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Fluctuating superconductivity in the strongly correlated two-dimensional organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ in an in-plane magnetic field

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We report magnetoresistance and magnetic torque measurements for the highly correlated 2D organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. Under magnetic field parallel to the conducting layers, we obtain convincing evidence of fluctuating superconductivity in a wide temperature and field range, where the magnetic torque shows diamagnetism but the resistance shows no appreciable decrease.

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In conventional superconductors, the superconducting transition is well characterized by zero resistance and diamagnetism due to exclusion of magnetic flux (Meissner effect).[1] Above the transition temperature (T_c), the amplitude of the order parameter $|\Psi|$, corresponding to density of Cooper pairs, vanishes and the bulk phase coherence ϕ is lost. In strongly correlated two-dimensional (2D) superconductors,[2,3] however, vortex-Nernst effect measurements show that fluctuating superconductivity (FSC), which has finite Cooper pair density but no bulk phase coherence, appears substantially above T_c. The FSC will be one of the most intriguing interpretations of the pseudogap formation, which is likely an intrinsic property in strongly correlated 2D superconductors.[4]

The FSC has been extensively studied with the vortex-Nernst effect in magnetic fields perpendicular to the conducting layers.[2,3] In highly 2D superconductors, as the magnetic field is rotated from the perpendicular direction to the parallel direction, the orbital effect, which is closely related to the nucleation of vortices, is reduced and then the critical field increases significantly. Because of the highly 2D nature of the superconductivity, the FSC will be also field-direction dependent. However, the anisotropic properties of the FSC have been rarely investigated so far.

The vortex-Nernst effect experiments under in-plane magnetic fields have been prevented for two reasons. First, under in-plane field, the flux lines penetrate only the insulating layers, forming Josephson vortices, but not the superconducting layers. Because of the platelike shape of the samples, it is hard to detect the Nernst effect of the Josephson vortices. Second, high magnetic field, which is not realized under normal laboratory conditions, is required to destroy the superconductivity at low temperatures especially for the high-T_c cuprates. Such high critical field makes it difficult to obtain the global phase diagram.

In this Rapid Communication, we report the magnetoresistance and magnetic torque measurements for a highly correlated 2D organic superconductor κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ with T_c of 10.4 K.[5] Under magnetic field parallel to the conducting layers, we obtained convincing evidence of FSC in a wide temperature and field range, where the magnetic torque shows diamagnetism but the resistance shows no appreciable decrease.

A charge transfer salt, κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ (hereafter κ-NCS) is one of the most studied highly correlated organic superconductors. The BEDT-TTF molecule layers form the highly 2D electronic state separated by the Cu(NCS)$_2$ anion (insulating) layers as shown in the inset of Fig. 1(a). The dimerization of the BEDT-TTF donors gives rise to a half-filled energy band. The isostructural salt, κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br (hereafter κ-Br), with a slightly higher T_c ($\sim$12 K) has smaller t/U than κ-NCS, where t and U are the transfer integral between the BEDT-TTF dimers and the Coulomb repulsion on the dimer, respectively. Therefore, the electronic state of κ-Br is closer to a Mott insulating phase than κ-NCS in the T vs t/U phase diagram.[6] Large Nernst signals are clearly observed in perpendicular fields well above T_c for κ-Br, but not for κ-NCS.[3] With decreasing t/U, the number uncertainty of the Cooper pairs N ($=|\Psi|^2$), which incurs a Coulomb energy penalty, is reduced.[7] From the uncertainty relation between the Cooper pair number and the bulk phase, $\Delta N \Delta\phi > 1$, the small t/U enhances the phase uncertainty, leading to phase fluctuation in the superconducting state.

A magnetic torque measurement is a powerful probe for detecting FSC under in-plane field. The magnetic torque is quite sensitive to diamagnetism even in the fluctuation regime where supercurrent induces only local diamagnetism.[8] The torque is given by $\tau = \mu_0(M \times H)$ where H is the applied magnetic field and M the magnetization. For highly 2D superconductors, the torque under strong in-plane field is written as $\tau \approx H_x M_z(H_z)$ where the $x(z)$ axis is parallel (perpendicular) to the conduction layers.[9] Therefore, one can obtain the perpendicular magnetization curve $M_z(H_z)$ under large H_x by dividing the toque τ by H_x. In addition, we can overcome the second difficulty for the highly 2D organic superconductors since the in-plane upper critical field is much lower than that of high-T_c cuprates.

