HIGHLIGHTS OF 1995

In this section we present scientific highlights of some of the Network's collaborations for the past calendar year.

Large Systems and Pseudopotentials: Pulling a piece of aluminium apart

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In recent decades, much research has focused on the properties of glamorous materials such as silicon and other semiconductros, magnetic layers, high temperature superconductors and many more. However the heart of materials science still lies in a sense in the mechanical strength of materials: why does the bridge not fall down, or rather how much money can be saved by making the girders thinner? The matter of mechanical strength is scientifically a difficult one, not only because of the complexity of the processes occurring in deformation and fracture, but because they span two length scales: the atomic scale of Angstroms and the mesoscopic scale of microns.

Both length scales are essential. The stress field around a crack tip and generation of dislocations belong to the mesoscopic scale, while fracture ultimately means overcoming the interactomic bonding forces on the atomic scale. It is in the latter where one might expect to see the difference between the brittle covalently bonded materials and ductile metals with atoms held by metallic bonding. Actually such a view was rather unfashionable until recently. It was thought that the only role of the interatomic forces was to determine the crystal structure, e.g. face centred cubic for many metals and, say, the diamond structure for silicon. After that, it was the propensity of the crystal structure to dislocation slip that was the dominant factor in ductile or brittle behaviour.

While that remains a large part of the answer, the actual interatomic forces at a crack tip have also been shown to matter in recent ab initio quantum mechanical calculations. In

metallic bonding the atoms are relatively free to slide over one another as long as the total coordination number is approximately maintained. This can be seen in the calculations on aluminium by Deyirmenjian, Payne, Lynden-Bell and Heine in Cambridge with Finnis at the Max Planck Institute for Metallurgy in Stuttgart. The computer sample of aluminium had rows of missing atoms, the rows about 1.6 nm apart, each such row being a defect something like an incipient crack. The sample was pulled gradually in one direction until near failure at an extension of 28%, the full quantum mechanics for the electron bonding and the atomic positions being solved at every small increment of the extension process.

Several interesting points could be seen in the simulations, but there were two findings of wider significance. The first concerns the role of metallic bonding. Whereas the quantum calculation for aluminium clearly gave ductile behaviour even at zero degrees Kelvin, a parallel calculation using a pairwise Morse interatomic potential gave brittle failure with identical geometry. The special nature of metallic bonding is therefore important in ductile behaviour. The second achievement was a basic improvement in the empirical Sutton-Chen model of metallic bonding for aluminium. The number of atoms (per superlattice cell) needed to simulate real deformation processes in a computer sample is too large to be treated by the ab initio quantum mechanical methods, so that one is forced to use empirical classical models of the interatomic bonding. Since the work of Finnis and Sinclair in 1984, a series of models have been devised to represent metallic bonding. Collectively sometimes called glue models, they incorporate approximately the quantum effects and are enormously better than the models preceding them. Deyirmenjian tested one of these due to Sutton and Chen in a parallel calculation, again with the identical starting geometry as the quantum simulation. It also showed ductile fracture, but with a long strong precursor effect in the deformation around the line of vacancies which was absent in the proper quantum calculation. In sp bonded metals, a quantity of basic importance is the local volume per atom available to the bonding conduction electrons. Finnis has recently developed a good definition and computable algorithm of the local atomic volume in an arbitrary configuration, and when this was used to modify the attractive 'glue' term in the Sutton-Chen model, the precursor disappeared almost completely. We therefore have here a guide for developing better glue models in the future, and the quantum calculation represents a large database with which empirical models can be compared. However it must be admitted that the accumulating experience is that empirical models will never do a really good job, no matter how well they are tuned up. But we must use them for many many simulations too large to be treated by the full quantum mechanical calculations, and therein lies a love/hate relation between the two approaches.

Where is the Cooper Force in the High Temperature Superconductors

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Eight years after the discovery of the High Temperature Superconductivity the physical mechanism behind this remarkable phenomenon remains a mistery. Many ingenous ideas have been tried [1] but so far they have failed to convince anyone except their inventors and their research students. Under these circumstances it may be worthwhile to approach the problem piecemeal, taking small steps at a time. Namely, one may attempt to isolate features of the problem which can be tackled without requiring a full solution. For instance, one might regard the establishement by Gough et al. [2] that the new superconductors, like the conventional ones, have to do with pairing of electrons, as the first move along this line. A similar but more dramatic step forward is the emerging consensus that the relative symmetry of the pair is d-type [3]. In this note we wish to highlight a new strategy for what might be an another useful manoeuvre. The aim is to determine at which site and in which state the members of a Cooper pair must be to experience the pairing force, without specifying its physical origin.

