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X-ray and resistance studies of the melting and freezing phase transitions for gallium in an opal

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Abstract. The melting and freezing processes and the structure of gallium in an opal were studied using x-ray powder diffraction within the temperature range 10 to 320 K. Four different modifications of solid confined gallium were found. Two of these modifications did not coincide with any known gallium structures; another two coincided with β -Ga and disordered α -Ga. The broadening of the total melting and freezing processes and reduction of the phase transition temperatures compared to bulk α -Ga phase were obtained. The size of confined gallium crystallites corresponding to the different modifications was estimated for cooling and warming. The reproducible freezing was treated as a result of the steep temperature dependence of the nucleation rate in supercooled melts. Additional measurements of resistance for the opal filled with gallium revealed that it was sensitive mainly to the melting and freezing within the gallium modification coinciding with disordered α -Ga. Melting–freezing hysteresis for this modification was found to depend on temperatures of pre-warming. It was suggested that the freezing of this modification is driven by the amount of frozen crystallites of the phase with the highest onset of freezing. The melting broadening and the lowering of the phase transition temperatures for the confined gallium modifications were discussed.

1. Introduction

Porous matrices with pore sizes under several hundred nanometres, including porous glasses and artificial opals, are promising materials for various applications. The structure of materials embedded into porous matrices and different processes within them are objects of continuing interest. Especially, phase transitions in materials confined within porous glasses have been studied intensively (see, for example, recent references [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 within porous glasses have been observed for materials such as water [13, 14], organic liquids [15–18], metals with low melting point [11, 19–22], helium [23–27], oxygen and some other simple liquids [10, 28, 29]. The melting and freezing within opals have not been so studied. The only work which is known to us [30] is devoted to NMR studies of gallium. Different experimental techniques were used in investigations of melting and freezing in confined materials. Some methods can provide only indirect information on the melting and freezing processes. For those methods, the phase transitions are registered upon alterations which they produce in properties of the sample, for instance, in ultrasound velocity or resistance. Nevertheless, the indirect methods make it possible

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to study special phenomena such as reversible and irreversible behaviour, percolation and relaxation. Other techniques, such as NMR, x-ray diffraction or neutron scattering, can give immediate information on the amount of liquid and frozen fractions. The x-ray powder diffraction technique seems to be very suitable for studying the melting and freezing phase transitions in porous media since it also shows the structure of confined materials and the size of nanoparticles formed within pores during cooling. However, until now x-ray diffraction measurements have been used only to determine the structure of frozen materials [2, 31, 32] and not to study the melting and freezing processes. Combining the x-ray diffraction with some other indirect methods seems to be also fruitful for further studies of the melting and freezing phase transitions and for comparing results obtained using different experimental techniques.

In the present paper we report results of x-ray diffraction and resistance studies of gallium inside an opal within the temperature range 10 to 320 K. Previous NMR measurements of liquid gallium embedded into an opal [30] showed that the melting and freezing of confined gallium were shifted to low temperatures compared to the bulk melting point with temperature hysteresis between melting and freezing. The NMR revealed also two well separated hysteresis loops in the liquid gallium amount during cooling and warming, strong asymmetry between freezing and melting and anomalies in structure of liquid gallium. After the first study of melting and freezing within opals reported in [30], a number of problems remained unclear. Some problems are general for any materials in confined geometries. The main ones are: the nature of thermal hysteresis between solidification and melting, the reasons for sharp or smeared melting and freezing and for their broadening and the origin of clear asymmetry between melting and freezing experimentally observed for many confined materials. In spite of the vast literature devoted to the melting and freezing phase transitions within porous glasses, the interpretation of these problems is controversial. Here again x-ray powder diffraction seems to be very useful since it allows us to examine alterations in sizes of confined solid particles during cooling and warming. In addition to the general problems, there are some particular problems for gallium within opals which remain unsolved. Namely, it is not clear whether the peculiarities in opals filled with gallium upon cooling and warming occur because of inhomogeneous freezing and melting within one crystalline structure or due to formation of two or more different solid gallium structures. The latter seems to be probable since bulk gallium is known to form various crystalline modifications under special conditions [33].

