Nodal Superconductors

*Peter Thalmeier and Kazumi Maki**

Degenerate interacting Fermi systems may exhibit instabilities due to pair condensation. An instability in the electron-electron channel leads to Cooper-pair formation and superconducting (sc) order. In the case of electron-phonon superconductors only gauge symmetry is broken, leading to Cooper pairs in a singlet s-wave state of zero orbital and spin angular momentum. The search for superconductors with more general pair states associated with the presence of 'nodal' gap functions and their theoretical description is a central topic in condensed matter physics. Three highly interesting examples of nodal superconductors have been investigated.

Unconventional superconducting states

It has been speculated soon after the advent of BCS theory that more general "unconventional" superconducting pair states than s-wave are possible in principle. They have finally been found in Ce- and U-based Heavy Fermion (HF) superconductors and later also in High-T_c cuprates and organic compounds. In real metals unconventional superconducting pair states have to be classified according to the crystal symmetry group. The sc gap function may be expanded in terms of basis functions $\psi_i^\Gamma(\mathbf{k})$ which transform like representations Γ of the crystal symmetry group (i=1-d is the degeneracy index) [1]. For spin singlet pairing one has

$$\Delta(\mathbf{k}) = \sum_{\Gamma,i} \eta_i^\Gamma \psi_i^\Gamma(\mathbf{k}) \equiv \Delta f(\mathbf{k}) \qquad (1)$$

In the spirit of the Landau theory only a ***single*** representation Γ with the highest T_c should be realized. Recently, however, cases with "hybrid" order parameters formed by superposition of a few representations have been found.

Unconventional superconductors exhibit the following aspects: Firstly, a non-s-wave pair state points to a non-phononic mechanism for the effective pair potential such as spin-fluctuation, magnetic-exciton or quadrupolar fluctuation exchange which may be very anisotropic in **k** space, i.e., have their largest attraction in a non-s-wave channel. Secondly, the anisotropic pair potential may lead to zeroes or 'nodes' in the gap function $\Delta(\mathbf{k})$ =0 not present in conventional superconductors. The nodal structure consisting of point nodes and/or line nodes on the Fermi surface is fixed by the specific symmetry class of $\Delta(\mathbf{k})$ defined by the set of η_Γ^i. Consequently quasiparticle states can be thermally excited at arbitrarilly low temperatures leading to power-law behaviour of physical quantities instead of exponential temperature behaviour for a conventional superconductor with nonvanishing $\Delta(\mathbf{k})$. Thirdly if Γ is a degenerate representation (i=1..d >1) the sc order parameter is a complex multicomponent vector instead of a scalar leading to entirely new properties like condensate magnetic moments and multiphase diagrams in the B-T plane.

Because the gap function is not a physical observable it is exceedingly difficult to determine its node structure, anisotropy and hence the irreducible group representation to which it belongs. On the other hand this is mandatory for understanding the properties of an unconventional superconductor. Traditionally the sc gap symmetry has been investigated by analyzing the temperature dependence of various physical quantities. Such investigations often lead to highly ambiguous or inconclusive results. For example it took almost a decade to discriminate betweeen the E_{1g} and E_{2u} states of UPt_3 in favor of the latter.

Magnetothermal properties in the vortex phase

Recently a new method has been used to obtain a much more detailed and direct access to the nodal structure of the gap. It consists of measuring the field-angle dependence of magnetothermal properties like specific heat and thermal conductivity in the vortex phase with a geometry indicated in the inset of Fig. 1. Its decisive advantage is that a quantitative analysis of temperature dependences in the sc regime is unnecessary, contrary to previous methods. It is sufficient to determine the extrema of specific heat and thermal conductivtity as function of field angles and their character (cusp for

