Superconducting properties of In-Ge mixture films

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We report on measurements of the perpendicular $H_{c\perp}$ and parallel $H_{c\parallel}$ upper critical fields of superconducting In-Ge mixture films in a wide range of In concentrations. The resistivities of the samples varied from about 10 $\mu\Omega$ cm, corresponding to high In concentration, up to about 1300 $\mu\Omega$ cm, corresponding to an In concentration close to the percolation threshold of the system. The critical temperatures of the samples in a zero external field have also been studied. For high metal concentrations the results have been analyzed and found to fit the predictions of the dirty limit for type-II superconductors. Near the threshold, however, where the normal-state resistivity goes to infinity, the critical fields saturate to a finite value. This result is in accordance with the prediction of percolation theory in the anomalous diffusion regime. As the threshold is approached the anisotropy ratio decreases to a constant value of 1.2 from its homogeneous type-II limit 1.69.

I. INTRODUCTION

It has been recognized for a long time that the high upper critical field H_{c2} of dirty superconducting alloys is due to the existence of a short impurity-limited mean free path[1] rather than to macroscopic inhomogeneities. Early results on solid-solution alloys[2] demonstrated that, in agreement with theoretical predictions, H_{c2} increases linearly with the normal-state resistivity ρ_n of the alloy (itself proportional to the impurity concentration).

Recently, an anomalous behavior of the upper critical field of percolating In-Ge films, has been reported.[3] Close to threshold it is characterized by a weaker dependence on the normal-state resistivity ρ_n than is observed in homogeneous dirty type-II superconductors. This behavior was interpreted as a crossover from a homogeneous to an inhomogeneous regime when the percolation correlation length ξ_p becomes longer than an effective superconducting coherence length $\bar{\xi}_s$. This interpretation was confirmed by detailed theoretical calculations.[4,5]

There remained, however, an apparently serious discrepancy between the theory[4] that predicted a saturation of the critical field beyond the crossover concentration, and the experiments which, from that concentration, indicated a variation of the critical field $H_c \propto \rho_n^{1/2}$ (Ref. 3) instead of a saturation. In order to clarify that point, we have made additional critical-field measurements, especially at concentrations close to the threshold. In that regime, we have indeed observed a saturation of the critical field, but only very close to the threshold.

II. EXPERIMENTAL TECHNIQUES

Samples were prepared by coevaporation of indium and germanium from two distinct electron-beam guns, spaced apart, onto a room-temperature glass substrate. Nine samples, about 2000 Å in thickness, were simultaneously evaporated onto one glass substrate, their indium concentrations varying by about 2% between neighboring samples, as a result of their different geometrical location. The pressure during the evaporation was held at approximately 1×10^{-6} Torr and never exceeded 5×10^{-6} Torr. In-Ge films prepared in this way have a random, rather than granular structure[6] with both constituents being crystalline. Their percolation threshold is close to 15 vol %, in agreement with theoretical predictions for percolation in a three-dimensional random continuous medium, and the In and Ge clusters have the ramified structure characteristic of percolating systems.[6]

The resistivity of the samples was measured by the four-terminals technique. The resistivity of a sample at 4.2 K was defined as the normal resistivity. The critical temperature and the critical field were defined as the temperature or the field, at which half of the normal resistivity was restored.

An alternative measurement technique has been utilized, based on the technique suggested in Ref. 7. In the apparatus, the superconducting to normal phase transition is detected by measuring the corresponding change in the sample magnetic susceptibility. The method employed uses the shift in the resonant frequency of a parallel LC circuit to monitor the change of the sample susceptibility, the sample being mounted in the inductor. Such an ac susceptibility measurement is a convenient way of determining H_{c2} or T_c because of the property of type-II superconductors that in both the Meissner and the mixed states a small ac field will be fully excluded from the sample. When a sample passes from the superconducting to the normal state, due to an increase of either temperature or dc field, its susceptibility, for small ac fields, changes. This produces a shift in the resonant frequency of the circuit and thus an out-of-phase output voltage.

III. EXPERIMENTAL RESULTS

All samples were evaporated under similar conditions, their normal-state resistivities varying from about 10 $\mu\Omega$ cm up to 1300 $\mu\Omega$ cm. They can be viewed as three-dimensional (3D) superconductors, $\bar{\xi}_s(T) < d$ except very close to the transition temperature T_c. The samples with

resistivity up to about 500 $\mu\Omega$ cm have a metallic behavior $d\rho/dT>0$; beyond that resistivity $d\rho/dT<0$. The samples show three distinct types of behavior according to their resistivities.