The approach is made possible by the particularly simple general form the attractive electron-electron interaction takes in the Density Functional Theory for superconductors [4]. Its pairing kernel $\lambda(\mathbf{r}, \mathbf{r}'; \mathbf{r_1}, \mathbf{r'_1})$ is given by functional derivatives of the exchange-correlation energy functional, of the charge density $n(\mathbf{r})$ and the pairing amplitude $\chi(\mathbf{r}, \mathbf{r}')$, with respect to the pairing amplitude. The superconducting analogue of the usual Kohn-Sham equations has the general form of the Bogolubov-de Gennes equations which involve the pairing potential $\Delta(\mathbf{r}, \mathbf{r}')$. The latter is determined through the pairing kernel $\lambda(\mathbf{r}, \mathbf{r}'; \mathbf{r_1}, \mathbf{r'_1})$ in terms of the pairing amplitude $\chi(\mathbf{r}, \mathbf{r}')$ as follows

$$\Delta(\mathbf{r}, \mathbf{r}') = \int \mathbf{d^3 r_1} \int \mathbf{d^3 r'_1} \lambda(\mathbf{r}, \mathbf{r}'; \mathbf{r_1}, \mathbf{r'_1}) \chi(\mathbf{r_1}, \mathbf{r'_1}). \tag{1}$$

Evidently, the great unknown in this theory is the pairing kernel, λ, which is, in general, a functional of both $n(\mathbf{r})$ and $\chi(\mathbf{r}, \mathbf{r}')$. Our semi-phenomenological approach is to express λ in terms of site- and orbital-dependent coupling constants which are treated as adjustable parameters and determined by fitting to experimental data from such searching probes as photoemission, spin-lattice relaxation rates, and neutron scattering experiments.

What lends impetus to this strategy is the conjunction of two fortunate circumstances. On the one hand, a relatively small set of coupling constants describes a rather large class

of mechanisms, and on the other, because these adjustable parameters are embedded in a fully first-principles calculation, a very large number of observables can be calculated without further adjustable parameters. Remarkably, when a set of coupling constants has been identified as being consistent with a variety of experiments, we have determined the orbital character and spatial location of the Cooper force without knowing its origin. Our hope is that such information will be suggestive concerning its nature.

A uniquely convenient starting point for our strategy is the eight-band model of Andersen et al. [5]. This model has the following features: **a)** it describes a Cu–O bilayer which is characteristic of many high T_c superconductors **b)** it has been obtained from first-principles (LMTO) calculations by a well controlled folding-down procedure **c)** it is of a required tight-binding form **d)** and finally, it has been shown to give a good quantitative account of the electronic structure, near the Fermi energy, in the normal state.

As a first step towards implementing the strategy outlined above, we have solved self-consistently the Bogolubov-de Gennes equations, corresponding to the eight-band model, for some 20 different choices of the coupling constants, and compared the resulting excitation spectra with those deduced from photoemission experiments [6]. In most cases we have studied we have assumed at most two different and non-zero coupling constants, with all the others set to zero. Concerning gap anisotropy, we have been able to assign a specific pairing interaction to each of the three different experimental scenarios for the superconducting gap anisotropy [7]. In particular, a gap of a zero value and a cusp along the (π, π) direction have been interpreted as arising from the nearest neighbour Cu $d_{x^2-y^2}$–Cu $d_{x^2-y^2}$ pairing interaction of 0.67 eV. A gap which is zero and a minimum along the (π, π) direction has been identified with the nearest neighbour Cu s–Cu $d_{x^2-y^2}$ pairing interaction of 2.3 eV, and finally, the most 'exotic' gap with a "hump" along the (π, π) direction has come out as a combined effect of the nearest neighbour Cu s–Cu $d_{x^2-y^2}$ pairing interaction of 2.7 eV and the nearest neighbour Cu p–Cu $d_{x^2-y^2}$ pairing interaction of 0.45 eV. Considering the magnitude of the pairing interaction of each studied case, the obvious favourite has to be the nearest neighbour Cu $d_{x^2-y^2}$–Cu $d_{x^2-y^2}$ pairing interaction, leading to a gap of d-type symmetry; which incidently is in line with the recently emerging consensus concerning the symmetry of the gap. Although we have been able to identify several different pairing interactions which also lead to a gap of d-type symmetry, their considerably larger magnitudes have inclined us to regard them, for the time being, as less physically likely. Thus, with some exaggeration to illustrate how our strategy can be useful, it can be said that we have deduced that the Cooper force operates between electrons on the nearest neighbour, in plane, Cu-sites and in the $d_{x^2-y^2}$ orbitals.