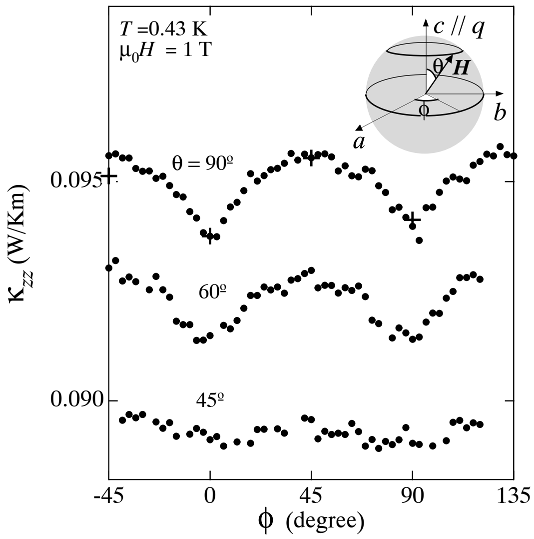

Fig. 1: Experimental c-axis thermal conductivity from Izawa et al. [4] as function of azimuthal field angle ϕ (inset) for various polar field angles θ.

point nodes or zero slope minima for line nodes). From this the nodal positions and their type may be directly obtained.

This method which has revolutionized the investigation of nodal superconductors is based on the "Volovik effect" [2] which can be understood in a quasiclassical picture. Because of the presence of nodes quasiparticles may channel into the intervortex region where their energy is shifted by a postion-(**r**-)dependent Doppler shift energy $\mathbf{v}_s(\mathbf{r})\,\mathbf{k}$ due to the superfluid velocity field $\mathbf{v}_s(\mathbf{r})$. This leads to a finite residual DOS at E = 0 which will depend both on field magnitude and direction:

$$\frac{N_s(E,\mathbf{H})}{N_0} \simeq \frac{1}{\Delta}\langle\langle|E - \mathbf{v}_s \cdot \mathbf{k}|\rangle\rangle \qquad (2)$$

The double average is performed both over the velocity field coordinate **r** and the quasiparticle momentum. It will depend on the direction of the magnetic field **H** determined by polar and azimuthal angles (θ,ϕ) with respect to the nodal directions leading to typical oscillations in the DOS as function of (θ,ϕ). Physically they are witnessed as oscillations in the specific heat $C_s(H,\theta,\phi)$ and thermal conductivity $\kappa_{ij}(H,\theta,\phi)$.

(Y,L)Ni_2B_2C: a rare case of nodal electron-phonon superconductivity

The rare earth nickel borocarbides ***R***Ni_2B_2C (***R***=Y, Lu, Tm, Er, Ho, and Dy) have attracted great interest in recent years due to superconductivity as well as its possible coexistence with antiferromagnetic order [3]. It has initially been thought that these materials can be understood by an isotropic s-wave pairing via the conventional electron-phonon coupling. However, recent various experimental results, particularly on the two nonmagnetic borocarbides Y(Lu)Ni_2B_2C, have unambiguously shown that the gap function is highly anisotropic with anisotropy ratio [4] $\Delta_{min}/\Delta_{max} \lesssim 10^{-2}$ from which the existence of nodes may be concluded. Indeed the $\pm\sqrt{H}$ dependence of the specific heat in the vortex state indicates a superconducting state with nodal excitations. Compelling evidence is now presented by Izawa et al. from the angular-dependent thermal conductivity in a magnetic field that the gap function of YNi_2B_2C has point nodes which are located along the [1,0,0] and [0,1,0] directions [4]. Thus, the previous isotropic s-wave theory has to be critically reconsidered.

Recently we have proposed a gap function for Y(Lu)Ni_2B_2C superconductors which is of hybrid (fully symmetric) s+g wave type with equal amplitudes which is consistent with these observations.

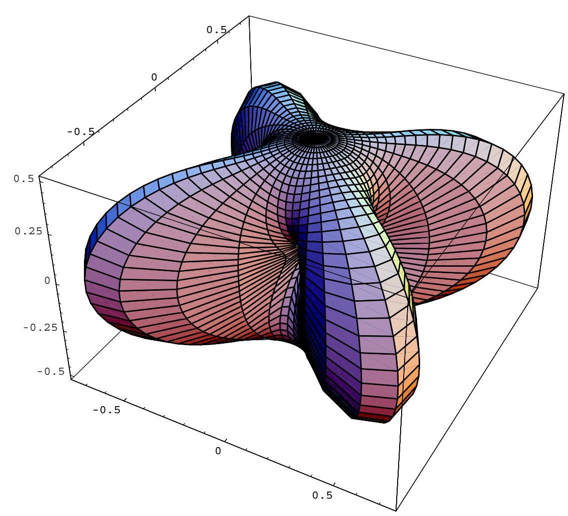

Fig. 2: Polar plot of gap function Δ(k) of the s+g model.

