PHYSICAL REVIEW B VOLUME 45, NUMBER 6 1 FEBRUARY 1992-II

# Superconducting properties of indium in the restricted geometry of porous Vycor glass

M. J. Graf
*Department of Physics, Boston College, Chestnut Hill, Massachusetts 02167*
*and Francis Bitter National Magnet Laboratory, Cambridge, Massachusetts 02139*

T. E. Huber*
*Lyman Laboratory, Harvard University, Cambridge, Massachusetts 02138*

C. A. Huber†
*Francis Bitter National Magnet Laboratory, Cambridge, Massachusetts 02139*

(Received 30 August 1991)

The superconducting transition of indium in 56-Å-pore Vycor glass has been studied through resistance and magnetic-susceptibility measurements. The confined indium behaves like a "dirty" type-II superconductor, and the superconducting transition consists of *two* transitions, which become well separated in applied magnetic fields. While the lower critical field $H_c^l$ follows de Gennes's prediction of $H_{c2}(T)$, the higher critical field $H_c^u$ has an unusual dependence of $(1-T/T_c)^{1/2}$. The possible origin of this transition is discussed in terms of the microstructure of the composite.

The material structure of superconductors strongly influences their properties, and modifications of the structure produce many physically interesting systems, as in, for example, artificially layered superconductor-insulator materials,[1] filamentary superconductors,[2] percolating superconductors,[3] and granular superconductors.[4] In the first two cases, additional properties arise when the characteristic sample size is made comparable to the bulk coherence length $\xi_0$, while in the latter two cases the conduction path is modified. In this work we investigate an interesting system which combines several aspects of those just mentioned: a pure type-I superconductor confined in a microporous host material. Because the metallic structure mimics the pore structure of the host, these composites have a highly reproducible microstructure, which can be varied by changing the host. We use porous Vycor glass[5] (PVG) as the host material because extensive studies on its structure have been carried out.[6] The use of PVG as a confining host has been particularly fruitful, for example, in studying the properties of superfluid helium,[7] liquid hydrogen,[8] and different aspects of molecular dynamics[9] in a restricted geometry.

Previous works[10] on indium in PVG have shown (from susceptibility measurements) that the superconducting transition temperature can be enhanced over the bulk value by 20% or more, and that the superconductor exhibits type-II behavior, with an upper critical field over 100 times greater than the critical field of the bulk (type-I) material. The enhanced $T_c$ is believed to arise from the large surface-to-volume ratio, which enhances the electron-phonon coupling constant, and thus $T_c$. To explain the enhanced critical field, a granular structure was assumed, where the grain size was limited by the pore size $d$. The resulting decrease in the electron mean free path $l$ reduces the coherence length from the bulk value. The upper critical field is related to the coherence length via[11]

$$H_{c2}=\frac{\Phi_0}{2\pi}[\xi(T)]^{-2}\ , \tag{1}$$

where $\Phi_0$ is the magnetic flux quantum, so one finds that the upper critical field is enhanced. For a "dirty" type-II superconductor,[11] $\xi \propto l^{1/2}$, and if $l \sim d$, then one would expect $H_{c2} \propto d^{-1}$, which was indeed observed. However, while $l$ was proportional to $d$, it was much smaller, on the order of 2 Å. It was then assumed that the superconducting grains were weakly coupled, with an intergrain transmission coefficient $\tau$ on the order of 0.04. Thus the effective mean free path is approximately $\tau d$, and the observed pore size dependence of $H_{c2}$ is explained.

In this work we focus on the transport and magnetic properties of pure indium ($T_c=3.41$ K, $H_c=0.03$ T) which has been injected into porous Vycor glass. We find an enhancement of $T_c$ and of the critical field, in agreement with previous works.[10] However, in contrast to those studies we find *two* distinct transitions at $T_c$. While in zero magnetic field these transitions are very closely spaced, as a magnetic field is applied they become quite distinct, and have qualitatively different phase diagrams. The lower-field transition is that described by Eq. (1), while the higher-field transition exhibits a different behavior, and has not been previously observed.