Interestingly, it is very difficult to reproduce the observed d-wave pairing with electrons on different Cu–O planes as required by the Anderson mechanism [1]. On the other hand, it is easy to imagine that the nearest neighbour Cu $d_{x^2-y^2}$–Cu $d_{x^2-y^2}$ pairing interaction is due to antiferromagnetic fluctuations. However, it is too early to draw firm conclusion from these preliminary results. Clearly, to lend further credence to this approach we

must go on to calculate the other observables we have mentioned at the beginning of this note. Particularly promising are calculations of the spin lattice relaxation rates, $1/T_1$, at the Cu-, O-, and other-sites. Since no further adjustable parameters are required, these should decisively eliminate a number of contending interactions.

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Magnetic Impurities in Alkali Metals

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At a first sight the magnetic properties of transition metal impurities in alkali or alkali–earth metals do not seem to be particularly exciting. As it is well known, 3d impurities like Mn or Fe are magnetic in noble metal hosts, having a local magnetic moment at the impurity site and showing a Kondo behaviour at low temperatures. Why should it be interesting to introduce a 3d impurity in one of the alkali metal hosts with their much larger volumes, when the same impurity is already magnetic in Cu?

The interesting new aspect is the development of an orbital moment, as requested by Hund's second rule for free atoms. In the dense noble metals the orbital moment of the 3d impurities is quenched due to the strong hybridization of the d–wavefunctions with the s electrons of the host. Now, in the alkali metals with their very low electron density the Fe atom acquires in addition to the spin moment also an orbital moment. This is basically the same localisation transition which is well known from the rare earth and actinide systems. In fact, one might take any impurity from the transition metal series and insert it into any of the alkali metals, the volumes of which change quasicontinuously in the sequence Cu, Ag, Li, Na, K, Rb, Cs by a factor of 10. Thus in these systems one can study the transition to the atomic limit in great detail and for many different impurities.

This field has been pioneered experimentally by D. Riegel of the Hahn–Meitner Institut in Berlin. He introduced the transition metal impurities into the alkali metals by ion–implantation, since the natural solubility for these elements is vanishingly small. Using nuclear spin rotation techniques he obtained a rich variety of interesting physical properties, of which we will only mention two: i) While 3d impurities normally have both spin– and orbital moments, in certain cases, e.g. for Fe in Na or K, two configurations are found, a substitutional Fe atom with fully developed spin and orbital moments and in addition an interstitial Fe with spin moment only. Apparently the higher electron density at the interstitial site quenches the orbital moment. ii) Gross and Riegel [1] find that also 4d impurities like Mo, Tc and Ru show in the heavier alkali metals a nearly atomic behaviour with spin and orbital moments.

This work motivated us to perform ab–initio calculations for transition metal impurities in alkali metals [2]. Based on the local density approximation the calculations partly apply the KKR–Green's function method, partly they adopt the more simpler jellium model. The electronic structure of all 3d and 4d impurities in all monovalent metals has been considered. For the 3d impurities very strong local moments are obtained, being practically saturated. Even the impurities at the beginning and end of the transition metal series, i.e. Sc and Ni, become magnetic in the heavier alkali metals. 4d impurities show nearly the same strong magnetic tendencies as 3d ones. For instance, Mo has in K, Rb and Cs a local moment of about 5 μ_B. Of all 3d and 4d impurities only Pd remains non-magnetic since it approaches the atomic d^{10} configuration. The impurities with large d–moments even develop sizeable s–moments, as it naturally occurs for the atoms.

To our surprise we found that 5d impurities which up to now have not been experimentally investigated, show a similar strong magnetic behaviour as 4d ones [3]. For instance, Ta or W impurities should have local moments of 4–5 μ_B in the heavier metals. Even more, the calculations show that 2sp impurities like B, C or N might be magnetic in these exotic hosts. In a recent paper [4] we have extended these calculation to the divalent alkali–earth metals. The results are dominated by the large elementary volumes of the earth alkali metals and are similar to the above results for the alkali metals.

While the above calculations represent an important progress in understanding the magnetic properties of these exotic systems there are two problems which require substantial future work. Because of the large size difference between the impurity and the alkali hosts, one expects very large lattice relaxations, which are neglected in the present calculations. The second and even more important problem concerns the occurence of ionic configurations with atomic orbital moments which cannot be described in local density functional theory. I. Solovyev and one of the authors have therefore studied this problem within the LDA+U approach [5], based on a realistic calculation of the Hubbard U and exchange parameters. While we do not want to discuss this work in detail, it is fair to say that the LDA+U approach describes the localized configurations quite well, but with the calculated U–parameters it fails to describe the transition between itinerant and localized behaviour.

