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Nuclear magnetic resonance, resistance and acoustic studies of the melting–freezing phase transition of gallium in Vycor glass

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Abstract. The melting–freezing phase transition of gallium confined within Vycor glass was studied by NMR, resistance and acoustic techniques. A single although broadened ^{71}Ga NMR line corresponding to melted gallium was observed in contrast to lineshapes found until now for liquid gallium in porous matrices. A difference between results obtained using the three methods was explained by formation of various confined solid gallium modifications. A depression of the freezing and melting phase transition temperatures and a pronounced hysteresis in the melting–freezing processes were found and are discussed. Heterogeneous nucleation was suggested to explain the dependence of crystallization on temperatures of pre-warming. Irreversible melting was observed for the second gallium modification.

1. Introduction

Phase transitions in low-dimensional systems are of continuing interest. Their investigation gives information which is valuable for deeper understanding the physics of phase transitions as well as for various technical applications. In particular, the superconducting phase transition and the melting–freezing processes in isolated metallic nanoparticles have been studied intensively ([1–10] and references therein). Another way of producing small metallic particles is to use porous glasses and other porous matrices with pore sizes in the range of several nanometres which are filled under pressure with low-melting metals. In this case, the ensemble of particles forms a partly interconnected network within porous matrices. The superconductivity of metals in confined geometry has been studied in a number of works ([11–16] and references therein). Melting and freezing of metals in porous matrices have been relatively seldom studied in contrast to melting and freezing of wetting nonorganic and organic liquids [17–29]. The common features of melting and freezing of confined metals are shifts of the phase transitions to low temperatures compared to the melting points for bulk metals and hysteresis between the melting and freezing processes [30–38]. However, the relation of the temperature shifts to pore sizes and geometry and the reasons for sharp or smeared melting and freezing observed for different samples as well as for the hysteresis and the role of nucleation processes are not yet clear. The interpretation of the experimental data is even more complicated since various experimental techniques sometimes lead to different results [32, 36, 37].

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In the present paper we report results of NMR, resistance and acoustic studies of the melting–freezing phase transitions for gallium embedded in Vycor glass. So far, melting and freezing of confined gallium have been studied for a porous glass with 200 nm pore sizes using NMR and acoustic techniques [32], for porous glasses with pore sizes of 4 nm using NMR [31], x-ray [38] and acoustic techniques [30] and for opals using x-ray and resistance methods [37] and NMR spectroscopy [33]. The results obtained depended strongly on pore sizes as well as on experimental methods used. In particular, solid gallium in porous matrices with nanometre pore sizes was found to occur in various crystalline modifications which generally differ from the known bulk gallium modifications [37–39]. Thus, it is of great interest to study the melting and freezing phase transitions of gallium for another confined geometry using a number of experimental techniques. We should emphasize that NMR is especially useful for such studies since it can provide direct data on the amount of gallium in the liquid state while resistance and acoustic measurements are convenient for revealing the reversible and irreversible behaviour upon cooling and warming.

2. Experiment

The sample of Vycor glass under study was supplied by Corning Glass Company. The total pore volume was 28% as measured by Corning Glass Company. According to our mercury intrusion porosimetry results, the average pore size was about 6 nm. The liquid gallium was introduced into the glass under pressure up to 9 kbar. The filling factor of the pore volume was about 85%.

NMR measurements were run using a pulse Bruker MSL 500 NMR spectrometer (resonance frequency of 152.48 MHz for ^{71}Ga). The temperature dependence of the ^{71}Ga NMR line from liquid gallium was studied in the temperature range 180 to 320 K covering the bulk gallium melting point (303 K). First, the sample under study was warmed up to 320 K to ensure that the total quantity of gallium in the pores was in the liquid state [30–33]. Then, the sample was cooled down to 180 K and warmed up again to room temperature. Similar temperature cycles were repeated several times. The rate of warming and cooling was very slow to prevent temperature overshoots, which did not exceed 0.2 K in our measurements. Prior to each measurement, the sample was kept at a fixed temperature for about 5 minutes. The accuracy of temperature control was better than 0.2 K. To detect the NMR signal, a single pulse sequence with phase cycling was applied with a pulse duration of 2.6 μs. The repetition time was 0.2 s. The intensity of the NMR signal was measured relative to the NMR signal from GaAs powder which was placed in the same tube. Note that the signal from solid confined gallium was not detected.