Single crystals of κ-NCS were grown electrochemically.[10] The crystals have platelike shapes, whose typical sizes used in the present experiments are 600 $\times$200 $\times$ 50 μm^3 for the resistance measurements and 200 $\times$ 100 $\times$ 20 μm^3 for

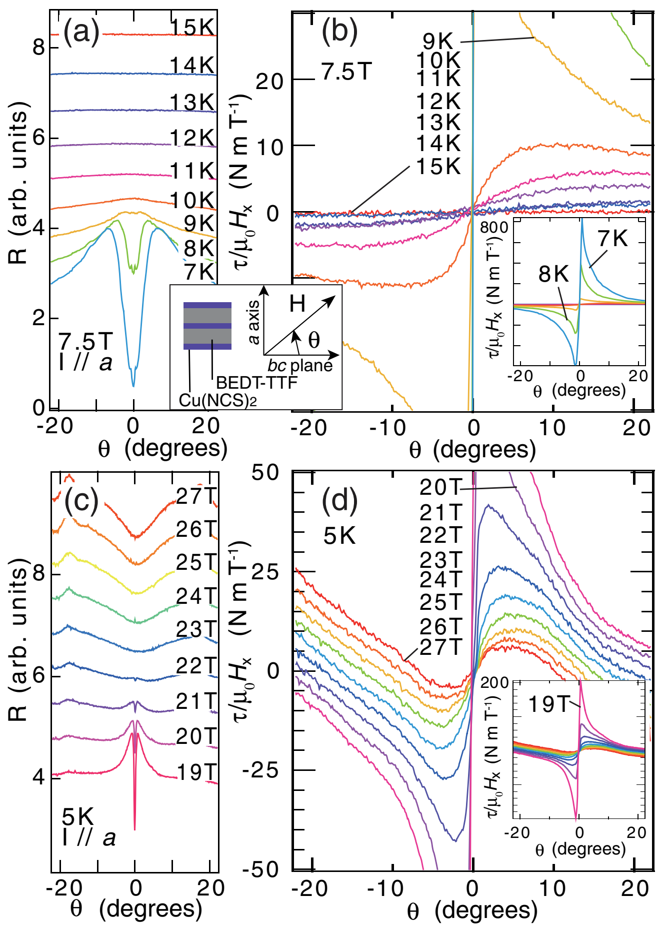

FIG. 1. (Color online) (a), (b): Angular dependence of the interlayer resistance R and magnetic torque τ at 7.5 T for various temperatures in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$. (c), (d): Angular dependence of the interlayer resistance and magnetic torque at 5 K for various magnetic fields. The inset of (a) shows a schematic of the crystal structure and the definition of the field angle θ. Each datum above 8 K in (a) and 20 T in (c) is shifted by a 0.5 Ω step for clarity. The insets of (b) and (d) show the overall views of the torque curves. The changes of the torque curves near $\theta = 0°$ show diamagnetism (negative M_z) of the sample.

the torque measurements. The samples 01-02 and 03-04 are used in the interlayer and in-plane resistance measurements, respectively, and samples 02, 05, and 06 are used in the torque measurements. The torque measurement for sample 02 is carried out after the resistance measurement. The magnetic torque was measured by a microcantilever technique.[11] The interlayer and in-plane resistances are measured with the standard four-terminal method with lock-in amplifiers with ac current of about 10 μA along the a axis and bc plane, respectively. Four gold wires of 10 μm in diameter are attached to the samples by carbon paste. These experiments were performed by a 20 T superconducting magnet with a ^{3}He cryostat or by a 30 T resistive magnet with a ^{4}He cryostat at Tsukuba magnet laboratories, NIMS.