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The Screened Korringa-Kohn-Rostoker (KKR) Method

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During the last decade, density-functional electronic-structure calculations have very substantially advanced the ability to understand and predict material properties from quantum-mechanical first principles. This progress can be attributed to the availability of powerful modern computers, but also to a large extent to the development of efficient numerical algorithms. A recent achievement in this respect is the discovery and development of the screened KKR method.

The use of screened structure constants is the main difference and advantage compared to the conventional, well-established method of Korringa, Kohn and Rostoker where the

structure constants are complicated and difficult to obtain. Originally a phenomenological prescription for the screening was suggested and applied with success for surface electronic-structure calculations [1]. Afterwards it was demonstrated that the screening can be obtained by an exact transformation. Physically the screened structure constants can be understood as representing the Green function of a periodic system of strongly repulsive (e.g. square well) potentials. For low energies this Green function decreases exponentially in space and can easily be calculated for a finite cluster of repulsive potentials [2]. This gives a reformulation of the original KKR method into a first-principles tight-binding like form. The screening is most effective in the important energy range of the occupied electronic states. With respect to the spectroscopically important unoccupied states, recent tests have shown that even the empty-space density of states can accurately be obtained up to, at least, 40 eV where the extended states represent a severe test for any tight-binding like description.

From computational point of view, the method is well suited for large systems. It does not require eigenvalue determinations, but only matrix inversions for which efficient algorithms exist on sequential as well as on parallel computers. Due to the exponential decay of the structure constants, interactions beyond next-nearest-neighbor distances can be neglected which results in sparse matrices. For general three-dimensional problems the best algorithms must still be found, but clearly the computing effort increases more slowly with system size than in conventional methods where it grows with the cube of the number of electrons involved.

For surface and interface calculations the sparsity is straightforwardly exploited and leads to computing times which increase only linearly with system size, i.e. with the number of layers taken into account. Current applications include first-principles calculations of magnetic anisotropies for overlayer and interface problems (in Vienna) and the development of computer programs for interlayer exchange couplings (in Jülich) and for giant magneto resistance (in Dresden).

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Magneto-optical properties of magnetically ordered solids

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The dependence of optical properties of a solid on the polarization of light is a well-known phenomenon. Using the dielectric or, equivalently, the optical conductivity tensor to describe the optical response, this property can be traced back to its crystallographic structure, i.e. its symmetry. Loosely speaking, the lower the symmetry the more pronounced is the polarization dependence of the optical response in the solid. From this it is not astonishing that reducing the symmetry by imposing magnetic ordering on a solid gives rise to a dependence of the optical properties on the magnetic ordering, i.e. to magneto-optical effects. As for the crystallographically induced effects studying magneto-optical properties gives insight into the various microscopic consequences of magnetic ordering. In addition one can go the opposite way and control the optical properties by controlling the magnetic properties. These are the main reasons that magneto-optical effects are of such a great academic as well as industrial interest at the moment. The most prominent example for the latter is the magneto-optical Kerr-effect that has been known for more than 100 years. The Kerr-effect denotes the fact that light reflected by a magnetized sample changes its polarization upon reflection. This is made use of in data-storage and sensor technology or as an analytical tool to study surface magnetism.

Since the mentioned symmetry reduction has an impact only because of the spin-orbit coupling the theoretical description of magneto-optical effects has to account for magnetic ordering as well as relativistic effects at the same time. The approach to deal with this complex and challenging situation adopted by the collaborating groups in Bremen (Banhart), Bristol (Györffy), Budapest (Szunyogh), Daresbury (Durham, Guo, Temmerman), Keele (Strange), Munich (Ebert) and Wien (Weinberger), is based on the fully relativistic Dirac formalism for spin–polarized systems. During the last years corresponding band structure program packages have been developed, extended and refined using the conventional $\mathbf{k}$–space as well as the more flexible multiple scattering formalism. Beside the magneto–optical Kerr–effect in the optical regime many new kind of spectroscopies in the X–ray regime have been studied using these codes. Here one has to mention the magnetic X–ray dichroism in absorption and emission, as well as the Faraday–effect in the X–ray regime. Recently corresponding studies of magnetic X–ray scattering have been performed. Application of the fully relativistic approach in combination with the Kubo–Greenwood–formalism gave access to the spontaneous magneto–resistance anisotropy and

anomalous Hall resistivity. These galvano–magnetic effects are both of great importance for sensor technology. A further recent extension of the fully relativistic formalism allowed for a description of magnetic dichroism in core level and valence band photo-emission spectroscopy. A corresponding project to deal with this phenomenon in Auger electron spectroscopy was started last year.

