Properties of gallium in porous glass

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11 December 1995; revised manuscript received 29 April 1996

We have studied the behavior of gallium in porous glass. Except for a few lines of α-Ga, the main pattern of the x ray does not fit in with any previously reported phase of gallium. By resistivity measurements, just above a superconducting transition, an anomalous peak at 6.3 K was observed. Lack of x-ray patterns of β-Ga and δ-Ga suggests that the 6.4 K transition might be due to a new phase of gallium or a β phase in strong disorder. [S0163-1829(96)02830-5]

Porous glass filled with different materials plays an important role in many aspects of science and technology. Properties of materials in confined geometries can differ significantly from those of bulk samples.[1,2] In this paper, we will discuss the properties of gallium in a porous glass.

The porous matrix was prepared from a sodium borosilicate glass. The pores had a rather narrow size distributions, and 95% of the pore diameters were lying within ± 4 Å of the average value. The pores together with narrow necks, which connect pores, form the random interconnected network in a glass bulk. The average distance between pores, according to small-angle diffractometry and electron microscopy, can be estimated to be 90 Å, about twice as large as the pore diameter. Before porous glass was filled with gallium, it was cleaned by H_2O_2 and heated up to 130 °C for the inner water evaporation. The liquid gallium was embedded into glass under high pressure up to 9 Kbar at 35 °C. The purity of gallium was 99.9%. The density of porous glass with gallium was 2.83 g cm^{-3} corresponding to about 80% filled total void volume.

Figure 1 gives the temperature dependences of resistance between 2 and 300 K. Electrical resistance was measured by a four-probe method. The schematic representation of the structure of porous glass with gallium and four probes is shown in the inset of Fig. 2. The sample was fixed tightly in the sample holder and four probes were pinned into the sample. A very small current 0.5 mA was used to measure the resistance. No self-heat effect was observed. The resistance of a sample was measured by averaging the voltages obtained with the current in the forward and reverse directions. As shown in Fig. 1, the resistance fluctuates between about 290 and 160 K. Except this temperature range, the resistance measurements are reversible and repeatable.

Figure 2 gives the temperature dependence of resistance R between 2 and 12 K. A very sharp superconducting transition is observed at 7 ± 0.01 K. At 7 K the resistance is near but still not zero. As shown in Fig. 2, there are many microchannels between A and B. As long as gallium in any one of the channels becomes superconductive, it will cause zero resistance between A and B.

Among the seven previously reported polymorphic modifications of gallium,[3–8] at least four of them, α-Ga, β-Ga, γ-Ga, and δ-Ga show superconducting phase transitions.[9–11] The superconducting transition temperatures T_c of α-Ga, γ-Ga, and δ-Ga are 1.082, 7, and 7.85 K, respectively. The transition temperature of β-Ga reported by different research groups was from 5.6 to 6.3 K.[11,12] The 7 K transition indicates a γ-Ga. However, the resistance does not reach zero at 7 K, which indicates only a tiny amount of gallium to be γ-Ga. Figure 3 gives the temperature dependence of resistance between 7 and 6 K using different currents. A dramatic feature in resistance measurement is the sudden increase of resistance associated with the onset of superconductivity at 6.30 ± 0.01 K. A similar two-stage superconducting transition of indium in porous glass was also observed by Graf *et al.*[13] To confirm the anomalous peak at 6.3 K was not an experi-

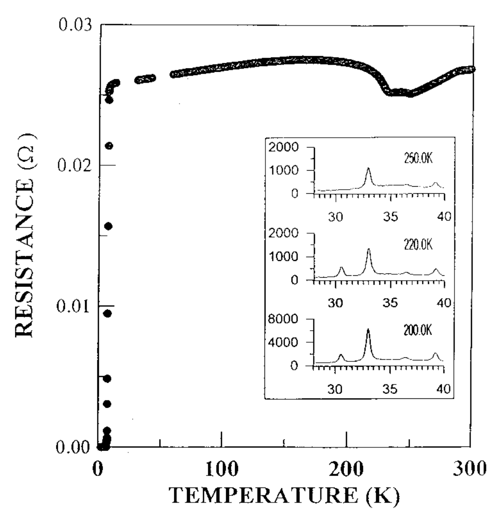

FIG. 1. The temperature dependence of resistance between 2 and 12 K. The inset gives x-ray spectra at 250, 220, and 200 K. The x axis of x-ray patterns is diffraction angle 2θ (deg) and the y axis is intensity with an arbitrary unit.

