Vortex-lattice melting in superconducting fullerene Rb_3C_{60}

M. F. Tai and G. F. Chang
Department of Physics, National Chung-Cheng University, Chia-Yi 621, Taiwan, Republic of China

M. W. Lee
Department of Physics, National Chung-Hsing University, Tai-Chung 402, Taiwan, Republic of China

(Received 15 December 1994; revised manuscript received 29 March 1995)

The temperature and field dependences of the dc magnetization have been characterized on a sample of Rb_3C_{60} fullerene with $T_c = 30.5$ K. The sample exhibits a rather large critical current density of about 2×10^6 A/cm^2 at $T = 5$ K and $H = 0$ T. An irreversibility line $H_{irr}(T)$ is defined by merging points of two sets of zero-field-cooling and field-cooling magnetization curves. The temperature dependence of the irreversibility field is in fairly good agreement with a power-law relation: $H_{irr}(T) = H_{irr}(0)[1 - T(H)/T_0]^\gamma$. The best fit of experimental data to this equation provides the following values: $\gamma = 2.04\pm0.16$, $H_{irr}(0) = 470\pm52$ kOe, and $T_0 = 30.4\pm0.2$ K. According to the nonlocal elasticity theory based on the Lindemann criterion, $\gamma = 2$ strongly suggests the occurrence of thermally activated vortex-lattice melting in our Rb_3C_{60} sample. The Lindemann number of $c \le 0.074$ is comparable to those of conventional type-II superconductors, but is much smaller than those for high-T_c oxides. Our data provide evidence of vortex-lattice melting in the superconducting fullerenes.

I. INTRODUCTION

Soon after the discovery of high-T_c oxide superconductors, Müller, Takashige, and Bednorz[1] investigated the magnetic behavior of the La-Ba-Cu-O superconductor and observed the presence of an irreversibility line within the region of the Abrikosov magnetic phase. This discovery prompted many experimental and theoretical investigations on the irreversibility line and vortex dynamics in subsequently discovered high-T_c superconductors.[2–17] These investigations have revealed that the possible causes of the irreversibility line may be flux creep,[2–5] the vortex-glass transition,[6–8] or vortex-lattice melting.[9–15] In the vortex-glass picture,[6–8] it is proposed that a second-order phase transition occurs when the vortex glass is transformed to a vortex-liquid phase. For example, the high-T_c layered cuprate oxides in the dirty limit[1,6–8] exhibit such a transition that appears to be continuous. The temperature width of this vortex-glass transition depends on the amount of disorder of the defects in the original phase. Thus, if a sample is free from defects, melting of the vortex lattice to form a vortex fluid would be a first-order phase transition. Such a transition has been observed based on the evidence of magnetic, transport, and oscillation measurements in high-quality untwinned single crystals, thin films of high-T_c superconductors,[9–13] and conventional low-T_c superconductors.[14,15]

The recent discovery of superconductivity in the alkali-metal intercalated fullerenes[16] presents another challenge. Some investigations[17–22] showed that the superconducting fullerenes are type-II superconductors of the conventional BCS model. Moreover, electrical conductivity measurements on single crystals revealed that the superconductivity is isotropic and three dimensional.[22] They are in contrast to ceramic superconductors that are highly anisotropic and two dimensional. The possible existence of irreversibility lines and vortex behaviors in fullerenes has received little attention up to now.[18–21] Recently, however, Lin *et al.*[17] studied the irreversibility lines and magnetic relaxation in K_3C_{60} and Rb_3C_{60} specimens. They demonstrated the existence of a superconducting glass and its transition to a vortex fluid in their polycrystalline specimens.

In this report we present data of dc magnetization for a powdered sample of Rb_3C_{60} measured at different temperatures and magnetic fields. These data allow the identification of an irreversibility line $H_{irr}(T)$ in the H-T plot. The position of this line is compared to theoretical predictions based on possible models of flux creep, vortex glass, and vortex-lattice melting. The results, based on the Lindemann criterion, strongly suggest the occurrence of a first-order transition of vortex-lattice melting. To the best of our knowledge, this represents the first observation of flux-lattice melting in a superconducting fullerene.