It is given by [4,5,6].

$$\Delta_{\mathbf{k}} = \frac{\Delta}{2}(1 - \sin^4\vartheta\cos 4\varphi)\ , \qquad (3)$$

where ϑ and φ are polar and azimuthal angles of **k**, respectively.

In the vortex phase the Volovik effect described above leads then to a residual field-angle dependent DOS. For the gap model of Eq.(3) it is given by [6]

$$N_s(0) = \frac{C_s}{\gamma_N T} = \frac{\tilde{v}\sqrt{eH}}{2\sqrt{2}\Delta} I_+(\theta,\phi) \qquad (4)$$

where $\tilde{\boldsymbol{v}} = \sqrt{\boldsymbol{v}_a \boldsymbol{v}_c}$ and $I_+(\pi/2,\phi) = \max(|\sin\phi|,|\cos\phi|)$. This function has a downward cusp at $\phi = n(\pi/2)$ when **H** is sweeping over the node points. Also the residual DOS exhibits naturally the experimentally observed $\sqrt{H}$-behaviour. It determines the angular dependence of the ***c***-axis thermal conductivity $\kappa_{zz}(H,\theta,\phi)$. This quantity has been investigated in detail both experimentally [4] and theoretically [6]. The geometry with heat current along c and **H** conically swept around c is shown in the inset of Fig.1. For in-plane field ($\theta = \pi/2$ (pronounced cusps in $\kappa_{zz}(\pi/2,\phi)$ are visible in Fig. 1 typical for the existence of point nodes in the gap function. When the polar field angle θ decreases the oscillations in $\kappa_{zz}(\theta,\phi)$ as function of azimuthal field angle ϕ are rapidly diminished. The theoretical prediction for the angle dependence of $\kappa_{zz}(H,\theta,\phi)$ is shown in Fig. 3. In addition, a comparison with the angular variation of $\kappa_{zz}(\theta,\phi)$ for an assumed d_{xy}-gap function $\Delta(\varphi)=\Delta\sin(\varphi)$ is given in this figure. In this case no cusp appears and the amplitude of $\kappa_{zz}(\theta,\phi)$-oscillation in ϕ is almost independent of θ. This speaks strongly in favor of the s+g wave order parameter as the correct model for YNi_2B_2C and possibly $LuNi_2B_2C$. This makes it the first confirmed case of a superconductor with (second order) node points in the gap functions. The only other known candidate is UPt_3 whose E_{2u} gap function in the B- phase is supposed to have point nodes on the poles. For the latter similar experiments as in Fig. 1 have yet to be performed for this compound.

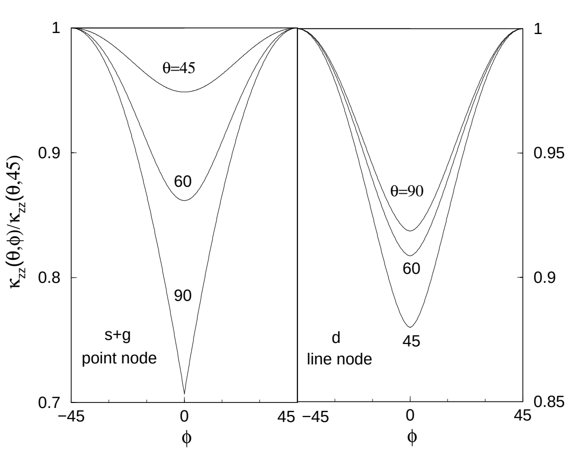

Fig. 3: Normalized c-axis thermal conductivity, comparison between s+g wave model and d-wave model.

Certainly the simple electron-phonon type pairing mechanism originally envisaged for the borocarbides has to be supplemented, for example by strongly anisotropic Coulomb interactions, to account for the s+g wave gap function found there.