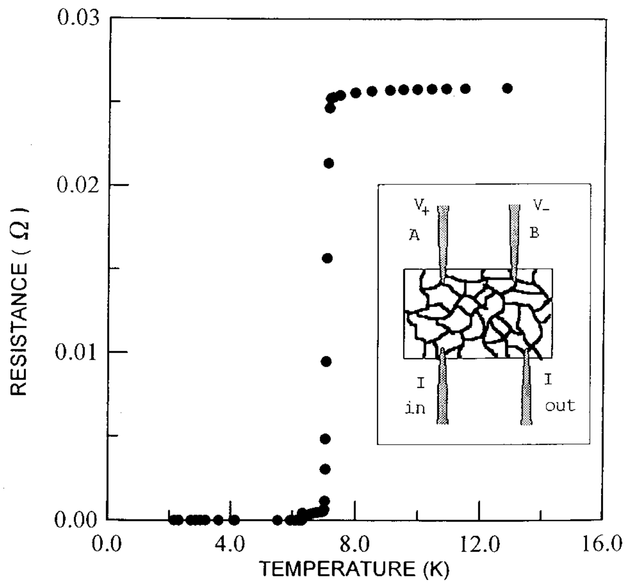

FIG. 2. The temperature dependence of resistance between 2 and 12 K. The inset is the schematic representation of the structure of the porous glass with gallium and four probes.

mental artifact, the resistances between 7 and 6 K were repeated by repositioning the leads. The peak at 6.3 K was always observed. However, if the leads changed, the microchannels between leads would be different and the shape of the 6.3 peak changed, too. When the current used to measure the resistance was increased, the peak was depressed. For currents larger than 4 mA, the peak vanishes. For resistance measurements between 300 and 2 K, the temperature at each data point was regulated by a Lake Shore DRC-93CA temperature controller. However, if the temperature was quenched directly to 10 K by putting in exchange gas, we measured the resistance after exchange gas was pumped out. The 6.3 K peak and 7 K superconducting transition disappeared. γ-Ga seems to fail to form in porous glass if it is quenched rapidly.

The x-ray-diffraction pattern of gallium in a porous glass is shown in Fig. 3. Since the absorption coefficient of gallium for Cu $K\alpha$ is 67.9 cm^2/g, x ray can penetrate several thousand microns into these samples, and we are able to observe the structure of gallium in the inner part of the glass bulk. As shown in Fig. 3(a), the x-ray spectrum indicates gallium in a liquid or amorphous phase at 300 K. The x-ray spectrum at 200 K is shown in Fig. 3(b). The material in porous media typically forms a confined interconnected three-dimensional network of channels of irregular size and shape. Except for a few lines of α-Ga, the main pattern of the x-ray spectrum of gallium in a porous glass at 200 K does not fit in with any previously reported phase of gallium.[14] According to Fig. 3(a), this main pattern is not observed at 300 K; therefore, it is unlikely caused by sodium borosilicate glass or impurities. This x-ray pattern might suggest a new phase of Ga. Within the x-ray technique, neither β-, γ-, δ-, ε-, η-, ζ-Ga, nor Ga II, nor Ga III is discovered. As shown in Fig. 3(c), α-Ga is strongly reduced at low temperature, and most Ga is left in this phase.

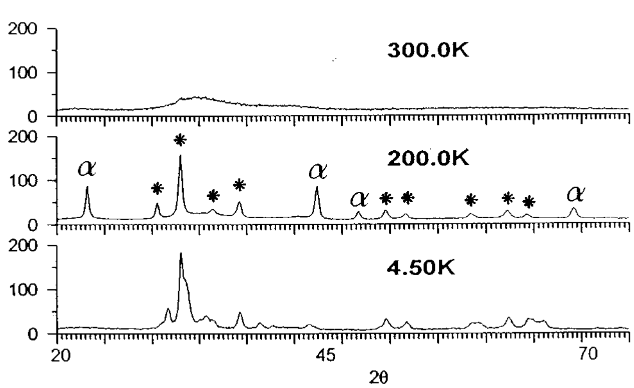

FIG. 3. The x-ray-diffraction pattern of Ga in a porous glass. At 200 K, the x-ray lines that do not fit in with any previously reported phase of Ga have been marked by *. The lines of α-Ga have been marked by α.

