Nuclear magnetic resonance and acoustic investigations of the melting - freezing phase transition of gallium in a porous glass

Nuclear magnetic resonance and acoustic investigations of the melting–freezing phase transition of gallium in a porous glass

B F Borisov†, E V Charnaya†, W D Hoffmann‡, D Michel‡, A V Shelyapin† and Yu A Kumzerov§

† Institute of Physics, St Petersburg State University, St Petersburg 198904, Russia
‡ Faculty of Physics and Geosciences, University of Leipzig, D-04103 Leipzig, Germany
§ A F Ioffe Physico-Technical Institute RAN, St Petersburg 194021, Russia

Abstract. The melting–freezing phase transition of gallium in a porous glass was studied by NMR and acoustical techniques. A depression of the freezing and melting phase transition temperatures and a pronounced hysteresis in the melting–freezing processes were found. An intricate ^{71}Ga NMR lineshape for liquid gallium was observed with a temperature coefficient of the Knight shift more than twice that measured for the bulk melt. The results are discussed on the basis of the Gibbs–Thompson equation and by means of a geometric freezing model.

1. Introduction

Porous glasses filled with different materials are the object of continuing interest [1]. Properties of materials in confined geometries differ significantly from those in bulk samples. They depend on many factors, such as pore size and geometry, interactions with the inner surface and between the particles in the pores themselves and wetting phenomena. Phase transitions, in particular, are strongly affected since they sensitively depend on the interference of short-range and long-range couplings. Hence, studying phase transitions in confined geometries the general problem arises of whether features of the embedded materials are chiefly determined by size effects for the particles in voids or by the common behaviour of the ensemble of particles which form a thoroughly interconnected network within the porous matrix.

So far, different phase transitions within pores of various geometries have been observed experimentally. Recently, the superfluid transition ([2–5] and references cited therein), the superconducting phase transition [6–8], the phase separation in liquids [9, 10] and references cited therein), phase transitions in liquid crystals [11, 12], the gas–liquid phase transition [13] and melting–freezing phase transition [13–22] have been intensively studied. It has been found that size and surface effects for isolated particles as well as the common behaviour can dominate. For example, a smearing out of the first-order nematic–isotropic phase transition in liquid crystals with decreasing pore dimensions [11] is evidently controlled by the pore geometry. However, some processes, such as the superconducting phase transition, remain well defined and occur in a narrow temperature range, thus revealing strong interconnections between the particles imbedded in the pores [7, 8].

In the present paper we report results of NMR and acoustical studies of melting–freezing phase transitions in gallium contained in porous glass. Although there are numerous experimental investigations of the melting–freezing phase transition in porous media, most of them have been performed for helium [4, 15, 20, 21], for some organic fluids [14, 17], for oxygen and for some other simple fluids [16, 22]. The investigations have shown some common features which appear to be characteristic for first-order phase transitions in confined geometries. In all cases, the freezing and melting transitions have been detected at temperatures well below the usual bulk melting point. Furthermore, a pronounced hysteresis has been observed with melting occurring at a higher temperature than freezing. Only a few papers are devoted to melting–freezing transitions in metals within porous glasses [18, 19]. For a narrow enough pore size distribution a clear asymmetry in the temperature behaviour was found during warming and cooling of gallium [18, 19]. This asymmetric behaviour has manifested itself, in particular, as a step-wise change in ultrasound velocity accompanied by only an abrupt decrease in ultrasound attenuation at gallium freezing in contrast to a smooth change in velocity and pronounced peaks of sound attenuation at gallium melting [18]. As opposed to sharp freezing this allowed the interpretation the melting process as a smeared phase transition, but with a transition temperature lower than in bulk gallium [18]. Also, results obtained in [18] have shown that a porous glass filled with gallium is a suitable model for acoustical measurements due to the low level of ultrasound attenuation below freezing. Further studies of porous glasses filled with gallium are of interest to obtain information on peculiarities of melting–freezing phase transitions in restricted geometries for different pore sizes. Note that NMR is especially useful for such studies since it can provide direct data on the amount of gallium in the liquid and solid states.