2. Sample and experiment

The opal sample under study consists of silica spheres with diameter near 250 nm. The silica spheres form a face-centred 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 opal under high pressure up to 9 kbar at about 35 °C. The filling of the total void volume was near 85%.

The x-ray diffraction measurements were performed using commercial powder diffraction equipment with Cu $K\alpha$ radiation and an 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 the α -modification of bulk gallium (303 K). Then it was slowly cooled down with a cooling rate less than 0.2 K min⁻¹ 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 change of temperature between measurements. Temperature overshoots

during cooling and warming were less than 1 K. At several temperatures we recorded the x-ray diffraction patterns within a large angle range 20 to 80 degrees with the scan speed of $0.5^\circ \text{ min}^{-1}$. 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 for angles from 28 to 35 degrees using the same scan speed.

Electrical resistance was measured using a four-probe method with a small current of 0.5 mA. The full temperature cycles of cooling and warming within the range 320 to 10 K were performed as described above for the x-ray diffraction measurements. Resistance was recorded during continuous slow cooling and warming. In addition, partial temperature cycling was used for studying reversible and irreversible behaviour under the conditions of incomplete phase transitions as described in section 3.2.

3. Results

3.1. X-ray diffraction

During cooling of the sample from 320 K, four different phases of solid gallium appeared consecutively. The x-ray patterns obtained upon cooling at 270, 240, 100 and 15 K are shown in figure 1. The phase denoted as 1 could be seen below 300 K; the phases denoted as 2 and 3 were seen below 255 and 210 K, respectively. These three gallium modifications were formed as a result of freezing of melted gallium since the broad x-ray peak belonging to liquid gallium was seen until 175 K. The phase denoted as 4 was seen only below 40 K and probably occurred due to some structural phase transition in solid gallium. The x-ray patterns of phases 1 and 4 do not coincide with those of any known gallium structures [34]. The peaks belonging to phase 2 coincide with slightly shifted peaks of α -Ga [34]. However, their relative intensities are quite different. It is known [36] that relative intensities in the x-ray patterns can be changed by structural disordering. Thus, we can suggest that the phase 2 of confined gallium is a disordered α -phase of bulk gallium with slightly modified lattice parameters. The x-ray peaks belonging to phase 3 coincide with those of β -Ga which normally occurs in supercooled liquid gallium [33]. Their intensities are also agreed with the β -Ga pattern [34]. This shows that the phase 3 is the rather ordered β -Ga structure. It should be noted that phase 1 and disordered α -modification were also found in a porous glass filled with gallium [4].

The relative intensities of different peaks in the x-ray patterns belonging to the particular solid gallium phases changed slightly during warming and cooling. The changes are approximately described by the Debye temperature factor which expresses an exponential decrease in peak intensity with increasing $\sin^2 \theta$ [35]. However, corrections for the Debye factor for low diffraction angles ($\theta < 20^\circ$) in the present case did not exceed 20%. Then we used the total intensities of some peaks observed at small angles to plot the relative amount of the phases 1 to 3 versus temperature. The most intensive peak at about $2\theta = 33^\circ$ was taken to estimate the amount of phase 1. For phase 2 we took the double peak near $2\theta = 30.5^\circ$, and for phase 3 the peak near $2\theta = 34.2^\circ$. The dependences obtained for a temperature cycle as described above in section 2 are shown in figure 2. The temperature dependence of the intensity of the broad peak corresponding to liquid gallium is also shown in figure 2.

