Phase diagram of reentrant and magnetic-field-induced superconducting states with Kondo impurities in bulk and proximity-coupled compounds

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Reentrant behavior is known to exist and magnetic-field-induced superconductivity has been predicted in superconductors with Kondo impurities. We present a simple framework for understanding these phenomena and generalize it to explain the long-standing puzzle of paramagnetic reentrance in thick proximity systems as being due to Kondo impurities.

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I. INTRODUCTION

Magnetic impurities, even in minute concentrations, can significantly change the behavior of their hosts, as has been discovered in several recent works.[1] In superconductors, magnetic impurities act as pair breakers since their interaction with the electrons breaks the time-reversal symmetry of the two members of each Cooper pair. Many works have dealt with the effect of magnetic impurities on superconductivity, and the landmark for these is Abrikosov and Grokov's calculation of the depression of the critical temperature of a superconductor in the presence of magnetic impurities.[2] Maki[3] expanded this work to include any pair-breaking mechanism in a universal manner through the pair-breaking energy α. When the pair-breaking energy is of the order of the critical temperature, superconductivity will be completely suppressed.

In 1970 Müller-Hartmann and Zittarz[4] expanded Abrikosov and Gorkov's work to include the Kondo effect. They predicted that due to the competition between superconductivity and spin-flip scattering off the Kondo impurities there will be, for certain impurity concentrations, not one but three critical temperatures; that is, as the temperature is lowered the superconductor will go into a superconducting state at T_{C1}, out of it at a lower temperature T_{C2}, and back into it at an even lower temperature T_{C3}. This happens because the Kondo impurities' spin-flip depairing is maximal around T_K, the Kondo temperature, and falls off far from it.[5] This reentrant behavior was confirmed experimentally as far as the existence of T_{C2}, a reentrance into a normal phase, is concerned[6] but the existence of a third transition and the conditions under which it will be observable are still a matter of debate.[7]

In 1989, in an often overlooked set of articles,[8] Podmarkov and Sandalov predicted the existence of magnetic-field-induced superconductivity in such systems. They predicted that, while for small temperatures and magnetic fields superconductivity will be suppressed by spin-flip scattering off the Kondo impurities, the application of magnetic field can polarize the impurities thus reducing the spin-flip scattering and restoring superconductivity.

In this work we shall use a simple interpolation in order to expand Müller-Hartmann and Zittartz's work to include the effect of a finite magnetic field and thus account for Podmarkov and Sandalov's predictions. We shall also see why such behavior should appear in other superconducting systems and since the reentrant phenomenon in thick cylindrical proximity systems, which has intrigued theoreticians since its discovery in 1990 by Visani *et al.*,[9] shows such behavior we will suggest that it arises due to the existence of Kondo impurities in the measured samples.

II. THE INFLUENCE OF MAGNETIC FIELDS ON SUPERCONDUCTING SYSTEMS WITH KONDO IMPURITIES

The Abrikosov-Gorkov formula for the depression of a superconductor's critical temperature due to magnetic impurities is

$$\ln\left(\frac{T_C}{T_{C0}}\right) = \Psi\left(\frac{1}{2}\right) - \Psi\left(\frac{1}{2} + \frac{\alpha}{2\pi T_C}\right), \tag{1}$$

with T_{C0} being the transition temperature without pair breaking, T_C the transition temperature, α the pair-breaking energy, and Ψ the digamma function. The critical temperature is completely suppressed when the pair breaking energy, α, reaches a critical value $\alpha_{\rm cr} \equiv \pi/2\exp(-\gamma)T_{C0} = 0.882\,T_{C0}$ with γ being the Euler constant.

Müller-Hartmann and Zittartz,[4] building on the works of Nagaoka[10] and Suhl,[11] arrived at an approximate form for the temperature dependence of the pair-breaking energy of small concentrations of Kondo impurities

$$\alpha(T) = \alpha_{\max}\frac{\pi^2 S(S+1)}{\pi^2 S(S+1) + \ln^2(T/T_K)}, \tag{2}$$

with T_K being the Kondo temperature, S being the spin of the magnetic impurities and $\alpha_{\max} = n_s/2\pi\nu$ with n_s being the density of the impurities, and ν being the density of states at the Fermi level. At low temperatures, $T \ll T_K$, this formula, known as the Nagaoka-Suhl formula, ceases to be valid and more refined methods have to be used (e.g., Ref. 5).