Figure 1(a) shows the angular dependence of the interlayer resistance of κ-NCS at 7.5 T for various temperatures. We observe the resistance drops at zero degrees due to superconductivity below 8 K but there is no sign of the superconductivity above 9 K. In Fig. 1(b), the torque curves are presented. The torque steeply increases as the field is tilted from zero degrees (in-plane field) below 9 K. This linear increase shows large diamagnetism [$M_z(H_z) < 0$]: A large number of the magnetic fluxes remain between the superconducting layers and are excluded from the superconducting layers. As the magnetic field is further tilted, the torque has a sharp peak and then rapidly decreases, showing that most of vortices start penetrating the superconducting layers. This behavior is interpreted in terms of a lock-in transition of flux lines, a transition from parallel flux lines to tilted flux lines.[12] At higher angles, the diamagnetism is gradually reduced and then the superconductivity is completely broken. As temperature increases, the diamagnetism is considerably reduced: The magnetic fluxes are only partially excluded even for small H_z, and the lock-in transition is smeared out. The quite unusual behavior is that the diamagnetic signal is evident at high temperatures up to 12 K whereas the resistance shows no appreciable decrease above 9 K. This diamagnetism above 9 K can be ascribed to FSC. Although the interpretation of the vortex-Nernst effect due to FSC seems still controversial,[13–17] the observation of the diamagnetism in κ-NCS provides convincing evidence of FSC. No appreciable hysteresis of the torque curve with field angle in the FSC region shows very weak pinning of the vortices, consistent with the picture of FSC. Figures 1(c) and 1(d) show the interlayer resistance and the torque at 5 K under fields from 19 to 27 T, respectively. No sign of superconductivity in the resistance is seen above 22 T. However, the diamagnetic signal is obviously observed even at 27 T in the torque curves, showing the significantly large FSC in the wide field range.

We can obtain the absolute values of the perpendicular magnetization from the magnetic toque. The inset of Fig. 2 shows the perpendicular magnetization vs the internal

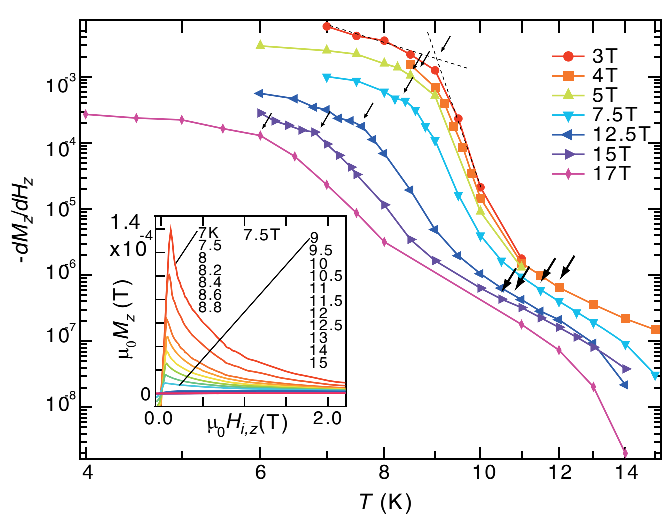

FIG. 2. (Color online) Temperature dependence of the diamagnetic susceptibility $-dM_z/dH_z$ for $H_z \to 0$. The perpendicular component of the magnetization $M_z(H_z)$ is derived from the relation $M_z(H_z) = \tau/(\mu_0 H_x)$. The inset shows $M_z(H_z)$ curves as a function of H_z for sample 05 at 7.5 T. Thick and thin arrows indicate the starting points of the upward curvatures and the saturation temperatures of $-dM_z/dH_z$ ($T_c^{\rm sat}$), respectively.

perpendicular magnetic field $H_{i,z} = H_z - nM_z$. The demagnetization factor of the sample, $n = 0.7$, is obtained from the ellipsoid approximation.[18] Figure 2 shows the temperature dependence of the slope of the τ/H_x curve as a function of H_z at zero degrees under various fields, corresponding to the diamagnetic susceptibility $-dM_z/dH_z$ for $H_z \to 0$. All the curves have qualitatively similar temperature dependence. At 3 T, for instance, $-dM_z/dH_z$ shows a steep increase at 11 K and tends to saturate below 9 K with decreasing temperature. The steep increase will correspond to the rapid growth of the phase coherence. We tentatively define $T_c^\star$ as the starting point of the upward curvature (thick arrows in Fig. 2). Different definitions of $T_c^\star$ will be acceptable, but our conclusions will not be affected by them. As field increases, the $-dM_z/dH_z$ curves shift to low temperatures: $T_c^\star$ is reduced with increasing field. At low temperatures, dM_z/dH_z tends to saturate, suggesting that the bulk phase coherence is almost achieved. The susceptibility $-dM_z/dH_z = 1$ corresponds to 100% diamagnetism (full Meissner effect along the z direction). As shown in Fig. 2, only a few percent of the Meissner volume fraction is obtained at low temperatures at 3 T. This small diamagnetism will be attributed to the fact that the perpendicular H_{c1} is too small to detect the full Meissner effect under large in-plane fields in the torque measurements. The lower critical field $\mu_0 H_{c1}$ in the perpendicular direction is only ~10 G at 7 K[19] and it corresponds to 0.006 degrees for $\mu_0 H = 10$ T. This value is smaller than the resolution of the rotation angle (~0.02 degrees).