Acoustic measurements were performed using the conventional pulse acoustic technique at the frequency of 4 MHz [40], which gave the relative longitudinal sound velocity value

$$\Delta v/v = [v(T) - v(T = 295\ \mathrm{K})]/v(T = 295\ \mathrm{K})$$

with an accuracy better than 10^{-5} and the relative attenuation coefficient $\Delta\alpha$ with an accuracy within 5%. Repeated cycles of slow cooling and warming similar to those used in the NMR studies were carried out. Prior to each measurement, the sample was kept at a fixed temperature for about 10–15 min.

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 150 K were performed as described above for the NMR measurements. The resistance was recorded during continuous slow cooling and warming. The samples for resistance and acoustic studies were cut from the same bulk specimen as the sample used for NMR.

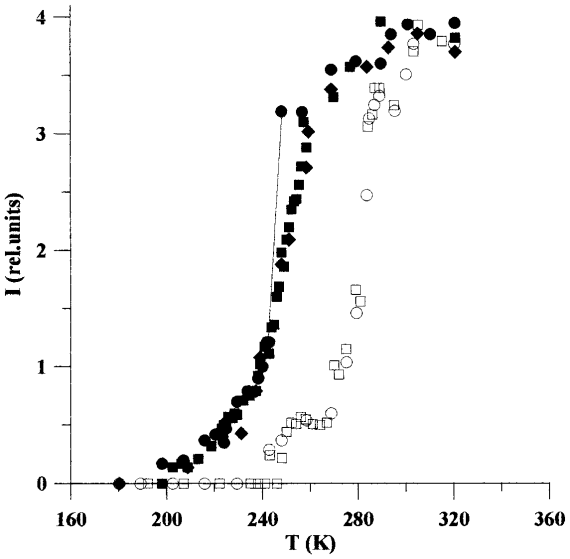

Figure 1. Intensity I of the ^{71}Ga NMR signal against temperature on cooling (solid symbols) and on warming (open symbols). Circles—cooling down from 320 K, diamonds and squares—cooling down from 300 K. The straight line provides a guide for the eye.

In addition, partial temperature cycling was performed during acoustic and electric measurements for studying reversible and irreversible behaviour under the conditions of incomplete phase transitions as described in section 3. Temperature cycling under the conditions of warming the samples up to temperatures below 320 K was also used in the NMR measurements.

3. Results

The NMR spectrum belonging to liquid confined gallium for the sample under study consisted of a single line in contrast to more complex spectra obtained for liquid gallium within an opal [33] and porous glasses with fine and coarse pores [31, 32]. This line was strongly broadened compared to that for bulk liquid gallium; its Knight shift at room temperature was smaller (by 140 ppm) than that in bulk gallium. Figure 1 shows the temperature dependence of the relative (integral) intensity of the NMR line which was measured for a full temperature cycle as already described. As seen from figure 1, the amount of liquid gallium remains nearly constant upon cooling from 320 K down to about 290 K. Then the amount of liquid gallium slightly decreases between 290 and about 245 K where it exhibits a sharp reduction, again reduces monotonically below 243 K and vanishes at about 195 K. Upon warming a pronounced hysteresis in the liquid amount of gallium can be observed; melting starts not before 245 K. When cooling was started after warming up to temperatures below 305 K, the freezing process was noticeably more smeared (figure 1).

