International Journal of Applied Engineering Research ISSN 0973-4562 Volume 12, Number 21 (2017) pp. 11107-11113


# Melting and Crystallization of a Ga-In alloy confined in a porous glass

**A.L. Pirozerski[1,3,*], A.I.Nedbai[1,4], Yu. A. Kumzerov[2,5], A. V. Fokin[2,6] and E.L. Lebedeva[1,7]**

*[1] Faculty of Physics, Saint-Petersburg State University, Saint-Petersburg, 198504, Russia.*
*[2] Ioffe Physical-Technical Institute, Russian Academy of Sciences, Saint-Petersburg, 194021, Russia.*
*[*] Corresponding author*
*[3]Orcid Id: 0000-0002-1495-2200 [4]Orcid Id: 0000-0003-1894-5929*
*[5]Scopus Id: 266 435 12700 [6]Scopus Id: 710 293 1309*
*[7]Orcid Id: 0000-0001-5064-3184*

**Abstract**

In this paper melting and crystallization of the indium-gallium alloy with indium content of 4 at. % embedded into the porous glass with pore size of 7 nm were studied using acoustic methods. Temperature dependencies of the velocity and attenuation of the ultrasound were measured in a wide temperature range. The expansion of the temperature range of the melting of α-Ga was observed. An anomaly on the temperature dependences of the ultrasound velocity and attenuation near ~223 K was revealed which is probably related with the formation of a small fraction of β-Ga.

**Keywords:** melting and crystallization in nanopores, nanocomposite, indium-gallium alloy, polymorphism, pulse-phase ultrasonic technique, size effects, confined geometry, porous glass

## INTRODUCTION

Last years the processes of melting and crystallization of small particles were actively studied. For isolated particles decrease of the melting temperature was predicted theoretically more than hundred years ago [1] and confirmed experimentally. The situation is considerably more complicated if particles are contained in a matrix of another material (so-called the confinement geometry conditions) because of the interaction of the particles with the matrix and with each other [2-5]. The features of the melting and freezing were studied for different materials embedded in pores of porous silica matrices [2-4, 6-8]. For gallium the appearance of polymorphs different from those known in the bulk case and stabilization of the phases which are metastable in the bulk were discovered [9, 10]. Nevertheless, for binary and, more generally, for multicomponent systems, in particular, for eutectic alloys, the influence of the size effects and of the confinement geometry conditions is still little-studied. Note that in contrast to the pure metals the melting and solidification of a bulk eutectic alloy occurs not at definite temperature but in a whole temperature range between the liquidus and the solidus, which degenerates to the single temperature point only for the alloy of the eutectic composition. For alloys in the pores at a given alloy composition, the position and length of this interval can be affected both by thermodynamic size effects and by interactions of the alloy with the porous matrix. If one or more components of the system are disposed to polymorphism, as it takes place for the gallium alloys, the situation becomes even more complicated. The crystalline structure, fraction and stability of arising phases can be dependent on the pore size, the pore network geometry, the pore filling factor, and chemical properties of the pore surfaces, and each of the formed phases will have its own temperature interval of the melting.

By now there are few papers devoted to melting and crystallization of gallium-indium alloys under confinement geometry conditions. In article [11] an alloy of the composition 90 at.% Ga and 10 at.% In embedded into a porous glass with pore size of 8 nm was studied using acoustic techniques. It was found that at freezing crystalline mixtures with α- and β-Ga arose in the pores. Similarly to the case of pure gallium [10], the stabilization of metastable in bulk β-phase occurred. In paper [12] four different In-Ga alloys with indium content of 4, 6, 9 and 15 at.% embedded into porous glasses with the pore size of 18 nm (below these glasses will be referred as LPG) were investigated using acoustic methods. Dependence of types of gallium polymorphous modifications arising upon freezing and of their relative fractions on the alloy composition was studied. In paper [13] alloys of the same compositions embedded into synthetic opal matrices with diameter of the silica balls of ~210 nm were studied with use of acoustic and NMR methods. The results obtained via acoustic methods were, in general, similar to that of [12]. The NMR studies gave different results that were explained by different temperature conditions. To get a deeper understanding of features of the melting and crystallization of In-Ga alloys under confinement geometry conditions it is

interesting to study nanocomposites on the base of porous matrices different from those studied earlier.