Müller-Hartmann and Zittartz obtained the impurity dependence of the superconductor's critical temperature by plugging $\alpha(T_C)$ from Eq. (2) into Eq. (1) and solving for T_C thus resolving self-consistently the interplay between superconductivity and Kondo impurities' pair breaking. The resulting dependence shows a striking reentrant behavior for certain impurity concentrations, see Fig. 1, which was confirmed experimentally.[6]

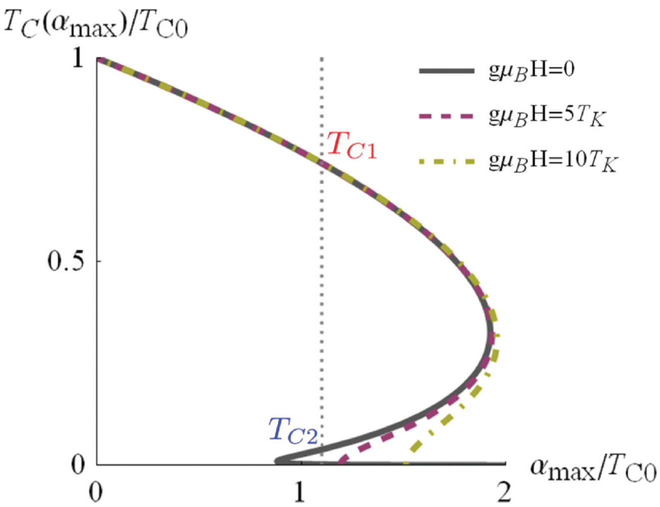

FIG. 1. (Color online) The critical temperature of a bulk superconductor in the presence of Kondo impurities, $T_C(\alpha_{\max})$, versus the maximal pair-breaking energy of the Kondo impurities $\alpha_{\max}$. Drawn from the self-consistent solution of Eqs. (1) and (3) for $T_K = T_{C0}/100$, $S = 1/2$, and three values of the Zeeman energy $g\mu_B H = 0$, $5T_K$, and $10T_K$ (in gray, dashed purple and dot-dashed yellow). The reentrant range for which there exists two or three transition temperatures is clearly visible and the magnetic field suppresses this reentrant behavior. The dotted gray line is the value of $\alpha_{\max}$ for which the dependence of the transition temperatures T_{C1} and T_{C2} (shown in red and blue measured in units of T_{C0}) on the magnetic field is plotted in Fig. 2. The third transition temperature, T_{C3}, which might exist at temperatures well below T_K is beyond the scope of this work.

As long as the Zeeman interaction is the dominant effect of the magnetic field on the system we can account for the effect of a finite magnetic field by using the interpolation[12]

$$\alpha(T,H) = \alpha_{\max}\frac{\pi^2 S(S+1)}{\pi^2 S(S+1) + \ln^2[\sqrt{T^2 + (g\mu_B H)^2}/T_K]} \quad (3)$$

with g being the Zeeman g factor, μ_B the Bohr magneton, and H the magnetic field. The magnetic field's dominant effect on the system is the Zeeman interaction when it is much smaller than the critical field of the superconductor, and other pair-breaking effects[3] are small compared to $\alpha_{\max}$. This equation interpolates between Eq. (2), which is the $g\mu_B H \ll T$ limit, and the $g\mu_B H \gg T$ limit where the Zeeman energy, $g\mu_B H$, replaces the temperature in that equation.[13]

While there have been several works regarding the crossover between these limits,[14] this simple interpolation, which disregards the pair-breaking energy's dependence on the electrons' energy, allows for an easy analysis of the system's behavior while giving the same qualitative results as other, more sophisticated methods[8] and allowing for easy generalization to other, similar systems (see below).