$PrOs_4Sb_{12}$: A second example of multiphase superconductivity

Superconductivity in the cubic (T_h symmetry) HF skutterudite $PrOs_4Sb_{12}$ with T_c = 1.8 K has provoked great interest since it exhibits a number of characteristics that suggest the presence of nodes. The specific heat results [7,8] indicate firstly a low temperature power law behavior and secondly the presence of two sc phases with two consecutive specific heat jumps at T_{c1} = 1.82 K and T_{c2} = 1.75 K somewhat reminiscent of UPt_3. More recent low temperature thermal conductivity results [4] in the vortex state confirm i) the presence of two superconducting A ($T < T_{c1}$) and B ($T < T_{c2}$) phases with different nodal structure and ii) the presence of point nodes in both A (H > 0.75 T, $T \ll T_c$) and B (H < 0.75 T, $T \ll T_c$) phase. More specifically, the thermal conductivity indicates the presence of four point nodes in $\Delta(\mathbf{k})$ along [1,0,0] and [0,1,0] in the A-phase while in the B-phase the two point nodes are located along [0,1,0]. Additional nodes may exist along [0,0,1]; this has yet to be confirmed.

The presence of two phases is most likely related to the degenerate Γ_3 ground state of Pr 4***f***-electrons associated with the tetrahedral crystal field. In U-based unconventional HF superconductors an exchange of (dipolar) spin fluctuations in the itinerant 5***f***-electrons is frequently implied as the mechanism for unconventional sc pair formation.

In the present case a new interesting possibility for pair formation is the exchange of quadrupolar fluctuations of the essentially localized $4f^2(\Gamma^3)$-electrons of Pr. Sofar there is no microscopic theory and various models for the gap function have been proposed on phenomenological grounds [10, 11]. It is impossible to explain the observed node structure with single representations of the tetrahedral symmetry group and therefore (as in the borocarbides) hybrid gap functions $\Delta(\mathbf{k}) = \Delta f(\mathbf{k})$ have to be involved for $PrOs_4Sb_{12}$ which have six and four nodal points respectively:

$$\begin{aligned} &(\mathrm{A})\ f(\mathbf{k}) = \frac{3}{2}(1 - k_x^4 - k_y^4 - k_z^4)\ , \\ &(\mathrm{B})\ f(\mathbf{k}) = 1 - k_y^4 - k_z^4\ . \end{aligned} \qquad (5)$$

The A-phase gap is again a superposition (hybrid `s+g-wave') of two fully symmetric T_h representations with equal absolute values of amplitudes. The B-phase gap function has lower symmetry and is three fold degenerate. A particular domain with nodes in the ***yz***-plane has been chosen.

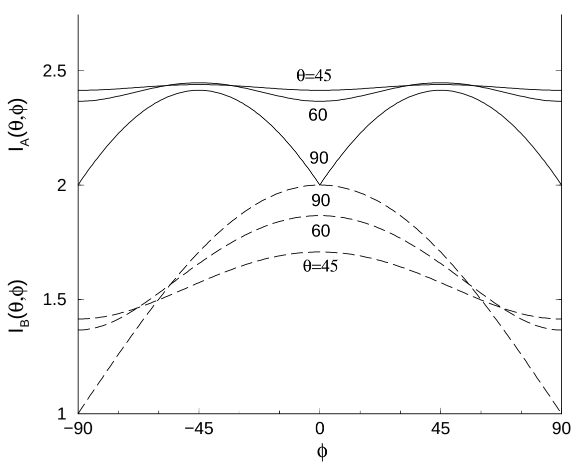

Fig. 4: Calculated angular dependence $I_A(\theta,\phi)$ (full lines) and $I_B(\theta,\phi)$ (broken lines) of $\kappa_{zz}(\theta,\phi)$ exhibits fourfold and twofold oscillations as function of ϕ.

