# Superconductivity of gallium in various confined geometries

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(Received 17 November 1997; revised manuscript received 2 March 1998)

The superconductivity of gallium in porous glasses with various pore sizes and in opals is studied using a superconducting quantum interference device magnetometer. The single and double superconducting phase transitions are observed for different samples. Magnetization hysteresis loops are also measured and found to be dependent on pore sizes and geometry. The changes in magnetization below about 6.4 K are treated within the framework of models for granular superconductors, while the alterations in magnetization near 7.1 K are treated as a result of the superconducting phase transition in a coexistent structural modification of confined gallium. X-ray diffraction measurements are performed to confirm the presence of such an additional gallium modification. The results obtained allow us to suggest that studies of magnetization at low temperatures can be used to get information about the geometry of the pore network and distribution of Josephson links in porous composite materials. [S0163-1829(98)07425-6]

## I. INTRODUCTION

Composites which consist of metals embedded into porous matrices with pore sizes under several hundred nanometers are promising materials for future applications. The first studies of superconductivity of metals in confined geometries were related with the problem of elevating temperatures of the superconducting phase transition and of developing new artificial hard superconductors.[1–5] The results are reviewed in Refs. 6 and 7. Later it was shown that when some metals are introduced into porous glasses and especially into opal-like matrices, a three-dimensional array of Josephson junctions is formed which could be used in microwave generators, detectors, parametric amplifiers, and other devices.[8] Such composite materials are also of interest for studying size effects in phase transitions under the condition of restricted geometries (see Ref. 9 and references therein). Recently, superconductivity in porous glasses filled with gallium and indium[10–14] was studied using various experimental techniques. It was obtained that below the superconducting phase transition porous glasses filled with metals exhibit properties of dirty type-II superconductors with some peculiarities. Double resistive transitions were found in some porous glasses with indium[10] and gallium,[14] while for other similar samples they observed only single superconducting phase transitions.[11–13] The temperature dependences of the upper critical field were deviated for low magnetic fields from predictions of the Landau theory.[2,13] In Ref. 10 different phase diagrams were obtained for observed two phase transitions. Detailed studies of a porous glass filled with gallium were performed in Ref. 13. A quantitative model was developed for the glass as a granular superconductor with effective sizes of grains much greater than the pore size. In particular, it was found that many general superconducting properties of porous glasses filled with metals occur due to the interplay of strong and weak links between metallic nanoparticles in pores. In this connection it is interesting to study superconductivity of metals in various confined geometries to reveal how pore sizes and configuration influence superconducting features.

In this paper we report results of magnetic studies of superconductivity for gallium embedded into porous glasses with different pore sizes and into opal-like matrices. Results of some additional x-ray measurements are also presented.

## II. EXPERIMENT AND SAMPLES

The samples of porous glass were made from phase-separated soda borosilicate glasses with pore structure produced by acid leaching.[15] The average pore sizes were determined by the mercury intrusion porosimetry method. Two specimens have pores of $4.0\pm0.4$ nm in diameter. They were cut from the same piece of a porous glass. The volume fraction of pores for them is about 22%. A third specimen has pores of $3.5\pm0.5$ nm in diameter. The volume fraction of pores for it is about 12%. The pores for the fourth specimen are $7.0\pm0.6$ nm in diameter with the volume fraction about 18%. Two opal samples consist of silica spheres with diameter near 250 nm forming a face-centered cubic lattice. Between touching spheres there are octahedral and tetrahedral voids of 100 and 50 nm, respectively. The total volume fraction of voids is about 26%. The liquid gallium was embedded into the glass and opal samples under high pressure up to 9 kbar at about 35 °C. For all samples under study the filling of the total void volume was near 85%. The specimens had the form of irregular cylinders. Two samples with 4 nm pores were about 10 mm in length and 2.5 mm in diameter. The sample with 3.5 nm pores was 5 mm in length and 1.5 mm in diameter. The samples with 7 nm pores and the first opal sample were about 4 mm in length and 1 mm in diameter. The second opal sample was about 7 mm in length and 3 mm in diameter.

