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Rolled-up nanomembrans form an ultra-compact energy storage element

Born-Oppenheimer molecular dynamics trajectory of TiSc$_2$N@C$_{80}$

Lorentz trajectories of the conduction electrons in real space for large mean free paths

Cross-section of a MgB$_2$ superconducting wire with Nb-sheathed filaments
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Superconductivity without nesting in LiFeAs iron pnictide
S.V. Borisenko, V. B. Zabolotnyy, D. V. Evtushinsky, T. K. Kim, I. V. Morozov, A. A. Kordyuk, G. Behr, B. Büchner

The particular shape of the Fermi surface can give rise to a number of collective quantum phenomena in solids, such as density wave orderings or even superconductivity. In many new iron superconductors this shape, the “nested” Fermi surface, is indeed observed, but its role in the formation of spin-density waves or superconductivity is not clear. We have studied the electronic structure of the non-magnetic LiFeAs ($T_c \sim 18$ K) superconductor using angle-resolved photoemission spectroscopy. We find a notable absence of the Fermi surface nesting, strong renormalization of the conduction bands by a factor of three, high density of states at the Fermi level caused by a Van Hove singularity, and no evidence for either a static or fluctuating order except superconductivity with in-plane isotropic energy gaps. Our observations set a new hierarchy of the electronic properties necessary for the superconductivity in iron pnictides and, possibly, in other materials.

The synthesis of another iron superconductor immediately attracted a considerable attention already for several reasons [1-3]. LiFeAs is one of the few superconductors which do not require additional charge carriers and has a considerable $T_c$ approaching the boiling point of hydrogen. Similar to $\text{AeFe}_2\text{As}_2$ (122) and $\text{LnOFeAs}$ (1111) parent compounds, LiFeAs consists of nearly identical ($\text{Fe}_2\text{As}_2)^2$ structural units and all three are isoelectronic, though the former do not superconduct. The band structure calculations unanimously yield the same shapes of the Fermi surfaces (FS), very similar densities of states and low energy electronic dispersions [4, 5] and even find in LiFeAs an energetically favorable magnetic solution which exactly corresponds to the famous stripe-like antiferromagnetic order in 122 and 1111 systems [5-7], though the experiments show rather different picture. The structural transition peculiar to 122 and 1111 families is remarkably absent in LiFeAs and is not observed under applied pressure of up to 20 GPa [8, 9]. Resistivity and susceptibility as well as $\mu$-spin rotation experiments show no evidence for the magnetic transition [10, 11]. The basic question is therefore why the isoelectronic and nearly isostructural FeAs blocks induce fundamentally different physical properties of the material? We show that this happens due to the important distinctions of the electronic structure and single out those which seem to be indispensable for the superconductivity to occur.

In Fig.1a we show the FS map of LiFeAs which is the momentum distribution of the photoemission intensity integrated within 5 meV around the Fermi level. Three clear features are visible on the map: a high-intensity butterfly-like shape at the $\Gamma$-point, a well defined barrel-like FS also centred at $\Gamma$, and a double-walled structure with somewhat obscure contours around M-point. Momentum-energy cuts along the selected directions passing near M and $\Gamma$ points and marked in panel a) by dashed lines are presented in Fig.1b and Fig.1c. While both dispersive features in Fig.1b as well as the left-most one in Fig.1c clearly cross the Fermi level thus supporting a double-walled electron-like FS around M and large hole-like FS around $\Gamma$ respectively, the other two features from Fig.1c only come close to the Fermi level without clear crossing, at least for the given cut through the momentum space. We have found that for certain excitation energies these features do cross the Fermi level resulting in very small hole-like FSs thus completing the analogy with the FS topology of 122 and 1111 systems: there are in total five FSs supported by five bands. The sketch in Fig.1a schematically shows all FS features centered in one point to facilitate the comparison of their sizes. The striking peculiarity of this FS shape is the absolute absence of the ($\pi$, $\pi$)-nesting peculiar to other pnictides.

Fig. 1: Fermi surface shape and topology. a) Momentum distribution map of the photoemission intensity integrated within 5 meV around the Fermi level. Solid black lines represent $\Gamma$-centered Fermi contours, black dashed lines – most pronounced M-centered Fermi contours. b, c) Momentum-energy cuts along the vertical directions marked by the white dashed lines in panel a).
According to the band structure calculations the FS of LiFeAs also consists of three hole-like FSs around the $\Gamma$-point and two electron-like ones at the corner of the Brillouin zone. In Fig. 2 we compare directly the calculated band structure and experimental data along the high-symmetry directions. We made a tight-binding fit to the best defined experimental band which supports the large $\Gamma$-barrel and found a remarkable qualitative agreement with the $d_{x^2-y^2}$ originated band from the LDA calculations. The ratio of the bandwidths turned out to be equal to 3.1 (1 eV vs. 0.326 eV). We then applied this renormalization factor to bring the experimental data and the calculated bands to the same energy scale. Overall agreement is very reasonable, taking into account that we have identified all bands in the vicinity of the Fermi level and associated them with the corresponding features in the ARPES spectra. Note that the electron-like pocket at M formed by another band is satisfactorily reproduced as well. As seen from the figure and confirmed by the calculations, a selective shift of the $d_{x^2-y^2}$ band (red curve in Fig. 2) by 150 meV with respect to the others perfectly reproduces the shape of the experimental Fermi surface and dispersion over the whole bandwidth. This agreement together with the extremely low temperatures at which we carried out our experiments clearly speaks in favor of a non-magnetic ground state realized in LiFeAs. This is supported by the fact that having explored the large portions of the k-space at different experimental conditions, we have not found any typical spectroscopic signatures of commensurate or incommensurate ordering appearing in a form of replica due to Fermi surface reconstruction or suppressed spectral weight due to gap, etc. [12, 13]. What is not captured by the LDA approach, which predicts magnetism in LiFeAs [5, 6], are the actual absence of nesting and renormalization by the factor of $\sim 3$. The energy gain from the opening of the gaps at or near the Fermi level due to the FS reconstruction is obviously more significant in a system with 3 times narrower bandwidth. That is probably why the SDW order does not disappear immediately upon doping in 122 and 1111 families of Fe-pnictides. In LiFeAs, where the $(\pi, \pi)$-nesting is absent, static magnetism disappears completely. Our results thus strongly imply the decisive role of nesting in the formation of SDW.

The apparent absence of the magnetism in LiFeAs seems to be not crucial for the superconductivity. We have clearly observed the opening of the superconducting gap in all $k_F$ points with the onset at the nominal $T_c$ of $\sim 18$ K. A typical example is presented in Fig. 3a where the crossing of the FS at point A is shown for two temperatures, above and below the transition. Upon entering the superconducting state, the usual BCS-like bending back of the dispersive feature is apparently seen in the lower panel. This is accompanied by the depletion of the spectral weight at the Fermi level due to the FS reconstruction is obviously more significant in a system with 3 times narrower bandwidth. That is probably why the SDW order does not disappear immediately upon doping in 122 and 1111 families of Fe-pnictides. In LiFeAs, where the $(\pi, \pi)$-nesting is absent, static magnetism disappears completely. Our results thus strongly imply the decisive role of nesting in the formation of SDW.

**Fig. 2:** High-symmetry momentum-energy cuts together with the results of the band structure calculations. Blue, green and red curves are the bands supporting the $\Gamma$-centred FSs. Yellow curves – the bands responsible for the electron-like FSs. Black curves – the bands which do not cross the Fermi level. Photon energy is 120 eV for the middle panel and 70 eV for the left and right panels.

**Fig. 3:** Superconductivity in LiFeAs. a) Fermi surface crossings of the largest hole-like FS (see Fig. 1c) taken above and below $T_c$ ($\sim 18$K). b) Energy distribution curves from panels a) corresponding to the $k_F$. c) Energy distribution curves corresponding to Fermi momenta on the largest hole-like electron-like FS measured above (20 K) and below (900 mK) $T_c$. 

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Disregarding for a moment any relation to other families of Fe-pnictides and thus possible presence of the so far not detected spin fluctuations capable of binding electrons in pairs [14], one may ask why a stoichiometric, nonmagnetic compound with a plane crystal structure is a multiband superconductor with considerable critical temperature and weakly in-plane anisotropic order parameter? The only remarkable property of the electronic structure of LiFeAs which makes it so special and intimately connects it to other superconductors like NbSe₂, A15 compounds, MgB₂ and the cuprates is the proximity of the Van Hove singularity to the Fermi level.

In Fig. 4 we suggest a very simple scenario which emphasizes the role of nesting for density wave orders and van Hove singularities for the superconductivity in pnictides and 2H-NbSe₂. In the parent compounds and in 2H-TaSe₂ the presence of the nesting reconstructs the original Fermi surface and induces the static density wave order resulting in the absence of the superconductivity (or its strong suppression). By doping the holes into the parent pnictide (or substituting Ta by Nb) we destroy the nesting and approach the bottoms of the electronlike bands (or saddle point in 2H-NbSe₂) thus bringing high density of states to the Fermi level. As a consequence, the density wave order is strongly suppressed and superconductivity occurs. The same holds for the electron-doped side of the phase diagram. Now the tops of the holelike bands show up at the Fermi level. In this sense LiFeAs appears to be similar to electron-doped pnictides since in this case the top of the holelike band coincides with the Fermi level already in the pristine compound.

The example of LiFeAs suggests that the intriguing presence of the density waves or their fluctuations in many families of the superconductors may turn out to be rather “technical”: they neighbour the superconductivity only because, purely from the topological considerations, the nesting is very probable to occur when tuning the system from one Van Hove instability to another by doping in multiband superconductors (see Fig. 4). On the other hand, the non-perfect nesting corresponding to the fading density wave order may result in still larger density of states at the Fermi level thus promoting the superconductivity [15]. However, in view of our present results, the Van Hove singularity close to the Fermi level seems to be a necessary condition for the onset of superconductivity, and not only in the pnictides [16].


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Coherent interfacial bonding on the FeAs tetrahedron in epitaxial Fe/Ba-122 bilayers


The production of thin films from the newly-discovered iron-based superconductors is critical to their assessment for applications and the investigation of their fundamental properties. A detailed microstructural investigation of Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ thin films fabricated at the IFW suggested that one way to achieve high quality films is through the use of an intermediate iron buffer layer. Films based on this new layer architecture, dubbed “Fe/Ba-122 bilayers,” exhibit excellent crystalline and electrical transport properties and additionally open up the route for novel thin film devices potentially suitable for all iron-based superconductors.

Essential to the understanding of key fundamental properties in the newly discovered iron-based superconductors and critical to their assessment for applications and devices is their fabrication into very high quality thin films. Thin films of the Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ phase – discovered by Sefat et al. [1] and commonly referred to as “Ba-122” – are particularly interesting since this compound appears to be resilient against oxidation and degradation due to water vapor [2], it is considerably easier to deposit compared to other iron-based superconductors, and it has a relatively high critical temperature. The search for optimal thin film growth parameters for this compound is currently the subject of a number of international research groups [2–11]. However, difficulties overcoming the poor metal/oxide bond at the interface of many substrates has necessitated the need for significant optimization of the deposition parameters [9,10] as well as the use of various intermediate layers [8] to produce well-textured films. In spite of these efforts, nearly all of these films contain an unintentional amorphous or iron-containing layer at the interface. While the nature of this interface is not yet fully understood, the disruption of local crystallographic ordering associated with it precludes the use of these films for interface-sensitive applications such as multilayers or heterostructures where coherent and chemically inert phase boundaries are required. Moreover, it may be responsible for the challenging growth of epitaxial Ba(Fe$_{1-x}$Co$_x$)$_2$As$_2$ (Ba–122) films in general [7,9] as well as the generation of pinning-active columnar defects observed to originate at this interface in some films [8].

At the IFW, a detailed investigation into the nature of this interface was initiated using the FEI Titan^3 300 kV Cs-corrected transmission electron microscope (TEM) available in-house. This microscope has a point resolution under 1 Å and provides access to a number of high resolution spectroscopic techniques. For Ba-122 deposited on top of bare (La,Sr)(Al,Ta)O$_3$ (LSAT) substrates, it was observed that significant amounts of textured body-centered cubic iron precipitate out at the substrate/film interface [9]. The formation of these iron regions is enabled by the interdiffusion of atomic species between the Ba-122 phase and the oxide substrate, thereby leading to the aforementioned localized

Fig. 1: Schematic model demonstrating that the mismatch between the (001) surface plane of bcc iron (left) and the iron sublayer in the Co-doped Ba–122 unit cell (right) is about 2%. Atomic radii are not to scale.
crystallographic disturbance. Furthermore, it was noted that the orientation of these textured iron regions is rotated 45° in-plane to both the substrate and the Ba–122 phase, providing a plausible explanation for the presence of an Fe (002) reflection in x-ray diffraction (XRD) patterns in nearly all Ba-122 films. In this orientation, the (001) surface plane of iron has an approximately 2% lattice mismatch with the square-planar iron sublayer defining the FeAs tetrahedron in the Ba–122 unit cell and thus offers a natural location for coherent interfacial bonding (Fig. 1).

One way to prevent the detrimental interspecies diffusion at the substrate interface is to preemptively deposit textured iron directly on the substrate prior to the deposition of the Ba-122 phase. Since the Fe/Ba-122 bond appears to be more stable than the oxide/Ba-122 bond, the resulting interface should be highly coherent and chemically stable. This new architecture has been dubbed “Fe/Ba-122 bilayers.”