The PVG used has an average pore diameter of 56 Å as determined by nitrogen adsorption and/or desorption measurements, with 96% of the pore volume being within 10% of this average. The interconnected network of pores occupies approximately 30% of the total sample volume. While the silica backbone structure is complex and interconnected, one can consider it as being made up of silica particles of a characteristic size.[12] This characteristic size was determined from small-angle x-ray scattering (SAXS) measurements to be approximately 260 Å, and is consistent with scanning electron micrographs taken of the empty Vycor.[13]

The samples are prepared by melting pure indium (99.9999%) and injecting it into the PVG by applying hydrostatic pressures of a few kilobars.[14] The shiny black samples have approximately 95% of the pore volume filled with indium. SAXS measurements of *selenium-injected* Vycor samples[13] show that the host matrix structure is unchanged by this injection process, and we assume this is also true for the indium-injected samples since they are prepared under similar conditions. X-ray diffraction studies on the composite show that the indium retains its tetragonal crystal structure. From the broadening of the x-ray diffraction lines a characteristic crystallite size of about 350 Å is inferred, significantly larger than the pore size of the Vycor.

The sample resistance was measured using a four-terminal ac technique, with frequencies of about 20 Hz and currents of 0.5 mA. Electrical contact was made via gold wires attached with silver epoxy. No effects from self-heating were observed. Data were taken by fixing the temperature and sweeping the magnetic field. Measurements of the ac magnetic susceptibility were also made. The samples were placed in the center of a pair of wrapped coils, and the change in the mutual inductance relative to an empty coil pair was measured using a Hartshorn-type bridge. Frequencies were on the order of a kilohertz, and the ac magnetic field amplitudes were a few gauss. Data were taken by fixing the magnetic field and changing the temperature.

At 300 K the resistivity of the composite is roughly 250 $\mu\Omega$ cm, and cooling to 4 K reduces this to 75 $\mu\Omega$ cm. The room-temperature conductivity is about 20 times smaller than that of the bulk indium used. This is consistent with a rough estimate for the conductivity of the composite $\sigma_c$ obtained from the empirical expression describing the conductivity of a porous system saturated with a conducting fluid,[15] $\sigma_c = \sigma_b \phi^m$, where $\sigma_b$ is the conductivity of bulk indium, $\phi = 0.30$ is the porosity, and $m$ is roughly 2. The resistance becomes essentially independent of temperature below 10 K, but $\partial\rho/\partial T$ is always positive, indicating the sample is metallic. The low-temperature magnetoresistance is small (0.2% in 20 T) and positive.

Three samples prepared in the same manner were found to have superconducting transition temperatures of 3.95, 3.98, and 4.03 K, with transition widths of approximately 0.05 K. These values of $T_c$ are enhanced over the bulk value for indium by 17%, in agreement with previous results.[10] In Fig. 1 we show the transition for the sample with $T_c = 4.03$ K. A break can be seen midway through the transition of the resistance versus temperature curve; this was also observed in the other samples. This is made clearer by plotting the temperature derivative of the resistance. If we interpret this as the occurrence of two distinct transitions, they are separated by roughly 50 mK. This effect becomes much more pronounced when a magnetic field is applied, as shown in Fig. 2 for the sample with $T_c = 3.98$ K. Two transitions separated by a plateau are observed, and they become further separated at lower temperatures. The transitions are hysteretic, and the curves shown are for increasing magnetic field transverse to the current. We find similar results with the field parallel to the current.

