driven electronic transition from a nearly-free-electron metal to a monovalent d transition metal. [I–51]
In this report we try to give an impression of the very many activities that have characterized our research in 1999. In the first part, the white pages, we give a quite detailed presentation of some of the most relevant results from our Departments and Service Groups. In the colored pages that make up the rest of the book, we give a complete list of publications as well as other useful information on our Institute. Details can be found in volume 3/98 of the series ‘Berichte und Mitteilungen’ of the Max-Planck-Gesellschaft as well as on our web site ‘http://www.mpi-stuttgart.de’.

In 1999 the Department of Martin Jansen began to be fully operational, while the new colleagues Bernhard Keimer and Klaus Kern started the process of building their Departments, a process which will be completed by the end of the year 2000. 1999 also saw the retirement of Manuel Cardona, the last of the founding fathers of the Institute still in active service. We wish him all the best and will continue to consult with him on all matters. The vacancy of the ‘Theory II’ Department has not yet been filled but we hope that very soon a new director will be appointed.

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. This is even more remarkable in a year in which so many changes have taken place.

Stuttgart – Grenoble

DAS KOLLEGIUM

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THEORETICAL PHYSICS

Electronic structure calculations, as a help for understanding the properties of condensed matter, are the main activity in the department headed by ANDERSEN. This involves ab initio density-functional calculations, developing methods for performing such calculations, deriving correlated Hamiltonians from them, as well as solving these many-body Hamiltonians. In 1999, we suggested that the unusual phases of Rb, Cs, and Si discovered in the high pressure group, derive from the fact that, at the beginning of a series, the corresponding type of electron (4d, 5d, 4p) makes a contribution to the bond pressure, which changes from repulsive to attractive. As a consequence, in a certain range of external pressures bond lengths become slack (‘Early Slackness’). A generalization of the LMTO method to arbitrary order in the polynomial approximation of the energy dependence of the wave functions was developed. The LDA+U linear-response method for the calculation of dynamical spin-susceptibilities was applied to buckled CaCuO$_2$, a model high-temperature superconductor. The work on hyperfine fields for a series of HTSCs was continued, using Wannier rather than Bloch functions. The Anderson impurity Hamiltonian was obtained for various cuprates, the corresponding core-level photoemission spectra were calculated, and the dimensionality and connectivity of the cuprate networks were related to the core spectra. Dynamical Mean-Field Theory enabled us to understand the stability of, and the photoemission from, striped phases in the La$_2$CuO$_4$ system. The development of quantum Monte Carlo methods for models with electron-electron or electron-phonon interactions was continued and applied to alkali-doped fullerenes. A metal-insulator transition was studied, focusing on the interplay between the Coulomb interaction, the Jahn-Teller effect, the Hund’s rule coupling and the lattice structure. The screening properties were shown to be important for understanding the superconductivity. Calculation of the resistivity provided an explanation for the observed lack of saturation at high temperatures. [I–16, I–100]

The main activity of the department headed by PARRINELLO is the simulation of the properties of matter from first principles. To this end the department develops algorithms and computer codes that allow these goals to be achieved with the maximum possible efficiency and accuracy. The computer codes developed are used to simulate static and dynamical properties of large molecules, solids, liquids, disordered systems, chemical and biochemical processes and are widely used throughout the world in both academia and industry. The group develops and maintains two simulation codes, one of which is a plane wave pseudopotential code (CPMD) for ab initio molecular dynamics which is very mature and fully developed. The other is the QUICKSTEP code that is based on Gaussian basis functions and is less developed. From the methodological point of view we have added new computational tools to the CPMD code, such as the ability to compute Raman scattering and NMR chemical shifts. These developments are of particular relevance to the interpretation of dynamical and chemical properties of disordered and liquid anharmonic systems. The QUICKSTEP code has been further improved to the point that it is now competitive with the CPMD code for special applications. We have also extended its capabilities to perform all-electron calculations. We have for the first time applied this code to a practi-
cal problem by studying a polymerization reaction. Also the mixed \textit{ab initio} and classical molecular dynamics code has found application in various enzymatic reaction problems. The study of water and hydrogen-bonded systems has been continued, as has the study of systems under pressure. Of relevance is a study of the complex chemical process by which water and sodium react in the controlled environment of a molecular cluster beam. [I–48]

The theory department, previously headed by FULDE and HEDIN, is mainly concerned with the electronic correlation problem in solids such as high-T\textsubscript{c} oxides, manganites and vanadates. We consider charge transfer, Kondo-lattice, Holstein, Hubbard, $t-J$ and coupled spin-orbital models. The employed methods include exact diagonalizations both at zero and finite temperatures, 1/N and 1/d expansions (N and d denote the number of spin-components and spatial dimensions, respectively), the use of local correlation operators, self-consistent or ‘GW’-type approximations. Substantial amount of research has been carried out in 1999 on high-T\textsubscript{c} superconductors, manganites and vanadates. We obtained results for the pair formation, instabilities towards superconductivity, or the possible occurrence of other structural phases due to stripes, spin- and charge-density, or bond-order waves. The interaction of these structural phases with superconductivity have been investigated. Possible scenarios for the breakdown of Fermi liquid theory have been investigated as well as the question how realistic the employed simplified models actually are for a description of these systems. Another central point of investigations dealt with the physics of the manganites. The spin- and orbital-dynamics and the appearance of long-range orbital order have been studied and results for the optical conductivity in these systems have been obtained. In the many-body problem of photoemission, the adiabatic to sudden transition for core-electron photoemission has been investigated. [I–65, I–82]

**EXPERIMENTAL PHYSICS**

CARDONA’s department is mainly concerned with optical spectroscopy of \textit{semiconductors} and \textit{high-T\textsubscript{c} superconductors} in the form of bulk samples, surface layers, and low-dimensional structures like quantum wells, quantum dots and superlattices. Central to the interest of the group is electron-phonon interaction, a topic of particular relevance to both material classes. Experimental methods used at present are Raman, hyper-Raman and Brillouin scattering off and in resonance, hot luminescence, spectroscopic ellipsometry (including synchrotron radiation as a source), optical measurements in high magnetic fields and under high pressure, photoelectron spectroscopy, scanning tunneling microscopy in ultra-high vacuum and X-ray techniques for interface and surface structure analysis. Close collaborations with the synchrotron laboratories in Hamburg (HASYLAB), Berlin (BESSY), Grenoble (ESRF) and Brookhaven (NSLS), the high pressure, technology, molecular beam epitaxy and crystal growth service groups at the MPI, the High Magnetic Field Laboratory and the Institut Laue-Langevin (ILL) in Grenoble have enabled the group to extend the variety of experimental techniques at its disposal. Surface X-ray diffraction and X-ray standing wave measurements are carried out at HASYLAB, ESRF
and NSLS, while at BESSY a vacuum UV ellipsometer (5–35 eV) is operated. At NSLS a Fourier ellipsometer for the far infrared spectral range has been built and optimized for measurements of extremely small samples. At ILL neutron scattering is used to study the lattice dynamics of isotopically pure and disordered single crystals. There is also a substantial theoretical effort in computing the electronic and vibronic band structure as well as electron-phonon coupling parameters of the materials under investigation. Topics of recent activities of the group are the vibrational and electronic properties of various compound semiconductors and superlattices, in many cases with controlled isotopic composition, the structure of semiconductor surfaces in the UHV and at the electrolyte interface, as well as electronic Raman scattering processes and crystal field excitations in high-$T_c$ superconductors. Considerable effort, partly in collaboration with the University of California at Berkeley and the Kurchatov Institute (Moscow), is spent in the growth and characterization of crystals with tailor-made stable isotope composition which are used to investigate isotope effects on a wide range of physical properties such as phonon dispersion, lattice constant, electronic band structure or thermal conductivity. [I–111, I–114]

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 as well as in high magnetic fields, spectral ellipsometry (including synchrotron radiation as a source), and optical and X-ray measurements under high pressure and high magnetic fields. Experiments at external neutron sources (ILL, Saclay, Risoe and NIST) are carried out on a regular basis, and a spectrometer at the new research reactor FRM-II in Munich is under construction. The latter instrument will use 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 is a member of the CMC-CAT consortium operating an insertion-device synchrotron beamline at the Advanced Photon Source at Argonne National Lab (USA), and maintains close contact with research groups at the NSLS at Brookhaven National Lab (USA). At the NSLS, the group also operates a Fourier ellipsometer for the far infrared spectral range and a high-field magnet for X-ray diffraction. The group pursues several activities in semiconductors, in particular inelastic X-ray scattering (at ESRF, France), Raman and other optical studies of isotope effects, spin-flip Raman scattering and Raman scattering in low-dimensional systems. Close collaborations also exist with the crystal growth service group at the MPI where large, high-quality single crystals of oxide compounds are prepared with state-of-the-art optical furnaces, as well as with the high pressure and technology service groups. [I–68, I–80]
Research efforts in the 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 ultra-thin 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 nanometer scale as well as tools to manipulate and assemble nanoobjects are developed. Of particular interest are: fundamentals of epitaxial growth and 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. [I–33, I–104]

Electronic properties of heterostructures, quantum wells, superlattices and molecular systems, 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 20 Tesla and temperatures down to 20 mK are used to characterize the systems. The quantum Hall effect is studied by analyzing electrical breakdown, time-resolved transport, edge channels and the behavior of composite fermions. Electron-phonon interactions in low-dimensional systems and the phonon transmission through interfaces are investigated with ballistic phonon techniques. Time-resolved photoconductivity, luminescence, and Raman measurements in magnetic fields are methods of characterizing the low dimensional electronic systems. A strong current interest is the preparation of nanostructures either by self-organized growth or by lithographic and synthetic routes (nanotubes and other synthetic nanoparticles) and the investigation of coupled two- and zero-dimensional electronic systems (electron drag, Kondo resonances, single electron transistor). The experiments are supported within the group by theoretical investigations of the transport and dynamic response of these low-dimensional electronic systems. [I–89, I–93, I–106]

WYDER’s department of our institute operates jointly with the French Centre National de la Recherche Scientifique (C.N.R.S.) the Grenoble High Magnetic Field Laboratory. During the first couple of years, there were two separate laboratories, the French and the German part, respectively; these have then been put together into one single laboratory on the basis of a contract for collaboration, Frenchmen and Germans working together, with one director and one single technical and scientific policy. This contract of collaboration between the C.N.R.S. and the MPG will expire at the end of 2004. The aim of the laboratory is to provide high magnetic fields with a wide range of scientific instrumentation (temperatures 30 mK to 1000 K, pressures up to 24 GPa, voltages nV to 50 kV, currents pA to several kA, etc.) allowing many interesting investigations. In the years 1990/1991, most of the technical installations were renewed and the dc-power supply was extended from 10 MW to 25 MW. We now have one of the world’s most modern power and cooling
installation for the generation of high magnetic fields in operation with a 20 MW resistive magnet producing a world record field of 30 Tesla in a bore of 5 cm. In addition, the MPG and the C.N.R.S. have decided to finance a new hybrid system for fields in the 40 Tesla range which will be working around the year 2001. All these magnets guarantee the leading role of the Grenoble-HML also in the years to come. In accordance with its mission, the in-house research at the HML shows a considerable diversification into several fields in condensed matter physics, where the use of high magnetic fields is interesting or necessary, such as the study of metals, semiconductors, 2D electronic systems, magneto-optics, high-field NMR and ESR, polymers and all sorts of soft matter and even some biological systems. [I–35]

SOLID STATE CHEMISTRY

Basic research in the field of preparative solid state chemistry with the goal of developing modern materials is the main emphasis of JANSEN’s department. Classes of materials currently under investigation include oxides and nitrides of nonmetals as well as fullerenes, e. g., new binary and ternary oxides synthesized under high oxygen pressure, superconducting oxides, 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, or by electrochemical methods. Besides optimizing the syntheses of these materials, 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 analysis serves as 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 predictive power of solid state chemistry, i. e., 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 using global optimization techniques, while on the preparative side kinetically controlled types of reactions that allow low-temperature synthesis of (possibly metastable) compounds, e. g. electrochemical reactions or the use of molecular precursors, are being developed. [I–24, I–39]

MAIER’s department is concerned with physical chemistry of the solid state, more specifically with chemical thermodynamics and transport properties. Of particular interest are ion conductors (such as proton, metal ion and oxygen ion conductors) and mixed conductors (especially perovskites). A major theme is the understanding of mass and charge transport, chemical reactivities and catalytic activities in relation to defect chemistry. Besides the clarification of local properties in terms of elementary mechanism, also their interplay to produce the overall system properties is investigated (inhomogeneous systems, espe-
cially multiphase systems and functional ceramics). In this context interfaces and nanosystems are in the focus of interest. The research ranges from atomistic considerations and phenomenological modeling to electrochemical and thermochemical experiments. Since electrochemical investigation immediately affects the coupling of chemical and electrical phenomena, the research is directed towards both basic solid state problems as well as energy and information technology (fuel cells, chemical sensors). [I–27, I–30, I–45]

SIMON’s department emphasizes the investigation of metal-rich compounds (main group metals, \(d\) and \(f\) metals). The purpose of the work is on the one side the development of concepts of structure and bonding (e. g., systematization of condensed cluster concept) and on the other side the search for new materials (e. g., metal-rich compounds, transition metal clusters, reduced rare earth halides, hydride, carbide, boride and boride carbide halides of the rare earth metals, alkali metal suboxides and alkaline earth subnitrides), phase relationships and relations between structure, chemical bonding and properties. Electron crystallography develops into a powerful tool in characterizing microcrystalline phases up to full structure refinement. Superconductivity is of special interest following a chemical view of the phenomenon in terms of a tendency towards pairwise localization of conduction electrons. Other fields of interest are structures of molecular crystals (in situ grown crystals of gases and liquids). Experimental techniques like diffractometry with X-rays and neutrons, XPS, UPS, HRTEM and measurements of magnetic susceptibility as well as electrical transport properties are used. [I–43, I–85]

**SERVICE GROUPS**

The CHEMIESERVICE GROUP (Kremer) develops techniques and provides experimental facilities to support all experimental groups of the institute with the characterization of the transport and magnetic properties of new compounds and samples. This objective requires a high versatility of all experimental methods including the development and cultivation of experimental setups to perform measurements on very small samples by contactless methods under inert gas conditions. Available are commercial SQUID magnetometers, ac-susceptometers which allow measurements down to 0.3 K and magnetic fields up to 12 Tesla, a contactless microwave transport method, ac- and dc-electrical transport measurements in magnetic fields up to 12 Tesla and temperatures down to 0.3 K. Materials currently under particular investigations are novel superconductors, unusual magnetoresistive materials, low dimensional and frustrated magnetic systems and intermetallic rare earth compounds. [I–70]

The COMPUTER SERVICE GROUP (Burkhardt) supports about 230 workstations in the departments and service groups of the institute. The services include hardware planning and maintenance, installation and administration of various UNIX-based operating systems (AIX, True64 Unix, HP–UX, Linux, Solaris and IRIX) and a common application software server for these systems. Furthermore the group administers 2 parallel computers (30-node
IBM SP/2 and 20-node CRAY T3E) for the Andersen and Parrinello theory groups, as well as several hundred PCs. The PC hard and software standard has been continuously adapted to the rapidly changing market. The use of free software like, e.g., the Linux operating system and the PC-Unix integration software Samba is growing dramatically. The ADSM backup and archive service is becoming increasingly popular as well, resulting in a total storage volume of 2.5 Terabyte at the end of 1999. The network has been modernized in close collaboration with the network support group (Winker), based on a new structured fiber-optic cabling scheme throughout the institute.

The CRYSTAL GROWTH GROUP (Schönherr) applies, modifies and develops techniques, such as Bridgman, top seeding, and traveling solvent floating zone (TSFZ with mirror furnace) methods to grow single crystals from the melt or solution. Typical examples are colossal magnetoresistance (CMR) oxides (RE1−xPbxMnO3, RE = rare earth), and superconducting oxides (REBa2Cu3O7−δ, RE2−xMxCuO4, Bi2Sr2Cax−1Cu4Oy, with n = 1 or n = 2 and M = Sr, Ce, Cd). The oxygen concentration of some oxide crystals is adjusted to thermo-gravimetrical technique. Gas phase methods are modified to grow crystals of II-VI and III-V compounds with defined isotopic components from low amounts of source materials. The growth kinetics and growth forms of crystals grown from the vapor are quantified by in situ observation. For optimizing the crystal growth from the vapor phase, vapor pressures and binary gaseous diffusion coefficients are experimentally determined. [I–74]

Research within the HIGH PRESSURE 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. The primary experimental methods are synchrotron X-ray diffraction and low-temperature optical spectroscopies. Materials currently under investigation are semiconductors and their heterostructures, transition metal oxides and inorganic low-dimensional solids. Laboratory facilities for optical spectroscopy and X-ray diffraction under pressure are available for use by other scientific groups (in-house and external). Pressure experiments in various research groups are supported through design and maintenance of pressure equipment. [I–51, I–56]

The X-RAY DIFFRACTION GROUP (Peters) is in charge of taking care of X-ray sources and diffraction cameras belonging to the ‘Röntgenpool’. Nondestructive investigations on single crystals and on powder samples can be performed with film exposing methods. For extended X-ray diffraction measurements of single crystals, four-circle diffractometers are available. The SIEMENS SHELXTLPLUS system is employed for solving, refining and displaying crystal structures from diffraction data.

The OPTICS AND SPECTROSCOPY GROUP (Kuhl) develops new optical instruments and components and measures optical properties of solid, liquid and gaseous samples. Available are grating and Fourier spectrometers for absorption and reflectivity studies within the spectral range from 180 nm to 1 mm wavelength. Investigations of optical properties of high-Tc superconducting materials have been emphasized. The construction and operation of optical instruments in other groups is supported by technical advice. The
research concentrates on generation of pico- and femtosecond optical pulses, as well as on studies of ultrafast relaxation of nonequilibrium carriers, excitons and phonons in semiconductors. Short optical pulses are used to generate and analyze pico- and subpicosecond electrical pulses by means of photoconductive switching and electro-optic sampling. These techniques are applied for characterization of high speed electronic and optoelectronic devices and coherent THz-spectroscopy on high-\textit{T}_c superconductors. [I–118]

Main subject in the MBE GROUP (Eberl) is the preparation and characterization of III/V and group IV semiconductor heterostructures. We apply molecular beam epitaxy (MBE) for the material systems (Al,Ga)As/GaAs, (In,Ga)As and (Al,In,Ga)P on GaAs substrate, and (Si,Ge)/Si on Si substrate. Our main interest is the preparation of low-dimensional structures. Lateral confinement is achieved by MBE-growth on patterned substrates, and by island formation in epitaxial growth of strained heterostructures. We are also investigating an atomically defined in situ etching technique based on AsBr$_3$ within the MBE system. The group IV element MBE activities are concentrated on the preparation of Si$_{1-x-y}$Ge$_x$C$_y$ alloy layers and Si/(Si,Ge) Esaki-diodes for new Si based devices. [I–108]

The TECHNOLOGY GROUP (Habermeier) offers service work in the fields of thin film deposition technologies, microlithography and fabrication of contacts to semiconductors and ceramic materials. The experimental facilities for the thin film work include the conventional high vacuum evaporation and sputtering (dc, rf and reactive) techniques. Additionally, pulsed laser deposition facilities are installed to prepare thin films with complex chemical composition such as high-temperature superconductors, perovskites with colossal magnetoresistance and ferroelectric materials. In the area of microlithography, simple masks with design rules down to 5 \textmu m can be realized in one photoreduction step. Recently, a Laser Mask Macro Projector has been installed which offers the possibility for improved mask making and direct, chemistry-free thin film patterning. The etching techniques available include wet chemical etching, ion milling and plasma etching as well. The research activities of the group are closely related to the service tasks. Thin film deposition of doped Mott insulators such as high-temperature superconductors and doped rare earth manganites exhibiting colossal magnetoresistance plays a central role. Pulsed laser deposition and rf sputtering are the techniques applied. The main focus of interest is currently the systematic study of epitaxial strain and associated defect creation at the substrate/film interface and their effect on the transport properties of the films. [I–62]

The LOW TEMPERATURE GROUP (Gmelin) comprises the research laboratory (TTL) and a technical service group (TTS), the latter belonging to the Max-Planck-Institut für Metallforschung. The research activities in TTL focus on the investigation of thermal properties of solids. Specific heat, thermal conductivity and thermal expansion are measured between 0.3 K and 320 K and partially within applied magnetic fields up to 16 Tesla; specific heats can be investigated up to 1700 K. Small samples (mg-range) are measured with a high-precision adiabatic-differential-scanning calorimeter. In 1999, with preference magnetic and electronic phase transitions have been studied by specific heat experiments. Members of the TTL were specifically engaged in working out interna-
tional standards for calibration of thermal analysis equipment in the cooling and heating modes. In TTS the service is currently offered for technical gases, vacuum pumps, liquid nitrogen and liquid helium supply, and for any type of cryogenic construction and design, e.g., ultra-high-vacuum cooling systems, nanometer and nanosecond resolving thermal systems (thermometers) and liquid helium cooled atomic-force-microscopy, documentation and consulting. About 220,000 liters of liquid helium were liquefied and distributed in 1999. [I–60]
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Developments in methods

Advances in our understanding of the solid state are driven by the development of new methods. The NMTO method allows the derivation of minimal basis sets for electronic structure calculations that are intelligible and accurate at the same time. The exploration of energy landscapes in configuration space helps to characterize structures and to understand structural transitions. By introducing generalized equivalent currents, chemical and electrical effects in solids can be dealt with on the same footing. With a novel optical method chemical transport across grain boundaries can be monitored \textit{in situ}. Finally it is shown how the femtosecond lifetimes of quasiparticles at metal surfaces can be measured using a scanning tunneling microscope.

Muffin tin orbitals of arbitrary order

O.K. Andersen, T. Saha-Dasgupta, C. Arcangeli, R.W. Tank, G. Krier, O. Jepsen and E. Pavarini

Introduction: For electrons in condensed matter, it is often desirable to express the single-particle wave functions, $\Psi_i(r)$, with energies $\varepsilon_i$ in a certain range in terms of a minimal set of state- and energy-independent orbitals, $\chi_{RL}(r)$. Here, $R$ spans the sites, and $L$ the local symmetry (e.g. $L \equiv \text{Im}$). A few examples: (a) In a crystal, the electrons belonging to an energy band which does not overlap any other band are most simply described in terms of the Wannier functions, $\chi(r-R)$, with $R$ spanning the lattice translations. (b) Model Hamiltonians are usually expressed in representations which for the electrons are assumed to be minimal and orthonormal. (c) In a density-functional calculation, the use of a minimal basis set for solving the Schrödinger equation self-consistently would ease the interpretation of the results and speed up the calculation. For realistic systems, however, it is hard to obtain a minimal basis of useful accuracy.

We have derived a general method for obtaining such minimal basis sets for cases where the wave functions are solutions of a Schrödinger equation which is locally separable,

\[ \mathcal{H}\Psi_j(r) = [-\Delta + V(r)]\Psi_j(r) = \varepsilon_j\Psi_j(r), \tag{1} \]

specifically, where the potential has the muffin tin form: $V(r) = \sum_R v_R(|r-R|)$. This work is part of an ongoing effort to develop an electronic-structure method which is generally applicable, intelligible, and computationally fast and accurate.

A MT potential divides space into MT spheres with radii $a_R$, where the potential is spherically symmetric, and a rest, the interstitial, where the potential is flat (zero). Inside each sphere and in the interstitial one may solve Schrödinger’s differential equation (numerically) for an energy, $\varepsilon$, chosen in the range of interest. In case the resulting partial solutions, $\phi(\varepsilon, r)$, can be matched continuously and differentiably at the spheres, they form
a wave function, $\Psi_I(\mathbf{r})$, with $\varepsilon_i = \varepsilon$. Such matching schemes (e. g. those of Wigner and Seitz and of Korringa, Kohn, and Rostoker (KKR)) are not very practical, however. Instead, we want to use the $\phi(\varepsilon, \mathbf{r})$'s to construct a set of energy-independent orbitals, $\chi^{(N)}(\mathbf{r})$, which span any wave function with energy $\varepsilon_i$ in the neighborhood of $N + 1$ chosen energies, $\varepsilon_0, \ldots, \varepsilon_N$, to within an error proportional to $(\varepsilon_i - \varepsilon_0) \ldots (\varepsilon_i - \varepsilon_N)$. Specifically, if the energy mesh is condensed onto one energy, $\varepsilon_0$, the error of a wave function with energy $\varepsilon_i$ will be proportional to $(\varepsilon_i - \varepsilon_0)^{N+1}$. These orbitals we call Nth-order muffin tin orbitals, or NMTOs. Note that N does not influence the size of the NMTO basis set, but the range of the individual orbitals. Let us now work this out in more detail.

**Kinked partial waves:** Inside the sphere at $\mathbf{R}$, the partial solutions are $\varphi_RI(\varepsilon, |\mathbf{r} - \mathbf{R}|) Y_L(\hat{\mathbf{r}}_R) \equiv \varphi_RI(\varepsilon, r_R) Y_L(\hat{r}_R)$, where the energy-dependent function is the regular solution of the radial Schrödinger equation. In the interstitial region, we use those solutions of the wave equation, $(\Delta + \varepsilon) \psi_{RL}(\varepsilon, \mathbf{r}) = 0$, which satisfy the following homogeneous boundary condition: The projection of $\psi_{RL}(\varepsilon, \mathbf{r})$ onto $\delta(R_R' - a_{RL}) Y_L(\hat{r}_{R'})$ is $\delta_{RL'} \delta_{L L'}$. As an example, $\psi_{RL}(\varepsilon = 0, \mathbf{r})$ is the electrostatic potential from a $2l$ multipole centered at $\mathbf{R}$ when all other spheres are grounded. The $\psi_{RL}(\varepsilon, \mathbf{r})$'s are called screened spherical waves. In fact, only those with $RL$ corresponding to the so-called active channels will be used, and only the projections onto other active channels vanish. For the projection of the screened spherical wave onto an inactive channel, the radial logarithmic derivative equals that of the solution to the radial Schrödinger equation. We can now form the set of so-called kinked partial waves: The kinked partial wave, $\phi_{RL}(\varepsilon, \mathbf{r})$, is $\varphi_{RL}(\varepsilon, r_R) Y_L(\hat{r}_R)$ inside its own sphere and for its own angular momentum. It is $\psi_{RL}(\varepsilon, \mathbf{r})$ in the interstitial region and, inside the sphere at $\mathbf{R}'$, it vanishes for any other $(R'L' \neq RL)$ active channel, but it is proportional to $\varphi_{RL'}(\varepsilon, r_{R'}) Y_L(\hat{r}_{R'})$ for an inactive channel. As a result, $\phi_{RL}(\varepsilon, \mathbf{r})$ is continuous (we normalize the radial solutions of the active channels such that $\varphi_{RL}(\varepsilon, a_R) \equiv 1$) and is a solution of Schrödinger’s equation with energy $\varepsilon$. But it has kinks at the spheres in the active channels and is therefore not a wave function.

![Si p kinked partial wave](image1)

![Si p Imto](image2)

Figure 1: $Si p_{x=y=z}$ kinked partial wave (KPW) and linear muffin tin orbital (LMTO).
The solid curve in the left-hand part of Fig. 1 shows the Si $p_{x-y-z}$ kinked partial wave for $\varepsilon$ in the middle of the valence band and for $\mathbf{r}$ along the [111]-line in the diamond structure from the central Si atom, through the nearest Si neighbor, and half-way into the back-bond void. The other curves will be explained later. The kinks at the $a$-spheres are clearly seen. Since this kinked partial wave is designed for use in a minimal $sp^3$-basis, only the Si $s$ and $p$ waves were chosen as active. The inactive partial waves – most notably Si $d$ – must therefore be provided by the tails of the kinked partial waves centered at the neighbors, and this is the reason for the strong Si $d$-character seen inside the nearest-neighbor sphere. Had we been willing to keep Si $d$-orbitals in the basis, the Si $d$-channels would have been active so that only partial waves with $l>2$ would have remained inside the neighbor spheres, whereby the kinked partial wave would have been more localized. Hence, the price for a smaller basis is a longer spatial range and a stronger energy dependence.

**Kink matrix and matching equations:** The central quantity of the present formalism is the Hermitian kink matrix, whose element $K_{RL',RL}(\varepsilon)$ is defined to be the kink of $\phi_{RL}(\varepsilon, \mathbf{r})$ at the $a_{RL}$-sphere, projected onto $Y_{L'}(\hat{r}_R)/a_{RL}^2$. Hence, it specifies how the Hamiltonian (1) operates on the set of kinked partial waves:

$$ (\mathcal{H}-\varepsilon) \phi_{RL}(\varepsilon, \mathbf{r}) = -\sum_{RL'} \delta(r_{RL'}^2 - a_{RL}) Y_{L'}(\hat{r}_{RL'}) K_{RL',RL}(\varepsilon). $$

(2)

Although an individual kinked partial wave is not a wave function, any smooth linear combination, $\sum_{RL} \phi_{RL}(\varepsilon, \mathbf{r}) c_{RL,i}$, is. Schrödinger’s equation may therefore be formulated as the matching- or kink-cancellation condition:

$$ \sum_{RL} K_{RL',RL}(\varepsilon_i) c_{RL,i} = 0 \quad \text{for all } R'L', $$

(3)

which is a set of homogeneous linear equations, equivalent with the KKR equations. Here, the indices run only over active channels. Since the kink-matrix is expensive to compute, it is not efficient to find a one-electron energy from $\det|K(\varepsilon_i)|=0$, and then solve the linear equations for the corresponding $c_{RL,i}$, but to construct an energy- and state-independent basis set of NMTOs, and then solve the generalized eigenvalue problem,

$$ \sum_{RL} \left< \chi_{RL}^{(N)} | \mathcal{H} | \chi_{RL}^{(N)} \right> c_{RL,i} = \varepsilon_i \sum_{RL} \left< \chi_{RL}^{(N)} | \chi_{RL}^{(N)} \right> c_{RL,i} \quad \text{for all } R'L', $$

(4)

resulting from the Raleigh-Ritz variational principle.