II. EXPERIMENTAL PROCEDURE

High-purity C_{60} crystallites were extracted from the soot of evaporated graphite by the usual method as reported earlier.[23,24] The C_{60} powder so obtained had a nearly crystalline morphology with cubic faces observable under a scanning electron microscope (SEM). The sizes of these crystallites were measured to be up to 100 μm with an average of about 50 μm. This average size appeared to be much larger than the penetration length of Rb_3C_{60} ($\lambda\sim3000$ Å).[18–20] A Rb_3C_{60} sample was successfully prepared from these C_{60} crystallites. This sample contained particles of about the same size as its source. The detailed sample preparation procedure for Rb_3C_{60} was described in a previous paper.[24]

 ©1995 The American Physical Society

All dc magnetic data were measured by a Quantum Design superconducting quantum interference device (SQUID) MPMSR2 magnetometer. Zero-field-cooled (ZFC) and field-cooled (FC) magnetizations were performed in various magnetic fields ranging from 1 mT to 1 T. dc hysteresis curves at various temperatures with 2.5 K intervals were performed over the field range of ± 1 T. The setting method of a point-by-point magnetic field was chosen for the field stability. The demagnetization correction due to sample geometry[25] was neglected because it is less than 2% of the measured data.

III. RESULTS AND DISCUSSION

The temperature dependences of the ZFC and FC susceptibility curves of the Rb_3C_{60} sample in applied fields of 10 and 500 Oe are shown in Figs. 1(a) and 1(b), respectively. Both low-field ZFC and FC diamagnetism give the same T_c value of 30.5 ± 0.2 K. The decline of diamagnetic signals for both FC and ZFC processes is more abrupt in our sample than that reported by others.[17–22] Moreover, the large ZFC diamagnetic signal of -1.94×10^{-2} emu/cm^3 G in our sample is accompanied by a very smaller FC diamagnetic signal of -1.38×10^{-3} emu/cm^3 G at $T=5$ K and $H=10$ Oe. Similar phenomena also appear at higher fields. These smaller-than-usual FC values may be attributed to the influence of a stronger effect of vortex pinning in our specimen. The influence is consistent with that interpreted by Tomioka *et al.*[26]

Tomioka *et al.*[26] proposed a model based on vortex-pinning control that explained the existence of a significantly smaller Meissner fraction in a specimen with a stronger pinning strength. Small Meissner fractions have been observed even in single crystals or powdered samples with high purity. Based on the flux distribution expected from Bean's critical-state model, they discussed how the ZFC (shielding effect) and FC (Meissner effect) magnetization curves of type-II superconductors with pinning deviate from the equilibrium case. In addition, they derived the dependence of ZFC and FC magnetization on certain factors such as the applied magnetic field and sample size. They concluded that the Meissner fraction (f_M) decreases monotonically with increasing field. Moreover, the saturated f_M values in low fields and low temperatures are significantly affected by the temperature dependence of J_c. For most superconductors, the temperature dependence of J_c has approximately the scaling relation of Eq. (1), which will be further discussed later. They argued that a larger pinning strength would yield a smaller m and consistently a smaller superconducting fraction of Meissner effect. Thus the saturated values of ZFC and FC magnetization in low temperatures and low fields would decrease with decreasing exponent m, especially these for FC (or Meissner fraction). According to this model, even in a field as small as 0.01 Oe, the low-temperature FC diamagnetism may be incomplete and unsaturated.

This model has been successfully used to explain the field-dependent ZFC and FC curves in polycrystalline samples of niobium and single crystals of $YBa_2Cu_3O_y$, $(La_{1-x}Sr_x)_2CuO_4$, and $Bi_2Sr_{1.8}CaCu_2O_8$.[26] The temperature and field dependences of the Meissner fraction for an unannealed Nb specimen with a higher pinning strength became approximately constant in low fields and had much smaller values than those for single crystals of oxide superconductors. This difference is attributed to the difference in the dependence of J_c on temperature in niobium and oxides. The temperature dependence of J_c in niobium, a typically metallic superconductor with a stronger pinning, was estimated as $J_c(T)\sim J_c(0)(1-T/T_c)$, while $J_c(T)$ for typical oxide superconductors, such as $YBa_2Cu_3O_y$, exhibits a more rapid decrease with increasing T, which has been reported as $J_c(T)\sim J_c(0)[1-(T/T_c)^2]^n$ with a larger exponent $n=3$–4.