Several of the above mentioned investigations pointed to a short-coming of the common theoretical basis: there is no feed-back of the spin-orbit induced electronic currents to the effective potentials. A way to overcome this problem meant to incorporate Brooks' orbital polarization approach into the multiple scattering formalism, which has recently been developed and successfully applied. A more satisfying way to achieve this would be to adopt current density functional theory. This route is explored at the moment in collaboration with Gross (Würzburg).

Finally one should emphasize that nearly all work mentioned above has been performed in close connection or collaboration with experimental groups. This is (at least partly) documented by the proceedings of a workshop on *Spin-Orbit Influenced Spectroscopies of Magnetic Solids* (published as Volume 466, in the Series "Lecture Notes in Physics", Eds.: H. Ebert and G. Schütz, Springer-Verlag, Berlin, 1996), that was attended to the same extent by theoretical and experimental workers in that field.

Magnetism of Transition–Metal Monolayers on Noble Metal Substrates

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It is well known that almost all transition metals are nonmagnetic in their bulk phases. Among the 30 different transition metals only five are magnetic in the bulk: Ni and Co are ferromagnetic, Cr is antiferromagnetic, and Mn and Fe, depending on their bulk crystal structures, are ferromagnetic or antiferromagnetic. On the other hand, all isolated transition metal atoms show large magnetic moments which are governed by Hund's first rule. From this one may expect magnetic properties to depend drastically on the dimensionality or coordination number of the arrangement of transition metal atoms. Confining the atomic arrangement of transition metal atoms to monolayer films may lead to an enhancement of the magnetic moments within the monolayer and to new magnetic monolayers, made of transition metals, which are nonmagnetic in the bulk. Monolayer magnetism has

been investigated experimentally in terms of transition metal monolayers on noble metal substrates, such as Ag, where the d bands lie about 3 eV below the Fermi energy and the d–d hybridization between a monolayer and the substrate is small.

Motivated by these arguments we have performed systematic *ab–initio* calculations for all $3d$, $4d$, and $5d$ transition metal monolayers on Ag(100) [1]. The calculations have been carried out using the FLAPW method in the film geometry within the density functional theory in the local spin-density approximation. They have revealed that practically all $3d$ monolayers are magnetic, even Ti and V, which are nonmagnetic in the bulk. The distribution of the magnitudes of the magnetic moments has turned out to be atomic–like with the maximum magnetic moment of about 4 μ_B at the center of the transition metal series (e.g. Mn in the $3d$ metal series).

To our great surprise we have also found magnetism in Tc, Ru, and Rh among the $4d$ metals, and Os and Ir among the $5d$ metals, associated with large magnetic moments between 1 μ_B and 2 μ_B. A closer look has revealed a strong deviation from simple atomic–like magnetism: The element with the largest moment among the $3d$, $4d$, and $5d$ monolayers has been shifted from Mn through Ru (isoelectronic to Fe) to Ir (isoelectronic to Co), respectively, while moving from $3d$, through $4d$ to $5d$ metals. We have argued that this deviation resulted from a two-dimensional bandstructure effect causing the magnetism of $4d$ and $5d$ monolayers to be strongly dependent on the coordination number of the film.

We have investigated this aspect further by repeating the above calculations for $3d$, $4d$, and $5d$ transition metal monolayers, but on a Ag(111) surface [2,3]. A comparison between (100) and (111) orientations has elucidated the dependence of monolayer magnetism on a change of coordination number from 4 to 6 within the monolayer plane. The calculations for the (111) substrate have exhibited the same trend for the magnetic moments as has been found for the (100) substrate. Magnetism has been found for all $3d$ monolayers, for Ru and Rh among the $4d$ metals, and for Ir among the $5d$ metals. The element with the largest magnetic moment among each series has remained unchanged, but for $4d$ and $5d$ metals the size of the magnetic moments has changed drastically with the change of the coordination number: The reduction of the magnetic moment of Ir (85%, 5d element) has been larger than for Ru (30%, 4d element), while the magnetic moment of Mn (3d element) remained practically unchanged.

