Unconventional superconductivity

Christoph Geibel [#], Andy Mackenzie, Mark E. Barber, Manuel Brando, Sandra Hamann, Clifford Hicks, Fabian Jerzembeck, Markus König, You-Sheng Li, Michael Nicklas, Helge Rosner, Alexander Steppke, Lishan Zhao

The research on superconductivity in our department focus on compounds which feature exotic properties very different from those expected and observed in standard superconductors. This makes these so-called unconventional superconductors paradigmatic systems for developing and testing new theories and thus, on a general level, for advancing our understanding of solid state physics. We are interested in very different kinds of systems, ranging from rare earth based intermetallic compounds to metallic oxides and including transition metal pnictides. Our department has specialized on the study of their magnetic, thermodynamic and transport properties at low temperatures, under magnetic field and under pressure, but other properties are studied as well, in collaboration with other groups all over the world. Recent highlights are the observation of superconductivity at 2 mK induced by a hybrid nuclear electronic order in the quantum critical system $YbRh_2Si_2$, the discovery of an unexpected fully gapped superconducting order parameter in the heavy fermion system $CeCu_2Si_2$, investigation of the interplay between density wave physics and bulk superconductivity in the cuprates and the $Lu(Pt_{1-x}Pd_x)_2In$ system and the demonstration of a huge effect of uniaxial strain on the superconductivity in Sr_2RuO_4.

The prominent feature which, at a conceptual level, distinguishes unconventional superconductors (SC) from standard ones is the symmetry of the SC order parameter, which in unconventional SC has a lower symmetry than the underlying crystalline structure. In a standard SC the superconducting gap, which can be taken as the SC order parameter, has the same sign for all directions of the electronic momentum, and is therefore named s-wave. In contrast in unconventional SC´s, the sign of the SC gap may e.g. change with the direction of the electronic momentum. This results in p-, d-, or even f-wave SC order parameters, depending on its angular dependence. Along the directions of sign change the gap has to disappear. The resulting nodes in the order parameter have a strong effect on many properties of the SC state. In unconventional superconductors the pairing mechanism is thought to differ from the standard electron phonon coupling. Generally a magnetic origin of the pairing interaction is favored, but in most cases this is still under strong debate and there is yet no consensus.

$CeCu_2Si_2$ was the first discovered unconventional superconductor [1]. It belongs to the family of Kondo lattices (KL), for which there are particularly strong reason to favor a p- or d- wave SC order parameter instead of an s-wave. KL are intermetallic compounds based on the rare earth elements Ce or Yb which feature strongly localized 4f electrons with a huge Coulomb repulsion U between f electrons on the same site. Accordingly, forming a bound state between two 4f electrons at the same site, which in a simple approximation would correspond to an s-wave, is very unlikely. Instead one expect the formation of bound states to occur between distant 4f electrons, which in a simple picture corresponds to a p- or a d-wave state. Thus the discussion of SC order parameters in KL almost exclusively focused on non-s-wave ones, especially d-wave. For the most extensively studied family of KL superconductors, the $CeTIn_5$ with T = Co, Rh, Ir compounds, there is indeed very strong experimental evidence that the SC order is a d-wave one [2, 3]. For long time the SC order parameter of $CeCu_2Si_2$ was also thought to be one of the standard d-wave type, although it was not clear which one.