A. Homogeneous limit
($\rho_n \leq 50\ \mu\Omega$ cm, indium volume fraction $x \geq 45\%$)

The superconducting transition of the samples of this group has a width of a few times 10^{-2} K and T_c is reduced down to $\simeq 3.3$ K (the pure In transition temperature is 3.4 K). For these samples the critical fields are in good agreement with the predictions for type-II dirty-limit superconductors.

An implicit formula for the critical field H_{c2} in a dirty superconductor, valid at all temperatures is[8]

$$\ln\left[\frac{T}{T_c}\right]=\Psi\left[\frac{1}{2}\right]-\Psi\left[\frac{1}{2}+\frac{\hbar D H_{c2}}{2\Phi_0 k_b T}\right], \tag{1}$$

where $\Psi(x)$ is the di-gamma function; $\Phi_0=hc/2e=2.07\times10^{-7}$ G cm^2 is the flux quantum; D is the diffusion constant of electron which is given by

$$D=[e^2N(0)\rho]^{-1}, \tag{2}$$

the Einstein relation.

The theoretical curve calculated from (1) for a sample with a normal resistivity of about 20 $\mu\Omega$ cm is presented in Fig. 1. Solid circles represent the experimental critical-field values obtained by susceptibility measurement; crosses by resistance measurement. Some comments have to be added at this point. The resistance critical field demonstrates a slight upward deviation from the theoretical curve when the temperature decreases. We understand this behavior as resulting from macroscopic inhomogeneities of the In-Ge film. This assumption is confirmed by the results of Ref. 9. It is seen in Fig. 1 that for every fixed temperature the susceptibility critical field is lower than the resistivity one. This result is qualitatively expected. While the susceptibility critical field is a bulk measurement, the resistivity critical field is that, at which the last superconductive path between the sample edges is suppressed. The volume fraction of this path is close to zero.

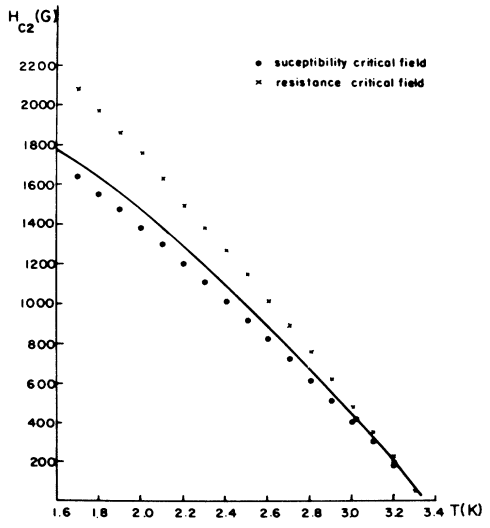

FIG. 1. Temperature dependence of the critical field of a sample with normal resistivity $\rho_n\simeq 20\ \mu\Omega$ cm, obtained by resistivity and susceptibility measurements. Solid line is the theoretical curve, predicted by the dirty-limit model without any adjustable parameter.

With these qualifications we can say that there is complete agreement between theory and experiment at all temperatures, without any adjustable parameter.

In the limit where T is close to T_c, formula (1) gives an explicit expression for H_{c2}:

$$H_{c2}=\frac{\Phi_0}{2\pi\xi^2(t)}, \tag{3}$$

where $t=T/T_c$

$$\xi(t)=0.85(\xi_0 l)^{1/2}(1-t)^{1/2} \tag{4}$$

for $l\ll\xi_0$, $t\to 1$; ξ_0 for indium is 4400 Å.[10]

The mean free path l can be found from the conductivity σ:

$$\sigma=\left[\frac{ne^2}{m}\right]\tau=\left[\frac{ne^2}{m}\right]\left[\frac{1}{\nu_f}\right]. \tag{5}$$

With the value $\rho_n l=m\nu_f/ne^2\simeq 0.57\times10^{-11}\ \Omega\,\text{cm}^2$, Eq. (2) takes the form (in cgs units):

$$H_{c2}=\frac{\Phi_0(1-t)\rho_n}{2\pi(0.85)^2\xi_0 0.57\times10^{-11}}, \tag{6}$$

or

$$H_{c2}\propto\rho_n(1-t), \tag{6'}$$

$$\frac{dH_{c2}}{dT}=52G/K\ \mu\Omega\,\text{cm}, \tag{6''}$$

with ρ_n expressed in $\mu\Omega$ cm.

