# Angle-Dependent Evolution of the Fulde-Ferrell-Larkin-Ovchinnikov State in an Organic Superconductor

R. Beyer,[1] B. Bergk,[1] S. Yasin,[1] J. A. Schlueter,[2] and J. Wosnitza[1]

[1]*Hochfeld-Magnetlabor Dresden (HLD), Helmholtz-Zentrum Dresden-Rossendorf, D-01314 Dresden, Germany*
[2]*Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA*
(Received 17 February 2012; published 11 July 2012)

We report magnetic-field and angular-dependent high-resolution specific-heat measurements of the organic superconductor $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$. When the magnetic field is aligned precisely within the conducting BEDT-TTF layer, at low temperatures a clear upturn of the upper critical field beyond the Pauli limit of 9.73 T is observed, hinting at the emergence of a Fulde-Ferrell-Larkin-Ovchinnikov state. This upturn disappears when the field is oriented out of plane by more than $\sim$0.5 deg. For smaller out-of-plane angles, the specific-heat anomaly at $T_c$ sharpens and a second peaky phase transition appears within the superconducting state.

DOI: 10.1103/PhysRevLett.109.027003 PACS numbers: 74.70.Kn, 65.40.Ba, 74.25.Bt, 75.40.Cx

In 1964, Fulde and Ferrell (FF) [1] as well as Larkin and Ovchinnikov (LO) [2] predicted independently the existence of novel inhomogeneous superconducting states at high magnetic fields and low temperatures. These FFLO states, having a spatially modulated superconducting order parameter, are relevant not only in condensed-matter physics, but as well for ultracold atoms, nuclear matter, and dense quark systems [3].

Here, we focus on the Cooper pairing of conduction electrons in metals. In type-II spin-singlet superconducting materials, the FFLO state may occur when the orbital critical field, $\mu_0 H_{\rm orb}$, is sufficiently larger than the Pauli paramagnetic limit, $\mu_0 H_P = \Delta_0/(\sqrt{2}\mu_B)$, with $\mu_B$ the Bohr magneton and $\Delta_0$ the superconducting energy gap at $T = 0$ [4]. More precisely, the Maki parameter, $\alpha = \sqrt{2}H_{\rm orb}/H_P$ [5], should be larger than 1.8 [6]. In addition, the superconductor must be in the clean limit with a mean free path, $\ell$, much larger than the coherence length, $\xi$. These rigorous conditions are fulfilled only by a few superconducting materials. Indeed, not many superconductors were reported to show manifestations of FFLO states. A number of these claims later had to be revised or are inconclusive. For a recent overview see Ref. [3].

Prime candidates for exhibiting the FFLO state are the quasi-two-dimensional (2D) organic superconductors. These are spin-singlet [7] and mostly, clean-limit superconductors, and when the magnetic field is aligned parallel to the conducting planes, the orbital critical field is greatly enhanced, much beyond the Pauli limit. Indeed, in some of the 2D organic superconductors indications for the existence of the FFLO state have been reported [3]. Recently, some of us could give true thermodynamic evidence for an upturn of the upper critical field, $H_{c2}$, beyond the Pauli limit and for the existence of a narrow superconducting phase below $H_{c2}$ in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ (BEDT-TTF stands for bisethylenedithio-tetrathiafulvalene) [8]. Assigning these features to the existence of the FFLO state was further supported by our magnetic torque data [9,10] and by recent nuclear magnetic resonance experiments [11].

In this Letter, we present specific-heat results for the organic superconductor $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ that shows an ideal 2D electronic structure with unresolvable interlayer coupling [12]. The modest critical temperature of $T_c = 4.3$ K and the concomitant low Pauli limit (9.73 T) allowed for a thorough investigation of the thermodynamic phase diagram as a function of temperature, magnetic field, and angle. The interesting region of the phase diagram can easily be reached by commercial superconducting magnets. As predicted for the FFLO state, the upturn of the critical field beyond the Pauli limit appears only for an almost perfect in-plane alignment of the magnetic field, when orbital effects are suppressed. A second phase transition within the superconducting state appears for a slight out-of-plane magnetic-field alignment.