The calculations for (111) oriented substrates have been possible due to the development of a new FLAPW film code which is capable to treat any surface unit cell, and which does not make any explicit use of two(three)-dimensional inversion symmetry. However, despite this apparent progress, two questions remain unanswered and require future work: (i) For $4d$ and $5d$ transition metals one expects large spin-orbit interactions, which have

been neglected in the present calculations. The large spin-orbit interaction may lead to a large magneto-crystalline anisotropy and a modification of the local moments [4]. (ii) For 3d monolayers on a (111) oriented substrate one also expects antiferromagnetic coupling of nearest neighbour atoms, leading to non-collinear magnetic phases.

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Theory of Pressure Induced Phase Transitions in the Cerium Pnictides

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The Cerium Pnictides CeN, CeP, CeAs, CeSb and CeBi have peculiar properties as a function of applied hydrostatic pressure. At ambient conditions they all crystallize in the rocksalt (B1) crystal structure. With the exception of CeN the lattice constants indicate a trivalent nature of the Ce ions, corresponding to a configuration with one localized f-electron on each Ce atom. This is corroborated by the Curie-Weiss type susceptibility observed at elevated temperatures. In contrast, CeN is closer to a tetravalent Ce configuration corresponding to itinerant f-electrons and behaves as a Pauli enhanced paramagnet. Thus, CeN is similar to the collapsed α phase of pure cerium, where the cerium f-electron contributes actively to the cohesive properties, while the other Ce pnictides at ambient conditions are more similar to the γ phase of cerium. When pressure is applied, discontinuous structural phase transitions occur in all the cerium pnictides, with the exception of CeN. In CeP a peculiar *isostructural* transition is observed at a pressure of $P_1 \sim 90$ kbar accompanied by a volume collapse of $\Delta V_1 \sim 3\%$. This transition is similar in appearance to the isostructural $\alpha \leftrightarrow \gamma$ phase transition in cerium metal,

and is usually attributed to a change from (predominantly) trivalent to (predominantly) tetravalent behavior of the cerium ions. At a higher pressure of $P_2 \sim 150$ kbar a second transition to the CsCl (B2) structure is observed, with a volume collapse of $\Delta V_2 \sim 10\%$. In CeAs, a single B1→B2 phase transition occurs at a pressure of $P \sim 145$ kbar with a volume collapse of $\Delta V \sim 11\%$. While some authors have claimed that no substantial change in Ce valency occurs at the transition, others conclude a significant change. In CeSb and CeBi a high pressure tetragonal phase is observed, at $P \sim 85$ kbar and $P \sim 90$ kbar, respectively, with volume collapses of $\Delta V \sim 11\%$ and $\Delta V \sim 9\%$, respectively. The tetragonal phase may be viewed as a uniaxial compression of the CsCl structure with a c/a ratio of 0.82 in CeSb and 0.84 in CeBi. In both cases the Ce ions are considered to remain trivalent across the phase transition.

In the present work a systematic theoretical investigation of the Ce pnictides has been undertaken. The electronic structure of the cerium pnictides was calculated with the self-interaction corrected local-spin density (SIC-LSD) approximation implemented with the LMTO method. This scheme offers the possibility of describing the Ce f-electrons as either localized or delocalized. By comparing calculations in different structures and different treatments of the f-electrons, all the phase transitions observed in the cerium pnictides are reproduced with excellent quantitative agreement, as demonstrated in Table I. The present calculations find the CeAs high pressure phase to be described with delocalized f-electrons. The isostructural B1(loc)→B1(deloc) transition is only barely missed, but the calculations do not offer a possibilty of a B1(loc)→B2(loc) transition.

The observed trends in the crystal structures of the cerium pnictides can be explained in a simple way: With increasing Z of the ligand, the specific volume (at zero pressure) increases while the ionicity of the compound decreases. The delocalization of Ce f-electrons is less favorable at large specific volumes (since interatomic hopping matrix elements are small), while the CsCl structure is favored over the NaCl structure with decreasing ionicity. The tetragonal structure observed at high pressure in CeSb and CeBi is almost degenerate with the undistorted CsCl structure.

The magnetic properties of the cerium pnictides are quite complicated with several antiferromagnetically ordered phases and phase transitions at low temperatures. The resistivities of the CeP, CeAS, CeSb and CeBi systems show semimetallic or small–gap semiconductive characteristics at ambient conditions. A negative slope of the resistivity as a function of temperatures indicates that Kondo type screening occurs in the ground state of the cerium pnictides. Calculations with the SIC-LSD method for CeP in the AFI structure confirm this semimetallic behaviour.