Figure 2 gives the variation of dH_{c2}/dT as a function

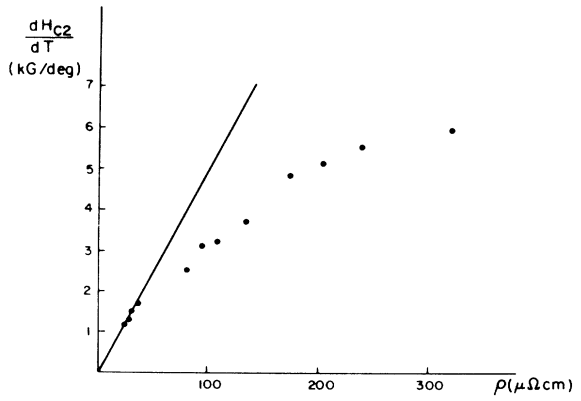

FIG. 2. dH_{c2}/dT as a function of ρ_n. The straight line is that predicted in the dirty limit for inhomogeneous type-II superconductors.

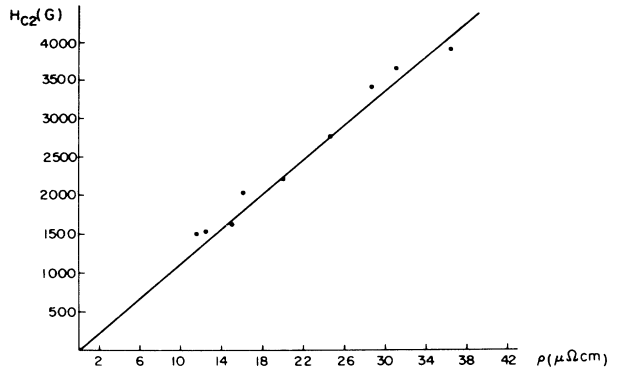

FIG. 3. Critical field at $T=1.6$ K as a function of ρ_n. Straight line is the dirty-limit prediction.

of ρ_n in the vicinity of T_c. For $\rho_n < 50\ \mu\Omega$ cm the data points can be fitted to a straight line with a slope of 49 ± 5 G/$\mu\Omega$ cm, in agreement with (6'). The same is true for the variation of $H_{c\perp}$ as a function of ρ_n at a fixed temperature (Fig. 3).

The behavior of the critical field in the homogeneous regime is somewhat surprising. Unlike a regular type-II superconductor, the resistivity of our samples arises not because of the local (microscopic) disorder, but because of the percolative topology of the infinite superconducting cluster. Then, according to theoretical predictions,[11] the critical field has to be normalized according to the superconductor mass reduction and H_{c2} has to be inversely proportional to the diffusion coefficient D rather than to the conductivity. According to (2), $D\propto(\rho P_\infty)^{-1}$, where P_∞ measures the mass of the infinite cluster. Near p_c, $D\propto(p-p_c)^{\mu-\beta}$ or $H_{c2}\propto\rho^{(\mu-\beta)/\mu}\propto\rho^{0.7}$ (3D value).

In contradiction to these predictions, the experiment gives $H_{c2}\propto\rho_n$, up to the concentration $(p-p_c)\simeq0.3$, where the measured value exceeds the above theoretical one by about a factor of 2. This may be understood by the fact that in the homogeneous region $(p-p_c)\geq0.3$ and the samples are very far from threshold; P_∞ there is almost equal to 1 and the diffusion coefficient D depends only on ρ, giving the homogeneous dirty-limit behavior.

The anisotropy ratio $H_{c\parallel}/H_{c\perp}$ (Fig. 4) of the samples of this group has been found to be constant in temperature and close to the theoretical value 1.69, which is expected for thick $[d>\xi_s(T)]$ type-II films $[H_{c\parallel}/H_{c\perp}=H_{c3}/H_{c2}=1.69$ (Ref. 8)]. For these samples, $\xi_s(T=0)$ varies from 500 Å for $\rho_n\simeq10\ \mu\Omega$ cm down to 200 Å for $\rho_n\simeq50\ \mu\Omega$ cm. Thus, the variation of $H_{c\perp}$ and $H_{c\parallel}$ as a function of T and ρ_n follows exactly the predictions for dirty type-II superconductors with no adjustable parameters for $\rho_n<50\ \mu\Omega$ cm, in spite of the fact that the increase of ρ_n is due to the percolative nature of the mixture rather than to an increase of the disorder on the atomic scale.