The investigated single crystal was prepared by a well-known electrochemical process described in more detail in Ref. [13]. The crystal with a mass of 2.242 mg and approximate dimensions of $4 \times 0.7 \times 0.4$ mm$^3$ was mounted by use of a small amount of Apiezon N grease on a sapphire platform that was firmly fixed by Nylon wires [see inset of Fig. 1(b)]. The specific heat was measured using the relaxation technique, similar as described in Ref. [8]. After heating up the sample and platform by 50 to 100%, this technique has the advantage to provide a large number of data points during a short (typical 5 to 10 s) relaxation time interval. For better statistics, we performed about 40 relaxation sweeps for each temperature range resulting in the high data point density visible in Figs. 1, 2, and 4. The calorimeter was mounted in a $^3$He cryostat equipped with a 20-T superconducting magnet. The thermometer was carefully calibrated in zero and applied magnetic fields. Reliable specific-heat data were obtained down to about 0.7 K, below which the fast relaxation times limited the accuracy. The calorimeter was

 

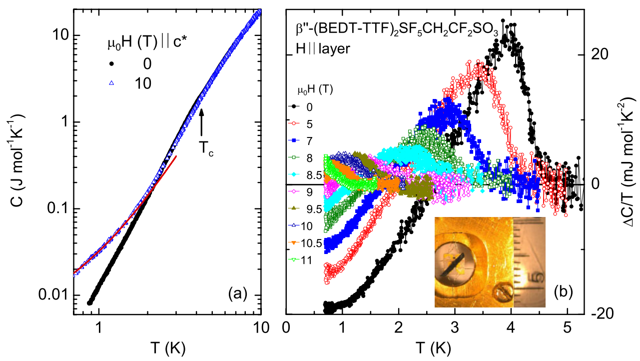


FIG. 1 (color online). (a) Specific heat of $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ at 0 and 10 T applied perpendicular to the layers as a function of temperature in a double-logarithmic scale. The solid line is a fit of the form $C = \gamma T + \beta T^3$ for the data up to 2 K. (b) Difference between the specific heat for selected in-plane magnetic fields and the normal-state specific heat, i.e., the 10-T data from panel (a), divided by temperature, measured as a function of temperature. The inset shows the investigated sample on the platform with a mm scale to the right.

mounted on a piezoelectric drive that allowed a precise *in situ* rotation with angular resolution of better than 0.02 deg. The accurate in-plane orientation was identified by finding the maximum transition temperature when rotating the sample in small steps in applied magnetic fields (see also Fig. 2). As becomes clear below, such an accurate alignment is a prerequisite for the observation of the FFLO state.

We first measured the specific heat for magnetic fields aligned perpendicular to the conducting planes. In Fig. 1(a), we show the data for $\mu_0 H = 0$ and 10 T. With the latter magnetic field, superconductivity is completely suppressed. We used the 10-T data set, representing the normal state specific heat, to determine the specific heat differences, $\Delta C$, shown in Figs. 1(b), 2, and 4. Below 2 K, these data can be well described by $C = \gamma T + \beta T^3$, yielding a Sommerfeld coefficient $\gamma = 19.0(5)$ mJ mol$^{-1}$ K$^{-2}$ and a Debye contribution with $\beta = 12.8(4)$ mJ mol$^{-1}$ K$^{-4}$ in very good agreement with previous results [14].

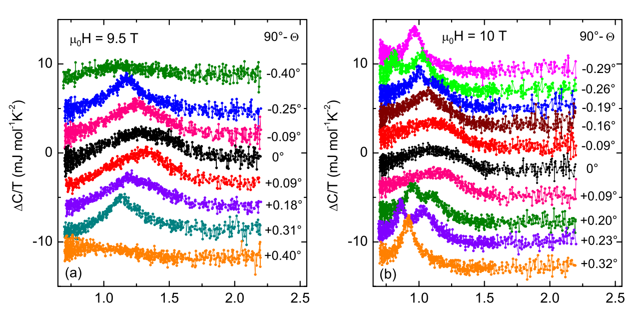


FIG. 2 (color online). Specific heat differences, $\Delta C$, divided by the temperature of $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ at (a) 9.5 and (b) 10 T for different angles close to in-plane field orientation. The data are plotted offset for clarity.