We can now insert Eq. (3) into Eq. (1), solve for T_C and obtain the dependence of the critical temperature on both impurity concentration and magnetic field as seen in Fig. 1 and the phase diagram of our system as can be seen in Fig. 2. For small temperatures and magnetic fields, $T, g\mu_B H \simeq T_K$, the system stops superconducting and goes

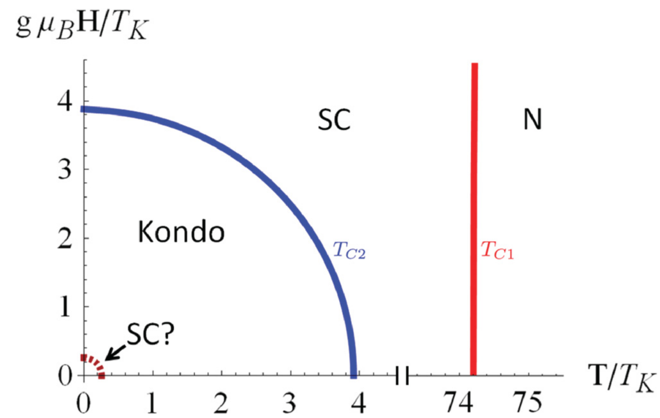

FIG. 2. (Color online) Phase diagram of a bulk superconductor with Kondo impurities in a small magnetic field, drawn from the self-consistent solution of Eqs. (1) and (3) for $T_K = T_{C0}/100$ and $\alpha_{\max} = 1.1T_{C0}$. At $T = T_{C1} \simeq 0.74T_{C0}$ the system has a phase transition from a normal phase into a superconducting one, which at $H \ll H_{C2}$ is almost field independent. At a low temperature, $T_{C2} \simeq 4T_K = 0.04T_{C0}$, the system undergoes a second phase transition into a non-superconducting phase dominated by spin-flip scattering from the Kondo impurities, which may be suppressed by a magnetic field of the order of $g\mu_B H = T_{C2}$. Thus the application of magnetic field in this phase can induce superconductivity. At even lower temperatures and magnetic fields ($T, g\mu_B H \ll T_K$) there might exist a transition back into a superconducting state.

into a phase dominated by spin-flip scattering off the Kondo impurities. For even smaller temperatures and magnetic fields there might exist another region of superconductivity, but since the Nagaoka-Suhl approximation is insufficient in that region we cannot contribute to the debate over its existence. However, we can mention that this extra region of superconductivity's extreme sensitivity to magnetic field might be a contributing factor in its experimental elusiveness.

In the Kondo phase, application of a magnetic field of the order of T_K/μ_B will cause the appearance of superconductivity by suppressing the Kondo effect. In this magnetic-field-induced superconductivity the Meissner effect will act to screen the magnetic field from the impurities, but since magnetic field is necessary for superconductivity a balance must be obtained and we shall therefore expect to see reduced Meissner screening which will increase at higher fields. There have already been several reports of systems with magnetic-field-induced superconductivity[15] including superconducting systems with magnetic impurities, but this type of behavior with both reentrance and magnetic-field-induced superconductivity is yet to be measured.

We can gain good insight into this system by looking at a graphical solution of the equations for T_C, Eqs. (1) and (2), in Fig. 3. The transition temperatures are the temperatures which co-solve these two equations, so graphically they correspond to the intersections of the two graphs $T_C(\alpha)$ from Eq. (1) and $\alpha(T)$ from Eq. (2). As we can see in Fig. 3 there is a range of $\alpha_{\max}$ for which there will be three intersections between the two graphs, and so there will be three critical temperatures. If $\alpha_{\max}$ is too small then there will be only one critical temperature close to T_{C0} while if $\alpha_{\max}$ is too large there will be only one critical temperature at $T \ll T_K$. Note that the validity of Eq. (2)