However, in 2014 a study of the specific heat of a superconducting $CeCu_2Si_2$ single crystal performed in a joint project between our Institute, the Institute of Solid State Physics (ISSP) in Tokyo, and further groups in Japan provided clear evidence for a fully gapped SC order parameter without nodes [4]. This was in strong disagreement with all previously considered d-wave order parameters, which where all expected to present nodes. This result, at odds with prevailing views, prompted new experimental studies to get more information on the SC order parameter in $CeCu_2Si_2$ as well as theoretical studies with new proposals for the nature of its SC state [5-12] (see also reports {Stockert} and {report Steglich}). An international team formed by our department, the group of Prof. Yuji Matsuda at the Kyoto University, the group of Antony Carrington at the University of Bristol, and further groups in France and Japan studied the London penetration depth $\lambda(T)$ and the thermal conductivity $\kappa(T)$ in the SC state of $CeCu_2Si_2$ [8]. The large exponent we observed in the T dependence of $\lambda(T)$ well below T_c (Fig. 1), as well as the very weak field dependence of $\kappa(T)$ for different directions of the thermal gradient and of the applied field [8] (not shown) provided further very strong evidence for the absence of nodes in the SC order parameter of $CeCu_2Si_2$. In a second step the same team studied the effect of irradiation on T_c, on the penetration depth λ(T) and on the residual resistivity [8, 9]. This study demonstrated that in $CeCu_2Si_2$, the superconducting state is extremely robust against radiation induced disorder. Thus not only T_c survives an increase of the residual resistivity to above 100 μΩcm (Inset of Fig. 1), but more importantly, the exponent in the T dependence of the penetration depth λ(T) stays well above 2 even in strongly irradiated samples with $\rho_0 > 100$ μΩcm (Fig. 1). This indicate the absence of impurity-induced low-energy states in irradiated superconducting $CeCu_2Si_2$, which is an evidence for the absence of sign change in the SC order parameter. In connection with further properties observed in the course of this study, it led to the conclusion that the SC order parameter in $CeCu_2Si_2$ has s-wave symmetry. This met strong skepticism in much of the community,

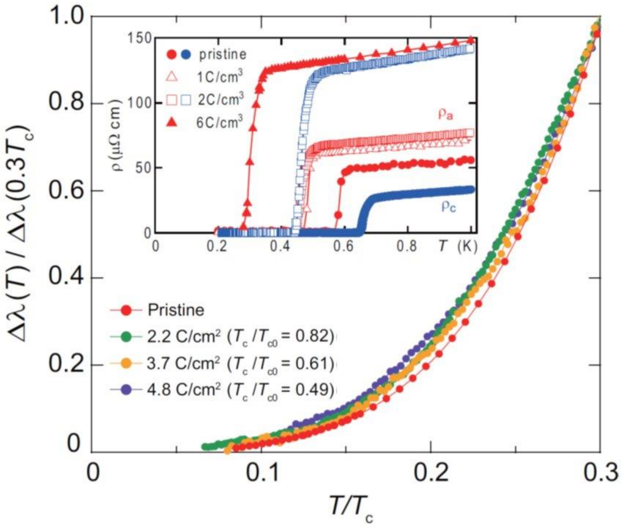

Fig.-1: Temperature dependence of the penetration depth λ(T) for pristine and irradiated $CeCu_2Si_2$ [8]. The increase in λ(T) with T reflects the abundance of low-energy electronic excitations. The strong curvature observed in the T-range well below T_c for both pristine and irradiated samples corresponds to a high exponent in a power law fit, indicating the absence of impurity- and defect-induced low energy states. Inset: T dependence of the resistivity along the basal plane (ρ_a) and the c direction (ρ_c) of the tetragonal structure in pristine and in irradiated $CeCu_2Si_2$ [9]. Bulk superconductivity with sizeable T_c is observed in irradiated samples even when the residual resistivity has been raised to values > 120 μΩcm, indicating the SC to be insensitive to potential scattering.

since an s-wave was generally supposed to be incompatible with the large coulomb repulsion between 4f electrons. However, one should note that in a recent study of the Kondo lattice model based on the sophisticated dynamical mean field approach, O. Bodensiek et al. found very robust s-wave superconductivity [13].