Thin layers of textured iron were grown on a number of substrates by our group, as presented in Fig. 2. On each of them, when the iron layer grows in a textured manner, the subsequent epitaxial growth of the Ba-122 phase was observed. The crystalline quality of the Ba-122 phase was of very high quality, exhibiting a sharp texture while retaining good superconducting properties. The presence of a stray texture component in the bilayer grown on the LSAT substrate is due to the growth of iron islands; in every case where an iron (001) facet grew parallel to the LSAT surface, textured Ba-122 was observed. Perhaps the most important criterion for high quality growth of thin films is the amount of current they are capable of transporting – known as the critical current density $J_c$ – particularly when an external magnetic field is applied. The bilayers on MgO exhibit $J_c$ values among the highest reported to date in thin films [8, 11, 13]. More significantly, however, is the lack of $J_c$ enhancement when the external magnetic field is applied parallel to the Ba-122 c-axis, as depicted in Fig. 3. This indicates that Ba-122 films grown in this manner do not have pinning-active correlated defects oriented along this direction, contrasting the results of other groups [8, 11]. Accordingly, these films can be considered suitable for a number of fundamental investigations where the intrinsic anisotropy of the Ba-122 phase is to be probed.

Controlled bilayers of this type lend themselves to an additional investigation of the nature of bonding at the interface. The interface between Fe and Ba–122 was studied using the microscope described above. Figure 4a shows a high resolution scanning transmission electron microscopy (HRSTEM) image obtained with a high angle annular dark field detector. Directly below, higher-resolution data obtained from a different sample region are presented. This image shows a mass-thickness contrast, meaning that atomic columns appear as bright dots. Hence, the location of individual atoms within their unit cell can be elucidated, as indicated in the lower portion of Fig. 4 through the use of artificial colors and a schematic model. The Ba–122 phase is observed to terminate on the upper As sublayer of the FeAs tetrahedron. As an independent confirmation of this analysis, high resolution TEM (HRTEM) was undertaken on a separate sample region and is presented in Fig. 4b. This focus of this image was adjusted such that the atomic columns also appear as white dots. Below it, the atomic positions are identified in the same manner as previously. Combined with the HRSTEM data in Fig. 4a, these observations constitute compelling evidence that the square-planar iron sublayer in the Ba–122 unit cell is directly replaced by the (001) surface plane of the bcc iron layer resulting in a coherent interfacial bond on the FeAs sublattice [12].

These results have opened up a number of new research directions for thin films of the iron-based superconductors. First, as demonstrated by figures 2 and 3, this architecture represents a means by which Ba-122 thin films with a very strong texture and minimal...
defects can be grown without seriously degrading its superconductive properties [13].
This provides researchers with the first thin films representative of the intrinsic Ba-122 phase without being tainted by defects. Second, the bilayer architecture enables the growth of iron-based superconductors on technical substrates such as hastelloy containing an MgO buffer layer that was deposited with Ion Beam Assisted Deposition (IBAD). Our group has produced the first such samples, and the results are shown in Fig. 5. Such thin film designs allow researchers to investigate the influence a grain boundary network exerts on superconductivity and additionally opens the way for in-situ strain investigations [14]. Finally, since the iron buffer layer bonds directly on the one structural feature common to all iron-based superconductors – the iron arsenic tetrahedron – it is likely that this same architecture will work for other families as well.

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Giant negative domain wall resistance in iron
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A domain wall-related magnetoresistance (MR) effect was discovered that may exceed the established MR-effects (Anisotropic MR, Giant-MR, Lorentz-MR etc.) by orders of magnitude. Phenomenologically it is a negative domain wall resistance (NDWR), caused by the formation of scattering-induced channels for the charge carriers around domain walls that can “shortcut” the Lorentz-MR (LMR) of magnetic domains. This fundamental influence of walls on the electric transport was not considered so far. The discovery was possible by choosing samples that allowed the separation of all superimposed effects by temperature-dependent resistance measurements and domain control. The samples were bulk single-crystalline iron cylinders (2 – 4 cm long, diameter $D \approx 1 – 4$ mm) [1, 2] with different orientations. They were of high purity and lattice perfection, characterized by residual resistance ratios $\text{RRR} = \rho(295 \text{K})/\rho(T \approx 2 \text{K})$ up to 5700, which are the highest values for bulk iron ever published. The domains of the rods were manipulated by small magnetic fields: (i) A circular “self-field” $H_{\text{circ}}$, caused by the (direct) measuring current $J$ along the rods and estimated at the surface to $\mu_0 H_{\text{circ}} = \mu_0 J/\pi D \leq 2 \text{ mT}$, and (ii) an external longitudinal field $\mu_0 H_{\text{long}} \leq 100 \text{ mT}$ along the rod axis ($J$). The domain structure and its field dependence was studied by longitudinal Kerr microscopy [3]. By suspending the rods on a rotation stage the whole surface was accessible. Fields and currents could be applied during imaging. So the resistivity measurements $\Delta \rho(B)$ could be interpreted in terms of the magnetization changes $B = \mu_0 (H+M)$.

In Fig. 1 the field-dependence of resistivity is plotted for the (100)- and (110)-oriented crystals. Reference state is the longitudinally saturated state, the resistance $\rho_{\text{long sat}}(T)$ of which is indicated by lines in Fig. 1a. Removing the saturation field, the resistivity rises (compare the $\rho_{\text{long sat}}(T)$-lines with the $H_{\text{circ}} = 0$ values in Fig. 1a). For increasing $H_{\text{circ}}$, Figs. 1a, b reveal a further resistivity increase — small circular fields of just 2 mT thus cause drastic resistivity changes up to factors of 100 for the (100)- and 30 for the (110)-crystal compared to the reference state (the different factors are primarily due to the different RRR). Superimposing then a longitudinal field of the same order of magnitude, nearly all the giant resistivity increase is canceled (Fig. 1c). An interpretation of these effects requires knowledge of the domains.
Figure 2 shows the domains on the (110)-crystal for some states along the curves in Fig. 1. There are 6 easy crystal directions (Fig. 2a): the [100], [-100] directions, called ±90°-directions (relative to the current axis), and the [010], [0-10], [001] and [00-1] directions called ±45°- and ±135°-directions. In an infinite crystal (which roughly applies to our bulk sample) and at zero external field, 1/3 of the volume is occupied by ±90° domains and 2/3 by ±45° and ±135° domains. The occupancy of the two main axes is visible in Fig. 2b. This relative distribution of domain phase volumes also applies to the zero-field state of Fig. 1a, where the resistance was measured with small current, i.e. at $H_{\text{circ}} < H_{\text{coercive}}$. The resistivity of this multidomain domain state is by a factor of 10 higher than that of the longitudinally saturated state because a substantial transverse LMR is caused by both, the ±90° domains and, to a lower degree, the ±45° and ±135° domains. The ±45°/±135° domains also contribute a longitudinal LMR, which, however, can only play a minor role: Due to their ‘short-cutting’ effect, the longitudinal LMR of these domains should lead to a total resistance in the same order of magnitude as that of the longitudinally saturated state. As this is not observed, we conclude that the transverse LMR of the ±45°/±135° phase volume dominates the resistance at zero-field.

When a circular field of only 2 mT is applied to this multidomain state, the resistivity strongly rises (Fig. 1b), accompanied by a change in the domain structure (Fig. 2c): domains with magnetization components parallel to $H_{\text{circ}}$ grow on expense of antiparallel domains. This leads to a reduction of the wall density at a stable transverse MR situation. The disappearance of domain walls must consequently be responsible for the resistivity rise. A conceivable (though not observed) partial phase transition from ±45° to ±90° domains, which would also lead to an increasing transverse LMR, can only play a marginal role. This fact is supported by the resistivity measurements on (111)-oriented crystals: For such crystals any kind of domain phase rearrangement cannot change the LMR configuration for symmetry reasons (all easy crystal axes have the same absolute angle relative to the current direction). Nevertheless, the resistance change in small magnetic fields (not shown) and the temperature dependence of resistivity have the same characteristics and order of magnitude. Again, there is only the difference in domain wall density left as an interpretation — changes in the longitudinal LMR components can be excluded for (111)-crystals.

If a longitudinal field of 1 mT is added to the circular field, the 180°-walls between the ±45° domains reappear (Fig. 2d) to create a longitudinal $M$-component. The domain phases are thus rearranged: the ±45° (or ±135°) volume is partly replaced by −45°.
(or −135°) volume, whereas the ± 90° phase volume will stay largely unchanged. Again, there is no significant redistribution of the (LMR-relevant) absolute $|90°|$ and $|45°|/|135°|$ phase volumes in the superimposed field. The resistivity, however, drops almost down to that of the longitudinally saturated state (compare Fig. 1b and c)! If the redistribution of 90° and 45°/135° phases would be responsible for this drop, the resistance should only decrease by a factor $[H/11270]2$, but not by (at least) an order of magnitude as measured. Again, it must be the domain walls that are responsible for the effect. Domain studies on the (100)-crystal (not shown) lead to the same conclusion.

The key to interpret the huge resistivity changes are the geometrical dimensions of the Lorentz trajectories of the conduction electrons in real space. They can be derived from Fermiology: The conductivity of iron is dominated by the Fermi surface (FS) of the 6th majority band sheet (Fig. 3c). The cyclotron orbits at the FS, caused by the Lorentz force, are transferred to helix-like trajectories around the induction $B$ (resp. magnetization $M$) in real space with an average diameter $d$ of 5 μm (Fig. 3b). As the mean-free electron path $\lambda$ in our perfect crystals can be up to 140 μm at low temperature (compared to ∼16 nm at room temperature) a spiral trajectory makes several turns $N$ before scattering. Thus the so-called “high field limit” $2\pi N = 2\lambda/d_{max} = \omega_c \tau > 1$ is realized (where $\omega_c$ is the cyclotron frequency, $\tau$ the relaxation time). Then for $\Delta\rho_{\text{Lorentz}}$ theory [6, 7, 8] yields

\[ \Delta\rho_{\text{trans}}(B, T)/\rho(B = 0, T) \propto (\omega_c \tau)^2 \propto B^2/\rho(B = 0, T)^2, \]

\[ \Delta\rho_{\text{long}}(B, T) = c_1 \rho(B = 0, T). \]

These equations for the transverse and longitudinal LMR hold for compensated metals (i.e. equal numbers of electrons and holes) with closed FS sheets, which both applies to iron. According to Eq. 1, $\Delta\rho_{\text{trans}}$ unboundedly increases with the number of orbits at the FS, which was indeed measured up to $B = 20$ T [9, 10]. The temperature dependence of the transverse LMR is determined by $\rho(B = 0, T)$ in the denominator of Eq. 1 (the numerator stays constant for a stable domain configuration with total or partial transverse $M$-components). The denominator in Eq. 1 decreases with falling temperature, explaining the negative temperature coefficient (TCR) of the transverse LMR that is measured in Fig. 1b.

Such behavior, however, can only occur if the electron helices propagate within sufficiently wide domains like in Fig. 2c. If a helix interacts with a domain wall, the Lorentz force changes and the spiral trajectory is interrupted. So within an effective width around the wall, given by roughly twice the average helix diameter, full helix turns cannot be
formed. Instead, short Lorentz trajectories, wiggling around the wall, will be generated (Fig. 3d). They are equivalent to highly conductive current channels along the wall, which may ‘shortcut’ the transverse LMR (and to a lower degree also the longitudinal LMR) if the walls have longitudinal orientational components. For our (110)-crystal this scenario is supported by domain observation: the angles between domain magnetization and electrical current direction stay largely constant in the low- and high-resistivity states (i.e. the last term in Eq. 1 remains unchanged), just the number of walls is different. The huge resistivity changes must consequently be caused by the creation and annihilation of domain walls. Within the channels the negative TCR of Eq. 1 cannot dominate the total resistivity. The TCR thus changes sign from negative to positive (Fig. 1a) when the wall density increases with decreasing circular field (Fig. 2b).

To summarize, our resistivity studies can only be explained conclusively by assuming that domain walls decrease the LMR, thus causing a NDWR. This “channeling” effect of walls, which is due to a change of the Lorentz trajectories and which is therefore a consequence of Fermiology at the end, can drastically exceed any (positive) DWR based on the carrier spin or diamagnetic models [11-14]. It is caused by the electron charge and thus independent of spin/wall interactions, being valid for both, electron transmission with spin tracking [15] or reflection with spin conservation [16]. The NDWR is huge at low temperatures, favored by the electronic structure of iron (compensation and closed FS sheets). The measurable features will be weaker e.g. in Co or Ni and in samples with reduced dimensions (like films) where the surfaces, which act like walls on the Lorentz trajectories [17], are dominating. Also at higher temperatures the effect will be reduced and most likely not be strong enough to be isolated from other MR or DWR effects. Nevertheless it is expected that the NDWR plays a role for all domain walls in any kind of magnetic material. Domain walls generally decrease the LMR, and because the LMR is inherent in every ferromagnet with more or less intensity, a negative domain wall resistance term exists as a matter of principle and has to be taken into account in any resistivity discussion! This effect was overlooked so far. For an extended description see ref. [18].