Magnetic properties of the porous matrices filled with gallium were studied using a Quantum Design superconducting

 

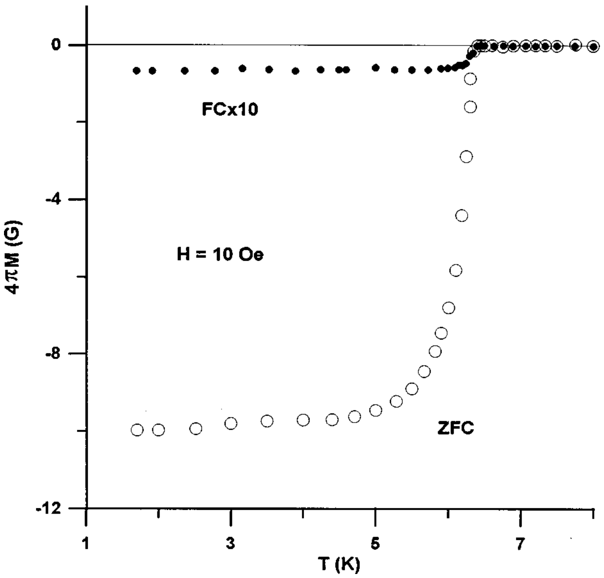


FIG. 1. ZFC and FC magnetizations for the first sample of porous glass with 4 nm pores measured at 10 Oe. The FC magnetization has been scaled by a factor of 10 for improved visibility.

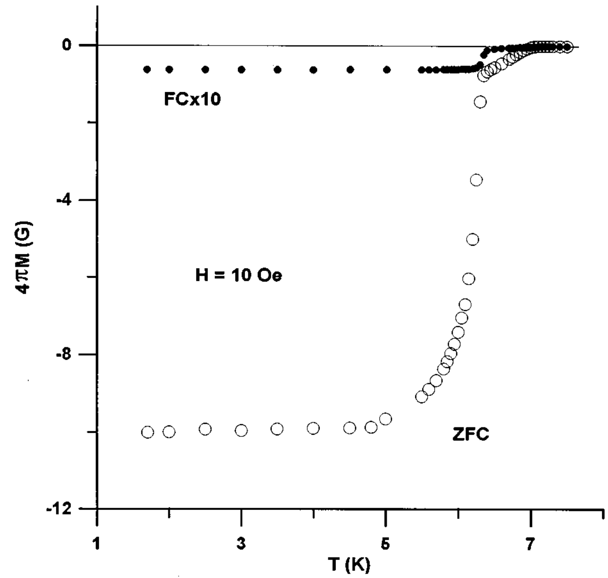


FIG. 2. ZFC and FC magnetizations for the second sample of porous glass with 4 nm pores measured at 10 Oe. The FC magnetization has been scaled by a factor of 10 for improved visibility.

quantum interference device magnetometer with a 7-T solenoid in the temperature range 1.7 to 20 K. The temperature during measurements was stabilized to within 0.01 K. To observe the diamagnetic shielding we used a special program to avoid the influence of temperature overshoots at the samples. Each step in the zero-field-cooled (ZFC) magnetization measurement consisted in setting the target temperature in zero field, switching on the field, measuring after a pause of 30 s, and switching off the field. The field-cooled (FC) magnetization was measured using the conventional procedure of cooling the samples in a constant applied field. The remanent magnetization was measured during warming only in the temperature range 1.7 to 3 K where temperature overshoots were very small. Before every measurement including those of the magnetization versus field, there was a pause of 30 s after stabilizing temperature or magnetic field. Additional x-ray diffraction measurements were performed using commercial equipment (Cu $K_\alpha$ radiation) at several temperatures in the range 4.5 to 300 K.

