Absence of effect of paramagnetic impurities on flux quantization in superconductors

Dragomir Davidović and M. Tinkham
Division of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138
(Received 19 February 1997)

In this work we investigate flux quantization effects in uniform superconducting rings doped with paramagnetic impurities. Several theories predicted that the impurity spins in weak links affect superconductivity by inducing phase shifts, which might result in half-integral fluxoid quantization. We tested whether these ideas could be extended to the case of uniform Mo rings doped with Fe, which is paramagnetic, but did not observe any such effects. We explain the absence of such effects within the de Gennes version of the Abrikosov-Gorkov theory of pair breaking. [S0163-1829(97)02626-X]

I. INTRODUCTION

A group of recent experiments which tested the symmetry of the superconducting state in high-temperature superconductors showed that a ring including such a superconductor may exhibit a half-integral flux quantization.[1–3] In such a ring, possible values of the fluxoid are $\pm\Phi_0/2, \pm 3\Phi_0/2, \ldots$, in strong contrast with conventional low-temperature superconducting rings where the fluxoid is quantized with values equal to $0, \pm\Phi_0, \pm 2\Phi_0, \ldots$. These experiments were done in order to test the idea that the order parameter in high-temperature superconductors has d-wave symmetry. The origin of half-integral (anomalous) flux quantization in a d-wave superconductor is an intrinsic phase shift of the superconducting order parameter between different crystalline directions. In a speculative alternative explanation,[4–6] it has been proposed that the anomalous flux quantization might be caused by phase shifts induced by spin-flip scattering on paramagnetic impurities, located at grain boundaries. The work reported here was motivated by a desire to test if these ideas can be applied to paramagnetic impurities in uniform superconducting rings.

In this work we measured fluxoid quantization in low-T_c superconducting loops doped with paramagnetic impurities. The rings were made by standard electron-beam lithography, and the impurity concentration was varied throughout the entire region of concentrations where T_c is nonzero. We find that paramagnetic impurities do *not* affect the type of flux quantization, and that the amplitude of the Little-Parks oscillations[7] is essentially independent of concentration of magnetic impurities. Experimental evidence indicates that paramagnetic impurities exist in bulk high-temperature superconductors.[6] Our work shows that those impurities cannot cause a half-integral flux quantization. We still do not rule out paramagnetic impurities as a possible explanation of the observed half-integral fluxoid quantization, because the quantization may be more sensitive to paramagnetic impurities in point contact weak links, as will be explained in the concluding section.

In Sec. II we give a brief background on pair-breaking effects in superconductors, in Secs. III and IV we discuss sample fabrication and results, and in Sec. V we give our conclusion.

II. BACKGROUND

In classic superconductors, paramagnetic impurities reduce the superconducting transition temperature; this is known as the pair-breaking effect. According to the Abrikosov-Gorkov theory,[8] pair breaking results from a difference in scattering amplitudes of paired electron states, where the scattering potential is the exchange interaction between conduction electrons and static magnetic impurities. de Gennes' version of the theory describes pair breaking by the properties of the time-reversal operator of a single electron in normal metal, subjected to forces that break its time-reversal symmetry.[9] Any two points in a sample are connected by many single-electron trajectories. The interference of the evolution of the time-reversal operator along those paths determines the correlation function of the superconducting pairing amplitude. Each time an electron passes near a magnetic impurity, the time-reversal operator rapidly acquires a phase,[10] which is of order Γ/E_F, where Γ is the exchange interaction between the electron and the impurity, and E_F is the Fermi energy of the metal. The phase shift is *dependent* on the relative orientation of the spins of the electron and the impurity. Because of the interference of different electron paths with different phase shifts, the superconducting correlations and the transition temperature are reduced in proportion to the concentration of paramagnetic impurities.

Another example of pair breaking in superconductors is an external magnetic field. In a magnetic field, the time-reversal operator of an electron along a trajectory evolves by acquiring a phase shift, which is equal to the Aharonov-Bohm phase of a Cooper pair.[9] This phase can be directly observed in the Little-Parks effect[7] or by interference in superconducting quantum interference devices (SQUID's). In contrast, explicit phase shifts induced by paramagnetic impurities in superconductors have not yet been seen experimentally.

It has been proposed that a Josephson junction containing paramagnetic impurities can have an intrinsic π phase shift originating from spin-flip scattering, and that a SQUID containing one such junction could exhibit half flux quantum pairing.[4] It was also predicted that anomalous flux quantization may appear with 50% probability in rings made from either disordered superconductors or granular superconductors doped with paramagnetic impurities and that phase shifts induced by the impurity spins are independent of the impurity spin orientation, which would make the phase shifts unaffected by thermal and quantum fluctuations.[5] Because our samples are well in the metallic regime, they are not necessarily the same as assumed in Ref. 5. However, the available evidence[11] and the Abrikosov-Gorkov theory[8] show that the pair-breaking effect does not depend on the amount of nonmagnetic disorder.