2. Experimental details

The sample under study was prepared from a phase-separated soda borosilicate glass whose pore structure was produced by acid leaching [23]. After acid leaching, the sample exhibits a well defined bimodal pore size distribution, with diameters around about 200 nm and near 7 nm for the coarse and the fine pores, respectively, as determined by mercury intrusion porosimetry and by electron microscopy. As is typical for partial leaching, the coarse pores show a broad variation in diameter, ranging from about 100 to 240 nm, with a distinct maximum at 200 nm. The fine-pore size distribution is fairly narrow with a variation of less than 1 nm. The total pore volume is 0.23 cm^3 g^{-1}. The volume fraction of the fine pores is about 40% of the total pore volume. The liquid gallium was introduced into the porous glass under pressure of up to 9 kbar. The filling factor of the pore volume is about 90%.

NMR measurements were run using a pulse Bruker MSL 500 NMR spectrometer. The temperature dependence of the ^{71}Ga NMR line in porous glass has been studied in the temperature range 185–310 K covering the bulk gallium melting point (303 K). First the sample under study was warmed up to 310 K, i.e. well above the bulk gallium melting temperature, to ensure that all the gallium in the pores was in the liquid state. Then, the sample was cooled down to 185 K and warmed up again to the room temperature. Similar temperature cycles were repeated several times. The rate of warming and cooling was very slow to prevent temperature overshoots, which were in our measurements no more than 0.5 K. Prior to each measurement, the sample was kept at a fixed temperature for about 5 min. The accuracy of temperature control was better than 0.5 K. Furthermore, the samples were held at several fixed temperatures for many hours to study whether this would result in any changes in NMR signal. To detect the NMR signal of both liquid and solid gallium,

the quadrupolar echo sequence was applied with a pulse duration of 1.9 μs and a resonance frequency of 152.487 MHz. The repetitive time was 0.1 s. The intensity of the NMR signal as well as the Knight shift was measured relative to the NMR signal from GaAs powder which was placed together with the sample under study.

Acoustical measurements were performed using the conventional pulse acoustic technique at the frequency of 7 MHz [24], which gave the relative longitudinal sound velocity value

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

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 that used in the NMR studies were carried out for the sample cut from the same bulk specimen as taken above. Prior to each measurement the sample was kept at a fixed temperature for about 15–20 min. The same procedure of holding the sample at a constant temperature for many hours was applied as already described for the NMR.

3. Results

The results of acoustical studies for one of the temperature cycles are presented in figure 1. As one can see from figure 1, the ultrasound velocity changes strongly on cooling in the temperature range of about 268–260 K. Below this range, a smooth and monotonic, but not linear, increase in velocity occurs down to the minimal temperature in our experiments of 185 K. On warming, there are two ranges of pronounced hysteresis. The first hysteresis loop, which reaches 4% of the velocity value at room temperature, is from about 260 to 287 K.
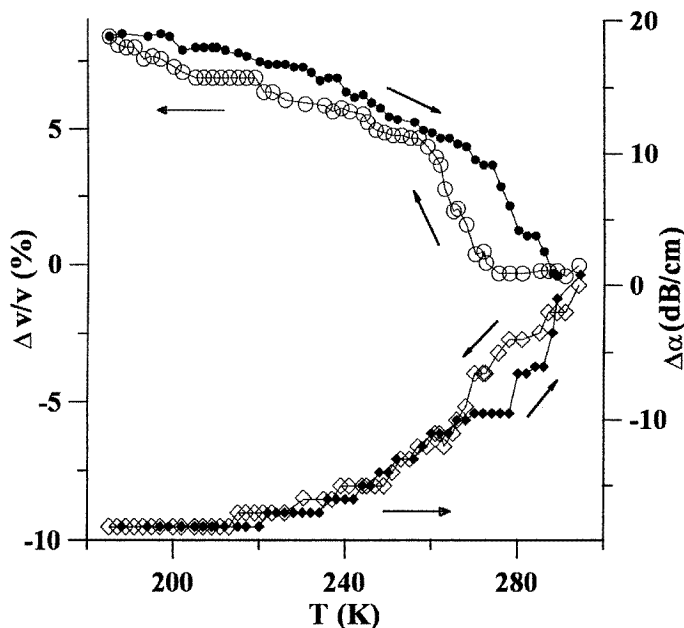