Of the seven reported polymorphic modifications, α-Ga is stable and always constitutes the majority of gallium but β-Ga appears to be metastable and is formed by supercooling. Ga II and Ga III are stable only above 11.4 kbar and 26.9 kbar, respectively. The remaining three phases δ-Ga, γ-Ga, and ε-Ga can be only observed with α-Ga and β-Ga as a small fraction.

The x-ray spectra at 200, 220, and 250 K are shown in the inset of Fig. 1. Comparing the x-ray spectrum at 300 K to the spectrum at 250 K indicates a crystallization below 250 K. The peak of the x-ray spectrum at $2\theta=33°$ as shown in Fig. 1 might be corresponding to lines at $2\theta=34.2490°$ and 34.965 81° of a β phase,[14] and the peak at $2\theta=30.5°$ might be corresponding to lines at $2\theta=30.2406°$ and 30.5371° of an α phase.[14] At 250 K, the disappearance of the peak at $2\theta=30.5°$ suggests a transition from α-Ga to β-Ga. Therefore, a possible explanation of the resistance measurements is that the fluctuation from about 250 to 220 K might be due to a transition from α-Ga to β-Ga and β-Ga melts at about 220 to 250 K. At atmospheric pressure the melting point of β-Ga is 256.5 K, much higher than 220 K. Molz *et al.*[2] claimed that on the occasion of fluids in porous glass the melting transitions are broadened and occur at temperatures below the bulk melting point. This argument is consistent with our results. Besides, a remarkable depression of the melting point of gallium due to the confinement has also been reported recently by Wolf *et al.*[15] for Ga precipitates within nanocrystalline tungsten.

If this argument is correct, above 250 K gallium is in an amorphous or liquid phase and α-Ga will not exist at high temperature. This result is inconsistent with the fact that α-Ga is the only stable phase at atmosphere. Besides, although the x-ray patterns of gallium in porous glass might be strongly broadened and shifted, the x-ray spectrum at 4.5 K hardly fits any Ga pattern previously reported. Therefore, another possible explanation of the resistance measurements is that there is a new phase to the α-Ga transition at about 160 K. To compare Fig. 3(b) to 3(c), α-Ga is strongly reduced at low temperature, which further supports a new phase to the α-Ga transition at about 160 K.

The low-temperature resistance measurement is shown in Fig. 2. The most possible explanation of the 6.4 K transition is a superconducting phase transition of β-Ga. Many different research groups measured the transition temperature of β-Ga and reported it from 5.6 to 6.3 K. Experiments indicated[16–18] that many weak-coupling superconductors showed an enhancement of T_c if they were made disordered. On the contrary, strong-coupling materials showed a small decrease of T_c with an increasing disorder.[17–19] By ion bombardment Goerlach *et al.*[19] demonstrated that the T_c of β-Ga could even increase up to 6.6 K. If the gallium in porous glass at low temperature is in a β phase, based on the x-ray spectrum, this β-Ga must be strongly disordered. However, the T_c of β-Ga and γ-Ga in porous glass are not shifted by disorder.

Suppose the 6.4 K superconducting transition is caused by β-Ga. The full diamagnetic shielding suggests that, in a porous glass, almost all gallium is in a β phase. If this argument is correct, based on the x-ray spectrum, this β-Ga must be strongly disordered.

However, it still cannot rule out the possibility that the 6.4 K superconducting transition might be caused by a new phase of gallium. Although indium, leads,[20] and mercury[21] in Vycor are known to have the bulk structure, Sokol *et al.*[22] reported that deuterium in Vycor has a nonbulk structure. Besides, Graf *et al.*[13] found that the superconducting transition of indium in Vycor occurred about 0.6 K higher than in bulk, even though the crystal structure in Vycor is the same as in bulk. This makes the identification of a possible β phase in gallium (largely based on the transition temperature being close to the bulk β phase transition) less convincing.

The properties of gallium are significantly changed in porous glass. The properties can be explained by either of the following. (1) Instead of the stable α phase, the gallium in porous glass is in the β phase with strong disorder. The melting point is smeared out and depressed to 220 K. Despite the remarkable disordering, the T_c of β-Ga and γ-Ga in porous glass do not shift. (2) There exists a new phase of gallium with T_c at 6.4 K. Contrary to a broad melting-freezing transition of metal in porous glass, the superconducting transition occurs sharply.

This work was supported by the National Science Council of the Republic of China under Contract No. NSC-84-2112-M006-001.

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