As shown in Fig. 1, we find that the FC magnetization for our sample also shows a very small Meissner fraction. This result is similar to those of niobium samples with strong vortex pinning. For our Rb_3C_{60} specimen, the $J_c(T)$ data also have the scaling-law relation of Eq. (1) which will be presented in the following section. The data fit described later shows that in the low-temperature region m is approximately equal to 1.4 for fields below 500 Oe with $T<T_c$; and $m\simeq 2$, for fields ranging from 500 Oe to 1 T. These m values in our sample are close to those of Nb specimens. The small m values and large $J_c(H,T)$ suggest the existence of a large pinning strength in our Rb_3C_{60} sample. Furthermore, these results explain the presence of small FC susceptibilities at low fields in our Rb_3C_{60} sample according to the vortex-pinning-control model. The calculation of the pinning potential

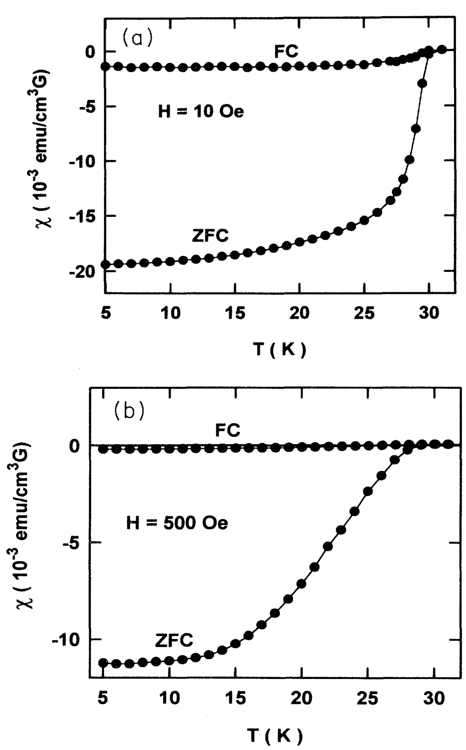

FIG. 1. dc ZFC and FC susceptibilities of Rb_3C_{60} as a function of temperature at an applied field of (a) 10 Oe and (b) 500 Oe.

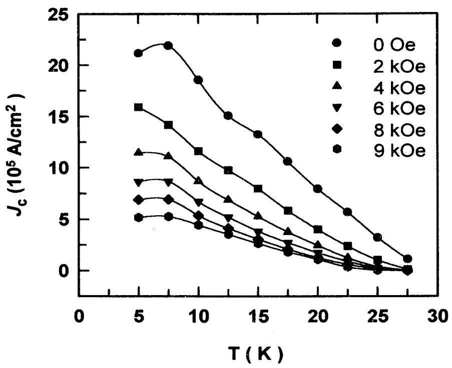

FIG. 2. Critical current density $J_c(T)$ of Rb_3C_{60} as a function of temperature at various field intensities.

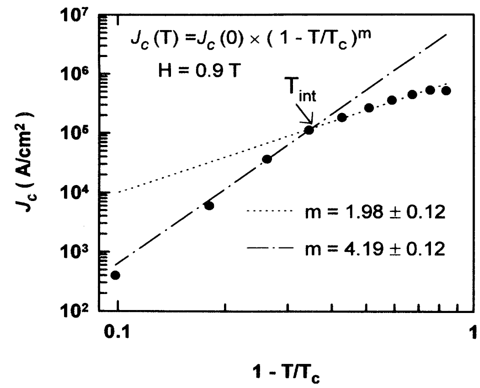

FIG. 4. Dependence of J_c on $(1-T/T_c)$ in $H=0.9$ T for Rb_3C_{60}. Both lines are regression curves of the empirical scaling equation of Eq. (1) for different m values.

will be presented elsewhere.[27]