The results of acoustic studies for one of the full temperature cycles are presented in figures 2 and 3. As one can see from figure 2, the ultrasound velocity changes strongly at 247 K upon cooling. Below this temperature, a smooth and monotonic, but not linear, increase in velocity occurs down to about 190 K. Below about 190 K, the velocity becomes again nearly constant. When warming, the nonlinear decrease in velocity becomes noticeable above

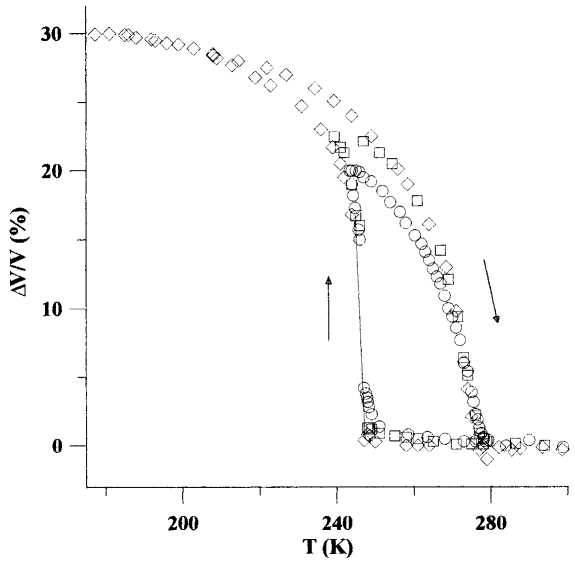

Figure 2. Longitudinal ultrasound velocity $\Delta v/v$ against temperature on cooling and warming. Arrows indicate the direction of changing temperature. Diamonds—cooling down from 320 to 175 K and warming up to 320 K; squares—cooling down to 239.5 K and warming up to 285 K; circles—cooling down to 243.5 K and warming up to 320 K. The straight line provides a guide for the eye.

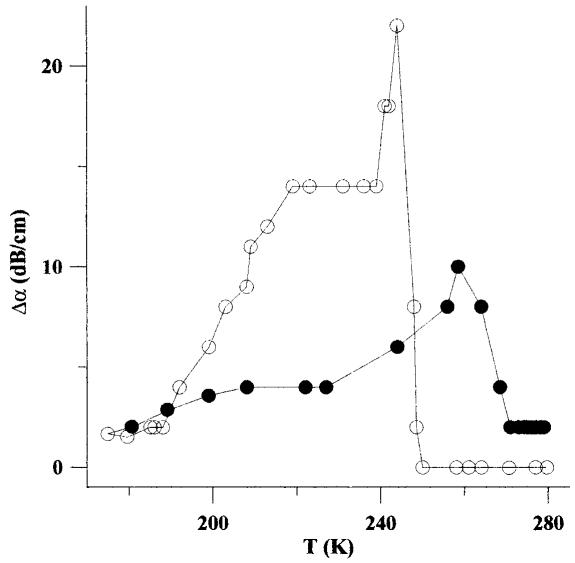

Figure 3. Longitudinal ultrasound attenuation coefficient $\Delta\alpha$ versus temperature for the same full cycle as shown in figure 2 by diamonds. Solid lines provide a guide for the eye. Open symbols correspond to cooling, solid symbols to warming.

200 K and the curves obtained upon cooling and warming merge together at 278 K exhibiting a large hysteresis loop between freezing and melting. A similar hysteresis was observed for ultrasound attenuation (figure 3). The behaviour of the acoustical features, similar to that