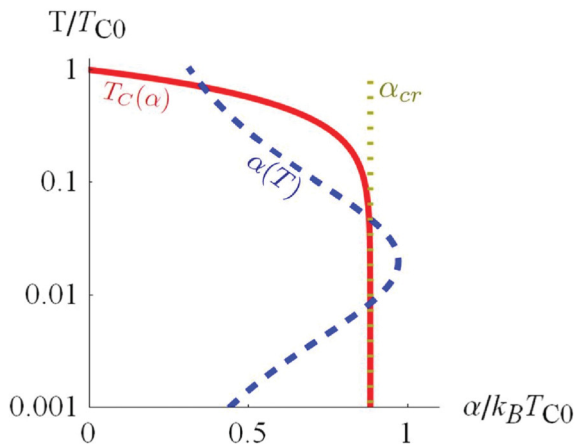

FIG. 3. (Color online) The shape of $T_C(\alpha)$ (in red), the critical temperature as a function of the pair breaking energy from Eq. (1), and $\alpha(T)$ (in dashed blue), the pair breaking energy as a function of temperature from Eq. (2). Also seen is $\alpha_{\rm cr}$ (in dotted mustard color), the critical pair breaking energy. Superconductivity will be seen at the range in which $\alpha(T)$ is below $T_C(\alpha)$ and so the the crossings of $\alpha(T)$ and $T_C(\alpha)$ represent critical temperatures. For a small enough T_K there can be values of $\alpha_{\rm max} = n_s/2\pi\nu$, the peak of the pair breaking energy, for which reentrance will occur, i.e., there will be multiple critical temperatures.

below T_K is dubitable and so the existence and properties of the sub-T_K transition are a matter of ongoing debate.[7]

In the limit $T_K < T_C \ll T_{C0}$ we can obtain approximate analytic expressions for the reentrant temperature and the range of impurity concentrations leading to reentrance which will be valid not only for bulk superconductors but also for other superconducting systems. At $T_C \ll T_{C0}$ Eq. (1) reduces to

$$\alpha = \alpha_{\rm cr} - O\left(T_C^2/T_{C0}\right), \tag{4}$$

and since $T_K \ll T_{C0}$ we can use the temperature-dependent α from Eq. (3) and set $\alpha(T_C) = \alpha_{\rm cr}$. Thus, at zero field, when the maximal spin-flip induced pair breaking exceeds the critical pair breaking energy, that is, when

$$\alpha_{\rm max} > \alpha_{\rm cr}, \tag{5}$$

there exists a transition from a superconducting phase into a nonsuperconducting phase when the pair breaking exceeds $\alpha_{\rm cr}$ at the temperature

$$T_{C2}(H=0) = T_K \exp\left(\pi\sqrt{S(S+1)(\alpha_{\rm max}/\alpha_{\rm cr}-1)}\right). \tag{6}$$

When $T_{C2} \sim T_{C0}$ this approximation breaks down, but that is exactly the limit where we expect reentrance to cease to exist, so we can use the condition $T_{C2} < T_{C0}$ with the above expression to obtain an upper bound for the reentrant range

$$\alpha_{\rm max} < \alpha_{\rm cr}\frac{\pi^2 S(S+1) + \ln^2(T_{C0}/T_K)}{\pi^2 S(S+1)}. \tag{7}$$

Using Eqs. (5) and (7) and the relation $\alpha_{\rm max} = n_s/2\pi\nu$ we obtain

$$2\pi\nu\alpha_{\rm cr} < n_s < 2\pi\nu\alpha_{\rm cr}\frac{\pi^2 S(S+1) + \ln^2(T_{C0}/T_K)}{\pi^2 S(S+1)} \tag{8}$$

for the range of impurity concentrations leading to reentrance at zero field.

For a finite magnetic field we find that

$$T_{C2}^2(H) + (g\mu_B H)^2 = T_{C2}^2(H=0) \tag{9}$$

and we see that as the field increases $T_{C2}(H)$ decreases. When $T_{C2}(H)$ goes below the sample's temperature the system will go out of the phase dominated by spin-flip scattering from the Kondo impurities and become superconducting; see Fig. 2.

The shape of Abrikosov and Gorkov's formula for $T_C(\alpha)$, Eq. (1), does not come into play in Eqs. (6), (8), and (9); only the value of $\alpha_{\rm cr}$ does. Since the shape of spin-flip induced Kondo impurity pair breaking is universal,[5] these equations should hold for any system where a critical pair-breaking energy destroys superconductivity and we should expect to see the behavior described above qualitatively in such systems even when Eq. (1) is not valid. Examples of such systems are thin superconducting films, dirty superconductors, and proximity induced superconductors (Kondo impurity induced reentrance has already been predicted for thin proximity systems[16]).

III. PARAMAGNETIC REENTRANCE IN PROXIMITY SYSTEMS

We now turn our attention to a system that shows a very similar behavior to the one we have just described, a behavior which has baffled theoreticians for over twenty years. The system in question is the thick proximity cylinders measured by Visani *et al.* and in subsequent experiments[9,17–19] which show both reentrant and magnetic-field-induced superconducting behavior, the two hallmarks of the physics described above.