**MTOs with $N=0$:** Since all wave functions with a certain energy may be expressed as linear combinations of the kinked partial waves with the same energy, the MTOs with $N=0$ are simply the kinked partial waves at the chosen energy: $\chi_{RL}^{(0)}(\mathbf{r})=\phi_{RL}(\varepsilon_0, \mathbf{r})$. In the basis of these, the Hamiltonian and overlap matrices are given by respectively:

$$ \left< \chi^{(0)} | \mathcal{H} - \varepsilon | \chi^{(0)} \right> = -K(\varepsilon_0) \quad \text{and} \quad \left< \chi^{(0)} | \chi^{(0)} \right> = \hat{K}(\varepsilon_0), $$

(5)

as may be found from Eq.(2) and the normalization. Here, $\varepsilon \equiv \partial / \partial \varepsilon$. The energy solutions of the generalized eigenvalue problem (4) have errors proportional to the square of the wave-function errors, that is, $\propto (\varepsilon_i - \varepsilon_0)^2$ when $N=0$. This also follows trivially from the fact that Eqs.(4)–(5) are merely the energy-linearization of the matching equations (3).
Green matrix and MTOs with $N > 0$: In order to construct MTOs with $N > 0$, it is useful first to define a Green matrix as the inverse of the kink matrix: $G(\varepsilon) \equiv K(\varepsilon)^{-1}$. As seen from (3), its poles are the one-electron energies. Next, by an equation of the usual type: $(\mathcal{H} - \varepsilon) \gamma_{RL}(\varepsilon, \mathbf{r}) = -\delta(r_{RL} - a_{RL}) Y_{L}(r_{R})$, we define a Green function, $\gamma_{RL}(\varepsilon, \mathbf{r})$, which has one of its spatial variables confined to the $a$-spheres, i.e. $\mathbf{r}' \rightarrow RL$. Considered a function of $\mathbf{r}$, this confined Green function is a solution with energy $\varepsilon$ of the Schrödinger equation, except at its own sphere and for its own angular momentum where it has a kink of size unity. This kink becomes negligible compared to the value of the function when $\varepsilon$ is close to a one-electron energy because the Green function has a pole there. Equation (2) shows that $\gamma(\varepsilon, \mathbf{r}) = \phi(\varepsilon, \mathbf{r}) G(\varepsilon)$. Here, and in the following, lower-case letters denote vectors and upper-case matrices ($\varepsilon$, $\varepsilon$, $RL$, and $N$ are numbers, though). The confined Green function is thus factorized into a Green matrix, $G(\varepsilon)$, which has the full energy dependence, and a vector of functions, $\phi(\varepsilon, \mathbf{r})$, which has the full spatial dependence and a weak energy dependence. The kind of energy range we are considering is such that for two energies within the range, $\phi_{RL}(\varepsilon, \mathbf{r})$ and $\phi_{RL}(\varepsilon', \mathbf{r})$ are never orthogonal. Finally, we want to factorize the $\mathbf{r}$ and $\varepsilon$-dependencies completely and, hence, approximate the confined Green function by $\chi^{(N)}(\mathbf{r}) G(\varepsilon)$. Subtracting from the Green function a function which is analytical in $\varepsilon$, obviously produces an equally good Green function, $\phi(\varepsilon, \mathbf{r}) G(\varepsilon) - \omega^{(N)}(\varepsilon, \mathbf{r}) \equiv \chi^{(N)}(\varepsilon, \mathbf{r}) G(\varepsilon)$, in the sense that both yield the same Schrödinger-equation solutions. If we can therefore determine the vector of analytical functions in such a way that each $\chi^{(N)}_{RL}(\varepsilon, \mathbf{r})$ takes the same value, $\chi^{(N)}_{RL}(\mathbf{r})$, at all $N + 1$ energies, $\varepsilon_0$, ..., $\varepsilon_N$, then

$$
\chi^{(N)}_{RL}(\varepsilon, \mathbf{r}) = \chi^{(N)}_{RL}(\mathbf{r}) + O((\varepsilon - \varepsilon_0) \ldots (\varepsilon - \varepsilon_N)),
$$

and, hence, $\chi^{(N)}(\mathbf{r})$ is the set of NMTOs. Now, since $\chi^{(N)}(\varepsilon_0, \mathbf{r}) = ... = \chi^{(N)}(\varepsilon_N, \mathbf{r})$, the $N$th divided difference of $\chi^{(N)}(\varepsilon, \mathbf{r}) G(\varepsilon)$ equals $\chi^{(N)}(\mathbf{r})$ times the $N$th divided difference of $G(\varepsilon)$. Moreover, if we let $\omega^{(N)}(\varepsilon, \mathbf{r})$ be a polynomial in energy of $(N-1)$st degree, its $N$th divided difference on the $\varepsilon_0, ..., \varepsilon_N$-mesh, $\Delta^N \omega^{(N)}(\mathbf{r}) / \Delta[0...N]$, will vanish. We have therefore found the following solution for the NMTO set:

$$
\chi^{(N)}(\mathbf{r}) = \frac{\Delta^N \phi(\mathbf{r}) G}{\Delta [0...N]} \left[ \frac{\Delta^N G}{\Delta [0...N]} \right]^{-1} = \sum_{n=0}^{N} \phi(\varepsilon_n, \mathbf{r}) L^{(N)}_n = \chi^{(N)}_{RL}(\mathbf{r}) + \frac{\Delta \phi(\mathbf{r})}{\Delta [N-1, N]} (E^{(N)} - \varepsilon_N) + ... + \frac{\Delta^N \phi(\mathbf{r})}{\Delta [0...N]} (E^{(1)} - \varepsilon_1) \ldots (E^{(N)} - \varepsilon_N).
$$

Here, the second expression may be interpreted as Lagrange interpolation of the energy-dependence of the kinked partial-wave set, but with the weights, $L^{(N)}_n$, being energy-independent matrices rather than $N$th-degree scalar polynomials in energy. Similarly, the last expression may be interpreted as Newton interpolation (Taylor expansion for a condensed mesh) with the energies substituted by (non-commuting and non-Hermitian) energy-independent matrices, $E^{(M)}$. Using the well-known expression:

$$
\frac{\Delta^N G}{\Delta [0...N]} = \sum_{n=0}^{N} \frac{G(\varepsilon_n)}{\prod_{m=0, \neq n}^{N} (\varepsilon_n - \varepsilon_m)} \rightarrow \frac{1}{N!} \frac{d^N G(\varepsilon)}{d\varepsilon^N} \bigg|_{\varepsilon_n},
$$

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for a divided difference, these matrices are seen to be given by:

\[ L_n^{(N)} = \frac{G(\epsilon_n)}{\prod_{m=0}^{N} \neq n (\epsilon_n - \epsilon_m)} \left[ \frac{\Delta^N G}{\Delta[0\ldots N]} \right]^{-1}, \]

\[ E^{(N)} = \epsilon_N + \frac{\Delta^{N-1} G}{\Delta[0\ldots N-1]} \left[ \frac{\Delta^N G}{\Delta[0\ldots N]} \right]^{-1} = \sum_{n=0}^{N} \epsilon_n L_n^{(N)}, \]

in terms of the values of the Green matrix on the energy mesh. Note that \( \sum_{n=0}^{N} L_n^{(N)} = 1. \) From the Newton expression (7), we realize that the NMTO equals a kinked partial wave at the same site and with the same angular momentum, plus a smoothing cloud of energy-derivative functions centered at all sites and with all angular momenta (NMTOs with \( N > 0 \) are smooth because the kinks \( (\mathcal{H} - \epsilon) \phi(\epsilon, \mathbf{r}) G(\epsilon) \) are independent of \( \epsilon \)). In the right-hand side of Fig. 1, the solid curve is the MTO with \( N = 1 \), the linear MTO (LMTO), and the dashed curve is the MTO with \( N = 0 \), shown by the solid curve in the left-hand side. Obviously, longer spatial range is the price for spanning wave functions of a wider energy range. This increase of range and smoothness with \( N \), follows from the relation:

\[ (\mathcal{H} - \epsilon_N) \chi^{(N)}(\mathbf{r}) = \chi^{(N-1)}(\mathbf{r}) \left( E^{(N)} - \epsilon_N \right), \]

which also shows that the energy matrices are transfer matrices between NMTO sets of different order.

**Variational eigenvalue equations:** Since from Eq.(6), the NMTO set has errors \( \propto \prod_{n=0}^{N} (\epsilon_i - \epsilon_n) \), solution of the variational eigenvalue equations (4) will yield energies with errors \( \propto \prod_{n=0}^{N} (\epsilon_i - \epsilon_n)^2 \). To exploit this, we need the following expressions:

\[ \langle \chi^{(N)} | \mathcal{H} - \epsilon_N | \chi^{(N)} \rangle = - \left[ \frac{\Delta^N G}{\Delta[0\ldots N]} \right] \left[ \frac{\Delta^{N+1} G}{\Delta[0\ldots N+1]} \right], \]

\[ \langle \chi^{(N)} | \chi^{(N)} \rangle = - \left[ \frac{\Delta^N G}{\Delta[0\ldots N]} \right] \left[ \frac{\Delta^{N+1} G}{\Delta[0\ldots N+1]} \right]. \]

for the Hamiltonian and overlap matrices. Here, \( \Delta^{M+N+1} G/\Delta[0\ldots M+N] \) is the \((M + N + 1)\)th derivative of that polynomial of degree \( M + N + 1 \) which takes the values \( G_0, \ldots, G_N \) at the \( N + 1 \) mesh points and the values \( \hat{G}_0, \ldots, \hat{G}_M \) of the first-derivative at the first \( M + 1 \) points. Note that this Hermite interpolation of \( G(\epsilon) \) is not supposed to approximate \( G(\epsilon) \), which usually has poles inside the mesh; the physical quantities are ratios of energy derivatives of such polynomial ‘approximations’. The Hamiltonian and overlap matrices may be expressed in terms of the values and first energy derivatives at the mesh of the smooth function \( K(\epsilon) \equiv G(\epsilon)^{-1} \), but as \( N \) increases, these expressions become increasingly complicated.

As a first example, we consider the simplest possible \( 1 \times 1 \) Green matrix, \( G(\epsilon) = \sum_j (\epsilon - \epsilon_j)^{-1} \), which is that of a single, normalized kinked partial wave: The variational energy relative to \( \epsilon_N \) can be worked out to be:

\[ \frac{\Delta^{2N} G}{\Delta[0\ldots N]} / \frac{\Delta^{2N+1} G}{\Delta[0\ldots N+1]} = \sum_j (\epsilon_j - \epsilon_N)^{-1} \prod_{n=0}^{N-1} (\epsilon_j - \epsilon_n)^{-2} / \sum_j \prod_{n=0}^{N} (\epsilon_j - \epsilon_n)^{-2}, \]

and the deviation from an exact
result, $\varepsilon_i - \varepsilon_N$, is therefore $\sum_{j \neq i} (\varepsilon_j - \varepsilon_N) \prod_{n=0}^{N} (\varepsilon_i - \varepsilon_n)^2 / (\varepsilon_j - \varepsilon_n)^2$, to leading order. This is in accord with the opening statement of this subsection. Fig. 2 shows how for the two-level system $G(\varepsilon) = \frac{1}{\varepsilon} + \frac{1}{\varepsilon - 1}$, this variational energy switches from 0 to 1 as the center, $x$, of the mesh sweeps from $-1$ to $+2$. The various curves refer to $N=0, 1, 2, and 4$. For $N > 0$, we used meshes of total width 0.4. We see that the switching curves sharpen up as $N$ increases, and that good results are obtained already with $N=1$, the chord-LMTO.

Density-functional calculations: In Fig. 3 we show for GaAs the LDA valence and conduction bands, 18 of which fall in the 35 eV-range displayed. The solid curves are the exact bands and the dotted curves are the bands calculated variationally using a basis of Ga $sp^3d^5$ and As $sp^3d^5f^7$ quadratic muffin-tin orbitals (QMTOS) with the three energies indicated in the right-hand panel. The good accuracy achieved with this basis of merely 25 orbitals/cell demonstrates the power of our method. Note that even for this large energy range, no radial quantum numbers are needed. In most cases (self-consistency iterations) one merely needs to describe the occupied states, which for GaAs are the five semi-core Ga 3$d$ bands at $-15$ eV, the As 4$s$-like band around $-11$ eV, and the three valence bands of dominant Ga 4$s4p$ and As 4$p$ characters extending from $-7$ to 0 eV. With a minimal Ga $sp^3d^5$ As $sp^3$ NMTO set, we find typical accuracies in the sum of the one-electron energies of 50 and 5 meV/GaAs respectively for LMTOs ($\varepsilon_0 \approx -15$ eV, $-5 < \varepsilon_1 < -2$ eV) and QMTOS ($\varepsilon_0 \approx -15$ eV, $\varepsilon_1 \approx -11$ eV, $-5 < \varepsilon_2 < -2$ eV).
**Wannier-like orbitals:** For cuprate high-temperature superconductors, one needs a one-band Hubbard Hamiltonian with realistic, material-dependent parameters. The conduction band obtained from angle-resolved photoemission, or with the LDA (Fig. 4), has antibonding O $p_x - Cu \, d_{x^2-y^2} - O \, p_y$ character, but it crosses, or hybridizes with a multitude of other bands below the Fermi level ($\sim -0.7$ eV), so that its Wannier function is long ranged and depends on irrelevant details. Rather than the Wannier function, one therefore wants an exponentially decaying orbital, which describes the band in a range around the Fermi level. The dotted band in Fig. 4 results from an $N = 3$ variational calculation, in which only the Cu $d_{x^2-y^2}$-channel was taken as active. It is seen to give a superb description of the conduction band in the regions where this band is isolated, including the extended saddle-point at X, and a smooth interpolation below -1.4 eV where the band is hybridized. The Fourier transform yields the hopping integrals.

![Figure 4: Band structure of CaCuO$_2$ with a 7$^0$-buckle, calculated in the LDA with a single, Bloch Cu $d_{x^2-y^2}$ CMTO (dotted) compared with the full band structure (solid).](image)

For calculating the Coulomb interaction and, more generally, for multiband model Hamiltonians, minimal orthonormal bases are required. With NMTOs, there is an efficient way to generate orthonormal sets, which goes via sets of so-called *nearly orthonormal* NMTOs. Before we indicate how this works, we recall that Löwdin orthonormalization is:

$\hat{\chi}(r) = \chi(r) \left\langle \chi \mid \chi \right\rangle^{-1/2}$, where the $\chi(r)$'s are normalized and where the matrix $\left\langle \chi \mid \chi \right\rangle^{-1/2}$ is obtained by Taylor-expansion in the non-orthonormality $1 - \left\langle \chi \mid \chi \right\rangle$, which is therefore required to be small. We also state, without proof, that the NMTO set, $\hat{\chi}^{(N)}(r)$, derived from the set, $\hat{\phi}(\epsilon, r) = \phi(\epsilon, r) \hat{T}(\epsilon)$, of transformed kinked partial waves, is a linear transformation of the original set, $\chi^{(N)}(r)$, and is given by hatted version of expressions (7). It now turns out to be a simple matter to find the transformation, $\hat{T}(\epsilon)$, which makes the sets $\hat{\chi}^{(M)}(r)$ nearly orthonormal, in the sense that $\left\langle \hat{\chi}^{(M-l)} \mid \hat{\chi}^{(M)} \right\rangle = 1$ for $l \leq M \leq N$. 

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and for instance $\hat{p}(\varepsilon_0, \mathbf{r}) = \hat{x}^{(0)}(\mathbf{r})$ is normalized. In such a representation, $\langle \hat{x}^{(N)} | \hat{x}^{(N)} \rangle$ is sufficiently close to the unit matrix that the non-orthonormality can be neglected, and if not, Löwdin orthonormalization will converge fast. The added bonus of a nearly orthonormal representation is that its energy matrices are Hamiltonians, as may be seen from the relation: $\hat{E}^{(M)} - \varepsilon_M = \langle \hat{x}^{(M)} | \hat{x}^{(M-1)} \rangle^{-1} \langle \hat{x}^{(M)} | \hat{H} - \varepsilon_M | \hat{x}^{(M)} \rangle$, derived from Eq.(8).

**Generating the kink matrix:** Having seen that both the NMTOs and the Hamiltonian and overlap matrices are expressed in terms of one matrix, $G(\varepsilon) \equiv K(\varepsilon)^{-1}$, let us finally indicate how the kink matrix is generated. The elements with $R \neq R'$ of the bare structure matrix, $B^0_{RL',RL}(\varepsilon) \equiv \sum_{m} 4\pi i^{l'+l'-l'} C_{Ll,lm} R_{RL}(\kappa | \mathbf{R} - \mathbf{R}' |) Y_{l'}^{m*}(\mathbf{R} - \mathbf{R}')$, specify how the spherical waves, $n_l(\kappa_{RL}) Y_L(r_R)$, are expanded in regular spherical waves, $j_{l'}(\kappa_{RL}) Y_{l'}(R_R)$. The expansions of the screened spherical waves are specified by the screened structure matrix, $B^\alpha(\varepsilon)$, which is obtained by matrix inversion of $B^0(\varepsilon) + \kappa \cot \alpha(\varepsilon)$. Here, $B^0_{RL',RL}(\varepsilon) \equiv 0$ and $\kappa \cot \alpha(\varepsilon)$ is a diagonal matrix with $\alpha_{RL}(\varepsilon)$ being the hard-sphere phase shift $[\tan \alpha_{RL}(\varepsilon) \equiv \eta_{RL}(\kappa_{ RL})/n_{L}(\kappa_{ RL})]$ if the channel is active, and the real phase shift $\eta_{RL}(\varepsilon)$ if the channel is inactive. With appropriate division into active and inactive channels, $B^\alpha(\varepsilon)$, defined via $B^\alpha(\varepsilon)^{-1} \equiv B^0(\varepsilon)^{-1} + \kappa^{-1} \tan \alpha(\varepsilon)$, has short spatial range and no poles in the energy-range of interest. Finally, the kink matrix is $K(\varepsilon) = -[\kappa n L(\kappa a)]^{-1} \{B^\alpha(\varepsilon) + \kappa \cot \eta^\alpha(\varepsilon) \} [\kappa n L(\kappa a)]^{-1}$, where $\eta^\alpha(\varepsilon)$ is the real phase shift in the medium of hard $a$-spheres $[\tan \eta^\alpha(\varepsilon) \equiv \eta(\varepsilon) - \tan \alpha(\varepsilon)]$.

**Overlapping MT-wells:** In closing, a point of considerable practical importance. The KKR and NMTO formalisms hold not only for straight MT-potentials, but for superpositions of overlapping MT-wells, to first order in the potential-overlap. In order to exploit this, we need to use kinked partial waves defined as in the left-hand part of Fig. 1: $\phi_{RL}(\varepsilon, \mathbf{r}) \equiv [\phi_{RL}(\varepsilon, r_R) - \phi^0_{RL}(\varepsilon, r_R)] Y_L(r_R) + \psi_{RL}(\varepsilon, \mathbf{r})$. Here, $\phi(\varepsilon, r)$ (dot-dashed) is the radial solution for the central MT-well, which extend to the radius $s (> a)$, and $\phi^0(\varepsilon, r)$ (dotted) is the phase-shifted wave proceeding smoothly inwards from $s$ to the central $a$-sphere, where it is matched with a kink to the screened spherical wave $\psi$ (dashed). Radial overlaps of up to 30% may be treated without changing the formalism, and overlaps up to 60% may be treated if a simple kinetic-energy correction is included. The NMTOs generated from such potentials are accurate for all cases we have considered so far.

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Understanding which compounds are capable of existence in a given chemical system, is a central goal of solid state chemistry. While the successful synthesis of these, perhaps even metastable, compounds is the final touchstone, theoretical investigations play an ever-increasing role, predicting not yet synthesized compounds, suggesting phase transitions, and yielding hints at possible synthesis routes. The key for this enterprise is the exploration of the energy landscapes of solids, which commonly exhibit a multitude of local minima and a highly complex barrier structure. Such complex landscapes are not only relevant to crystalline solids. The dynamic and static features of a large variety of systems ranging from the relaxation dynamics in glasses and spin glasses, over the folding transformation in proteins and the study of the properties of clusters and polymers, to the efficiency of combinatorial optimization algorithms, are intimately related to the structure and properties of their respective energy surfaces.

Thus, we have been developing methods to determine important global and local features of energy landscapes that are typically present in all types of complex systems, e.g., local minima and larger basins containing many minute local minima, the energetic and entropic barriers between them, the saddle points and transition regions, and the local densities of states. The algorithms we employ are based on random walks on the potential energy surface of the system. For the purpose of illustration, the landscape of CaF$_2$ (two formula units per simulation cell, $Z = 2$) is considered, where empirical potentials have been used for the energy evaluation.

Starting points in such an exploration are the critical points of a landscape, in particular the local minima, which in solids correspond to compounds that should be capable of existence at least at low temperatures. A large number of methods exist for their determination, although, for typical complex systems, only a small fraction thereof can actually be determined with a reasonable effort. However, in certain systems, e.g., the crystalline solids we are investigating, many of these minima are essentially equivalent with respect to their physical properties, e.g., differing only by very minor distortions of an ideal structure. Unless such variations are of special interest, one collects all the corresponding local minima in one large basin or minimum region.

For the next step, the determination of the energetic barriers separating such regions, we have developed the so-called threshold algorithm. Starting from a local minimum, one performs a random walk, where every step is accepted, as long as a prescribed energy lid is not crossed. Periodically during this so-called threshold phase, quench runs (random walks, where only steps that decrease the energy are accepted) are performed. Such threshold runs are repeated for a sequence of increasing energy lids. For very low lids, the quench runs will always end in the starting minimum. The first lid value, where another minimum is found, gives an upper bound on the energetic barrier between the two minima involved. Using this information, a tree-graph representation of the energy landscape
follows by using the minima as end-nodes of the tree, which are connected by internal nodes at the energy barrier between the minima (see Fig. 5). Here, the global minimum (\textit{VIII-a}) corresponds to the experimentally observed structure.

Figure 5: Tree-graph diagram for CaF$_2$. Connections of lines mark lid values where a transition to other minima is found for the first time. The height of the bars on the minima indicates the energy up to which 100\% (dark) and 80\% (light) of the threshold runs ended at the starting minimum. The shaded ellipse indicates the energy region, where the entropically stabilized structure ‘\textit{VII-a}’ is located.

Such threshold runs involve many millions of energy evaluations. By sampling the energies during such a run, we gain information about the local density of states accessible during the random walk. By combining the samples for many lid values, we can derive accessible local densities of states for each of the minimum regions. In principle, this information can be used to give estimates of the thermodynamic properties of each local minimum region, e.g., the specific heat. Furthermore, the local density of states can also have an effect on the kinetics of the system, if the growth of the local density of states with energy is exponential with growth factor $\alpha$. In this case, a random walker at temperature $T$ will not be able to leave the region for $T < 1/\alpha = T_{\text{trap}}$, while for $T > 1/\alpha$, the walker cannot enter the region. Such approximately exponentially growing densities of states have already been observed in a number of systems ranging from spin glasses, lattice glasses and polymers to crystalline solids [Sibani \textit{et al.}, Comp. Phys. Comm. \textbf{116}, 17 (1999); Wevers \textit{et al.}, J. Phys. Cond. Matter \textbf{11}, 6487 (1999)].
Clearly, the barrier between two minimum regions cannot be completely described by the energy of, e.g., a saddle point alone. Instead the entropic barrier, measuring the difficulty of finding a path from one region to the other, must be estimated, too. Such barriers make themselves felt in e.g., transition probabilities between two minima, which remain essentially zero even though it is known that a low-energy path exists. We have cast this behavior in the form of so-called return-energies that indicate the energies up to which a certain percentage of threshold runs does not leave the starting minimum region (see Fig. 5). This is complemented by the so-called transition maps, where we represent the energy-dependent transition probability matrix in diagrammatic form (see Fig. 6).

Figure 7: Quench and low-temperature Monte-Carlo runs, exhibiting the entropically stabilized region ‘VII-a’.
Another effect is the entropic stabilization of regions of the landscape that do not correspond to a local minimum, but exhibit nevertheless long residing times. A beautiful example is found in the CaF$_2$ system, where an intermediate region of the landscape, called VII-$a$, has been observed at the end of simulated annealing runs. A closer investigation shows that no local minimum is associated with this region. But nevertheless, Fig. 7 shows that essentially all quench runs and low-temperature (i.e. $T < T_{\text{trap}} (\text{VII}-a)$) Monte-Carlo runs reside for a very long time in this region before reaching the global minimum VIII-$a$. This result might also be of relevance regarding the question of possible intermediates in the high-pressure phase transition of RuO$_2$ from rutile over a CaCl$_2$-intermediate to the fluorite structure, which corresponds to the VI-$f \rightarrow$ VIII-$a$ transition. Our results suggest that a structure like VII-$a$ might occur as an intermediate between CaCl$_2$ and fluorite, supporting a proposal [Haines et al., Phys. Rev. B48, 13344 (1993)] of a hypothetical intermediate very similar to our VII-$a$–structure. In addition, a very slow kinetics of the phase transformation was observed, which is a first hint that the transition region might be entropically stabilized.

Chemical and electrical effects described by generalized equivalent circuits

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In view of the complexity of solid state chemical processes a representation in terms of equivalent circuits with well-defined circuit elements would be extremely helpful. Charge carrier transport, which is a basic step in solid state processes, is in general composed of fluxes of ionic and electronic charge carriers. On the level of irreversible thermodynamics the fluxes are proportional to the gradients of the corresponding electrochemical potentials, and mass and charge conservation is taken into account by continuity equations. Electrodynamics is taken into account by Poisson’s equation, as long as magnetic fields can be neglected. Thus, in order to describe a situation in a mixed conducting solid with one ionic and electronic charge carrier a set of at least five differential equations is needed.

As far as the treatment of purely electrical transport or of electrode kinetics is concerned, the use of equivalent circuits has a long tradition. In the case of combined chemical and electrical effects a description in terms of an equivalent circuit would be particularly helpful but, simultaneously, the correspondence between the differential equations and the circuit is rather difficult to establish. A few contributions in this respect are available in the literature, but are restricted, however, to cells under applied voltage. In the following we describe our general equivalent circuit which takes into account both applied voltages and chemical potentials and we demonstrate the power of the circuit by means of two specific, but highly relevant problems.
The circuit elements to be considered are in addition to electrical resistors and capacitors the respective chemical analogues. While the implementation of chemical effects in resistors is rather trivial (electric potential drops have to be extended to electrochemical potential drops), the implementation of chemical capacitors is more tricky. We define them as the increase of particle density with increasing chemical potential. The chemical capacitors are, in contrast to the electrostatic ones, proportional to thickness and independent of dielectric constant; they depend (linearly in a dilute case) on the carrier concentration.

Figure 8 shows such a generalized circuit which describes chemical and electrical transport as well as the internal chemical reaction in a laterally homogeneous mixed conducting solid. The horizontal coordinate (referring to the driving forces $\nabla \mu$, $\nabla \phi$) describes the transport while the vertical one (referring to the driving force $\delta \mu$) characterizes the local internal reaction. The constant of proportionality between the individual fluxes and the gradients of the electrochemical potentials, $\nabla \tilde{\mu}$, is given by electrochemical resistors $R$: the upper rail refers to electronic (eon) and the bottom one to ionic (ion) fluxes. The force acting on resistors is not caused by a voltage drop, but by a drop of electrochemical potentials (see Fig. 8b)). The electrostatic capacitors ($C^q$) arranged in the center rail reflect Poisson’s equation, and chemical capacitors ($C^\mu$) – implemented vertically – the mass conservation. While the electro-chemical resistors take into account both electrical ($\nabla \phi$) and chemical ($\nabla \mu$) driving forces simultaneously, two substantially different elements are needed to describe the storage of electrostatic and chemical energy, respectively. This lies in the fact that both storage mechanisms are distinguishable. We have shown that this circuit is equivalent to the set of underlying differential equations while the terminal elements of the circuit reflect on the boundary conditions. As shown in Fig. 8b), the circuit separates transport from local reaction.

Figure 8: a) Equivalent circuit of a sample simultaneously exposed to different component chemical potentials $\delta \mu'$, $\delta \mu''$ (e.g. oxygen partial pressures) and a voltage drop (resulting in $\Delta \tilde{\mu}_{eon}$). Although the potentials are different by nature they still obey Kirchhoff’s law. b) The horizontal lines refer to the transport, the vertical ones to the local reaction. The symbols $z$ and $e$ denote the carrier’s charge numbers and the absolute value of the electronic charge.
Let us give two examples:

(i) With this circuit it was possible to solve elegantly a long lasting problem in the field of impedance spectroscopy. It is well known that the impedance response of a mixed conductor (ionic and electronic conductivities) sandwiched between two metal electrodes consists of a low frequency ‘arc’, the left side of which is linear with a slope of 45° (Fig. 9a), Warburg impedance). If we now let the electronic contribution tend to zero so that we have a pure ionic conductor, an extremely extended Warburg impedance is expected. This is, however, fundamentally different from what we obtain if we neglect electronic carriers right from the beginning and, from what is observed experimentally, namely a sharp capacitive 90° rise as shown in Fig. 9b).

![Figure 9: Typical impedance spectra of a) a mixed conductor and b) a pure ion conductor, connected with two metal electrodes.]

As we have demonstrated this paradox disappears if both electrical and chemical effects are considered according to Fig. 8. In impedance spectroscopy the excitation is caused by $\Delta \mu_{\text{con}}$, we can thus omit outer chemical sources $\delta \mu'$ and $\delta \mu''$. Now (1) both response types can be directly derived as limiting cases, and (2) the decisive materials parameter which determines the type of the response is easily identified: it is the ratio of the electrostatic (electrode) capacitance and the component chemical capacitance (series combination of $C^\delta_{\text{con}}$ and $C^\delta_{\text{ion}}$, see Fig. 8). If the concentration of ionic or electronic defects vanishes, the component chemical capacitance will be negligibly small, and a type (b) response will be observed. In the opposite limit the electrode capacitance can be neglected yielding a type (a) response.

