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Superconductivity and structure of gallium under nanoconfinement

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Abstract
Superconductivity and crystalline structure were studied for two nanocomposites consisting of gallium loaded porous glasses with different pore sizes. The superconducting transition temperatures were found to differ from those in known bulk gallium modifications. The transition temperatures 7.1 and 6.7 K were ascribed to two new confined gallium structures, ι- and κ-Ga, observed by synchrotron radiation x-ray powder diffraction. The evolution of superconductivity on decreasing the pore filling with gallium was also studied.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Studies of nanostructured composite materials are of high priority in modern physics because of their importance for various technical applications. A great deal of attention has recently focused on composites consisting of nanoporous matrices loaded with various substances: metals, semiconductors, ferroelectrics, liquid crystals, and others (see, for instance, a review [1]). It has been shown that nanoconfinement can strongly affect many properties of substances embedded into small pores including atomic mobility in the liquid and solid states, crystalline structure, and phase transitions of different natures (see [2–5] and references therein). In particular, superconductivity of pure metals was reported to be drastically influenced by confined geometry, the porous matrices filled with metals behave in magnetic fields as dirty type II superconductors, often with shifted superconducting transition temperatures (see [6–9] and references therein).

Studies of superconductivity in porous glasses and opal photonic crystals loaded with gallium revealed superconducting transition temperatures remarkably different from that in common α-Ga, which is stable under ambient conditions [6, 10–12]. To treat the alterations in the superconducting transitions observed it was suggested that gallium within pores crystallizes into various modifications. Such suggestions were supported by x-ray powder diffraction studies of a confined gallium structure [13–15]. A new tetragonal gallium crystalline modification was observed in [15] which did not coincide to the known bulk tetragonal Ga(III) [16]. However, while the superconducting transition temperatures were found to differ significantly for gallium embedded into porous glasses with different pore sizes, the structural studies were restricted to a porous glass with 4 nm pores [13, 15]. Therefore, no correlations were established between superconductivity and the structure of gallium under nanoconfinement.

The main purpose of the present paper is to study superconductivity and the structure of gallium in two samples of porous glasses with different pore sizes. It will be shown that the shifted phase transition temperatures are related to two new gallium structures which occur under nanoconfinement. In addition, the evolution of the superconducting properties caused by a decrease in the filling of pores with gallium will be observed. The superconducting transition temperatures will be found to be independent of the pore filling while the diamagnetic screening is extremely sensitive to it.

2. Experiment and samples

Two samples of porous glasses with mean pore diameters of 7.0 ± 0.5 and 3.5 ± 0.5 nm were used as nanoporous matrices. They were made from phase separated soda borosilicate glasses with a pore structure produced by acid leaching. The pore size and pore size distribution were determined by mercury porosimetry and electron microscopy. The volume

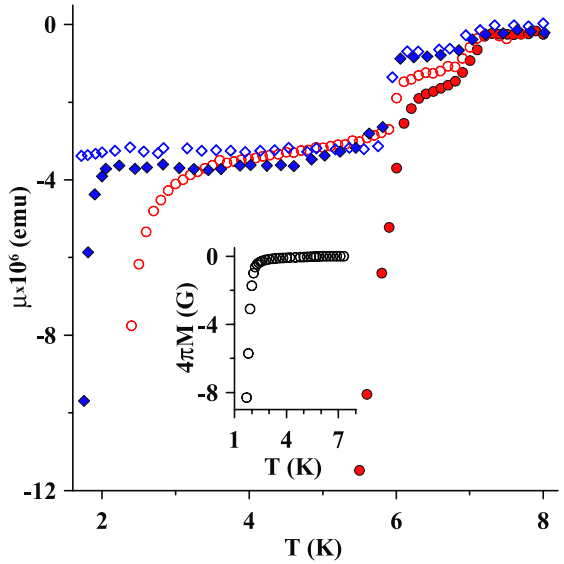

Figure 1. Temperature dependences of the ZFC (closed symbols) and FC (open symbols) magnetic moment μ for the gallium loaded porous glass with 7 nm pores measured at 20 Oe. Circles and triangles correspond to the pore filling 80 and 50%, respectively. The inset shows the temperature dependence of the ZFC magnetization at 80% filling.