In 1990, Visani *et al.*[9] measured the magnetic response of relatively clean thick proximity cylinders of superconducting material (Nb, Ta) coated with normal metal (Ag, Cu). As the samples were cooled the superconductor started to show full diamagnetic Meissner screening at $T \simeq T_{CS} \sim 10$ K, the critical temperature of the bulk superconductor. Around $T \simeq T_A \sim 1$ K, the Andreev temperature (see definition below), the normal metal in the samples started to also show the Meissner effect due to the proximity effect as expected.

In some samples at a lower temperature ($\sim$20 mK) a paramagnetic response came into play that tended to cancel the diamagnetic screening. This response increased gradually as the temperature was decreased until it saturated at $T \sim 1$ mK.[19] In some of the samples the normal metal's diamagnetic response was entirely canceled out by the paramagnetic effect, and in one sample the paramagnetic effect was reported to cancel out the superconductor's signal as well. A small magnetic field, of the order of 20 Oe, was shown to be enough to destroy the paramagnetic signal and return the sample to a screening fraction close to that which would have been expected if it was not for the reentrant effect. These measurements, which have stimulated a very lively discussion among theoreticians,[20–26] can be simply understood, in light of the theory presented above, as due to the existence of Kondo impurities in the normal metal. This approach does not rely on geometry and should apply equally to proximity cylinders and slabs.

For a thick proximity sample the relevant transition temperature is the Andreev temperature,[27] $T_A = v_F/2\pi d \ll T_{CS}$ with d being the thickness of the normal metal and v_F being the Fermi velocity. It is around this temperature that the normal side of the sample will start showing the Meissner effect, and it plays the role of T_{C0} when applying our results to this system and so $\alpha_{\rm cr} \sim T_A$. The field in which the supposed Kondo region breaks down is 20 Oe which correlates to a Zeeman energy of ∼5 mK, of the same order of the reentrant transition temperature as expected from Eq. (9), and therefore the Kondo temperature of the impurities is ∼1 mK. With these parameters and Eq. (8) the impurity concentration needed to explain the reentrant phenomenon can be estimated to be ∼100 ppm, though since this estimate relies on several unknown factors, especially the exact value of $\alpha_{\rm cr}$, the actual concentration may be much smaller.

While the source materials for these samples were reported to be very clean[27,28] the complex mechanical treatment involved in sample fabrication may have introduced magnetic impurities into the samples or created in them dislocations and/or two-level systems which can act as effective Kondo scatterers. The varnish used for isolating the samples[29] may also have introduced magnetic impurities into them. Notice that the nature of the impurities and their position within the sample (on the surface, in the bulk, or at the interface) might have major consequences for the effect in question. For example, the destruction of the superconductor's Meissner effect in one of the samples may be explained if the impurities permeated into the superconductor itself.

Past research into this reentrant phenomenon has led to two main approaches. One approach by Fauchére *et al.*[21] attributed this phenomenon to repulsive net electron-electron interactions in the normal metal. While attracting much theoretical attention[22–24,26] recent experimental results[30,31] indicate that such repulsive interactions do not exist in the relevant metals. Another approach by Bruder and Imry[20] suggested the phenomenon might be due to the contribution of glancing states. Bruder and Imry took the magnetic field to be constant in space in their argument but calculations that treated the magnetic field self-consistently with the Meissner current have shown that the effect of these states is too small to explain this phenomenon.[25,32]

The approach presented here explains, at least qualitatively, this phenomenon and can easily be verified experimentally either by characterizing the original samples or by fabricating new samples with controlled amounts of Kondo impurities. The existence of magnetic impurities in the original samples may be detected by a Curie-Weiss term in their magnetic response above T_{CS}, and the net paramagnetic magnetization in the original samples slightly above T_{CS}[19] may be a sign of such a term.

IV. CONCLUSIONS

We have presented a simple approach for understanding reentrant and magnetic-field-induced superconducting behavior in systems with Kondo impurities and have used it to show that the existence of such impurities can explain the paramagnetic reentrant effect which has been measured in proximty samples.

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1F. Pierre, A. B. Gougam, A. Anthore, H. Pothier, D. Esteve, and N. O. Birge, Phys. Rev. B **68**, 085413 (2003); H. Bary-Soroker, O. Entin-Wohlman, and Y. Imry, Phys. Rev. Lett. **101**, 057001 (2008).