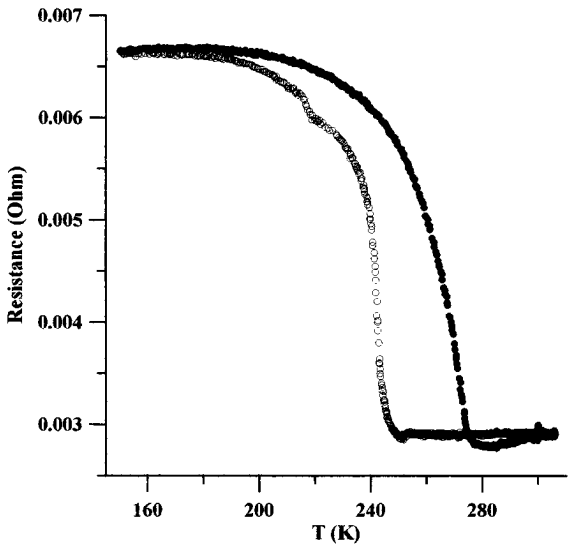

Figure 4. The temperature dependence of resistance obtained during a full temperature cycle. Open circles—cooling, solid circles—warming.

shown in figures 2 and 3, was quite reproducible for all other full consecutive temperature cycles: the temperatures of freezing could change within 2 K and the temperatures of melting were stable within experimental accuracy. When the sample under study was cooled down to some temperatures between 245 and 200 K which corresponded to incomplete freezing and then warmed up, the melting branches of hysteresis loops for such partial cycles firstly ran below the melting branch for the full cycle and then merged with it at higher temperatures. Some examples are shown in figure 2. When the sample was pre-warmed up to temperatures between about 305 and 280 K and then cooled down, the steep change in velocity at freezing was only slightly smeared (figure 2) in contrast to shifts of freezing to higher temperatures observed for an opal sample filled with gallium [37].

The temperature dependence of the resistance during a full temperature cycle is shown in figure 4. The hysteresis loop for the resistance is quite similar to that found by acoustic techniques. Results obtained for partial temperature cycles are shown in figures 5 and 6. In addition to cycles for incomplete freezing similar to those for acoustic measurements (figure 5), we performed partial cycling for incomplete melting (figure 6). In both cases the partial hysteresis loops were confined within the hysteresis loop for the full cooling–warming cycle; the temperatures of complete freezing or melting did not alter noticeably.

4. Discussion

The three experimental methods used showed that freezing and melting of gallium embedded in Vycor glass occur well below the melting point of the α-structure into which bulk gallium crystallizes at ambient conditions (303 K). However, while freezing starts at about 247 K according to the acoustic and resistance data, the decrease in intensity of NMR line begins at much higher temperatures (figures 1, 2 and 4). Since NMR provides direct information on the liquid gallium amount unlike indirect acoustic and resistance methods which detect changes in some properties during melting and freezing, we should conclude that the latter methods are

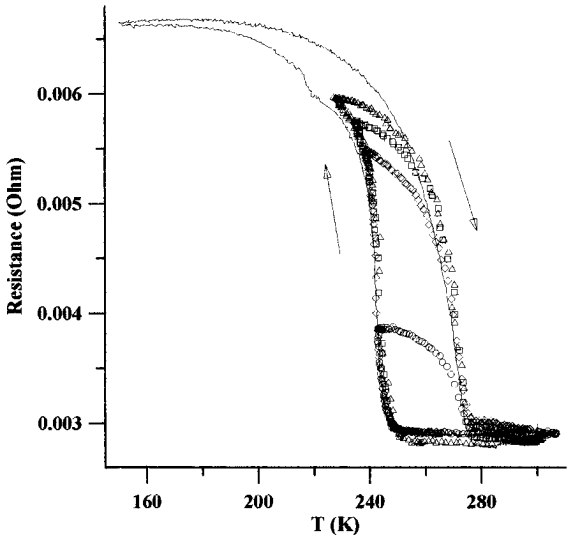

Figure 5. The temperature dependence of resistance obtained during four consecutive partial cooling–warming cycles. Circles, diamonds, squares and triangles correspond to cooling stopped at 242, 238, 235 and 226 K, respectively. Arrows indicate the direction of changing temperature. The solid line shows changes in resistance during the full temperature cycle from figure 4.