Towards ballistic heat transport of quantum spin excitations

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Fundamental conservation laws predict ballistic, i.e., dissipationless transport behaviour in one-dimensional quantum magnets. Experimental evidence, however, for such anomalous transport has been lacking ever since. Here we provide experimental evidence for ballistic heat transport in a $S = \frac{1}{2}$ Heisenberg chain. In particular, we investigate high purity samples of the chain cuprate SrCuO$_2$ and observe a huge magnetic heat conductivity $\kappa_{\text{mag}}$. An extremely large spinon mean free path of more than a micrometer demonstrates, that $\kappa_{\text{mag}}$ is only limited by extrinsic scattering processes, which is a clear signature of ballistic transport in the underlying spin model.

The integrability of the one-dimensional (1D) antiferromagnetic $S = \frac{1}{2}$ Heisenberg chain implies a divergent magnetic heat conductivity $\kappa_{\text{mag}}$ at all finite temperatures $T$ [1–4]. Despite this rigorous prediction, experimental evidence for ballistic heat transport in quantum magnets is lacking. Such experimental $\kappa_{\text{mag}}$ is always finite, since extrinsic scattering processes due to defects and phonons are inherent to all materials and mask the intrinsic behavior of the chain. A promising large $\kappa_{\text{mag}}$ has been observed in a number of cuprate compounds, which realize 1D $S = \frac{1}{2}$ Heisenberg antiferromagnets [5–9]. The compound SrCuO$_2$ is a prominent example [8, 9]. However, a quantitative analysis of $\kappa_{\text{mag}}$ has always been difficult in this compound, since the phononic and magnetic heat conductivities are of similar magnitude at low temperatures. Here we report evidence for ballistic heat transport as a result of a huge enhancement of $\kappa_{\text{mag}}$ upon increasing the samples purity [10].

The main structural element in SrCuO$_2$ is formed by CuO$_2$ zig-zag ribbons, which run along the crystallographic $c$-axis, as shown in Fig. 1. Each ribbon can be viewed as made of two parallel corner-sharing CuO$_2$ chains, where the straight Cu-O-Cu bonds of each double-chain structure result in a very large antiferromagnetic intrachain exchange coupling $J/k_B = 2100–2600$ K of the $S = \frac{1}{2}$ spins at the Cu$^{2+}$ sites [11, 12]. The frustrated and much weaker interchain coupling $|J'|/J = 0.1–0.2$ [11] and presumably quantum fluctuations prevent three-dimensional long range magnetic order of the system at $T > T_N = 1.5–2K$ [13, 14]. Hence, at significantly higher $T$ the two chains within one double chain structure can be regarded as magnetically independent, which is consistent with results by inelastic neutron scattering [12].

Fig. 1: Crystal structure of the spin chain compound SrCuO$_2$. The symmetry is $Cmcm$ with lattice constants $a = 3.56\AA$, $b = 16.32\AA$, $c = 3.92\AA$ [16]. The main building block of the crystal, the double spin chain consisting of CuO$_2$ plaquettes is shown in the right picture.

Fig. 2 presents our results for $\kappa_a$ and $\kappa_c$ of SrCuO$_2$ for both 99% (2N) and 99.99% (4N) purity as a function of $T$. We first describe the data for 2N purity, which are in good agreement with earlier results by Sologubenko et al. [9]. A pronounced low-$T$ peak is found for $\kappa_{c,2N}$, perpendicular to the chains. This peak and a $-T^{-1}$-decrease at $T \approx 150$ K towards a small value at room temperature, represent the characteristic $T$-dependence of phonon-only heat conductivity $\kappa_{\text{ph}}$. A similar low-$T$ peak is also present for $\kappa_{c,2N}$ parallel to the chains. It is however larger and exhibits a distinct shoulder at $T \approx 40$ K. $\kappa_{c,2N}$ decreases at higher $T$, but remains much larger than $\kappa_{c,2N}$ even at room temperature. The apparent large anisotropy, together with the unusual $T$-dependence of $\kappa_{c,2N}$, is the signature of a large magnetic fraction of $\kappa_{c,2N}$ over a large $T$-range [8, 9].

Fig. 2: Thermal conductivities $\kappa_a$ and $\kappa_c$ of SrCuO$_2$ for 2N (99%) and 4N (99.99%) purity. Closed (open) symbols represent $c$-axis ($a$-axis) data, circles (diamonds) correspond to 4N (2N) purity. We now turn to the new data which have been obtained for the high-purity compound.

The heat transport perpendicular to the chains ($\kappa_{c,4N}$) is slightly enhanced as compared to $\kappa_{c,2N}$. This reflects a somewhat reduced phonon-defect scattering. However, a much more drastic and unexpected large effect of the enhanced purity is observed in the heat transport parallel to the chains, $\kappa_{a,4N}$. Instead of a narrow low-$T$ peak and a shoulder, as observed in $\kappa_{a,2N}$, a huge and broad peak centered at $-28$ K is present in $\kappa_{a,4N}$. This peak exceeds $\kappa_{a,2N}$ at $T \approx 70$ K by more than a factor of 2. For $70K \leq T \leq 200$ K we observe $\kappa_{a,4N} > \kappa_{a,2N}$ and interestingly both curves approach each other. At $T \approx 200$ K both curves
phononic heat conductor, the overall similar, but clear differences are present at low-
spinon-phonon scattering becoming increasingly important. Both curves are very a general Umklapp process with a characteristic energy scale furthe r scattering process, which leads to

Second, the spinon-defect scattering length is more than a factor of 3 higher than the largest reported \( \kappa_{\text{mag}} \) [9]. The peak is followed by a strong decrease upon raising \( T \). Similar to the typical \( T \)-dependence of a clean phononic heat conductor, the overall \( T \)-dependence of \( \kappa_{\text{mag}} \) suggests, that, in a simple picture, two competing effects determine \( \kappa_{\text{mag}} \). These are at low-\( T \) the scattering of spinon on defects and for higher \( T \) spinon-phonon scattering. \( \kappa_{\text{mag}} \) of the 2N sample is qualitatively very similar. However, the absolute value at the peak is much lower (\(-172 \text{ W/mK}\)) and the position of the peak is shifted to a higher \( T \) (\(-55 \text{ K}\)). We analyze \( \kappa_{\text{mag}} \) quantitatively by extracting the spinon mean free path \( l_{\text{mag}} \) according to [5, 6]

\[
l_{\text{mag}} = \frac{3\hbar}{\pi N_b k_B T} - \kappa_{\text{mag}},
\]

where \( N_b = 4/ab \) is the number of spin chains per unit area. As can be inferred from Fig. 4, \( l_{\text{mag}} \) of both samples shows a strong decrease with increasing \( T \), which directly reflects spinon-phonon scattering becoming increasingly important. Both curves are very similar, but clear differences are present at low-\( T \), where \( l_{\text{mag}} \) of the 2N sample is somewhat lower, in accordance with a higher spinon-defect scattering. We evoke Matthiesen’s rule to model the \( T \)-dependence of \( l_{\text{mag}} \) and to account for both scattering processes viz.

\[
l_{\text{mag}}^{-1} = l_0^{-1} + \left( \frac{k_B T}{A_T T^*} \right)^{-1}\frac{\exp(T/T^*)}{A_T T^*},
\]

which can be used to fit the data with \( l_0, A_T \) and \( T^* \) (\( A_T \) describes the coupling strength) as free parameters. We find an excellent agreement between such fits and the experimental \( l_{\text{mag}} \). Inspection of the fit parameters [17] yields two remarkable aspects, which corroborate our previous qualitative findings. First, the parameters \( A_T \) and \( T^* \), which determine the spinon-phonon scattering are practically the same for both samples. In fact, a good fit is obtained if the same \( T^* \) is used for both curves. Note that the extracted \( T^* - 200 \text{ K} \) is of the order of the Debye temperature \( \Theta_D \) of this material and thus leads to the conjecture, that mostly acoustic phonons are involved in this scattering process. Second, the spinon-defect scattering length \( l_0 \), which represents a lower bound for the low-\( T \)-limit of \( l_{\text{mag}} \) and which should significantly depend on the samples purity turns out to be drastically different for both cases. To be specific, we find \( l_0 = 300 \mu\text{m} \) for the 2N compound and an extraordinary \( l_0 = 1.6 \mu\text{m} \) for the 4N sample. These distances correspond to more than 750 and 4100 lattice spacings, respectively.

Fig. 3: \( \kappa_{\text{mag}} \) of SrCuO\(_2\) for different purities. Open symbols represent low-\( T \) \( \kappa_{\text{mag}} \), which is disregarded in the further analysis. The shaded areas show the uncertainty of the estimation of \( \kappa_{\text{mag}} \) due to the phononic background.

Fig. 4: Magnetic mean free paths of SrCuO\(_2\) for different purities. The solid lines were calculated according to Eq. 2. The shaded area illustrates the uncertainty from the estimation of the phononic background. The inset shows the same set of curves on a double logarithmic scale.
These findings provide a further confirmation, that for 2N and 4N purity, $\kappa_{\text{mag}}$ is determined by the same spinon-phonon scattering process and that the difference between the two curves can be described by the different defect density only. A major outcome of our study is the unambiguous identification of the extrinsic scattering processes as the only relevant ones. Intrinsic spinon-spinon scattering, on the other hand, plays no role in our analysis, even in the case of the very clean sample. The strong enhancement of $\kappa_{\text{mag}}$ upon a reduced number of impurities, thus appears as the manifestation of ballistic heat transport of the underlying spin model, where $\kappa_{\text{mag}}$ is rendered finite by extrinsic scattering processes only. A simple analysis reveals a remarkable lower bound for the low-temperature limit of the spinon mean free path $l_{\text{mag}}$ of more than a micrometer. This renders SrCuO$_2$ an intriguing candidate for future spin transport experiments.

[17] For the 4N compounds we get $l_{\text{0},4N} = (1.56 \pm 0.16) \, \mu m$, $T_{\text{u},4N}^* = (204 \pm 11) \, K$, $A_{\text{s},4N} = (59 \pm 5) \times 10^{-6} \, 1/\text{mK}$. Setting $T_{\text{u},2N}^* = T_{\text{u},4N}^*$ gives $l_{\text{0},2N} = (320 \pm 13) \, \text{nm}$ and $A_{\text{s},2N} = (72 \pm 5) \times 10^{-6} \, 1/\text{mK}$ for 2N. The errors account for the accuracy of the fit.

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Endohedral metallofullerenes (EMFs) – i.e. fullerenes encapsulating one or more metal atoms or a cluster in their inner space – are characterized by a high degree of internal electron transfer between the encaged metal and the host carbon cage. The vast majority of EMFs is limited to encaged metals of group I - group III. As a rule theses metals are found in their highest oxidation states in such EMFs. The frontier molecular orbitals (MOs) of EMFs are thus essentially carbon cages’ MOs, and therefore electrochemical activity of EMFs is mainly determined by the properties of the carbon cage. The situation is similar for the large group of nitride clusterfullerenes (NCF), i.e. the EMFs with three metal atoms bonded to a central nitride ion inside the fullerene cage, which are the most stable endohedral fullerene structures available so far.

The electronic state of the endohedral metal atoms remains thus barely constant irrespective of the charge of the whole EMF molecule. Therefore any electrochemical reaction does not change the redox state of the encaged species. One of the notable exclusions from this rule is Sc3N@C80, which has Sc-localized LUMO. Both the chemical and the electrochemical reduction of Sc3N@C80 leads to the change of the valence state of all three Sc atoms which can be especially well observed in the ESR spectrum of the anion-radical, which exhibits large 45Sc hyperfine coupling constant (hfc) and shift of g-factor from the free-electron value. So far, all other metallic-nitride clusterfullerenes (NCFs, the EMFs with composition of M3N@C2n, where M is Sc, Y and lanthanides, while 2n can vary from 68 to 100) have carbon cage-based frontier orbitals, and hence the valence state of endohedral metal atoms in NCFs cannot be manipulated by chemical and electrochemical techniques.

The world of NCFs has been severely enlarged by the development and implementation of the procedures for the synthesis and separation of mixed-metal NCFs (i.e. NCFs with two different metal atoms in one M3N cluster). To get isolated mixed-metal nitride clusterfullerenes (MMNCFs) of high isomeric purity, the application of high level recycling chromatography is required. The change in the metal composition of the endohedral species opens the way to EMFs with unprecedented electronic properties. By this approach, it is now possible to synthesize and isolate MMNCFs with those metal atoms which do not form homometallic M3N clusters. For instance, Ti3N@C80, NCFs cannot be synthesized up till now, but the MMNCF with mixed Sc-Ti cluster, TiSc2N@C80, is readily available in the arc burning process. Besides, in the MMNCFs the single metal atom combined with two others can exhibit specific properties, which are not available in the homometallic clusters. This has been demonstrated in the recent study for the valence state of a metal ion which can be tuned electrochemically in certain MMNCFs.