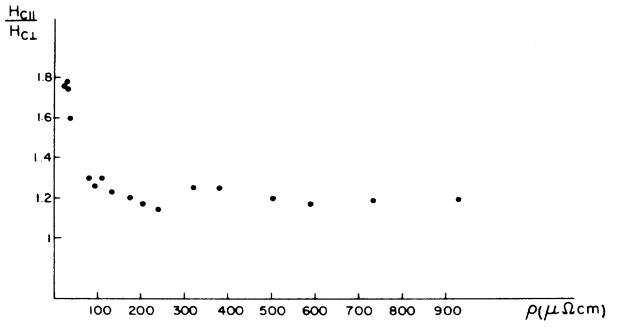

FIG. 4. Anisotropy ratio as a function of ρ_n.

B. Crossover range
(50 $\mu\Omega$ cm $\leq\rho_n\leq$ 300 $\mu\Omega$ cm, 25% $\leq x\leq$ 45%)

In this range we confirm the results of Ref. 3. The behavior of the critical fields near T_c is still linear with temperature, but the slope is smaller than predicted by the dirty-limit theory and the deviation becomes larger as ρ_n increases. The anisotropy ratio $H_{c\parallel}/H_{c\perp}$ drops to a value $\simeq1.2$ already for $\rho_n\leq100\ \mu\Omega$ cm (Fig. 4).

C. Inhomogeneous limit
[300 $\mu\Omega$ cm $<\rho_n\leq$ 1300 $\mu\Omega$ cm, $0\leq(x-x_c)\leq10\%$]

The critical fields $H_{c\perp}$ and $H_{c\parallel}$ and the electrical transition of a sample with a normal resistivity 730 $\mu\Omega$ cm, are shown in Fig. 5. The transition temperature is reduced to 2.8 K and the width of the transition increases to 0.5°. The critical field does not increase linearly with temperature near T_c, as is clearly seen in Fig. 5. The critical field increases quickly near the transition temperature, the slope at T_c seems to go to infinity as the resistivity increases, i.e., when $x\rightarrow x_c$. The critical field is fitted rather well by the form $H_{c\perp}\propto(T_c-T)^\alpha$ with $\alpha<1$ and $\alpha\rightarrow0.65\pm0.05$ when $x\rightarrow x_c$ (Fig. 6). This power law

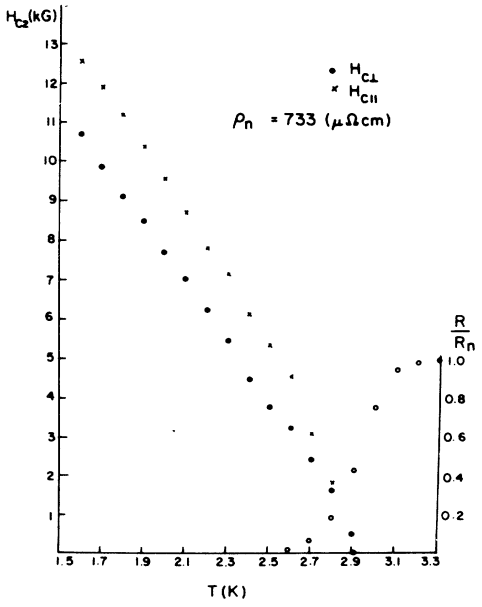

FIG. 5. Critical fields and electrical transition of a sample with normal resistivity $\rho_n=733\ \mu\Omega$ cm.