The absence of gap nodes in the SC order parameter of $CeCu_2Si_2$ has meanwhile be confirmed by a further study of the penetration depth [11], as well as by a recent NMR study [10]. Therefore a fully gapped SC order parameter can now be considered as well-established in $CeCu_2Si_2$. In contrast there is a strong and controversial debate on whether the order parameter presents a change in sign or not. In the course of this debate it became clear that all the experimental results which were previously considered to be the "smoking gun" for a change in sign of the SC order parameter do not have the significance they were claimed to have. Thus our surprising new results on the superconducting state of $CeCu_2Si_2$, with the strong challenge that they present for established theories, revived the field of heavy fermion superconductivity and stimulated new theoretical approaches.

The Kondo lattice $YbRh_2Si_2$ is a very prominent system in the field of quantum criticality [14]. In this compound the competition between a strong Kondo screening interaction and the RKKY intersite exchange shifts the antiferromagnetic ordering temperature T_N to merely 70 mK and reduces the size of the ordered moment to tiny 0.002 μB. This places this compound in immediate proximity to the quantum critical point (QCP) separating the magnetic ordered from the paramagnetic ground state. Although unconventional superconductivity is commonly observed at QCP´s, and high quality samples with low residual resistivity are available, no evidence for superconductivity had been observed in $YbRh_2Si_2$ until recently. In a long-standing cooperation between our department and E. Schuberth at the Walther-Meissner Institute in Munich, we achieved to measure the magnetic susceptibility of this compound down to a temperature of about 0.7 mK [15]. Anomalies in the ac and dc susceptibility observed with different set ups and on different single crystals provide clear evidence for the presence of 2 magnetic transitions at 10 mK and at 2 mK (Fig. 2), and preliminary evidence that the transition at 2 mK is connected with the onset of superconductivity [15] (see also report Steglich). The extremely low ordering temperatures suggests the nuclear moments of Yb to play an important role.

Comparing the relevant hyperfine coupling strength with the relevant electronic magnetic energy scales indeed indicate that they are of similar magnitude. Therefore, the 2 mK transition was proposed to be a hybrid nuclear-electronic order, and the 10 mK transition to be a precursor [15]. A hybrid nuclear-electronic transition which combines magnetism and superconductivity is a unique situation in solid state physics.

However, a deeper analysis and understanding of the nature of these transitions is prevented by the very limited information provided by the present susceptibility measurements. It is essential to collect more experimental information. An independent proof of superconductivity based on resistivity measurements is e.g. highly desirable. A resistivity measurement seems to be a rather simple and standard task, but this is only the case for temperatures above 20 mK. At lower temperature it becomes an extreme challenge, because the tiniest amount of energy dissipated in the sample results in enough heating to prevent reaching these very low temperatures, the critical dissipation power level being of the order of 0.01 pW. The major problem arises from the resistance at the current contacts to the sample. An approach to overcome this problem is to replace the standard bar shaped sample by a micro-structured meander. Because of the much smaller cross-section and the increased length of the current channel, the same voltage drop can be obtained using a much smaller current and thus strongly reducing the power dissipated at the current contacts. The challenge is to avoid a deterioration of the sample during the micro structuring process. After some optimization we are now able to prepare meanders with very high quality (Inset of Fig. 3). This is evidenced by the T dependence of the resistivity and a high resistivity ratio, which are both the same in the micro-structured meander as in the original bulk single crystals (Fig. 3). These micro-structured samples are now being used for further measurements in the 1 - 10 mK range in the group of Prof. John Saunders at Royal Holloway, University of London. The results of these experiments will be crucial for determining the nature of the transitions in $YbRh_2Si_2$ and obtaining an insight into the underlying mechanism.

