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X-ray studies of the melting and freezing phase transitions for gallium in a porous glass

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We use x-ray powder diffraction to study the melting and freezing processes for gallium within a porous glass. The only modification to solid gallium was found above 20 K, in contrast with previous x-ray studies of confined gallium. The size of gallium crystallites remained nearly constant during cooling and warming, while both the melting and freezing processes were smeared. The size of confined gallium crystallites was estimated as 22 nm, which is significantly larger than the pore size. The reasons for the phase-transition broadening and hysteresis between freezing and melting are discussed on the basis of the results obtained.
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Porous glasses with pore sizes under several hundred nanometers have various applications. The structure of materials embedded into porous glasses and the different processes within them are objects of continuing interest. Phase transitions in confined materials are studied intensively (see, for example Refs. 1–12 and the references therein). Among various phase transitions, the melting and freezing phase transitions are of particular interest since they are purely first order and are well studied for bulk substances. Until now, the melting and freezing in confined geometries have been observed for materials such as water,[13,14] organic liquids,[15–18] metals with low melting point,[11,19–23] helium,[24–28] oxygen, and some other simple liquids.[10,29,30] In spite of a lot of papers devoted to these phase transitions, treatment of some general problems remains controversial. In particular, the melting and freezing broadening and the origin of hysteresis between melting and freezing were interpreted completely differently by various authors.[10,11,17,23] To solve many such problems, the x-ray powder-diffraction technique seems to be very suitable since it shows directly the size of nanoparticles formed within pores during cooling as well as the structure of confined materials and the amount of frozen fractions. However, until now the x-ray-diffraction measurements have been used only to determine the structure of frozen materials[2,4,31,32] and not to study the melting and freezing processes. In the present paper we report results of the first x-ray-diffraction studies of gallium inside a porous glass with pores of 4 nm in diameter within the temperature range 10–320 K. The temperature independence of the sizes of confined metallic crystallites upon cooling and warming will be shown, both the melting and freezing processes being smeared. It will be also shown that in contrast with the samples of porous glasses studied earlier,[4] only one modification of solid gallium is formed during freezing in the sample under study.

The sample under study was prepared from a phase-separated soda borosilicate glass whose pore structure was produced by acid leaching.[33] After acid leaching, an interconnected network of fine pores was formed with an average pore diameter of 4 nm as determined by mercury intrusion porosimetry. The pore-size distribution is fairly narrow with 95% of the pore diameters lying within 0.4 nm of the average size. The volume fraction of pores was about 22%. The liquid gallium was introduced into the porous glass under high pressure up to 9 kbar at 35 °C. The filling factor is about 85% of the total pore volume.

The x-ray-diffraction measurements were performed using commercial powder-diffraction equipment with Cu $K\alpha$ radiation and a RINT2000 wide-angle goniometer. The experimental procedure was as follows. First, the sample under study was warmed up to 320 K well above the melting point of bulk gallium (303 K). Then it was slowly cooled down with a cooling rate less than 0.2 K/min to the first and consecutive temperature points of measurements until 10 K. During measurements the temperature was stable within 0.1 K. Then the sample was again warmed up to 320 K with the same rate of changing temperature between measurements. Similar cycles were performed several times. Temperature overshoots during cooling and warming were less than 1 K. At several temperatures we recorded the x-ray-diffraction patterns for the large-angle range 20°–80° with the scan speed of 0.5 deg/min. For other temperatures to obtain information on the relative amount of frozen gallium and on possible alterations in sizes of solid gallium nanoparticles, we observed diffraction only within the angle range from 28° to 35° using the same scan speed. In that range the most intensive diffraction peak was found to be set.

Almost within the whole temperature range under study, only a single structure of solid gallium was observed. This contrasts with the x-ray data presented in Ref. 4 where several modifications of gallium were found upon its solidification in a porous glass with the same pore size. The difference obtained means that the structure of confined gallium is very sensitive to minute deviations in pore geometry. At temperatures below 20 K, the presence of another solid gallium structure was found. The second gallium modification occurs probably because of a solid-solid phase transition. The x-ray patterns obtained upon cooling at 250, 100, and 10 K are