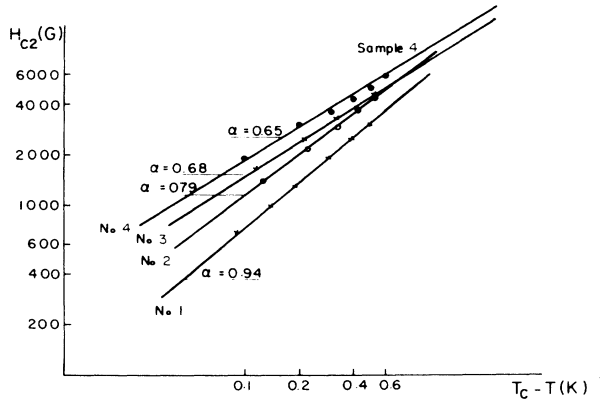

FIG. 6. Critical field as a function of $(T_c - T)$ in the vicinity of T_c. log-log plot, showing a power-law behavior. The normal resistivities of the samples are as follows (in $\mu\Omega$ cm): No. 1, 322; No. 2, 590; No. 3, 733; No. 4, 930.

remains correct also if we will determine $H_{c\perp}$ as a field at which 90% or 10% of normal resistivity was restored. In this case T_c is also determined as a temperature at which 90% or 10% of normal resistivity was restored. A saturation of the critical field $H_{c\perp}(\rho_n)$ is observed in this regime (Fig. 7). The anisotropy ratio remains constant (Fig. 4) and equal to 1.2.

The critical temperature as a function of resistivity is shown in Fig. 8. The dots are values of T_c and the arrows show the transition width (10—90% of normal resistivity). The points on the graph belong to the samples evaporated on three different substrates, i.e., under slightly different conditions. In spite of the width discrepancy, the transition-temperature curve is smooth and matches well at the transition between substrates. The reduction in T_c seems to be linear even at high film resistivities, with a slope of 0.65×10^3 K/Ω cm. Granular superconductors may be roughly divided into two classes. In the first, the grains are strongly coupled and the grain-size distribution is rather wide. In the second class, the grains are weakly coupled, either by a thin bridge of metal, i.e., a weak link, or by the Josephson coupling which connects two superconducting grains separated by a thin insulating layer. It is usually assumed that the grains are equal in size and only the widths of insulating layers are distributed. In Ref. 12 the second class of granular superconductors is discussed and linear reduction of critical temperature is predicted. In-Ge mixture film belongs to the first class mentioned above and its critical temperature dependence on sample resistivity cannot be explained in the frame of percolation theory. Percolation, being a purely classical phenomena cannot by itself affect the superconducting transition. The critical temperature depression can be discussed and understood by the interplay between electron localization and superconductivity. Localization theory predicts a linear decrease in critical temperature of 2D samples, but, following Ref. 13 the expected slope is about 5 times lower than the measured one. Our experimental results fit the picture proposed in Ref. 14, which interprets the metal-insulator transition in terms of percolation-localization crossover. The assumption is that the length scale for disorder is responsible for the character of the transition. In large grained systems like Pb-Ge and Al-Ge, all transport properties are governed by percolation and T_c would remain close to that of bulk material.[6,15] By contrast, in amorphous films like Bi-Kr,[16] where the characteristic length scale for disorder is the interatomic distance, T_c is depressed significantly at relatively low values of ρ_n. The observed T_c depression in In-Ge is consistent with a structure intermediate between that of the large grained and amorphous systems.

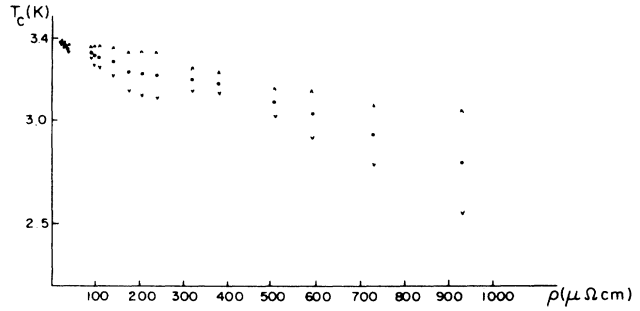

FIG. 8. Critical temperature as a function of ρ_n. Arrows show the transition width (10—90 % of the normal resistivity).

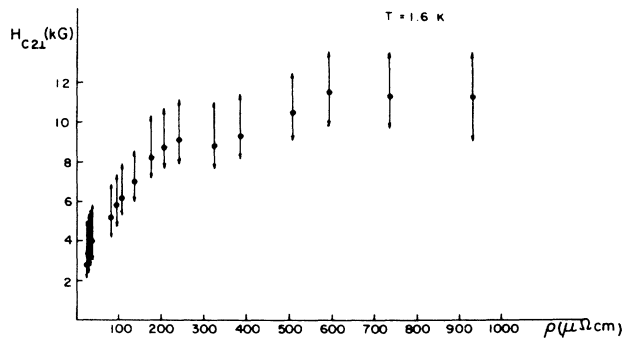

FIG. 7. Critical field at $T=1.6$ K as a function of ρ_n. Arrows show the transition width (10—90 % of the normal resistivity).