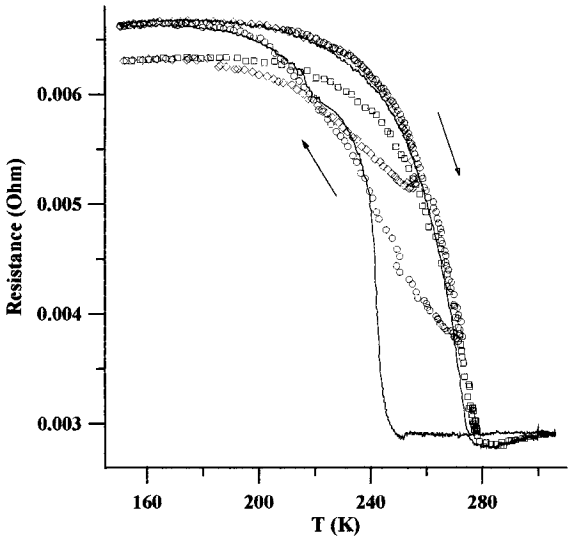

Figure 6. The temperature dependence of resistance obtained during consecutive partial warming–cooling cycles. Circles—warming up from 150 to 272 K and cooling down to 150 K; diamonds—warming up to 256 K and cooling down to 150 K; squares—warming up to 307 K. Arrows indicate the direction of changing temperature. The solid line shows changes in resistance during the full temperature cycle from figure 4.

not sensitive to freezing in the temperature range between about 290 and 247 K. These results can be explained if we take into account that confined gallium in porous matrices can freeze up into different structural modifications as shown in [37] and [39] by x-ray powder diffraction.

Thus, within the temperature ranges of about 290 to 247 K upon cooling and of about 280 to 300 K upon warming, gallium occurs in a modification which is not detected by acoustic and resistance techniques. According to [41], the modification which forms under the conditions of confined geometry at such temperatures differs from any known crystalline modifications of bulk gallium and has a tetragonal symmetry with lattice parameters 0.325 and 0.495 nm. As obtained in [37], resistance is rather insensitive to the formation of such a tetragonal phase. Below 247 K, another modification of confined gallium starts solidifying which is detected by resistance and acoustic techniques. The NMR data (figure 1) show that the relative amount of this second modification in the Vycor glass is much greater than the amount of the tetragonal modification. Using results of x-ray studies [37], we can suggest that the second modification coincides with a disordered α-phase of bulk gallium.

The reduction of melting temperatures in restricted geometry is normally treated as a result of thermodynamic size effects [3, 4, 42]. However, since the structure of the first tetragonal solid gallium modification in the sample under study is different from the α-structure of bulk gallium, one cannot expect direct relations between the pore sizes and lowering of its melting temperature compared to that for bulk gallium. The shift of the melting temperature for the second confined gallium modification compared to the melting point for the bulk α-phase can be influenced by structural disordering observed in [37]. Besides, the size of metallic nanoparticles within porous matrices can noticeably differ from pore diameters [35, 37, 38]. Nevertheless, if we neglect the role of disordering and take into account that the surface to volume ratio is mainly determined by surface curvature, that is by the pore size, we can apply the model developed for spherical small particles [4] to estimate roughly the melting temperature depression

$$\Delta T_m = 4\gamma v_0 T_m / Ld = K/d \tag{1}$$

where d is the pore 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 $\Delta T_m \cong 25$ K for the offset of melting and $K \cong 1500$ K nm for α-Ga.