The thermal conductivity along [001] for A,B phases is again determined by the angular dependence of the residual DOS in the vortex state described by functions $I_{A,B}(\theta,\phi)$. In Fig. 4 the ϕ-dependence is shown for various fixed θ. Qualitatively this corresponds to the experimental observation where a transition from the twofold oscillation pattern in ϕ to the fourfold oscillation pattern is observed at $H^* = 0.75$ T at low temperature. Following the twofold-to-fourfold transition

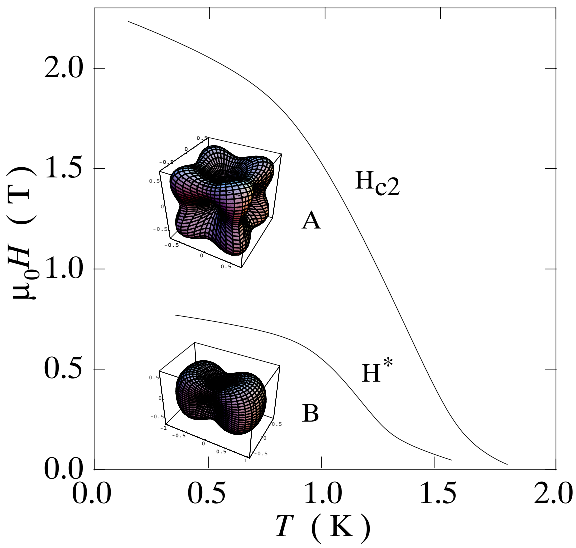

Fig. 5: B-T phase diagram of $PrOs_4Sb_{12}$ exhibiting B-phase with twofold symmetry and A-phase with fourfold symmetry in a cubic plane. Insets show polar plots of A-phase and B-phase gap functions defined in Eq. (5) with six and four node points respectively, including the still unproven nodal points along [001] direction.

field H^* as function of T leads to the multiple sc phase diagram shown in Fig. 5.

As a preliminary conclusion it seems clear that $PrOs_4Sb_{12}$ is a very unconventional multiphase HF superconductor of potentially the same interest as UPt_3. Recalling that heavy quasiparticles are presumably caused by hybridization with a nonmagnetic quadrupolar $4f$ ground state one is lead to speculate that sc in $PrOs_4Sb_{12}$ might also imply the presence of a novel pairing mechanism based on the exchange of quadrupolar fluctuations. In addition to the spin-fluctuation and the magnetic- exciton exchange mechanism this would be the third possibility for Cooper pair formation relevant in HF compounds.

UPd_2Al_3: first magnetic exciton mediated nodal superconductor

The well-known unconventional Heavy Fermion superconductor UPd_2Al_3 (T_c = 1.8 K) [12] with γ = 140 mJ/molK^2 shows coexistence of nodal superconductivity and “large” moment (μ = 0.85 μ_B) antiferromagnetism (T_N=14.3 K). Only recently it has turned out to be the first case where a non-phononic mechanism for Cooper pair formation has been directly proven [13]. The electronic configuration ($5\boldsymbol{f}^3$) of UPd_2Al_2 can be described within a dual electronic model. Two of the 5***f***-electrons form localized atomic-like crystalline electric field (CEF) states while the remaining forms a band of conduction electrons. Localized and itinerant 5***f*** electrons are seen in complementary experiments: inelastic neutron scattering (INS) and quasiparticle tunneling, respectively. INS probes localized magnetic 5***f***-excitations and tunneling experiments probe the current due to sc quasiparticles. In both experiments interaction effects of localized and itinerant 5***f*** electrons are essential. Quantitative analysis of these complementary results leads to the conclusion that the exchange of ***magnetic excitons*** are responsible for the formation of Cooper pairs in UPd_2Al_2 [13,14].

Magnetic excitons are propagating CEF excitations of the localized 5***f***-electrons (inset Fig. 6) whose dispersion is caused by inter-site magnetic exchange J(**q**) according to

$$\omega_E(\mathbf{q}) = \delta - \alpha^2 J(\mathbf{q}) \tag{6}$$

where α is an effective dipolar matrix element between the lowest CEF split δ singlet states of the $5\boldsymbol{f}^2$ configuration. Calculations and experimental results for the magnetic exciton dispersion in UPd_2Al_2 are shown in Fig. 6. The remaining 5***f***- electron forms a conduction band whose main Fermi surface sheet is shown in the same figure. Localized and itinerant 5***f*** electrons have strong interaction which has two main effects: (i) Broadening of the magnetic excitons; however, they remain propagating modes in contrast to overdamped AF paramagnons in fully itinerant spinfluctuation models. (ii) Exchange of magnetic excitons $\omega_E(\mathbf{q})$ between itinerant carriers leads to an effective pair potential $V_E(\mathbf{q},\omega)$ determined by the magnetic exciton dispersion $\omega_E(\mathbf{q})$ [14].