This paper presents the results of acoustic studies of melting and crystallization of the indium-gallium alloy with indium content of 4 at. % embedded into the porous glass with average pore size of 7 nm. Acoustic methods are shown to be very suitable for the investigations of the phase transitions [14-20] and have some advantages due to possibility to use different temperature modes of the measurements and to high speed of the measurements at each temperature point.

## SAMPLES AND EXPERIMENT

Nanocomposite under study represents a porous glass matrix with the pores filled by a gallium-indium alloy. The size of the pores determined via nitrogen sorption-desorption was about 7 nm. The alloy composition was 4 at.% In, 96 at.% Ga. The alloy was embedded into the pores in liquid state under pressure up to 9 kbar.

Measurements of the ultrasound velocity and attenuation were carried out using an enhanced version [20] of the single-pulse pulse-phase ultrasonic technique [21] developed previously for strongly absorbing samples. The experimental setup and the measurement procedure are described in detail in [20]. Acoustic contacts between the sample and the acoustic ducts were made using the vacuum grease Apiezon N.

The acoustic measurements were carried out on longitudinal waves with the frequency of 7 MHz. The temperature dependences of the relative changes of the ultrasound velocity $\Delta v / v_0 = (v(T) - v_0)/v_0$ and of the ultrasound attenuation $\Delta\alpha = \alpha(T) - \alpha_0$ (where $v_0$ and $\alpha_0$ are, respectively, the velocity and the attenuation at room temperature) were measured at full and partial cooling-heating cycles after preliminary heating to 310K.

## EXPERIMENTAL RESULTS AND DISCUSSION

The temperature dependence of the ultrasound velocity at a full cooling-heating cycle is shown in Fig.1. In this cycle, the sample was heated up to ~310 K (not shown in Fig.1), then cooled to 133 K and heated again to 310 K. The heating and cooling rates were about 0.7 K/min. The phase transitions of melting and crystallization appear on the curve of the temperature dependence as regions of strong nonlinear changes of the velocity. Cooling and heating branches of the curve differ from each other forming a pronounced hysteresis loop.

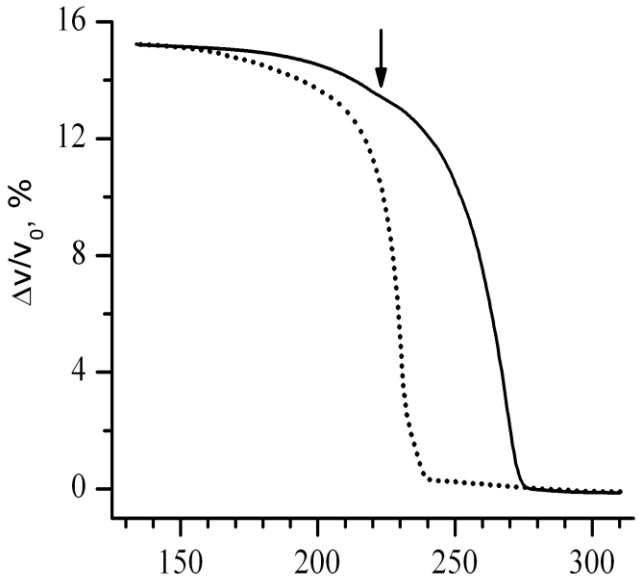


**Figure 1:** Temperature dependence of the ultrasound velocity at complete cooling-heating cycle. Dotted line corresponds to the cooling, solid line – to the heating. The arrow indicates an anomaly near ~223 K.

Upon cooling the crystallization begins sharply at ~239 K. To 215 K the relative velocity change reaches 12% (which is about 80% of its maximal value), indicating that the most part of the alloy in the pores is frozen, and the velocity change rate ( |dv/dT| ) decreases. The crystallization of the alloy in the pores completely terminated at ~155 K that is confirmed by the fact that the cooling and heating branches coincide with each other in the temperature range 155–132 K.

Upon heating the deflection of the temperature dependence curve from straight line became noticeable at ~188 K that may be considered as the onset of the melting. From this temperature toward ~255 K the melting rate increases gradually but at ~ 223 K a slight knee on the temperature dependence of the velocity can be noticed (marked by arrow in Fig.1). It appears more distinctly on the temperature dependence of the derivative $d(\Delta v/v_0)/dT$ shown in Fig.2.

In the temperature range 255–274 K a strong almost linear decrease of the ultrasound velocity occurs.