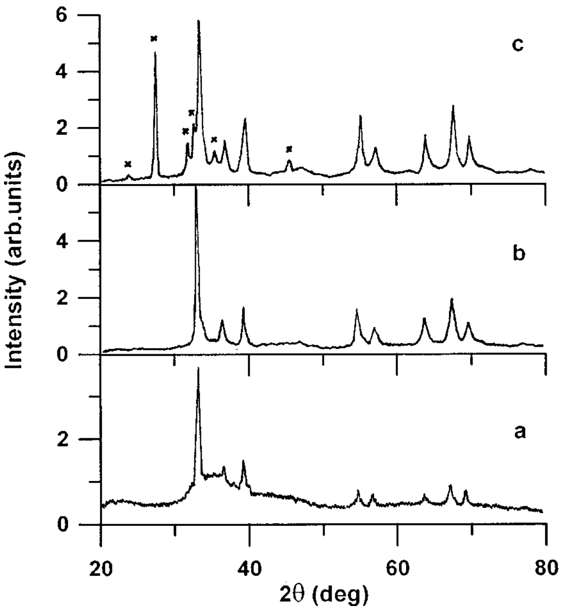

FIG. 1. The x-ray patterns at (a) 250, (b) 100, and (c) 10 K. Peaks, corresponding to the second solid gallium modification, are marked by asterisks in pattern *c*.

shown in Fig. 1. Peaks corresponding to the second structure are marked by asterisks in Fig. 1(c). Both observed modifications of confined gallium do not coincide with any of known bulk gallium structures.[34,35]

The width of different peaks in the x-ray patterns at various temperatures was practically independent of the diffraction angle and was significantly greater than the instrumental broadening. This shows that effects of strains within confined gallium are unimportant.[36] Hence, we can calculate the average size of metallic crystallites within pores from the peak broadening using the Scherrer equation:[36]

$$B(2\theta)=0.94\lambda/(d\cos\theta), \tag{1}$$

where B is the half-maximum intensity width of powder pattern peaks, θ is the diffraction angle, λ is the wavelength of x-ray radiation, and d is the particle size. Taking into account corrections for instrumental broadening, the average size of confined gallium particles can be estimated as 22 nm. Within the limits of experimental accuracy (of about 15%) the x-ray peak broadening was independent of temperature. Only a slight tendency to the peak narrowing within 15% was observed at decreasing temperature (and the corresponding broadening at increasing temperature). This means that changes in gallium particle sizes during warming and cooling the sample, including the ranges of freezing and melting, were very small. This conclusion is significant for treating the melting and freezing within porous matrices.

The obtained size of confined particles is more than five times larger than the pore diameter. For nonwetting materials this result was not necessarily expected. In fact, the particle size for confined mercury was found in Ref. 22 to be equal to the pore diameter (7 nm), while for indium in Vycor glasses it was equal to about 35 nm, which is much greater than the pore size.[2,32] Note that similar differences in pore diameters and particle sizes were obtained for wetting liquids such as O_2 and D_2 (40–70 nm) (Ref. 37) and CO_2 (16 nm) (Ref. 31) in Vycor glasses. The large confined gallium particle size implies that the front of crystallization spreads at least over several adjacent pores upon freezing.

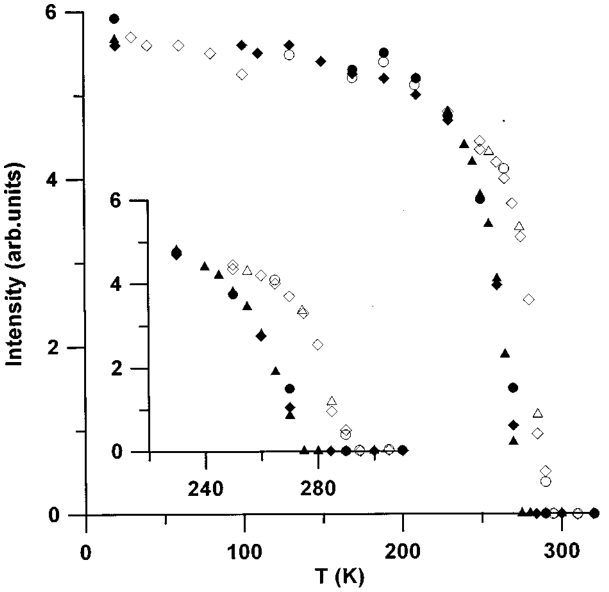

FIG. 2. The temperature dependence of the relative intensity of the x-ray-diffraction peak at $2\theta\cong 33°$. Solid symbols, cooling; open symbols, warming. Circles, triangles, and diamonds mark data obtained during three consecutive temperature cycles. The inset shows the scaled hysteresis.