Additional low-field specific-heat data for $H$ aligned perpendicular to the planes (not shown) allow us to estimate an extrapolated zero temperature upper critical field of $\mu_0 H_{c2} \approx 1.4$ T for this field orientation. The corresponding coherence length is about 15 nm. This critical field is much lower than was previously estimated from magnetization [15] and earlier, less accurate, specific-heat data [14]. Although we did not measure the mean free path for this particular sample, numerous measurements of quantum oscillation for many other samples showed consistently scattering rates of $\tau^{-1} \approx 5 \times 10^{11}$ s$^{-1}$ [15,16]. Together with the known Fermi energy of about 12 meV and the effective mass of 1.9 free-electron masses, a mean free path of $\ell \approx 100$ nm can be assumed for the studied specific-heat sample. Consequently, the superconductor is in the clean limit with $\ell/\xi \approx 7$.

In search for the expected FFLO state, we measured the specific heat for accurate in-plane orientation of the magnetic field. The differences between the specific heat for selected in-plane fields and the normal-state specific heat is shown in Fig. 1(b). The data for $H = 0$ allow us to determine the coupling strength and the superconducting gap, $\Delta_0$, with good precision. $\Delta C$ can be well described, except for the data close to $T_c$, when assuming a BCS-like temperature dependence of the gap scaled with the adjustable parameter $\alpha = \Delta_0/k_B T_c$, which in the weak-coupling limit is 1.76. In the present case, the best fit is obtained with a moderate strong coupling of $\alpha = 2.18$ which nicely agrees with our previous result $\alpha = 2.15$ [14]. From that, we now can extract the Pauli-limiting field $\mu_0 H_P = \Delta_0/(\sqrt{2}\mu_B) = 9.73(3)$ T quite accurately.

The field-dependent superconducting transition temperatures were determined from data as shown in Fig. 1(b) by using an equal-entropy (or equal-area) construction. Starting at $T_c = 4.3$ K, the specific-heat anomaly first shifts only slightly with increasing field (see Fig. 3). From the initial slope of the critical field, $-\mu_0 dH_{c2}/dT \approx 25$ T/K, we obtain the orbital critical field $\mu_0 H_{\text{orb}} = -0.7\mu_0 T_c dH_{c2}/dT \approx 75$ T. This, obviously, is much larger than $\mu_0 H_P$. Consequently, in the spin-singlet superconductor $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ the limiting effect on superconductivity at higher magnetic fields becomes the Zeeman energy. Indeed, the steep initial slope quickly levels off at higher fields upon reaching the Pauli limit. However, below about 1.6 K (above 9.3 T), $H_{c2}$ rises steeply to much larger values than expected for a Pauli-limited superconductor (dashed line in Fig. 3). This is a clear indication for the emergence of the FFLO phase.

When comparing the present data with the specific-heat results obtained for $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ [8], we find remarkable differences. First, the anomaly from the normal to the superconducting state becomes very sharp (first order) for the $\kappa$-phase material; whereas, it remains rather broad in the present case. Moreover, in the data shown in Fig. 1, no indication for a second phase transition is found,

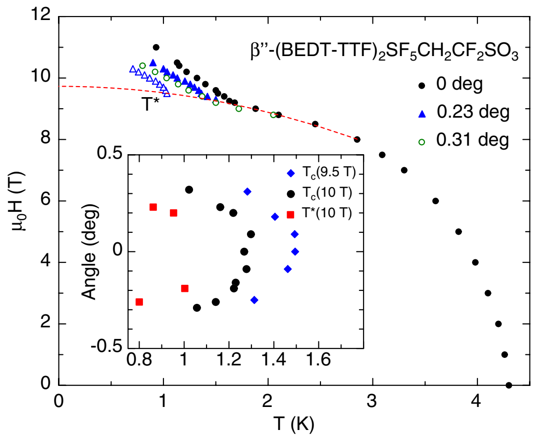


FIG. 3 (color online). Phase diagram of $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ for fields aligned parallel to and by 0.23 and 0.31 deg out of the superconducting layers. The data of the second anomaly observed at 0.23 deg (Fig. 4) are labeled by $T^\star$ (open blue triangles). The dashed line is a rough extrapolation of the data between 2 and 3 K to the Pauli limit of 9.73 T. The inset shows the angular dependence of $T_c$ and $T^\star$ at 9.5 and 10 T.