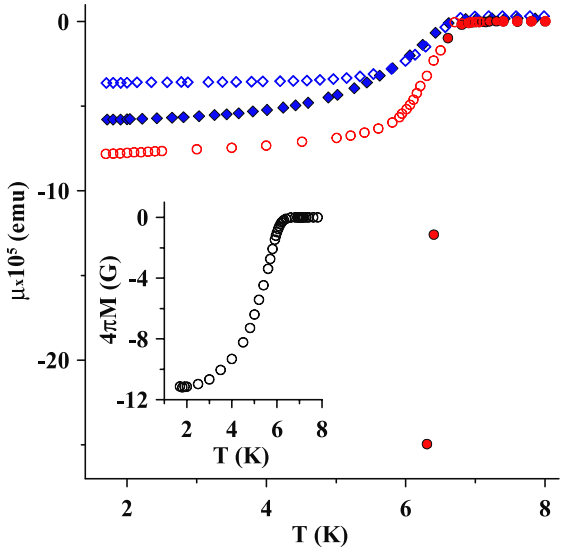

Figure 2. Temperature dependences of the ZFC (closed symbols) and FC (open symbols) magnetic moment μ for the gallium loaded porous glass with 3.5 nm pores measured at 20 Oe. Circles and triangles correspond to the pore filling 80 and 55%, respectively. The inset shows the temperature dependence of the ZFC magnetization at 80% filling.

fraction of pores for the samples under study was about 17 and 12%, respectively. The sample volumes were 4.1 and 18 mm^3. The liquid gallium was embedded into pores under pressure up to 9 kbar. The initial filling of the total void volume was near 85% for both samples and then was gradually reduced by heat treatment to 50 and 55% for the samples with 7 and 3.5 nm pores, respectively.

Magnetic properties of the gallium loaded porous glasses were studied using a Quantum Design superconducting quantum interference device magnetometer with a 7 T solenoid in the temperature range 1.7–295 K. The temperature during measurements was stabilized to within 0.01 K. The zero-field-cooled (ZFC) and field-cooled (FC) magnetization was measured using the conventional procedure of cooling down the samples at zero field to the lowest temperature, switching on a magnetic field, then warming up the samples at a constant applied field to a temperature ranging from 10 to 295 K, and subsequent cooling.

Powder x-ray diffraction was performed at the BL01C2 beamline of the Taiwan National Synchrotron Radiation Research Center with the wavelength λ of 0.774 91 Å. Two-dimensional diffraction patterns were recorded by a Mar345 imaging plate system. The diffraction angle θ was calibrated with Si powders (NBS640b) and silver behenate. One-dimensional x-ray powder diffraction profiles were integrated from selected fan-like areas of the symmetrical 2D powder rings. The temperature was changed with a rate of about 5 K min^{-1}. Before measurements the sample was kept at a target temperature for about 7 min. Upon monitoring the x-ray spectra, the temperature was stable within 0.01 K. The sizes d of confined gallium crystallites were evaluated using Scherrer's equation $d = k\lambda/(B\cos\theta)$ with the shape correction constant $k = 0.95$ and full width at half maximum B of the related Bragg peaks [17]. X-ray patterns were obtained for the minimal filling of the pore volume equal to 50 and 55% for the samples with 7 and 3.5 nm pores, respectively.

3. Experimental results

ZFC and FC magnetizations at a magnetic field of $B = 20$ Oe obtained at two different pore fillings for the samples with 7 and 3.5 nm pores are shown in figures 1 and 2, respectively.