The phase diagram of κ-NCS under the in-plane field is shown in Fig. 3, where $T_c^\star$ and T_c are the critical temperature determined by the torque and resistance measurements, respectively. The T_c values are defined as the temperatures where the resistances drop by 10%, which are in good agreement with the previous reports.[20] The $T_c^\star$ values are apparently higher than T_c, showing that FSC appears in the wide temperature and field region.

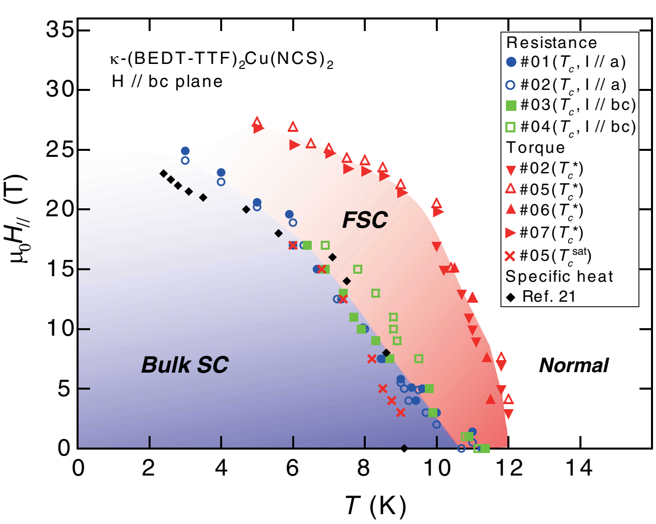

FIG. 3. (Color online) Phase diagram of κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ under the in-plane magnetic field. Circles and squares indicate $T_c(H)$ determined from the interlayer resistance ($I \parallel a$) and the in-plane resistance ($I \parallel bc$ plane), respectively. Triangles represent $T_c^*(H)$ determined from the magnetic torque measurements. Diamonds indicate $T_c(H)$ determined from the specific heat measurement (Ref. 21). Bulk SC and FSC indicate bulk superconductivity and fluctuating superconductivity, respectively.

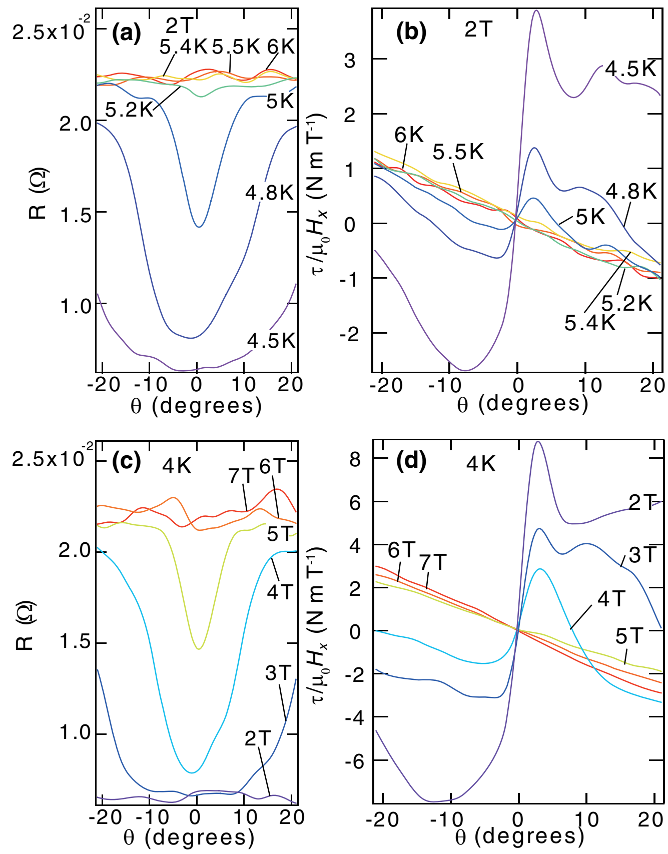

FIG. 4. (Color online) (a), (b): Angular dependence of the interlayer resistance and magnetic torque at 2 T for various temperatures in a typical anisotropic superconductor NbSe$_2$. (c), (d): Angular dependence of the interlayer resistance and magnetic torque at 4 K for various magnetic fields in NbSe$_2$. The wavy torque curves are probably caused by unknown pinning effects of the vortices.