## III. RESULTS

The temperature dependences of the ZFC and FC magnetization obtained for the samples under study in the magnetic field of 10 Oe are shown in Figs. 1–6. The magnetization was calculated without taking into account the demagnetizing factor. It can be seen that the ZFC and FC curves are rather distinctive for different samples. The simplest behavior was observed for the first sample with pores of 4 nm in diameter (Fig. 1). There is a very sharp onset of diamagnetism near 6.35 K with complete diamagnetic shielding at lower temperatures. For the second sample with the same pore size the onset of weak diamagnetism occurs near 7.1 K and an abrupt change in the ZFC magnetization up to complete diamagnetic shielding occurs near 6.35 K as for the first sample (Fig. 2). For the sample with pores of 3.5 nm, the ZFC magnetization starts decreasing smoothly at about 6.5 K, diamagnetic shielding at low temperatures is also complete (Fig. 3). For the sample with pores of 7 nm diamagnetism becomes strong only below 2.5 K, while the onset of measurable diamagnetism occurs at 6.2 K (Fig. 4). For the first opal sample there is a region of incomplete diamagnetic shielding below 6.2 to about 3 K and then the ZFC magnetization decreases below 3 K (Fig. 5). The onset of fairly remarkable diamagnetism for the second opal sample is seen at 6.2 K as for the first opal sample, then diamagnetic shielding increases below 2.1 K, but achieves only one twentieth of complete shielding at 1.7 K (Fig. 6). Note, that for this sample as well as for the samples with 3.5 and 7 nm pores, hardly measurable diamagnetism was seen until about 7.1 K.

As can be seen from Figs. 1–6, the relation of the FC magnetization to the ZFC magnetization varies strongly for

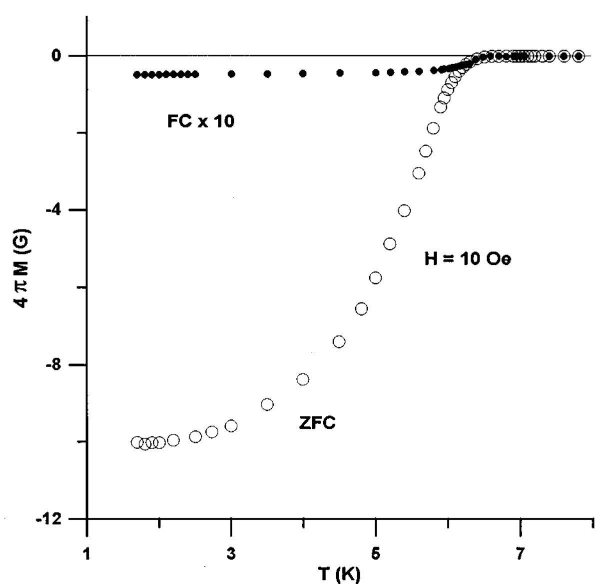


FIG. 3. ZFC and FC magnetizations for the porous glass with 3.5 nm pores measured at 10 Oe. The FC magnetization has been scaled by a factor of 10 for improved visibility.

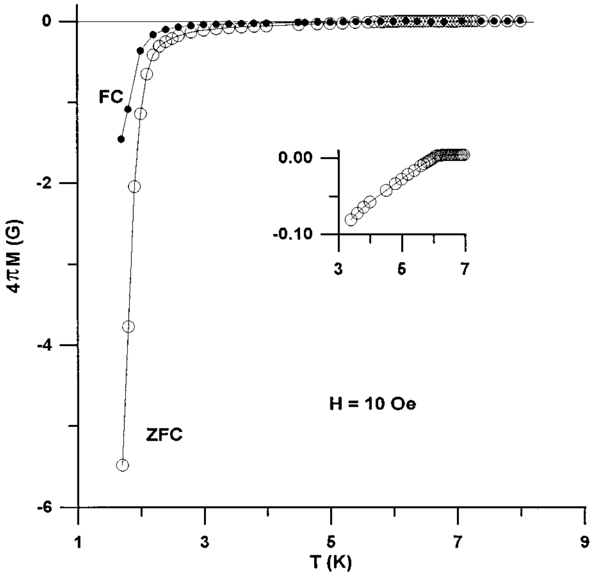


FIG. 4. ZFC and FC magnetizations for the porous glass with 7 nm pores measured at 10 Oe. The lines provide a guide for the eye. The inset shows the ZFC magnetization near the superconducting phase transition.

different samples and in different temperature ranges. Note, that the FC magnetization is weak compared to the ZFC magnetization for the samples with 4 and 3.5 nm pores when diamagnetic shielding becomes near complete at low temperatures (Figs. 1–3).