The width of different peaks in the x-ray patterns at various temperatures did not depend practically on the diffraction angle. This shows that effects of strains within confined gallium are unimportant [35]. The width of peaks belonging to phase 1 was greater than the instrumental broadening (0.176°). Hence, one can evaluate the average size of metallic

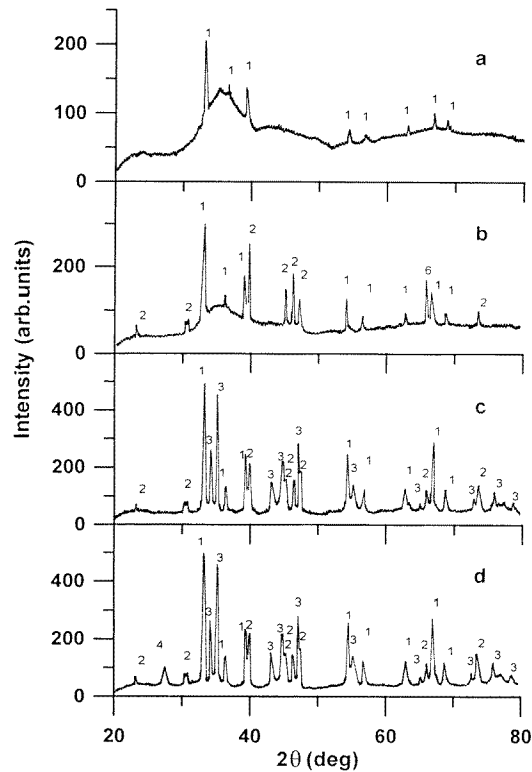


Figure 1. The x-ray patterns of gallium confined within the opal at 270 (a), 240 (b), 100 (c) and 15 (d) K. Peaks corresponding to the various solid gallium modifications are marked by corresponding numbers.

crystallites of phase 1 within pores from the peak broadening using the well known Scherrer equation [35]. After taking into account corrections for instrumental broadening, the average size of confined gallium particles of the phase 1 can be estimated as 120 nm on cooling within the temperature range 290 to 265 K. The number of large crystallites of phase 1 in this temperature range is very small as can be seen from figure 2(a). Below 265 K the average size of crystallites decreases and becomes constant and equal to about 25–30 nm from 250 K when the most of phase 1 starts freezing. Upon warming, the average size of the gallium crystallites of phase 1 did not change within the limits of experimental accuracy (about 15%) and remained equal to about 25–30 nm until complete melting. Peaks belonging to phase 2 were very narrow; their width was due to instrumental broadening. This makes it possible to estimate only the lower limit of the average size as 140 nm. The size of gallium crystallites of phase 3 was independent of the temperature and can be estimated as 30 nm. The size of crystallites of phase 4 was smaller and equal to about 15 nm.

Results obtained during a second full temperature cycle roughly reproduced those for the first cycle. However, when warming was stopped at 294 K and cooling was started again, the temperature dependence of the amount of the frozen phase 1 almost reproduced measurements during previous warming. In addition, some phase 2 appeared even at 285 K; this phase was more disordered than after cooling from 320 K.

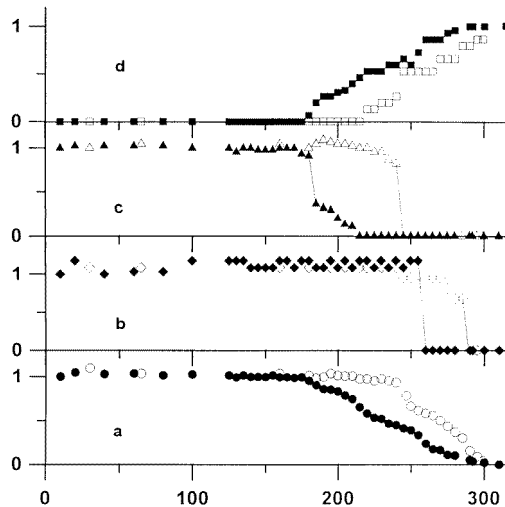


Figure 2. The temperature dependences of the relative intensity of x-ray diffraction for the first (a), second (b) and third (c) solid gallium modifications and for liquid gallium (d). Solid symbols—cooling, open symbols—warming. Solid lines provide a guide for the eye.

3.2. Resistance

The temperature dependence of resistance during a temperature cycle, as described for the x-ray measurements, is shown in figure 3. Only slight changes in resistance can be seen during cooling until 265 K. Then the resistance drops down in a steplike manner at about 265 K and decreases smoothly when cooling to low temperatures. Results obtained on warming reproduce those obtained on cooling below the step. However, on warming the resistance starts increasing only near 285 K forming a hysteresis loop. The curves corresponding to cooling and warming are about merged above 295 K.