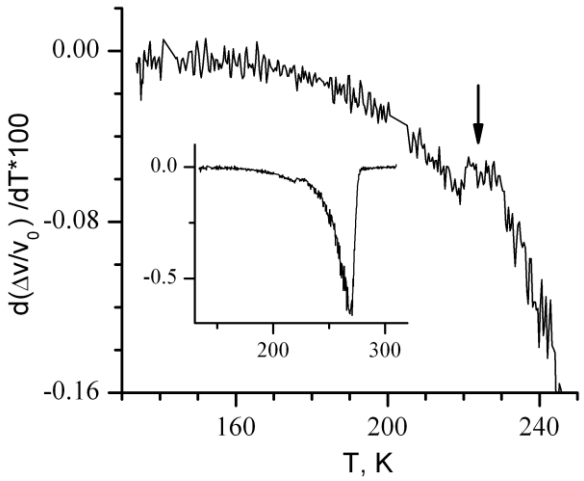


**Figure 2:** Temperature dependence of the ultrasound velocity change rate $d(\Delta v/v_0)/dT$ in the temperature range 133-245 K upon heating. The arrow indicates the same anomaly as in Fig.1. Insert: temperature dependence of the ultrasound velocity change rate for the whole heating branch.

Above 276 K the heating and cooling branches coincide with each other indicating that the melting is completed to this temperature.

The temperature dependence of the ultrasound attenuation has a more complicated character, see Fig. 3. Upon cooling, $\Delta\alpha$ decreases almost linearly in the temperature interval 310-240 K. Then a narrow peak of the attenuation was observed with maximum at ~231 K. (Note that at this temperature the relative increase of the velocity was only 3.9%). The peak was followed by an abrupt decrease of the attenuation in the temperature range 231–225 K. Then the attenuation decrease became smoother and a local minimum was observed near ~200 K. Next, a small step-like increase of the attenuation occurs (199–196 K) followed by a plateau (196–180 K) and, finally, a weak linear decrease of the attenuation lasted up to 133 K.

Upon heating the ultrasound attenuation increased linearly in the temperature range 132–214 K, and below ~180 K the heating branch of temperature dependence of the attenuation nearly coincided with the cooling branch.

Next, in the temperature range 214–225 K the attenuation stayed nearly constant. Note that such a behavior can be regarded as a local minimum superimposed on the linear increase. This temperature range closely matches to that where the anomaly of the ultrasound velocity was observed so we assume that both anomalies have common physical cause.

In the temperature range 225–271 K the ultrasound attenuation increased rapidly. Then two bends was observed on the curve $\Delta\alpha(T)$ with inflexion points at ~271.5 K and 276 K. At higher temperatures the heating and cooling branches nearly coincide with each other.

The low-temperature partial heating-cooling cycle is shown in Fig.4. After preliminary heating to 310 K and subsequent cooling down to ~130 K, which are not shown in Fig.4, the sample was heated from ~130K to ~260 K. The temperature dependence of both the velocity and the attenuation nearly coincided with those of the full cycle, indicating a good reproducibility of the experimental results. At 260 K the temperature control system was programmed to maintain this temperature for about 45 min. As seen from Fig.4, during this period both the ultrasound velocity and attenuation stayed virtually constant suggesting, firstly, that melting of the alloy occurred via the quasi-equilibrium way and, secondly, that temperature gradients in the sample were sufficiently small to do not affect considerably the measurement results.

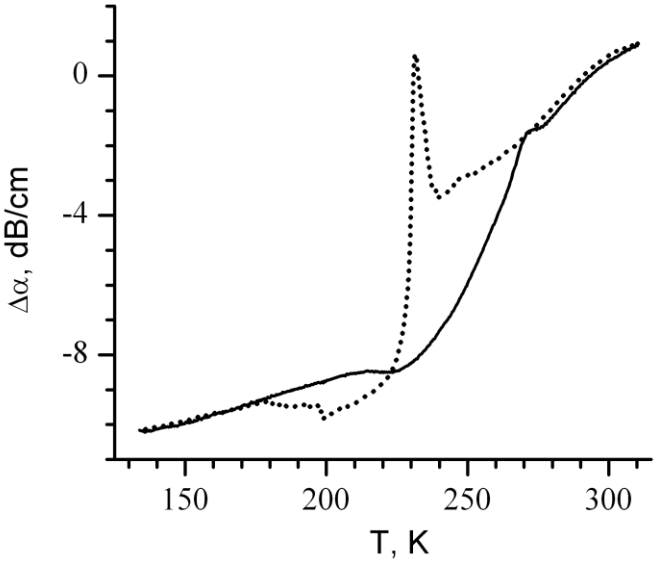


**Figure 3:** Temperature dependence of ultrasound attenuation at the same complete cooling-heating cycle as shown in Fig.1. Dotted line corresponds to the cooling, solid line – to the heating.