IV. DISCUSSION

We have listed three physical parameters that deviate simultaneously from the dirty-limit behavior. These are the critical field, its temperature derivative near T_c, and the anisotropy ratio. For all three the deviation occurs when ρ_n is of the order of 40—50 $\mu\Omega$ cm. It can be shown that this point corresponds approximately to the value of x, where the superconductive correlation length $\bar{\xi}_s$ equals the percolative correlation length $\bar{\xi}_p$. By using $\bar{\xi}_s^2=\Phi_0/2\pi H_{c2}$ and $\bar{\xi}_p=d(x-x_c)^{-\nu}$ we can estimate the value of x at the crossover. With $d=150$ Å as an indium grain dimension, $\nu=\nu(3D)=0.85$, we obtain $x_{cr}-x_c\simeq0.3$ and $\rho(x-x_{cr})\simeq40$ $\mu\Omega$ cm in fair agreement with experiment. The choice of $\nu(3D)$ is justified by the fact that at $x=x_{cr}$, $\xi_p=400$ Å which is significantly smaller than the

film thickness.

We interpret this change in behavior as a crossover between two regimes: a homogeneous type-II regime at low resistivities and high metal concentrations, and a percolation dominated regime at high resistivities near the percolation threshold. When $\bar{\xi}_s \gg \xi_p$, the medium is effectively homogeneous on the scale of $\bar{\xi}_s$ and the structure of the infinite cluster is unimportant for the superconducting properties. This is the regime where $H_{c\parallel}/H_{c\perp} \propto H_{c3}/H_{c2}$ and $(dH_{c\perp}/dT)_{T_c} \propto \rho_n$. In the opposite limit, the structure of the infinite cluster is important, the topology has a direct influence on the value of the upper critical field.

The saturation of H_{c2} with ρ_n and its anomalous temperature dependence near T_c are expected in the fractal regime $\xi_s(T) < \xi_p$.[4] The saturation of H_{c2} reflects the fact that any property of the infinite cluster on a scale smaller than ξ_p is independent of $(x - x_c)$ and therefore of ρ_n.

The critical field behavior as a function of temperature in the vicinity of T_c for x close to x_c is predicted to be as follows. In the fractal regime $L < \xi_p$ the diffusion coefficient depends on the length scale

$$D \propto L^{-\theta} , \tag{7}$$

where $\theta = \mu - \beta/\nu$ is the diffusion index. It can also be expressed as being time dependent:

$$D(\tau) \propto \tau^{-\theta/(2+\theta)} . \tag{8}$$

In the dirty limit

$$\bar{\xi}_s^2 = D(\tau)\tau , \tag{9}$$

where

$$\tau = \frac{k_b}{\hbar}(T_c - T)^{-1} . \tag{10}$$

Noting that the critical field is proportional to $(\xi_s^2)^{-1}$, we obtain

$$H_{c2} \propto (\xi_s^2)^{-1} \propto \tau^{-2/(2+\theta)} \propto (T_c - T)^{2/(2+\theta)} . \tag{11}$$

For samples close to the threshold considered here, ξ_p is larger than the film thickness and we must use the 2D value of $\theta = 0.9$. The power $2/2+\theta$ is then very close to the observed value 0.65.

Measurements of the critical-field anisotropy can be used to check specific models of the infinite cluster. The nodes-and-links model, which completely neglects the fact that at short times diffusion is faster than at long times, seems to fail to explain the observed anisotropy value in the inhomogeneous regime. As the fibers take on the average, a random orientation with respect to the applied field, we expect an anisotropy ratio of 1. The fact that our experiments give a constant value 1.2 means that the structure of the infinite cluster is more complicated.

In conclusion, we have observed the fractal regime predicted by theory for percolating superconductors. However, further theoretical work is required for the understanding of the very broad crossover region, observed experimentally. The behavior of the anisotropy ratio is also quite interesting but requires a theoretical interpretation. We believe that its saturation value 1.2 is related to the anomalous dimensionality of the infinite cluster on scales smaller than ξ_p, which is intermediate between the Euclidean dimensionality (3) and that of 1D strands.

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