Another major avenue of research on superconductivity is motivated by the continued quest to understand the order parameter of the celebrated *p*-wave candidate material Sr_2RuO_4 [16]. The realization that the ability to apply both compressive and tensile uniaxial pressure to Sr_2RuO_4 would give important new insights to this decades old problem provided the primary motivation for the development by members of this department of an entirely new concept for how to perform uniaxial pressure measurements [17, 18]. This technology has formed the basis for on-going technical advances discussed in (report Hicks) and has also led to the surprising observation that the T_c of Sr_2RuO_4 can be raised by a factor of 2.3 if the *a* or *b* axis is strained by approximately 0.6% [19]. This is accompanied by a large increase of the critical field H_{c2} for magnetic fields applied perpendicular to the conducting planes and a much more modest one for fields applied in-plane. Taken together, and combined with theoretical analysis from the group of Steve Simon at Oxford University, these findings suggest the possibility of an order parameter change from *p*-wave at zero stress to *d*-wave in the highly strained samples. We are following this work up with extensive investigations into critical fields, specific heat, muon spin rotation (in collaboration with the TU Dresden group of Hans-Henning Klauss), scanning SQUID

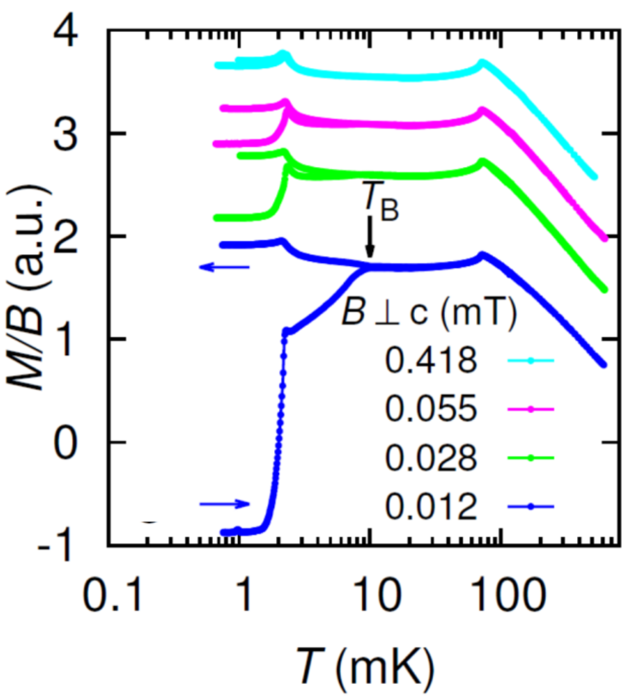

Fig.-2: dc susceptibility of $YbRh_2Si_2$ in the temperature range 0.1 mK < T < 600 mK [15]. The negative value of the zero-field-cooled susceptibility below 2 mK and its large increase when approaching 2 mK are preliminary evidence for a Meißner-Ochsenfeld effect due to the formation of a superconducting state below 2 mK. The peak observed at 2 mK at higher fields indicate the onset of the hybrid nuclear-electronic order at 2 mK. The opening of the hysteresis at T_B =10 mK in low field is likely a precursor transition.

microscopy (in collaboration with Kathryn Moler's group at Stanford) and nuclear magnetic resonance (in collaboration with Stuart Brown's group at UCLA). The new 'high-T_c' Sr_2RuO_4 that we can create with our uniaxial pressure has therefore added a new dimension to research on this material, and we anticipate further research on the strained material in the years to come.

Among further results on superconductivity obtained in our department, two are of special interest, since they evidence completely different kinds of unconventional superconductivity. In the alloy $Lu(Pt_{1-x}Pd_x)_2In$, we observed a strong enhancement of the superconducting transition temperatures just at a Charge Density Wave Quantum Critical Point, indicating a new type of interaction between charge density fluctuation and superconductivity. These results are presented and discussed in (report Brando). The compound $LaNiGa_2$ attracted some interest because a μSR study observed the breaking of time reversal symmetry at the onset of superconductivity [20]. We performed a detailed study of its superconducting properties, which provided strong evidence for a two-gap nodeless SC order parameter instead of the nodes expected from the breaking of the time reversal symmetry. In order to reconcile the seemingly contradicting experimental results we proposed a novel triplet superconducting state based on interband pairing [21].