Within the de Gennes' description of pair breaking in superconductors, if we consider an electron path closing the loop such that the total phase accumulated along the path is closer to $(2n+1)\pi$ than to $2n\pi$, then such a path would favor a half flux quantum pairing. We note that because magnetic flux and fluxoid must be antisymmetric with respect to the applied magnetic field, due to the overall time-reversal symmetry of the ring, and because the spacing between consecutive fluxoid quantum values in a superconductor is equal to Φ_0, only integral or half-integral flux quantizations are allowed.

The type of flux quantization in our samples was determined by measuring the Little-Parks oscillations[7] near T_c. If the quantization were half-integer, then the induced circular supercurrents and their kinetic energy would have the highest magnitude when the applied flux is equal to $0, \pm\Phi_0, \pm 2\Phi_0, \ldots$, and the kinetic energy would be zero when the applied flux is equal to $\pm\Phi_0/2, \pm 3\Phi_0/2, \ldots$.[4] Thus, the superconducting critical temperature would have a maximum at the applied flux equal to $\pm\Phi_0/2, \pm 3\Phi_0/2, \ldots$, and the resistance vs field curves near T_c would be shifted by half a flux quantum relative to the conventional Little-Parks oscillation.[7]

III. SAMPLE FABRICATION

For this experiment, we selected Mo as the superconductor and Fe as the impurity. Fe dissolved in Mo has a magnetic moment,[12] and it has a dramatic effect on the superconducting transition temperature.[14] Only about 0.01 at. % Fe is enough to render bulk Mo nonsuperconducting.

MoFe alloy films were obtained by e-beam lithography, magnetron sputtering, and liftoff. A bilayer resist technique was used to achieve a large resist undercut, which is necessary for a successful liftoff of sputter deposited films. Mo and Fe were mixed by sputtering from two different targets. The first target, which we will refer to as pure Mo, contained about 0.003 at. % Fe, as specified by the manufacturer. The second target was a Mo target to which we added a dot of pure Fe. The area and the position of the dot were determined so that film deposited from that target alone contained approximately 0.02% Fe. Films with arbitrary Fe concentration were grown as multilayers Mo-$MoFe_{0.02\%}$-Mo-$MoFe_{0.02\%}$ ... $MoFe_{0.02\%}$-Mo, with a Mo layer thickness 40 Å and a $MoFe_{0.02\%}$ layer thickness ranging from 0 to 40 Å. Total film thickness was ≈ 500 Å. Since the superconducting coherence length of the films inferred from H_{c2} measurement was 400 Å, which greatly exceeds the layer thickness, the mixture can be regarded as uniform. Four films with different Fe concentration were deposited on a given pump-down of the sputtering chamber. Each film was patterned into four or five wires with widths ranging from 100 to 300 nm and six rings with diameter 1 μm and average width 150 nm. The total area covered by samples with a particular Fe concentration was only 50 μm$\times$50 μm, which assured a uniform Fe concentration. One ring sample is shown in Fig. 1.

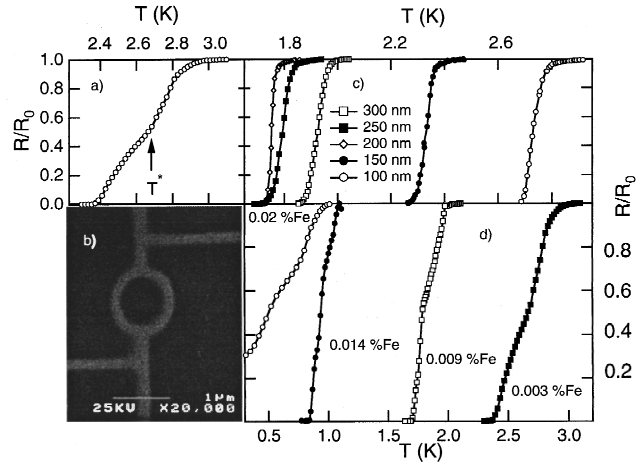

FIG. 1. (a) Superconducting transition curve of an undoped Mo ring. $T^{\star}$ is the temperature at which phase fluctuations are small enough that we can just observe Little-Parks oscillation. (b) Scanning electron micrograph of a Mo ring. (c) Superconducting transition curves of five Mo wires with different widths, showing nonmonotonic width dependence. (d) Superconducting transitions of four MoFe rings of different Fe concentration.