Figure 1. Ultrasound velocity $\Delta v/v$ and attenuation coefficient $\Delta\alpha$ against temperature on cooling (open circles and diamonds) and on warming (solid circles and diamonds).

The pronounced hysteresis of sound attenuation running up to 6 dB cm^{-1} is observed in the same temperature range (figure 1). The smaller velocity hysteresis loop, with an alteration of 1.5%, occurs in the temperature range between 205 and 245 K. In the same range the sound attenuation decreases monotonically with decreasing temperature and shows only an insignificant hysteresis behaviour within the limits of accuracy of measurements. Holding the sample under study at any fixed temperature for more than 15 h has not led to noticeable changes in either ultrasound velocity or attenuation coefficient. The behaviour of acoustical features, similar to that shown in figure 1, was quite reproducible for all other consecutive temperature cycles.
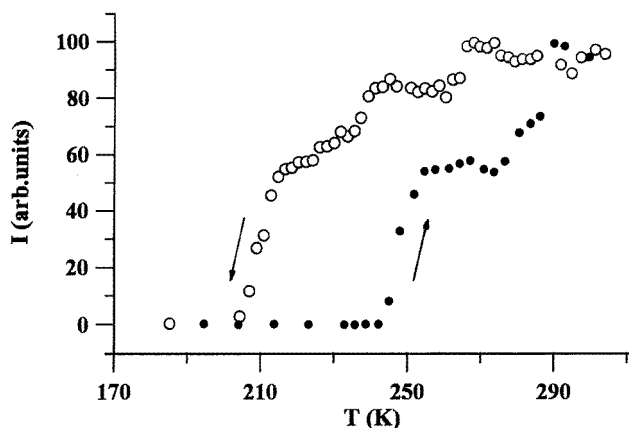

Figure 2. Intensity I of the Ga^{71} NMR signal against temperature on cooling (open circles) and on warming (solid circles).

Figure 2 shows the temperature dependence of the relative (integral) intensity of that part of the NMR spectrum which is attributed to liquid gallium and which was measured for a temperature cycle similar to that already described. At cooling down from 213 K, the NMR signal from solid gallium can be distinctly observed. When the NMR signal from liquid gallium vanishes at about 202 K, only the broad signal from the solid phase is seen (figure 3). However, its relative intensity was found to be only one-third of the integral liquid gallium signal obtained at temperatures where confined gallium is completely melted in rough agreement with the fact that only the central part of the solid state NMR spectrum is observed in this case. Note that the liquid state of gallium was observed down to a temperature of 202 K, well beyond the melting temperature of the bulk gallium.