The onset of weak diamagnetism in the sample with 7 nm pores was seen at $T_c = 7.1 \pm 0.1$ K (figure 1) independently of the pore filling. Then, at lower temperature near 6.0 there was another increase in diamagnetism. Between 7.1 and 6 K the ZFC and FC magnetization curves were rather similar and did not change significantly when the filling of pores with gallium was decreased. Below 6 K a strong dependence of the diamagnetic shielding was observed on the pore filling. At high filling, the diamagnetic shielding at the lowest temperature achieved was almost complete, as can be seen in the inset to figure 1 for the 80% filling. At the minimal filling a noticeable increase in the diamagnetic shielding was seen only below 2 K. The volume fraction f_{sc} of the sample in the superconducting state at 1.7 K can be estimated using the relationship

$$f_{sc} = \frac{4\pi\mu}{HV}, \tag{1}$$

where μ is the magnetic moment measured under ZFC, H is the applied magnetic field, and V is the sample volume. The fraction f_{sc} evaluated in such a way at a field of 20 Oe is shown in figure 3. It decreased with decreasing pore filling and was only 1.5% for the 50% filling.

The superconducting transition for the gallium loaded porous glass with 3.5 nm pores is seen at a temperature of

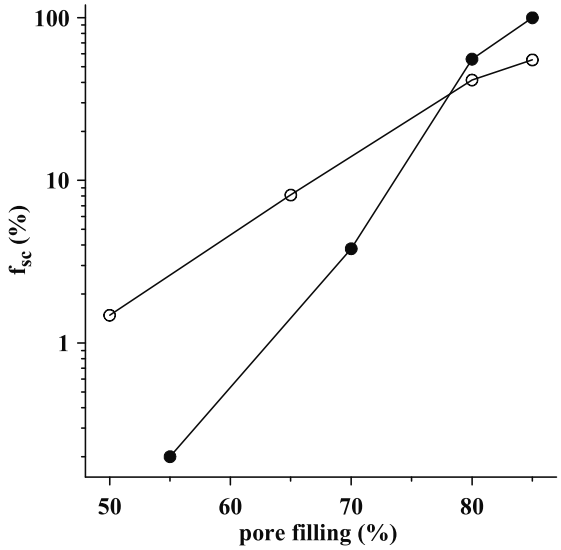

Figure 3. The volume fraction in the superconducting state f_{sc} at 20 Oe versus the pore filling at 1.7 K for the samples with 7 (closed symbols) and 3.5 nm (open symbols) pores. The solid lines are guides for the eye.

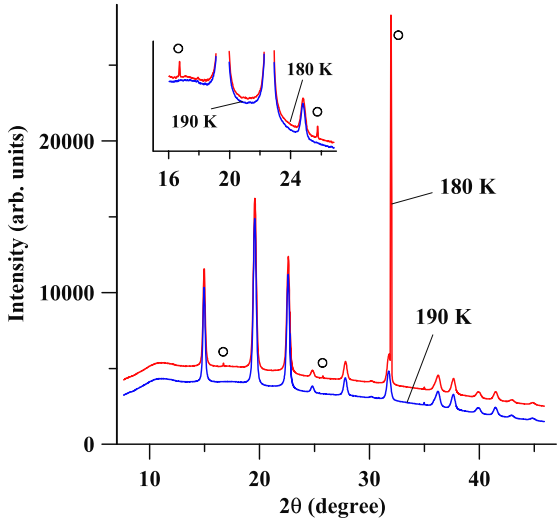

Figure 4. X-ray patterns of the gallium loaded porous glass with pore size 7 nm at 190 K (blue) and 180 K (red) obtained upon cooling. The patterns are shifted vertically for better visibility. The inset shows scaled patterns at 190 and 180 K. The peaks belonging to ι-Ga are marked by circles.

$T_c = 6.7 \pm 0.1$ K (figure 2), which is noticeably lower than the onset of superconductivity in the sample with 7 nm pores. As in the first sample, the diamagnetic shielding was close to complete at higher filling and decreased with decreasing amount of confined gallium. For the minimal pore filling 55% only 0.2% of the sample volume was in the superconducting state at the lowest temperature 1.7 K. The observed phase transition temperature did not change on decreasing the pore filling (figure 2). The fraction f_{sc} versus pore filling for the sample with 3.5 nm pores is also shown in figure 3 along with the data for the sample with 7 nm pores.