The most intense powder pattern peak belonging to the first structure was seen near $2\theta=33°$. We used the total intensity of this peak to plot the relative amount of the first solid gallium modification as a function of temperature above 20 K. The dependence obtained for three temperature cycles as described above is shown in Fig. 2. It should be noted that during warming and cooling the relative intensities of different peaks in the x-ray patterns belonging to the first structure of solid gallium changed slightly. One can see by comparing the patterns at various temperatures that these changes are approximately described by the Debye temperature factor that expresses an exponential decrease in peak intensity with increasing $\sin^2\theta$.[36] It is easy to show that corrections for the Debye factor for low diffraction angles ($\theta < 20°$) in the present case do not exceed 20%. In the narrower temperature ranges, corresponding to the gallium melting and freezing phase transitions, the error in relative intensity cannot exceed 10%. Thus, the use of the visible intensity of the peak near $2\theta=33°$ as a measure of the frozen gallium amount is quite reasonable.

As can be seen in Fig. 2, the freezing and melting processes within the first gallium modification are shifted to low temperatures compared to the bulk gallium melting point (303 K). However, the results obtained have shown that any direct relations between the pore size and reduction of temperatures of the phase transitions cannot exist since the confined gallium modification differs from the bulk one.

In Fig. 2 one can also see that the freezing is strongly broadened and there is pronounced hysteresis between the freezing and melting processes, the width of the hysteresis loop is about 20 K. Hysteresis between freezing and melting was found earlier for all materials confined within porous glasses. However, the freezing can be sharp or smeared depending on particular materials and pore configuration. For instance, the freezing of gallium was steplike according to acoustic and NMR measurements within a sample of porous glass with the same average pore size.[19,20] Explanations of the different character of freezing and of its shift-relative melting remain controversial (see, for example, Refs. 10, 17, and 23). The results obtained in the present paper show that the broadening of freezing is not related to alterations in sizes of metallic crystallites. This contradicts the model of geometric freezing. The broadening and hysteresis could be explained by independent crystallization of supercooled confined liquids in different parts of the sample. It was not clear, however, why the freezing was rather reproducible and did not depend on the cooling rate. We suppose that reasons for such behavior are as follows. It is known that the temperature dependence of the homogeneous nucleation rate for bulk materials is very steep, especially for metals.[38,39] Then, really, the homogeneous crystallization occurs at quite definite temperatures well below the bulk melting point.[38] This could explain the reproducible freezing for materials within porous glasses. On the other hand, under the conditions of confined geometries, the heterogeneously catalyzed crystallization can play the main role. In fact, the heterogeneous crystallization was suggested in Ref. 23 for In within a Vycor glass. The heterogeneous crystallization can be induced by the inner surface of porous glasses or by small oxide crystallites. The temperature dependence of the heterogeneous crystallization rate is also very steep.[38,39] Besides, the heterogeneous crystallization within porous glasses can be limited by some additional factors, including size and geometric factors. In particular, sizes of heteronuclei should exceed the critical nucleus size.[38] All this yields restrictions for heterogeneous nucleation until some temperatures and explains the hysteresis between melting and freezing. This also can lead to some indirect relations of pore sizes with temperatures of freezing.

Since the size of confined gallium crystallites was about constant during melting, the broadening of the melting process cannot rise due to particle-size distribution as has been assumed in most papers devoted to the melting and freezing phase transitions in porous matrices. The broadening cannot be related directly with the pore size distribution either, since the gallium crystallites are much larger than the pores. Thus, we have to suggest another mechanism of the melting broadening. For separated spherical metallic nanoparticles it was shown experimentally that the melting broadening arises because of formation of a liquid skin around solid cores.[40] Similarly, formation of a liquid skin can lead to the broadening of the confined gallium melting. In the case of confined gallium, the complex shape of crystallites that occupy several adjacent pores should lead to some ‘‘island’’ formation of the liquid skin; the effective size of crystallites obtained by x-ray diffraction remains near unchanged. Since the lowering of the melting temperature as well as formation of the liquid skin for small particles depend on the surface-to-volume ratio,[41–44] there should exist an indirect relation of the melting broadening with pore sizes and their distribution.

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