We also measured the remanent magnetization at low temperatures up to 3 K for all samples under study. The ratio of the ZFC and remanent magnetizations for the field of 10 Oe was about unity for the glasses with 4 and 3.5 nm pores and increased up to 1.3 for the opals and the glass with 7 nm pores.

The temperature dependence of the upper critical field was studied in details for the first sample with 4 nm pores. The results are depicted in Fig. 7. The values of $H_{c2}$ were

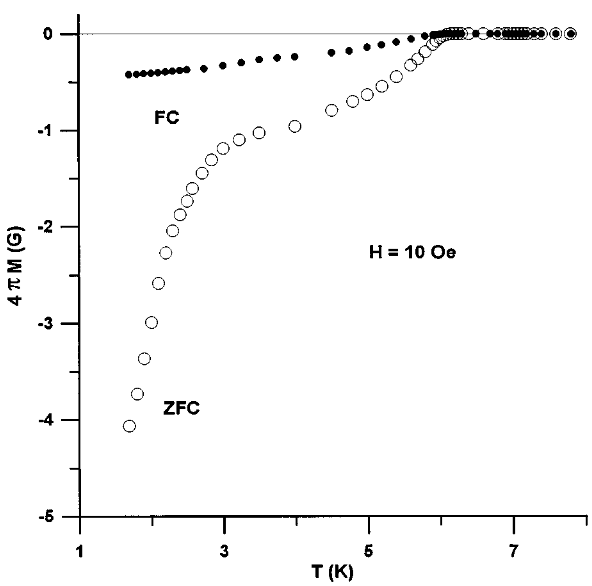


FIG. 5. ZFC and FC magnetizations for the first opal sample measured at 10 Oe.

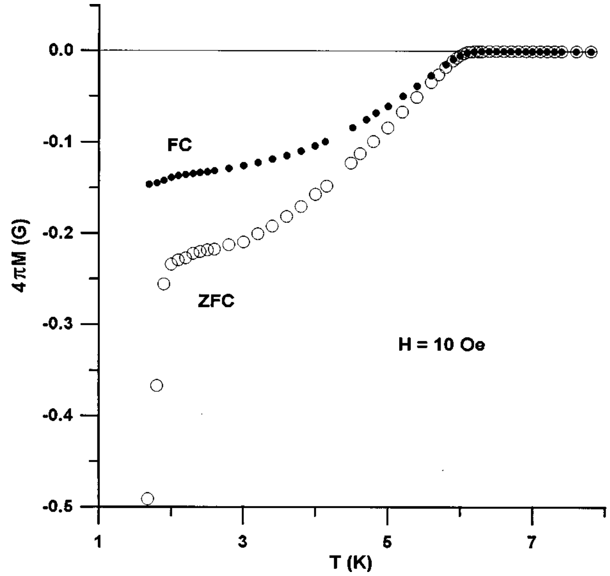


FIG. 6. ZFC and FC magnetizations for the second opal sample measured at 10 Oe.

obtained from hysteresis loops measured at different temperatures and from the onset of superconductivity in different applied fields. In full agreement with previous results for porous glasses filled with indium[2] and gallium,[13] the upper critical field increased roughly linearly with decreasing temperature following the Landau theory law but deviated from the linear dependence in the low-field region.