Searching for MMNCFs with unexpected properties of the encapsulated metal atoms the case of CeLu2N@C80 is of special importance opening the route to a new redox reaction at EMFs. NMR spectroscopic studies have shown that Ce in this MMNCF is in the III valence state with a single localized 4f electron (its spin can be followed by the characteristic temperature dependent shift in 13C NMR spectra). All previous electrochemical studies of Ce(III)-containing EMFs in comparison to their La and lanthanide analogues (including M@C82, M2@C72,78, M3N@C88,92,96) have not revealed any special redox behaviour of endohedral Ce. That is, redox potentials of Ce-based endohedral metallofullerenes were always close to those of the non-Ce analogues. However, for CeLu2N@C80 we have found that its oxidation potential is shifted by 0.6 V from the values of all other M3N@C80 NCFs (Fig. 1). Such a strong shift of the redox potential indicates that
it’s origin is not based on changes of the carbon cage MOs of the EMF but is obviously grounded in the change of the valence state of the Ce atom in the encaged cluster. Indeed, DFT calculations have shown that the removal of the 4f electron from Ce atom in CeLu2N@C80 is 0.43 eV more favorable than oxidation of the carbon cage. Thus, CeLu2N@C80 is the first Ce-based endohedral metallofullerene exhibiting redox activity of endohedral Ce(III), which can be reversibly oxidized into the Ce(IV) state. In this way a new type of redox reactions at fullerenes is described being the matter of a new branch in electrochemistry, called endohedral electrochemistry. Moreover, CeIVLu2N@C80+ cation is the first EMF with the tetra-valent cerium atom.

The existence of the CeIVLu2N@C80+ cation is by no means a single case of endohedral electrochemistry in action. Unprecedented electrochemical properties of endohedral fullerenes were also revealed for the MMNCF TiSc2N@C80.8 This MMNCF is paramagnetic and ESR spectroscopic as well as DFT computational studies have shown that Ti is in the III-valence state in the neutral form of the MMNCF. Single-occupied MO (SOMO) and hence the spin density as well are to a large extent localized on the Ti atom (Fig. 2). Unlike all other M3N@C80 NCFs either with a homometallic or a mixed-metal nitride cluster, which exhibit electrochemically irreversible (but chemically reversible) reductions, the TiSc2N@C80 has three electrochemically reversible reductions and one reversible oxidation step (Fig. 2). The redox behaviour which is different from all other known NCFs is caused by the new route of endohedral electrochemistry. Both reduction and oxidation of TiSc2N@C80 proceed through the change of the valence state of Ti atom: from Ti(II) in the TiSc2N@C80– anion through Ti(III) in the neutral state to Ti(IV) in the TiSc2N@C80+ cation. TiSc2N@C80 is the first example of EMF with metal-only redox system in which endohedral metal is electrochemically active in both reduction and oxidation.

It is to be mentioned that exohedral derivatization can also significantly alter the properties of NCFs. The studies of Sc3N@C80(CF3)2 have shown that addition of only two CF3 groups drastically changes dynamics of the cluster and electrochemical properties of Sc3N@C80 core.3 Sc3N@C80(CF3)2 exhibits two single-electron oxidation and three single-electron reduction steps, all of them are electrochemically reversible even at low voltammetric scan rates. High stability of the charge states in solution enabled an in situ ESR spectroscopic characterization of the electrochemically generated charged paramagnetic states (cation, anion, and trianion; Sc3N@C80(CF3)2− is the first trianion of any EMF ever characterized spectroscopically). Analysis of the 45Sc hyperfine structure of the anion and trianion has shown that exohedral addition of two CF3 groups hinders rotation of the Sc3N cluster (in Sc3N@C80 the cluster rotates freely). The study also revealed a mixing of the fullerene and cluster states in the frontier orbitals of the derivative and, as a result, the mixed cage-cluster distribution of the spin density in the derivative with the exceptionally high spin population on one Sc atom in the trianion.
Localization of the spin density in EMFs on the endohedral cluster and fast dynamics of the endohedral clusters raises the question of their mutual influence. Detailed DFT studies have shown that spin density distribution in such EMFs is very flexible; even slight reorientation of the cluster results in considerable changes of the spin populations of the metal atoms. This conclusion was further corroborated by the DFT-based Born-Oppenheimer molecular dynamics, which provided details of the spin density dynamics (dubbed as the spin flow). Fourier transformation of the time dependencies of the spin populations resulted in the spin-flow vibrational spectra, which reveal the major spin-flow channels. In particular, for TiSc2N@C80 it is shown that the cluster-cage spin flow is selectively coupled to one vibrational mode.

In general, the judicious choice of synthetic and separation techniques and target EMFs opens the way to compounds with chemically and electrochemically tuneable valence states of the endohedral species. In the studies of such EMFs, the new field of electrochemistry, endohedral electrochemistry, is emerging. An interesting question still to be addressed in more details is the mechanism of the electron transfer to and from endohedral species through the formally inert carbon cage. The first studies of the electron density distribution2,8 have revealed that the formal change of the valence state of the endohedral atoms is accompanied by the spatial spin-charge separation.

Fig. 3: (a–b) Experimental and simulated ESR spectra of (a) Sc3N@C80(CF3)− and (b) Sc3N@C80(CF3)3−; (c) spin density distribution in Sc3N@C80(CF3)−, Sc3N@C80(CF3)3−, and Sc3N@C80−.

Fig. 4: (a) Born-Oppenheimer molecular dynamics trajectory of TiSc2N@C80 (10 ps at 300 K, displacements of carbon atoms are not shown); (b) spin-flow vibrational spectra of TiSc2N@C80 (note that the scale for Ti is an order of magnitude higher than the scale for Sc and N atoms).


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Towards controlled graphene properties:
Direct synthesis on dielectrics and Tuning via stress
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Interest in graphene since its isolation in 2004 has rapidly escalated. It has been described as nature’s thinnest elastic material and its exceptional mechanical and electronic properties make it an extremely exciting material. Within the realm of electronics, it is its one atoms thickness, planar geometry, high current-carrying capacity and thermal conductivity and potential to open a gap when existing as a narrow ribbon that hold particular promise. These features make it ideally suited for further miniaturizing electronics to form ultra-small devices and components for future semiconductor technology.

In order for graphene to realize its potential in electronics various obstacles need to be overcome. One of the more important aspects is its actual synthesis. Various routes exist to synthesize graphene; however, most are not best suited for integration into current silicon technology. The primary routes are through graphite exfoliation, epitaxial graphene, graphene oxide and chemical vapor deposition. Most of these routes require the graphene to be transferred onto a dielectric or, as in the case of SiC, require high temperatures. To use graphene as the basis of field-effect transistors at room temperature one needs to modify graphene’s semi-metallic nature so as to open a band gap. When existing as narrow strips (nanoribbons) quantum confinement effects lead to band gap formation. Most band gap engineering routes use multiple lithographic steps to fabricate a graphene device. This leads to contamination and disorder to the flake. Dry lithography-free techniques can help, nonetheless technical difficulties still remain.

Another approach is chemical modification, for example, graphene oxide in which hydroxyl and other chemical groups attach to graphene. Although the technique is able to lift the degeneracy of the $\pi$ band at the Fermi level of graphene, it is difficult to control its electronic properties and avoid defect formation.

A more attractive route to control graphene’s properties is through mechanical strain engineering which modifies graphene’s geometrical structures. For example, substrate-induced sublattice symmetry breaking in exipitaxially grown graphene can give rise to energy gaps; scanning tunneling microscopic studies show evidence for strain-induced spatial modulations in the local conductance of graphene on $\text{SiO}_2$; strain with triangular symmetry induces strong gauge field that effectively act as a uniform magnetic field exceeding 10 T. However most of these experiments are based on graphene layers with fixed static strain. Thus, new techniques allowing for strain on demand are quite important in order to intentionally tune and understand the interplay between geometry and electronic properties of graphene.

Uniaxial strain on graphene has been experimentally controlled by bending graphene on a plastic substrate, and using Raman spectroscopy to probe its phonons. However, this bending-substrate geometry is not practical for many experiments. Moreover, uniaxial strain moves the relative positions of the Dirac cones and induces a significant influence in the intervalley double-resonance processes. Thus, biaxial strain, which ensures a planar-substrate geometry and avoids complicate perturbations to the Dirac cones, would be more suited to control the graphene’s properties.

Recently we developed a method by utilizing a piezoelectric substrate to control the properties of micro-/nanostructures. [1-2] The same approach has been successfully applied to the strain engineering of single layer graphenes (SLG). [3] We use a 300 $\mu$m [Pb(Mg1/3Nb2/3)O3]0.72-[PbTiO3]0.28 (PMN-PT) substrate overgrown with a thin (~20 nm) epitaxial layer of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSMO) acting as top contact, see Fig. 1. The backside is coated with gold. A bias voltage $V$ applied to the PMN-PT results in an out-of-plane electric field $F$ which leads to an in-plane strain $\varepsilon_{ij}$. After the deposition of a 1 $\mu$m-thick $\text{SiO}_2$
The substrate is spin-coated with a 60 nm-thick PMMA (polymethyl methacrylate) layer. We fabricate the graphene samples from highly ordered pyrolytic graphite (HOPG) by mechanical cleavage with the scotch tape technique. The tape is then placed onto the substrate followed by a baking process at 120 °C for 10 min [Fig. 1(a)]. The glue-like PMMA layer becomes solid and the graphene layers are transferred onto the piezoelectric actuator [Fig. 1(b)].

The thickness of the interfacial SiO₂/PMMA layers has been carefully optimized to visualize the SLGs under an optical microscope. Figure 1(c) shows the typical Raman spectrum (measured at 300 K) of a SLG after transfer onto the piezoelectric substrate. The characteristic Raman features are the so-called D, G, 2D, and 2D' peaks, which locate at 1339 cm⁻¹, 1581 cm⁻¹, 2671 cm⁻¹, and 3245 cm⁻¹, respectively. Many of the measurements on graphene need to be performed at low temperature. The advantage of using PMN-PT crystal is that it is capable of exerting either compressive or tensile stresses at very low temperature. Figure 2(a) presents the color-coded intensity map of the Raman peaks of one SLG sample as a function of the voltage V applied to the PMN-PT actuator (measured at 15 K). V is swept several times between −550 V and 1100 V with steps of 20 V, to demonstrate the reversibility of the strain tuning technique. The maximum voltage is only limited by our power supply, in fact, with a thinner PMN-PT substrate it is possible to achieve the same out-of-plane electric field F (therefore, the same in-plane strain ε₁) with much smaller voltage. For V < 0 the graphene experiences an in-plane tension (T) and the Raman peaks show roughly a linear shift to lower frequency, as reported before. In-plane compression (C) on the graphene is also feasible with this piezoelectric actuator, just by applying a positive voltage V > 0 to the substrate. From Fig. 2(a) we do not see any hysteresis over multiple compressing/stretching cycles.

The Grüneisen parameters describe the strain sensitivity of the phonon frequencies, and are thus an important fundamental set of parameters for graphene. There have been
several attempts to measure the Grüneisen parameters under uniaxial strain or hydrostatic strain. As discussed before the D, and 2D peaks are zone-boundary phonons activated by intervalley double resonances, the relative movement of the Dirac cones changes the phonon wave vector we are probing. Therefore, it would be more suitable to measure the D mode Grüneisen parameter under biaxial strain. After the strain calibration by the movement of G mode,[3] we can plot the strain-dependent shifts of all Raman peaks in Fig. 2(b). All peaks show smooth and linear shifts with biaxial strain, indicating that neither slippage nor corrugation of the graphene occurs during the experiment. Linear fits of all data (under either compressive or tensile strain) yield the Grüneisen parameters $\gamma_D = 1.8$, $\gamma_D' = 2.30$, $\gamma_{2D} = 2.98$, and $\gamma_{2D'} = 1.73$. Our results are in good agreement with values derived from first-principles calculations for graphene, and experimental values for carbon materials under hydrostatic pressure (for example, carbon fibers and graphite), suggesting that graphene has similar strain dependencies of the Raman frequencies with graphite. There are some differences between our results and the values derived from uniaxial experiments, which might be explained by the reasons stated above. In the experiments we found different strain sensitivities of the D mode and its overtone 2D mode, i.e., different Grüneisen parameters. This peculiar phenomenon has been theoretically predicted for two-dimensional graphite. Our experimental studies[3] suggest that the defect-activated D mode is in fact associated with intervalley double-resonance scattering with two different phonon processes. The inelastic scattering by a phonon and the elastic scattering by a defect can happen at reversed time sequences, thus involving phonons with different wavevectors. The 2D mode, however, does not need defects for its activation and only involves the elastic scattering process. The linewidth analysis of the D and 2D modes at different applied strain supports this conclusion.[3]

Although we have shown the potential of graphene strain engineering via piezoelectric actuation there exists a technical drawback, similar to the for graphene based FETs, namely the need to transfer the material onto the piezoelectric material (or gate dielectric in the case of FETs). Transferring graphene generally leads to damage and impurity deposition which can adversely affect its performance. For example the PMMA gluing layer in aforementioned technique can be a drawback when performing STM analysis. Thus, the fabrication of graphene devices with atomically uniform dielectrics which can provide a uniform electric field and/or uniform stress induction across the active region is attractive. To this end we are developing thermal CVD techniques to deposit graphene directly on dielectrics at temperatures below 500°C. In Fig. 3, a variety of micrographs are seen which show we are able to grow graphene flakes on the surface of magnesium oxide and tune the growth from single to multi layers. The multi layers shown in the overview of Fig. 3(a) are grown from cyclohexane at 775°C and 100 mbar. With these conditions, the reaction stops when the catalyst is fully encapsulated by graphitic layers. We found that the number of layers can increase up to nine. In Fig. 3(c) we highlight the closely spaced parallel lattice fringes of the crystals are those of (100) planes on top of which there is epitaxial graphitic carbon. Furthermore, as indicated by the arrow, the multilayers are ubiquitously anchored into step edges on the (100) surfaces. We propose that, similar to observations in silicon carbide growth, these step sites initiate the growth of graphitic layers. We argue that these step sites are not only nucleation sites, but also growth sites because growth appears to stop once the particle is fully encapsulated. In this regard, this work corroborates previous studies suggesting the cooperative role of oxide supports in the growth of multiwalled carbon nanotubes. We also investigated zirconium oxide to further elucidate the atomic surface structure required for graphitic synthesis on oxides. This catalyst has recently been extensively explored for the synthesis of carbon nanotubes. In our case, the synthesis of graphitic layers is performed on nanocrystallites which following the reaction are in the baddeleyite form and the graphitic layers are anchored on a face with (020) at its surface normal.