As seen from figure 2, the amount of liquid gallium remains nearly constant on cooling from room temperature to about 268 K. Then the amount of liquid gallium decreases to 83% between 268 and 260 K, again remains constant to 243 K, reduces monotonically to about 52% in the temperature range 215 K and vanishes fast to 202 K. On warming pronounced hysteresis in amount of liquid gallium manifests itself; the melting starts near 243 K. Between 243 and 254 K about 52% of the gallium melts. The temperature behaviour of the NMR signal remains similar to that on cooling excluding a temperature shift of 40 K. However, above 254 K the process of melting differs significantly from that of freezing. This difference manifests itself also in the temperature dependence of the lineshape. It should be noted that in almost the whole temperature range the ^{71}Ga signal of the liquid phase shows
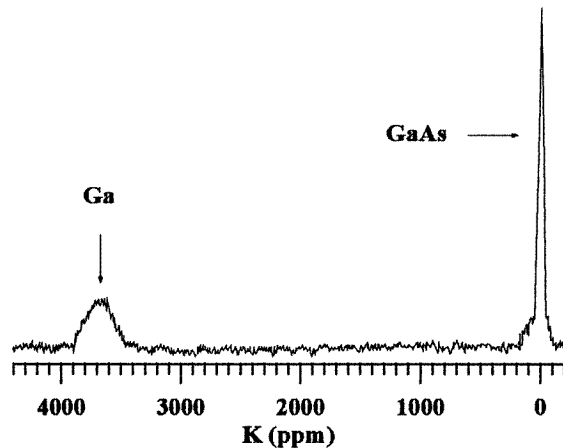
Figure 3. The Ga[71] NMR signals from solid gallium in the porous glass and from the GaAs reference sample at 200 K.

a splitting into two or three well separated components (figure 4). However, during the process of melting only two components in the lineshape are observed (figure 4(b)). Below 210 K the splitting in the lineshape for liquid gallium is no longer visible. The component of the resonance line with the lowest frequency can be detected over the whole temperature range of existence of liquid gallium. The Knight shift of this low-frequency component of the NMR line is shown in figure 5. With decreasing temperature, the Knight shift of the low-frequency component increases linearly (figure 5). The temperature coefficient of the shift, $\delta K/\delta T = -0.7$ ppm K^{-1}, evaluated from the plot in figure 5, is more than twice that in bulk liquid gallium [25]. The Knight shift for the high-frequency component also increases linearly with decreasing temperature, the splitting of the low- and high-frequency components remains nearly constant and equal to 55 ± 3 ppm. The third component of the liquid gallium NMR line can be observed only in a narrow temperature range between 270 and 260 K on cooling (figure 4). As already mentioned for the acoustical measurements, the NMR spectra do not change with time if the sample is kept at any fixed temperature for a longer interval.

4. Discussion

Shifting the melting and freezing phase transitions to low temperatures for materials confined within porous matrices has been examined in both theory and experiment. The melting temperature depression is usually interpreted as a result of a large surface to volume ratio. Assuming the spherical form of both pores and particles within pores, the melting temperature depression ΔT_m is given by the same Gibbs–Thompson equation [26] as for small isolated crystals [27–29]:

$$\Delta T_m = 4\gamma v_0 T_b / Ld \qquad (1)$$

where d is the pore diameter, γ is the surface tension of the solid, L is the latent heat of fusion, T_b is the bulk melting temperature and v_0 is the molar volume of the solid. To
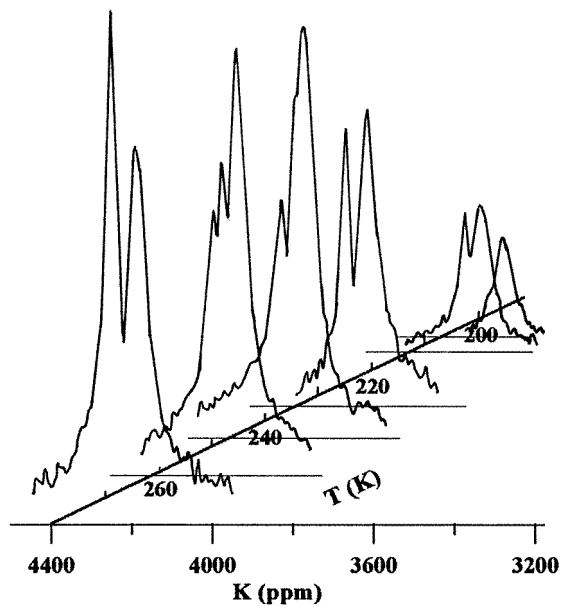
(a)
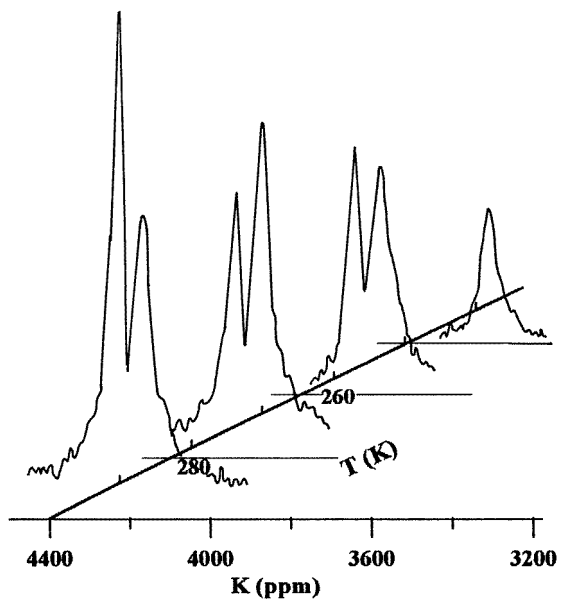
(b)

Figure 4. The Ga[71] NMR line shape for several values of temperature (a) on cooling and (b) on warming.

obtain (1), the assumption was made [29] that the melting temperature T_m of small particles is equal to the triple point where solid and liquid phases and vapour are in equilibrium. This
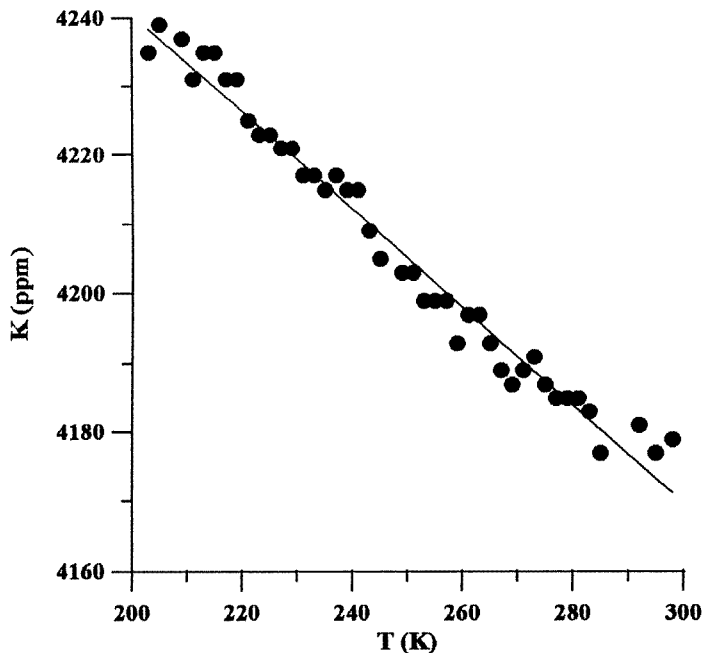
Figure 5. The temperature variation of the Knight shift K for the low-frequency component of the Ga^{71} NMR line. The straight line is the result of linear fitting.

starting assumption agrees with the experimental fact that the vapour pressure of minute crystal near melting is notably higher than that of the bulk material [30, 31]. It follows from (1) that the temperature shift is inversely proportional to the surface curvature, that is to the pore size.

Experimentally it was also found for different materials that the shift of the melting point from T_b increases monotonically with decreasing pore size [16, 17]. Since ΔT_m is related to pore dimensions, the distribution of pore sizes should result in broadening the process of melting. Such an idea was used in some studies to determine small-particle and pore size distribution from the melting process [17, 32]. On the other hand, it was found for small metallic particles [33–37] that the melting process can be smeared in the case of very narrow particle size distribution due to different phenomena which reveal with decreasing characteristic dimensions. A similar broadening can manifest itself for metals in porous glasses [18]. Within the framework of such models, a melting temperature depression results due to increasing surface to volume ratio, but a broadening of the temperature range of melting results due to size effects, that does not exclude the role of the size distribution.