Magnetization versus field hysteresis loops obtained also varied for different samples and temperature regions. For the specimens with 4 and 3.5 nm pores in the total temperature range of superconductivity, the hysteresis loops were typical for hard type-II superconductors. An example for the second sample with 4 nm pores at 6.6 K is shown in Fig. 8. For the glass with 7 nm pores the hysteresis loops below 2 K were

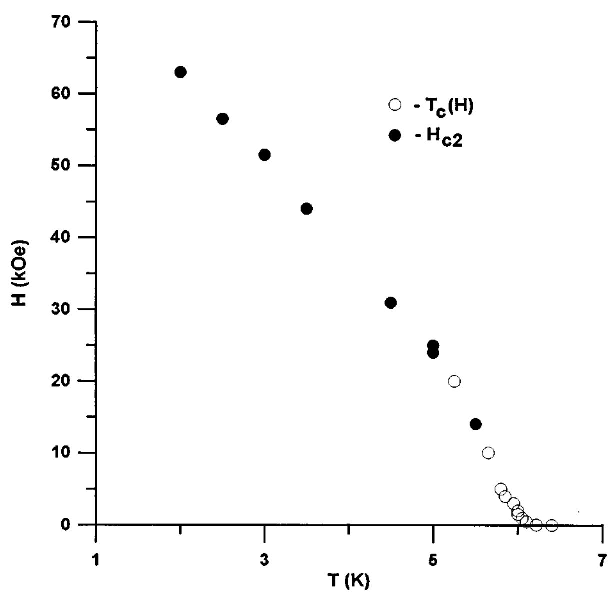


FIG. 7. The H-T phase diagram for the first sample of porous glass with 4 nm pores. The closed circles are the upper critical fields found from hysteresis loops. The open circles are the temperatures of the onset of superconductivity.

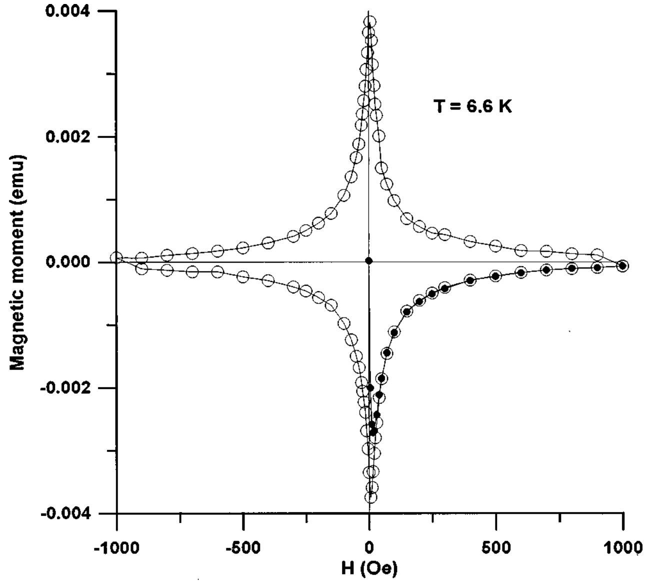


FIG. 8. The magnetization hysteresis loop for the second sample of porous glass with 4 nm pores measured at 6.6 K. The closed symbols correspond to first increasing the magnetic field after the sample was cooled in zero applied field. The open symbols correspond to consecutive decreasing and increasing the field.

similar to those for hard superconductors but their shape was butterflylike (Fig. 9). However, for the opal samples in the whole temperature range under study and for the sample with 7 nm above 2 K in the temperature range of partial diamagnetic shielding, the magnetic behavior was almost reversible (see Fig. 10). Note, that some reversibility at high magnetic fields was obtained in Ref. 13 for gallium confined within a porous glass with pores of 4 nm in diameter.