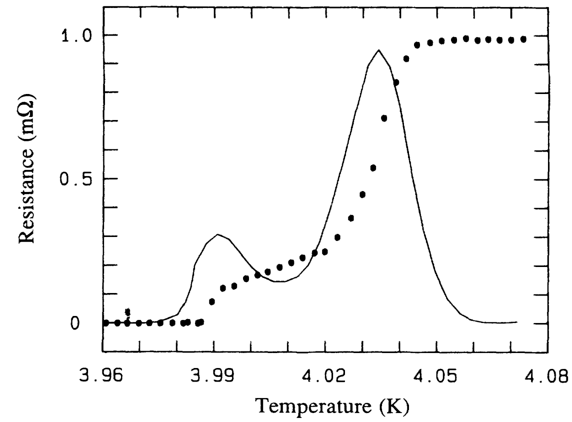

FIG. 1. The zero-field resistive transition of indium-injected PVG with $T_c = 4.03$ K (full circles). Also shown is the calculated derivative $dR/dT$ (solid line) in arbitrary units.

In Fig. 3 we show the phase diagram of the observed resistive transitions for all three samples studied. We call the transition at low fields $H_c^l$ and at high fields $H_c^u$. The temperature dependence of $H_c^l$ is well described by de Gennes's theory for a "dirty" type-II superconductor,[16] which gives an implicit form for $H_{c2}$ as a function of reduced temperature $t = T/T_c$. This is shown in Fig. 3 (solid line), taking $l$ as 4 Å and the Pippard coherence length, corrected for the enhanced $T_c$, as 3700 Å.[17] On the other hand, the high-field transition $H_c^u$ has a much different behavior than that expected for bulk type-II superconductors, and cannot be fitted by de Gennes's theory. We find that the data are best described away from $T_c$ by $H_c^u(t) \propto (1-t)^{1/2}$ (dashed line in Fig. 3).

The previous studies on this system showed only one transition as determined from a peak in the imaginary part of the susceptibility, $\chi''$.[10] To compare our results we have also made ac susceptibility measurements on a sample studied via transport ($T_c = 3.98$ K). In Fig. 4 we show the real ($\chi'$) and imaginary ($\chi''$) parts of the susceptibility versus temperature at a fixed field of 0.3 T. $\chi'$ begins to change near 3.8 K, and a second (less obvious)

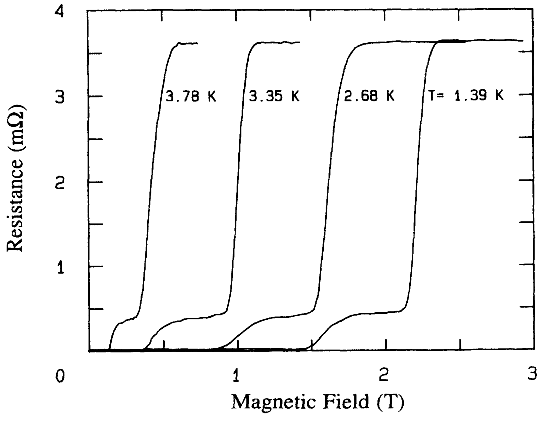

FIG. 2. The magnetic-field-induced transitions at four temperatures below $T_c = 3.98$ K.

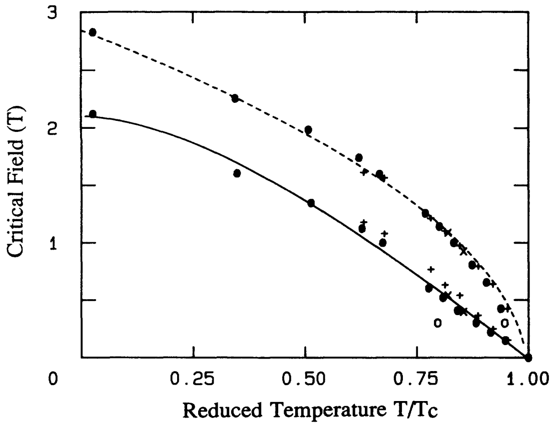

FIG. 3. Phase diagram generated from resistivity (+, $T_c=3.95$ K; ●, $T_c=3.98$ K; and ×, $T_c=4.03$ K) and susceptibility (○, $T_c=3.98$ K). The solid line is a fit to the theory of Ref. 16, and the dashed line is proportional to $(1-T/T_c)^{1/2}$.

change occurs at 3.2 K. These two points are shown as open circles in the phase diagram of Fig. 3. The observed transition temperatures are slightly lower than the resistive transitions, probably due to the relatively large amplitude of the oscillating field.[10] In contrast to $\chi'$, a significant change in $\chi''$ only occurs at 3.2 K, the low-field transition. From this fact and the temperature dependence of $H_c^l$, we conclude that the low-field transition is the one previously observed; the high-field transition is most readily observed via resistance measurements.