Recently, heat capacity measurements have been done under in-plane field up to 23 T, whose T_c values are also plotted in Fig. 3 for comparison.[21] We note that our T_c values well agree with those determined by the heat capacity measurements for $\mu_0 H > 8$ T. At zero field, our T_c (about 10.8 K) is higher than the reported value $T_c = 9.1$ K. This difference, however, will give no profound influence on our conclusion. The saturation temperatures of dM_z/dH_z, T_c^{sat}, showing the bulk phase coherence, are also plotted. The T_c^{sat} values are in good agreement with T_c. This agreement will provide further evidence showing that the bulk phase coherence is achieved at T_c.

For comparison, we have performed the same experiments for a typical anisotropic superconductor NbSe$_2$ with $T_c = 7.2$ K.[22] Figures 4(a) and 4(b) show the angular dependencies of the resistance and the torque, respectively, at various temperatures. We note that reductions of resistance and diamagnetic signal due to superconductivity near zero degrees (in-plane field) disappear simultaneously above 5 K. As shown in Figs. 4(c) and 4(d), both the resistance drop and diamagnetism at 4 K also disappear above 5 T. At T_c (4.9 K) for 2 T, for instance, we obtain $-dM_z/dH_z$ ($H_z \to 0$) $\sim 2 \times 10^{-5}$, which is two orders of magnitude smaller than that for κ-NCS. These results lead us to conclude that FSC is not observed under the in-plane field for $NbSe_2$. There will be two possible reasons for the absence of the FSC: The electronic state is not highly 2D and/or the electron correlation is not sufficiently strong. To clarify this point, further investigation will be necessary.

In conventional BCS superconductors, the amplitude fluctuation is considered to be dominant: Phase fluctuation is negligible. As discussed in the literature,[23] there are two types of phase fluctuation, classical (thermal) and quantum fluctuations. For the classical phase fluctuation, "phase stiffness" of the order parameter is generally determined by the superfluid density $n_s(0)$: The smaller the density, the more the phase fluctuation. The density is given by $n_s(0) \sim m^\star/\lambda(0)^2$, where $m^\star$ and $\lambda(0)$ are the effective mass and penetration depth, respectively. Since $\lambda(0) \sim 8000$ Å for κ-NCS and $\lambda(0) \sim 200$ Å for $NbSe_2$,[24] $n_s(0)$ is about three orders of magnitude smaller for κ-NCS. The quantum fluctuation arises from the number-phase uncertainty relation, $\Delta N \Delta\phi > 1$. For layered structures, the charge fluctuation between the neighboring layers will be suppressed (because of the charge neutrality), which will enhance the quantum phase fluctuation. In this way, the phase will be much more fluctuated for κ-NCS than for $NbSe_2$. Therefore, the large FSC for κ-NCS is likely dominated by the phase (not by amplitude) fluctuation.

Surprisingly the vortex-Nernst effect measurements of κ-NCS show almost no FSC above T_c under perpendicular fields.[3] The fact suggests that the orbital effect of the in-plane field plays a crucial role in the emergence of FSC: The phase fluctuation is enhanced by the in-plane field. In Fig. 3, we actually note that the FSC region seems wider at higher fields although the measurements are limited in a relatively low field region at present.

Because of the layered structure, the interlayer transport is described as a quantum tunneling for κ-NCS. The interlayer tunneling conductance of layered structures under in-plane field has been studied theoretically[25] and experimentally.[26] Under in-plane field ($H \parallel y$), the interlayer tunneling, which requires the momentum and energy conservation, is suppressed since the field ($H \parallel y$) causes a momentum shift for the tunneling carriers, $k_x = eHd/h$, where d is the layer spacing. Therefore, for layered superconductors such as κ-NCS, the interlayer tunneling of the Cooper pairs is suppressed by the in-plane field: The Cooper pairs are confined in each superconducting layer. The confinement will reduce the number uncertainty ΔN, and consequently, enhance $\Delta\phi$. It may explain why the FSC is evident only under the in-plane field.