To study reversible and irreversible behaviour of confined gallium during freezing and melting, we performed measurements of resistance during partial temperature cycles. Some of the results are presented in figures 4 and 5. The data obtained show that hysteretic behaviour depends strongly on the temperature up to which the sample was warmed before measurements. When the sample was pre-warmed above 310 K and then cooled down, the temperature dependence of resistance roughly reproduced that shown in figure 3 (figure 4, circles). When the sample was pre-warmed up to temperatures between about 295 and 310 K, the freezing was steep but shifted to high temperatures. An example is shown in figure 4, diamonds. When the sample was warmed from low temperatures to temperatures near and below 295 K, the resistance behaviour upon consecutive cooling became rather reversible with smeared and very narrow hysteresis loops (figure 4, squares, and figure 5).

4. Discussion

As can be seen in figure 2, the freezing and melting processes within the solid gallium modifications 1 to 3 are shifted to low temperatures compared to the bulk α -gallium melting point (303 K). However, the results obtained have shown that one cannot expect direct relations between the void sizes and reduction of temperatures of the phase transitions

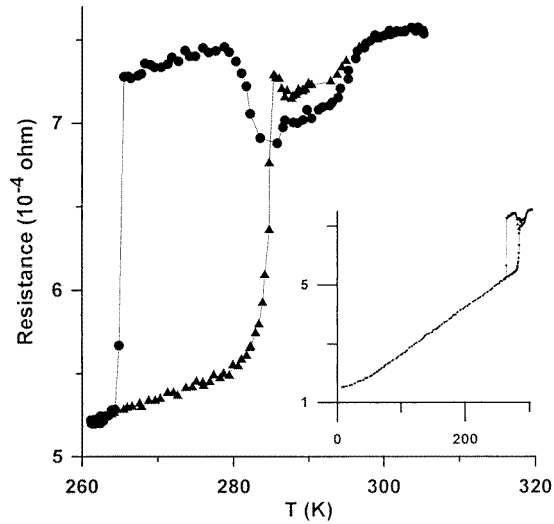


Figure 3. The temperature dependence of resistance between 260 and 305 K obtained during a full temperature cycle. The inset shows all results for this cycle. Closed circles correspond to cooling, closed triangles to consecutive warming. Solid lines provide a guide for the eye.

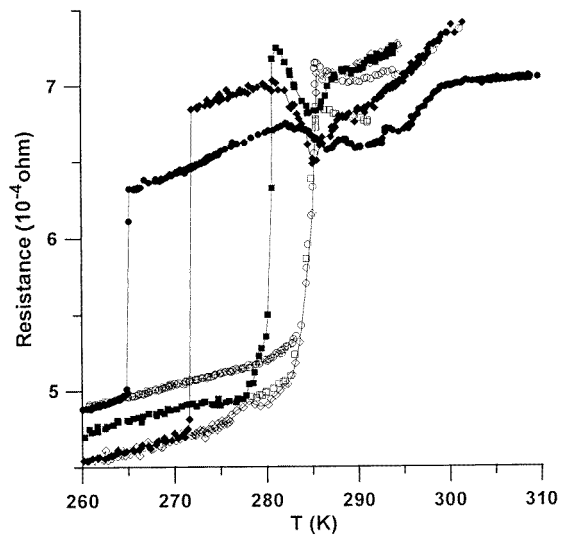


Figure 4. The temperature dependences of resistance obtained during three consecutive partial cooling-warming cycles. Circles correspond to the first cycle after pre-warming up to 320 K. Diamonds correspond to the second cycle after the sample was warmed to 301.6 K during the first cycle. Squares correspond to the third cycle after the sample was warmed to 294.6 K during the second cycle. Closed symbols—cooling, open symbols—warming. Solid lines provide a guide for the eye.

for phase 1 since it differs from the bulk α -Ga phase. Nevertheless, it is interesting that this phase completely melts near the α -Ga melting point. Phase 2 is strongly disordered compared to the bulk α -phase. Thus, the lowering of its melting temperatures may arise not