Based on a modified Bean's model,[25] for a powdered sample with an average particle size of d (in cm), the magnetic critical current density J_c (in A/cm^2) may be estimated from the following formula:

$$J_c = 30\Delta M/d \ .$$

Here, ΔM (in G) $=M_+ - M_-$, where M_+ and M_- represent the magnetization values measured during decreasing- and increasing-field branches, respectively. Figure 2 shows the temperature dependence of the calculated magnetic critical current densities, J_c, at various fields. Note that J_c values appear to be rather large at lower temperatures/fields. For example, at $T=5$ K, $J_c = 2.1\times10^6$ A/cm^2 for $H=0$ T and 5.2×10^5 A/cm^2 for $H=0.9$ T. As the temperature increases to 25 K, the J_c value still remains at 3.2×10^5 A/cm^2 for zero applied field. The J_c values so calculated are rather large for a powdered sample of a superconductor. These large J_c values suggest the presence of strong pinning in our sample.

The dependence of J_c on temperature may follow the empirical scaling relation

$$J_c(T) = J_c(0)(1-T/T_c)^m \ , \tag{1}$$

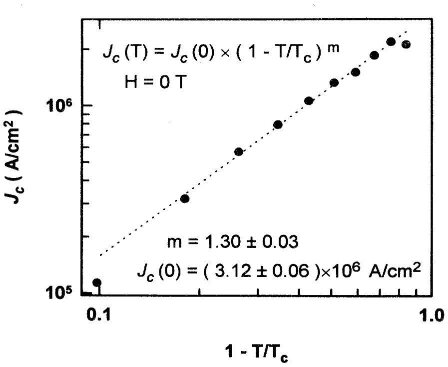

FIG. 3. Dependence of J_c on $(1-T/T_c)$ in $H=0$ T for Rb_3C_{60}. The line is a regression curve of the empirical scaling equation of Eq. (1) based on the experimental data.

where $J_c(0)$ is the extrapolated critical current density at $T=0$ K and T_c is the superconducting transition temperature. For zero applied field, as shown in Fig. 3, a data fit of $J_c(T)$ yields $m=1.30\pm0.03$ and $J_c(0)=(3.12\pm0.06)\times10^6$ A/cm^2 for $5<T<30$ K. For the field range from 0.4 to 0.8 T, Eq. (1) yields $m\sim2$. In the higher-field region, two types of scaling curves may apply to different temperature ranges. For $H=0.9$ T, as shown in Fig. 4, $m=1.98\pm0.12$ and $J_c(0)=(9.60\pm0.55)\times10^5$ A/cm^2 are obtained for the lower temperature range of $5<T<20$ K. In the higher-temperature range of $20<T<30$ K, the larger values of $m=4.19\pm0.12$ and $J_c(0)=(9.7\pm1.2)\times10^6$ A/cm^2 are applicable. Each curve represents a flux-density distribution. Both curves intersect at $T=20$ K which defines the intersecting temperature T_{int}, as indicated in Fig. 4. It appears that T_{int} corresponds to T^+ as reported by Tomioka *et al.*[26] According to them, T^+ will decrease with increasing field. If this is the case, we expect T_{int} to decrease with rising field also. When applied to our sample, we obtain $m\leq2$ for T below T_{int} and $m\geq4$ for T above T_{int}.

An irreversibility line $H_{irr}(T)$ can be defined by the merging points of ZFC and FC magnetization curves. Lin *et al.*[17] also studied the irreversibility lines $H_{irr}(T)$ of the same system (M_3C_{60} with $M=$K and Rb). Figure 5 compares $H_{irr}(T)$ of Rb_3C_{60} for the data of Lin *et al.* and ours. Both irreversibility lines can be expressed by the following power-law relation:

$$H_{irr}(T) = H_{irr}(0)[1-T/T_0]^\gamma \ . \tag{2}$$

Here, $H_{irr}(0)$, T_0, and γ are treated as fitting parameters. $H_{irr}(0)$ is obtained by extrapolating the irreversibility field to $T=0$ K and T_0 is the irreversibility temperature at zero applied field, i.e., $T_{irr}(H=0)$. T_0 also corresponds to the zero-field superconducting critical temperature, i.e., $T_c(H=0)$. For $T_0=T_c(H=0)=30.5$ K, the best fit of our data yields these values: $\gamma=2.04\pm0.16$ and $H_{irr}(0)=470\pm52$ kOe. If the γ value is assumed to be exactly 2, then T_0 would be 30.4 ± 0.2 K. γ values as re-