Freezing can be treated in a different manner also. On the one hand, a shift of freezing relative to melting can occur as a result of supercooling. Then the freezing process should be mainly controlled by nucleation kinetics and not by the pore geometry. In this case, physical characteristics at freezing for materials confined in porous glasses would change in a step-wise manner. Also, the onset of freezing should obviously depend on the cooling rate. On the other hand, the geometric freezing model has been discussed for porous media [16, 22]. According to this model, the freezing occurs when the gain in volume free energy for the whole particle in a pore compensates the necessary surface energy. In other words,

the freezing is considered similarly to different structural phase transformations [38]. Then the freezing is controlled by pore geometries and the depression of freezing point T_f relative to the bulk point T_b for spherical pores is given by the following equation:

$$\Delta T_f = 6\alpha v_0 T_b / L d \tag{2}$$

where α is the surface energy at the liquid–solid interface. Within the frameworks of the geometric freezing model, the distribution of pore sizes leads to a broadening of the freezing phase transition since ΔT_f depends on the particle diameter d.

Let us discuss now results described in section 3. Since the depression of both freezing and melting ranges increases as the pore size decreases, we can attribute the first step in the NMR signal intensity at cooling near 260 K (figure 2) to solidification of liquid gallium inside the pores with largest sizes, namely in pores of about 200 nm. In the same temperature range a considerable increase in the ultrasound velocity is measured (figure 1). From comparison of figures 1 and 2 one can see that the rather small change in NMR intensity corresponds to the maximal alteration in acoustical velocity and attenuation. A further change in the NMR signal intensity near 240 K can be ascribed to freezing within coarse pores with smaller diameters than 200 nm, which could be formed during incomplete leaching [23]. The step in the temperature dependence of the amount of liquid gallium near 210 K arises obviously due to freezing gallium within fine pores. Note that the ultrasound velocity and attenuation change faintly near 210 K. This means that acoustical parameters are almost insensitive to the phase transition inside fine pores in the sample under study. However it does not mean that acoustical properties are not generally sensitive to the freezing–melting phase transition for gallium inside pores with small diameters. In [18] alterations in the ultrasound velocity of about 10% were found in freezing and melting processes for gallium in a porous glass with only fine pores of 4 nm. Thus, we can speculate for glasses with a large pore size distribution that acoustical parameters are mostly sensitive to the phase transformation within the largest pores in a specimen.

At warming one can similarly assume that gallium would first start to melt within fine pores. Then, the step in the amount of liquid gallium near 250 K measured by the NMR technique corresponds to the melting of gallium within fine pores (figure 2). The intensity gain above 274 K should be attributed to the melting process of gallium in coarse pores (figure 2). In contrast to the freezing process with two steps in the intensity dependence, there is only one distinct step in the NMR signal intensity during the melting process corresponding to liquefaction of gallium in coarse pores. Moreover, the whole range of melting in coarse pores from about 275 to 287 K, determined by NMR, coincides with the temperature range of pronounced change of the ultrasound velocity and attenuation (figure 1). According to the situation discussed above, the velocity and attenuation hysteresis loops are assigned to melting–freezing processes within pores with diameters of about 200 nm. Thus, one should assume that the melting of confined gallium which freezes in the broad temperature range near 240 K superimposes with the melting in pores with sizes of about 200 nm. The superimposition of the melting processes for gallium confined within pores of various sizes is in obvious contradiction with the Gibbs–Thompson equation. The reason for this behaviour is not quite clear. A probable explanation for the non-monotonic temperature shift of melting with changing pore size consists in different forms of pore of distinct sizes [23], fine pores having a quasi-spherical form and coarse pores being quasi-cylindrical. Since the Gibbs–Thompson equation has been written for spherical particles, the alterations in pore form and form of gallium nanoparticles within pores can affect the size dependence of T_m. Another probable explanation for this is based on results of x-ray studies of gallium embedded in glass with pores of 4 nm which were briefly reported in [7]. According to