**Fig. 3:** Multilayer graphene synthesized over MgO from cyclohexane at 775 °C and 100 mbar. The attachment of graphene layers to the (100) oxide step edges can be observed.
Preliminary first principles density functional theory investigations using MgO (100) surfaces with step sites as a model system for oxides show acetylene does not easily adsorb on the surface but does so more readily at steps sites. More over, acetylene dissociation on the surface is shown to be endothermic whilst at a step site the process is exothermic. Complimentary diffusion studies show a diffusion barrier of ca. 0.38 eV for C and 0.2 eV for H over an oxygen atom on the MgO (100) surface. This points to C remaining on the surface whilst H simply flies away. We propose a graphene formation mechanism involving four distinct sub-process; the adsorption of the carbon feedstock molecules on the substrate surface, dissociation of hydrogen from the precursor, surface diffusion and addition of carbon atoms to the network. These sub-processes are shown in Fig. 4.

Conclusions
In conclusion we have achieved several milestones towards the controllable modification of the graphene properties. First, we demonstrate that tunable modification of the graphene Raman modes can be realized by applying external biaxial strains. The experiment utilizes a newly developed piezoelectric actuator-based technique. The key mechanical characteristics of graphene, i.e., the Grüneisen parameters, are studied under biaxial strain. Combining graphene with the piezoelectric actuator promises new opportunities to study and control the strain-related behaviors of graphene, such as the ballistic conductance, the basal-plane hydrogenation, and the thermal conductivity, with unprecedented details. Second, we are aiming at the direct synthesis of graphene on dielectric substrates, which could avoid the use of PMMA gluing layer and provide a uniform electric field and/or uniform stress induction across the active region. Regards the thermal CVD investigations, our experimental and theoretical data indicate high K dielectrics have potential for the catalytic formation of graphene via thermal CVD at temperatures below 500°C.


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Transformations in glassy CuZr-based alloys

Monolithic bulk metallic glasses (BMGs) are known to be extremely prone to shear localisation upon mechanical loading. Macroscopically, this behaviour reflects in the formation of so-called shear bands, which have characteristic thicknesses of tens of nanometres [1]. The operation of shear bands becomes apparent once their propagation creates a shear step on the surface of the specimen. Even though the strain within these shear bands is surprisingly high (ε ≈ 10) [2] the low shear band density leads to catastrophic failure without detectable plastic strain, especially under tensile loading conditions. In order to exploit the unique combination of mechanical properties like high strength, large elastic limit and low Young modulus for instance in structural applications, the deformation behaviour of BMGs has to be understood and ways have to be found to overcome their intrinsic brittleness.

In principle there are two stages of shear localisation at which one can interfere in order to postpone fracture: either at the early stage of shear band evolution or at a later stage during propagation of existing shear bands. The latter approach has been successfully implemented for BMG matrix composites, in which a crystalline phase is embedded in a glassy matrix [3]. Blocking, deflection and substantial branching of shear bands has been shown to significantly enhance the plastic strain in these composites [3]. However, to date no mechanisms are known, which could impede and retard the generation of shear bands in monolithic BMGs at the early stages of their nascent.

The current understanding of how shear bands evolve in BMGs is based on the concept of so-called shear transformation zones (STZs). These entities consist of up to several hundreds of atoms [4] and represent the fundamental units of plasticity [5]. Upon shearing, the atoms of a given STZ rearrange in a cooperative manner passing through a transition state. The latter configurational state becomes “jammed” and thus renders this rearrangement irreversible – or plastic [6]. The formation of a shear band is the result of the percolation of STZs in each others’ direct vicinity [6] and their lateral expansion [7].

Surprisingly, in the case of certain (Cu0.5Zr0.5)100-xAlx bulk metallic glasses (e.g. x = 5, 6, 8) there is a clear deviation from linearity at high stresses upon tensile deformation, which is in contrast to the typical brittleness of BMGs (Fig. 1). As the inset of Fig. 1 shows, this small ductility is not accompanied by shear steps, which means shear bands do not appear to be the carriers of plastic deformation in the present case. Instead, transmission electron microscopy (TEM) reveals that in these alloys, which are glassy apart from sparse nanocrystals with diameters around 2-5 nm (Fig. 2), nanocrystals precipitate and substantially grow during deformation (Fig. 3 (a)). Furthermore, some of these crystals exhibit a contrast reminiscent of twinning. The Fast-Fourier-Transformation (FFT) of high-resolution TEM images clearly reveals that the nanocrystals consist of the B2 CuZr phase (Pm-3m) (Fig. 3 (c)). The larger nanocrystals undergo twinning, which is corroborated by the occurrence of additional diffraction spots in the corresponding FFT (Fig. 3 (b)).

It is noteworthy that the B2 CuZr phase is thermodynamically stable only at temperatures above 988 K and should not precipitate at room temperature [8].

In the following, this unique deformation mechanism is discussed in the framework of the potential energy landscape (PEL) theory [9,10]. The potential energy function of BMGs is relatively complex and consists of broad minima, so-called inherent states and smaller undulations, which are separated by low-energy barriers (Fig. 4 (a)). Upon loading, the external elastic stress field is superimposed on the potential energy function of the system (Fig. 4 (a)). This effectively reduces the potential energy barrier, ΔV, between two inherent states and biases flow of the material in the respective direction (Fig. 4 (a)). Moreover, simulations show that elastic energy flattens out the minima [12]...
and thus reduces the energy barrier height (Fig. 4 (b)), which has a strong impact on the elastic constants of the material as will be shown below. The simplest function to capture the potential energy landscape is a sinusoidal function, similar to a Frenkel landscape [13]:

\[
\frac{\Phi}{\Phi_0} = \sin^2 \left( \frac{\pi \gamma}{8 \gamma_c} \right),
\]

(1)

where \(\Phi\) is the potential energy, \(\Phi_0\) is the amplitude of the energy function, \(\gamma\) is the shear strain and \(\gamma_c\) is a critical shear strain limit. The second derivative of the potential energy with respect to the shear coordinate (representing the curvature of the potential energy function at \(\gamma = 0\)) yields the instantaneous shear modulus, \(G\):

\[
\frac{\text{d}^2 \Phi}{\text{d} \gamma^2} \bigg|_{\gamma=0} = G = \left( \frac{\pi^2}{8 \gamma_c^2} \right) \Phi_0.
\]

(2)

This means the flattening out of the inherent states during loading represents a decrease of the shear modulus, which facilitates structural rearrangements or flow. The total barrier height, which has to be surmounted to initiate structural rearrangements, \(\Delta F(T)\), is the product of the amplitude of the potential energy function, \(\Phi_0\), and the size of the cooperatively rearranging zone, \(\Omega\) [14]:

\[
\Delta F(T) = \Phi_0 \Omega = \frac{8 \gamma_c^2}{\pi^2} G \Omega.
\]

(3)

Viscosity, \(\eta\), can be expressed as [13]:

\[
\eta = \eta_0 \exp \left( \frac{\Delta F(T)}{k_B T} \right),
\]

(4)

the pre-exponential constant \(\eta_0\) being the viscosity at infinite temperature, \(\Delta F(T)\) being the temperature dependent activation energy, \(k_B\) being the Boltzmann constant and \(T\) being the temperature. Inserting eq. (3) into eq. (4) establishes a link between the flow behaviour (viscosity) and the shear modulus. In short, the elastic energy imposed onto the system reduces the shear modulus of the BMG and biases structural rearrangements and thus reduces the viscosity.

The structural rearrangements can now lead to two competing processes, namely the formation of STZs and, as in the present case, to the precipitation of B2 CuZr nanocrystals (Fig. 3 (a)). The fact that the thermodynamically unstable B2 phase forms instead of the equilibrium phases Cu10Zr7 and CuZr2 implies that kinetics play the crucial role. Since the B2 phase is polymorphous to the composition of the glass there might be a similar coordination in the glass as in the B2 phase itself. Consequently, only marginal atomic
rearrangements are required to precipitate B2 CuZr crystals during deformation, which rivals the minor atomic rearrangements disemboguing in STZs. The volume change associated with the crystallisation and the differences in the elastic properties most likely reduce the stress concentrations in the glass, which would otherwise lead to the evolution of additional STZs in their vicinity. As a consequence the amount of STZs, which form in the course of deformation, is effectively reduced. Besides, the nanocrystals represent obstacles for the propagation of a shear band at the later stages of deformation and hence fracture is postponed. A similar effect is achieved by the twinning process, which is found in the larger nanocrystals. The volume changes during this diffusionless transformation also interact with the stress fields in the matrix and impede the generation and subsequent percolation of STZs into shear bands.

B2 CuZr is a shape memory alloy exhibiting a reversible martensitic transformation [15]. However, due to the small grain size, the confinement by the rigid glassy matrix and due to the dissolved Al atoms the B2 phase is distorted and the deformation-induced phase transformation rather proceeds in form of twinning. Since both precipitation of nanocrystals and twinning consume energy, the formation of STZs and with it the formation of detrimental shear bands is retarded and macroscopic plasticity combined with work hardening can be measured during tensile deformation [16].

The development of glassy alloys derived from shape memory phases such as the present Cu-Zr-Al BMGs, could open up an alloy design strategy for the development of advanced BMGs with an increased tolerance towards failure.


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**Damascene light weight metals**


In a broad field of applications, as e.g. for mobile applications, transport systems and the required components as well as for optimised light weight design elements, there is a huge demand for materials with a high specific strength (strength divided by the mass density). One possible way to improve strength is to refine the materials microstructure. A variety of such ultra-fine grained (ufg) or even nanocrystalline (nc) materials is available in laboratory scale, however, useable semi-finishes products with the right property combination are commonly not yet available. Research on nc materials has been found to reveal some exciting combinations of properties. In this context, magnetic, superconducting, biomedical as well as mechanical properties are strongly affected by a nc microstructure. For example, the saturation magnetisation as well as the Curie temperature [1] of Ni can be reduced significantly when the microstructure becomes nanocrystalline. An increase in cell proliferation by more than one order of magnitude has been observed for commercially pure Titanium when the grain size is reduced from 4.5 μm to 200 nm [2]. The mechanical properties also undergo a remarkable change when the microstructure is refined to the nc range. In particular, some nc materials exhibit a high ultimate tensile strength while retaining a reasonable elongation [3, 4], which is essential for their applicability. Deforming bulk, coarse grained materials to very high strains is one possibility to reaching a nc, or an ultra-fine grained microstructure [5]. Severe plastic deformation allows to build large quantities of ufg materials without impurity issues, as it is the case for compacting nc powders to dense work pieces.

The presently used technology allows to producing semi-finished parts in the shape of wires with tuneable density and high specific strength [6]. In this respect, use is made of the good mechanical properties of ufg microstructures, which is combined with the ability to produce a common semi-finished product. One further goal is to improve the specific strength, which is of great interest in constructive light weight design. This already suggests the use of common light weight metals such as Ti, Al or Mg for processing. Fig. 1 shows the processing technique for a macro composite consisting of a Ti tube (green), a Nb tube (red) and an Al rod (blue), which is repetively swaged up to a logarithmic strain of η = 8.4. The composite is cold deformed to η = 4.3, cut into 37 pieces, bundled and stacked in a Ti tube and swaged again. The process is theoretically arbitrarily repeatable. It reminds on the production of the so called damascene steel in past centuries. However, the two-dimensionality of stacking and the application to light weight metals are rather new.

The heavy cold work causes a strong grain refinement of the starting materials (see Fig. 2). In the processed composite, Niobium acts as a diffusion barrier. Consequently,

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**Fig. 1:** Repeatable swaging and bundling processing route for composite materials, here: Ti tube (green), Nb tube (red), Al rod (blue).