(ii) By allowing for chemical sources but omitting the electrical source the circuit shown in Fig. 8 can be used to describe pure mass transport, e.g. chemical diffusion of oxygen in an oxide. It turns out that in this representation the chemical diffusion coefficient is inversely proportional to the product of the effective resistance (series combination of electronic and ionic resistances) and the component chemical capacitance. The representation is especially convenient if diffusion in an inhomogeneous material, such as a polycrystal, is considered.
Since most of the oxygen will be stored in the bulk rather than in the boundaries the bulk contribution to the chemical capacitance will dominate. Just the opposite is true for the resistance if the boundaries are ‘blocking’ for mass transport. Thus, the resistive term of the effective diffusion coefficient will be composed of the boundary resistance but the capacitive term of the chemical capacitance of grain interior (Fig. 10a)). In the other extreme of highly conductive boundaries (Fig. 10b)) the effective diffusion coefficient is determined solely by the properties of the grain’s interior. It is straightforward to show that not only can the diffusion processes visualized in Fig. 10 be quantitatively mapped but that analytical expressions for these effective diffusion coefficients can also be easily derived.

Chemical transport across grain boundaries

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Internal mass transport is one of the most significant processes of solid state science. In contrast to bulk diffusion the chemical transfer step through internal boundaries is largely terra incognita, even though a problem of pronounced relevance, for example, with respect to the response time of chemical sensors, the rate of permeation experiments and for solid state reactions in general. This is due to the lack of (1) an adequate quantitative phenomenological understanding, (2) adequate methods for investigating such processes, and (3) most often the knowledge of the crystallographic, chemical and defect-chemical properties of boundaries. In the following we briefly demonstrate how chemical transport through grain boundaries can be quantitatively described and how it can be measured in situ as a function of time and space. The electrical and chemical analysis is accompanied by high resolution TEM to elaborate the atomistic structure.
We decided to study two characteristic grain boundaries in SrTiO$_3$, one being close to a \( \Sigma 13 \) boundary (Fig. 11a)), which represents a significant structural perturbation, and the other a \( \Sigma 3 \) boundary (Fig. 11b)) of lower energy, reflecting only a slight structural variation. Impedance analysis of the bicrystal reveals back-to-back Schottky barriers which are negatively charged and hence depleted of holes. We know from electrical measurements that the space charge potential is \( \approx 500 \) mV for the \( \sim \Sigma 13 \) boundary and much less, \( \approx 250 \) mV for the \( \Sigma 3 \) boundary. In the first case, the impact at a high space charge potential on equilibrium ion redistribution can be seen by energy loss spectroscopy. Since the ionic carriers (doubly ionized oxygen vacancies) are also expected to be depleted, the effect on oxygen transport should be visible for the \( \sim \Sigma 13 \) boundary. We therefore extended the optical in situ technique, developed in our department, to study chemical diffusion as a function of space and time, to observe oxygen transport across such boundaries (see Fig. 11).
The technique relies on the dependence of the redox state of deep acceptors on the local oxygen chemical potential. As can be seen in Fig. 11c) and d), the Σ 13 boundary shows a distinct colour jump (Fig. 11c)) from which one can extract concentration profiles displayed in Fig. 11e). Conversely, in the case of the Σ 3 boundary the grain boundary is obviously ‘overlooked’ (Fig. 11d) and f)).

A quantitative treatment which describes such phenomena was recently developed by us. In the present case the analysis is considerably simplified since core effects are not of relevance and since the boundary is much thinner than the bulk. The effective rate constant can then be obtained by integration of the harmonic mean of the ionic and electronic conductivities over the grain boundary. Fig. 12 shows the measured rate constant, $k_{gb}$, and the space charge potential, $\Delta \phi$, derived from it, as a function of temperature. In addition, the space charge potential obtained by impedance spectroscopy is shown. This agreement is particularly meaningful as impedance spectroscopy refers to the (singly charged) holes while the chemical transport is primarily influenced by the (double-charged) oxygen vacancies that perceive the electric field within the grain boundary much more sensitively.

In summary: we showed (i) that it is possible to follow chemical transport across boundaries in situ and spatially resolved; (ii) that the process can be quantitatively analyzed; (iii) the parameters extracted can be consistently explained in terms of the grain boundary chemistry.

Figure 12: Temperature dependence of the grain boundary rate constant, $k_{gb}$, and of the space charge potential, $\Delta \phi$, which determine the boundary barrier height. The space charge potentials were independently derived from chemical (triangles) as well as from electrical (squares) experiments.
Phase coherence length of hot surface state electrons

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The phase relaxation length $L_{\phi}$, i.e., the distance a quasiparticle can propagate without losing its phase memory, is a key quantity in solid state physics. Quantum mechanical interference phenomena can prevail only if $L_{\phi}$ is larger than any other relevant length scale. Examples include Aharonov-Bohm oscillations, quantum Hall effect, Friedel oscillations, and localization. With respect to surface physics the lifetime of the quasiparticle $\tau_{\phi}$ is of particular interest, since it governs the dynamics of charge transfer and electronic excitations in surface chemistry.

We have developed a novel approach to measure the phase relaxation length and femtosecond lifetime of quasiparticles on metal surfaces. The approach is based on the quantitative analysis of the decay of quantum mechanical interference patterns of surface state electrons probed by scanning tunneling microscopy (STM). Under well-defined conditions the surfaces of noble metals show features which look like ripples of water spreading out in circles from each defect and moving in straight lines from each step edge (Fig. 13). These waves are caused by the interference of ‘electron waves’ moving towards and away from each defect or step. But the ripples die away within a short distance of the surface features because electrons eventually scatter from one quantum state into another, destroying the pattern. So the lifetime during which an electron remains in a specific quantum state before scattering is directly reflected in the distance over which the ripples persist away from a step edge.

Figure 13: Steps and defects on a Cu(111) surface lead to electron waves under the right conditions, which can be measured directly in scanning tunneling microscopy. Analysis of these ‘electron ripples’ gives fundamental properties of the surface electrons.

$V_t = 13 \text{ mV}, I_t = 0.32 \text{ nA}$ 1000 X 1000 Å²
We have measured the persistence lengths of the wave patterns as a function of temperature and bias voltage for Ag and Cu(111) probing the thermal damping and hot-electron dynamics of these surfaces. The thermal damping of the electron standing waves is described quantitatively within a simple plane wave model accounting for thermal broadening due to the broadening of the Fermi-Dirac distributions of sample and tip, for beating effects between electrons with different \( k \parallel \) vectors, and for inelastic collisions of the electrons, e.g., with phonons. From the quantitative analysis of the damping we can determine the phase relaxation length \( L_\phi \) of the surface state electrons. In contrast to photoelectron spectroscopy we measure \( L_\phi \) close to \( E_F \) and also locally. The latter eliminates residual line widths due to surface defect scattering embarrassing integral measurements such as photoemission. Our STM-results therefore provide currently the best absolute estimates of \( L_\phi \). Our values can be combined with photoemission results on \( dL_\phi /dT \) to derive the inelastic lifetime of surface state electrons at any \( T \).

![Figure 14: Femtosecond lifetime of hot surface state electrons as a function of excess energy.](image)

In order to probe the dynamics of hot surface state electrons we analyzed quantitatively the spatial decay of interference patterns in the energy range 0.5–3.5 eV above the Fermi energy at a sample temperature of 4.9 K. This decay is governed by inelastic electron-electron scattering and allows for a direct determination of the corresponding lifetime of the injected quasiparticles. As shown in Fig. 14, we find a \((E - E_F)^{-2}\) energy dependence of the hot electron lifetimes for both Ag and Cu surface state electrons, and our values are comparable to bulk electron lifetimes of the corresponding metals. This indicates that electron-electron interaction of hot Ag and Cu surface state electrons with the Fermi sea is dominated by the underlying bulk electrons.
New materials and reaction mechanisms

In this chapter we present some of the experimental and theoretical approaches employed at the Institute with the aim of developing new materials and of elucidating reaction mechanisms. In the former case a diverse range of materials are covered, from complex clusters to amorphous fibers and from ceramics to metals. Such diversity is also evident in the two reports on reaction mechanisms, one an experimental study of magneto-chiral anisotropy, the second a quantum mechanical molecular dynamics simulation on the reaction between sodium and water clusters.

Enantioselective magneto-chiral photochemistry

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In biology, chemistry and physics one often deals with systems that can occur in two forms that are each others mirror image. This phenomenon of chirality (from the Greek cheiros = hand) plays a particularly important role in biochemistry, since in most biochemical reactions only one enantiomer (mirror image) of the molecules involved can participate. In physical terms, chirality is equivalent to breaking of parity. It is clear on symmetry grounds that in order to obtain a chiral result from any reaction, it has to contain a chiral component or it has to be subjected to some external chiral influence. A well-known example of this principle is the use of circularly polarized light as a chiral agent in certain photochemical reactions, where the handedness of the light determines the handedness of the reaction product. It has often been attempted to use magnetic fields to induce chirality in chemical reactions, but so far in vain. Recently we have observed a new magneto-optical effect, called magneto-chiral anisotropy (MChA) that establishes a coupling between chirality and magnetic fields and that can discriminate between the two enantiomers of chiral systems. Here we show experimentally that through this effect, a magnetic field can lead to an enantiomeric excess in a photochemical reaction with unpolarized light.

Natural optical activity, which occurs exclusively in chiral media, and magnetic optical activity, which is induced by a longitudinal magnetic field, show a strong phenomenological resemblance. In both cases, the polarization of light is rotated during propagation through the medium. Interpreting magnetic optical activity as a sign of magnetically induced chirality, Pasteur was the first to search for an enantioselective effect of magnetic fields, followed by many others. These searches were in particular motivated by the hope of finding an explanation for the homochirality of life. They were however unsuccessful as symmetry forbids a magnetic field per se to induce chirality.

The recently discovered MChA effect can be regarded as a cross-effect between natural optical activity and magnetic optical activity, with its own characteristic symmetry properties. It is described by an extra term in the dielectric constant; for chiral isotropic media
like gases, liquids, or cubic crystals, and light propagating with wave vector \( \mathbf{k} \) in a magnetic field \( \mathbf{B} \), this term is proportional to \( \mathbf{k} \cdot \mathbf{B} \), and of opposite sign for the two enantiomers, i.e. it is enantioselective. Amongst others, MChA leads to a difference in absorption coefficient for unpolarized light in a magnetic field for the two enantiomers, proportional to \( \mathbf{k} \cdot \mathbf{B} \). As a photochemical reaction rate is proportional to the absorption coefficient, this will lead to different rates for the two enantiomers, and therefore in general could lead to an excess of one enantiomer over the other.

We have studied the implementation of this principle on the Cr(III)tris-oxalato complex (see inset Fig. 15), as this is expected to show a relatively large MChA. This complex, that exists in a right and a left handed version, is unstable in solution and spontaneously dissociates and re-associates. In equilibrium, one has equal concentrations of right and left handed complex. The dissociation is accelerated by the absorption of light, so under irradiation with unpolarized light in a magnetic field, one enantiomer will dissociate more often, whereas the re-association is random. This leads to an excess of the less absorbing enantiomer, the handedness of which depends on the relative orientation of \( \mathbf{k} \) and \( \mathbf{B} \). If this process, called photoresolution, is much faster than the thermal racemization (the return to a 1:1 mixture), the size of the excess in dynamic equilibrium should be given by \( g_{\text{MChA}}/2 \), where \( g_{\text{MChA}} \) is the MChA asymmetry factor which equals

\[
2\left\{ \epsilon(\mathbf{k} \uparrow \downarrow \mathbf{B}) - \epsilon(\mathbf{k} \downarrow \uparrow \mathbf{B}) \right\}/\left\{ \epsilon(\mathbf{k} \uparrow \uparrow \mathbf{B}) + \epsilon(\mathbf{k} \downarrow \downarrow \mathbf{B}) \right\},
\]

\( \epsilon \) being the optical extinction coefficient.

Figure 15: Experimental setup for determining photochemistry of the Cr(III)tris-oxalato complex. Monochromatic irradiation is performed with a Ti:sapphire laser around 696 nm, with a polarization state that can be selected between linear, circular and unpolarized. The latter was obtained after passing the light through 10 meters of 1 mm diameter optical fiber. The inset shows the molecular model of the Cr(III)tris-oxalato complex. (LA: lock-in amplifier, PEM: photoelastic modulator, GreNe: helium-neon laser at 543 nm).
Figure 15 shows the experimental setup to generate and detect the enantiomeric excess (ee). Irradiation is done by a Ti-sapphire laser around the spin-forbidden transition $^4A_{2g} \rightarrow ^2E_g$ of the Cr$^{3+}$ ion. Detection of the excess is done by measuring the natural circular dichroism at the $^4A_{2g} \rightarrow ^4T_{2g}$ transition, the value of which known for the enantiopure compound.

Figure 16 shows the obtained excess as a function of magnetic field. For fields parallel to the irradiation direction $k$, we observe a strictly linear relation, for perpendicular fields no significant excess can be detected, in agreement with the prediction.

![Figure 16: Enantiomeric excess obtained after irradiation with unpolarized light during 25 minutes at $\lambda=695.5$ nm, as a function of magnetic field, with an irradiation direction $k$ either parallel or perpendicular to the magnetic field $B$.](image)

Figure 17 gives the obtained excess as a function of irradiation wavelength, which shows a characteristic derivative-type line shape, indicative of so-called $A$-terms, implying that the magnetic field influence on the optical properties is through the Zeeman effect. This behavior was predicted for the MChA of the Co(III)tris-oxalato complex, but no detailed prediction for the Cr(III) complex is available. We have found earlier that for a given electronic transition, the order of magnitude of $g_{MChA}$ can be estimated by $g_{NCD} \cdot g_{MCD}$, where $g_{NCD}$ and $g_{MCD}$ are the asymmetry factors for natural and magnetic circular dichroism. At $\lambda=701$ nm this yields an estimate of $ee/B = 1.3 \cdot 10^{-6}$ T$^{-1}$, close to the observed value of $ee/B = 1.7 \cdot 10^{-6}$ T$^{-1}$. 

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MChA has been suggested as an explanation for the homochirality of life. So far, the two possible causes for this homochirality considered as most likely, are photochemistry with circularly polarized light, and the electroweak interaction. The latter, although never observed in this context, is predicted to lead to extremely small ee ($\approx 10^{-17}$). The photochemistry with circularly polarized light can yield ee close to unity. At this moment it is unknown how large a prebiotic ee is required in order to arrive at homochirality. We can therefore only wonder if the magnetic fields observed in nature, ranging from the Earth’s magnetic field of $10^{-4}$ T, up to the stray field of neutron stars ($10^8$ T on the surface), might through MChA lead to sufficiently large ee. Furthermore, issues of spectral, spatial and temporal averaging have to be addressed. Clearly the question of the origin of the homochirality of life is far from answered. Our results merely suggest that MChA merits consideration in this discussion.
High temperature ceramics: from molecule to fiber


The application of high-temperature engine has been limited by the performance of metal alloys and carbide fiber composites at elevated temperatures. Random inorganic networks composed of silicon, boron, nitrogen, and carbon represent a novel class of ceramics with outstanding durability at elevated temperatures, which should lead to a new generation of high-temperature engines with great economic and ecological benefits [Baldus et al., Science 285, 699 (1999)].

The design concept behind these ceramics is to generate a strongly bonded three-dimensional covalent random network in a ternary or quaternary system containing, e.g., nitrogen or carbon, where a high degree of interconnectivity is expected to suppress rapid crack propagation in the bulk. In order to avoid spatial inhomogeneity, which might induce phase separation and even crystallization during the processing or the lifetime of the final ceramic, we have chosen the polymer route for synthesis. Starting from a ‘single source’ precursor, in a first reaction stage a polymer is produced, consisting of a multitude of oligomers of various sizes. This is then pyrolyzed to yield a dense amorphous ceramic in form of a powder (see Fig. 18). Alternatively, the polymer can be spun into a fiber (see Fig. 19), which can be employed in a fiber-matrix composite material.

Figure 18: A: Synthesis of the precursor molecule ‘TADB’. B: Pyrolysis and polymerization of ‘TADB’.
As a first step, we have synthesized appropriate precursor molecules, of which two, Cl₃Si–NH–BCl₂ (‘TADB’) and Cl₃Si–CH(CH₃)–BCl₂ (‘TSDE’), have proved to be particularly advantageous. The rapid polymerization is achieved by ammonolysis or aminolysis at low temperatures, resulting in two types of polymers, one without and one with N-bonded Methyl–groups (called ‘PBS- Me’). The final pyrolysis takes place at about 1000°C, with either ammonia or N₂ being used as the reactive gas. In the former case (NH₃), both types of polymers transform into the ternary nitride Si₃B₃N₇, while in the latter one, ‘PBS-Me’ yields SiBN₃C.

Both Si₃B₃N₇ and SiBN₃C are amorphous according to X-ray diffraction. Their exact compositions have been determined by chemical analysis to be Si₃B₃N₇ and SiBN₂₃C₀₈, respectively. Their thermal stabilities are impressively high. The onset of N₂ evolution in Si₃B₃N₇ begins at 1650°C, 160°C higher than for the corresponding (thermodynamically stable) ceramic composite (Si₃N₄)·(3BN). With respect to weight loss, SiBN₃C is stable up to 1800°C, at which point it begins to decompose into Si, N₂, BN, and SiC. Remarkably, no changes in microstructure are detectable up to that temperature. Regarding the technologically important oxidation resistance, a fortuitous feature makes SiBN₃C superior to all known carbides and nitrides. Exposing the material to air at elevated temperatures (≈1400°C) results in the formation of a protective double layer (SiO₂/BN).
The outer layer, rich in Si and O but depleted of B due to the evaporation of B$_2$O$_3$, acts as a diffusion barrier for oxygen, while the inner layer, rich in N and B, but with less Si (because of Si diffusion to the surface) suppresses further cation diffusion (see Fig. 20). This double layer is probably also the reason for the inertness of the ceramic to corrosion by liquid metals, such as Cu or Si, allowing the use of the liquid insertion technique when synthesizing a matrix composite. The hardness of SiBN$_3$C is comparable to that of sapphire, and the density of the fibers produced either by melt-spinning or by a dry-spin process is ≈ 1.8 g/cm$^3$.

In order to gain further understanding into the physical and chemical properties of these high-temperature resistant ceramics, a large number of physical experiments have been performed on the precursors, the intermediate polymers and the final powders. In particular, we have investigated the atomic structure of these amorphous ceramics, using for part of this work the extensive array of experimental probes available in the SFB 408 at Bonn university.

IR-measurements on the polymers and the ceramics show that, e.g., Si-H–vibrations can only be observed up to ≈600°C, while the Si-N– and B-N–vibrations are clearly present in the fully developed ceramics. Thus, one can conclude, in agreement with the elemental analysis results, that essentially all hydrogen has been removed by the time the ceramics has been formed. Of central importance is the question, whether the amorphous nature of the ceramics, as indicated by X-ray diffraction, electron diffraction, and neutron diffraction, extends down to the atomic scale. Electron spectroscopic imaging (ESI) in collaboration with Prof. Mader in Bonn shows that the distribution of the elements in the compound is homogeneous down to at least the length scale of ≈0.7 nm. One experimental probe that is able to analyze the immediate environment and might be extendable up to a few Ångstrom, is solid state NMR. We find that Si and B are essentially always fourfold (tetrahedral) and threefold (trigonal planar) coordinated by N, respectively. Similarly, nitrogen appears to exhibit threefold coordination in an approximately trigonal planar arrangement, as
confirmed by NMR-spectroscopy of $^{15}$N-enriched samples of Si$_3$B$_3$N$_7$. This confirms the deductions from the analysis of the pair correlation functions taken from X-ray, neutron, and electron diffraction.

A final tool for analyzing amorphous compounds are computer simulations that are employed to model the structure and, if possible, even the route by which the compound has been synthesized. Their special contribution is the ability to analyze the amorphous networks on length scales which are currently not accessible experimentally.

In particular the connectivity of the network can be studied in detail, and various (observable and currently unobservable) physical properties can be computed. Together with the group of Prof. Lengauer at the GMD in Bonn, we have developed and are currently refining various structure models (see Fig. 21), which already exhibit a satisfactory agreement with experimentally observed quantities, such as the pair correlation function (see Fig. 22).
Tb$_{16}$Br$_{23}$B$_4$: A new interstitial-stabilized cluster

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The structures of metal rich rare earth halides REX$_y$ ($1 \leq y \leq 2$) are characterized by the presence of discrete and condensed RE clusters. The centers of the clusters can be empty or occupied by interstitial atoms or molecules [Mattausch et al., Inorg. Chim. Acta 289, 174 (1998)]. In RE$_7$I$_1$C single octahedral RE$_6$C clusters are found which are linked to infinite chains in RE$_4$X$_5$C, double chains in RE$_6$X$_7$C or RE$_3$X$_3$C, and layers in RE$_2$X$_2$C or RE$_2$X$_2$C$_2$. Following the concept of condensed clusters [Simon et al., Angew. Chem. Int. Ed. Engl. 20, 1 (1981)] compounds with structures lying between these 0-, 1- and 2-dimensional extremes are expected, and have been synthesized with the compounds Gd$_{10}$Cl$_{18}$C$_2$, Gd$_{10}$Cl$_{17}$(C$_2$)$_2$, Gd$_{10}$I$_{16}$(C$_2$)$_2$ [Simon et al., Angew. Chem. Int. Ed. Engl. 20, 1013 (1981)]. The structures are characterized by two Gd$_6$(C$_2$) octahedra condensed through a common edge. The double octahedron is the first step in the condensation of RE$_6$X$_{12}$ clusters to the infinite chain.

Boride halides of rare earth metals offer a particularly rich new structural chemistry as illustrated by just one example, Tb$_{16}$Br$_{23}$B$_4$. The preparation procedure follows by annealing of stoichiometric mixtures of B, TbBr$_3$ and Tb at 1100°C in welded Ta ampoules under Ar (yield: 80%) and results in black, needle like crystals. The electrical resistivity shows semiconducting behavior and the magnetic moment has the expected value for Tb$_{3+}$ of $\mu = 9.6 \mu_B$. At $\approx 10$ K it orders antiferromagnetically.

Figure 23: a) A quadruple octahedron Tb$_{16}$B$_4$ – the characteristic building unit in the structure of Tb$_{16}$Br$_{23}$B$_4$ (Tb atoms: red; B: yellow). b) The environment of Tb$_{16}$B$_4$ unit by Br atoms (green) in i- and a-type functions.

In the crystal structure of Tb$_{16}$Br$_{23}$B$_4$ (C2/m; $a = 1752.3(4)$, $b = 1200.8(2)$, $c = 1190.1(2)$ pm and $\beta = 103.9(1)^\circ$) the Tb atoms form octahedra centered by boron. The Tb$_6$B units are connected to quadruple octahedra (Fig. 23a)) through five sharing edges. The Tb$_{16}$B$_4$ entity results in view of the different connectivity function of the terbium atoms

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as \((\text{Tb}_3\text{Tb}_{1/2}\text{Tb}_{1/2}\text{Tb}_{1/3}\text{B})_2\) for the two ‘outer octahedra’ with two edges in common and \((\text{Tb}_2\text{Tb}_{1/2}\text{Tb}_{1/2}\text{Tb}_{1/3}\text{B})_2\) for the two ‘inner octahedra’ with three edges in common. The Br atoms (Fig. 23b)) surround the well separated \(\text{Tb}_{16}\text{B}_4\) constituents above the octahedral edges and corners as \(\text{Br}^i\) and \(\text{Br}^a\), respectively, as in the \(\text{M}_6\text{X}_{12}\) cluster type.

![Figure 24: The interconnection of different \(\text{Tb}_{16}\text{B}_4\) units by Br atoms. Two additional units (not drawn in this figure) are connected via \(\text{Br}^r\) above and below the central cluster.](image)

From Fig. 24 the interconnection pattern can be derived as
\[
\text{Tb}_{16}\text{B}_4(\text{Br}^{r-a-a})_{6/3}(\text{Br}^{a-i})_{4/2}(\text{Br}^{i-a})_{4/2}(\text{Br}^{i-r})_{10/2}(\text{Br}^i)_{12}.
\]
The formula shows that some of the Br atoms coordinate only one \(\text{Tb}_{16}\text{B}_4\) unit (\(\text{Br}^i\)), others (\(\text{Br}^{r-a}, \text{Br}^{a-i}\) and \(\text{Br}^{i-r}\)) connect the clusters 2-dimensionally, and the third kind (\(\text{Br}^{a-a-a}\)) connects them 3-dimensionally.

![Figure 25: In the structure of \(\text{Tb}_{16}\text{Br}_{23}\text{B}_4\) the Br and B atoms are arranged in closed packed sheets. In two of three sheets 2/9 of the Br atoms are substituted by B atoms. The Tb atoms fill the octahedral voids around the B atoms.](image)
Tb$_{16}$Br$_{23}$B$_4$ is a member of a series of compounds with the common formula RE$_{6n+4}$X$_{5n(n-1)+18}$Z$_2n$, where Z is the interstitial atom and n is the number of condensed double octahedra. In addition to the described Tb quadruple octahedron with n = 2, only the double octahedron with n = 1 and Z = C$_2$ in Gd$_{10}$Cl$_{18}$($C_2$)$_2$ is known. With n = $\infty$ a double chain compound RE$_6$X$_5$Z$_2$ can be expected, and would be a third structural variant (cf the well known RE$_6$X$_7$Z$_2$ and RE$_6$X$_6$Z$_2$) with the same characteristic structural feature of two condensed octahedral metal chains, but with different interconnection by the halogen atoms. Similar to these two types of compounds the Br and B atoms form closed packed sheets in the structure of Tb$_{16}$Br$_{23}$B$_4$ parallel to (001) (Fig. 25). In two of three sheets 2/9 of the Br are substituted by B atoms resulting in (Br$_9$)(Br$_7$B$_2$)(Br$_7$B$_2$)···. The occupation of all octahedral voids around the B atoms by the Tb metal atoms leads to the composition Tb$_{16}$Br$_{23}$B$_4$. From this point of view it seems plausible to transfer all valence electrons from the electropositive Tb metal atoms to the Br and B atoms, and thus according to the Zintl-Klemm concept (Tb$^{3+}$)$_{16}$$(Br^-)_{23}$(B$^{5-}$)$_4$ there is an excess of 5 valence electrons which form metal-metal bonds localized in the Tb$_{16}$B$_4$ unit.

**Stable oxides with high proton conductivity**

A. Fuchs, K.D. Kreuer, W. Münch and J. Maier

The generation of protonic defects in acceptor-doped oxides and the occurrence of proton conductivity are experimentally well established phenomena. Both are of high significance for a fundamental understanding of proton transport in solids as well as for electrochemical applications. We have shown over the years that the proton transport in these oxides is due to a phonon assisted proton hopping rather than to (OH$^-$) hopping or proton tunneling.

It is generally believed that high stability and high proton conductivity cannot be achieved simultaneously, and hence application of such proton conducting oxides in fuel cells is not promising. However, we will outline that this pessimistic view ignores substantial entropy effects which stabilize protonic defects and it is indeed possible to combine high conductivity with sufficient thermodynamic stability. Consequently we propose that Y-doped BaZrO$_3$ is a promising candidate. Our treatment relies on a comprehensive study of the formation and transport of protonic defects by experimental and simulation techniques.

**Generation of protonic defects**

The major reaction leading to the generation of protonic defects in oxides is the dissociative dissolution of water involving oxygen vacancies ($V^{\cdot\cdot}_O$) according to:

$$\text{H}_2\text{O} + V^{\cdot\cdot}_O + \text{O}_0^{\cdot\cdot} \rightarrow 2\text{OH}_0^{\cdot\cdot}.$$  (9)
Two internal (OH) groups ($\text{OH}_i$) are formed in this reaction, and, therefore, correlations are expected between the enthalpy of this exothermic reaction and the basicity of the corresponding oxides. Such trends are indeed observed for several systems. In addition the thermodynamic data we obtained from the hydration isobars of a variety of cubic, acceptor-doped perovskite-type oxides reveal an unexpectedly high influence of the reaction entropy on the thermodynamic stability of such defects.

The isobars shown in Fig. 26 demonstrate that for BaCeO$_3$ the increase in the concentration of Y-acceptor dopants thermodynamically destabilizes protonic defects, although the heat of hydration becomes more negative. Even more surprising is the high stability of protonic defects in significantly less basic Y-doped BaZrO$_3$. The hydration enthalpy is about half of that of BaCeO$_3$, but the significantly less negative hydration entropy stabilizes protonic defects to quite high temperatures.

**Proton conduction mechanism and transport rates**

The long range diffusion of protonic defects in oxides involves proton transfer reactions to neighboring oxygens and subsequent reorientation. The latter is brought about by rapid rotational diffusion, which has been evidenced by quasi-elastic neutron scattering (QNS) and muon spin resonance ($\mu$-SR) experiments and quantum molecular dynamics (QMD) simulations. On the other hand, strong hydrogen bonding between the protonic defect and the oxygen neighbors, as indicated by the IR spectra, suggests a stronger orientation confinement. A detailed analysis of QMD simulation data, reveals some unexpected features of the hydrogen bond in this unusual environment. The hydrogen bonds are indeed found to be very strong, but the free energy decrease of the system due to the hydrogen bonding is almost compensated by the effect of the lattice distortion (the OH/O separation has to be reduced significantly to form a hydrogen bond) over a wide range of OH/O separations (Fig. 27).
Figure 27: Lattice softening in the vicinity of a protonic defect in BaZrO$_3$ as obtained from a quantum molecular dynamics simulation. Top: The free energy of the system as a function of the hydrogen bond separation (OH···O) is extremely flat as a result of the balance of the contributions from hydrogen bond formation itself and the corresponding lattice distortion. Bottom: OH-stretching dynamics in the fluctuating hydrogen bond being formed between the protonic defect and one of the eight oxygen neighbors.