Further results of what we believe to be considerable significance have been obtained from collaborative work on cuprates with the group of Séamus Davis at Cornell, with the leading PhD student, Stephen Edkins, co-supervised by Davis and Andy Mackenzie. In this work, important results on the form factor of the cuprate density wave [22] were followed by an innovative experiment demonstrating the feasibility of scanned Josephson spectroscopy, in which a Josephson junction instead of a standard tunnel junction is established between tip and sample. Scanned Josephson spectroscopy had been achieved previously using conventional superconducting tips [23, 24], but in this experiment it was shown that a flake of high-T_c superconductor can be picked up in-situ and used to terminate a conventional tip, producing Josephson tunneling between two large-gap superconductors. The excellent spatial resolution achieved in the research further enabled the first direct observation of a spatially modulated Josephson current, the expected signal from the long-sought pair density wave [25].

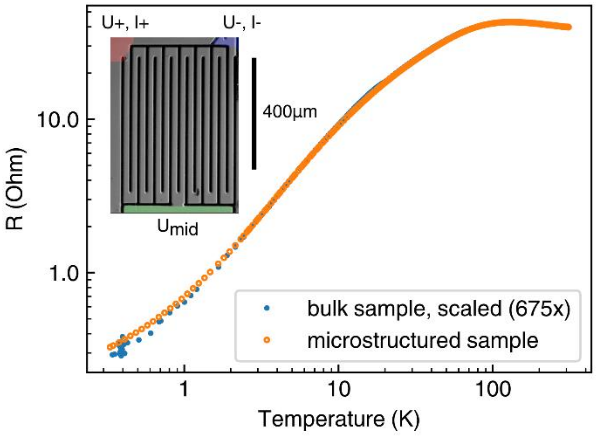

Fig.-3: Temperature dependence of the resistivity of the $YbRh_2Si_2$ meander shown in the inset, and of the original bulk single crystal it was made from. The perfect overlapping of both curves demonstrates that the micro-structuring process do not lead to a degradation of the $YbRh_2Si_2$ material. The very large residual resistivity ratio of about 270 in both the meander and the single crystal demonstrate that both are of very high crystalline quality.

External Cooperation Partners

K. Machida (Ritsumeikan University, Japan); T. Sakakibara (ISSP, Japan) ; Y. Matsuda (Kyoto University, Japan) ; T. Shibaudi (University of Tokyo, Japan) ; A. Carrington (University of Bristol, Great Britain); K. Ishida (Kyoto University, Japan); E. Schuberth (Walter Meissner Institute, Garching, Germany); Q. Si (Rice University Houston, USA); C. Krellner (University Frankfurt, Germany); J. Saunders (RHUL London, UK); H. Q. Yuan (Zhejiang University, China); J. C. Davis (Cornell, USA); H.-H. Klauss (TU Dresden, Germany); K. Moler (Stanford); S.E. Brown (UCLA, USA)

References

[1] *Superconductivity in the presence of strong Pauli Paramagnetism: $CeCu_2Si_2$, F. Steglich, J. Aarts, C. D. Bredl, W. Lieke, D. Meschede, W. Franz and H. Schäfer, Phys. Rev. Lett.* ***43*** *(1979) 1892.*

[2] *Angular position of nodes in the superconducting gap of quasi 2D heavy fermion superconductor $CeCoIn_5$, K. Izawa, H. Yamaguchi, Y. Matsuda, H. Shishido, R. Settai and Y. Onuki, Phys. Rev. Lett.* ***87*** *(2001) 057002.*

[3] *Visualizing nodal heavy fermion superconductivity in $CeCoIn_5$, B. B. Zhou, S. Misra, E. H. da Silva Neto, P. Aynajian, R. E. Baumbach, J. D. Thompson, E. D. Bauer and A. Yazdani, Nature Physics* ***9*** *(2013) 474.*