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**Fig. 2:** Microstructure of the constituents after deformation up to η = 8.4. Grain sizes in cross section: Al: ~0.2 μm, Nb: ~0.2–0.5 μm, Ti: ~100 nm.
no intermetallic phase formation of Ti and Al can be detected by X-Ray diffraction after deformation (Fig. 3). The mechanical properties of the wires are shown in Fig. 4 in comparison to other materials. After being deformed to a logarithmic strain of \(\eta = \ln \left( \frac{A_f}{A_0} \right) = 8.4\) (where \(A_0\) and \(A_f\) are the starting and final cross sectional area), the wires show an ultimate tensile strength of 790 MPa, whereas 540 MPa were obtained after deformation up to \(\eta = 4.3\. These values are shown in Fig. 4 with respect to their absolute mass density. The obtained strength of 790 MPa is equivalent to a specific strength of 200 MPa/(g/cm³). This value is comparable to the upper limits of conventional Ti, Al or Mg alloys (refer to the upper dashed line in Fig. 4) and is therefore in direct competition with the conventional high strength alloys of the different classes. These values are promising, since the used Ti, Nb and the Al alloy are easily available. Furthermore, there is potential of optimisation with respect to e.g. reduction of the grain size, an increase of the frequency of high angle grain boundaries due to re-bundling and during further cold working, as well as the possible introduction of heat treatments during or after processing.

There are a number of properties that are changed intrinsically by the used processing route, such as: dislocation density, mass density, elastic constants, texture, grain size and distribution, the frequency of high and low angle grain boundaries as well as the total amount of internal interfaces. These properties interact in a rather complex way. Although the bulk properties are easily accessible, their individual character as well as their interaction is yet not well understood. Furthermore, the characterisation of the microstructure of the processed wires is a challenging task. One main goal for future activities deals with the characterisation of the mentioned features, including their distinctness, as well as the characterisation of their interactions. This understanding of the mechanisms will allow a further improvement of the specific strength.


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Energy storage elements based on hybrid organic/inorganic nanomembranes

C. C. Bof Bufon, J. D. C. Gonzales, D. J. Thurmer, D. Grimm, M. Bauer and O. G. Schmidt

In this work we demonstrate the fabrication of three-dimensional ultra-compact hybrid organic/inorganic energy storage elements, manufactured in parallel on a single chip. The inorganic version of our elements exhibit capacitances per footprint area higher than their state-of-the-art planar counterparts and specific energy comparable with supercapacitors (\(\sim 0.55\) Wh/kg). In addition, the electronic properties of these devices were precisely controlled by incorporating self-assembled molecular layers.

The evident progress in the miniaturization of electronic devices and circuits as well as the substantial reduction of their power consumption gave rise to the concept of Energy Autonomous Systems (EAS). EAS by definition is an electronic system that has been designed to operate as long as possible in any environment providing, elaborating and storing information without being connected to a power grid. Such a system could potentially operate in external natural or industrial environments as well as for in-vivo applications in the diagnostic and therapeutic area. Regarding to the nowadays status-of-the-art, EAS should have the ability to operate with less than hundreds of \(\mu\)W of power within less than some cubic centimeter. Examples of such systems are nomadic devices operating at ultra low power (wireless sensor networks, in-vivo sentinel and actuators, ambient intelligence devices, “smart dust”). EAS can be divided in 4 basic modules: the energy harvester, the energy storage element, the operation module and communication interface.

Over the past decade a lot of research has been dedicated to create new ways for efficient energy harvesting (vibrational, thermal, photovoltaic and RF energy based systems), circuit power management and low power RF modules. However, the available solutions for energy storage are still based on electrochemical batteries which occupy large footprint areas. Several approaches have been described for the development of micro batteries, however, none of them are fully suitable for EAS since criteria like small foot print (<1cm\(^2\)), life time (>10 years), high number of charge-discharge cycles (several thousands) and short charging time (1-10) has still not been achieved. As an alternative to batteries, electrostatic storage elements like solid-state capacitors can be an approach to supply energy to EAS. Being an electrostatic element, capacitors have the capability to deliver high power densities for a short period of time in conventional electronic circuits but also supply sufficient energy densities (0.01-1Wh/Kg) for EAS. Due to the nature of the dielectric used, capacitors can be charged very fast (1-60s), perform several thousand charge-discharge cycles and have a life time longer that 10 years. Nevertheless, to reach a minimum level of energy density to operate an EAS, the capacitor has to be made larger than the acceptable criteria for EAS.

Nowadays, self-assembly is widely accepted as a standard technique to generate complex structures on many length scales [1]. One of such self-assembly processes was reported 100 years ago when Stoney noticed that strained metal layers spontaneously “curl up into beautiful close rolls” once they detach from their host substrate[2]. It was not until a decade ago however, that the great potential of this phenomenon was recognized as appropriate for exciting new perspectives and applications in micro- and nanotechnology [3]. The self-rolling of patterned thin layers elegantly combines top-down and bottom-up approaches to generate ordered micro- and nanostructured building blocks of almost arbitrary material combinations on a single chip [4]. Applying the self-rolling phenomenon, however, we achieve an approach that is fully integrative on a chip, and components can be fabricated in parallel using well-established semiconductor processing technologies (see the fabrication scheme in Fig. 1).

![Fabrication process](image1)

**Fig. 1**: Fabrication process. (a) Deposition of the multi-stack layer. (b) The selective etching of the sacrificial layer releases the hybrid nanomembrane to form the roll-up device. (c) Illustration of a parallel array of ultra-compact energy storage elements (after [5]).

![Typical SEM images](image2)

**Fig. 2**: Typical SEM images of nanomembrane-based UCCaps highlighting the high reproducibility of the process (after [5]).
Here, we demonstrate that self-assembly methods combined with standard top-down approaches are suitable for fabricating three-dimensional ultra-compact hybrid organic/inorganic electronic devices, such as self-wound capacitors (UCCaps), manufactured in parallel on a single chip (Fig. 2) [5]. In addition to reducing the device footprint by the rolling process, the bottom metallic plate (red strip in Fig. 1) mechanically touches the top oxide layer so that the final active capacitor area increases. For a large number of rotations (N), this effect is equivalent to connecting two unrolled capacitors in parallel. Figure 3 shows the capacitance increase due to the rolling. To the best of our knowledge, the inorganic UCCaps, based on Al₂O₃ thin layers, exhibit capacitances per footprint area (see Fig. 3b) higher than their state-of-the-art planar counterparts [6] and specific energy comparable with supercapacitors (∼0.55 Wh/kg). While their small size may limit their application range to low power systems, apart from being suitable for EAS, we believe that rolled up supercapacitors with high specific energy could find many uses in stand-alone microelectronic systems where other supercapacitor structures would be far too bulky. Additionally, the incorporation of solid-state-electrolytes could lead to ultra-compact batteries extending the application range to system where shorter life time and longer charging periods are acceptable.

Due to the synthetic tailorability of molecular systems, their incorporation in inorganic elements gives rise to novel devices with almost limitless chemical and biological functionalities. To demonstrate this advantage, we have self-assembled phosphonic acid anchor groups (SAM) into the inorganic capacitor structure (Fig. 1) [5]. The integration of organic molecules provides further free parameters to tune the properties and extend the range of applications of the final self-wound device (Fig. 4). Replacing the phosphonic acids by magnetic molecules may represent a route towards organic spin-electronics in the near future.


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Precise control of thermal conductivity at the nanoscale via individual phonon scattering barriers


The ability to precisely control the thermal conductivity ($\kappa$) of a material is fundamental in the development of on-chip heat management or energy conversion applications. Nanostructuring permits to dramatically reduce $\kappa$ of single-crystalline materials, as recently demonstrated for silicon nanowires. However, silicon-based nanostructured materials with extremely low $\kappa$ are not limited to nanowires. By engineering a set of individual phonon scattering nanodot-barriers we have accurately tailored the thermal conductivity of a single-crystalline SiGe material in spatially defined regions as short as $\sim 15$ nm. Single barrier thermal resistances between $2-4 \times 10^{-9}$ m$^2$ K/W were attained, resulting in a room temperature $\kappa$ down to about 0.9 W/m-K, in multilayered structures with as little as 5 barriers. Such low thermal conductivity is compatible with a totally diffuse mismatch model for the barriers, and it is well below the amorphous limit.

Tailoring the thermal conductivity of nanostructured materials with high spatial resolution is a fundamental challenge for micro and nanoelectronics heat management, and for micro/nano scale energy conversion on a chip [1-4]. Previous work on nanoscale thermal transport has demonstrated that in some cases nanostructuring can reduce the thermal conductivity of a material below that of its disordered alloy counterpart [5-7], and can even beat the amorphous limit [8], which for a long time was believed to represent a bound to the minimum attainable thermal conductivity of a material with a given composition [9]. In dislocation-free SiGe/Si multilayered materials however, it has not been clear how low the thermal conductivity can be pushed. A plausible lower bound when the SiGe layers are very thin would be given by a model in which ballistic Si layers are separated by interfaces, or phonon barriers (the thin SiGe regions), where phonons are scattered in a completely diffusive way. This is the diffuse mismatch model, DMM, in the particular case of no acoustic mismatch between the two sides of the interface [10]. In general, however, previous works only showed a weakly diffusive behavior of the interfaces, with layer resistances lower than those predicted by the DMM. This raises the question: is it possible to achieve highly diffusive interfaces in SiGe/Si systems? Besides, most previous measurements were performed on systems above 1 $\mu$m thick and comprising over a hundred periods. Thus, it was unclear whether much thinner systems would still preserve the individually additive character of the single interface resistance, or whether ballistic effects across multiple periods might occur, rendering the concept of thermal conductivity inadequate for such thin regions [11].

We have answered the two questions above, and showed that: (1) highly diffusive interfaces can be achieved in dislocation-free SiGe/Si nanodot systems; and because of this, (2) a well defined thermal conductivity can be accurately tailored for material regions as short as $\sim 15$ nm, comprising just a small number of periods.

The studied structures (see sketch in Fig. 1a) consist of 5 and 11 layers of epitaxial Ge nanodots separated by Si spacers with thickness $t_Si$. The first island layer was obtained by deposition of about 6 monolayers (ML) Ge leading to the formation of small (105) faceted islands on top of a 3-4 ML thick wetting layer (Fig. 1c). Dots have an average height of $1.2 \pm 0.2$ nm and a surface density of $\sim 8 \times 10^{10}$ cm$^{-2}$, with a fractional area coverage of about 70%. In the upper layers, the Ge coverage was reduced in order to prevent the occurrence of misfit dislocations. In comparison with most of the previous works [7,12-14], our multilayers were grown at lower substrate temperature (500°C),
resulting in smaller dots (“hut-” instead of “dome-” and “pyramid-” shaped clusters) with higher Ge content and higher surface densities.

In order to characterize the cross-plane thermal conductivity, $\kappa$, of the samples, HPTR measurements were carried out at the University of Bordeaux on the samples with 5 and 11 Ge layers, and independent 3$\omega$ measurements were carried out at IFW Dresden on samples with 11 Ge layers, yielding results consistent with those from HPTR. The results are shown in Fig. 2, where the cross-plane thermal resistance per interface $R$ (Fig. 2a) and the thermal conductivity of all the samples (Fig. 2b) are plotted as a function of multilayer period thickness $L$. ($L$ is estimated as the sum of $t_{Si}$ and the average amount of Ge per dot layer $t_{Ge}$.)

It is illuminating to normalize the thermal resistance values of Fig. 2a by the average amount of Ge contained in each interface, given in terms of its thickness $t_{Ge}$. When this is done, one obtains a nearly constant thermal resistivity, of about 4.5 m K W$^{-1}$ for a single layer, independent on the period (Fig. 2c). This strongly suggests that transport through the Si regions is ballistic, and resistance is produced by the independent nano-dot layers: each layer acts as an individual barrier, and the total thermal resistance is the sum of the individual barrier resistances. Such a picture is consistent with the fact that the average phonon mean free path in Si is larger than a hundred nm [15]. The phonon mean free path is thus determined by scattering with the SiGe nanodots, which are arranged in individual layers, perpendicular to the direction of heat propagation, and separated by a distance $L$ between each consecutive layer. In an overly simplistic view, a fully diffusive barrier will have equal transmission and reflection probabilities of $\frac{1}{2}$, yielding the limit $\lambda \sim L$ for the mean free path. The thermal conductivity can now be evaluated as an integral over frequencies [16], obtaining the DMM limit shown by the solid line in Fig. 2b. The measured thermal resistance associated to one individual interface is around 2.5-4 · 10$^{-9}$ m$^2$K/W. This is close to the DMM value in the totally diffuse case (see Fig. 2b), and it is 2-3 times larger than the values reported in Refs. [6, 7].

The above implies that a very precise control over the thermal conductivity value of the nanostructured material can be achieved by varying the period length. As a result of the highly diffusive character of the interfaces, we are able to reach the very low thermal conductivity value of $(0.9 \pm 0.1)$ W/m-K when using periods of $\sim 3.7$ nm (5 nanodot layers separated by 4 Si spacings, with a total thickness of 15.5 nm and an average barrier resistance of 3.5 · 10$^{-9}$m$^2$K/W in this case). This thermal conductivity is the lowest reported so far for bulk-like Si or SiGe samples, and it is well below the amorphous Si
limit of 2.5 W/m-K [17]. A smaller thermal conductivity of 0.76 W/m-K was reported only for 10-nm-wide Si nanowires [18]. A value of 1.2 W/m-K was independently reported on rough Si nanowires [19].

The additive character of the individual interface thermal resistances allows us to engineer regions with accurately defined values of $\kappa$, with good spatial resolution down to the 10 nm level. In our samples, the shortest measured region was $\sim 15$ nm thick, consisting of 5 interfaces [20]. This demonstrated ability to tailor thermal conductivity with 1W/m-K precision and a spatial resolution below the 20 nm range is very relevant to the development of integrated miniaturized energy harvesting or thermal management devices, fully compatible with silicon nanoelectronics. The highly diffusive interfaces achieved permit the precise control of thermal conductivity at the local level, via the sole distance between interfaces. A similar approach could be used with other materials, thus extending the range of thermal conductivities available, and possibly being able to simultaneously tailor electronic properties as well.