[7], the solid gallium in the porous glass has several structures which differ from the bulk one and depend not only on temperature but also on the temperature history of the sample. One can speculate that different solid gallium modifications are formed also in the porous glass under study and this leads to more intricate dependences of melting temperatures on d than the Gibbs–Thompson equation predicts. Such a suggestion does not contradict the non-linear dependence of freezing temperature shifts on $1/d$ (see figure 2) and the different NMR line shapes on warming and on cooling (figure 4). Further investigations should be performed to clear the peculiarities on melting and freezing gallium in coarse pores.

As one can see from figure 2, the temperature range of freezing in fine pores is broadened. Nevertheless, the whole range of freezing is shifted to low temperatures by 40 K relative to the corresponding melting process. Moreover, the broadening of melting in fine pores is about the same as that of freezing. Together with the time independence of the amount of liquid gallium at fixed temperatures on cooling as well as on warming, this supports the geometric freezing model. Assuming the validity of the relationship (2) for gallium in fine pores, one can estimate the width of the fine-pore diameter distribution from the NMR data as 1 nm. This estimation coincides with the fact that the distribution of fine pore sizes usually is rather narrow [23]. Nearly the same estimation (of 1.2 nm) can be evaluated from the melting data. The closeness of the estimations probably points to the main role of pore geometry both in freezing and in melting processes. It seems not to be possible to make similar estimations for coarse-pore distributions due to the intricate temperature dependences of melting and freezing as discussed above. Nevertheless, the fact that there was no indication of any time variation of amount of liquid gallium in the range of melting and freezing within coarse pores, which would be expected if nucleation kinetics were important, also supports the geometric freezing model.

The origin of freezing–melting hysteresis is not quite clear when the geometric freezing model is accepted [16]. However, we can formally assume that freezing occurs when surface and volume energies compensate each other at the temperature given by (2), whereas melting corresponds to equilibrium of liquid and solid states with vapour at the temperature given by the Gibbs–Thompson equation (1). Then the hysteresis arises from the difference between ΔT_f and ΔT_m.

The complex shape of the ^{71}Ga NMR line of liquid gallium (figure 3) also should be discussed. It is seen from figure 3 that solidification of gallium within coarse pores does not lead to a simplification of the line shape. Thus, there are no plausible reasons to assign a certain component of the spectrum to gallium within pores of various size. Hence, one cannot explain the observed line shape with the size effect for the Knight shift only. We have to speculate then that the gallium melt within pores is the strongly correlated liquid with a structure depending on both temperature and pore size. This hypothesis is consistent with the difference in the temperature coefficients of the Knight shift for confined and bulk liquid gallium. Note that the values of the Knight shift for the confined liquid and solid gallium differ from the corresponding values for the bulk gallium. We will devote a special paper to this problem.