X-ray powder patterns of confined gallium seen upon temperature variations were completely different for the samples with pores 7 and 3.5 nm. The evolution of the gallium structure in the former sample upon cooling from 320 down to 180 K and consecutive warming is illustrated in figure 4. Gallium remains in a liquid state until about 260 K. A crystalline structure with peaks similar to those shown for 190 K first appears upon cooling at 255 K. On further cooling the intensities of the peaks slightly increased without noticeable changes in their ratios. This set of peaks corresponds to the most pronounced peaks of the x-ray pattern for α-Ga [18] except for the missing one at $2\theta \cong 11.5°$. Therefore, the peaks can be ascribed to α-Ga where freezing is affected by confinement. However, confined α-Ga is most likely disordered because of the lack of the peak at 11.5° and deviations in relative peak intensities from those in bulk α-Ga.

At 180 K another set of peaks appears upon cooling (figure 4). One of them (at $2\theta \cong 31.95°$) is very intensive, two others (at $2\theta \cong 25.77°$ and $2\theta \cong 16.73°$) are very weak (see inset in figure 1). This set of peaks does not correspond to patterns of any known bulk gallium crystalline structures including high pressure ones. It was not reported previously under nanoconfinement, either, and was observed for the first time. Upon subsequent warming, the intensity of these three

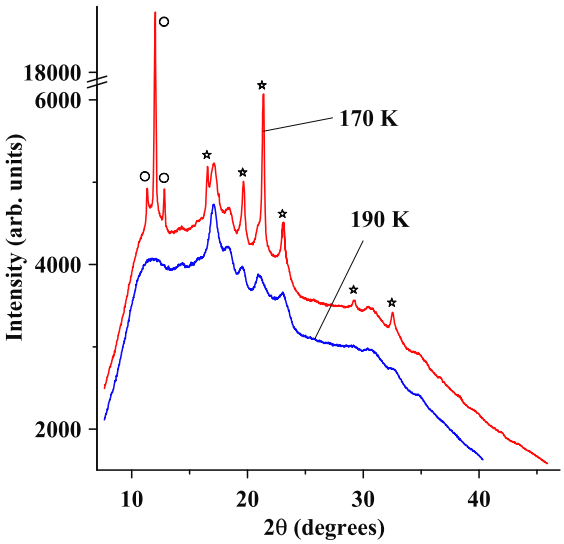

Figure 5. X-ray patterns of the gallium loaded porous glass with pore size 3.5 nm at 170 K (red) and 190 K (blue) obtained upon warming from 70 K. The patterns are shifted vertically for better visibility. The pattern at 190 K shows only peaks corresponding to δ-Ga. The peaks belonging certainly to κ-Ga and other narrow peaks (see text) at 170 K are marked by circles and asterisks, respectively.

peaks was about the same until 240 K. Then it decreased due to melting and the peaks were no longer seen at 255 K.

The crystalline gallium structure within pores of smaller sizes is still more complex. Upon cooling from 320 K, confined gallium remains in the supercooled state until about 140 K. Then upon further cooling, a single peak at $2\theta = 12.05°$ appears. At lower temperatures another set of broad peaks emerges combined with narrower peaks. Such patterns are seen below 130 K down to the lowest temperature achieved (70 K) during the x-ray measurements and upon sequential warming up to about 175 K. Figure 5 shows, as an example, a pattern

at 170 K obtained upon warming. Above 175 K, the gallium responsible for narrow peaks melt and only the set of broad peaks survives up to about 220 K. A pattern consisting of broad peaks at 190 K is shown in figure 5. All broad peaks coincide well with strong peaks in the δ-Ga x-ray powder diffraction pattern [18]. It should be noted that the relative intensities of the confined δ-Ga peaks follow the pattern for bulk δ-Ga which means that confined δ-Ga structure is quite ordered. A set of narrower peaks at $2\theta = 12.05°$, 11.35°, and 12.85° (figure 5) does not belong to any known bulk crystalline modifications of gallium as in the case of the sample with 7 nm pores and was not reported previously for nanoconfined gallium. Detailed studies of the temperature evolution of the x-ray spectra for two new confined gallium structures and their melting and freezing processes will be published elsewhere.