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Catalytic and Biocatalytic Microbots
S. Sanchez, A. A. Solovev, S. Schulze, S. M. Harazim, Y. F. Mei and O. G. Schmidt

Introduction
The development of useful micro- or nanomachines which could one day be manipulated inside the human body, remains a challenging dream in nanotechnology and biomedicine [1]. Over the last five years, there has been substantial interest in the use of chemistry to propel tiny engines in a similar fashion that nature uses biochemistry to power biological motors [2,3].

Motor proteins powered by chemical fuel have inspired scientists to design hybrid and synthetic nano/micromachines which efficiently generate locomotion (propulsion power) autonomously from their surroundings (chemical). In eukaryotic cells, kinesin motors convert chemical energy from adenosine triphosphate (ATP) into mechanical energy to move intracellular cargo along microtubules where they “walk” [4]. These impressive molecular motors have inspired scientists to search for versatile nanomachines which can swim in diverse conditions while transporting cargo in a controlled manner.

There are three main challenges that researchers try to conquer when engineering artificial nanomachines: i) efficient self-propulsion, demonstrated by the catalytic breakdown of H2O2 by Pt [3,5], Ni [6,7] catalysts and catalase enzyme [8] contained in nanomotors; ii) motion control, achieved by the incorporation of Ni or Fe segments and subsequently using external magnetic fields to orient the nanomotors [9,10] and; iii) the development of useful task such as the transport of cargo in fluid [11].

Rolled-up microtubes containing a Pt catalyst [10] or catalase enzyme [8] in their inner layer can trigger the breakdown of the hydrogen peroxide fuel wherein they are immersed. The hollow structure generates a thrust of oxygen microbubbles in their interior released from one of the tubular openings. The motion of laminar fluid through the interior of the microtube sucks the cargo towards its front opening, permitting a large variety of microobjects to be easily transported without the need of functionalization [7].

Here we describe our recent advances on the controllable manipulation of microbots in microfluidic channels and the transport of biological material such as cells. Moreover, the coupling of catalytic biomolecules such as enzymes and artificial nano/microdevices are a promising alternative to the first generation of catalytic nanomotors containing Pt metal as a catalyst towards the finding of higher efficiency conversion, versatile configurations, more physiological conditions and biocompatible fuels.

Microbots swimming in microfluidic channels
The easy loading and delivery of cargo within a lab-on-a-chip microchannel network remains a big challenge for this class of nanomotors, motivating the search for versatile nanomachines which can swim in diverse conditions while transporting cargo in a controlled manner.

The accurate stirring of autonomous microbots swimming within PDMS microfluidic channels is shown in Fig. 1. First, the Ti/Fe/Pt microbots were suspended along with polystyrene microparticles (5 μm diameter) into a reservoir chamber (1 cm²) containing hydrogen peroxide solution (8.75 % v/v) and soap (5 % v/v). Immediately, the microbots
start to self-propel by the oxygen released from one of the openings of the microtubes as described before. The optical images in Fig. 1 depict the microbot travelling and being directed from the wide microfluidic channel (Fig. 1.A) towards the narrower areas (Fig. 1.B and Fig. 1.C) wherein microparticles are ultimately loaded and transported. As an example, a microbot against a flow of 73 μm s⁻¹ travels at 78 μm s⁻¹. This speed significantly overcomes Brownian motion, proving a high power output from the rolled-up microbots into the fabricated microchannels. The microbot’s motion is controlled by a magnetic field generated by a small NdFeB magnet bar placed underneath the microfluidic chip. The ability of artificial micromachines to swim against a continuous flow is of particular interest for future applications since living systems contain moving fluids rather than static ones (Fig. 2).

In addition, the transport of spherical particles in the flowing streams of microchips is achieved (Fig. 1.D)[12].

**Transport of animal cells**

The controlled transport of cells is of significant importance since it is clearly the next step towards the use of artificial nanomachines in future biomedical applications. Animal cells can be transported within a fluid in a controllable manner by using artificial microbots [13]. The Ti/Fe/Pt rolled-up catalytic microbot is guided towards a specific cell, which is moved to a desired location where it is released (Fig. 3, A-C). Its motion is coordinated by an external magnetic field, which –once is turned rapidly–, enables the release of the loaded cell at a desired target (small insets of Fig. 3 A-C).

We describe the pick-up, transport and release, of multiple neuronal CAD cells (Cathecolaminergic cell line from the central nervous system) in fluid by using catalytic microbots. Although “large” cells are loaded at the front end of the microbots (diameters ranging from 10 to 15 μm), their motion is not totally halted. One would expect that microbots with diameter larger than 15 μm will suck the cell through the tube body due to the fluid pumping, whereas microbots with a very small size will not be suitable for the manipulation of very large cell. Therefore, we optimized the fabrication parameters to produce microbots with diameters from 6 to 10 μm (see SEM image in Fig. 3, D).

Sophisticated micromachines are required for the performance of multiple tasks. For instance, the consecutive loading of several cells is beneficial for complex applications such as cell sorting. Therefore, high power output and easy loading mechanisms are demanded for this purpose.

**Biocatalytic microbots, increasing the power**

The versatile rolled-up technique allows on-demand fabrication of microtubes by deposition of different materials [14]. Therefore, we fabricate rolled-up microtubes containing Au as inner layer instead of Pt (i.e. Ti/Au), and modify them with an enzyme which decomposes peroxide, catalase, in a very efficient manner. By using low concentration of hydrogen peroxide (1.5 % v/v), the hybrid microengines move at 10 body length sec⁻¹ at the air-water interface compared with 1 body length sec⁻¹ from the Pt based-microengines. The high efficiency of these microengines is of significant importance.
Fig. 4: A) Open view of the hybrid biocatalytic microengine. B) Surface modification of inner Au layer and enzymatic decomposition of peroxide fuel towards the design of more powerful nanomachines. In order to bind the enzyme to the inner layer of the microtubes., we functionalized the thin Au layer with self assembled monolayers (SAM) of 3-mercaptopropionic acid (3-MPA) where the enzymes covalently bond (Fig. 4). This was the first report on the effective use of enzymes as catalysts in self-propelled microengines [8]. Moreover, as a proof of concept, the specific enzyme-binding into the microtubular structures demonstrates that new configurations can be used for autonomous motion towards the finding of more biocompatible fuels, e.g. glucose.

In summary, our work clearly indicates that our microbots could be suitable in the near future for the development of bioanalytical and biomedical applications using different kind of cells.

For instance, the microbots can be used for cell sorting or to move one single cell into an analytical device (e.g., lab-on-a-chip) to analyse the changes in biochemistry, physiology or metabolism of the single cell.

On the other hand, the hybrid biocatalytic microengines pave the way to other chemical configurations to induce motion and towards the finding of biocompatible fuels and why not, to biochemically sense their environment. This novel approach leads to faster, more powerful and more efficient microengines compared with those based on a Pt catalyst, as well as using lower concentrations of peroxide fuel.

All together, the integration of “smart and powerful” microbots with different microchip schemes can lead to multiple functions in Lab-on-a-chip devices such as the separation and sorting of drugs or cells, and also biosensing. Other visionary tasks could be the translocation of stem cells on-demand to build up new tissues or to replace disease cells or tissues.


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Direct alignment of rolled-up tubes in a fluid suspension by surface acoustic waves

X. H. Kong, Ch. Deneke, H. Schmidt, and O. G. Schmidt

Rolled-up micro-/nanotubes cover a wide range of potential on-chip applications such as optofluidic components [1], ultra-compact capacitors [2], and meta material fiber optics [3]. Apart from on-chip integration, free floating rolled-up tubes have been engineered to create self-propelling catalytic microjet engines [4]. Control over position and motion has been exerted by means of magnetic fields or confinement into small channels, but a rigorous control over whole ensembles of tubes is still challenging. Meanwhile, surface acoustic waves (SAWs) have been employed to align and control single as well as ensembles of micro-objects in a fluid [5].

Here, we demonstrate that SAWs can be used as a versatile tool to align metallic rolled-up tubes suspended in a fluid. Using carefully designed interdigital transducers (IDTs), SAWs are excited on a LiNbO3 surface. A droplet of the tube suspension is deposited between the IDTs — in the first case a two-port device, in the second case a four-port device — and tube alignment was monitored. We find that tubes can be aligned periodically, where the periodicity is defined by the wavelength of the SAW. Furthermore, tubes can be rotated and in this way manipulated by the four-port device offering rigorous control over these micro-objects in the fluid environment [6,7].

Figure 1(a) shows a schematic diagram of the two-port SAW devices in our experiments. The devices were fabricated on 128° rotated Y-cut single-crystal LiNbO3 substrates with SAW propagation along the X axis. A pair of opposing IDTs composed of Cr/Au (20/70 nm) layers were patterned on each device using optical lithography and electron-beam evaporation. The acoustic path length between the split-finger IDTs was 3.6 mm with an IDT finger-width of 16.2 μm. The IDT finger pitch was roughly 130 μm which defines the SAW wavelength \( \lambda_{\text{SAW}} \) according to the formula \( \lambda_{\text{SAW}} = \frac{\nu_{\text{SAW}}}{f} \), where \( \nu_{\text{SAW}} \) is the acoustic velocity and \( f \) is the high-frequency of the applied signal. The as-designed IDT device launched SAWs with a wavelength of 130 μm at a corresponding frequency of about 30 MHz. Signal powers were added to the IDT device by two signal generators for the tube alignment experiments where each signal generator provided a 0 - 13 dBm output power at 30 MHz.

Rolled-up Cr microtubes with lengths of 30, 50, and 80 μm were used in our study (tube layer thickness and tube diameter were 10 nm and 7 – 9 μm, respectively). For the experiments, one drop of PC-solvent (propylene carbonate) followed by a drop of tube suspension were placed in the capillary gap between the LiNbO3 substrate and a glass cover, as illustrated in Fig. 1a. The PC-solvent was applied to decrease the liquid evaporation. The glass cover was pressed onto the tube suspension parallel to the substrate surface with a spacing of 50 μm or less in order to create a microfluidic channel. SAW induced motion of the microtubes was monitored by an optical microscope connected to a high speed camera.

At the start of each experiment, the rolled-up microtubes in the fluid are randomly dispersed on the LiNbO3 substrate, as shown in Fig. 1b. When two rf-signals of 30 MHz with equal power are applied to the two IDT ports simultaneously, a standing SAW pattern forms on the LiNbO3 surface. Under this condition, the rolled-up metallic Cr microtubes are aligned in one direction, with their axis parallel to the propagation direction of the SAWs, as seen in Fig. 1c. Furthermore, it is observed that Cr tubes are located in equi-spaced columns perpendicular to the SAW propagation direction, similar to particle alignment reported previously. These columns are marked by the green dashed lines in Fig. 1c. The space between the columns is around 65 μm, close to \( \lambda_{\text{SAW}}/2 \), corresponding to the separation of the SAW standing wave nodes.

Interestingly, Cr tubes are able to link together and form bridges by increasing the tube concentration. As shown in Fig. 1d, linked Cr tubes appear as shorter or longer micro...
chains, parallel to the SAW propagation direction. Up to 17 Cr tubes can be linked together (Fig. 1e), forming a long tube-chain.

A set of sequential optical images obtained from a video is depicted in Fig. 2 to display the dynamic process of the tube-chain formation. Once the rf-signal power is activated, the randomly dispersed Cr tubes are immediately (in 0.2 s) aligned parallel to the SAW propagation direction. Only those tubes strongly adhering to the substrate need more time to be aligned, such as the one pointed at by the red triangle (1.2 s). Once aligned, the tubes are in a thermodynamically metastable state and oscillate inside well defined columns (green dashed lines) due to a microfluidic background flow and mechanical vibration forces caused by the SAWs. When the instability of a tube’s position is too large, the tube moves to a neighboring column. As shown in Fig. 2, the tube marked by the red triangle originally oscillates around column 2 for about 1.2 s. It hops to column 3 (2.4 s) and later to column 4 after leaving its initial equilibrium position. Subsequently, it leaps to column 5 (7.2 s) and attaches to another tube there. Finally, the two tubes are linked together and oscillate as a whole entity. Similar behavior is observed for the tube marked by the blue triangle in Fig. 2. It oscillates around column 3 originally, then jumps to column 4 and connects with another tube. Afterwards the two merged tubes connect with a third tube (marked by the green triangle) and form a small tube-chain. Longer tube-chains are formed in a similar way.

By systematically tuning the experimental conditions, we find out that the percentage of microtubes aligned by SAWs at a certain frequency depends on the size of the tubes and the applied signal power. Cr tubes with equal layer thicknesses and diameters, but with lengths less than $\lambda_{SAW}/2$ are easier aligned than those being longer than $\lambda_{SAW}/2$. Additionally, tubes align faster when the applied rf-signal power is increased.

To obtain further control over the microtubes in solution, a four port device is used. In this case, two IDT pairs are perpendicular to each other allowing for exciting the SAW field along both major directions of the substrate parallel to the edges.