Several experimental facts show that the high-field transition is not caused by extrinsic effects, such as impurities or the existence of a second phase. First, the temperature dependence of $H_c^u$ is much different than that of a typical bulk type-II superconductor. Also, the x-ray diffraction measurements do not reveal any evidence for a second phase. Finally, indium extruded from the pores has a critical temperature and critical field like those of pure bulk indium. We conclude that the presence of two distinct transitions is an intrinsic effect associated with the microstructure of indium in the porous Vycor glass host. However, we do not believe that the two transitions are related to the distribution of pore sizes. A wide distribution of pore sizes would only broaden the transition, and a bimodal distribution with two characteristic pore diameters (as in the "ink-bottle" model[18] of porous Vycor) would not result in a different temperature dependence for the low- and high-field transitions.

Somewhat similar composites have been studied in the past: for example, grains of indium[19] or aluminum[20] imbedded in germanium. for Al-Ge samples near the percolation threshold, two closely spaced transitions are observed in zero field: a high-temperature transition at which the individual grains become superconducting and a low-temperature one at which phase coherence extends from grain to grain. This effect has been studied in several granular-type systems, including high-temperature superconductors,[21] and is most obvious in electrical transport as the grain and grain-boundary resistances add in series. This picture qualitatively describes our zero-field results well. To the best of our knowledge, however, none of those systems exhibit two qualitatively different transitions in field, as observed in our case. One possible explanation lies in the large indium crystallite size as compared to the Vycor pore diameter. The individual indium crystallites may have a filamentary "internal structure" which makes the transition to superconductivity for each crystallite at $H_c^u$ different from the "bulk" transition at $H_c^l$ (when all the crystallites are coupled). For example, thin Al wires have an upper critical field (perpendicular to the current) which varies as $(1-T/T_c)^{1/2}$,[22] the result we find for $H_c^u$. The superconducting state with all the crystallites coupled should be three dimensional, however, as the coherence length is much larger than the pore diameter at all temperatures. This would result in two distinct critical fields with different temperature dependences. Further work, both experimental and theoretical, is required to investigate this possibility.

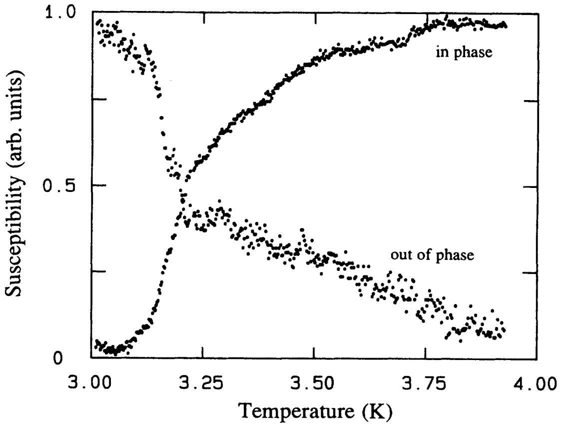

FIG. 4. $\chi'$ ("in phase") and $\chi''$ ("out of phase") vs temperature in an applied magnetic field $H=0.3$ T.

In summary, we have studied the superconducting transition of a three-dimensional metal-insulator nanocomposite synthesized by indium injection of a 56-Å pore diameter Vycor glass. In an applied magnetic field two qualitatively different transitions are observed through both electrical transport and magnetic susceptibility: a low-field transition characteristic of bulk inhomogeneous type-II superconductors, and a new high-field transition which we believe is related to the microstructure of the indium in the porous host. Further studies of samples with different pore sizes, and also of the current-voltage characteristics and vortex formation and flow, are planned to help understand the relation of the microstructure to the observed phenomena.