The results shown in figures 1 to 4 reveal the pronounced hysteresis between the freezing and melting processes. Hysteresis between freezing and melting were found earlier for all materials confined within porous glasses, while freezing and melting could be sharp or smeared depending on the particular pore geometry. The treatment of its origin is controversial [17, 21, 22, 32]. The most obvious explanation is that the hysteresis arises due to supercooling the liquids in pores. This suggestion seemed, however, to be in contradiction with the reproducibility of temperatures of freezing and, in particular, with its independence of the cooling rate. Note, that because of reproducible freezing, the geometric freezing model was developed ([21] and references therein) where freezing was considered similarly to various structural phase transitions [43]. However, the geometric freezing model itself cannot explain the origin of the hysteretic thermal behaviour and, therefore, additional speculative assumptions are necessary. Thus, in spite of the reproducible character of freezing, one can 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 [44, 45], and in reality the homogeneous crystallization in bulk metals occurs at quite definite temperatures well below the bulk melting point [44]. This could explain the reproducible freezing for materials within porous matrices. In addition, under the conditions of confined geometry, heterogeneously catalysed crystallization can play the main role. Note, that in most experimental papers devoted to melting and freezing in porous matrices, heterogeneous crystallization was not considered likely due to strong depression of freezing compared to melting. Nevertheless, heterogeneous nucleation was suggested in [35] for metallic indium within Vycor glass to explain results of calorimetric

studies. 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 the other gallium modification. The temperature dependence of the heterogeneous crystallization rate is also very steep [44, 45] which leads to reproducible temperatures of freezing. Besides, heterogeneous crystallization within porous matrices can be limited by some additional factors, including size and geometric factors [44]. All this yields restrictions for heterogeneous nucleation until 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 for the first tetragonal modification. For the second modification which solidifies well below the temperature where the first one starts freezing, the heterogeneous crystallization induced by crystallites of the first modification seems to be most probable. It may be that the rather steep freezing of the second gallium modification during complete temperature cycling arises because of heterogeneous crystallization. In fact, freezing within a single crystalline modification for confined metals was found to occur in a smeared way [36, 38].

It follows from figures 2, 5 and 6 that both melting and freezing of the second confined gallium modification are irreversible. These results contradict the reversible behaviour of mercury in a porous glass during most of the temperature range of melting [36]. One can suppose that the melting phase transition of the second confined gallium modification is affected by the melting of the first modification while the melting of mercury was treated within the framework of the model of liquid skin on a solid core. It follows also from figure 6 that in spite of the irreversibility, the solidification starts immediately when cooling begins after incomplete melting. Note, that this agrees with the suggestion about heterogeneous crystallization. The same is valid for melting after incomplete freezing (figures 2 and 5). Nevertheless, the temperatures of complete freezing remain equal to those obtained for full temperature cycles in contrast to the noticeable narrowing of the hysteresis loops observed for gallium confined within an opal [37]. More studies are necessary to explain the different behaviour of metals within porous matrices during partial temperature cycling.

It should be also noted that slight increases in ultrasound velocity and resistance upon warming during temperature cycles started being noticeable at about 200 K while the NMR signal from liquid gallium appeared only at about 245 K. It is possible that the intensity of the NMR line is very low between 200 and 245 K because of the small amount of melted gallium and the NMR signals cannot be seen through noise. Thus, melting of the second modification of confined gallium seems to be more broadened than found by means of NMR and occurs in the temperature range of about 80 K.

In conclusion, NMR, acoustic and resistance measurements on gallium melting and freezing within Vycor glass were performed. They revealed different temperature ranges of melting and freezing. This was treated as a result of forming two crystalline modifications of confined gallium in agreement with x-ray data; the acoustic and resistance techniques were sensitive only to the modification which solidifies at lower temperatures. Thus, it was shown that indirect experimental methods such as acoustic or resistance can give incomplete information on melting and freezing when confined materials occur in several solid modifications. Freezing of the low-temperature modification was found to be affected by the presence of the first solid gallium modification; heterogeneous crystallization played an important role. Lowering of the melting temperatures for confined gallium was treated as a result of the great surface to volume ratio. The large hysteresis between freezing and melting was observed and treated as a result of supercooling under the specific conditions of confined geometry. Partial temperature cycling revealed irreversible behaviour upon cooling and warming which differed from that for gallium in other confined geometries.

Acknowledgments

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