Because of the strong coupling between itinerant and localized 5***f***-electrons both types of electrons can be seen both in INS and tunneling experiments. In the latter the exchange of magnetic excitons leads to typical strong coupling signatures in the tunneling DOS similar to the phonon signatures in electron phonon superconductors. Since the energy of the exchanged bosons (- 1 meV) visible in the tunneling current corresponds to those of the magnetic excitons seen in INS around the antiferromagnetic Bragg point one has to conclude that the latter are indeed the glue that bind the unconventional Cooper pairs in UPd_2Al_2. A comparison of low energy magnetic excitons from INS around **Q** = (0,0,0.5) (in r.l.u.) and the calculated model tunneling DOS from Eliashberg theory is shown in Fig. 7.

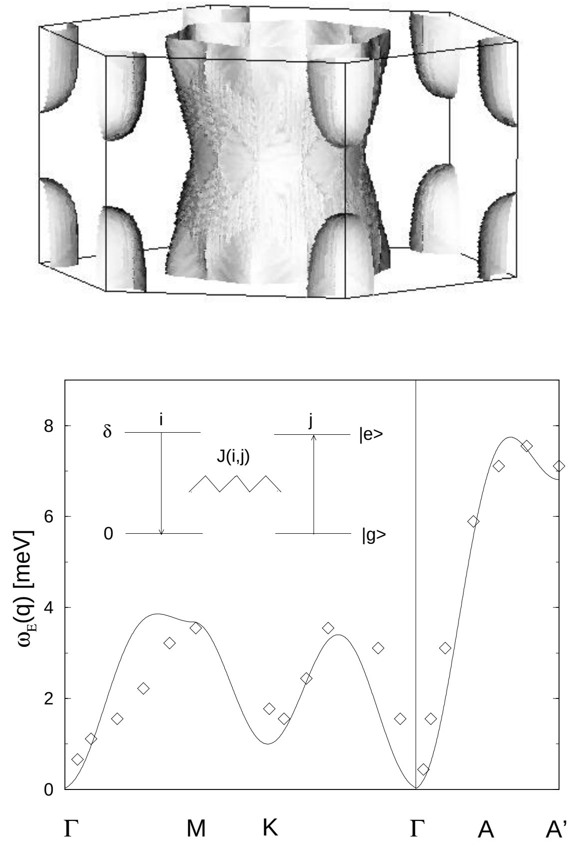

Fig. 6: The $5f^3$ configuration in UPd_2Al_3 has a dual nature. above: main Fermi surface cylinder of itinerant 5f-electrons. below: theoretical (full line) and experimental (diamonds) magnetic exciton dispersion of localised 5f-electrons in the hexagonal BZ [14]. Insert shows their origin as propagating singlet-singlet (g-e) CEF excitations caused by intersite exchange J(i,j).

Presently, the symmetry of the gap function cannot predicted. The most frequently proposed even parity gap function $\Delta(\mathbf{k}) = \Delta f(\mathbf{k})$ with $f(\mathbf{k}) = \cos \boldsymbol{k_z}$ has node lines on the AF Bragg-planes $\boldsymbol{k_z} = \pm(\pi/2)$. For a definite confirmation of this choice magnetothermal investigations in the vortex phase as in the two compounds discussed before are necessary [15].