[4]* *Multiband superconductivity with unexpected deficiency of nodal quasiparticles in $CeCu_2Si_2$, S. Kittaka, Y. Aoki,*

Y. Shimura, T. Sakakibara, S. Seiro, C. Geibel, F. Steglich, H. Ikeda and K. Machida, Phys. Rev. Lett. ***112*** *(2014) 067002.*

[5] *Emergent Loop-Nodal s+/- -wave superconductivity in $CeCu_2Si_2$: Similarities to the iron-based Superconductors, H. Ikeda, M. T. Suzuki and R. Arita, Phys. Rev. Lett.* ***114*** *(2015) 147003.*

[6]* *Thermodynamic study of gap structure and pair-breaking effect by magnetic field in the heavy-fermion superconductor $CeCu_2Si_2$, S. Kittaka, Y. Aoki, Y. Shimura, T. Sakakibara, S. Seiro, C. Geibel, F. Steglich, Y. Tsutsumi, H. Ikeda and K. Machida, Phys. Rev. B* ***94*** *(2016) 054514.*

[7]* *Superconducting gap and vortex lattice of the heavy-fermion compound $CeCu_2Si_2$, M. Enayat, Z. Sun, A. Maldonado, H. Suderow, S. Seiro, C. Geibel, S. Wirth, F. Steglich and P. Wahl, Phys. Rev. B* ***93*** *(2016) 045123.*

[8]* *Fully gapped superconductivity with no sign change in the prototypical heavy Fermion $CeCu_2Si_2$, T. Yamashita, T. Takenaka, Y. Tokiwa, J. A. Wilcox, Y. Mizukami, D. Terazawa, Y. Kasahara, S. Kittaka, T. Sakakibara, M. Konczykowski, S. Seiro, H. S. Jeevan, C. Geibel, C. Putzke, T. Onishi, H. Ikeda, A. Carrington, T. Shibauchi and Y. Matsuda, Science advances* ***3*** *(2017) e1601667.*

[9]* *Full-Gap superconductivity robust against disorder in heavy-fermion $CeCu_2Si_2$, T. Takenaka, Y. Mizukami, J. A. Wilcox, M. Konczykowski, S. Seiro, C. Geibel, Y. Tokiwa, Y. Kasahara, C. Putzke, Y. Matsuda, A. Carrington and T. Shibauchi, Phys. Rev. Lett.* ***119*** *(2017) 077001.*

[10]* *Magnetic and superconducting properties of an s-type single-crystal $CeCu_2Si_2$ probed by ^{63}Cu nuclear magnetic resonance and nuclear quadrupole resonance, S. Kitagawa, T. Higuchi, M. Manago, T. Yamanaka, K. Ishida, H. S. Jeevan and C. Geibel, Phys. Rev. B* ***96*** *(2017) 134506.*

[11] *Fully gapped d-wave superconductivity in $CeCu_2Si_2$, G. Pang, M. Smidman, J. Zhang, L. Jiao, Z. Weng, E. M. Nica, Y. Chen, W. Jiang, Y. Zhang, W. Zie, H. S. Jeevan, H. Lee, P. Gegenwart, F. Steglich, Q. Si and H. Yuan, PNAS 1720291115 (2018).*

[12] *Gap Symmetry of heavy fermion superconductor $CeCu_2Si_2$ at ambient pressure, Y. Li, M. Liu, Z. Fu, X. Chen, F. Yang and Y. F. Yang, arXiv:1801.01690.*

[13] *Unconventional superconductivity from local spin fluctuations in the Kondo lattice, O. Bodensiek, R. Zitko, M. Vojta, M. Jarell and T. Pruschke, Phys. Rev. Lett.* ***110*** *(2013) 146406.*

[14]* *The break-up of heavy electrons at a quantum critical point, J. Custers, P. Gegenwart, H. Wilhelm, K. Neumaier, Y. Tokiwa, O. Trovarelli, C. Geibel, F. Steglich, C. Pepin and P. Coleman, Nature* ***424*** *(2003) 524.*