The corresponding free energy curves of the system as a function of the length of the transient OH/O bond shows a very shallow minimum. In other words the lattice is 'softened' in the vicinity of the protonic defect, and the resulting 'liquid-like' dynamics corresponds to high defect entropies and produce configurations, which favor defect reorientation, and configurations which are favorable for proton transfer reactions (Fig. 27).

Figure 28: Proton conductivity of different acceptor-doped perovskite-type oxides at a water partial pressure of 23 hPa. The oxide ion conductivity of a 9% Y-doped zirconia (YSZ) is shown for comparison.
The situation is found to be particularly advantageous for the amphoteric, cubic perovskite-type Y-doped BaZrO$_3$ ($Y \text{ : BaZrO}_3$). For this system, not only the highest mobility of protonic defects is measured, but due to the high defect concentration (see above) also the highest proton conductivity in such oxides is observed (Fig. 28).

**High proton conductivity and phase instability**
Proton conducting oxides with high conductivities contain earth alkaline metals and are generally considered to degrade in CO$_2$ containing atmospheres (as in high temperature fuel cells) to form carbonates. Their instability versus acidic gases, such as CO$_2$ and SO$_3$, was especially thought to be the price paid for a sufficiently large concentration of protonic charge carriers.

The observation that high ground state entropies of protonic defects which thus stabilize compounds also stabilize the charge carriers and can even promote their mobility in ‘amphoteric’ oxides, is hence of great significance for the application of such compounds in electrochemical cells, such as fuel cells and electrochemical sensors.

These considerations point toward BaZrO$_3$-based compounds as most promising: They are thermodynamically stable at the CO$_2$-levels of air at temperatures above about 300°C. We could show that up to about 700°C, the protonic conductivity of Y-doped BaZrO$_3$ is even higher than that of Y-stabilized zirconia (YSZ, see also Fig. 28), the standard electrolyte material for many electrochemical applications.

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**Microsolvation and chemical reactivity of sodium and water clusters**
Ch.J. Mundy, J. Hutter and M. Parrinello

It has long been known that sodium and water react violently yielding sodium hydroxide and hydrogen gas. Although this is a show case reaction, the mechanism is still not fully understood. Motivated by recent experimental findings [Buck et al., J. Phys. Chem. A 102, 7333 (1998); Bewig et al., J. Phys. Chem. A 102, 1124 (1998)] we report a novel mechanism of the reaction of sodium and water in a molecular beam through a detailed first principles molecular dynamics investigation. While it is clear that the bulk phase reactions proceed without difficulty, special conditions are necessary in order for the same reaction to occur in a beam.

The experimental observations have indicated that at least three sodium atoms must be present to initiate the chemistry. More specifically, it is the presence of a solvated sodium atom and its interaction with a sodium dimer that will give rise to the reactive species. In order to explain this unexpected observation, we used the Car-Parrinello molecular
dynamics (CPMD) method. Using the experimental conditions as a guide, we started with initial conditions (reactants) of an equilibrated sodium water cluster \((\text{Na}(H_2O)_6)\) and a sodium dimer.

Our novel mechanism begins with the following initial step: the dissociation of the sodium dimer to yield a polarized \(\text{Na}^-\) and a solvated \(\text{Na}^+\). To explain this prediction we examine the electronic structure of \(\text{Na}(H_2O)_6\) cluster. To obtain a chemically intuitive description of the electronic structure we used the Boys localization criterion which obtains localized orbitals that minimize the spatial spread for each electronic state. This methodology also affords us the centroid and spread. The remarkably delocalized 3s electron of the sodium atom is shown in Fig. 29. It shows a snapshot of the density of the localized 3s electron of the isolated \(\text{Na}(H_2O)_6\) undergoing CPMD. During the finite temperature dynamics (roughly 100K in accordance with experiment) this is a highly polarizable species. This delocalized electronic state acts as a catalyst to aid in the dissociation of the sodium dimer to form the reactive \(\text{Na}^-\) intermediate (see Fig. 30).

After 3 ps of CPMD we can analyze the electronic structure of the full system (three sodiums and six waters) in the same fashion (Fig. 30). Here we find that instead of one state with a large spread, there are three electronic states with a spread of roughly 3 Å. One of the extended states is the 3s electron of the solvated sodium (as shown in Fig. 29),

![Figure 29: A snapshot of an isolated \(\text{Na}(H_2O)_6\) cluster undergoing CPMD. The blue denotes sodium, the red water and the hydrogens are white. The yellow sphere is the centroid of the localized function. The extended 3s electron of the sodium is represented by the transparent yellow mesh with isosurface value of 0.165 \(e^-/\text{Bohr}^3\).](image-url)
and the two others are the spin polarized $3s$ states of the Na$_2$. The spontaneous cleavage of the Na$_2$ is evident. It is this polarized Na$^-$ that is the reactive intermediate. Thus, the dipolar Na$^-$ acts as a Lewis base and will attack a proton to form sodium hydride (NaH) completing the chemical process and yielding NaOH and H$_2$. However, it is the formation of NaH that is the rate determining step, and thus requires some care to gain understanding into its mechanism.

Figure 30: A snapshot of the full system, Na$_3$(H$_2$O)$_6$ during the formation of NaH. The color coding is the same as in Fig. 29 except for the addition of a light blue sphere and transparent mesh denoting the ‘spin down’ centroid and localized electron, respectively. All electron densities are represented by an isosurface value of 0.397 $\text{e}^/\text{Bohr}^3$. It is clear from this figure that the Na$_2$ is severed and the electrons are spin polarized (blue and yellow spheres are not overlapping) located closer to one sodium, thus forming the reactive intermediate, Na$^-$.

Because of the time-scales involved in the experiment (e.g. microseconds) constraint algorithms must be employed to aid in sampling the reaction barrier. We would like to utilize a set of constraints that enable the reaction path to evolve in a natural way, rather than following the bias of the simulator. To this end, we use the coordination number constraint algorithm of Sprik [Faraday Discuss., 110, 437 (1998)]. By slowly decreasing the coordination number of the oxygen, we believe that the system is nearly equilibrated at every time step and a reasonable, upper bound to the reaction barrier to form NaH can be obtained. Thus, we find a barrier of 14 kcal/mole which translates into a reaction time of roughly a microsecond at the temperatures realized in the simulation which is in good agreement with experiment.

After the formation of NaH, the reaction proceeds spontaneously to produce H$_2$ gas. We then outline our mechanism in the language of chemistry. First, a single sodium atom is solvated by six waters on the picosecond time scale: Na + (H$_2$O)$_6$ → Na(H$_2$O)$_6$. Second, cleavage and solvation of a sodium dimer: Na$_2$ + Na(H$_2$O)$_6$ → Na$_3$(H$_2$O)$_6$. Third, formation of sodium hydride and sodium hydroxide: Na$_3$(H$_2$O)$_6$ → (NaH)(NaOH)Na(H$_2$O)$_5$. 

I-50
Fourth, formation of a second sodium hydroxide and molecular hydrogen: \((\text{NaH})(\text{H}_2\text{O})_5 \rightarrow (\text{NaOH})(\text{H}_2\text{O})_4 + \text{H}_2\). This reaction mechanism is able to explain experimental observations: in order to observe NaOH as a product the molecular beam interaction time must be on the order of a microsecond and molecular sodium (Na\(_2\)) must be present. The first is corroborated by our upper bound on the reaction barrier. The second can be understood from the fact that the formation of Na\(^-\) is impossible from interactions of the cluster with neutral sodium atoms. It can be explained further by the novel observation that the role of the extended state of the Na(H\(_2\)O)\(_5\) could act as a catalyst in ‘cleaving’ the Na\(_2\) bond. The analogy of a catalyst could be further emphasized by the fact that it is consumed during the chemical process and is seemingly regenerated after the final products are formed, namely the remaining sodium atom will be again stabilized by solvating waters. This could lead to the additional formation of (NaOH)\(_2\) that is observed in experiments.

Complex crystal structures of heavy alkali metals at high pressures

K. Syassen, U. Schwarz (MPI/CPFS Dresden), A. Grzechnik and I. Loa; M. Hanfland (ESRF Grenoble); K. Takemura (NIRIM Tsukuba)

The alkali metals have played an important role in developing the nearly-free electron picture for simple sp band metals. With increasing pressure, however, these metals become less free-electron like. In particular, at sufficiently high compression the heavy alkali metals K, Rb, and Cs essentially turn into monovalent d transition metals. The pressure-driven s \(\rightarrow\) d transition is believed to be the driving force for destabilizing the common, highly symmetric, low pressure structures (bcc and fcc) with respect to lower symmetry structures. In fact, at intermediate densities both Rb and Cs adopt a body centered tetragonal structure (denoted Cs-IV-type, see Fig. 31), where the atoms are only eightfold coordinated. The existence of a variety of other high-pressure phases (cf Fig. 31) has been inferred from optical reflectivity measurements, electrical transport studies, and X-ray diffraction measurements. Solving the crystal structures of most of these other high-pressure modifications was possible only recently.

Figure 31: Schematic representation of the phase sequence of heavy alkali metals as a function of relative density. The density \(\rho_0\) corresponds to the respective ambient pressure value. Question marks refer to phases with unknown or unconfirmed crystal structures.
Based on angle-dispersive synchrotron powder X-ray diffraction diagrams measured at the ESRF Grenoble, we have been able to solve the structures of the phases Rb-IV and Rb-VI [Schwarz et al., Phys. Rev. Lett. 83, 4085 (1999); Schwarz et al., Sol. State Commun. 112, 319 (1999)]. In particular, the structure of Rb-IV is found to be surprisingly complex.

The X-ray diffraction patterns were recorded at room temperature using a wavelength near 0.45 Å and a flat image plate detection system. Pressure was generated in a diamond anvil cell. Indexing, structure solution, and refinements of diffraction diagrams were performed using standard crystallography software packages. Both, the high angular resolution and the high sensitivity of the experimental setup were essential for solving the crystal structures.

Figure 32: Image plate pattern and integrated diffraction diagram of Rb-IV at 16.9 GPa.

Figure 32 shows the full diffraction pattern of the phase Rb-IV, measured at a pressure of 16.9 GPa and the corresponding integrated powder diagram. The 52 reflections of this diagram can be indexed on the basis of a tetragonal cell with lattice parameters $a \approx 2 \times c$. The systematic extinctions are compatible with the space groups (SG) I4/mcm, I4cm and I4c2. Solutions of the crystal structure were thus performed in the centrosymmetric SG I4/mcm. Applying direct methods reveals that one set of Rb atoms occupies the Wyckoff positions 16k $(x, y, 0; x \approx 0.79, y \approx 0.08)$. The resulting arrangement of Rb1 atoms (see Fig. 33) consists of columns of face-sharing square antiprisms interconnected by short Rb1-Rb1 contacts (red lines in Fig. 33). The closest separation between Rb1 atoms (3.04 Å at 16.9 GPa) corresponds to twice the ionic radius of Rb$^+$ (1.52 Å).
The Rb1 framework hosts chains of a second set of Rb atoms as evidenced by electron density maxima in the difference Fourier map (see Fig. 34). Maxima occur at the 8g (0.5, 0, z) site. The Fourier map in combination with the maximum possible number of 20 atoms per unit cell, as inferred from atomic volumes of neighboring phases, thus suggest an average Rb2 arrangement with statistical occupation of 8g sites and an occupation factor of 0.5. However, for such an arrangement within the chains the average interatomic distance would be only 2.6 Å, which is difficult to accept because it is 15\% smaller than the ionic radius of Rb\(^+\).

We therefore conclude that the number of Rb2 atoms in chain sites is less than four per unit cell. A refinement of the 16.9 GPa diffraction diagram, in which occupation factors of sites along the chains are treated as free parameters, converges to occupation numbers corresponding to 19.48 atoms per cell or an average chain atom separation of about 2.97 Å.
We have not observed any supercell reflections which would indicate a commensurate ordering of the chain atoms with respect to the framework of Rb1 atoms. On the other hand, some diffraction patterns of Rb-IV show a single extra reflection corresponding to a d-value of about 3.0 Å, i.e., at the position marked by a triangle in Fig. 32. If interpreted as a reflection arising from the intrachain ordering, the absence of other additional reflections would indicate that the chains are uncorrelated with respect to each other.

There is a quite surprising resemblance of the Rb-IV structure to the metal atom sublattice of the W$_5$Si$_3$-type structure, which is rather common among binary alloys. Furthermore, it has been pointed out by Nesper and v. Schnering, that the Cs-IV–type structure, which is also adopted by the phase Rb-V, corresponds to the metal sublattice in the ThSi$_2$-type structure. This leads to a more general concept, namely, that at intermediate densities the alkali metals adopt crystal structures, that represent metal sublattices of binary intermetallic compounds.

![Figure 35: The orthorhombic crystal structure of Rb-VI and Cs-V. The conventional unit cell contains 16 atoms in two crystallographically non-equivalent positions \[8f (0, y, z)\] and \[8d (x, 0, 0)\] in Wyckoff notation. The corresponding sites are denoted as 1 and 2, respectively. The structure can be viewed as an alternating sequence of planar layers formed by five-coordinated nets and puckered nearly-square layers. The shortest interatomic distances are marked by red lines.](image)

When Rb is pressurized to 48 GPa it undergoes the transition to the phase Rb-VI (cf Fig. 31). Again based on monochromatic diffraction data, we have solved the structure of this phase. It is found to be isotypic to Cs-V, which we had previously determined [Schwarz et al., Phys. Rev. Lett. 81, 2711 (1998)]. The structure has space group $\text{Cmca}$ and 16 atoms per orthorhombic unit cell (oC16 in Pearson notation). A schematic view of this structure is shown in Fig. 35. Characteristic features are flat layers of Rb1 atoms on
the Wyckoff 8f position alternating along the [100] direction with puckered nearly square layers of Rb2 atoms on the position 8d. The unit cell extends over four layers. The deviation of the cell parameters from a tetragonal metric is extremely small ($b/c \approx 1.005$). One of the Rb1–Rb1 distances is particularly short which suggests that the Rb1 atoms on the 8f position condense into Rb2 units. The Rb1 and Rb2 atoms are eleven and tenfold coordinated, respectively. In other words, for Rb (and also Cs) the atomic coordination increases again after having passed through the eight-coordinated Cs-IV-type structure.

The increase in coordination number continues at higher pressure. At least in the case of Cs, we could recently show that the structure adopted by Cs-VI (70 GPa to at least 184 GPa) is double hexagonal close packed with a $c/a$ ratio corresponding to an ideal close packing of spheres [Takemura et al., Phys. Rev. B, submitted]. At the highest pressure of 184 GPa Cs is compressed to 14% of its ambient-pressure volume.

In conclusion, we have determined the crystal structure of the phase Rb-IV based on high-resolution monochromatic synchrotron X-ray diffraction. The results demonstrate that the pressure-driven breakdown of the nearly-free electron character of a simple metal induces a phase transition to a rather complex structure. The present work partly closes the gap in our knowledge about the phase transition sequence in heavy alkali metals during the early stages of the $s \to d$ transition. Furthermore, having solved the structures of Rb-VI and Cs-VI we have made an important step in understanding the structural evolution of heavy alkali metals, when they are fully turned into monovalent $d$-transition metals by the application of pressure. Our results have implications for developing a detailed picture of the electronic structure, chemical bonding, and physical properties of heavy alkali metals during the progression of the $s \to d$ transition.
Materials and magnetism

The magnetic behavior of materials is an intellectually interesting subject and also one of enormous technological importance. In both these respects, one group of materials, the 3d transition metal oxides, has attracted a great deal of attention in recent years. Research at the institute has concentrated in particular on doped LaMnO$_3$ compounds, which show a range of unusual properties including colossal magnetoresistance.

Pressure-induced break-down of Jahn-Teller distortion and insulator to metal transition in LaMnO$_3$

I. Loa, P. Adler, A. Grzechnik and K. Syassen; U. Schwarz (MPI-CPFS Dresden); M. Hanfland (ESRF Grenoble)

Perovskite-type manganites have recently gained renewed interest after the observation of a colossal negative magnetoresistance (CMR) effect in La$_{1-x}$(Ca, Sr)$_x$MnO$_3$. Materials of the class R$_{1-x}$A$_x$MnO$_3$ (where R is a trivalent rare earth and A a divalent alkaline earth element) are currently under intense investigation. The interest stems partly from a wealth of interesting physical effects: CMR, charge and orbital ordering, metal-insulator, magnetic, and magnetic-field induced phase transitions, which are due to an intimate interplay of structural, spin, and electronic degrees of freedom. In addition, these compounds are examined as possible magnetoresistance sensor materials.

We have investigated the effect of hydrostatic pressure on the structural and electronic properties of LaMnO$_3$ – the parent compound of the CMR materials – by angle-dispersive synchrotron X-ray powder diffraction and optical reflectivity spectroscopy. This study was motivated in part by the observation that the CMR effect is strongly pressure sensitive and the close relation between structural, magnetic, and electronic properties. Only for a small number of distorted perovskites the structural changes under pressure have been studied up to date. Deviation from the ideal cubic perovskite structure is generally attributed to a mismatch of ionic sizes. Decreasing as well as increasing distortion under pressure have been found. In contrast to other perovskites studied under pressure so far and also differing from the typical CMR materials, an additional pronounced distortion of MnO$_6$ octahedra occurs in LaMnO$_3$ due to the Jahn-Teller effect arising from a localized t$_{2g}^3$e$_g^1$ electron configuration of the Mn$^{3+}$ ions. Application of pressure is expected to enhance the Mn–O–Mn interactions and consequently the itinerancy of the electronic system. This leads to the expectation that the Jahn-Teller effect in LaMnO$_3$ could be reduced at high pressure which might result in structural phase transitions to higher symmetry perovskite structures.
Figure 36: Crystal structure of LaMnO$_3$ at ambient conditions (space group Pnma).

The crystal structure of orthorhombic LaMnO$_3$ is sketched in Fig. 36 for ambient conditions. The Mn ions are surrounded by corner-sharing oxygen octahedra which form a three-dimensional network. Cooperative Jahn-Teller distortion of the octahedra leads to alternating long and short Mn–O distances in the ac-plane. The tiltings of the octahedra can be described by rotations about two axes which would be parallel to the $a$- and $b$- axis in an undistorted structure. The La ions are located in the voids between the octahedra. Qualitatively, the same structure is adopted by the lightly doped manganites La$_{1-x}$Am$_x$MnO$_3$ with $x < 0.1$.

The pressure dependence of the crystal structure of LaMnO$_3$ up to 40 GPa under hydrostatic conditions was studied by angle-dispersive X-ray powder diffraction at the European Synchrotron Radiation Facility (Grenoble) using diamond anvil cell (DAC) techniques. The relative changes of the lattice parameters with pressure are illustrated in Fig. 37a). At low pressures, the $a$-axis compressibility is $\sim 4$ times larger than that of the $b$ and $c$ axes. This can be attributed to a pressure-induced reduction of the Jahn-Teller distortion of the MnO$_6$ octahedra which is evident from the evolution of the Mn–O distances shown in Fig. 37b). Extrapolation of the experimental data suggests the Mn–O bond lengths to become nearly equal around 17 GPa, where the $a$-axis compressibility exhibits a distinct change (cf Fig. 37a)). Besides the usual overall compression of the lattice, the important effect of pressure on the crystal structure of LaMnO$_3$ is a reduction of the Jahn-Teller induced distortion of the MnO$_6$ octahedra and also a decrease of the octahedral tiltings.
With respect to the *doped manganites*, these findings support the suggestion that the increasing temperature of maximum resistivity and maximum magnetoresistance with pressure is due to a straightening of the Mn–O–Mn bond angles towards 180° and decreasing Mn–O distances. This would induce an increase of the overlap between the manganese *d* orbitals and the oxygen *p* orbitals which is a crucial parameter for the electronic conductivity. Altogether, it would lead to a stabilization of the low-temperature metallic state and hence to the observed pressure effects in the doped manganites.

The structural changes of LaMnO₃ under pressure strongly affect its electronic properties. Figure 38 shows optical reflectivity spectra in the pressure range 11–38 GPa at ambient temperature. The broad spectral feature around 2 eV corresponds to an optical excitation gap in agreement with an insulating ground state. Up to 20 GPa, there is no major change in the optical response, although the Jahn-Teller distortion of the octahedra is mostly suppressed in this pressure range. Above 25 GPa, the near-infrared reflectivity increases strongly. The inset in Fig. 38 shows an increase of the reflectance at 0.6 eV by two orders of magnitude, indicating an insulator to metal transition. The important effect of pressure appears to be a strengthening of the Mn–O–Mn interactions, leading to enhanced itinerancy of the system.
Figure 38: Optical reflectivity spectra of LaMnO₃ at room temperature as a function of energy. 
$R_d$ denotes the absolute reflectivity of the interface between sample and diamond of the pressure-generating DAC. The inset shows the pressure dependence of $R_d$ at 0.6 eV.

Apparently, high pressure in LaMnO₃ leads to a similar electronic situation as in the cubic perovskite SrFeO₃ where isoelectronic Fe⁴⁺ ions occur. Enhanced covalency of the iron-oxygen bonding results in a suppression of the Jahn-Teller effect and metallic conductivity in SrFeO₃ already at ambient pressure. Also, doping of LaMnO₃ with divalent alkaline earth elements, which leads to Mn³⁺/Mn⁴⁺ mixed-valence compounds, gives rise to similar structural and electronic changes. Moderate pressures up to $\approx 15$ GPa continuously suppress the Jahn-Teller effect – as does doping up to $x \approx 0.1$. In an intermediate range (pressure 15–25 GPa; doping $x \approx 0.1$–0.2), there is no Jahn-Teller distortion, but the system remains insulating. At higher doping levels, the system becomes metallic and adopts a rhombohedral structure. In analogy, pressure above 25 GPa moves LaMnO₃ into a metallic regime and there are in fact indications for a transition to a higher symmetry crystal structure.
The effect of Zn-substitution on the para-to-ferromagnetic transition temperature of La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$

CMR materials

V.P.S. Awana and E. Gmelin

The discovery of high-temperature superconductivity (HTSC) in perovskite oxide cuprates stimulated the research into similar perovskite oxides which were neither cuprates or even not superconductors. A class of materials, with the nominal formula RE$_{1-x}$Ea$_x$MnO$_{3+\delta}$ (where RE = La, Pr, Nd, Sm, etc., Ea = Ca, Sr, Ba, Pb, etc.) was re-investigated in 1993. These compounds show a very large colossal magnetoresistance (CMR), that makes them interesting for practical application and for fundamental research of the CMR phenomena.

At the present time it is known that $T_p$, the paramagnetic-to-ferromagnetic (pm-fm) transition temperature, where the CMR occurs, is highly sensitive to $x$, the doping concentration, and $\delta$, the oxygen deficiency, in RE$_{1-x}$Ea$_x$MnO$_{3+\delta}$ samples. By changing $x$ with fixed $\delta$ or vice-versa, one essentially changes the Mn$^{3+}$/Mn$^{4+}$ ratio in these compounds; Mn$^{4+}$ amount has a clear relationship with $T_p$. In fact, the doping mechanism for changing the Mn$^{3+}$/Mn$^{4+}$ ratio is similar to that as followed for the HTSC compounds to control the effective Cu valency (Cu$^{2+\epsilon}$) which is directly correlated to the superconducting transition temperature $T_c$. For both CMR and HTSC, Mn and Cu, respectively, can be substituted partially by other 3d metals like Co, Ni, Fe and Zn. Several studies of magnetic 3d metal substitution in CMR compounds have been carried out. The monotonic decrease of $T_p$ found with increasing $x$ (e.g. for Fe) was explained in terms of a changed Mn$^{3+}$/Mn$^{4+}$ ratio. However, no systematic study of the influence of nonmagnetic ions, e.g. Zn, has been reported so far, and in addition, very few studies deal with the thermal properties, in particular the specific heat and the magnetic entropy, related to $T_p$. The latter was the aim of present study.

Samples of La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ (with $0.0 < x < 0.5$) were synthesized by solid state reaction as described in the literature. Neutron diffraction results, performed at the University of Missouri, as well as X-ray diffraction patterns, show that Zn-substitution occurs isostructurally in the La$_{0.67}$Ca$_{0.33}$Mn$_{1-x}$Zn$_x$O$_3$ system, at least up to $x = 0.3$ and that the oxygen content remains nearly invariant. Rietveld analysis of these data allowed the determination of the lattice parameters, the oxygen stoichiometries and selected bond lengths. Measurements of the electrical resistivity (showing large anomalies around $T_p$ as expected from other CMR substances), magnetization and heat capacity curves as a function of temperature clearly show the pm-fm transition at $T_p$ for $x < 0.15$; it gradually disappears for $x > 0.15$. The transition takes place over an increasingly broader temperature range, between 5 K to 50 K, depending on $x$. $T_p$ decreases with increasing $x$ with a rate of $dT_p/dx$(Zn) $4.9$ K/at%, similar to values observed for other 3d metal substitutions on Mn site.
Figure 39: Left: $\Delta S_{\text{trs}}$ as a function of the Zn-concentration $x$. Right: Heat capacity $C_p$ versus temperature plots for $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ system, measurements have been made down to 100 K.

Plots of the heat capacity $C_p$ versus temperature $T$ are shown in Fig. 39. The samples ($x = 0, 0.03, 0.05, 0.075$) show well defined transition peaks, a less pronounced hump for $x = 0.1$ and no anomaly for $x = 0.15$ and 0.30, similar to the resistivity and magnetization results. The transition temperature $T_p(C_p)$, as determined from $C_p(T)$, shifts to lower temperatures with increased $x$ values and coincides excellently within about 2 K with that found from the magnetization curves, $T_p(M)$. Values are given in Tab. 1.

Table 1. Paramagnetic-to-ferromagnetic transition temperatures $T_p$ for $La_{0.67}Ca_{0.33}Mn_{1-x}Zn_xO_3$ samples (with various concentration $x$ of Zn substituting Mn), as deduced from magnetization ($T_p(M)$) and heat capacity ($T_p(C_p)$) curves, change of entropy ($\Delta S_{\text{trs}}$) calculated from the specific heat curves in the range 100 K to 300 K and taking $x = 0.30$ as reference, and $\Delta S_{\text{trs}}$, the transition entropy corrected by contributions estimated from below 100 K (see text) and from the magnetic part of the sample with $x = 0.30$.

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<th>Zn-concentration $x$ [%]</th>
<th>$T_p(M)$ [K]</th>
<th>$T_p(C_p)$ [K]</th>
<th>$\Delta S_{\text{trs}}$ [J/molK]</th>
<th>$\Delta S_{\text{trs}}$ [J/molK]</th>
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<td>185</td>
<td></td>
<td>2.3</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The change of entropy ($\Delta S_{\text{trs}}$) associated with $T_p$ was calculated from $C_p(T)$ by subtracting the lattice contribution. Theoretically, the expected entropy change $\Delta S_{\text{trs}}$ for a magnetic ordering of a mixture of Mn$^{4+}$/Mn$^{3+}$ ions is: $\Delta S_{\text{trs}} = 0.67 R \ln 5 + 0.33 R \ln 4 = 12.8$ J/molK, since for $La_{0.67}Ca_{0.33}MnO_3$ (similar to other CMR compounds) 1/3 of the Mn ions are in
the Mn$^{4+}$ state, with spin $S = \frac{3}{2}$, and 2/3 of them are Mn$^{3+}$, with $S = 2$. Obviously, the specific heat anomalies, displayed in Fig. 39, show only $\Delta S_{\text{trs}} \ll 12.8 \text{ J/molK}$, a phenomenon also observed by other groups for other CMR materials. However, we notice that for a magnetic transitions near 280 K, a considerable part of entropy may be contained in $C_p(T)$ below 100 K. For this reason, we approximated the pure lattice heat (in the range 100–300 K) by the $C_p(T)$-curve of the sample with $x = 0$ and subtracted this curve from all others. The resulting variation of $\Delta S_{\text{trs}}'$ as a function of $x$ is represented in Fig. 39: $\Delta S_{\text{trs}}$ decreases, and the values are listed in Tab. 1. The following estimate, however, evidences that the expected full entropy is presumably engaged for the $x = 0$ sample: (i) the entropy below 100 K amounts to $\Delta S^\text{cor}_{\text{trs}}(<100 \text{ K}) \approx 2.5 \text{ J/molK}$, (ii) assuming a magnetic heat of 2.5 J/molK for $x = 0.3$ (the present lattice-reference) leads to an additional contribution $\Delta S^* \approx 3.7 \text{ J/molK}$. As a consequence, the full entropy estimated by this way, including these corrections, yields: $\Delta S_{\text{trs}} = [(6.4 + 2.5 + 3.7) \pm 1.5] = 2.6 \text{ J/molK}$ for $x = 0$. The values are listed in Tab. 1 also and correspond to what is expected (in the case of $x = 0$) whereas several contributions in the literature interpret the lack of magnetic entropy as a characteristic feature of CMR materials. In contrast to literature, our specific heat results and entropy evaluation, show that the full magnetic entropy ($\Delta S_{\text{trs}} = 12.8 \text{ J/molK}$) is removed between 0 K and 280 K, a result that may presumably be also valid for all other CMR materials.

Evidence of anisotropic transport properties in La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films studied by laser-induced transient voltages

H.-U. Habermeier and X.-H. Li

The observation of a colossal magnetoresistance (CMR) close to the spin ordering temperature, $T_c$, in doped rare earth manganites of the type Ln$_{1-x}$B$_x$MnO$_3$ (with Ln = La, Pr, Nd and B = Ca, Sr, Ba, Pb) has generated considerable research activities due to their peculiar electronic and magnetic properties caused by strong electron correlation. The CMR materials have a perovskite-type crystal structure in which the corner-sharing oxygen octahedra surrounding the Mn ions can cooperatively rotate around the cubic [110] or [111] direction, causing a reduction of the original cubic to an orthorhombic or rhombohedral symmetry. It is now accepted that both, double exchange and Jahn-Teller (JT) lattice distortions, play an important role in determining their electronic and magnetic properties. If the JT distorted oxygen octahedra surrounding the Mn$^{3+}$ ions are not distributed randomly in the material, an anisotropy of the transport properties can be expected in addition to the anisotropy introduced by spin ordering at temperatures below the spin ordering temperature.
In principle, experimental studies of anisotropy effects in transport properties can directly be performed using sufficiently large single crystals or – in the case of unavailability of the appropriate crystals – with single-crystalline thin films. In reality, using the thin film approach, the technological problems for the measurement of the out-of-plane properties can only be overcome if, e.g., the electrical conductivity in plane and out-of-plane differ by orders of magnitude. In our experiments, we use an unconventional thin film approach to study anisotropy effects and describe experimental evidence of a pronounced anisotropy in the transport properties of doped LaMnO$_3$ that is not compatible with a cubic symmetry or faintly distorted cubic symmetry.