IV. RESULTS AND DISCUSSION

An undoped Mo ring and its superconducting transition curve are shown on the left part of Fig. 1. We also show five transition curves obtained by measuring five wires of different widths deposited at the same time, in the top right graph. Resistance was measured by a four-probe method with an ac excitation current of 0.1 μA and frequency 20 Hz, in both wires and rings. The ac response signal was linear and it was measured by an analog lock-in amplifier. Experiments were made in a ^{3}He cryostat, which was placed inside a shielded room. All external leads were filtered to reduce rf noise. As the width of wires decreases, T_c first decreases. But, when the width is about 200 nm or less, this trend reverses, and T_c becomes larger as the wire gets narrower. The initial T_c vs width dependence can result from weak localization enhancement of electron-electron interactions[15] or possibly from the enhancement of the pair-breaking strength of Fe, due to the finite-size Kondo effect.[16] The sheet resistance of the film $\sim 1\ \Omega$ is much smaller than the resistance quantum; thus the weak localization effects should be negligibly small. The increase in T_c when the width becomes smaller than 200 nm is probably caused by the reduction in stress in Mo. It is known that narrow wires made by magnetron sputtering and liftoff have less stress and smaller thickness than the bulk film, due to the shadowing effects of the resist mask.[13] We measured that the narrowest wires were about 15% thinner by atomic-force microscopy.

All the rings that we measured have dimensions as shown in Fig. 1. The field that generates one flux quantum in a 1 μm diameter circle is 25 G. Flux quantization effects in an undoped Mo ring are shown in Fig. 2. The curves show

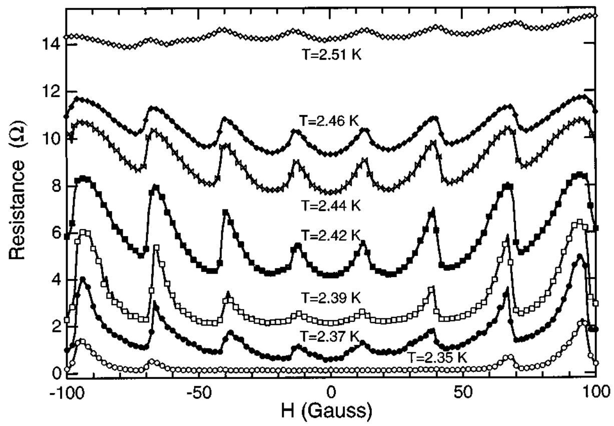

FIG. 2. Resistance vs magnetic field of the purest Mo ring at different temperatures. The oscillations represent the Little-Parks effect. No oscillations are observed above $T^\star$ as indicated in Fig.1(a).

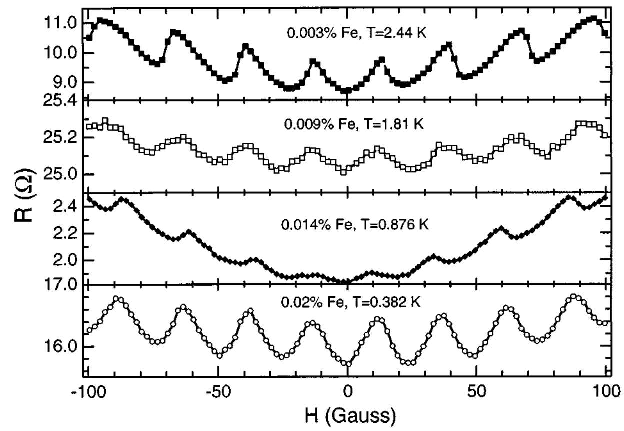

FIG. 3. Little-Parks effect of Mo rings vs concentration of Fe. Note that only integer flux quantization is observed, independent of Fe concentration.

resistance vs magnetic field applied perpendicular to the ring. We see that the oscillations in resistance have a minimum at zero field, and the first maximum at 12.5 G, which is the field for a half flux quantum in the ring, exactly as expected in the usual Little-Parks effect. As the temperature is reduced, the oscillations of the resistance as a function of magnetic field first appear at $T \approx 2.6$ K. Above this temperature, the resistance is nearly constant in this range of fields. We note that there is an inflection point in the resistance vs temperature curve in Fig. 1(a), indicated by $T^\star$, just above the temperature at which the oscillations in resistance begin. Thus $T^\star$ is identified as the temperature at which the entire ring becomes superconducting, in a sense that phase fluctuations are small enough that we can observe Little-Parks oscillations. $T^\star$ is much smaller than the temperature of the onset of the transition because of the strong width dependence of T_c in narrow Mo wires. Since the average width of the wire is ≈ 150 nm<200 nm, and since the wire is wider near electric contacts, superconductivity first nucleates at two points which are furthest away from the contacts. As the temperature is reduced, superconducting regions spread, and at $T^\star$, we can observe phase coherence along the entire ring circumference.