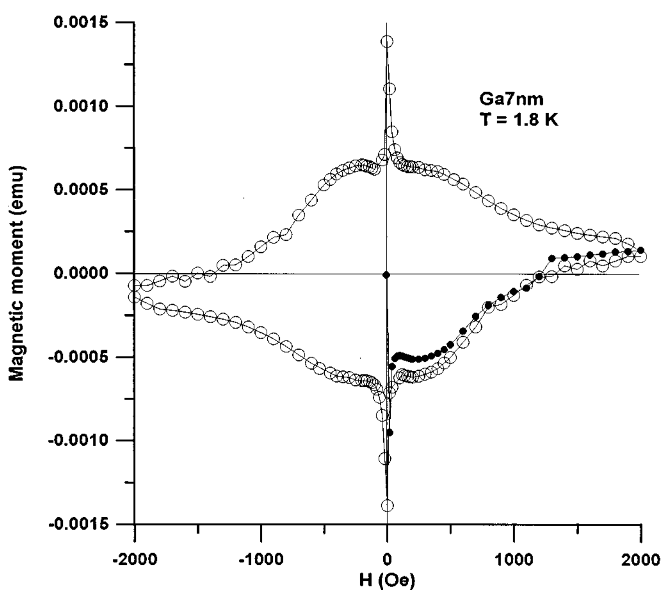


FIG. 9. The magnetization hysteresis loop for the porous glass with 7 nm pores measured at 1.8 K. The closed symbols correspond to first increasing the magnetic field after the sample was cooled in zero applied field. The open symbols correspond to consecutive decreasing and increasing the field.

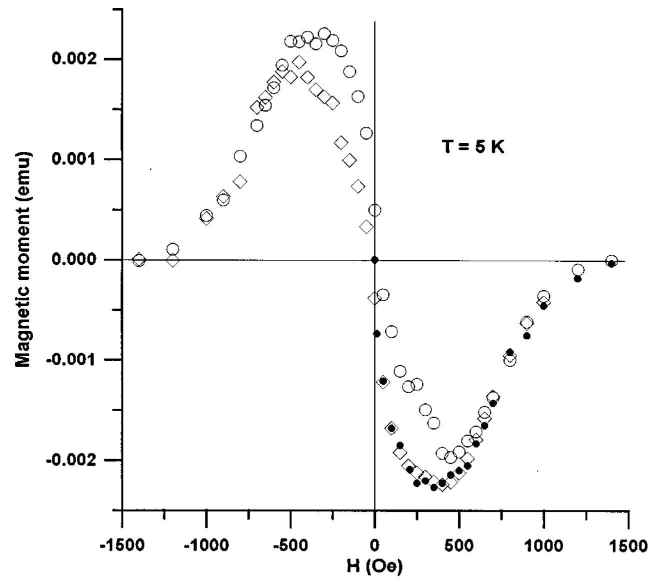


FIG. 10. The magnetization hysteresis loop for the second opal sample measured at 5 K. The closed circles correspond to first increasing the magnetic field after the sample was cooled in zero applied field. The open circles and diamonds correspond to consecutive decreasing and increasing the field, respectively.

## IV. DISCUSSION

As can be seen from the results described above, the magnetic properties of the samples under study in the superconducting state are rather different. Nevertheless, diamagnetic shielding is complete or strong enough at low enough temperatures for all specimens. This evidences that screening superconducting currents are spread over gallium in at least several neighboring pores and that the external magnetic field is extruded from the most volume of the samples in agreement with a model of porous glasses filled with metals developed in Refs. 12 and 13.

Let us discuss the nature of the different temperature dependences of the ZFC magnetization in the samples under study. One can separate in Figs. 1–6 three temperature ranges where the ZFC magnetization undergoes noticeable alterations: around 6.4 K for all samples, below 3 K for the glass with 7 nm pores and for the opals, and near 7.1 K for the second sample with 4 nm pores. As has been shown in Ref. 14, gallium in a porous glass with pores of 4 nm between 4.2 and about 150 K can occur in two coexistent structural modifications, both are different from the known bulk phases. Thus, the two steps in magnetization near 6.4 and 7.1 K for the second sample of porous glass (Fig. 2) might be due to consecutive superconducting phase transitions within those two modifications of confined gallium. This suggestion seems to be reasonable if we take into account that the step of 6.35 K is very sharp and coincides with the onset of superconductivity in the first sample with the same pore size. The shape of the hysteresis loop at 6.6 K (Fig. 8) also confirms this suggestion. Moreover, our studies have shown that superconductivity in the intermediate temperature range between these two steps can be completely suppressed at higher magnetic fields while the phase transition at 6.35 K is only shifted and broadened. To confirm the suggestion we performed x-ray diffraction studies of both samples with 4 nm pores. For the second sample after gallium had com-