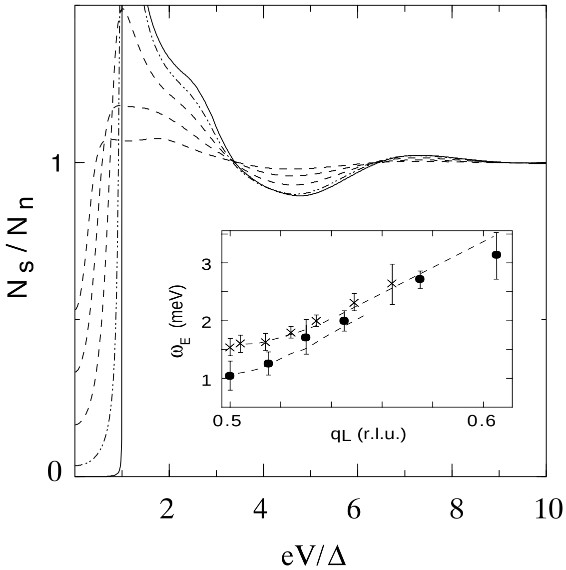

Fig. 7: Calculated tunneling DOS for T/T_c= 0.025 – 0.95 (from below at V=0) [13]. Inset shows magnetic exciton dispersion $\Omega_E(q)$ (q)=(0,0,q_L) close to AF point q_L= 0.5 (r.l.u. =$2\pi/c$) from high resolution INS [13] above T_c (crosses) and below T_c (circles). 2Δ = 5.6 k_BT_c = 0.87 meV.

Nodal superconductors are a most active subject of research. The classification of their gap function according to their symmetry properties is on one hand a fascinating theoretical challenge and on the other hand a necessary prerequisite for understanding their low-temperature physical properties. This task has been very much simplified by the advent of field angle-dependent magnetothermal analysis in the vortex phase which has given a direct access to determination of the nodal structure of the superconducting gap. Its knowledge is an essential prerequisite for the investigation of more microscopic models for the sc state. The three investigated compounds show that the appearance of nodal gaps is not specific to the common spin fluctuation pairing mechanism but is also possible for quadrupolar fluctuation or magnetic exciton exchange mechanism and in rare cases even for electron-phonon superconductors.

References

[1] ***G. E. Volovik and L. P. Gor'kov***, Sov. Phys.- JETP **61**, 843 (1986)

[2] ***G. E. Volovik,*** Pisma Zh. Eksp. Teor. Fiz. **58**, 457 (1993) [JETP Lett. **58**, 469 (1993)].

[3] ***A. Amici, P. Thalmeier and P. Fulde,*** Phys. Rev. Lett. **84**, 1800 (2000)

[4] ***K. Izawa, K. Kamata, Y. Nakajima, Y. Matsuda, T. Watanabe, M. Nohara, H. Takagi, P. Thalmeier and K. Maki,*** Phys. Rev. Lett. **89**, 137006 (2002).

[5] ***K. Maki, P. Thalmeier and H. Won,*** Phys. Rev. B **65**, R140502 (2002).

[6] P. ***Thalmeier and K. Maki,*** cond-mat/0210364.

[7] ***E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf and M. B. Maple,*** Phys. Rev. B **65**, R100506 (2002).

[8] ***R. Vollmer, A. Faißt, C. Pfleiderer, H. V. Löhneysen, E. D. Bauer, P.-C. Ho and M. B. Maple,*** cond-mat/0207225.

[9] ***K. Izawa, Y. Nakajima, J. Goryo, Y. Matsuda, S. Osaki, H. Sugawara, H. Sato, P. Thalmeier and K. Maki,*** cond-mat/0209553.

[10] ***K. Maki, P. Thalmeier, Q. Yuan, K. Izawa and Y. Matsuda,*** cond-mat/0212090.

[11] ***J. Goryo,*** cond-mat/0212094

[12] ***Ch. Geibel, C. Schank, S. Thies, H. Kitazawa, C. D. Bredl, A. Böhm, M. Rau, A. Grauel, R. Caspary, R. Helfrich, U. Ahlheim, G.Weber and F. Steglich,*** Z. Phys. B **84**, 1 (1991)

[13] ***N.K. Sato, N. Aso, K. Miyake, R. Shiina, P. Thalmeier, G. Varelogiannis, C. Geibel, F. Steglich, P. Fulde and T. Komatsubara,*** Nature **410**, 340 (2001).

[14] ***P. Thalmeier,*** Eur. Phys. J. B **27**, 29 (2002)

[15] ***P. Thalmeier and K. Maki,*** Europhysics. Lett. **58**, 119 (2002).

* Department of Physics and Astronomy, USC, Los Angeles