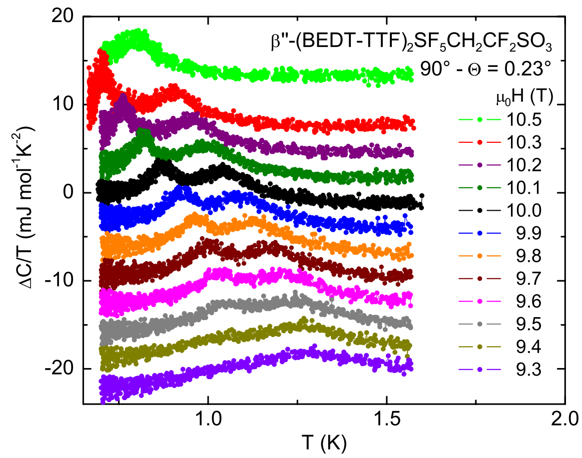


FIG. 4 (color online). Specific-heat differences, $\Delta C/T$, for different magnetic fields aligned 0.23 deg out of the conducting plane. The data are plotted offset for clarity.

contrary to the sharp first-order transition in the $\kappa$-phase compound.

The highly accurate rotation mechanism allowed us, for the present sample, to carefully investigate the angular dependence of the FFLO phase. By rotating the sample in small steps at constant magnetic fields around in-plane ($\Theta = 90$ deg) alignment, we measured the specific heat close to the phase transition. At 9.5 T [Fig. 2(a)], the specific-heat anomaly moves towards lower temperatures, but sharpens when rotating away from $\Theta = 90$ deg. When being off by merely 0.4 deg from in-plane orientation, no clear anomaly is discernible anymore down to 0.7 K. This means the upturn of the $H_{c2}$ line, indicating the FFLO state, is absent when the magnetic-field alignment is less accurate than about half a degree. At 10 T [Fig. 2(b)], a similar rapid reduction of $T_c$ and sharpening of the phase transition is seen. However, in addition, a second sharp anomaly, just below $T_c$, appears when the magnetic field is rotated out of plane by just $\pm 0.2$ deg. Both anomalies move out of the temperature window for slightly larger angles. The angular dependences of the observed anomalies for the two magnetic fields are shown in the inset of Fig. 3. The second anomaly below $T_c$ is labeled $T^\star$ [17].

In order to investigate this second anomaly in more detail, we measured the specific heat for a number of different fields close to and above the Pauli limit at an out-of-plane angle of 0.23 deg (Fig. 4). Starting at about 9.4 T, the $T^\star$ anomaly appears. With increasing magnetic field, the two anomalies move in parallel to each other to lower temperatures keeping a distance of about 0.3 K. At 10.5 T, the lower, $T^\star$, anomaly is moved out of the accessible temperature window.

These data at 0.23 deg closely resemble the specific heat anomalies observed in $\kappa$-(BEDT-TTF)$_2$Cu(NCS)$_2$ [8]. This strongly points towards a small out-of-plane component of the magnetic field for the latter case. There, the sample was mounted in a fixed orientation and no *in situ* rotation was possible. The temperature difference between the two anomalies showed a similar value of about 0.2 K (see Fig. 3 in [8]).

Figure 3 comprises all phase-transition points that we determined by use of our specific-heat data. In order to visualize the hypothetical low-temperature upper critical field without the appearance of an FFLO state, we extrapolated the data between 2 and 3 K to the Pauli limit of 9.73 T at $T = 0$. For the precise in-plane field alignment (0 deg), the strongest upturn of the critical-field line appears. A less strong upturn starting at somewhat lower temperature, together with the $T^\star$ anomaly, is measured for $90\ \mathrm{deg} - \Theta = 0.23$ deg. For an offset angle of 0.31 deg (data not shown), the upturn is further reduced and shifted to lower temperatures without any discernible second specific-heat anomaly in our temperature window. For out-of-plane angles larger than about 0.5 deg, no upturn of $H_{c2}$ beyond the Pauli limit, i.e., no FFLO state, appears. Obviously, already such small out-of-plane angles induce orbital currents that prevent the emergence of the FFLO state.