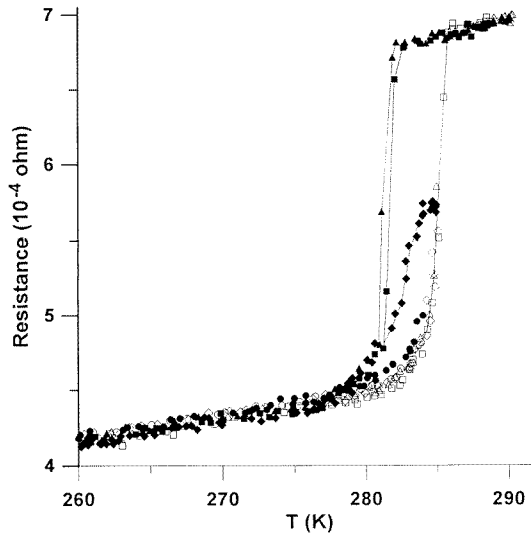


Figure 5. The temperature dependences of resistance obtained during four consecutive partial warming–cooling cycles. Before the measurements, the sample was warmed up to 320 K and cooled down to 260 K. Circles, diamonds, squares and triangles correspond to the first, second, third and fourth cycle with warming to 283.9, 285, 288.6 and 290.3 K, respectively. Closed symbols—cooling, open symbols—warming. Solid lines provide a guide for the eye.

due to size effects but due to influence of disordering. In contrast, the melting temperature reduction to about 235 K for phase 3 (figure 2(c)) compared to the bulk melting point of β -Ga (256.5 K) can be treated as a result of size effects, namely of a large surface to volume ratio [36,37]. Since the melting of phase 3 is rather steep and the average size of confined crystallites is smaller than the void sizes, one could apply the Gibbs–Thompson equation for rough interpretation of the melting temperature depression assuming the spherical form of the crystallites [37]:

$$\Delta T_m = 4\gamma v_0 T_m / Ld = K/d \quad (1)$$

where d is the crystallite diameter, γ is the surface tension of the solid, L is the latent heat of fusion, T_m is the bulk melting temperature and v_0 is the molar volume of the solid. It follows from our measurements that $K \cong 600$ K nm for β -Ga.

In figure 2 one can also see pronounced hysteresis between the freezing and melting processes. Hysteresis between freezing and melting was found earlier for all materials confined within porous glasses. Explanations of its origin are controversial [10, 11, 17, 23]. The most obvious explanation is that the hysteresis arises due to supercooling of the liquids in pores. It was not clear, however, why the freezing was rather reproducible and did not depend on the cooling rate. Because of reproducible freezing, the geometric freezing model was developed by several authors (see [10] and the references therein) where the freezing was considered similarly to different structural phase transitions. Within the framework of that model, the broadening of freezing and melting is caused by wide distribution of confined crystallite sizes; the hysteresis is due to some geometric factors. In agreement with our results, we suppose that the hysteresis arises because of supercooling; the reasons for reproducible freezing in porous matrices are as follows. It is known that the temperature dependence of the homogeneous nucleation rate is very steep, especially for metals [38, 39].

Then, really, homogeneous crystallization occurs at quite definite temperatures well below the bulk melting point [38]. This could explain the reproducible freezing for materials within porous matrices. In addition, under the conditions of confined geometries, heterogeneously catalysed crystallization can play the main role. Actually, heterogeneous crystallization was suggested in [23] for In within a Vycor glass. Heterogeneous crystallization can be induced by the inner surface of porous matrices, by small oxide crystallites or, for the sample under study, by crystallites of other phases. However, the temperature dependence of the heterogeneous crystallization rate is also very steep [38, 39]. Besides, the heterogeneous crystallization within porous matrices 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 to certain temperatures and explains the hysteresis between melting and freezing. Both the models of independent homogeneous and heterogeneous crystallization within different ranges of the sample can be applied to explain the hysteretic behaviour and the freezing broadening for phase 1. For phases 2 and 3, which solidify well below phase 1 starts freezing, the heterogeneous crystallization induced by crystallites of the phase 1 seems to be more probable.