Our experiment is designed in analogy to the well established so called thermopile effect in YBa$_2$Cu$_3$O$_7$ (YBCO) single crystal thin films grown on vicinal cut STO single crystal substrates. This approach probes the anisotropic thermoelectric properties of a material rather than the dc conductivity. The origin of the thermopile effect lies in the generation of thermoelectric fields transverse to a temperature gradient, $\nabla T$. The thermoelectric fields are caused by the nonzero off-diagonal elements of the Seebeck tensor $S_{ij}$. Off-diagonal Seebeck coefficients occur in tetragonal, trigonal, hexagonal and orthorhombic crystals only, if $\nabla T$ has an orientation not along the low indexed crystallographic axes. In the thermopile experiment, the non-crystallographic system orientation is realized by depositing YBCO thin films onto SrTiO$_3$ (001) single crystal substrates intentionally miscut by an angle $\theta$ towards the [010] direction as shown schematically in Fig. 40. This causes the CuO$_2$ planes of the YBCO to grow with a tilt angle $\theta$ with respect to the substrate surface plane. An illumination of the film with a short laser pulse generates a transient temperature gradient $\nabla T$, which gives rise to a voltage, $U$. Quantitatively, the integration of the Seebeck equation

$$\nabla \Phi_i = S_{ij} \nabla j T$$

yields:

$$U_{[0\bar{1}0]} = l/2t \nabla T \nabla S \sin 2\alpha$$

and

$$U_{[100]} = 0$$

(10)

($l =$ length of illuminated film strip, $t =$ film thickness, $\nabla T =$ temperature difference of top and bottom of the film, $\nabla S = S_{ab} - S_c$, the difference of the Seebeck coefficients in the ab-plane and along the c-axis). In YBCO the signals detected at room temperature even for
A moderate laser fluence of 50 mJ/cm² can be as large as 18 V for a sample with \( t = 250 \) nm and an illuminated length of 2 mm. The experiments reported here, demonstrate the existence of an unexpected laser-induced voltage (LIV) in \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) thin films in the order of 1/10 of those measured in YBCO. The existence of these laser-induced signals suggests a microscopic mechanism comparable to that in YBCO implying a substantial anisotropy of the thermoelectric properties of \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \).

![Figure 41: a) Laser-induced voltage signals measured at room temperature for \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) thin films of thickness 180 nm in [100] and [010] direction, b) as a function of illuminated length, c) as a function of illuminating laser energy density, d) and the vicinal angle of the substrate.](image)

Expitaxial \( \text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3 \) films were prepared on STO (001)-oriented substrates with intentional miscut angles \( \theta \) using the standard pulsed laser deposition technique, subsequently patterned and contacted by the usual lithographic and deposition procedures. The films consist of single-phase material with properties typical of epitaxial CMR thin films. The thermoelectric experiment is performed using an excimer laser (KrF, \( \lambda = 248 \) nm, pulse duration 28 ns) as energy source in conjunction with an Oxford optical cryostat allowing measurements in the range 10 K < \( T < 300 \) K. Figure 41a) shows the original raw
data as recorded for a specimen deposited on a perfectly oriented (001) substrate together with the signals for a specimen deposited on a substrate with 100 tilt vs. the [010] direction. As shown in Fig. 41a), the existence of a laser-induced voltage in La$_{2/3}$Ca$_{1/3}$MnO$_3$ thin films oriented not along the principal crystal axes, suggests its thermoelectric origin. Consequently, the predictions of Eq.(10) such as its dependence on the crystallographic orientation, length, thickness and laser fluence, i.e., $\nabla T$ must hold. The results of the most crucial experiment are given in Figs. 41a) – d) for La$_{2/3}$Ca$_{1/3}$MnO$_3$ films deposited on vicinal cut substrates and patterned in a L-shape with branches oriented along the [010] and [100] directions, respectively. According to Eq.(10), $U$ must vanish. for the strip oriented along [100]. Along the tilt direction [010], however, $U$ should be nonzero and scale linearly with the illuminated length, laser fluence and the tilt angle $\theta$. The data given in Fig. 41a) – d) are in accordance with the predictions of the Seebeck equation. A careful study of the temperature dependence $\nabla S(T)$ and $\rho(T)$ suggests a close relationship between these quantities supporting the validity of the predictions of Eq.(10).

In conclusion, we have demonstrated the existence of a laser-induced voltage in La-Ca-Mn-O thin films deposited on vicinal cut substrates which is compatible with the predictions given by a model based on the existence of off-diagonal elements of the Seebeck tensor. This implies the presence of an anisotropy of the material. We ascribe the origin of this anisotropy to the interplay of the Jahn-Teller distortion caused by the Mn$^{3+}$ ions and biaxial interfacial strain of the films.

**Charge and orbital order in half-doped manganites**

J. van den Brink and G. Khaliullin

Manganese oxides with the general composition R$_{1-x}$A$_x$MnO$_3$ (where R and A are rare earth and alkaline earth ions, respectively) have attracted considerable attention because of their unusual magnetic and electronic properties. Most of the perovskite manganites show a ferromagnetic (FM) ground state when the holes are optimally doped (usually $0.2 < x < 0.5$) and anisotropic antiferromagnetic (AFM) phases for $x > 0.5$. The half-doped manganites, with $x = \frac{1}{2}$, are very particular. Magnetically these systems form FM zig-zag chains that are coupled AFM (see Fig. 42) at low temperatures, the so-called magnetic CE-phase. The ground state is, moreover, an orbital-ordered and charge-ordered insulator. The insulating charge-ordered state can be transformed into a metallic FM state by application of an external magnetic field, a transition that is accompanied by a change in resistivity of several orders of magnitude.
Figure 42: View of the CE-phase in the x-y plane. We choose our basis orbitals such that the gray lobes of the shown orbitals have a negative sign. The dots at the bridge-sites represent a charge-surplus.

We address the nature of the charge ordering at $x = \frac{1}{2}$ and show that (i) the insulating CE-phase results from a particular ordering of orbitals, (ii) this state is stable only in a narrow concentration range around the commensurate value and that (iii) the zig-zag chains are intrinsically charge ordered due to on-site Hubbard correlations.

Figure 43: Top: Topology of the interactions in a zig-zag chain, where $t_1 = \frac{t}{2}$, $t_2 = \frac{t}{\sqrt{3}}$, and $U$ is the Coulomb interaction between electrons on the same site. Left: Electron dispersion in the zig-zag chain of the CE-phase for $U = 0$ and electron dispersion in a straight chain, as in C-phase (dashed line). Right: Total energy per site for the CE-, C- and FM-phase. The Maxwell-construction in the phase separated (PS) region is shown by the thin dashed line.
The strong spatial anisotropy of the hopping, combined with the competing kinetic and superexchange energy can give rise to low dimensional spin and charge structures. As in the double-exchange framework electrons can only hop between sites with FM aligned core-spins, in the CE-phase only hopping processes within the zig-zag chains are possible, rendering the system one-dimensional for low-energy charge fluctuations. The topology of the electron hopping integrals is shown in Fig. 43.

The essential observation is that an electron that passes a corner-site of the zig-zag chain, acquires a phase that depends on the orbital through which it passes. This leads to an effective dimerization that splits the bands and opens a gap at the Fermi-surface, see Fig. 43. The gap is very robust as it is a consequence of the staggered phase-factor that is itself fully determined by the topology of the system. At the same time not all orbitals are fully occupied, leading to an orbital-polarized ground state. Our most surprising observation is that the experimentally observed charge order is directly obtained from the degenerate double-exchange model when the Coulomb interaction (the Hubbard $U$) between electrons in different orbitals, but on the same site, is included. This can be understood from the fact that in the band-picture on the corner-sites both orthogonal orbitals are partially occupied, but on the bridge-site only one orbital is partially filled. The on-site Coulomb interaction acts therefore differently on the corner- and bridge-sites: charge is pushed away from the effectively correlated corner-sites to the effectively uncorrelated bridge-sites. We calculate the charge order parameter with three different methods: exact diagonalization (ED), in mean-field (MF) and with the Gutzwiller-projection (GP). Figure 44 shows the charge-disproportionation $\delta$ defined as $\langle n_B - n_A \rangle$, where $\langle n_B \rangle$ ($\langle n_A \rangle$) is the expectation value for finding an electron on a bridge- (corner-) site.

![Figure 44: Charge-disproportionation as a function of Coulomb interaction and doping (inset). The full line is obtained from exact diagonalization (ED). The dashed lines for small and large $U$ are obtained by the mean-field and Gutzwiller approximations, respectively. The dots in the inset are the ED results for $U \rightarrow \infty$.](image)

The on-site Coulomb interaction causes a charge-surplus on the bridge-sites in the x-y plane. In the CE-structure the zig-zag chains are stacked AFM along the z-direction, which implies that above each bridge-site there is another bridge-site in the next plane. So we find that the charges actually accumulate on sheets formed by the bridge-sites.
along the z-direction. This is in remarkable agreement with experiment and at the same
time excludes the possibility that the charge-order is driven by longer range Coulomb in-
teractions because the Madelung-sum is always minimized for a rock salt-type charge-order.
Figure 44 shows that the charge disproportionation is strongly doping dependent. For $x > \frac{1}{2}$
the holes that are doped into the lower band efficiently suppress charge-order. In this dop-
ing range, however, the CE-phase becomes unstable with respect to the so-called C-phase.
Figure 43 shows that the energy of the C-phase is lower for $x > 0.57$. For $x < \frac{1}{2}$ the en-
ergy per site of the CE-phase, $E_{CE}$, is constant because the extra electrons are doped in the
nondispersive bands at zero energy, which causes a kink of $E_{CE}$ at $x = \frac{1}{2}$. For lower hole-
doping the homogeneous FM-phase is lower in energy, as is expected. Due to the kink in
$E_{CE}$ at $x = \frac{1}{2}$, one finds that for $x < \frac{1}{2}$ the FM-phase and CE-phase coexist. We conclude
that there is a strong asymmetry for doping lower and higher than $\frac{1}{2}$, as phase separation
between the CE- and FM-phases is only present on the lower doping side.

In summary, the CE-phase with one-dimensional ferromagnetic zig-zag chains is stable
for $x = \frac{1}{2}$ and due to staggered phase factors in the hopping, the chains are insulating and
orbital-ordered. The striking feature of our model is that the strong Coulomb interaction be-
tween electrons on the same Mn-site leads to the experimentally observed charge ordering.
In a magnetic field we expect the chains to be unstable with respect to the ferromagnetic
metallic state. This might offer a likely explanation for the large magnetoresistance at the
metal-insulator transition for the half-doped manganites.

**Spin dynamics and orbital fluctuations in LaTiO$_3$+$\delta$**

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Y. Taguchi and Y. Tokura (Univ. Tokyo)

In the layered cuprates exemplified by the series La$_{2-x}$Sr$_x$CuO$_{4+\delta}$, the transition from
a 3$d^9$ antiferromagnetic insulator at $x=\delta=0$ into an unconventional metallic and super-
conducting state with increasing hole concentration ($x, \delta > 0$) has received an enormous
amount of attention. The magnetic spectra of these materials, determined by inelastic neu-
tron scattering, have played a key role in efforts to arrive at a theoretical explanation of
this transition. The pseudocubic perovskite La$_{1-x}$Sr$_x$TiO$_{3+\delta}$ undergoes an analogous tran-
sition from a 3$d^1$ antiferromagnetic insulator at $x=\delta=0$ to a metallic state with increasing
hole concentration. In the titanates, however, the metallic state shows conventional
Fermi liquid behavior, and no superconductivity is found. Momentum-resolved probes
such as angle-resolved photoemission spectroscopy and inelastic neutron scattering have
thus far not been applied to the titanates, and the origin of the very different behavior of the
metallic cuprates and titanates is still largely unexplored. We have carried out an inelastic
neutron scattering study of the parent compound of the titanate series, LaTiO$_3$, that pro-
vides insight into the microscopic interactions underlying this behavior. Not surprisingly, the low temperature spin dynamics of LaTiO$_3$, which orders antiferromagnetically below $T_N = 130$ K, are described by the usual spin wave theory. The nearest-neighbor superexchange constant extracted from the spin wave spectrum (Fig. 45) is $J = 15.5$ meV, and the anisotropy gap (due to deviations of the superexchange Hamiltonian from Heisenberg symmetry) is 3 meV. This nearly isotropic spin wave spectrum is, however, very difficult to reconcile with a conventional scenario in which orbital order breaks the twofold orbital degeneracy of the Ti $t_{2g}$ multiplet at high temperatures and locks in the exchange interactions that drive the magnetic order at low temperatures. If this were correct, one would expect a large unquenched orbital angular momentum which would in turn introduce a large anisotropy into the spin wave spectrum due to spin-orbit coupling.

![Figure 45: Magnetic spectrum of LaTiO$_3$ along the (111) direction of reciprocal space. $\xi = 0$ and $\xi = 0.25$ are at the antiferromagnetic zone center and zone boundary, respectively. The points with vertical (horizontal) error bars result from constant-momentum (constant-energy) scans. The line is the result of a fit to a standard spin wave dispersion.](image)

This observation could be explained if strong orbital fluctuations average out the spin-space anisotropy. In order to test this scenario, we have conducted extensive resonant X-ray scattering experiments that have recently been established as a very sensitive probe of orbital ordering in transition metal oxides. With the X-ray energy tuned near the Ti K-edge, superlattice reflections indicative of orbital ordering were not found. Both neutron and X-ray data are thus consistent with an unusual state in which orbital order is very weak or absent, yet magnetic long range order is present. This situation is in stark contrast to the layered cuprates where orbital degrees of freedom are quenched due to the large Jahn-Teller distortion of the CuO$_6$ octahedra. Orbital fluctuations may hence act to reduce the effective Coulomb correlations in the metallic state of the titanates, which could help explain the very different electronic properties of the superficially rather similar cuprates and titanates.
Effect of pressure on the magnetic phase transition in 
$\alpha'$-NaV$_2$O$_5$

R.K. Kremer, I. Loa, F.S. Razavi and K. Syassen

The spin-Peierls (SP) transition in its simplest form may occur in antiferromagnetically coupled $S=1/2$ Heisenberg or XY chains, if magnetoelastic coupling causes a spin-lattice dimerization which induces a gap in the magnetic excitation spectrum. The gap separates the diamagnetic ground state from a continuum of excited states. The SP transition traditionally has gained renewed interest triggered by the discovery of a low-temperature phase transition in CuGeO$_3$ which showed the signatures of a SP transition below 14 K.

Lately, the compound $\alpha'$-NaV$_2$O$_5$ was suggested to represent the second inorganic SP system. A magnetic phase transition occurs in $\alpha'$-NaV$_2$O$_5$ at $T_C \approx 34$ K, below which the spin susceptibility, $\chi_{\text{spin}} \to 0$ as $T \to 0$. A gap of about 10 meV develops and a lattice distortion appears. Based on the original crystal structure determination, $S=1/2$ chains in $\alpha'$-NaV$_2$O$_5$ were supposed to originate from V$^{4+}$ ions being arranged in chains along the $b$-axis. This structure model was strongly guided by the assumption of a charge disproportionation and the formation of two different V moieties, namely V$^{4+}$ and V$^{5+}$, in a non-centrosymmetric crystal structure. New determinations of the crystal structure at room temperature indicated that rather $\alpha'$-NaV$_2$O$_5$ crystallizes in a centrosymmetric structure. The new structure model retains the general arrangement of the atoms but finds all V atoms to be identical with an average oxidation state of +4.5. A local density approximation analysis proposed the electrons to be distributed in molecular type wavefunctions across a V–O–V rung of V–O ladders which run along the $b$-direction. Consequently the notion of a quarter filled ladder system has been introduced for $\alpha'$-NaV$_2$O$_5$, which provides a natural explanation for the insulating character of $\alpha'$-NaV$_2$O$_5$.

The nature of the state below the phase transition originally proposed to be a conventional SP state is currently strongly disputed. The detection of two inequivalent V sites by NMR is ascribed to charge disproportionation associated with the formation of the singlet magnetic ground state. In contrast to CuGeO$_3$, charge degrees of freedom therefore appear to be an essential feature of the phase transition in $\alpha'$-NaV$_2$O$_5$.

Here we report a high-pressure ($< GPa$) Raman scattering and magnetization investigation of the transition temperature of $\alpha'$-NaV$_2$O$_5$. By applying pressure the transition temperature of $\alpha'$-NaV$_2$O$_5$ decreases, in contrast to CuGeO$_3$ for which a remarkable increase with pressure has been detected. We discuss our findings: (1) with respect to the results of a recent high-pressure X-ray crystal structure investigation which reveals a pronounced anisotropy of the compressibilities, and (2) with respect to theoretical predictions for the pressure dependence of the transition temperature in SP systems.

Figure 46(a) shows Raman spectra of $\alpha'$-NaV$_2$O$_5$ in the temperature range of 5–18 K at a pressure of 0.55 GPa. The transition to the low-temperature phase manifests itself in the Raman spectra by the appearance of additional peaks due to the folding of the Brillouin
zone and changes to the magnetic excitation spectrum. In our configuration, Raman modes intrinsic to the low-temperature phase could be observed at 657 and 950 cm\(^{-1}\). From the temperature dependence of the intensity of the 950-cm\(^{-1}\) peak (inset Fig. 46(b)), \(T_C\) at a given pressure could be deduced. Figure 46(b) displays \(T_C\) versus pressure \(P\). The zero-pressure value of \(T_C\) determined by this method is a few degrees lower compared to accurate determinations from specific heat or magnetic susceptibility measurements which yield \(T_C = 33.2(2)\) K. This deviation is mostly due to heating of the sample by the incident laser beam. The heating effect should, however, hardly affect the pressure dependence of \(T_C\). Figure 47(b) shows \(T_C\) as a function of pressure. The transition temperature decreases rapidly with increasing pressure at a rate of -15(5) K/GPa. No signature of a phase transition was detected at pressures above 1.2 GPa and temperatures down to 5 K. This finding indicates a suppression of the phase transition at relatively low pressures. In this respect, \(\alpha'\)-NaV\(_2\)O\(_5\) behaves similar to most organic SP compounds.

![Raman spectra of \(\alpha'\)-NaV\(_2\)O\(_5\) at 0.55 GPa for temperatures of 4.7–17.9 K.](image)

![Transition temperature of \(\alpha'\)-NaV\(_2\)O\(_5\) versus pressure as deduced from the intensity measurements of the Raman peak at 950 cm\(^{-1}\).](image)

Figure 46: (a) Raman spectra of \(\alpha'\)-NaV\(_2\)O\(_5\) at 0.55 GPa for temperatures of 4.7–17.9 K. (b) Transition temperature of \(\alpha'\)-NaV\(_2\)O\(_5\) versus pressure as deduced from the intensity measurements of the Raman peak at 950 cm\(^{-1}\) (see inset).
Figure 47: (a) Magnetic susceptibility of $\alpha'$-NaV$_2$O$_5$ measured at different external pressures, 0, 0.32, 0.46 and 0.71 GPa, from right to left, respectively. The inset displays the temperature derivative of $\chi_{mol} \cdot T$ with $\chi_{mol}$ taken at ambient pressure.

(b) Pressure dependence of the SP transition temperature of $\alpha'$-NaV$_2$O$_5$. The full line represents a fit of a linear decrease ($T_C[K] = 34.0 - 10.2(7) P[\text{GPa}]$) to all data, the dotted line a fit with a parabola (see text). Different symbols refer to samples taken from different batches.

$T_C$ can be determined more accurately from the sharp drop in the magnetic susceptibility below the transition. The magnetic susceptibility of $\alpha'$-NaV$_2$O$_5$ at various pressures is shown in Fig. 47. The magnetization of the empty cell has been subtracted. The high signal-to-noise ratio allows a reliable determination of $T_C$ from the peak temperature of the quantity $d(\chi_{mol} \cdot T)/dT$ (inset Fig. 47(a)). There was no indication of hysteresis when cycling the pressure in the range up to 1 GPa and back to ambient pressure. $T_C$ decreases with increasing pressure as is shown in Fig. 47(b). This result confirms the observation of the Raman scattering experiments and confirms the decrease of the transition temperature with increasing pressure. The average linear pressure coefficient for $T_C$ is -10(1) K/GPa, somewhat lower than observed in the Raman scattering results but within error. From the
magnetization experiments the pressure dependence appears to be nonlinear with a negative curvature. A fit to a parabolic decrease gives $T_C[K] = 34.0 - 6.1(2.6)P - 6.0(3.7)P^2$, where pressure $P$ is in GPa and fits the data with an improved $\chi^2$ parameter, however, in view of the error bars this presumption requires further experimental confirmation.

The phenomenology of the magnetic transition on $\alpha'$-NaV$_2$O$_5$ closely resembles that of a SP transition in quasi-one-dimensional spin systems. The variation of $T_C$ with pressure in organic SP systems has been studied by Bray. Using the expressions for $T_C$ as derived by Pytte and by Cross and Fisher, we expect a decrease in $T_C$ with pressure, as has been observed, for instance, in the organic SP system TTF-CuBDT.

An increase of $T_C$ with pressure, as experimentally realized, e.g., in (MEM)-(TCNQ)$_2$, has theoretically been explained by Lepine by taking into consideration an anharmonic coupling of the (anharmonic) SP soft mode to the average lattice strain along the chains. Depending on the sign of the coupling energy between the soft mode and the lattice strain along the chain, $T_C$ can either decrease or increase with pressure.

The above scenario, which is based on an essentially one-dimensional picture and intra-chain interactions only, does not fully explain to $\alpha'$-NaV$_2$O$_5$. Recent crystal structure determinations under pressure show that $\alpha'$-NaV$_2$O$_5$ is rather incompressible along the chain axis ($b$-axis) as well as perpendicular to the chains in the $a$-axis direction and hence most of the overall volume change is due to the large compressibility along the $c$-axis. The enhanced interlayer interaction affects in particular the apex oxygen atoms of the VO$_4$ units, as evidenced, for instance, by the pronounced softening of the out-of-plane vibrations of these oxygen atoms with increasing pressure. It therefore appears plausible that it is the enhanced interlayer coupling under pressure which plays a major role in determining the pressure dependence of $T_C$. On the one hand, the large reduction of the $c$-axis clearly affects the intralayer elastic properties as is indicated by the unusual pressure dependence of the $a$ and $b$ lattice parameters. These show negative compressibility at pressures above 4 GPa and near ambient pressure, respectively. Secondly, in view of the suggested charge disproportionation associated with the magnetic transition in $\alpha'$-NaV$_2$O$_5$, there may also be an additional more subtle electronic aspect specific to the transition in $\alpha'$-NaV$_2$O$_5$, namely an increase in the screening of Coulomb interactions with increasing pressure. To our knowledge, microscopic theoretical models proposed so far for $\alpha'$-NaV$_2$O$_5$ deal with intrachain or intralayer couplings only and do not take into account the interlayer interactions.

In summary, from magnetization as well as Raman measurements the magnetic transition temperature in $\alpha'$-NaV$_2$O$_5$ is found to be strongly pressure dependent. It decreases with pressure at an average rate of -10 K/GPa. In this respect the behavior of $\alpha'$-NaV$_2$O$_5$ differs from that of CuGeO$_3$ which shows a pronounced increase of $T_{SP}$ under pressure. Based on the evolution of structural parameters under pressure and anomalous pressure effects on lattice vibrational modes we argue that enhanced interlayer interactions are likely to play a major role in the suppression of the transition in $\alpha'$-NaV$_2$O$_5$ under pressure.
Superconductivity

The quality of experiments on high temperature superconductors is often limited by the quality of the samples. Using a new optical furnace it was possible to grow large, high quality single crystals of the cuprate family Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Inelastic neutron scattering experiments on these samples showed a resonance peak similar to the one observed in YBCO. On the theoretical side the phase diagram of the $t$–$J$ model with nearest neighbor Coulomb interaction has been determined using a $1/N$ expansion, and the formation of stripes, induced by electron-phonon interaction, has been investigated.

**Growth of Bi$_{2+x}$Sr$_{2-x}$Ca$_{n-1}$Cu$_n$O$_{2n+4+\delta}$ crystals using a traveling solvent floating zone method**

C.T. Lin and E. Schönhe"r

The growth of crystals of the high-$T_c$ oxide superconductors has been hampered by the complexities of the materials and their phase diagrams. The most common crystal growth technique adopted for these oxides is the ‘flux’ method, where the starting materials are dissolved in a melt, which is usually formed by excess CuO and BaO or a KCl/NaCl mixture. The crystals are produced by slow cooling of the melt. This method, however, suffers from several disadvantages: (1) the crystals are contaminated with the crucible material, (2) the crystals are difficult to remove from the crucible, (3) the crystals contain flux inclusions. In most cases these drawbacks can be overcome by the ‘traveling solvent floating zone’ (TSFZ) method. Moreover, this method is suitable for growing crystals from incongruently melting compounds and has been thus successfully used to grow large crystals of the high-$T_c$ La$_{2-x}$Sr$_x$CuO$_4$ and Bi$_{2+\delta}$Sr$_{2-x}$Ca$_{n-1}$Cu$_n$O$_{2n+4+\delta}$ (denoted as 2201 for $n = 1$ and 2212 for $n = 2$) superconductors. In this work we report the growth of large and high quality 2201 and 2212 crystals as well as their characterization.

The TSFZ image furnace, shown schematically in Fig. 48, forms a melting zone by focusing the light of 4 halogen lamps on to a feeding rod. For this purpose each lamp is positioned at one focus of an ellipsoidal half chamber and the 4 chambers are then symmetrically placed around the feeding rod axis. For high light reflectivity the walls of the chambers are plated with aluminum. The sample temperature is adjusted by the current through the lamps. A video camera allows the direct observation of the melting zone and is thus used to monitor the crystal growth. The sample is enclosed in a fused silica tube to enable crystal growth in various gas atmospheres up to 9 atm pressure. Through the slow movement of the mirror arrangement, single crystals are obtained by passing a molten zone (floating zone) from the lower seed rod along the upper feed rod. The seed and the feed rod are rotated contrariwise to ensure efficient mixing and uniform radial temperature distribution in the molten zone.
The melting behavior of the Bi-Sr-Ca-Cu-O system is very complicated with a wide range of compositions, where \((\text{Bi, Sr})_4\text{CuO}_2\) or \((\text{Bi, Ca, Sr})_5\text{Cu}_2\text{O}_z\), partially or totally melt in the temperature range 890–1000°C. Thus growth of a thick \(\text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}\) crystal from a regular flux is rather difficult. These disadvantages are circumvented by the TSFZ procedure. In order to explain the growth process, we consider a typical pseudobinary equilibrium phase diagram of an incongruently melting compound, schematically shown in Fig. 49 where the metastable extension is represented by a broken line. The incongruently melting compound we require crystallizes from a melt with composition between \(C_0\) and \(C_1\) in the temperature range \(T_0\) to \(T_1\). We arrange the experiment with the seed crystal of composition \(C_S\), the molten zone with \(C_0 < C_L < C_1\), and the feed rod with \(C_S\). \(\Delta x\) is the path of the upward moving molten zone. An amount of \(\Delta x\) with composition \(C_S\) is crystallized from the molten zone with the composition \(C_L\), if an equivalent amount of \(\Delta x\) with \(C_S\) is solved from the feed rod at the upper zone end. Therefore continuous growth of crystals having the chemical composition of \(C_S\) is expected from the zone with the fixed composition \(C_L\) which is independent of the zone traveling distance \(\Delta x\).

A pellet of \(\approx 0.5\) g of solvent is placed on the seed to form the initial zone. The feed rod and the growing crystal are then rotated at 30 rpm in opposite directions. To obtain stoichiometric and thick crystals in the \(c\)-axis, a low growth rate of <0.5 mm/h and pure oxygen pressures of 100, 200, 300, 500 and 700 kPa is applied throughout the growing procedure.

Figure 48: Schematic illustration of the four ellipsoidal infra-red image furnace.
The final feed rod must meet three requirements, namely, (1) its composition should be similar to that of the desired crystal (2) the rod should be straight and of uniform diameter to avoid trembling and (3) of high density, i.e., \( \rho > 90\% \) compared to that of the crystal. Starting feed and solvent materials were prepared from \( \text{BiO}_1\text{Sr}_1\text{CaCO}_3 \) powders of 99.9% purity. For the 2201 feed and solvent, ratios of \( \text{Bi}:\text{Sr}:\text{Cu} = 2.1:1.9:1.0 \) and 2.3:1.9:1.3 were used, and for the 2212 feed and solvent those of \( \text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 2.1:1.9:1.0 \) and 2.6:1.9:1:1.6, respectively. The well mixed powders were calcined at 880°C for 48 hours. After grinding and milling they were formed into cylindrical shapes of \( \phi 10 \times 100 \) mm by pressing at a hydrostatic pressure of \( \approx 70 \) MPa. The feed rod and solvent mixtures were then sintered in flowing oxygen for 48 hours at 850°C and 820°C, respectively. Finally, the high density required for the rod was obtained through the (TSFZ) premelting with the mirror furnace. Figure 50 shows a sintered and subsequently predensified feed rod, respectively.