4. Discussion

Ga is a low melting point metal which occurs in different polymorph crystalline phases. In addition to the, stable at ambient conditions, α-Ga (melting point 303.3 K), several other structures (β-, γ-, δ-, and ε-Ga) with lower melting temperatures were also observed at ambient pressure [19–23]. Two more phases (ζ- and η-Ga) were reported to emerge upon cooling below room temperature [24]. There are also at least four high pressure crystalline phases of gallium, labeled Ga(II), Ga(III), Ga(IV), and Ga(V) [16, 25–27]. The stabilization of β-, γ-, and δ-Ga, which are metastable in bulk, was reported for gallium droplets of submicron sizes dispersed in polymethacrylate matrix and within epoxy resin [28–30] and for gallium encapsulated in carbon nanotubes [31]. A new crystalline phase named θ-Ga was suggested for gallium with an admixture of some particulate materials which revealed itself in an unusual superconducting transition temperature [32].

The superconducting transition temperature of bulk α-Ga is $T_c(\alpha) = 1.0833$ K. Other crystalline gallium structures have higher temperatures ranging from 6.07 to 7.85 K. They are listed, for instance, in [32].

According to figure 4, two crystalline modifications of gallium emerge at lower temperatures within 7 nm pores, the disordered α-Ga and another modification with a previously unreported x-ray powder diffraction pattern. Continuing the list of gallium crystalline structures, this phase can be named ι-Ga. As can be seen from figure 4, the peaks belonging to confined α-Ga are broadened. To estimate the size of gallium crystallites formed within pores we chose the peak at $2\theta \cong 19.6°$ since it is a singlet. The Scherrer equation yields a size of 140 Å, which is about twice as large as the pore diameter. The size of confined ι-Ga crystallites evaluated with the Scherrer equation is noticeably bigger than the pore size (about 280 Å) as the x-ray peaks associated with this modification are twice as narrower as those of confined α-Ga. It means that ι-Ga crystallites should have a dendrite-like shape following the tortuous pore network.

Since α-Ga has a superconducting transition temperature below the lowest achieved temperature 1.7 K in our measurements, the superconductivity in the porous glass with 7 nm pores arises due to the ι-Ga modification. Therefore, $T_c(\iota) = 7.1$ K.

Table 1. Temperatures T_c of the superconducting phase transition in confined gallium.

Crystalline phase	ι-Ga	κ-Ga	λ-Ga
T_c (K)	7.1	6.7	6.3 [6]

Superconductivity in the gallium loaded sample of porous glass with 3.5 nm pores emerged at 6.7 K. Such a temperature was not observed in known modifications of bulk gallium, as can be seen from data collected in [32]. In particular, it is lower by more than 1 K than the superconducting phase transition temperature observed once for δ-Ga [33]. Therefore, one can suggest that the onset of superconductivity at 6.7 K in gallium loaded porous glass with 3.5 nm pores is caused by the superconducting transition in the newly found gallium structure occurring under nanoconfinement. Continuing the list of reported gallium crystalline modifications, this gallium phase is labeled as κ-Ga.

Note, that several other narrower peaks appear in the x-ray patterns for the gallium loaded sample with 3.5 nm pores at about the same temperatures as the three low-angle peaks attributed to κ-Ga. The temperature dependences of their intensity do not quite coincide with that of the κ-Ga peaks. These peaks could also belong to κ-Ga, the variations of the relative intensity with temperature being caused by changes in the lattice ordering. However, two peaks at $2\theta = 21.4°$ and 23.15° could belong as well to β-Ga [18] formed within pores, other peaks being suppressed by lattice disorder. Three peaks at $2\theta = 16.57°$, 19.7°, and 32.6° coincide with intensive lines belonging to a confined gallium phase previously found in porous glasses with pore sizes 4 nm and opal photonic crystals [13, 14]. That modification was identified with a *bc* tetragonal structure with lattice constants $a = b = 0.325$ nm and $c = 0.495$ nm [15]. The confined tetragonal phase was found in [6] to respond for superconductivity with a phase transition temperature of 6.3 K. No Greek letter was attached to it, thus, continuing the list of the reported gallium modifications we label it as λ-Ga. Figure 2 does not show any visible anomalies at the superconducting transition temperatures in β-Ga ranging from 6.0 to 6.4 K according to different studies (see [34] and references therein) or λ-Ga. Thus, one can suggest that κ-Ga is mostly responsible for superconductivity in the sample with 3.5 pores and $T_c(\kappa) = 6.7$ K. For convenience, the superconducting transition temperatures in structural modifications of nanoconfined gallium are collected in table 1.