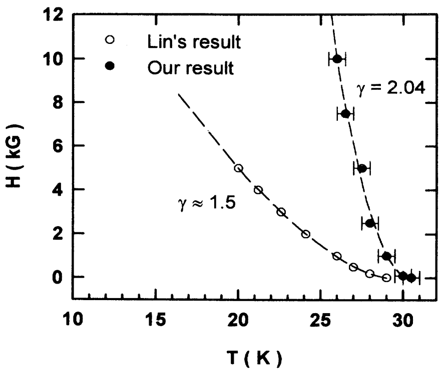

FIG. 5. Comparison of irreversibility lines of Rb_3C_{60}. Solid and open circles represent our data and the data of Lin *et al.* (Ref. 17), respectively. Both lines are regression curves of the power law of Eq. (2).

ported in the literature[9–15,28] are very close to 2 for many superconducting samples that are defect-free, e.g., the untwinned single crystals of $YBa_2Cu_3O_7$,[11] and $Bi_2Sr_2Ca_2Cu_3O_{10}$,[9] Nb thin films,[14] etc. Thus our data are consistent with the theoretical predictions based on models of vortex-lattice melting, but they are in disagreement with other mechanisms, such as flux creep and the vortex glass.

Houghton, Pelcovits, and Sudbø[9] proposed a nonlocal elasticity theory based on the Lindemann criterion to investigate the thermally activated flux-lattice melting for type-II superconductors. They calculated the effective stiffness of the lattice as a function of field and temperature. They defined the degree of susceptibility α as follows:

$$\alpha=2\times10^5[H_{c2}(0)/T_c^2]^{1/2}(m/m_z)^{1/2}(c/\kappa)^2 \ . \tag{3}$$

Applying the Lindemann criterion and α, they derived an implicit relationship for the melting field at the melting point and obtained the melting criterion due to thermal fluctuations as follows:

$$\frac{t}{\sqrt{1-t}}\frac{\sqrt{b}}{1-b}\left[\frac{4(\sqrt{2}-1)}{\sqrt{1-b}}+1\right]\geq\alpha \ . \tag{4}$$

Here, $t=T/T_c$, $b=H(T)/H_{c2}(T)$, and κ $(=\lambda/\xi)$ is the Ginzburg-Landau parameter. The value m/m_z is the ratio of in-plane and out-plane effective masses. In this model they applied the Ginzburg-Landau results of

$$H_{c2}(T)=H_{c2}(0)[1-T/T_c(H=0)] \ ,$$

where $H_{c2}(0)$ is the upper critical field at $T=0$ K. In Eq. (3), the parameter c is the so-called Lindemann number with a typical value of 0.1. This criterion is strictly valid only for $H \ll H_{c2}(T)$. This inequality is fairly well satisfied for high-T_c superconducting systems over the temperatures investigated so far. But a rather larger Lindemann number c than the typical value is obtained, about 0.4.[9,28] The result may be attributed to its high anistropicity (large m/m_z value).

For isotropic superconductors with $m/m_z\sim1$, because α is inversely proportional to κ^2, therefore, the effect of thermally activated melting is more pronounced with increasing κ. Due to the large value of κ, the above theory predicts that the melting curves are suppressed well below the mean-field transition line $H_{c2}(T)$ between the superconducting and normal states. Furthermore, these melting lines would be linear with temperature over a wide range of high magnetic fields.

For Rb_3C_{60} fullerenes that are isotropic and are extreme type-II superconductors, the following values are applied: $\kappa\sim100$, $H_{c2}(0)\sim35$ T, and $m/m_z\sim1$.[28,29] In this case, if $c=0.1$, then $\alpha\sim1$ would be estimated by Eq. (4). This value is sufficient to widen the region of lattice melting in the H-T phase diagram. According to this model, the melting curve is linear when the field is high. But when T approaches T_c the melting line is given by $H_m(T)\sim H_m(0)(1-T/T_c)^2$. This expression is identical to that predicted by Eq. (2) when γ is assigned the value of 2. Thus the fact that the γ value is 2 strongly suggests the existence of a first-order phase transition of vortex-lattice-melting type in our pure Rb_3C_{60} sample. In this case, the irreversibility line can be interpreted as a melting line. The melting appears to be induced by the conventional thermally activated fluctuations.