Figure 50: Feed rod of \( \text{Bi}_{2.1}\text{Sr}_{1.9}\text{Cu}_2\text{O}_{8+ \delta} \), the longer one (10 cm) sintered at 850°C, 48 hours in flowing oxygen and the shorter one is a premelted and highly dense rod.
A large crystal could be obtained by a low growth rate under 0.5 mm/h and a long feed rod over 10 cm in length. Figure 51(left) shows a cross section of a 2201 crystal ingot grown at a rate of 0.4 mm/h. After polishing of the cross section three growth states were revealed, i.e., molten zone (solidified melt), convex solid-liquid interface and as-grown crystals. At the initial stage the crystals grew along the \( a \)-direction by spontaneous nucleation and the grain size gradually increased in its diameter with length, while the number of the grains was reduced, as shown in Fig. 51(right). This indicated that the longer the ingot is grown the larger the crystal is obtained.

**Figure 51:** A cross section of the \( \text{Bi}_{2+x}\text{Sr}_{2-x}\text{Cu}_2\text{O}_6+\delta \) ingot consisted of as-grown crystals, convex interface and molten zone (solidified melt) grown by TSFZ method (left) and the grain size increasing while the grain number decreasing with dimension of the ingot – a preferential growth (right).

Figure 52(left) shows a typical \( \text{Bi}_{2.1}\text{Sr}_{1.9}\text{CaCu}_2\text{O}_8+\delta \) crystal ingot obtained at a growth rate of 0.2 mm/h; the crystal grains in the polished surface were visible under polarized microscope. The X-ray Laue patterns showed that grains were preferably grown along the crystallographic \( a \)-axis (parallel to the rod axis). Figure 52(right) displays platelets with dimension of \((20 \times 5 \times 1.3)\) mm cleaved from the ingot mechanically. In Table 2 the compositions of the cations are listed as determined from the analysis by the Inductive Coupled Plasma-Optical Emissions Spectroscope (ICP-OES). Study of the thermal stability and structural features indicates that the proximity of the ionic radii of \( \text{Bi}^{3+} \) and \( \text{Sr}^{2+} \) allows easily a mutual site exchange between the two cations. Thus, the solid solution phase \( \text{Bi}_{2+x}\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_{n+1}\text{O}_{2n+4+\delta} \) with \( x = 0 \) was very difficult to obtain. By applying oxygen pressure during the TSFZ growth, the Sr content of the crystals was determined.
to increase with increasing the pressure. The Bi$_{2+x}$Sr$_{2-x}$CuO$_{6+\delta}$ ($x \approx 0.1$) crystals were obtained under the pressures of 200, 300, 500 and 700 kPa, and those of Bi$_{2}$Sr$_{2-x}$CuO$_{6+\delta}$ ($x = 0.21$) under 100 kPa. For the 2212 compound $x \approx 0.1$ was found under 200 kPa, and $x \approx 0.2$ in air. Notice that a high solubility of strontium was achieved with a high oxygen pressure.

Figure 52: A well aligned rod with the rod axis along the crystallographic a-axis (left) and platelets cleaved from the as-grown ingot (right).

The 2201 crystals obtained under oxygen pressure of $\leq 500$ kPa showed a C-centered monoclinic symmetry, while those grown at 700 kPa displayed a tetragonal structure. The 2212 compounds were determined to have an orthorhombic structure. Table 2 lists the crystal symmetry and lattice constant identified by a four-circle diffractometer SIEMENS P4.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Crystal structure</th>
<th>Lattice constant ($\AA$)</th>
<th>Excess oxygen</th>
<th>$T_c$ (K)</th>
<th>Oxygen pressure (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$<em>{1.98}$Sr$</em>{1.79}$CuO$_{6+\delta}$</td>
<td>Monoclinic</td>
<td>$\alpha$: 26.83, $b$: 5.382, $c$: 26.90, $\beta$: 113.44</td>
<td>0.05</td>
<td>10</td>
<td>100</td>
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<tr>
<td>Bi$<em>{2.10}$Sr$</em>{1.80}$CuO$_{6+\delta}$</td>
<td>Monoclinic</td>
<td>$\alpha$: 26.83, $b$: 5.369, $c$: 26.90, $\beta$: 113.46</td>
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<td>7.5</td>
<td>200</td>
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<tr>
<td>Bi$<em>{2.12}$Sr$</em>{1.86}$CuO$_{6+\delta}$</td>
<td>Monoclinic</td>
<td>$\alpha$: 26.85, $b$: 5.382, $c$: 26.86, $\beta$: 113.46</td>
<td>0.16</td>
<td>7</td>
<td>300</td>
</tr>
<tr>
<td>Bi$<em>{2.13}$Sr$</em>{1.91}$CuO$_{6+\delta}$</td>
<td>Monoclinic</td>
<td>$\alpha$: 26.87, $b$: 5.382, $c$: 26.89, $\beta$: 113.43</td>
<td>0.35</td>
<td>5</td>
<td>500</td>
</tr>
<tr>
<td>Bi$<em>{2.15}$Sr$</em>{1.90}$CuO$_{6+\delta}$</td>
<td>Tetragonal</td>
<td>$\alpha$: 5.403, $b$: 5.403, $c$: 24.77</td>
<td>0.54</td>
<td>7</td>
<td>700</td>
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<tr>
<td>Bi$<em>{2.21}$Sr$</em>{1.88}$Ca$<em>2$CuO$</em>{8+\delta}$</td>
<td>Orhtorhombic</td>
<td>$\alpha$: 27.10, $b$: 30.95, $c$: 5.44</td>
<td>0.20</td>
<td>90</td>
<td>air</td>
</tr>
<tr>
<td>Bi$<em>{2.21}$Sr$</em>{1.90}$Ca$<em>2$CuO$</em>{8+\delta}$</td>
<td>Orhtorhombic</td>
<td>$\alpha$: 5.41, $b$: 5.42, $c$: 30.89</td>
<td>0.32</td>
<td>95</td>
<td>200</td>
</tr>
</tbody>
</table>

By means of the hydrogen reduction thermogravimetry method, the oxygen content was estimated in as-grown crystals, as seen in Tab. 2. The amount of oxygen of the crystals increased linearly with the oxygen pressure applied during the growth process.
Figure 53: Electrical resistivity of the Bi\(_{2+\delta}\)Sr\(_{2-x}\)CuO\(_{6+\delta}\) crystals as a function of temperature for different pressures.

All 2201 crystals were superconducting at \(T_c \approx 5–10\) K and 2212 crystals at 90–95 K according to the SQUID measurements, as listed in Tab. 2. The resistivity measurement in the \(ab\)-plane for the 2201 crystals is shown in Fig. 53. The crystals with a high amount of Sr or oxygen (i.e., \(x = 0.14, \delta = 0.16\); \(x = 0.09, \delta = 0.35\) and \(x = 0.10, \delta = 0.54\)) showed a nearly perfect linear decrease of the resistivity with the temperature down to \(T_c\). This resistivity in CuO\(_2\) plane exhibited metallic behavior in the normal state. However, this feature for the Bi\(_{2.10}\)Sr\(_{1.89}\)CuO\(_{6.07}\) compound of a low oxygen indicated a semiconductor-like behavior and was more pronounced on the Bi\(_{1.99}\)Sr\(_{1.79}\)CuO\(_{6.05}\) sample. In general, the electric properties of the crystals were affected by both the contents of oxygen and Sr.
Magnetic excitations in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Inelastic neutron scattering provides incisive information about collective magnetic excitations that is required to develop a microscopic description of correlation effects in the copper oxide superconductors. However, since the discovery of high-temperature superconductivity more than a dozen years ago, only two of the many families of cuprates have been amenable to investigations by this technique: $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$. Suitably large single crystals of other copper oxide compounds could not be grown. While the magnetic spectra of both materials bear certain similarities, there are also pronounced differences that have hampered a unified description of the spin dynamics in the copper oxides. In particular, a sharp resonant spin excitation dominates the spectrum in the superconducting state of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, but is not found in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

This unusual excitation has recently emerged as a key factor in the phenomenology of the copper oxides. In particular, prominent features in angle-resolved photoemission and optical conductivity spectra have been attributed to interactions of this bosonic mode with fermionic quasiparticles. The implications of these observations for the mechanism of high-temperature superconductivity are under intense scrutiny, especially following suggestions that spectral weight of the mode (which is present only below the superconducting transition temperature, $T_c$) provides a measure of the condensation energy of the superconducting state. Several fundamentally different microscopic descriptions of the neutron data have been proposed. Some of these attribute the resonance peak to the threshold of the particle-hole spin-flip continuum at $2\Delta_{SC}$, where $\Delta_{SC}$ is the energy gap in the superconducting state, others to a magnon-like collective mode whose energy is bounded by the gap. Although these calculations differ in many details, the excitations corresponding to the neutron peak are described by the same quantum numbers (spin 1 and charge 0). In a completely different approach, however, the neutron data are interpreted in terms of a collective mode in the particle-particle channel whose quantum numbers are spin 1 and charge 2.

In order to select the correct theoretical model and establish the origin of the differences between the spin excitations in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$, we have made a concerted effort to obtain large single crystals of a third cuprate family, $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. This project was initially started as a collaboration with external groups, but recently large, high quality single crystals have also been synthesized by the crystal growth group at the Max-Planck-Institute using a new optical furnace.

Fig. 54 shows an energy profile obtained by inelastic magnetic scattering on a single crystal of optimally doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$. The sharp feature shown has the same properties as the well known resonance peak in superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$; for instance, the
magnetic intensity falls to background level above the superconducting transition temperature (Fig. 55). The observation of a resonance peak in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ rules out the possibility that this phenomenon is due to a conspiracy of structural or chemical parameters peculiar to YBa$_2$Cu$_3$O$_7$. Rather, it is an intrinsic feature of the copper oxides whose explanation must be an integral part of any theory of high-temperature superconductivity. Further, because of its superior surface properties, Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ is the system of choice for angle-resolved photoemission (ARPES), so that our results now enable a detailed, quantitative comparison between the single-electron spectral function measured by ARPES and the collective spin dynamics measured by neutron scattering.

**Figure 54:** Difference spectrum of the neutron intensities at $T = 10 \, \text{K} \ (\lt T_c)$ and $T=100\, \text{K} \ (\gt T_c)$, at a wave vector $q=(\pi/a,\pi/a)$, where $a$ is the Cu-Cu distance. For comparison, the resonance peak in optimally doped YBa$_2$Cu$_3$O$_{6+x}$ is observed at the same wave vector and energy $41 \, \text{meV}$. The bar represents the instrumental energy resolution, the line is a guide-to-the-eye. The negative difference at low energies comes from the temperature dependence of the phonon background.

**Figure 55:** Temperature dependence of the integrated intensity of the resonance peak shown in Fig. 54. Note that the superconducting transition temperature is $91 \, \text{K}$.

Finally, we have now begun to explore the overdoped state in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ which is difficult to access in YBa$_2$Cu$_3$O$_{6+x}$. Our data indicate that the resonance peak shifts to lower energies in this regime, a finding that will be important both for the comparison with ARPES and for its theoretical interpretation. It means that the peak energy is controlled by the superconducting transition temperature and not by the carrier concentration, as the particle-particle theory had predicted. The new neutron data therefore help to resolve a long-standing theoretical controversy on this issue.
The most relevant model for the low-energy physics of the CuO$_2$ planes in high-T$_c$ oxides is the $t$–$J$ model. In the undoped, half-filled case it consists of a Heisenberg interaction with coupling constant $J$ between spin densities localized on the sites of a square lattice. After doping with holes the holes may hop between nearest neighbor sites with a hopping amplitude $t$ in such a way that double occupancies are avoided. In addition we include in the model a screened Coulomb interaction between holes. Its strength can be characterized by its nearest-neighbor interaction, $V_{nn}$. Unfortunately, neither numerical simulations nor analytic treatments are presently able to make reliable predictions of the above model in the interesting range of model parameters, of the temperature $T$, and the doping $\delta$, without further assumptions. In our analytic study of this model we therefore employed a 1/N expansion where the two spin degrees of freedom per site have been increased to N degrees of freedom and 1/N is taken as a small expansion parameter in a perturbation expansion directly in terms of Hubbard’s X-operators. The resulting expressions become asymptotically exact at large N’s describing a kind of mean-field solution for strongly correlated systems and small fluctuations around this solution.

Figure 56: Phase diagram in the $T$–$\delta$ plane for $J = 0.3$ and different Coulomb interaction strengths, characterized by the nearest-neighbor constant $V_{nn}$. N, SC, FL, and ICDW denote the normal, superconducting, flux, and incommensurate charge density wave phases, respectively. To the left of the dash-dotted line in the upper panel, the normal state phase-separates.

Figure 56 shows the calculated phase diagram in the $T$–$\delta$ plane for $J = 0.3$ and three different strengths of the Coulomb interaction $V_{nn}$. The energies are given in units of twice the hopping energy between nearest neighbors, i.e., roughly in eV. The dot-dashed line
in the upper panel, which refers to the case without Coulomb interaction, describes the instability line of the normal state with respect to phase separation. At small dopings the system splits into two spatially separated parts with different hole concentrations wiping out other possible structural phases. Only the superconducting phase below the solid line is stable against phase separation. Its most stable order parameter has $d$-wave symmetry and its transition temperature $T_c$ is monotonically increasing with decreasing doping. Due to symmetry requirements this superconducting state transforms continuously into the Affleck-Marston RVB-state of the undoped antiferromagnet at rather high temperatures which makes the increase of $T_c$ with decreasing $\delta$ plausible.

Turning on the Coulomb interaction (middle panel of Fig. 56) the phase separation line shifts to smaller dopings (dot-dashed line) and describes now the instability of the normal state with respect to an incommensurate charge density wave. More important, however, is a new instability line separating the normal state from a flux or bond-order wave state (dashed line). The corresponding complex order parameter is $\langle c_i^\dagger c_j \rangle$ where $c_i^\dagger$, $c_j$ are electron creation and annihilation operators subject to the constraint of no double occupancies of sites. This order parameter has $d$-wave symmetry with respect to the direction of the two sites (i.e., different signs if $i-j$ lies along the $x$- and $y$-axis). Furthermore, the dependence on $i-j$ is modulated by a wave vector $\mathbf{Q}$. Figure 56 has been calculated with $\mathbf{Q}=(\pi,\pi)$. For $T<0.01$ $\mathbf{Q}$ actually becomes incommensurate which, if taken into account, removes the strange back-bending of the instability line at low temperatures. Both the flux and the superconducting order parameters have $d$-wave symmetry and thus repel each other. Since the flux wave instability is much stronger than the superconducting one the flux phase suppresses the superconducting phase strongly at smaller dopings. As a result $T_c$ shows a well-pronounced maximum near the onset of the flux phase. To the left of the maximum is the underdoped regime with coexisting superconducting and flux order parameters at low temperatures and a pseudogap phase above $T_c$ caused by the nonvanishing $d$-wave flux order parameter. Taking also fluctuations into account only the solid line and the $T=0$ points of the dot-dashed and dashed lines would be associated with phase transitions and long-range order, yielding thus a quantum critical point scenario. In our case the structural phase is neither a charge- nor a spin-density but a flux phase. Moreover, optimal doping is obtained from the competition between the superconducting and the flux phase which explains in a natural way the coincidence of optimal doping and quantum critical point. Increasing the strength of the Coulomb interaction further (lower panel in Fig. 56) the regions where the charge and the flux phases are stable do not change much whereas the superconducting phase has vanished due to the strong Coulomb repulsion. The middle panel in Fig. 56 agrees with many experimental data in high-$T_c$ superconductors, in particular, thermodynamic and photoemission data. Recent measurements suggest that the situation may be more complex: electronic Raman scattering and tunneling experiments found a pseudogap behavior well inside the overdoped region and in some systems even more than one $T^*$ curve at low dopings.
Experimentally small amounts of Zn impurities suppress $T_c$ in such a way that the $T_c$ lines in the phase diagram collapse with increasing impurity concentrations to one point at $T=0$. In contrast to that the $T^*(\delta)$ line associated with the pseudogap is nearly unaffected by the impurities. We have calculated the influence of Zn impurities on the phase diagram in Fig. 56 describing the scattering of holes from Zn atoms by a phenomenological scattering rate $\Gamma$ which accounts for strong potential scattering and scattering from Zn-induced magnetic moments. The solid lines in Fig. 57 show the calculated suppression of $T_c$ as a function of doping for different scattering rates $\Gamma$. The corresponding changes in $T^*(\delta)$, depicted in Fig. 57 by the grey region, are very small at low temperatures. Fig. 57 is in excellent agreement with the corresponding curves in Zn doped (Y,Ca)-123 and La-214. The different behavior of the two d-wave order parameters with respect to impurities is related to the fact that the superconducting instability occurs in the particle-particle channel and is rather weak whereas the flux instability occurs in the particle-hole channel, is strong and localized in momentum space near ‘hot’ spots. Roughly speaking, the impurity scattering causes an additional smearing in fermionic distribution functions acting like an increase in temperature. $T^*$ is, however, practically independent of the temperature in the region shown in Fig. 57 and thus insensitive to impurities.
Phonon induced stripe formation and the isotope effect on $T^{*}$ in high-$T_c$ superconductors

A. Bussmann-Holder

A theoretical understanding of the mesoscopic striped phase, common to many HTSC, is still incomplete. Specifically it remains unclear, whether and how the stripes are related to superconductivity. At present the formation of the striped phase is mostly thought to arise from antiferromagnetic fluctuations which also act to drive the hole pairing through a d-wave order parameter. The two new independent experimental findings of: (i) a correlation of hole doping with phonon anomalies; and (ii) a huge isotope effect on the stripe formation temperature $T^{*}$, question the role of antiferromagnetic fluctuations as driving mechanism, and certainly suggest strongly that electron-phonon interaction induced effects have to be incorporated in any model for HTSC.

In the following it will be shown that the striped phase can be related to charge ordering stemming from strong electron-phonon interactions reminiscent of polaron or Jahn-Teller polaron formation, but extended to account for nonlinear effects. In order to simplify the complex dynamics of the copper oxides we concentrate on the CuO$_2$ planes only and model them by a two-dimensional nonlinear electron-phonon interaction Hamiltonian. This Hamiltonian can be diagonalized with respect to electronic and phononic degrees of freedom where both subsystems, electrons and phonons, experience strong renormalizations. Even though similar approaches have been used previously, the present model is extended here to account for nonlinear effects (proportional to $\lambda_4$ in Eq.(11) below) by using higher order density-density multiphonon interactions and combining them with linear onsite, proportional to $\lambda_1$, and intersite, with strength $\lambda_2$, electron-phonon couplings:

$$-\lambda_1 \sum_j u_j^{(1)} n_j - \lambda_2 \sum_j \left( u_{j+1}^{(2)} - u_{j-1}^{(2)} \right) n_j + \lambda_4 \sum_j \left[ u_j^{(1)} n_j \left\{ 3u_j^{(1)} n_j - 2 \left( u_j^{(1)} \right)^2 - 4n_{j+1} n_{j+1} \right\} \right]$$

(11)

Here $u_j^{(1)}$, $u_j^{(2)}$ are the displacement coordinates of the oxygen, copper ion, respectively, in the $j$’th unit cell with $j=1 \ldots N$. The p electron density at site $j$ is given by $n_j = c_j^+ c_j$. In our approach the electron-phonon coupling to the oxygen p-electrons is onsite and included since this is known to be the dominant term in transition metal oxides. A phonon mediated p-d charge transfer is possible through the intersite coupling term proportional to $\lambda_2$. The higher order density-density multiphonon terms stabilize the $2p^6$ configuration of O$^{2-}$. The exact nonlinear solutions for the lattice frequencies and displacement coordinates have been described previously where a two mode model was used. In order to obtain the electron-phonon and doping induced effects on the electronic structure, we relate the ratio of $\lambda_1 / \lambda_4$ to doping, i.e., the strength of harmonic coupling to the density-density multiphonon terms simulates the effects of doping which increases the local instability of the oxygen ion. The electronic energies are renormalized through the electron-phonon coupling as:
$$E_{k,q}^2 = \epsilon(k, k-q)^2 + \Delta^2(q),$$

where $\epsilon(k, k-q)$ is the band energy and

$$\Delta^2(q) = \pi \epsilon F \left[ \sqrt{\lambda_2 \omega_q u_q(2)} + \sqrt{\lambda_3 \omega_q u_q(1)} \right] \left[ 1 + \frac{\lambda_4}{\lambda_1} \left[ u_q u_q(1)^2 + u_q^2 \left( u_q(1)^2 \right) \right] \right], \quad (12)$$

where the $\omega_q, u_q$, respectively, are the momentum $q$-dependent lattice frequencies and displacement coordinates obtained from solving the nonlinear equations of motion of the coupled system. The Fourier transform of Eq.(12) describes the real space charge modulations caused by strong electron-phonon coupling.

Figure 58: Real space variations of the electron-phonon interaction induced gap with $\lambda_3 / \lambda_4 = 0.138$ a), $= 0.276$ b), $= 0.413$ c) along <10> and <11> direction with lattice constant $a$.

Figure 59: Real space variations of the electron-phonon interaction induced gap with $\lambda_3 / \lambda_4 = 0.138$ a), $= 0.276$ b), $= 0.413$ c) along <10> and <11> direction with lattice constant $a$. The oxygen ion mass is enhanced by a factor $18/16$ as compared to Fig. 58.
The results are shown in Fig. 58 for various ratios of \( \lambda_1 / \lambda_4 \). For small values of this ratio (Fig. 58a) modulations in the charge distribution already show up along <10> and <11>. For larger values of the ratio a striped phase clearly appears along <11> and changes periodicity with increasing \( \lambda_1 / \lambda_4 \) with additional features growing in the <10> direction. It is important to note that the dynamical ionic displacements are inserted in Eq.(12) and directly cause the excitation spectrum described above. This strong correlation between ionic and electronic degrees of freedom is clearly reminiscent of polaron formation. In order to correlate the above features with the experimental data we first replace the \(^{16}\text{O}\) oxygen ion mass by its \(^{18}\text{O}\) isotope and carry out the same self-consistent iteration scheme to solve for frequencies and displacement coordinates to determine \( \Delta \) and its real space equivalent. The results are shown in Fig. 59 for the same parameters as those used in Fig. 58. It is evident from Fig. 59 that even for small ratios of \( \lambda_1 / \lambda_4 \) charge ordering is present and persists also at higher values but with a different periodicity. It is especially striking that the amplitude of the charge modulation is much more enhanced as compared to Fig. 58. The stripe formation temperature \( T^* \) can be related to the electron-phonon interaction induced gap:

\[ k_B T^* = 2.28 \varepsilon_F \exp(-2b) \]

with

\[ 2b = \int_0^{\varepsilon_F} dx \ tanh \frac{1/2\beta F}{F} + \ln 2 + O \left( \frac{\Delta^2}{\varepsilon_F^2} \right) \quad \text{and} \quad F = \sqrt{x^2 + \Delta^2} \]

The gap varies strongly in real space, but we provide an estimate for the effect on \( T^* \) by comparing the average gap value \( \Delta \) for the same parameters calculated for \(^{16}\text{O}\) with those found in \(^{18}\text{O}\). \( T^* \) and \( 2b \) can then be evaluated self-consistently for fixed \( \varepsilon_F \) and representative results are given in Tab. 3.

<table>
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<tr>
<th>( \Delta ) [meV]</th>
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<th>( T^* ) [K]</th>
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<td>138.4</td>
</tr>
<tr>
<td>60</td>
<td>0.247</td>
<td>155.03</td>
</tr>
<tr>
<td>80</td>
<td>0.186</td>
<td>164.7</td>
</tr>
</tbody>
</table>

From e. g., Figs. 58b) and 59b) an enhancement in \( \Delta \) by at least a factor of 3 is observed which leads to an enhancement factor of \( T^* \) of 1.41. Even though this is less than observed experimentally our result provides the correct trend. It is important to note here that the experimental observation of the isotope effect is limited by three factors which have to be present simultaneously. (i) The time scale of the experiment has to be faster than \( 10^{-14} \) s.
in order to capture the additional ionic dynamics; (ii) the length scale must be local, i.e., of the order of a few lattice constants in order to reproduce the local spatial variations in the charge distribution and the ionic displacements; (iii) the spatial experimental resolution must be better than \(10^{-9}\) cm, since this is the scale of the ionic displacements contributing to the stripe formation. Correspondingly the experimental detection of an isotope effect on \(T^*\) will be limited to very few methods.

To summarize, it has been shown that stripe formation with charge ordering follows from strong nonlinear electron-phonon effects which lead to strong modulations in the phonon induced gap in the electronic degrees of freedom. The isotope effect on \(T^*\) is a natural consequence of these effects. Yet it should be kept in mind that the time and length scales of these effects are restricted and consequently limit their experimental detectability. Q-dependent anomalies in the phonons are expected at an incommensurate wave vector, and a variation of these anomalies with doping is expected. Even though our model oversimplifies the dynamics of HTSC, it yields qualitative agreement with striking new experimental data.
Investigations of the optical and electrical properties in crystalline materials with reduced dimensionality have become one of the most fascinating and active fields of solid state physics during the last decade due to the rapid progress in sample fabrication techniques. The ‘top-down’ approach starts from a 3-dimensional crystal in which the carrier and phonon propagation is confined in one, two or even three dimensions by nanostructuring or self-organizing growth techniques which create quantum wells, quantum wires and quantum dots, respectively. The opposite ‘bottom-up’ process starts from the atomic or molecular level and forms clusters with increasing number of atoms. Examples for the latter approach are fullerenes and carbon nanotubes which are shown to exhibit attractive features from both fundamental or technical points of view.

Studies of a 2D electron gas in high quality quantum wells placed in a perpendicular magnetic field reveal the influence of the interaction between electron spins and nuclear spins on the transport properties in in the fractional quantum Hall effect regime. The essential physical properties of strongly correlated 2D electron systems subjected to high magnetic fields demonstrate that the description of the fractional quantum Hall effect in terms of composite fermions assembled from one electron and two fictitious flux quanta works very well.

**Anomalous interaction between electron and nuclear spins in the fractional quantum Hall effect regime**

W. Dietsche, S. Kronmüller and K. von Klitzing; G. Denninger (Univ. Stuttgart); W. Wegscheider (Garching)

The integer and the fractional quantum Hall effect can be observed in two-dimensional electron gases subjected to a perpendicular magnetic field. These charge gases form either at interfaces between two dissimilar semiconductors (heterostructures) or inside a semiconductor layer (quantum well) which is sandwiched between two other ones with larger conduction band energies. The quantum Hall effect manifests itself by a vanishing longitudinal and a quantized transverse (Hall) resistance. In the integer case, this gap is due to the Landau quantization of the orbital motion of the electrons which follows from the single particle properties of the electrons. In the fractional case, however, the gap is caused by an interplay between the Coulomb and the Zeeman energy which are of comparable magnitude. No satisfactory and generally applicable theory has been developed yet for the fractional case.
In recent experimental work at the MPI für Festkörperforschung, it was found that under certain conditions the normally observed fractional behavior, i.e. the existence of a gap turns into a dissipative (gapless) behavior. It has furthermore been demonstrated that this behavior is connected with a strong interaction of the conduction electrons with the spins of the nuclei of the host material. This gives rise to the first observation of a resistively detected nuclear magnetic resonance (NMR).

In our experiment, the two-dimensional electron gas is defined by a 150 Å wide modulation doped quantum well and is shaped in a standard Hall-bar geometry. This quantum well contains a much narrower 2DEG compared to the more commonly used interface heterostructures. The electron mobility of this sample is \(1.8 \times 10^6 \text{ cm}^2/\text{Vs}\) at a carrier density of \(1.3 \times 10^{11} \text{ cm}^{-2}\). This is the highest mobility ever reported for electrons in a quantum well of this thickness. The sample was grown at the Walter-Schottky Institut in Garching.

![Figure 60](image.png)

**Figure 60**: Longitudinal resistance for two different carrier densities. The longitudinal resistance maximum (HLR) at filling factor \(2/3\) is clearly developed for the two carrier densities at the slow sweep rates (0.002 T/min) of the magnetic fields. The numbers denote the filling factors of the Landau levels.

Figure 60 shows the longitudinal resistance for an 80 μm wide Hall bar measured with a source-drain current of 100 nA. The dotted and dashed curve correspond to slightly different electron concentrations. Both curves are measured with a sweep rate of the magnetic field of 0.7 T/min and show the expected vanishing longitudinal resistance at the integer filling factors of the Landau levels (numbers in the figure). The fractional quantum Hall effect at \(\frac{2}{3}\) is not yet fully developed at this temperature of 0.4 K but a clear minimum can already be observed. If, however, the sweep rate of the magnetic field is substantially reduced to 0.002 T/min then huge maxima in the longitudinal resistance (‘HLR’) are observed in the longitudinal resistance. The HLR-maximum is clearly related.
to the existence of the fractional quantum Hall effect because it is only observed if the fractional effects are visible in fast sweeps. Most likely, its occurrence is connected with the unique combination of small well widths and high mobility in our samples. Therefore, this phenomenon has not been observed in the samples used in earlier research.

Figure 61: (a) Setup for the NMR experiment. A wire is wrapped around the sample to create an RF-field perpendicular to the static magnetic field. (b) The longitudinal resistance versus RF-frequency for the $^{75}$As nuclei for two different electron densities causing the resonance to occur at two different magnetic fields. Unexpectedly, the resonances are split in four sublines. (c) The nuclei have spin $\frac{3}{2}$ which means they split in an external magnetic field in four equidistant energy levels. Three transitions at the same frequency are possible.