Since the size of confined gallium crystallites of phase 1 was about constant during melting, the broadening of the melting process for this phase cannot rise due to particle size distribution. For separated spherical metallic nanoparticles it was shown experimentally [40] that the melting broadening arises because of formation of a liquid skin around solid cores which was predicted theoretically (see, for example, [41, 42] and references therein). Similarly, formation of a liquid skin can lead to the broadening of the confined gallium melting. Note, that existing of a liquid skin on the surface of mercury confined in a porous glass was recently suggested in [43] on the base of acoustic and NMR measurements. In the case of confined gallium, the complex shape of crystallites should lead to some 'island' formation of the liquid skin; the effective size of crystallites obtained by x-ray diffraction remains nearly unchanged. The melting within phases 2 and 3 is abrupt. Hence, there is no direct sign of existence of a liquid skin. For phase 2 this might be related to large sizes of confined crystallites. One can also speculate that the melting as well as the freezing within phases 2 and 3 is strongly influenced by the phase transformations within phase 1.

Comparing the changes in resistance with those in the x-ray diffraction patterns (figure 2), one can conclude that resistance was sensitive mainly to freezing and melting within phase 2. The phase transitions within phase 1 probably give rise to small alterations in resistance between 280 and 300 K. The freezing and melting within phase 3 do not manifest themselves in the resistance measurements. This makes it possible to suggest that percolation phenomena within a gallium network in the opal are dominated by phase 2. However, the relatively high sensitivity of resistance to the structural transformations within phase 2 is not related to the largest amount of solid gallium in this modification as can be seen from the temperature dependence of the intensity of the x-ray peak belonging to liquid gallium (figure 2(d)). Then, the studies performed show that data on melting and freezing within porous matrices obtained using indirect methods such as resistance or acoustic measurements should be treated very carefully, especially when confined materials can form various modifications.

On the basis of measurements depicted in figures 4 and 5 we can suggest that the freezing of phase 2 depends on the amount of frozen gallium in phase 1 and is driven by heterogeneous crystallization. After pre-warming above 310 K where total gallium is completely melted, the amount of phase 1 upon cooling is smaller than after pre-warming up to lower temperatures and corresponds to figure 2(a). This correlates with the lowest and

reproducible temperature of supercooling within phase 2 under these conditions (figures 3 and 4). When the sample is pre-warmed below 295 K (figure 5), the heterogeneous crystallization can be induced by crystallites of phase 1 as well as of phase 2. This explains why the hysteresis loops in figure 5 are narrow. After pre-warming up to intermediate temperatures between 310 and 295 K, the temperature of freezing in phase 2 elevates gradually because of the greater amount of phase 1 formed during cooling.

In conclusion, the melting and freezing and the structure of gallium in an opal were studied for the first time using x-ray powder diffraction and resistance measurements. Four different solid modifications of confined gallium were found. Three modifications appeared during freezing of liquid gallium. Two of them coincided with disordered α -Ga and with β -Ga. The fourth modification was observed only below 40 K and occurred as a result of phase transformations within solid gallium. The sizes of the most of crystallites for phase 1 were estimated as 25–30 nm, of crystallites for phase 3 as 30 nm and for the low-temperature phase 4 as 15 nm, while for phase 2 only the lower limit was found equal to 140 nm. The size of crystallites of phase 1 was nearly constant during cooling below 250 K and during warming, while both the freezing and melting transitions were strongly smeared. The reproducible freezing and the hysteresis between melting and freezing were treated as a result of the steep temperature dependence of the nucleation rate in supercooled melts. The melting broadening was suggested to be caused by formation of a liquid skin. The coefficient in the Gibbs–Thompson equation for confined β -gallium modification was calculated. The phase transitions within phase 2 and 3 were found to be driven by crystallites of phase 1. The resistance of opal filled with gallium was found to be most sensitive to the melting and freezing within the second gallium modification coinciding with disordered α -Ga.

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