The effect of Fe on T_c of Mo rings is shown by Fig. 1(d). The depression of T_c is approximately proportional to the Fe content. The width of the transition is nearly independent of Fe concentration, when the concentration is smaller than 0.015%. At the highest measured Fe concentration, the transitions become wider. The origin of this broadening is not clear, but it may be due to the antiferromagnetic correlation between Fe spins, which is well established in MoFe alloys with large Fe concentration.[12] The slope of the depression of T_c is approximately $dT_c/dC \approx 1.4$ K/0.01 at. %, which is close to the literature value.[14] The normal-state resistance in all the samples is between 37 and 57 Ω, and its value does not depend on Fe concentration. The temperature dependence of the resistance above T_c and below 8 K is barely measurable, but the samples with Fe concentration larger than 0.01% have a negative temperature slope, which is caused by the Kondo effect in Mo.[17]

The Little-Parks effect in the MoFe rings is shown in Fig. 3. A close inspection in Fig. 1(d) shows that there is an inflection point in all three doped samples, just as the point denoted by $T^\star$ for an undoped sample in Fig. 1(a). Flux quantization effects were observed only at temperatures below the corresponding inflection points. At all the temperatures where oscillations in resistance are nonzero, and for all the Fe concentrations, the phase of the Little-Parks oscillation is given by integral flux quantization. The amplitudes of the oscillations are not the same in all the curves because they were obtained at different relative temperatures $(T_c - T)$. Nonetheless, the magnitude of the oscillation in resistance is about the same in the purest Mo and the most highly doped sample at the corresponding temperature. We may conclude that the Little-Parks effect is not strongly affected by doping with paramagnetic impurities.

V. CONCLUSION

Fluxoid quantization effects in micron-sized Mo rings doped by magnetic Fe impurities were measured, as a function of Fe concentration. We found that integral flux quantization is the only observed quantized regime. Within the de Gennes' formalism, the explanation for the absence of any anomalous flux quantization is that the phase shifts induced by paramagnetic impurities do not survive averaging over different electron paths around the loop. When the length of an electron path enclosing the ring is of the order of the mean free path for spin-flip scattering, then the accumulated phase is of order 1. Because the superconducting state is formed when electrons condense in many paired electron states, and because the width of the wires is much larger than the mean free path to elastic scattering, phase shifts vary randomly from pair to pair, and so the average phase shift along the loop is zero. This situation would be different if the diameter of the wire forming the ring were narrow enough to make it essentially one-dimensional, so that all the electrons circling the loop are subjected to the same exchange potential; however, our samples are not that narrow. A loop with a nanometer-size point contact, doped with magnetic impurities might satisfy this requirement in an experimentally accessible way.

ACKNOWLEDGMENTS

This research was supported by NSF Grant No. DMR92-07956 and MRSEC Grant No. DMR-94-00396. We thank K. K. Likharev and Philip Phillips for useful discussions.

[1] D. A. Wollman, D. J. Van Harlingen, W. C. Lee, D. M. Ginsberg, and A. J. Leggett, Phys. Rev. Lett. **71**, 2134 (1993).
[2] C. C. Tsuei, J. R. Kirtley, C. C. Chi, L. S. Yu-Jahnes, A. Gupta, T. Shaw, J. Z. Sun, and M. B. Ketchen, Phys. Rev. Lett. **73**, 593 (1994).
[3] A. Mathai, Y. Gim, R. C. Black, A. Amar, and F. C. Wellstood, Phys. Rev. Lett. **74**, 4523 (1995).
[4] L. N. Bulaevskii, V. V. Kuzii, and A. A. Sobyanin, Pis'ma Zh. Eksp. Teor. Fiz. **25**, 314 (1977) [JETP Lett. **25**, 290 (1977)].
[5] B. I. Spivak and S. Kivelson, Phys. Rev. B **43**, 3740 (1991).
[6] V. Kresin, S. Wolf, Yu. Ovchinikov, A. Bill, S. Adrian, O. Dolgov, and S. Shulga, J. Low Temp. Phys. **106**, 159 (1997).
[7] W. A. Little and R. D. Parks, Phys. Rev. Lett. **9**, 9 (1962).
[8] A. A. Abrikosov and L. P. Gorkov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].
[9] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Addison-Wesley, Reading, MA, 1989), pp. 247–272.
[10] P. G. de Gennes and M. Tinkham, Physics **1**, 107 (1964).
[11] R. Hilsch, G. v. Minnigerode, and K. Schwidtal, *Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962* (Butterworths, London, 1963), p. 155.
[12] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).
[13] T. Shiota, T. Imamura, and S. Hasuo, IEEE Trans. Supercond. **2**, 1 (1992).
[14] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Lett. **8**, 313 (1962).
[15] J. M. Graybeal, P. M. Mankiewich, R. C. Dynes, and M. R. Beasley, Phys. Rev. Lett. **59**, 2697 (1987).
[16] P. Phillips (private communication).
[17] B. R. Coles, Philos. Mag. **8**, 335 (1963).