One of the most striking property of the HLR-maximum is its timescale. It can take up to one hour (depending on the sample width) for the resistance maximum to develop completely. These long timescales point already strongly to an involvement of the nuclear spins in this effect. The most direct way to show the relation between the HLR-maximum and the nuclear spins is a nuclear magnetic resonance (NMR) measurement. One loop of a wire is wrapped around the sample (Fig. 61(a)). Oscillating current is applied to this loop for creating a radio frequency (RF) magnetic field perpendicular to the static magnetic field. Initially the sample is put in the HLR state by applying the appropriate constant magnetic field and passing current until the HLR maximum is fully developed. Then the RF is applied and its frequency is swept while the resistance is monitored as a function of the RF-frequency. Indeed, a very substantial resistance drop of the order of 5–10% is observed for the frequencies corresponding to the three nuclei ($^{69}$Ga, $^{71}$Ga, $^{75}$As) present in the quantum well. In Fig. 61(b) the As resonance of $^{75}$As is shown, strikingly it is fourfold split just as the two Ga resonances. Obviously, the HLR-Maximum can be influenced by changing the nuclear spin polarization. Usually, the nuclear spin polarization is too small and the nuclear relaxation rates are too slow to affect the electronic conductivity.
Therefore, the nuclear resonances are very rarely observed in the resistance of solids of any type. It is not clear why the behavior of the nuclear polarizations is totally different under the HLR conditions.

It is very likely that the strong nuclear polarization is a consequence of spin flips in the electronic systems which lead to spin flips in the nuclear spin system because of angular momentum conservation. One possible scenario is based on the fact that the fractional quantum Hall effect at filling factor $\frac{2}{3}$ can exist both with a spin polarized and an unpolarized ground state. It is possible that the two ground states are nearly energetically degenerated. Then a domain structure of different polarized domains could form in the two-dimensional electron gas. The scattering of the electrons at the domain boundaries could cause the huge longitudinal resistance and would be connected with electron spin flips required for the observed nuclear polarization.

This model would describe the observed resistance behavior, it does not, however, solve the problem of the fourfold splitting of the NMR lines. All three nuclei in the quantum well have a nuclear spin of $I = 3/2$ (Fig. 61(c)), which means that due to the Zeeman splitting four energetically equidistant energy levels exist in a magnetic field. Therefore, one expects normally only one resonance line in an NMR experiment. Perturbations like the dipole-dipole coupling between the neighboring nuclei causes a broadening of the resonance in the order of 1–3 kHz. The hyperfine interaction with the electrons leads to a Knight shift, i.e. a shift of the resonance by a few kHz but not to a splitting. The possible splitting via the interaction between the electrical quadrupole moment of the nuclei and an electrical field gradient, would only result in three sublines. Thus, at this time no conceivable interaction mechanism leads to a fourfold splitting.

Thus, in addition to the puzzling novel resistance maximum and the novel detection of the nuclear resonances in the resistance, one needs to find an explanation for the unusual splitting of the resonances. It is likely that these phenomena are initiated by an effective reduction of the g-factor of the electrons in the narrower quantum well. The Coulomb interaction between the electrons is at the same time slightly enhanced. Therefore the ratio of the Zeeman and Coulomb energy which is crucial to the formation of the fractional quantum Hall effect is modified. It seems that this modification may even lead to another unexpected electronic state where the interaction with the nuclei of the host semiconductor plays an important role.
Commensurate composite fermions in weak periodic electrostatic potentials: direct evidence of a periodic fictitious magnetic field

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The two-dimensional electron system (2DES), subjected to a strong perpendicular magnetic field, exhibits the spectacular correlation phenomenon of the fractional quantum Hall effect (FQHE). The crucial ingredients for its theoretical description are weak disorder and finite gaps in the excitation spectrum induced by the interaction among the electrons. Much of our understanding of the FQHE is due to Laughlin. He proposed a very elegant and succinct many-particle trial wave function for the most prominent FQHE state at filling $\nu = 1/3$, i.e., when the number of electrons in the sample divided by the number of elementary flux quanta threading the sample equals 1/3. Recently, a conceptually different way of thinking about the FQHE in terms of composite particles has emerged. These so-called composite fermions are assembled from one electron and a flux tube containing two fictitious flux quanta that point in the direction opposite to the external applied magnetic field (a pedestrian’s description of a Chern-Simons gauge field transformation). Each of them experiences not only the external applied magnetic field, but also the fictitious field associated with the flux quanta attached to the other composite particles. To simplify matters a mean field approximation is adopted, in which the granularity of the fictitious magnetic field is given up and the effect of the attached flux quanta is smeared homogeneously across the system. Since two flux quanta are attached per composite fermion, the external magnetic field is cancelled exactly at filling $\nu = 1/2$. At this filling, a metallic state of composite fermions (CFs) forms and the effective magnetic field is zero. The attractiveness of this CF-picture is based on the assertion that dressing the electrons with two flux quanta constitutes the main effect of the interaction between the 2D electrons. The residual interaction is treated as weak, so that in many instances the system can be considered as a Fermi liquid of noninteracting composite particles in zero effective magnetic field. A deviation from exact half-filling results in the appearance of a nonzero effective magnetic field. It quantizes the CF motion and discretizes their energy spectrum into Landau levels, much the same way as what occurs at small fields for electrons. Within this composite fermion construction, the FQHE is a manifestation of Landau quantization of CFs and the integer quantum Hall effect of CFs maps onto the FQHE of the electrons. The hard-to-visualize many-body wave functions can be put aside to some extent and the experimentalist can revert to easy-to-grasp single particle concepts to describe the strongly interacting two-dimensional electron system.

Recently, experiments have been devised to demonstrate unequivocally the fundamental property of flux attachment in the composite fermion picture. Consider a two-dimensional electron system in which the density is periodically modulated. In regions with a deficit or surplus $\Delta n$ of composite fermions with respect to the average density $\bar{n}$, a certain density
of fictitious flux quanta, $2\Delta n$, is either missing or excessive to compensate the external magnetic field at half-filling. As a result, a strong local effective magnetic field with amplitude $\Delta B_{\text{eff}} = B_1\Delta n/\bar{n}$ is produced. Therefore, a 2DES, on which a periodic modulation of the density has been imposed, represents a marvelous test-case of the flux attachment. CFs in this system are forced to not only move through a periodic modulation of density, but also through a periodic fictitious magnetic field. Its presence should leave signatures in the resistivity. Indeed, at least for electrons near zero external field it is well known that the resistance of a 2DES subjected to either a weak one-dimensional periodic electrostatic potential or a periodic magnetic field displays $1/B$-periodic oscillations in the resistance when the homogeneous external magnetic field $B$ is swept and current flows along the modulation direction. They reflect the commensurability between the classical cyclotron radius $R_c$ at the Fermi energy $E_F$ and the period $a$ of the modulation. Minima appear in the resistance when the cyclotron diameter equals $a \times (\lambda \mp 1/4)$, where $\lambda = 1, 2, \ldots$ is an integer oscillation index and with the ‘−’ or ‘+’ sign for a periodic electrostatic and magnetic field, respectively. The position of the commensurability minima on the magnetic field abscissa allows one to distinguish between electrostatic and magnetic modulation. An example of low field data for a 2DES subjected to a periodic electrostatic potential is depicted in the insert to Fig. 62.

![Figure 62: The inset shows a blow-up of the resistivity at small magnetic fields and an SEM-picture of the etched grating to induce a periodic variation of the density. The minima of the $1/B$-periodic commensurability oscillations due to the imposed electrostatic modulation are marked by solid triangles. The high-field data are presented for current flow along the modulation (black curve) and perpendicular to the modulation direction (red) [Smet et al., Phys. Rev. Lett. 80, 4538 (1998)]. For the latter case, the data are similar to those obtained on an unpatterned sample, whereas for the former a strong response due to the density modulation is observable.](image-url)
A similar scenario should hold for composite fermions around half-filling. The commensurability conditions remain valid if the CF cyclotron radius (set by the effective magnetic field rather than the truly applied external magnetic field) is substituted for the electron cyclotron radius. This provides a clear road map for how to look for experimental verification of the flux attachment. Our strategy was to impose only a periodic electrostatic potential, i.e., a periodic change in the density. It is expected that a periodic effective magnetic field is simultaneously generated for CFs and thus the commensurability minima should be shifted toward the magnetic commensurability condition (‘+’ sign). The periodic density modulation has been implemented in two ways. In one method, an array of lines written by electron beam lithography is transferred onto the heterostructure with the aid of a shallow etch (for example the data in Fig. 62). The difference in Fermi level pinning and surface condition produces a periodic change in the conduction band profile. A less invasive technique uses holographic illumination. It exploits the persistent photoionization of DX-centers in AlGaAs-based heterostructures after brief illumination at low temperatures with the interference pattern of two beams of a coherent light source (an example is shown in Fig. 63). Figure 62 demonstrates that an electrostatic modulation along the direction of the current induces a dramatic response near half-filling.

![Diagram](image)

**Figure 63:** The longitudinal resistivity $\rho_{xx}$ near half-filling of the lowest Landau level for a periodic modulation of the density (top left inset) imposed by holographic illumination (bottom left inset) [Smet et al., Phys. Rev. Lett. 83, 2620 (1999)]. The blue triangles correspond to the position of the primary minimum for pure electrostatic modulation, the red triangles are for a periodic magnetic modulation.
If the period of the modulation is sufficiently small it is indeed possible to observe commensurability effects as shown in Fig. 63. The blue and red triangles indicate the position of the primary commensurability minimum ($\lambda = 1$) for electrostatic and magnetic modulation, respectively. Minima occur if a periodic magnetic field is present. To further support our assertion, the same experiment was repeated for other periods. The result is summarized in Fig. 64.

In all cases the observed minima lie at $2R^c_{CF} = a \times (1 + 1/4)$. They make a strong case for magnetic commensurability effects. It is the clearest demonstration of attached fictitious flux to the CFs reported so far. Note the strong damping of the oscillations due to the much smaller mean free path of CFs. Only the first minimum with index $\lambda = 1$ can be discerned for these state-of-the-art heterostructures, in contrast to the low field data where oscillations up to $\lambda = 9$ can be observed.

Figure 64: The magnetic field difference between the primary minima in the longitudinal resistivity, due to commensurate orbits, as a function of the modulation period $a$ for etched gratings and holographic illumination [Smet et al., Phys. Rev. Lett. 83, 2620 (1999)]. The approximate theoretical dependencies for a periodic electrostatic potential or a periodic magnetic field are also included (solid curves) for the fundamental period and second harmonic of the modulation. In the case of magnetic modulation, the result of a more accurate theoretical model has also been included. It follows more closely the experimental data. The inset displays the shift of the minima with decreasing period (indicated in nm) for some of the data with holographic modulation.
The linearized Boltzmann equation for CFs was solved numerically and its solution yields good overall agreement with experiment, provided one incorporates an anisotropic scattering cross-section and goes beyond the second order approximation in the modulation strength in order to include the effect of channeled or so-called *snake orbits* (Fig. 65).

Figure 65: Resistivity near filling factor $\nu = 1/2$, $a = 275$ nm, $n = 2 \cdot 10^{11}$ cm$^{-2}$; solid black line: experimental data; dashed brown line: numerical solution of the Boltzmann equation up to second order including anisotropic scattering, but without the inclusion of channeled orbits; solid red line: numerical solution beyond second order in the modulation amplitude ($\Delta n/n = 3.6\%$) taking into account channeled orbits [Zwerschke et al., Phys. Rev. Lett. 83, 2616 (1999)]. The inset shows the low field (black curve) and the corresponding numerical simulation (blue curve). The oscillations at higher fields in the experimental data are the well-known Shubnikov-de Haas oscillations. Also at low fields, an anisotropic scattering cross-section is essential to obtain a good overall fit to the experimental data.
These are particle trajectories wiggling around lines of zero total effective magnetic field along the direction of the stripes. Each time such a line is crossed the curvature of the local CF cyclotron orbit changes sign as illustrated in Fig. 63. They enhance the longitudinal resistivity and cause the significant positive magnetoresistance consistently observed close to $B_{\text{eff}} = 0$. Nevertheless, their contribution saturates as soon as the average effective magnetic field exceeds the amplitude of the periodic effective magnetic field component.

As demonstrated by the above example, the composite fermion picture and its seemingly crude mean-field approximation work astonishingly well and seem to capture the essential physics in the vicinity of the half-filled lowest Landau level. Its relative simplicity, conciseness and perspicuity has made a valuable contribution to our understanding of the strongly correlated 2DES in high magnetic fields.

Is $C_{60}$ a ‘hard sphere’?

W. Branz, N. Malinowski, H. Schaber and T.P. Martin

Two $C_{60}$ molecules begin to repel one another only at very short distances (compared with their diameter), that is, they might be expected to behave like hard spheres. Indeed, solid $C_{60}$ has the close-packed crystalline structure expected for hard spheres. Several years ago, we performed experiments clearly indicating that fullerene clusters, $(C_{60})_n$, can have icosahedral symmetry. However, in the ‘hard sphere’ limit, icosahedral structures are unstable since the spheres within a shell-like layer do not touch one another, Fig. 66.

Support was given to the hard sphere model by several theoretical groups that found $(C_{60})_n$ clusters prefer close-packed structures for $n > 13$ using a variety of hard intermolecular potentials. These groups attributed our observation of icosahedra to the fact that experiments were performed on positively charged clusters while the calculations were for neutral clusters. This year we performed experiments on neutral $(C_{60})_n$ clusters – and found again icosahedral structures. However, by looking more closely into the cluster formation process, we believe we have found the reason for the apparent discrepancy between intuition and experiment.
Figure 67: Mass spectra of $(C_{60})_n$ clusters as-grown at 100 K (top), after heating to 510 K (middle) and after heating to 600 K (bottom). Representative structures obtained by energy minimization are shown, whereby each $C_{60}$ molecule is represented by a sphere. The structures obtained after moderate heating have an icosahedral motif, those obtained after more intense heating are close-packed.
Clusters of $\text{C}_60$, entrained in He gas, were heated by allowing them to pass through an oven. They subsequently cooled by the evaporation of molecules. A mass spectrum of unheated clusters is shown at the top of Fig. 67. No cluster size is unusually prominent in the size distribution of clusters freshly formed at 100 K. Evaporation from heated clusters results in an overall shift in the size distribution to lower values. More importantly, certain cluster sizes are particularly stable and resist evaporation, leading to anomalously intense mass peaks. The mass spectrum of clusters heated to 510 K demonstrates a series of intense mass peaks which are easily identified as corresponding to highly stable icosahedral structures. The third mass spectrum in Fig. 67 indicates that clusters heated to 600 K assume close-packed structures. In principle this transition could be caused by (1) the increasing contribution of entropy to the free energy at high temperature, or (2) by the kinetics of annealing from an initially disordered state. The experimental results combined with a computational examination of the total energy surfaces support explanation (2).

Computations of the total energy surfaces indicate that icosahedral clusters have large catchment basins. That is, they are ‘easy-to-find’ when minimizing the energy from arbitrary disordered conformations using an appropriate intermolecular potential. The close-packed structures, although lower in energy, are represented on the energy surface by narrow basins. In order to indicate the types of geometries obtained after annealing, the structure of clusters corresponding to several prominent mass peaks are shown in Fig. 67. Simply stated, low annealing temperatures followed by quenching, yield easy-to-find, icosahedral structures. Higher annealing temperatures allow the clusters to find the global energy minima corresponding to close-packed structures. $\text{C}_60$ does indeed behave like a hard sphere.

**Resistivity of metallic fullerenes: is there a lower limit to the mean free path?**

O. Gunnarsson and J.E. Han

The electrical resistivity $\rho$ of a metal is usually interpreted in terms of a mean free path $l$, i.e., the average distance an electron travels before it is scattered. As the temperature $T$ is raised, $\rho$ is increased and $l$ is reduced. In this semiclassical picture, however, $l$ cannot become (much) shorter than the distance $d$ between two atoms. The resistivity should then saturate at a value corresponding to $l \sim d$. This has been confirmed for many systems and was considered a universal behavior. Recently, a few apparent exceptions were found, e.g., alkali-doped fullerenes and high-temperature superconductors. These systems could, however, be in exotic states where only a small fraction of the conduction electrons contribute to the conductivity, and $l > d$ could then still be satisfied. It is therefore interesting to ask if there is some general principle, limiting the resistivity of a metallic system at large $T$.  

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To address this problem, we have constructed a model of $A_3C_{60}$, where the electrons are scattered by intramolecular vibrations. For this model we have performed an essentially exact calculation of the resistivity, using a quantum Monte Carlo (QMC) method.

The conduction in $A_3C_{60}$ takes place in a partly filled $t_{1u}$ band. The $T$-dependent part of the resistivity is assumed to be due to scattering against phonons with $H_g$ symmetry. We therefore consider a model with a threefold degenerate $t_{1u}$ level and a fivefold degenerate $H_g$ Jahn-Teller phonon on each molecule, the hopping between the molecules and the coupling between the electrons and the phonons. The hopping takes into account that there is an orientational disorder of the molecules.

We have performed a finite temperature calculation, using a determinantal QMC method. The current-current correlation function is calculated for imaginary times and a transformation to real frequencies is made, using a maximum entropy method. This gives the optical conductivity and the resistivity. The QMC method has no ‘sign-problem’, and the resistivity of the model can be calculated essentially exactly down to quite small $T$.

Figure 68: The resistivity as a function of $T$ according to the full QMC calculation, the Boltzmann equation (Bloch-Grüneisen) and the bubble diagram. The symbol $\times$ shows the $\rho(T=0)$ due to the orientational disorder. The figure illustrates that $\rho$ can become extremely large, that the bubble calculation is quite accurate and that there is no qualitative break-down of the Boltzmann equation at high temperatures.

Figure 68 shows the resistivity for a cluster of 48 $C_{60}$ molecules with the dimensionless electron-phonon coupling constant $\lambda = 0.53$ and the phonon frequency $\omega_{ph} = 0.2$ eV. The QMC calculation (full line) shows that the resistivity can become very large, corresponding to $l \sim 0.7 \, \text{Å}$ at $T = 0.5$ eV. This should be compared with the separation $d = 10 \, \text{Å}$ between two $C_{60}$ molecules, i.e., $l \ll d$. By considering also unrealistically large temperatures, we emphasize the lack of a general principle of the type $l > d$. To interpret these results we have used a diagrammatic approach. In the Kubo formalism this requires the calculation of a bubble diagram including vertex corrections (see Fig. 69a)). We have neglected the vertex and calculated the bubble diagram using the electron Green’s function from the QMC calculation. The resulting resistivity (dashed line in Fig. 68) is practically identical to the QMC result, justifying the neglect of vertex corrections for the present model. It was shown by Holstein that in the limit of a broad electronic band, all vertex corrections except ladder diagrams can be neglected and that a Boltzmann equation can be derived. Holstein’s derivation is not strictly valid for the narrow band
considered here (width $\sim 0.6$ eV), but our calculations show that his arguments are still qualitatively right. For our model with a $\mathbf{q}$-independent electron-phonon coupling, even the ladder diagrams can be neglected. Essentially following Holstein we obtain approximately a Boltzmann like conductivity

$$\sigma(T) \sim \int d\omega N(\omega) \left( -\frac{df(\omega)}{d\omega} \right) \frac{1}{\text{Im}\Sigma(\omega)} |j_k|^2_{\omega_\mathbf{k} = \omega}, \quad (13)$$

where $N(\omega)$ is the density of states, $f$ is the Fermi function, $\Sigma(\omega)$ is the electron self-energy, $j_k$ is the current matrix element for a state with the label $k$ and the energy $\varepsilon_k$. We interpret $\text{Im}\Sigma$ as the inverse of the relaxation time. For a large $T$, $\text{Im}\Sigma$ becomes comparable to or larger than the one-particle band width and the quasi-particle concept breaks down.

![Figure 69: Diagrams for the current-current response function a) and two approximations to the electron self-energy b) and c). The full and dashed lines represent electron and phonon Green’s functions. Self-consistent Green’s functions are used in a) but not in b) or c).](image)

The resistivity thus depends crucially on $\Sigma$. To understand its behavior, we considered the diagram in Fig. 69b) calculated with bare Green’s functions and for simplicity neglecting the orbital degeneracy

$$\Sigma^{(1)}(\mathbf{k},\omega) = g^2 \sum_{\mathbf{q}} \left[ \frac{n_B(\omega_{\mathbf{ph}}) + 1 - f(\varepsilon_{\mathbf{q}})}{\omega - \omega_{\mathbf{ph}} - \varepsilon_{\mathbf{q}}} + \frac{n_B(\omega_{\mathbf{ph}}) + f(\varepsilon_{\mathbf{q}})}{\omega + \omega_{\mathbf{ph}} - \varepsilon_{\mathbf{q}}} \right], \quad (14)$$

where $g$ is the electron-phonon coupling constant and

$$n_B(\omega_{\mathbf{ph}}) = \frac{1}{e^{\omega_{\mathbf{ph}}/T} - 1} \quad \rightarrow \quad T \to \infty \quad \frac{T}{\omega_{\mathbf{ph}}} \quad (15)$$

is the Bose occupation number. For large $T$, the number of phonons $n_B$ becomes large, leading to a large $\text{Im}\Sigma$, a small $\sigma$ and a large $\rho$.

It is interesting to compare this with the resistivity due to the electron-electron scattering. Using the dynamical mean-field theory (DMFT) we have calculated the resistivity for a nondegenerate Hubbard model with the band width $W$ and a simple cubic lattice with the lattice parameter $a = 1$ Å. We focused on the half-filled case, which is relevant for A$_3$C$_{60}$, and we do not consider the case of a doped Mott insulator. Figure 70 shows $\rho(T)$ for different values of the on-site Coulomb interaction $U$. For $U < W$ the system is a metal and $\rho(T)$ grows with $T$, while for $U > W$ it is an insulator and $\rho(T)$ decreases with $T$. 

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In the metallic case $\rho(T)$ saturates at $\rho \approx 0.4 \text{ m}\Omega \text{ cm}$, which corresponds to $lla \approx 1/3$. Thus, in contrast to the electron-phonon scattering case, electron-electron scattering does not lead to an $l$ which is very much smaller than $a$ in the metallic state of the half-filled Hubbard model.

To understand this, we have studied the electron self-energy $\Sigma$ to second order in $U$, since $\Sigma$ determines $\rho$ in the DMFT. For low $T$, there is little scattering due to the small phase space available, as controlled by the Fermi functions. As $T$ increases, the available phase space grows and $\rho$ increases. However, for large $T$, $\rho$ essentially saturates, since the Fermi functions approach a constant value. This is in strong contrast to the Bose occupation numbers (Eq.(15)), that increase with temperature. The qualitative difference between the two scattering mechanisms for large $T$ can then be traced to the difference between fermions and bosons.

We have also addressed the validity of the Boltzmann equation for the case of the electron-phonon scattering in view of $l \ll d$. We have calculated the resistivity using the Ziman solution of the Boltzmann equation (Bloch-Grüneisen) and added the resistivity due to the orientational disorder as a $T$-independent contribution (dotted line in Fig. 68). Although the Boltzmann result is larger than the QMC result for large $T$, there is no qualitative break down of the Boltzmann equation even when $l \ll d$. The justification for the Boltzmann equation in the limit $l \ll d$ is not the semi-classical derivation, but the (approximate) derivation from the full quantum mechanical Kubo formulation (Eq.(13)). The proper language in this limit is not in terms of a very short mean free path, but in terms of a very broad spectral function, as discussed above.

The QMC calculation gives an approximately linear $T$ dependence. This agrees with the experimental result that $\rho$ is linear down to about 100–200 K. The result may seem surpris-
ing, because at small $T$ the probability of exciting finite energy phonons is exponentially small as is the contribution to $\rho$. Calculating the bubble diagram with the QMC electron Green’s function also gives a linear behavior, while the use of a Green’s function with the self-energy in Fig. 69b) gives an exponentially small contribution. The QMC Green’s function also involves processes like in Fig. 69c), where a virtual phonon is created followed by the decay of this phonon into an electron-hole pair. The excitation energy of such a pair can be arbitrarily small, which leads to a $\rho$ which is quadratic in $T$. In our model this goes over to an approximately linear behavior already for very small $T$.

### Patterned films of carbon nanotubes

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Carbon nanotubes have attracted a great deal of attention in recent years, due to their unique physical properties. Several interesting technological applications exploiting these properties have been proposed of which one is the use of carbon nanotubes as field-emission electron sources. At first glance, the idea of using carbon nanotubes as cold electron sources looks very promising. However, practical experience shows that several major problems have to be solved first before this will be possible.

One important prerequisite to using carbon nanotubes in such applications, for example, as electron emitters for flat panel displays, is the need to apply them in a controlled way to the substrate in order to define pixels. It has been shown recently that substrates can be patterned with carbon nanotubes using standard lithographic techniques. Compared to such standard photolithographic techniques, soft lithography is useful in several applications for which photolithography is not appropriate or very expensive, for example, patterning of large areas in one single process step or patterning of nonplanar surfaces. One way to use soft lithography is microcontact printing, $\mu$CP. This technique uses a patterned and inked elastomeric stamp to print molecules or assemblies of molecules as a pattern onto substrates. Recently inorganic solutions have been used as an ink to print catalysts on surfaces. Substrates patterned with such catalysts are in turn able to induce chemical reactions that are inhibited at bare surfaces, e.g., the electroless deposition of metals or the decomposition of hydrocarbons for the growth of multiwalled carbon nanotubes. $\mu$CP of catalysts is a fast and easy to use one-step process with the advantage of not using any photoresist or costly machines such as evaporators or mask aligners. The choice of $\mu$CP to pattern silicon wafers allows one also to vary the density of the catalyst on the substrate by changing the concentration of the transition metal in the ink.
We have developed a simple but powerful way to use \( \mu \)CP to pattern silicon wafers with transition metal catalysts followed by the growth of multiwalled carbon nanotubes on the activated regions by acetylene decomposition. The samples show patterns of high contrast and the pixels are covered by multiwalled carbon nanotubes about 10 nm in diameter and with well graphitized walls. The directed growth of the carbon nanotubes was found to depend critically on the choice and preparation of the catalyst and the appropriate combination of substrate and catalyst.

![Figure 71: Morphology of the patterned carbon nanotube films as a function of the concentration of the printed catalyst \((\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O dissolved in ethanol)}\): a) 10 mM, b) 25 mM, c) 40 mM, d) 70 mM and e),f) 50 mM.]

A key advantage of microcontact printing catalysts is the possibility to tune the density and morphology of the carbon nanotubes in the printed pattern. This can easily be achieved by varying the concentration of the catalyst in the ink. Figure 71 shows the influence of the catalyst concentration on the morphology of the deposited film. At low concentrations only a few single nanotubes are randomly distributed over the printed zones (10 mM). Increasing the concentration of the catalyst to 20–40 mM is accompanied by the formation of a film of entangled nanotubes. Using a concentration around 50 mM results in arrays of nanotubes aligned perpendicularly to the surface. The side walls are flat and no tubes are branching away. The transition from an entangled film at low catalyst concentrations in the ink to a well aligned film of carbon nanotubes at high concentrations is associated with the increased density of catalytically active particles. Nanotubes grow from the nucleation...
centers and are forced to extend along the direction normal to the substrate because neighboring nanotubes force them to grow unidirectional. Finally for concentrations higher than about 60 mM, the growth of nanotubes is almost inhibited and the pattern is decorated by particles of amorphous carbon.

The morphology of the nanotube patterns are an important factor influencing the emission behavior of the samples. We performed a series of preliminary experiments showing that the emission images taken by a tip scanning at constant height over the sample reproduce the printed pattern. A clear contrast between the emitting structures of multiwalled carbon nanotubes and the bare substrate is visible and demonstrates the selectivity of the printing and in turn the ability of the nanotubes to emit electrons.

Carbon nanotubes as electromechanical actuators – ‘artificial muscles’

S. Roth, C. Journet, O. Jaschinski and G. Gu;
an international cooperation involving groups in America, Australia, and Italy

Since their discovery in 1991 carbon nanotubes have attracted considerable attention. Carbon nanotubes are thin and long tubes. Their diameter is only one or a few nanometers, their length can be several micrometers and even millimeters. So in their cross-section, they are like molecules whereas along the axis they are ‘infinite’ solids. In electronics, these nanotubes are discussed as quantum wires and quantum dots. They can be used as components of nanostructured field effect transistors and single electron transistors. Their mechanical strength enables applications in nanocomposite materials and, because of the large surface area per unit weight, nanotubes are good candidates for all sorts of adsorption processes, including hydrogen storage for sustainable energy supplies.

Figure 72: What looks like a plate of spaghetti is an electron micrograph of the bucky paper. The noodles (about 10 nm thick) are not the individual nanotubes but bundles or ropes of several hundred tubes. The ropes are entangled to form the paper. The particular bucky paper shown here was made by C. Journet, delegated from Montpellier to Stuttgart in the frame of the European Network NAMITECH.
From X-ray investigations of graphite, we know that the graphite hexagons expand if the graphitic sheets are electrically charged. This effect is understood by rationalizing that adding electrons will populate anti-bonding states and adding holes will depopulate bonding states. In both cases, the carbon-carbon bond weakens and the bond length increases. Model calculations predict that this is also true for carbon nanotubes: the tubes will increase their length if we change the number of electrons sitting on a tube. This effect can be used for electromechanical actuators. Actuators are the moving parts in robotics (‘artificial muscles’). The relatively large length change and the high elastic modulus lead to very large figures of merit for carbon nanotube actuators. At the moment, mechanical experiments with individual nanotubes are still difficult, but the effect can easily be demonstrated with ‘Bucky Paper’. Bucky paper is a free standing film of bundles of nanotubes (Fig. 72).

Figure 73: Strip actuator. Strips of bucky paper are on both sides of a scotch tape. Electrochemically, one side is charged negatively (with positive sodium counterions), and the other side positively (with negative chloride counterions). Both sides expand (in neutral bucky paper chemical bonding is optimized), but the positive side expands more than the negative and the whole structure bends, like a human arm bends by contracting a muscle on one side and expanding its antagonist on the opposite side.

Figure 74: Length change of a straight strip of bucky paper. In this first experiment a length change of about half a promille was observed when a potential of 1 Volt was applied. This seems to be a very small change. But compared to other actuator materials (e. g. piezoelectrics) it is fairly large, and the voltage needed is fairly small. Moreover the nanotube actuators work in aqueous environment, and in particular in salt water – like in sea water or under physiologic conditions.