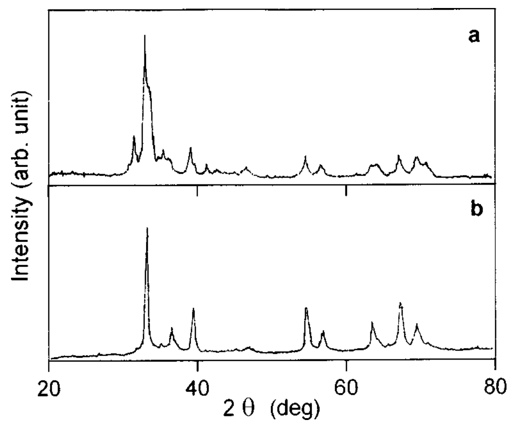


FIG. 11. The x-ray diffraction patterns obtained at 10 K for the second (a) and for the first (b) samples with pores of 4 nm in diameter.

pletely frozen, we observed at low temperatures a spectrum corresponding to at least two gallium modifications [Fig. 11(a)] which could be easily separated during warming and cooling the sample since they appear and disappear at various temperatures. The spectrum obtained coincides with the pattern presented in Ref. 14. In contrast, for the first sample there was only one set of lines arising from one of the structural modifications in the second sample [Fig. 11(b)]. Reasons for occurring different solid gallium modifications inside the first and second samples which were cut from the same piece of porous glass are unclear. Probably, slight distinctions in pore geometry or in filling factor can influence the process of gallium freezing. Taking into account the x-ray results we can attribute the superconducting phase transition at 6.35 K to the structural modification of confined gallium which is common for both samples while the transition at 7.1 K occurs within the modification which is specific for the second sample. Note that the fact that gallium in porous matrices occurs in structural modifications different from the bulk phases explains the elevated temperatures of the superconducting phase transitions observed. Negligible diamagnetism above 6.5 K for some other samples under study could be ascribed to the presence of small amount of the gallium modification with the transition temperature near 7.1 K, however, it also might arise due to thermodynamic fluctuations in gallium particles near the superconducting phase transition.[6,7]

The different magnetic behavior of the samples under study below about 6.4 K can be treated within the framework of models for granular superconductors or arrays of Josephson junctions that were already used in Ref. 13 and are consistent with the structure of porous glasses and artificial opals. In fact, these porous matrices have within them an interconnected network of pores with average sizes which are determined by mercury porosimetry. After liquid gallium had been introduced in pores under high pressure and elevated temperatures and the pressure had been put off at room temperature, some metallic crystallites were formed within pores during further cooling. Since gallium does not wet the inner glass surface and does not fill the total void volume, the metallic network in pores should be broken down. Thus, the confined metallic crystallites should be small enough. Their size can be estimated from the x-ray linewidth measured at low temperatures when confined gallium is in the solid state. The measurements performed for the samples with 4 nm pores gave a value of about 20 nm which is significantly larger than the pore size. We can expect that crystallites with sizes greater than the pore size are formed in all samples under study, excepting maybe the opals. Note that a similar estimate was obtained for indium crystallites in Vycor glass (35 nm).[10,11] These crystallites are linked weakly or strongly between each other depending on the local configuration of necks which connect pores, on the distance between pores, and the pore filling factor. We could expect that the superconducting properties of the samples under study should be governed by these links. Thus, following Ref. 13 we can model the samples as a disordered three-dimensional network of grains formed by strongly coupled metallic crystallites, the grains are connected by weaker Josephson links. The superconducting properties of the grains are described by the theory of type-II superconductors. (Note, that in Ref. 13 the size of grains for a porous glass with 4 nm pores was estimated from low-field hysteresis loops as about 1 $\mu$m.) It is known that three-dimensional arrays of Josephson junctions can undergo a well resolved double superconducting phase transition depending on intergranular resistance at temperatures when links responsible for intergranular phenomena are in the normal state.[16,17] First, at higher temperatures the single grains become superconducting, then at lower temperatures the phases of the order parameter of the individual grains become coherent. The depression of the phase ordering transition temperature $T_j$ obeys[17,18] fairly well the following relation similar to that derived by treating the phase coherence within a mean-field approximation:

$$\frac{T_j}{T_c}=\frac{1}{1+\beta R/R_0}, \tag{1}$$

where $T_c$ is the temperature of the superconducting transition in grains, $\beta$ is the numerical coefficient of the order of 0.1, $R$ is the normal-state intergrain resistance, and $R_0=\hbar/e^2$ is a characteristic resistance. The relationship (1) is obtained assuming grains to be equal and neglecting distribution in barrier resistance. Percolative disordering also leads to reducing the temperature of the transition to global superconductivity.[17,19] Both enhancement in tunneling resistance and percolative disorder broaden the temperature range of the superconducting phase transition. Note that double resistive transitions were observed experimentally for some electron-doped granular superconductors.[18,20–23] It then follows from Eq. (1) that when $R \ll R_0$ the shift of $T_j$ is negligibly small and the superconducting phase transition is sharp. This is the case of the samples with 4 nm pores. The roughly linear temperature dependence of the upper critical field (Fig. 7) agrees with such a conclusion. The sole superconducting transition in the sample with 3.5 nm pores is slightly broadened probably due to smaller sizes of effective grains.[7] In fact, the distance between pores is greater for this sample because of smaller total void volume. Thus, the coupling of confined metallic crystallites between each other should weaken. For the other samples the bend on the magnetization curves below 3 K together with incomplete diamagnetic shielding above 3 K indicates the presence of Josephson links with high normal resistance and probably wide distribution in tunneling barriers. For the opal samples one can speculate that the regions of strictly ordered silica spheres form ''grains.'' Between these grains there are disordered areas which serve as weak Josephson links with high resistance in normal state. The rather reversible behavior of the opals filled with gallium in a magnetic field (Fig. 10) within a temperature range where most of intergranular links are still in normal state (that is, above 3 K) then signifies that the number of pins within the grains is very small. This agrees with regular local packing of silica spheres in opals seen by electron microscopy.[8] Note that the difference between the temperatures of the local superconducting transition in the sample with 3.5 nm pores (6.5 K), in the samples with 4 nm pores (6.35 K), and other samples (6.2 K) probably arises due to size effects.[7]

The butterflylike hysteresis (or fishtail) similar to that observed at low temperatures for the sample with pores of 7 nm (Fig. 9) has been found in many high-$T_c$ superconductors (see, for instance, Refs. 24–27, and references therein). This effect can be treated differently. In particular, a Josephson-junction model of fishtail was discussed in Refs. 28 and 29. This model agrees well with the model of strongly and weakly coupled metallic crystallites in porous matrices assumed above. However, further studies should be made to elucidate this phenomenon for porous glasses filled with metals.

In conclusion, we studied superconductivity of gallium in various confined geometries. The single and double superconducting phase transitions were observed for different samples. The changes in magnetization below about 6.4 K were treated within the framework of models for granular superconductors, while the alterations in magnetization near 7.1 K were treated as a result of the additional superconducting phase transition in another structural modification of confined gallium. The results obtained allow us to suggest that measurements of magnetization at low temperatures can be used to get information about the geometry of the pore network and distribution of Josephson links in such composite materials.

## ACKNOWLEDGMENT

The present work was supported by the National Science Council of Taiwan under Grant No. 87-2811-M-006-0009.

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