In a recent report, a possible FFLO state in $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$ was already suggested [18]. This was based on in-plane penetration-depth measurements by use of a tunnel diode oscillator technique. The observed features, however, are tiny and only visible in the second derivative of the frequency changes. The shape of the phase-transition line in [18] is qualitatively in line with our results (Fig. 3), but quantitatively considerable discrepancies are found. Nevertheless, our thermodynamic data allow us to extract a much more robust and reliable phase diagram.

In our specific-heat measurements for accurate in-plane field alignment, we could not resolve any feature signaling the expected transition from the FFLO state to the homogeneous superconducting state. However, in case this transition would follow the dashed line in Fig. 3, as some theories [3] and other experiments [10,18] suggest, our specific-heat measurements are not well suited for its detection. Since we are sweeping the temperature at constant magnetic field, we either would run parallel to, or would cross at a very shallow angle, the transition line. A better way to detect this transition, obviously, is to cross the line perpendicular, i.e., at constant temperature while sweeping the magnetic field. The proper thermodynamic technique for that are magnetocaloric-effect experiments. Indeed, we performed such kind of measurements. However, due to the fast relaxation times of our calorimeter we could not resolve any reliable magnetocaloric-effect data [19].

For precise in-plane field alignment, all observed phase transitions from the normal to the superconducting state, whether homogenous or FFLO-type, are second order; i.e., no latent heat could be resolved in our experiments. Indeed, the question whether the transition from the normal to the inhomogeneous state is first or second order appears somewhat controversial. However, to answer this question theoretically, as well as performing an explicit evaluation of the full phase diagram, requires the calculation of the free energy for general inhomogeneous order parameters which is a formidable task [3]. Experimentally, our specific-heat data for small out-of-plane angles show a prominent sharpening of the phase transition when entering the FFLO phase. The transition at $T^\star$ as well reflects a sharp anomaly. Although this may indicate first-order-type transitions for offset angles, we could not resolve any latent heat or hysteresis within our resolution.

The origin of the $T^\star$ anomaly is unclear so far. It most probably is not related to the transition from the FFLO to the homogeneous state since that is expected to appear at the Pauli-limiting field (dashed line in Fig. 3). One might speculate that this anomaly signals a transition between possible different types of periodic structures within the FFLO state, such as predicted theoretically for an $s$-wave two-dimensional superconductor [20]. In the theory, however, such a narrow FFLO phase running parallel to $H_{c2}$ is not expected. Probably, the $T^\star$ anomaly indicates the appearance of some kind of vortex phase in the inhomogeneous superconducting state.

In summary, we presented high-resolution angular-dependent specific-heat measurements in high magnetic fields. Our data show a pronounced upturn of the upper-critical-field line when the Pauli-limiting field is reached at low temperatures. This behavior is most prominent for precise in-plane field alignment. It disappears rapidly for small out-of-plane orientation of the magnetic field; i.e., when orbital effects become important. This is strong thermodynamic evidence for the emergence of the FFLO phase. The appearance of a second phase transition within this phase for small out-of-plane angles indicates a possible vortex phase of unknown character. Microscopic measurements, such as NMR or neutron scattering, are the obvious next step for gaining better knowledge on the FFLO state, especially since only modest magnetic fields are needed in $\beta''$-(BEDT-TTF)$_2$SF$_5$CH$_2$CF$_2$SO$_3$.

We would like to thank P. Fulde, R. Lortz, and G. Zwicknagl for helpful discussions. Part of this work was supported by EuroMagNET II (EU Contract No. 228043). Research at Argonne National Laboratory was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Contract No. DE-AC02-06CH11357.