This work was supported in part by the NSF through Grants DMR-9013127 and DMR-9007890 and by Boston College. Some experiments were performed at the Francis Bitter National Magnet Laboratory, which is supported by the NSF at the MIT. We would like to thank B. A. Allor and A. P. Salzberg for technical help with some of the experiments. C.A.H. acknowledges partial support by Radcliffe College. The hospitality of D. Heiman at the Francis Bitter National Magnet Laboratory and of I. Silvera at Harvard University is also acknowledged.

[*] Present address: Department of Physics, Polytechnic University, Brooklyn, NY 11201.

[†] Present address: Naval Surface Warfare Center, Silver Springs, MD 20903.

[1] I. K. Schuller, Phys. Rev. Lett. **44**, 1597 (1980); S. T. Ruggiero, T. W. Barbee, Jr. and M. R. Beasley, *ibid.* **45**, 1299 (1980).

[2] E. Maxwell and M. Strongin, Phys. Rev. Lett. **10**, 212 (1963); V. N. Bogolomov, N. A. Klushin, and Yu. A. Kumzerov, Pis'ma Zh. Eksp. Teor. Fiz. **26**, 79 (1977) [JETP Lett. **26**, 72 (1977)].

[3] *Percolation, Localization, and Superconductivity,* edited by A. M. Goldman and S. A. Wolf (Plenum, New York, 1984).

[4] J. Rosenblatt, Rev. Phys. Appl. **9**, 217 (1974); G. Deutscher, O. Entin-Wohlman, S. Fishman, and Y. Shapira, Phys. Rev. B **21**, 5041 (1980).

[5] Vycor glass is manufactured by Corning Glass Works, Corning, New York.

[6] For example, P. Wiltzius, F. S. Bates, S. B. Dierker, and G. D. Wignall, Phys. Rev. A **36**, 2991 (1987).

[7] For a review, see M. W. H. Chan, Physica B **169**, 135 (1991).

[8] R. H. Torii, H. J. Maris, and G. M. Seidel, Phys. Rev. B **41**, 7167 (1990).

[9] For a review, see J. M. Drake and J. Klafter, Physics Today **43**(5), 46 (1990).

[10] J. H. P. Watson, Phys. Rev. **148**, 223 (1966); N. K. Hindley and J. H. P. Watson, *ibid.* **183**, 525 (1969).

[11] M. Tinkham, *Introduction to Superconductivity* (Krieger, Malabar, Florida, 1975).

[12] A. Höhr, H.-B. Neumann, P. W. Schmidt, P. Pfeifer, and D. Avnir, Phys. Rev. B **38**, 1462 (1988).

[13] T. E. Huber, P. W. Schmidt, J. S. Lin, and C. A. Huber (unpublished).

[14] C. A. Huber and T. E. Huber, J. Appl. Phys. **64**, 6588 (1988).

[15] P. Weng, J. Koplik, and J. P. Tomanic, Phys. Rev. B **30**, 6606 (1984).

[16] P. G. de Gennes, *Superconductivity of Metals and Alloys* (Benjamin, New York, 1966).

[17] $\xi_0$ of bulk indium is taken to be 4400 Å. P. N. Dheer, Proc. R. Soc. London, A **260**, 333 (1961).

[18] R. H. Tait and J. D. Reppy, Phys. Rev. B **20**, 997 (1979).

[19] G. Deutscher, I. Grave, and S. Alexander, Phys. Rev. Lett. **48**, 1497 (1982).

[20] G. Deutscher and M. L. Rappaport, J. Phys. (Paris) Colloq. **39** C6-581 (1978).

[21] K. A. Müller, M. Takashige, and J. G. Bednorz, Phys. Rev. Lett. **58**, 1143 (1987); K. Härkönen, I. Tittonen, J. Westerholm, and K. Ullakko, Phys. Rev. B **39**, 7251 (1989).

[22] P. Samanatham, S. Wind, and D. E. Prober, Phys. Rev. B **35**, 3188 (1987), and references therein.