To estimate the crystallite size of confined δ-Ga the peak at $2\theta = 23.3°$ was used because it is the only peak strong enough and well separated from intensive neighbors. The Scherrer equation gives a size of 60 Å, about twice as large as the pore diameter. For κ-Ga crystallites, the Scherrer equation gives an estimate of 350 Å. It shows that the crystallization front went through several neighbor pores and the κ-Ga crystallites should have a dendrite-like shape similar to those of the ι-Ga phase.

Note, that for both porous glasses with 3.5 and 7 nm pores the size of gallium crystallites of known and new structures were found to be rather different. The known structures formed crystallites which were only about twice as large as the pore sizes, while ι- and κ-Ga formed much larger dendrite-like crystallites. This result allows us to suggest that the connectivity of liquid gallium within pore networks could play a crucial role in the formation of particular gallium crystalline modifications which are associated with unusual superconducting transition temperatures.

The fact that the onset of superconductivity in the samples under study was not changed on decreasing the pore filling (figures 1 and 2) is evidence of the occurrence of sufficient amounts of the ι- and κ-Ga modifications within pores independently on the filling.

The different magnetic behavior of the samples under study upon decreasing the pore filling can be treated within the framework of models for granular superconductors or arrays of Josephson junctions that were already used in [6, 10] and are consistent with the structure of porous glasses. In fact, after liquid gallium had been embedded into pores under high pressure and then the pressure had been backed off, some amount of gallium flowed from pores leaving a partly interconnected network of confined particles. The remaining amount corresponded to the initial filling. During further cooling small metallic crystallites of various modifications emerge within pores. The size of the crystallites was evaluated here using the Scherrer equation. These crystallites are linked weakly or strongly between each other depending on the local configuration of necks which connect the pores, the interpore distance, and the pore filling. The superconducting properties of a given sample as a whole should be governed by these links. Therefore, the samples can be modeled as a three-dimensional network of grains formed by strongly coupled crystallites, the grains being connected by weaker Josephson links. First, at higher temperatures, only the single grains become superconducting. In the samples under study the superconducting transitions in grains occur at 7.1 and 6.7 K for crystallites of the ι and κ modifications of gallium, respectively. At lower temperatures the phases of the order parameter of the individual grains become coherent and the superconducting currents envelop larger areas of the samples. The depression of the phase ordering transition, compared to T_c, is driven by the normal-state intergranular resistance (see [35, 36] and references therein). When the filling of the total pore volume with gallium is high, the intergranular resistance is reduced and the diamagnetic shielding is almost complete while only a part of the sample volume consists of superconducting grains. When the filling decreases, the phase ordering transition shifts to low temperatures and the diamagnetic shielding remains incomplete at accessible temperatures as is seen in figure 3. Such a model explains why diamagnetism near the onset of superconductivity in the nanocomposites under study depends weakly on the pore filling despite strong alterations in the ZFC magnetization magnitude at lower temperatures.

It should be noted that $T_c(\iota) = 7.1$ K is rather close to the superconducting phase transition temperature observed in [32] for bulk θ-Ga, $T_c(\theta) = 7.23$ K. Thus, one cannot exclude the possibility of a coincidence between the ι- and θ-structures. However, the decisive conclusion is prevented by a lack of structural data on θ-Ga.

In conclusion, studies of superconductivity in gallium loaded porous glasses with pore sizes 7 and 3.5 nm revealed unusual superconducting transition temperatures which differ from those in known bulk gallium structures. The synchrotron radiation x-ray powder diffraction studies allowed them to be related to two new crystalline gallium structures, ι- and κ-Ga. The onset of superconductivity did not shift when the filling of pores with gallium was decreased while the diamagnetic shielding of the nanocomposite volumes was found to be affected drastically by the pore filling.

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