Although the irreversibility line reported by Lin *et al.*[17] also agreed with the power-law of Eq. (2), it yielded different fitting values for Rb_3C_{60}, i.e., $\gamma=1.59\pm0.05$, $H_{irr}(0)=27.2\pm1.7$ kOe, and $T_0=29.1\pm0.1$ K. Lin *et al.* explained these parameters based on the spin-glass state as predicted by de Almeida–Thouless theory. In this case, the γ values would be about $\frac{3}{2}$ in their samples (K_3C_{60} and Rb_3C_{60}). We believe that their low γ values may be caused by a large amount of grain boundaries in their polycrystalline samples, as described in their paper. Hence the pinning energy attracting the vortices to the defect sites could dominate. As a result the vortex glass-fluid transition in the samples of Lin *et al.* may become second order instead of first order as observed in our sample.

If we assume an upper bound of $\kappa=150$ for the Rb_3C_{60} compound,[17–20] the data fit of $H_{irr}(T)$ will yield an α value about 0.4. Using these values of α and κ, the upper bound of c is calculated to be 0.074. This upper bound of the Lindemann number is substantially smaller than those for high-T_c superconducting materials.[9] But this value is larger than the c value of 0.065 for Nb_3Sn magnetic wire as determined by Suenaga *et al.*,[30] and the upper bound of $c=0.04$ for a Nb film as reported by Schmidt, Israeloff, and Goldman[14] Even so, the Lindemann criterion is still lower than the typical value of 0.1. these results are consistent with Brandt's prediction[10] and the calculation of Ryu *et al.* based on Monte Carlo simulations.[31]

Brandt[10] indicated that the mechanism of thermal fluctuations of vortices from their equilibrium positions is not unique for flux-lattice melting. He calculated, using Schmucker's criterion,[10] the thermal fluctuation at the shear stress required to deform a lattice plastically. The result allowed him to derive a melting curve that is similar to Eq. (2) with $\gamma=2$. Brandt also predicted c could be as small as 0.05. He offered five possible explanations of the origins of such a small value of c.

Ryu *et al.*[31] also used the Lawrence-Doniach model to calculate the melting curve for a Bi-Sr-Ca-Cu-O sample as reported by Houghton, Pelcovits, and Sudbø.[9] They found that as the field shifts downward the flux-line density decreases. Moreover, the interlayer coupling becomes more dominant than that of the intraplane. These results allow the construction of a three-dimensional (3D) lattice made of straighter flux lines such that a lattice would yield a lower Lindemann criterion. Using Monte Carlo simulations, Ryu *et al.* obtained a field-dependent Lindemann criterion for the lattice melting. They found that c decreased with decreasing flux-line density and/or field strength. The above model can also apply to the results for films of Nb and Nb_3Sn and magnetic wires of Nb-Ti. According to the above speculation, the Lindemann criterion in our isotropic Rb_3C_{60} sample is consistent with a lower c value, as we obtained.

IV. CONCLUSIONS

Our superconducting Rb_3C_{60} fullerene has a strong pinning strength. The sample exhibits a large critical current density of about 2×10^6 A/cm^2 at $T=5$ K and $H=0$ T. The irreversibility line with $\gamma=2$ strongly supports the existence of a first-order vortex-lattice-melting transition. This transition occurred in our sample with a crystalline morphology. According to the nonlocal elasticity theory of Houghton, Pelcovits, and Sudbø the Lindemann criterion would be smaller in such a sample than in high-T_c superconductors. However, our c value is comparable to those of conventional type-II superconductors, such as $NbSn_3$ and Nb-Ti magnetic wire and Nb film. These smaller Lindemann numbers are well understood based on the models of Brandt and Ryu *et al.*

ACKNOWLEDGMENTS

The authors are grateful to Professor J. B. Shi for fruitful discussions and S. C. Luo for assistance in sample preparation for this research. This research was supported by the National Science Council of the R.O.C. under Contract No. NSC-84-2112-M194-005.