The exact ground states of the cerium pnictides are bound to be much more complicated

Compound	Character	P_t/kbar		$\Delta V/V_0$	
		exp.	theo.	exp.	theo.
CeP	B1(loc)→B1(deloc)	90	71	3%	8%
CeP	B1(deloc)→B2(deloc)	150	113	10%	12%
CeAs	B1(loc)→B2(deloc)	145	114	11%	18%
CeSb	B1(loc)→tet(loc)	85	70	10%	11%
CeSb	tet(loc)→tet(deloc)	-	250	-	4%
CeBi	B1(loc)→tet(loc)	90	88	9%	9%

Table 1: Experimental and theoretical phase transition pressures and volume collapses in the cerium pnictides.

than the simple picture offered by the SIC-LSD method, which still, like the LDA, describes the system in terms of a single Slater determinant. The good agreement between the SIC-LSD theory and experiments shows, however, that the method is accurate enough to reproduce the cohesive properties of correlated electron materials. In particular, the energy of localization, which in the SIC-LSD is given as the self-interaction correction of the localized f-electron, has the correct magnitude. In CeP this energy is ~ -65 mRy, which is countered by the 'band-formation energy' to produce the delicate balance between the trivalent and tetravalent configurations. It remains a challenge for the coming years to extend the accuracy of the present calculational scheme and to augment the formalism in such a way that other physical properties may be considered, like e.g. photoemission experiments.

Rennes[1] - Zürich[2] collaboration on the electronic and dynamical properties of molecular charge-transfer compounds

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P. E. Blöchl *(IBM Zürich, Switzerland)*[2]

Charge transfer salts exhibit a dazzling variety of different structural and electronic phase transition. Members of this class are superconductors, ferroelectrics, antiferro- and ferrimagnets, and exhibit Peierls and neutral to ionic transitions. Close to the transition spin and charge solitons have been observed. The transitions can be driven by pressure, temperature, photoirradiation etc. Charge transfer salts are molecular crystals with typicaly two types of large organic molecules assembled in low dimensional structures. Thus

they exhibit features ranging from zero to three dimensions. These structures are an ideal ground for fundamental studies, which may help in the understanding of other low dimensional and correlated materials.

Despite active research over several decades, a detailed microscopic understanding of these materials is still elusive. The structural complexity has prohibited accurate first-principles calculations in the past. Only recently this situation changed owing to new simulation techniques such as the Projector Augmented Wave method developed at the IBM Zürich Research Laboratory.

In our quest to obtaining a global understanding of these materials and their transitions, we have selected the prototypical material for neutral to ionic transitions, namely tetrathiafulvalene-chloranil or short TTF-CA. So far we have studied the vibrational spectra depending on charge state of chloranil in order to make contact with experiments that deduce the ionicity of the crystal from the measured i.r. and Raman spectra. This work will soon be published in Physical Review. Currently we are proceeding to deriving the parameters that are essential for the transition. We have so far evaluated ionization energies and electron affinities, the intra– and inter–molecular Coulomb interaction, spin splitting parameter, hopping integrals and as of writing this article we are in the process to extract the relevant phonon interactions. Once the model is completed, it will allow us to *derive* a consistent description, from which the complex nonlinear exitations and phase transitions can be simulated and elucidated.

The expertise gained in this study is expected to be useful to understand materials of technological interest such as organic magnets, superconductors, and dyes, conducting polymers and materials for light emmitting diodes.

This collaboration has been initiated in 1994, by a joint project between IBM-Zürich and the University of Rennes, and has been partially funded by the Psik-network. This project has started with the training of C. Katan (young researcher in Rennes) in the CP-PAW method, to reach a perfect knowledge of all the possibilities of the code. During the course of this collaboration, C. Katan spent in total 2.5 months at IBM-Zürich research Laboratory.

Highlights of the collaboration between T.U. Vienna and IBM Zurich Research Laboratory

Adsorption of water and methanol in zeolites

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Zeolites are microporous aluminasilicates, which are important catalysts in petrochemistry used for cracking and the production of fine chemicals. The catalytic function of zeolites rests with steric hindrance inside the pores and cages with catalytic centers distributed over the internal surface of zeolites. The most common catalytic centers are acid sites, namely AlOH fragments, which replace a SiO fragment of the framework. Despite the critical importance of the interaction of polar molecules with acid site centers for the catalytic reactions, the adsorption properties of even simple molecules such as water and methanol have not yet been resolved.

The most direct experimental information is available through ir spectroscopy. However, owing to the unusual bonding arrangements in zeolites, the interpretation of these results depends largely on their comparison with theoretical calculations. Previous quantum chemical calculations have been limited to small clusters and the inability to investigate finite temperature behavior, and hence have been unable to reproduce the experimental spectra.