In Fig. 3 the 90° rotation process of Cr tubes by a single switching of SAW propagation direction is demonstrated. At the beginning (0 s) tubes are aligned in the x-direction due to the SAW propagation along this direction. Then the signal power for the x-directed IDT is turned off and the y-propagating SAW is activated. Consequently, tubes begin to rotate gradually. The adhesive force from the substrate and a cover slip as superstrate is the main resistance for the tube rotation. Some tubes with less adhesion to the environment can be rotated easier (e.g. No. 3, 4, 5, 10). Most tubes can be finally rotated with time going on. Of the ten tubes shown in Fig. 3, five tubes (No. 1, 3, 4, 5, 10) rotate clockwise while the other five (No. 2, 6, 7, 8, 9) rotate counter-clockwise.
Rotation direction is determined by the balance of moments from dielectrophoresis [6] and the viscosity of the tube solution at the beginning of SAW propagation. In this SAW-based operation, the angular tube orientation is manipulated at certain places by the formation of a proper piezoelectric field distribution only, whereas the lateral tube location can be only affected by the fluidic flow caused by SAW-induced acoustic streaming.

The different kinds of relationships between rotational tube alignment and corresponding SAW propagation are summarized in Fig. 4. The basic operation modes are illustrated by the upper three cases: If SAW (counter-)propagate along one direction, metallic tubes can be aligned with their axis parallel to the SAW direction due to the presence of a well-defined piezoelectric field. But if SAW propagate along two or more directions (for example, if power signals were applied to all four ports simultaneously), the tubes will not be aligned. If the SAW propagation direction is switched after proper tube alignment, the tubes will rotate accordingly until their axes are parallel to the current SAW propagation direction. This behavior can be repeated many times, as far as the dielectrophoretic force is strong enough to overcome the tube adhesion to substrate and cover slip, respectively (Fig. 4, lower cases).

The SAW-based dielectrophoretic manipulation of rolled-up metallic microtubes in a microfluidic system was demonstrated. Within this setup, the SAW-induced piezoelectric fields act as contactless tweezers for sensitive manipulation of the angular tube orientation as well as of their lateral location. In this sense, SAW-controlled microtube manipulation opens up new perspectives for on-chip microfluidic applications.

**Fig. 4:** Relation of the tube alignment and rotation in relation to the SAW propagation direction.

<table>
<thead>
<tr>
<th>SAW Direction</th>
<th>Tube Alignment Type</th>
<th>SAW Switch</th>
<th>Tube Rotation Type</th>
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<tr>
<td>↖ ← ↖</td>
<td>![Diagram of tube alignment]</td>
<td>![Diagram of SAW switch]</td>
<td>![Diagram of tube rotation]</td>
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MgB₂ superconducting wires with high critical current density for MRI magnets

MgB₂ was found to be superconducting with a critical temperature $T_c$ of 39 K, the highest value found amongst the common metallic compounds. Therefore the potential operating temperature range is between the one of low temperature superconductors like NbTi or NbSn₃ and high temperature superconductors like YBCO and BSCCO. Two properties are recognized to be crucial for potential applications: the lack of weak-link behaviour and the capability of the microstructure of MgB₂ to allow for an effective flux pinning. Whereas the applicability of NbTi and NbSn₃ is limited to operating temperatures around 4 K, MgB₂ can be operated even at temperatures above 10 K and is therefore cost-effectively useable in cryogen-free systems (refrigerator cooling).

Already reported high upper critical fields and large critical current densities [1,2] as well as the low cost of the constituent elements makes the material a candidate for superconductor applications including MRI-magnets [3]. Prototypes such as current leads in a Japanese satellite and a liquid Hydrogen level sensor [4] have been presented already.

The material is in an early stage of commercialization. Two pre-commercial prototype producers of MgB₂-wires are on the market, Columbus Superconductors in Italy [5] and Hypertech in the USA [6]. In this context, IFW is cooperating in the development of MgB₂ wires with Bruker EAS in Hanau, one of the world leading producers of superconductors [7].

The IFW has a long standing experience in the preparation and characterization of MgB₂-wires in the laboratory scale [8-10]. The distinctive feature of our technology is the usage of mechanically alloyed precursor powders.

Mechanical alloying is an excellent technique to adjust the microstructure in the MgB₂ precursor powder. The basic principle of this method is shown in Fig. 1. The resulting nanocrystalline particle size serves for a high amount of grain boundaries acting as pinning sites and therefore is beneficial to obtain high critical current densities in the material.

Facing the challenge of introducing MgB₂ wires and tapes into application, it is also essential to adapt its preparation to the industrial scale. Only a reasonable interplay of both key parameters, current carrying capability and an appropriate preparation route, will allow for a widespread use of MgB₂ conductors. To allow for a reliable production of MgB₂ wires on the kilometer scale, it is indispensable to make use of a precursor which can be deformed properly within the sophisticated architecture of a conductor as required for all different aspects of the application.

The deformability of the precursor strongly depends on the powder morphology, which can be tailored by the imparted energy during ball milling. Fig. 2 (left side) shows a series of SEM micrographs of the as milled precursors with varying milling energy from gently mixed powders (50 J) to extreme processing conditions (10 MJ), an intermediate energy level (0.3 MJ) is shown also.

All stages of a mechanically alloyed ductile-brittle powder system are present. With increasing imparted energy, from mixing to high energy mechanical alloying, an ongoing refinement of the powder can be observed. Additionally, an increasing homogeneity and also a higher densification of the precursor powder can be obtained, as can be seen from the longitudinal images of the as prepared wires in Fig. 2 (right side). At the same time
the flowability of the powder within the sheath material and therefore the deformability of the conductor as a whole will deteriorate when used in the conductor preparation. This is also shown by the misshaping of the filament cross-section and the formation of shear-bands in the filament of the wire with the precursor of the highest imparted energy (10 MJ).

The critical current density of tapes prepared from precursors with varied milling treatment show clearly that an increasing imparted energy results in a higher ampacity of the conductor (Fig. 3). This is explained by the declining crystallite size due to the intensification of the mechanical alloying resulting in an increasing number of grain boundaries acting as pinning sites in the material. Furthermore it is shown that independently from the set of processing parameters, the total amount of imparted energy transferred is determining the critical current density of the MgB$_2$. This is shown by the $j_c$-curves of tapes prepared with an imparted energy of approximately 0.3 MJ, but clearly different processing parameters in terms of milling time, speed and ball-powder-ratio.

The used standard preparation setup (250 rpm, 50 h, ball-powder-ratio of 36) equals an imparted energy of around 5 MJ, representing a compromise of high performance and adequate deformability at the same time.

Wires were prepared using the powder-in-tube-technique (PIT). As sheath materials for the monofilamentary wires a double tube of Nb as diffusion barrier in an ODS-Cu-tube is utilized. The filled tube is deformed by swaging. For the preparation of multifilamentary tapes 21 monofilamentary wires were stacked in an outer Monel-tube. This compound is deformed further. First deforming steps are carried out by swaging. Starting at a diameter of about 7 mm the deformation is switched to wire drawing. It has to be mentioned that interstage annealing has to be applied in the temperature range of 300°C to 500°C in Ar atmosphere to reduce work hardening respectively to decrease mechanical stresses in the sheath. The final diameter of the wire is 0.85 mm, a typical cross-section of such a multifilamentary wire is shown in Fig. 4.

Wire drawing of such a compound material with nanocrystalline precursor powder is a sophisticated process, because the precursor powder is already reacting to MgB$_2$ at temperatures $>$ 500°C. Thus an increasing hardness of the filaments is degrading the drawing ability of the conductor. Therefore the drawing process has to be optimized by applying an optimal cycle of deformation/annealing steps using an appropriate lubricant.

The final heat treatment for the complete formation of MgB$_2$ is carried out in Ar at temperatures between 550°C and 700°C. With the best combination of peak temperature,
dwell time and heating/cooling rates engineering critical current densities $j_e$ of 170 A/mm² at short samples could be realized. Medium length samples obtained $j_e$-values of 120 A/mm² in a magnetic field of 5 T at 4.2 K. At 20 K a critical current density of about 50 A/mm² was found at fields of 3 T. The n-value at 4.2 K is about 40 for magnetic fields ≤ 5 T.

The collaboration with Bruker EAS succeeded in the preparation of a single piece multifilamentary wire exceeding a 1000 m in length (Fig. 5) with a $j_e$ of up to 91 A/mm² at 4.2 K and 5 T. In Fig. 6 the $j_e(B)$-curves of a wire with 21 filaments at 4.2 K are shown in comparison to commercial wires.

This conductor, using a mechanically alloyed in-situ MgB₂ precursor prepared at the IFW, was manufacturedly under industrial production conditions at Bruker EAS. The wire was already successfully twisted for reducing the AC-losses and the thermal stabilization was improved by the wire-in-channel-technique (soldering of the wire into a Cu-profile). One focal point of further development of wires is the increasing of the filling factor from 10 % to about 20 % to further increase the engineering critical current density.


Cooperation: Bruker EAS GmbH (Hanau), Slovak Academy of Science - Institute of Electrical Engineering (Bratislava)

Funding: Bruker EAS GmbH, DAAD, NESPA
Application Laboratory for Metastable Alloys
W. Pfeiffer, U. Kühn

Leibniz application laboratories stand for a new technology transfer initiative of the Leibniz Association. They represent a platform permitting potential customers and cooperation partners from industry and public areas to receive information on application-oriented research results, and to prepare the transfer of such results to practical applications in the form of projects and joint ventures.

IFW Dresden operates the Leibniz application laboratory "Amorphous Metals". Considering the unique properties of amorphous metals, also known as "metallic glasses", they can be advantageously used in a wide range of applications. The recognition of the research results achieved so far in this field – they were awarded the 2009 Leibniz Prize – reflects the great expectations of the industry regarding the utilization of these results. Therefore, it is the purpose of an IFW project initiated under the "industry meets science" research program, to apply and improve in industrial applications manufacturing technologies that have so far been primarily oriented toward scientific research and communication, and to create and present multi-faceted practicable application schemes for amorphous metals by using the IFW plant and equipment existing in a Leibniz application laboratory as is detailed below.
In particular, the equipment added in previous years for doing research work on these innovative materials - for example special melting and casting equipment, rapid solidification as well as modern rapid prototyping equipment - is planned to be efficiently used also for making prototype products. In this context, the project will focus on the addition to previously applied technologies of a hot-rolling process for amorphous sheet metals and an impact extrusion process for complex amorphous components. What is most important, however, is the establishment of an application centre, e.g. in the form of an exhibition area, which aims at improving communication with the industry and uses specific marketing activities to this end.

The funding received for the implementation, and carrying out the work required in the project phase of approx. 2 years (July 2009 – June 2011) amount to kEUR 360. The persons financed in connection with the technology transfer project work in close cooperation with the scientists in the field so as to ensure the proper implementation of the work schedule.

Essential activities within this project were the enlargement of the presentation area and the provision of more exhibits as a basis for the permanent establishment of the application laboratory for the purpose of permitting especially small and middle sized companies the access to research and development technologies as well as production resources that are mature to be used in practical applications. This goal was reached in October 2010, and the show and advisory service space so created can now be made use of by the scientists.

Under aspect of an economic utilisation of the technologies the research fields and work teams have been subdivided into following development lines:

- Casting of amorphous metal alloys
- Thermoplastic forming
- Selective laser melting (SLM)
- High-strength iron base alloys

The objective of the “casting of amorphous metal alloys” development line is to translate the current know-how of massive metallic glasses in such a way that it can be used in the two technologically oriented development lines „thermoplastic forming” and „3D laser melting” for the development of marketable semi-finished products and prototypes. In the process, the characteristic properties of amorphous metal alloys, such as high hardness, near-net-shape castability, elastic formability and/or good corrosion behaviour shall be maintained or even improved. Another objective is the optimisation of the alloy systems in dependence of the economic and ecological requirement profile.
The "thermoplastic forming" line aims at transferring for the first time production methods known from the plastics and glass industry to the processing of massive metallic glasses, thus permitting metallic glass components to be produced economically and in large quantities. This approach is based on the particularity that in a certain temperature range metallic glasses can be processed in the same way as conventional (oxidic) glass or polymer materials. It is the goal of the research team to develop automatable manufacturing processes in which, starting from a suitable semi-finished product (granulate), a component can be manufactured in a few production steps and in large numbers.

It is the purpose of the "3D laser melting" line to transfer this technology from conventional metallic alloy systems to massive moulded bodies of metallic glass. Using conventional metal powders, this 3D laser melting process is meant to allow the manufacture of components featuring complex structures on the one hand, and offer new potentials for the economical production of prototypes and small batches of metallic glass components on the other.

The "high-strength iron base alloys" line is designed to develop innovative iron-based materials with extreme mechanical properties, and to lay the foundation for their use in practical applications. This class of materials is characterized by high hardness, high strength, high wear resistance, a high energy absorption potential and good plasticity, and is therefore ideal for a wide range of applications. First tests carried out in industry, in which these materials were used for cutting tools and wearing parts of building machinery (digging teeth), showed that their tool life was up to ten times longer than that of conventional materials.

As a result of the project, it will be possible to manufacture and design a much greater range of simple components and semi-finished products of metallic glass which will facilitate the transfer of the technology for industrial applications.