Acknowledgments

References

[1]   Klafter J and Drake J M (ed) 1989 *Molecular Dynamics in Restricted Geometries* (New York: Wiley)
[2]   Chan M H W, Blum K I, Murphy S Q, Wong G K S and Reppy J D 1988 *Phys. Rev. Lett.* **61** 1950
[3]   Finotello D, Gillis K A, Wong A P Y and Chan M H W 1988 *Phys. Rev. Lett.* **61** 1954
[4]   Beamish J R, Hikata A, Tell L and Elbaum C 1983 *Phys. Rev. Lett.* **50** 425
[5]   Larson M, Mulders N and Ahlers G 1992 *Phys. Rev. Lett.* **68** 3896
[6]   Graf M J, Huber T E and Huber C A 1992 *Phys. Rev.* B **45** 3133
[7]   Charnaya E V, Kumzerov Yu A, Tien C and Wur C S 1995 *Solid State Commun.* **94** 635
[8]   Charnaya E V, Tien C, Wur C S and Kumzerov Yu A 1996 *Physica* C **269** 313
[9]   Dierker S B and Wiltzius P 1991 *Phys. Rev. Lett.* **66** 1185
[10] Pricaupenko L and Treiner J 1995 *Phys. Rev. Lett.* **74** 430
[11] Iannacchione G S, Crawford G P, Zumer S, Doane J W and Finotello D 1993 *Phys. Rev. Lett.* **71** 2595
[12] Uzelac K, Hasmy A and Jullien R 1995 *Phys. Rev. Lett.* **74** 422 and references therein
[13] Duffy J A, Wilkinson N J, Fretwell H M and Alam M A 1995 *J. Phys.: Condens. Matter* **7** L27 and references
         therein
[14] Jackson C L and McKenna G B 1990 *J. Chem. Phys.* **93** 9002
[15] Beamish J R, Mulders N, Hikata A and Elbaum C 1991 *Phys. Rev.* B **44** 9314
[16] Molz E, Wong A P Y, Chan M H W and Beamish J R 1993 *Phys. Rev.* B **48** 5741
[17] Strange J H, Rahan M and Smith E G 1993 *Phys. Rev. Lett.* **71** 3589
[18] Borisov B F, Charnaya E V, Kumzerov Yu A, Radzhabov A K and Shelapin A V 1994 *Solid State Commun.*
         92 531
[19] Shabanova E, Charnaya E V, Schaumburg K and Kumzerov Yu A *Physica* B at press
[20] Brewer D F, Cao Liehao, Girit C and Reppy J D 1981 *Physica* B **107** 583
[21] Thomas A L, Brewer D F, Naji T, Haynes S and Reppy J D 1981 *Physica* B **107** 581
[22] Warnock J, Awaschalon D D and Shafer M W 1986 *Phys. Rev. Lett.* **57** 1753
[23] Varshal B G (ed) 1991 *Two-phase Glasses: Structure, Properties, Applications* (Leningrad: Nauka)
         (in Russian)
[24] Charnaya E V and Rakhimov I 1990 *Ferroelectrics* **112** 45
[25] Cornell D A 1967 *Phys. Rev.* **153** 208
[26] Defay R, Prigogine I, Bellemans A and Everett D H 1966 *Surface Tension and Absorption* (London:
         Longmans Green)
[27] Pawlow P 1909 *Z. Phys. Chem.* **65** 545
[28] Hanszen K-J 1960 *Z. Phys.* **157** 523
[29] Buffat Ph and Borel J-P 1976 *Phys. Rev.* A **13** 2287
[30] Lisgarten N D, Sambles J R and Skinner L M 1971 *Contemp. Phys.* **12** 575
[31] Piuz F and Borel J-P 1972 *Phys. Status Solidi* a **14** 129
[32] Wronski C R M 1967 *Bri. J. Appl. Phys.* **18** 1731
[33] Hahn M Y and Whetten R L 1988 *Phys. Rev. Lett.* **61** 1190
[34] Ajayan P and Marks L 1989 *Phys. Rev. Lett.* **63** 279
[35] Berry R and Wales D 1989 *Phys. Rev. Lett.* **63** 1156
[36] Ercolessi P, Andreoni W and Tosatti T 1991 *Phys. Rev. Lett.* **66** 911
[37] Nagaev E L 1992 *Sov. Phys.–Usp.* **35** 747 and references therein
[38] Morokhov I D, Trusov L I and Lapovok V N 1984 *Physical Phenomena in Ultradispersed Media* (Moscow:
         Energoatomizdat) (in Russian)