2A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

3K. Maki, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969).

4E. Müller-Hartmann and J. Zittartz, Z. Phys. **234**, 58 (1970).

5T. Micklitz, A. Altland, T. A. Costi, and A. Rosch, Phys. Rev. Lett. **96**, 226601 (2006).

6M. B. Maple, W. A. Fertig, A. C. Mota, L. E. DeLong, D. Wohlleben, and R. Fitzgerald, Solid State Commun. **11**, 829 (1972).

7T. Matsuura and Y. Nagaoka, Solid State Commun. **18**, 1583 (1976); E. Müller-Hartmann, E. B. Schuh, and J. Zittartz, *ibid.* **19**, 439 (1976); K. Winzer, *ibid.* **24**, 551 (1977); D. Borycki and J. Maćkowiak, Supercond. Sci. Technol. **24**, 035007 (2011).

8A. N. Podmarkov and I. S. Sandalov, Supercond. Sci. Technol. **2**, 66 (1989) [Sov. Phys. JETP **68**, 1291 (1989)].

9P. Visani, A. C. Mota, and A. Pollini, Phys. Rev. Lett. **65**, 1514 (1990).

10Y. Nagaoka, Phys. Rev. **138**, A1112 (1965).

11H. Suhl, in *Many-Body Description of Nuclear Structure and Reactions*, Proceedings of the International School of Physics "Enrico Fermi," Course XXXVI, 1966, edited by C. Bloch (Academic, New York, 1967).

12F. B. Anders and M. Huth, Eur. Phys. J. B **19**, 491 (2001).

13P. Mohanty, J. Phys. Soc. Jpn. **72** Suppl. A, 13 (2003).

14G. Göppert, Y. M. Galperin, B. L. Altshuler, and H. Grabert, Phys. Rev. B **66**, 195328 (2002); M. G. Vavilov and L. I. Glazman, *ibid.* **67**, 115310 (2003).

15H. W. Meul, C. Rossel, M. Decroux, O. Fischer, G. Remenyi, and A. Briggs, Phys. Rev. Lett. **53**, 497 (1984); S. Uji, H. Shinagawa, T. Terashima, T. Yakabe, Y. Terai, M. Tokumoto, A. Kobayashi, H. Tanaka, and H. Kobayashi, Nature (London) **410**, 908 (2001).

16A. B. Kaiser, J. Phys. F **7**, L339 (1977).

17A. C. Mota, P. Visani, A. Pollini, and K. Aupke, Physica B **197**, 95 (1994).

[18] R. Frassanito, P. Visani, M. Nideröst, A. C. Mota, P. Smeibidl, K. Swieca, W. Wendler, and F. Pobell, Czech. J. Phys. **46**, 2317 (1996).
[19] F. B. Müller-Allinger and A. C. Mota, Phys. Rev. Lett. **84**, 3161 (2000).
[20] C. Bruder and Y. Imry, Phys. Rev. Lett. **80**, 5782 (1998).
[21] A. L. Fauchère, W. Belzig, and G. Blatter, Phys. Rev. Lett. **82**, 3336 (1999).
[22] F. Niederer, A. L. Fauchère, and G. Blatter, Phys. Rev. B **65**, 132515 (2002).
[23] O. T. Valls, M. Bryan, and I. Zutic, Phys. Rev. B **82**, 134534 (2010).
[24] T. Löfwander, Phys. Rev. B **70**, 094518 (2004).
[25] W. Belzig, C. Bruder, and Y. V. Nazarov, J. Low Temp. Phys. **147**, 441 (2007).
[26] K. Maki and S. Haas, Phys. Lett. A **272**, 271 (2000).
[27] F. B. Müller-Allinger, A. C. Mota, and W. Belzig, Phys. Rev. B **59**, 8887 (1999).
[28] A. C. Mota, P. Visani, and A. Pollini, J. Low Temp. Phys. **76**, 465 (1989).
[29] A. C. Mota (private communication).
[30] M. Wolz, C. Debuschewitz, W. Belzig, and E. Scheer, Phys. Rev. B **84**, 104516 (2011).
[31] W. Belzig (private communication).
[32] Yuval B. Simons, M.Sc. thesis, Weizmann Institute of Science, 2012.