Therefore, we have performed finite-temperature simulations of methanol and water in a zeolite called sodalite at low and high coverages (E. Nusterer, P.E. Blöchl and K. Schwarz, Angew. Chem. 1996 in press). Our approach, the projector augmented wave method combined with the ab-initio molecular dynamics scheme of Car and Parrinello, allows periodic zeolite crystals to be studied and provides access to finite-temperature dynamics. Simulations of methanol at low coverages, i.e. one methanol molecule for every second cage of sodalite, have been performed for 20 psec. The calculations reproduce all main features related to hydrogen bonds observed by experiment, but also provide us with a microscopic picture of the structure and dynamics. We observed that methanol forms one very strong hydrogen bond with the acid site, whereas a second hydrogen bond can exchange between several hydrogen bond acceptors of the framework. One of the two types of structures observed has not yet been proposed because it involves framework oxygen atoms that are too distant to have been included in previous quantum chemical calculations.

At high coverages, however, the picture changes qualitatively (E. Nusterer, P.E. Blöchl and K. Schwarz, submitted to Chem. Phys. Lett.) Although no protonation of wa-

ter and methanol have been observed when only one methanol was adsorbed per acid site, two molecules already result in almost perfect protonation and in the formation of hydroxonium-like structure adsorbed via hydrogen bonds to the zeolite framework. This finding has important consequences on the catalytic reactions in zeolites: reactions typically performed at larger coverages therefore qualitatively resemble those in a similar acid-catalyzed reaction in the liquid, except for a dramatically increased proton concentration. The structural changes upon increasing coverage is reflected in a qualitative change of the measured adsorption spectra, which are well reproduced by our simulations.

Not only are the changes of the spectra upon increasing partial pressure well reproduced, but also selective deuteration experiments are in line with our predictions, lending strong support to our model of the adsorption of small polar molecules in zeolites.

Structure and vibrational properties of metallocenes

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In preparation of investigations of catalytic reactions using transition metalorganic complexes we have investigated structural and dynamical studies of metallocenes such as ferrocene (P. Margl, K. Schwarz and P.E. Blöchl, J. Chem. Phys. 100, 8194 (1994)) and beryllocene (P. Margl, K. Schwarz and P.E. Blöchl, J. Am. Chem. Soc. 116, 11177 (1994), *ibid* J. Chem. Phys. 103, 683 (1995). Ferrocene is a sandwich compound with an Fe(II) ion sandwiched between two aromatic cyclopentadienyl rings $C_5H_5^-$. This molecule is a classical test system and has been studied extensively using quantum chemical methods because its bonding is severely influenced by electronic correlations not present in the Hartree–Fock approach. On the other hand its size is small enough to allow accurate correlated methods to be applied. The trajectories from finite temperature simulations have been analyzed to obtain the vibrational modes and frequencies using an approach inspired by previous work of Kohanoff and Parrinello. A comparison reveals deviations of the order of a few percent in the vibrational spectrum. Furthermore our work has resulted in a reassignment of the experimental absorption spectra. The dynamical properties of a related molecule, which in contrast to the rather stable ferrocene shows fluxional behavior, have been elucidated with the present approach. Thus we have successfully tested the Car–Parrinello projector augmented wave method for two limiting cases of organometallic behavior.

These calculations have opened the door for investigations of organometallic catalytic reaction mechanisms performed to date. They include the enantioselective allylic amination using Pd(II) catalysts with bidentate P-N,ferrocenyl ligands (P.E. Blöchl and A. Togni,

submitted to J. Am. Chem. Soc.), polymerization reactions using zirconocene catalysts (P. Margl, J.C.W. Lohrenz, T. Ziegler and P.E. Blöchl, submitted to J. Am. Chem. Soc.) and to carbonylation of methane using an Rh catalyst (P. Margl, T. Ziegler and P.E. Blöchl, J. Am. Chem. Soc. 117, 12625 (1995), *ibid* submitted).

About the collaboration between T.U. Vienna and IBM Zurich Research Laboratory

The collaboration between the group of Prof. K. Schwarz at the Technical University of Vienna and Dr. P.E. Blöchl at the IBM Zurich Research Laboratory has been very active. This has included regular, extended visits of Ph.D. students of Prof. K. Schwarz, namely E. Nusterer, P. Margl and J. Sarnthein, in Zurich, one extended stay of P.E. Blöchl at the Technical University of Vienna, and several short visits of the project coordinators.