[1]K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987).
[2]Y. Yeshurun and A. P. Malozemoff, Phys. Rev. Lett. **60**, 2202 (1988).
[3]Y. Xu and M. Suenaga, Phys. Rev. B **43**, 5516 (1991).
[4]E. Zeldov *et al.*, Appl. Phys. Lett. **56**, 1700 (1990).
[5]C. W. Hagen and R. Griessen, Phys. Rev. Lett. **62**, 2857 (1989).
[6]P. L. Gammel *et al.*, Phys. Rev. Lett. **66**, 953 (1991); J. Appl. Phys. **67**, 4676 (1990).
[7]D. S. Fisher, M. P. A. Fisher, and D. A. Huse, Phys. Rev. B **43**, 130 (1991).
[8]R. H. Koch *et al.*, Phys. Rev. Lett. **63**, 1511 (1989); M. P. A. Fisher, *ibid.* **62**, 1415 (1989).
[9]A. Houghton, R. A. Pelcovits, and A. Sudbø, Phys. Rev. B **40**, 6763 (1989).
[10]E. H. Brandt, Phys. Rev. Lett. **63**, 1106 (1989).
[11]D. E. Farrel, J. P. Rice, and D. M. Ginsberg, Phys. Rev. Lett. **67**, 1165 (1991).
[12]R. G. Beck *et al.*, Phys. Rev. Lett. **68**, 1594 (1992).
[13]L. I. Glazman and A. E. Koshelev, Phys. Rev. B **43**, 2835 (1991).
[14]M. F. Schmidt, N. E. Israeloff, and A. M. Goldman, Phys. Rev. Lett. **70**, 2162 (1993); Phys. Rev. B **48**, 3404 (1993).
[15]G. Blatter and B. Ivlev, Phys. Rev. Lett. **70**, 2621 (1993).
[16]A. F. Hebard *et al.*, Nature 350, 600 (1991); K. Holczer *et al.*, Science **252**, 1154 (1991).
[17]C. L. Lin *et al.*, Phys. Rev. B **49**, 4285 (1994); Solid State Commun. **90**, 629 (1994).
[18]M. Baenitz *et al.*, Physica C **228**, 181 (1994).
[19]A. M. Neminsky *et al.*, Phys. Rev. Lett. **72**, 3092 (1994); J. G. Hou *et al.*, Physica C **228**, 175 (1994); Y. J. Uemura *et al.*, Nature **352**, 605 (1991).
[20]C. E. Johnson *et al.*, Phys. Rev. B **46**, 5880 (1992); G. Sparn *et al.*, Phys. Rev. Lett. **68**, 1228 (1992); K. Holczer *et al.*, *ibid.* **67**, 271 (1991).
[21]K. Tanigaki *et al.*, Nature **356**, 419 (1992), and references therein.
[22]X. -D. Xiang *et al.*, Nature **361**, 54 (1993).
[23]M. W. Lee, M. F. Tai, and H. J. Lee, J. Vac. Soc. R.O.C. **6**, 11 (1993).
[24]M. W. Lee, M. F. Tai, S. C. Luo, and J. B. Shi, Physica C **245**, 6 (1995).
[25]*Magnetic Susceptibility of Superconductors and Other Spin Systems,* edited by R. A. Hein *et al.* (Plenum, New York, 1992), p. 173; A. M. Campbell and J. E. Evetts, Adv. Phys. **21**, 199 (1972).
[26]Y. Tomioka *et al.*, Physica C **223**, 347 (1994); **215**, 297 (1993).
[27]M. F. Tai and M. W. Lee (unpublished).
[28]D. E. Farrell, in *Physical Properties of High Temperature Superconductors IV,* edited by D. M. Ginsberg (World Scientific, Singapore, 1994), Chap. 2.
[29]M. S. Dresselhaus, G. Dresselhaus, and R. Saito, in *Physical Properties of High Temperature Superconductors IV* (Ref. 28), Chap. 7.
[30]M. Suenaga *et al.* Phys. Rev. Lett. **66**, 1777 (1992); Supercond. Sci. Technol. **5**, 1 (1991).
[31]S. Ryu *et al.*, Phys. Rev. Lett. **68**, 710 (1992).