In conclusion, we performed systematic measurement of the angular dependence of the magnetoresistance and magnetic torque for a highly correlated 2D organic superconductor κ-NCS. Our work provides clear evidence of the diamagnetism due to the FSC in a wide temperature and field range under the in-plane fields. Since the vortex-Nernst effect measurements of κ-NCS show almost no FSC above T_c under perpendicular fields, the orbital effect of the in-plane field plays a crucial role in the emergence of the FSC. Moreover, no appreciable FSC in $NbSe_2$ gives an important insight into the origin of the FSC; strong electron correlation and/or high two dimensionality will be crucial for the FSC.

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[1] M. Tinkham, *Introduction to Superconductivity*, 2nd ed. (Dover Publications, Mineola, NY, 2004).
[2] Y. Wang, L. Li, and N. P. Ong, Phys. Rev. B **73**, 024510 (2006).
[3] M. Nam, A. Ardavan, S. J. Blundell, and J. A. Schlueter, Nature (London) **449**, 584 (2007).
[4] T. Timusk and B. Statt, Rep. Prog. Phys. **62**, 61 (1999).
[5] H. Urayama, H. Yamochi, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, Chem. Lett. **17**, 55 (1988).
[6] B. J. Powell and R. H. McKenzie, J. Phys.: Condens. Matter **18**, R827 (2006).
[7] S. Doniach, Phys. Rev. B **24**, 5063 (1981).
[8] Y. Wang, L. Li, M. J. Naughton, G. D. Gu, S. Uchida, and N. P. Ong, Phys. Rev. Lett. **95**, 247002 (2005).
[9] J. C. Martinez, S. H. Brongersma, A. Koshelev, B. Ivlev, P. H. Kes, R. P. Griessen, D. G. de Groot, Z. Tarnavski, and A. A. Menovsky, Phys. Rev. Lett. **69**, 2276 (1992).
[10] H. Anzai, J. M. Delrieu, S. Takasaki, S. Nakatsuji, and J. Yamada, J. Cryst. Growth **154**, 145 (1995).
[11] C. Rossel, P. Bauer, D. Zech, J. Hofer, M. Willemin, and H. Keller, J. Appl. Phys. **79**, 8166 (1996).
[12] D. Feinberg and C. Villard, Phys. Rev. Lett. **65**, 919 (1990).
[13] H. Kontani, Phys. Rev. Lett. **89**, 237003 (2002).
[14] I. Ussishkin, S. L. Sondhi, and D. A. Huse, Phys. Rev. Lett. **89**, 287001 (2002).
[15] B. Dora, K. Maki, A. Vanyolos, and A. Virosztek, Phys. Rev. B **68**, 241102 (2003).
[16] S. Tan and K. Levin, Phys. Rev. B **69**, 064510 (2004).
[17] A. S. Alexandrov and V. N. Zavaritsky, Phys. Rev. Lett. **93**, 217002 (2004).
[18] J. A. Osborn, Phys. Rev. **64**, 351 (1945).
[19] M. Tokumoto, H. Anzai, K. Takahashi, K. Murata, N. Kinoshita, and T. Ishiguro, Synth. Met. A **27**, 305 (1988).
[20] G. Saito, H. Yamochi, T. Nakamura, T. Komatsu, M. Nakashima, H. Mori, and K. Oshima, Physica B **169**, 372 (1991).
[21] R. Lortz, Y. Wang, A. Demuer, P. H. M. Bottger, B. Bergk, G. Zwicknagl, Y. Nakazawa, and J. Wosnitza, Phys. Rev. Lett. **99**, 187002 (2007).
[22] S. Foner and E. J. Mcniff Jr., Phys. Lett. A **45**, 429 (1973).
[23] V. J. Emery and S. A. Kivelson, Nature (London) **374**, 434 (1995).
[24] J. E. Sonier, R. F. Kiefl, J. H. Brewer, J. Chakhalian, S. R. Dunsiger, W. A. MacFarlane, R. I. Miller, A. Wong, G. M. Luke, and J. W. Brill, Phys. Rev. Lett. **79**, 1742 (1997).
[25] L. N. Bulaevskii, M. J. Graf, and M. P. Maley, Phys. Rev. Lett. **83**, 388 (1999).
[26] J. P. Eisenstein, T. J. Gramila, L. N. Pfeiffer, and K. W. West, Phys. Rev. B **44**, 6511 (1991).