[15]* *Emergence of the canonical heavy-electron metal $YbRh_2Si_2$, E. Schuberth, M. Tippmann, L. Steinke, S. Lasuberg, A. Steppke, M. Brando, C. Krellenr, C. Geibel, R. Yu, Q. Si and F. Steglich, Science* ***351*** *(2016) 485.*

[16]* *Even odder after twenty-three years: the superconducting order parameter puzzle of Sr_2RuO_4, A. P. Mackenzie, T. Scaffidi, C. W. Hicks and Y. Maeno, NPJ Quantum Materials* ***2*** *(2017) 40.*

[17]* *Strong increase of T_c of Sr_2RuO_4 under both tensile and compressive strain, C. W. Hicks, D. O. Brodsky, E. A. Yelland, A. S. Gibbs, J. A. N. Bruin, M. E. Barber, S. D. Edkins, K. Nishimura, S. Yonezawa, Y. Maeno and A. P. Mackenzie, Science* ***344*** *(2014) 283.*

[18]* *Piezoelectric-based apparatus for strain tuning, C. W. Hicks, M. E. Barber, S. D. Edkins, D. O. Brodsky and A. P. Mackenzie, Rev. Sci. Inst.* ***85*** *(2014) 65003.*

[19]* *Strong Peak in T_c of Sr_2RuO_4 under uniaxial pressure, A. Steppke, L. Zhao, M. E. Barber, T. Scaffidi, F. Jerzembeck, H. Rosner, A. S. Gibbs, Y. Maeno, S. H. Simon, A. P. Mackenzie and C. W. Hicks, Science* ***355*** *(2017) aaf9398.*

[20] *Nonunitary Triplet Pairing in the Centrosymmetric Superconductor $LaNiGa_2$, A. D. Hillier, J. Quintanilla, B. Mazidian, J. F. Annett and R. Cywinski, Phys. Rev. Lett.* ***109*** *(2012) 097001.*

[21]* *Two-Gap Superconductivity in $LaNiGa_2$ with Nonunitary Triplet Pairing and Even Parity Gap Symmetry, Z. F. Weng, J. L. Zhang, M. Smidman, T. Shang, J. Quintanilla, J. F. Annett, M. Nicklas, G. M. Pang, L. Jiao, W. B. Jiang, Y. Chen, F. Steglich and H. Q. Yuan, Phys. Rev. Lett.* ***117*** *(2016) 027001.*

[22]* *Atomic-scale electronic structure of the cuprate d-symmetry form factor density wave state, M. H. Hamidian, S. D. Edkins, Chung Koo Kim, J. C. Davis, A. P. Mackenzie, H. Eisaki, S. Uchida, M. J. Lawler, E.-A. Kim, S. Sachdev and K. Fujita, Nature Physics* ***12*** *(2016) 150.*

[23] *On the use of STM superconducting tips at very low temperatures, J. G. Rodrigo, H. Suderow and S. Vieira, European Physical Journal B* ***40*** *(2004) 483.*

[24] *A 10 mK scanning tunnelling microscope operating in ultra high vacuum and high magnetic fields, M. Assig, M. Etzkorn, A. Enders, W. Stiepany, C. R. Ast and K. Kern, Rev. Sci. Inst* ***3*** *(2013) 033903.*

[25]* *Detection of a Pair Density Wave in $Bi_2Sr_2CaCu_2O_{8+x}$ Using Scanned Josephson Tunneling, M. H. Hamidian, S. D. Edkins, Sang Hyun Joo, A. Kostin, H. Eisaki, S. Uchida, M. J . Lawler, E.-A. Kim, A. P. Mackenzie, K. Fujita, Jinho Lee and J. C. Davis, Nature* ***532*** *(2016) 343.*

Christoph.Geibel@cpfs.mpg.de