The actuator effect of carbon nanotubes has been demonstrated in a multinational cooperation involving the group in Stuttgart and partners in America (Ray Baughman, Allied Signal, Coordinator), Australia, and Italy (Science 21 May 1999). For this purpose, a strip of bucky paper has been dipped in salt water and electrochemically charged by changing the potential to ±1 V versus a standard electrode. The length expansion has been made visible by sticking the bucky paper on a piece of inert material (e. g. scotch tape, Fig. 73). If the bucky paper expands (Fig. 74), the bi-strip bends and the motion can easily be seen by the naked eye.
Carriers and phonons in solids

Tailoring of the crystal structure and composition is a powerful tool to control the electronic and lattice features. Optimization of the structural quality and the doping profiles of Si/SiGe/Si (p+/i/n+) layered structures led to interband tunneling diodes with improved electrical characteristics for digital circuit applications. Application of novel Raman techniques utilizing ultrashort laser pulses or the availability of isotopically pure crystals are demonstrated to solve important questions concerning the dynamics of phonon generation and decay which have puzzled people for a long time.

Si/SiGe interband tunneling diodes

R. Duschl, O.G. Schmidt and K. Eberl

Semiconductor tunneling structures have been studied intensively for many years since the pioneering work by Esaki in 1958. The interest arises mainly from possible applications in high-frequency and fast digital devices. Especially in the case of logic circuits the introduction of structures with negative differential resistance (NDR) can reduce the circuit complexity and/or increase the speed and reduce the power consumption compared to conventional logic circuits. For realistic applications, a peak current density (PCD) of about 10 kA/cm² and a peak to valley current ratio (PVCR) of at least 5 is required.

In principle there are two different types of tunneling structures exhibiting NDR: resonant tunneling diodes (RTD) based on double barrier quantum wells and Esaki interband tunneling diodes exploiting the band bending at a p+/n+ junction. The performance of state-of-the-art Si/SiGe RTDs, however, is strictly limited by their intrinsic properties. In particular large effective masses and relatively low barrier heights in Si/SiGe heterostructures cause PVCRs which are not much larger than one at room temperature. For this reason, Si(Ge) Esaki diodes are under detailed investigation. First Si interband tunneling diodes produced by an alloy process showed a PCD of about 1 kA/cm² and a maximum PVCR of 3.9 but these values are difficult to reproduce. Due to severe problems in growing high-quality Si/SiGe layers with very high and abrupt doping profiles the PVCR reached in first epitaxially grown structures were limited to about two.

We performed a detailed growth study of Si/SiGe/Si (p+/i/n+) interband tunneling diodes. The doping profiles and the structural quality of the highly doped Si layers were carefully optimized and investigated by secondary ion mass spectroscopy, reflection high energy electron diffraction and X-ray diffraction [Duschl et al., Electr. Lett. 35, 1111 (1999)]. The investigated structures consist of a B doped Si p⁺ (5·10¹⁹ cm⁻³) buffer layer, followed by a p-type d-doping layer (1·10¹⁴ cm⁻²), a 0–1 nm Si/2–4 nm Si₁₋ₓGeₓ / 1 nm Si intrinsic i-zone, a n-type d-doping layer (1·10¹⁴ cm⁻²) and a P doped Si n⁺ (6·10¹⁹ cm⁻³) cap layer. All samples were annealed for 1 min at 700°C after growth to reduce point defects formed during the low temperature growth (T = 360°C), which is
needed to avoid dopant segregation. For the measurements, mesa diodes were defined by standard optical lithography and wet chemical etching. The active area of the mesas ranges from 4 \( \mu \text{m}^2 \) to 4000 \( \mu \text{m}^2 \).

The tunneling barrier of the structures is determined by the energy gap, which can be tuned by the Ge content, and the width of the intrinsic or depleted region (inset of Fig. 75). At small applied forward voltages, electrons can tunnel from the occupied states in the conduction band (CB) at the n side to the empty states below the valence band (VB) at the p side. Since molecular beam epitaxy allows the realization of heterostructures with very sharp and well defined profiles the dependence of the relevant values, the PCD and the PVCR, on the different parameters is given quantitatively.

![Figure 75: RT I-V characteristics and PVCR for diodes with 2, 2.5, 3, 3.4, and 4 nm Si\(_{0.52}\)Ge\(_{0.48}\) embedded between two 1 nm Si layers within the i-zone. The schematic band structure is shown in the lower right part.](image)

Fig. 75 shows the RT I-V characteristics as a function of SiGe layer thickness for a Ge concentration of 48%. The thickness is varied from 2 nm to 4 nm. The shift of the peak voltage with increasing current is explained by a serial resistance within the measurement setup. A pronounced increase of the current with decreasing width of the i-zone is observed, as would be expected for thinner barriers and hence increased tunneling probabilities. The resulting PCD for the 200 \( \mu \text{m}^2 \) mesas is about 0.4 kA/cm\(^2\) for the structure with 4 nm SiGe and reaches a maximum value of 12.6 kA/cm\(^2\) for the structure with 2 nm SiGe. The PVCR shows a maximum of 5.1 for the tunneling diode with 3 nm SiGe (Fig. 75). Since a thickness of 3 nm is at the upper limit for the epitaxial growth of Si\(_{0.52}\)Ge\(_{0.48}\) a further increase of the layer thickness causes an increase of the defect density, which reduces the PVCR. A very thin SiGe layer (2 nm) would avoid these problems but leads to an increase of the leakage current.

For a further optimization, the amount of Ge was varied for the structure with 3 nm SiGe. The strain in the SiGe layer, however, limits the Ge content for pseudomorphic growth. A higher Ge content for a fixed layer thickness has the same consequences as an increase of layer thickness for a fixed Ge content as was discussed in Fig. 75. The position of the
SiGe layer within the i-zone was found to be crucial for the tunneling probability and therefore for the I-V characteristic [Duschl et al., Physica E (2000), in print]. Growing the SiGe layer directly at the δP layer without any Si spacer layer deteriorates the device performance. Whereas the growth of the SiGe layer directly at the δB layer reduces the B diffusion and supports the transfer of the holes into the SiGe layer. Both effects increase the tunneling probability. For this reason the 1 nm Si spacer between the δB and SiGe layers was left out for the optimized structure with 3 nm Si₀.₅₂Ge₀.₄₈. The influence on the j-V characteristic is demonstrated in Fig. 76. The PCD increases from about 3 kA/cm² to more than 8 kA/cm² for the structure without spacer. Even more important is that, despite these high PCD, the PVCR raises from 5.1 to 5.45. This is the highest value ever reported for Si based interband tunneling diodes.

![Figure 76: RT current density (j)-voltage characteristics of the tunneling structure with 1 nm Si/3 nm Si₀.₅₂Ge₀.₄₈/1 nm Si in the i-zone (with Si spacer), compared to a structure with 3 nm Si₀.₅₂Ge₀.₄₈/1 nm Si in the i-zone (without Si spacer).](image-url)

In conclusion, our study demonstrates the high potential of epitaxially grown Si/SiGe interband tunneling diodes. By changing the thickness of the intrinsic SiGe layer the PCD can be varied in a wide range from 0.4 kA/cm² to 12.6 kA/cm². An optimization of the structure regarding Ge content, thickness and position of the SiGe layer results in a diode with a high PCD of 8 kA/cm² and a record PVCR of 5.45 for Si based interband tunneling diodes. The results imply that the aforementioned minimum requirements for an application in the field of digital circuits can be fulfilled with Si based structures.
Spin-orbit splitting of acceptor states in Si and C

J. Serrano, A. Wysmolek, T. Ruf and M. Cardona

The knowledge of acceptor levels allows one to evaluate the effects of different dopant atoms on the carrier concentration. This is of crucial importance in the development of devices, such as transistors or diodes, which are widely employed in electronic systems. Despite the intensive study of these acceptor levels, especially by means of optical spectroscopies, there are some aspects of the observed spectra which are not completely understood. In the case of Si, a splitting, $\Delta_0^a$, has been observed for B, In, Be$^-$, Zn$^-$ substitutional impurities. This splitting varies from 23.7 meV to 0.3 meV depending on acceptor. Its tentative assignment to spin-orbit interaction requires an enormous reduction of the corresponding spin-orbit splitting of the $\Gamma^+_{2s}$ valence band states, $\Delta_0 \simeq 44$ meV. In the case of diamond, the reported experimental spin-orbit splitting is 6 meV, but a value of 13 meV was calculated by using relativistic LMTO, while for the boron acceptor the experimental value is reduced to 2 meV.

We report here calculations for the spin-orbit-induced splitting of substitutional acceptors in silicon and diamond. A Green’s function method is used to estimate the splitting of $\Gamma_8$ and $\Gamma_7$ ground state levels for different impurities, using as input parameter only the experimentally determined value of the binding energy for the acceptor under consideration, $E_{ab}$. In order to calculate the Green’s function, the full-zone $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian is used with a Slater-Koster ansatz for the impurity potential (this ansatz is equivalent to assuming that the hole interacts with the acceptor only if both are in the same primitive cell). This allows us to obtain the binding energy of an acceptor level $\Gamma, E_{ab}^\Gamma$, by using the equation

$$\frac{1}{V_0} \simeq G_r \left( E_{ab} \right),$$

where $V_0$ represents approximately the average of the potential over the primitive cell, and $G_r^\Gamma$ is the real part of the $\Gamma$-projected Green function. $G_r^\Gamma$ is obtained from the imaginary part of the Green function, $G_i^\Gamma$, by using a Hilbert transform. $G_i^\Gamma$ is related to the $\Gamma$-projected density of states through

$$G_i^\Gamma \left( E \right) = -\pi N^\Gamma \left( E \right).$$

$N^\Gamma \left( E \right)$ is calculated from the $30 \times 30$ full-zone $\mathbf{k} \cdot \mathbf{p}$ Hamiltonian using the tetrahedron method with a grid of $\approx 3 \cdot 10^5$ tetrahedra. The density of states is projected via $\Gamma_8^+$ and $\Gamma_7^+$ admixture coefficients interpolated for each tetrahedron. Finally, we made the plausible assumption of equal values of $V_0$ for $\Gamma_8^+$ and $\Gamma_7^+$. The $\Gamma_8 - \Gamma_7$ acceptor splitting $\Delta_0^a$ is then found by solving Eq.(16) for $E_{ab}^\Gamma(\Gamma_8)$ after having determined $V_0$ using also Eq.(16) and the experimental value of $E_{ab}^\Gamma(\Gamma_8)$. The values of $\Delta_0^a$ obtained for silicon by this procedure vs. $E_{ab}^\Gamma$ are displayed in Fig. 77 (solid line).
We have also performed Raman measurements in Si : X samples, X being B, Al, Ga and In. Most samples were cut from bulk material but we also used epitaxial layers. The carrier concentrations were in the $10^{16} – 10^{18}$ cm$^{-3}$ range. The 7993 Å krypton laser line was used for excitation in backscattering configuration with low power densities. A cold finger cryostat was used to hold the samples at 11 K. A Dilor XY multichannel spectrometer and a charge-coupled device detector were used to record the spectra. The spectral resolution was 1.5 cm$^{-1}$.
In Fig. 78, we show typical Raman spectra in the range of 4–30 meV, displaying structure that can be attributed to $\Delta_0^{a}$, the $\Gamma_8 - \Gamma_7$ spin-orbit splitting of the corresponding acceptor ground state levels. The observed values of 22.8 meV (B) and 4.1 meV (In) are in good agreement with those previously reported at 22.7 meV and 4.2 meV, from Raman and EDSR experiments, respectively. However, a strong broad structure was obtained for Si:Al. This increases the error for the determination of the splitting, although the energy at the maximum is in reasonable agreement with what would be expected from the calculations, as can be seen in Fig. 77. In the case of Si:Ga, two peaks occur in the range of interest, we thus cannot unambiguously assign one of them to $\Delta_0^{a}$; on the basis of the general systematics (see Fig. 77), we assign the lower one (10 meV) to $\Delta_0^{b}$. Tentatively, however, we assign the additional peaks observed for Ga to disorder activated TA phonons (DATA). The shoulder in the Si:In spectrum at 8 meV is likely to be due to vibronic structure (dynamic Jahn-Teller effect).

Our experimental data are compared with the calculation in Fig. 77 where we also show some results of Electric-Dipole Spin Resonance (EDSR) measurements from H. Schroth et al. [phys. Stat. Sol. (b) 210, 747 (1998)]. The open circles represent the EDSR data, while the open squares stand for the Raman results. The theoretical curve describes the trend of the experimental data, namely a reduction of $\Delta_0^{a}$ with increasing $E_0^{a}$, although considerable differences exist between the magnitudes of experimental and calculated splittings. These differences are less conspicuous if we look at the data in terms of the quenching of the $\Gamma_8^+ - \Gamma_7^+$ band splitting which amounts to 44 meV for the experimental value in the case of the Zn$^+$ acceptor and 41 meV for the calculated one.

Similar calculations have been performed for acceptor states in diamond. While lending support to the value of $\Delta_0 = 13$ meV calculated ab initio with the relativistic LMTO method by M. Willatzen et al. [Phys. Rev. B50, 18054 (1994)] for intrinsic diamond, they lead to a calculated value of $\Delta_0^{a} = 3.9$ meV. This is in reasonable agreement with the 2 meV observed experimentally for substitutional boron, the only clearly identified acceptor. We also performed a calculation of the value $\Delta_0^{exc}$ reported for the splitting of the edge (indirect) excitons in diamond with a method similar to that used for acceptor levels, modified so as to take into account the indirect nature of the edge exciton. We obtained the value $\Delta_0^{exc} = 8.6$ meV in rather good agreement with the experimental one ($\simeq 7$ meV).

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Anomalous Raman line shape of the TO phonon in GaP

F. Widulle, T. Ruf, E. Schönherr and M. Cardona

The Raman spectrum of the transverse optic (TO) phonon in GaP is known to exhibit an asymmetric line shape at room temperature. We performed high resolution Raman experiments on natural GaP crystals at low temperature that revealed a characteristic fine structure in the line shape of the TO phonon. Variation of the isotopic composition in semiconductor crystals has proven to be a powerful tool for investigating phonon properties. By this procedure, the resulting changes of lattice-dynamical properties can be tuned, thus allowing one to trace phonon parameters in great detail. Hence, we studied systematically the changes in the anomalous Raman line shape with varying Ga isotope abundance. The different measured line shapes are found to originate from anharmonic coupling of the TO Raman phonon with a continuum of two-phonon states \[ \text{Widulle et al., Phys. Rev. Lett. 82, 5281 (1999)} \].

Many elements found in nature consist of more than one stable isotope and possess a characteristic natural isotopic composition. In such systems the virtual crystal approximation (VCA) is applied where the phonon frequencies of an elemental semiconductor with average isotope mass $\bar{M}$ obey, in the harmonic approximation, the mass dependence $\omega \propto \bar{M}^{-1/2}$ which is valid for all phonon branches in the entire Brillouin zone (in binary compounds $\bar{M}$ is replaced by a reduced mass $\mu$). Anharmonic phonon-phonon interactions also depend on the isotopic composition and affect the phonon properties. Isotope effects beyond those found within the VCA arise from the random distribution of the isotopes in the crystal lattice (isotope mass disorder). Both mechanisms – anharmonicity and mass disorder – contribute to the phonon self-energy which leads to additional line shifts of the harmonic Raman frequency and determines the broadening of the observed spectral peaks. It is not known a priori which mechanism contributes predominantly.

The average Ga mass can be varied between the masses of the stable isotopes $^{69}\text{Ga}$ and $^{71}\text{Ga}$ whereas phosphorus is isotopically pure ($^{31}\text{P}$). Natural Ga ($^{\text{nat}}\text{Ga}$) contains 60.11% $^{69}\text{Ga}$ and 39.89% $^{71}\text{Ga}$. In addition to the $^{\text{nat}}\text{GaP}$ specimens, two isotopically pure crystals with highly enriched contents of $^{69}\text{Ga}$ (99.7%) and $^{71}\text{Ga}$ (99.6%) were grown. Another isotopically disordered ‘anti-natural’ sample ($^{\text{nat}}\text{GaP}$) with an isotopic Ga composition of $^{69}\text{Ga}_{0.4}^{71}\text{Ga}_{0.6}$, complementary to that of $^{\text{nat}}\text{Ga}$, allows us to better interpolate between the data of the isotopically pure crystals and probe possible disorder effects.

Figure 79 shows the measured low temperature TO Raman spectra (symbols) together with the results of line shape calculations (solid lines) and the respective two-phonon density of states (DOS, dashed lines). The vertical lines represent the bare harmonic TO phonon at $\omega_0$ ($\delta$-function). The Raman lines of all investigated samples are nonsymmetric and shoulders are observed. Compared to the LO phonon (linewidth $\Gamma \approx 0.3 \text{ cm}^{-1}$) and most Raman phonons in other semiconductors, the TO phonon ($\Gamma \approx 3 \text{ cm}^{-1}$) in natural GaP is

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unusually broad even at low temperature. Our measurements and calculations show that isotope disorder does not account for this fact since the linewidths of the two isotopically pure samples, with almost zero mass disorder, are also quite large and, intriguingly, they differ significantly by almost a factor of two.

Figure 79: Raman spectra of the TO phonon of (a) $^{69}$GaP, (b) $^{nat}$GaP ($^{69}$Ga$_{0.6}$,$^{71}$Ga$_{0.4}$P), (c) $^{nat}$GaP ($^{69}$Ga$_{0.4}$,$^{71}$Ga$_{0.6}$P), and (d) $^{71}$GaP at $T = 6$ K. The solid lines are fits to the experimental data (symbols) using the indicated two-phonon DOS, $\rho_2(\omega)$, (dashed lines), respectively. The vertical lines at $\omega_0$ represent the $\delta$-function-peaks of the harmonic TO phonons prior to renormalization.

We calculate the Raman spectrum of the TO phonon based on the assumption that solely third-order anharmonicity is responsible for the broadening. The renormalized Raman line shape can be approximated as

$$\mathcal{A}(\omega) \propto \frac{\Gamma(\omega)}{[\omega - \omega_0 - \Delta(\omega)]^2 + [\Gamma(\omega)]^2}. \quad (18)$$

The complex phonon self-energy $\Sigma(\omega) = \Delta(\omega) - i \omega \Gamma(\omega)$ renormalizes the bare harmonic phonon at $\omega_0$. Its frequency dependent real and imaginary part $\Delta(\omega)$ and $-\Gamma(\omega)$, respectively, are related to each other via a Kramers-Kronig transformation. If they do not depend strongly on frequency, $\Delta(\omega)$ induces a frequency shift with respect to $\omega_0$ whereas $\Gamma(\omega)$ gives an almost constant broadening of the Raman line. $\Gamma(\omega)$ is directly proportional to the two-phonon DOS $\rho_2(\omega)$

$$\Gamma(\omega) = |V_3|^2 \rho_2(\omega). \quad (19)$$
The parameter $V_3$ determines the effective coupling between the three phonons that participate in the anharmonic scattering process. The values of $|V_3|^2$ around 57 cm$^{-2}$ found in this study indicate a somewhat smaller anharmonic coupling strength compared to $|V_3|^2 = 70$ cm$^{-2}$ obtained for the more ionic CuCl.

Equation (18) represents a Lorentzian as long as the self-energy does not depend significantly on frequency. Here, we consider the general case where $\rho_2(\omega)$, and correspondingly $\Gamma(\omega)$ and $\Delta(\omega)$, depend strongly on frequency. Consequently, the Raman line shape deviates from a Lorentzian, leading to the observed asymmetries. The degree of distortion is determined by the shape of $\rho_2(\omega)$ within that frequency range where the spectral density function $\mathcal{A}(\omega)$ yields significant values, i.e., around the (renormalized) phonon frequency. If the self-energy contains one or more strongly frequency dependent features (peaks, kinks) within the spectral range of interest, these features are reflected in the Raman spectrum. Extreme renormalization can even lead to richly structured spectra with multiple peaks, as seen in the TO phonon line shape of CuCl.

![Graphical representation](image)

Figure 80: Effect of Raman line shape distortion in isotopic GaP. (a) Simulated TO Raman spectra for different gallium masses calculated with Eq. (18) using the complex phonon self-energy (one line type defines a set). (b) and (c) Complex TO phonon self-energy in GaP. The harmonic phonon is indicated by the vertical line, and its frequency $367$ cm$^{-1} \lesssim \omega(\mu) \lesssim 368$ cm$^{-1}$ set to zero in each case.

Figure 80(b) and (c) show the imaginary and real parts of the phonon self-energy, respectively, around the TO frequency for various Ga isotope compositions. According to Eq. (19), $\Gamma(\omega)$ reflects the frequency dependence of the two-phonon DOS which, in the range of interest here, can be parametrized as
where $c_1$ and $c_2$ are positive constants. This parametrization models the two-phonon DOS around the TO phonon frequency calculated from a lattice-dynamical model. The constant DOS below the kink at $\omega_k$ stems from close-lying two-phonon combinations of the acoustic branches along the X–K direction in the Brillouin zone. These are the states the Γ-point phonon can decay into, i.e., $\text{TO}(\Gamma) \rightarrow \text{LA}(X-K) + \text{TA}(X-K)$. The dispersion of these branches causes a Van Hove singularity of type M at $\omega_k$. Figure 80(c) shows the corresponding real part $\Delta(\omega)$ which exhibits a sharp peak at $\omega_k$. $\Gamma(\omega)$ and $\Delta(\omega)$ are displayed at four different spectral positions of $\omega_k$ relative to the corresponding harmonic phonon frequency $\omega_0$ in order to simulate the case of four GaP crystals with different isotopic compositions. In order to keep the harmonic frequency fixed, we have chosen as abscissa $\omega - \omega_0$. The spectral dependencies of $\Gamma(\omega)$ and $\Delta(\omega)$ result in the characteristic line shapes, shown in Fig. 80(a), which reproduce the corresponding experimental Raman spectra (see also Fig. 79, solid lines). The linewidths of the topmost (solid line, $^{69}\text{GaP}$) and bottom (dot-dashed line, $^{71}\text{GaP}$) Raman peaks differ significantly since in the first case the phonon frequency $\omega_0$ is located inside the range of the constant and large two-phonon DOS whereas it is outside this region in the latter case. The topmost Raman spectrum (solid line, $^{69}\text{GaP}$) is somewhat more shifted to lower frequencies compared with the others. The amount of the shift is approximately given by the solution of $\Delta(\omega) = \omega - \omega_0$. This equation can be solved graphically; and the respective crossing points of $\Delta(\omega)$ and $\omega - \omega_0$ are marked as circles in Fig. 80(c). They reveal a more negative frequency shift for $^{69}\text{GaP}$. 

Note that fits of lattice-dynamical models to inelastic neutron scattering data must be very accurate near $\text{TO}(\Gamma)$ and the LA and TA frequencies along X–K in order to provide a realistic two-phonon DOS around $\text{TO}(\Gamma)$. Conversely, our Raman experiments can be used as an extremely sensitive tool for probing details of the two-phonon DOS. In the case presented here, isotope substitution is the method of choice for a systematic investigation since it allows a fine tuning of the effect in highly resolved steps. Our theoretical approach, based on third-order anharmonic phonon-phonon interaction and an analytical model two-phonon DOS, explains all measured low temperature Raman line shapes in remarkable detail. Isotope disorder effects and higher-order anharmonic contributions are found to be unimportant.
Coherent phonon dynamics studied by impulsive stimulated Raman scattering

J. Kuhl, T.E. Stevens and R. Merlin

In the last decade, pump/probe experiments with ultrashort optical pulses have been developed as a powerful tool for time-domain studies of coherent lattice dynamics. Following recent advances in laser technology, notably the advent of practical and reliable sub-10-fs sources, it is now possible to excite coherent vibrations in solids and molecules with energies up to more than 500 cm\(^{-1}\) by a strong pump pulse which impacts onto the sample for a time shorter than the phonon period. Subsequently the relaxation properties of the photoexcited phonons are investigated with a time-resolution as short as a few femtoseconds by measuring the modulation of the sample transmission or reflectivity associated with the coherent lattice vibration as a function of the delay between the pump and the probe pulse.

Here we report on the mechanisms of phonon generation by fs optical pulse excitation in opaque materials. The question of the mechanism of light-induced phonon generation has been discussed extensively in the literature. While there exists general consensus that impulsive stimulated Raman scattering (ISRS) is the driving force in transparent media, alternative proposals such as the so-called displacive excitation of coherent phonons (DECP) have been considered for opaque materials. DECP assumes that real excitation of carriers from bonding to anti-bonding states changes the equilibrium positions of the atoms and then generates a coherent vibration. It was originally proposed to account for early time-domain experiments in semimetals that revealed the fully-symmetric A\(_{1g}\) but not the E\(_g\) mode. However, recent observations of the E\(_g\) mode in Sb and Bi as well as theoretical work on resonant ISRS have challenged the notion that DECP represents an alternative mechanism for phonon generation. To enhance our understanding of the generation process, we have measured the photon-energy dependence of the amplitude of the coherent A\(_{1g}\) mode in Sb using excitation near the E\(_2\) critical point at \(\approx 1.95\) eV. The experiments use a standard pump-probe setup in the reflection geometry to measure changes in the dielectric function caused by coherent phonon oscillations. As a source, we used an optical parametric amplifier (OPA) pumped by a 250 kHz regenerative Ti:sapphire amplifier that produced continuously tunable 85 fs pulses with an energy of 50 nJ and central wavelength in the range 500–700 nm. The maximum differential change in the reflected intensity was \(\approx 10^{-3}\).

Extending the model of impulsive stimulated Raman scattering in transparent media to absorbing materials, we have calculated the dependence on the width and central energy of the pulse of (i) the amplitude and phase of the phonon and (ii) the phonon-induced change in reflectivity. Our theory applies to materials for which two-band processes dominate and pulse-widths that are small compared to the width of the Raman resonances. Under these assumptions, the coherent phonon parameters can be expressed in terms of the real and imaginary parts of the index of refraction. An important prediction of our model is that,
in general, the resonant energy at which the phonon amplitude is largest does not occur at
the peak of the spontaneous Raman cross section. This is due to differences in the pole
structure of the tensors associated with the phonon generation and the scattering process.
Specifically, the approximate expression for the scattering tensor is

\[ R_S(\omega, \omega \pm \Omega) \approx \left[ \frac{\varepsilon(\omega) - \varepsilon(\omega \pm \Omega)}{\pm \Omega} \right] \Omega \to 0 \text{ Re} \left( \frac{d\varepsilon}{d\omega} \right) + i\text{ Im} \left( \frac{d\varepsilon}{d\omega} \right) \]

while the tensor involved in the generation of coherent phonons can be approximated by

\[ R_Q(\omega, \omega \pm \Omega) \approx \left[ \frac{\varepsilon(\omega) - \varepsilon^*(\omega \pm \Omega)}{\pm \Omega} \right] \Omega \to 0 \text{ Re} \left( \frac{d\varepsilon}{d\omega} \right) + \frac{2i}{\Omega} \text{ Im}(\varepsilon). \]

Here, \( \varepsilon \) is the frequency (\( \omega \))-dependent dielectric function and \( \Omega \) is the phonon frequency.

Fig. 81 shows the \( A_{1g} \) phonon amplitude \( Q \) and the atomic displacement \( u \) at 300 K as a
function of laser pulse energy and distance \( z \) from the surface of the crystal. In the calculations,
we used a Gaussian pulse shape and ignore phonon decay. The phonon amplitude is
largest at \( z = 0 \) and decreases into the crystal due to absorption. The maximum atomic dis-
placement reaches values of approximately 1 pm. The calculated time-dependence of the
oscillation is of the form \( \cos(\Omega t + \varphi) \) where \( \varphi \approx 0 \) across the entire energy range shown.
The amplitude decreases with increasing energy, following primarily the absorption, i.e.,
\( \text{Im}(\varepsilon) \). We note that these resonant-ISRS predictions are the same as those of the DECP
model. Hence, there is no need to invoke a new mechanism for phonon generation.

In Fig. 82, we compare the theoretical prediction for the normalized change of the re-
reflectivity \( \Delta R/R \) with our experimental results. The optical constants from Cardona et al.
[Phys. Rev. 133 A, 1685 (1964)] were used both to calculate the two-band approximation

![Figure 81: Phonon amplitude Q and atomic displacement u in Sb as a function of central pulse energy. Values for two depths below the surface are shown.](image-url)
to $\Delta R/R$ and to fit the spontaneous Raman cross-section measured by Renucci et al. [phys. Stat. Sol. (b) 60, 299 (1973)] which is shown in the inset. We consider the agreement between theory and experiments as satisfactory in that the calculation reproduces the general shape of the ISRS data. However, there are important discrepancies in regard to the position (the experimental data are shifted to lower energies by an amount of the order of the phonon energy $\hbar/2\pi\Omega$) and width of the resonance that we tentatively ascribe to small differences in the optical constants of the different samples, on which the Raman cross-section depends sensitively. We note that the calculated maximum of $\Delta R/R$ is lower in energy than the peak of the spontaneous cross-section. This feature does not depend on small variations in the indices of refraction and is explained by the different dependence of $R_Q$ and $R_S$ on the real and imaginary part of the complex dielectric function (see the corresponding equations given above).

Figure 82: Phonon-induced change in reflectivity in Sb as a function of central pulse energy. A Lorentzian (dashed line) has been drawn through the data (black squares) to guide the eye; the theory yields the solid line. The optical constants used in the calculation of $\Delta R/R$ are those used to fit the spontaneous Raman cross-section (black squares), taken from Renucci et al. [phys. Stat. Sol. (b) 60, 299 (1973)], shown in the inset. The two-band approximation was used to compute both solid curves. The gray Gaussian curve represents a typical electric field distribution of the laser pulse.

Finally it should be mentioned that further experimental proof of our theoretical model should be attainable from a systematic measurement of the phonon phase in dependence on the detuning of the laser field from the material resonance. As discussed above, the coherent phonon oscillations which are sine-like for transparent media should switch to a cosine-like behavior in the presence of strong absorption. Unfortunately the current experimental accuracy in determining the zero time positions of the pump/probe signals for different wavelength tunings of the OPA prevents a precise measurement of the phase of the scattered probe field.