[1] P. Fulde and R. A. Ferrell, Phys. Rev. **135**, A550 (1964).
[2] A. I. Larkin and Y. N. Ovchinnikov, Zh. Eksp. Teor. Fiz. **47**, 1136 (1964) [Sov. Phys. JETP **20**, 762 (1965)].
[3] G. Zwicknagl and J. Wosnitza, in *BCS: 50 years* edited by L. N. Cooper and D. Feldman (World Scientific, Singapore, 2011) p. 337–371; Int. J. Mod. Phys. B **24**, 3915 (2010).
[4] A. K. Clogston, Phys. Rev. Lett. **9**, 266 (1962).
[5] K. Maki and T. Tsuneto, Prog. Theor. Phys. **31**, 945 (1964).
[6] L. W. Gruenberg and L. Gunther, Phys. Rev. Lett. **16**, 996 (1966).
[7] Clear evidence for spin-singlet superconductivity in the BEDT-TTF salts has been given by NMR data [see, e.g., S. M. De Soto and C. P. Slichter, Phys. Rev. B **52**, 10364 (1995); and H. Mayaffre, P. Wzietek, D. Jerome, C. Lenior, and P. Batail, Phys. Rev. Lett. **75**, 4122 (1995)] as well as by the Pauli-limited upper critical fields as seen, e.g., in the specific heat (Fig. 3).
[8] R. Lortz, Y. Wang, A. Demuer, P. H. M. Böttger, B. Bergk, G. Zwicknagl, Y. Nakazawa, and J. Wosnitza, Phys. Rev. Lett. **99**, 187002 (2007).
[9] B. Bergk, A. Demuer, I. Sheikin, Y. Wang, J. Wosnitza, Y. Nakazawa, and R. Lortz, Physica (Amsterdam) **470C**, S586 (2010).
[10] B. Bergk, A. Demuer, I. Sheikin, Y. Wang, J. Wosnitza, Y. Nakazawa, and R. Lortz, Phys. Rev. B **83**, 064506 (2011).
[11] J. A. Wright, E. Green, P. Kuhns, A. Reyes, J. Brooks, J. Schlueter, R. Kato, H. Yamamoto, M. Kobayashi, and S. E. Brown, Phys. Rev. Lett. **107**, 087002 (2011).
[12] J. Wosnitza *et al.*, Phys. Rev. B **65**, 180506(R) (2002); J. Wosnitza, J. Hagel, O. Ignatchik, B. Bergk, V. M. Gvozdikov, J. A. Schlueter, R. W. Winter, and G. L. Gard, J. Low Temp. Phys. **142**, 331 (2007).
[13] U. Geiser, J. A. Schlueter, H. H. Wang, A. M. Kini, J. M. Williams, P. P. Sche, H. I. Zakowicz, M. L. VanZile, and J. D. Dudek, J. Am. Chem. Soc. **118**, 9996 (1996); J. A. Schlueter *et al.*, Synth. Met. **85**, 1453 (1997).
[14] S. Wanka, J. Hagel, D. Beckmann, J. Wosnitza, J. A. Schlueter, J. M. Williams, P. G. Nixon, R. W. Winter, and G. L. Gard, Phys. Rev. B **57**, 3084 (1998).
[15] J. Wosnitza, J. Hagel, P. J. Meeson, D. Bintley, J. A. Schlueter, J. Mohtasham, R. W. Winter, and G. L. Gard, Phys. Rev. B **67**, 060504(R) (2003).

[16] D. Beckmann, S. Wanka, J. Wosnitza, J. A. Schlueter, J. M. Williams, P. G. Nixon, R. W. Winter, G. L. Gard, J. Ren, and M.-H. Whangbo, Eur. Phys. J. B **1**, 295 (1998).
[17] As the criterion determining $T^{\star}$, we used the maximum of the specific-heat anomaly in the $\Delta C/T$ data.
[18] K. Cho, B. E. Smith, W. A. Coniglio, L. E. Winter, C. C. Agosta, and J. A. Schlueter, Phys. Rev. B **79**, 220507(R) (2009).
[19] The relaxation time of our calorimeter (about 5 s below 1.5 K) is similar to the possible sweep rate of the magnetic field in our superconducting magnet. Therefore, no significant field-induced temperature changes could be resolved.
[20] Y. Matsuda and H. Shimahara, J. Phys. Soc. Jpn. **76**, 051005 (2007).