After the temperature stabilization period, the sample was cooled down to 130 K. As seen from Fig. 4, the cooling branch of the temperature dependence of the ultrasound velocity at the partial cycle differs from both the heating and cooling branches of the full cycle at the temperatures above ~160 K (i.e., near to the low-temperature limit of the full cycle hysteresis). This implies a partial irreversibility of the melting process, and probably related with the presence of solid alloy clusters which serve as crystallization centers. The temperature dependence of the attenuation upon the cooling followed close to the heating branch up to ~220 K. This behavior is very different from that of the cooling branch of the full cycle, especially, there is no attenuation peak. Below 220K, the curve of the temperature dependence of the attenuation goes, on the contrary, close to the cooling branch of the full cycle, in particular, it has the minimum near ~200 K.

Fig.5 shows a high-temperature partial cooling-heating cycle. After a preliminary heating to 310 K, the sample was cooled down to the temperature of 232 K, at which the relative velocity change was ~6.3%, i.e. about 40% of the total velocity increase during crystallization at the full cycle. Then the temperature control system was switch to the temperature stabilization mode. The period of the operation in this mode can be conventionally divided into two stages. At the stage 1 (of duration ~ 20 min), the system tried to bring the sample temperature near to a predefined set point. At the stage 2, the system kept the temperature at the set point with accuracy better than 0.1 K during ~30 min. After the temperature stabilization period the sample was heated to 310 K.

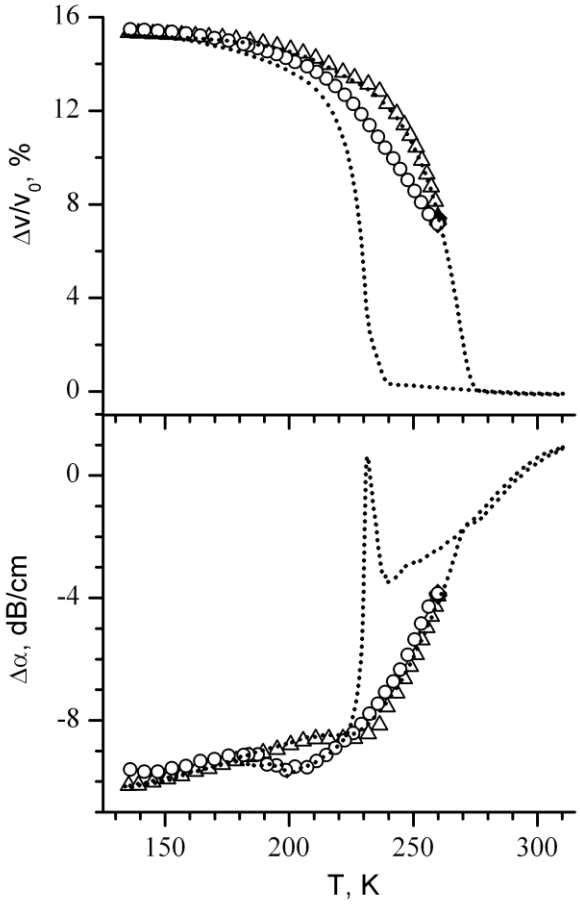


**Figure 4:** Temperature dependences of the ultrasound velocity and attenuation at a partial heating-cooling cycle. Open triangles correspond to heating, open circles – to cooling and closed diamonds – to the temperature stabilization period (see the text for details). Dotted line represents the full cooling-heating cycle shown in Fig.1

As seen from Fig.5, upon cooling the temperature dependencies of both the velocity and the attenuation are close to those measured in the full cycle, but the onset of the alloy freezing and the attenuation peak are shifted to higher temperatures by ~2.3 K as compared with the full cycle. This can imply that a supercooling of the alloy takes place at freezing. The increase of the velocity by ~1.6% and the decrease of the attenuation by ~1.5 dB/cm during the stage 1 of the temperature stabilization period agree with this assumption but the relaxation of the temperature gradients in the sample may play a more significant role in these changes. At the stage 2 the changes of the relative velocity and of the attenuation do not exceed 0.2 % and 0.3 dB/cm, respectively, indicating that the semi-equilibrium state is attained.

Upon heating the temperature dependence of the ultrasound velocity approaches the heating branch of the full cycle only near to the end of the alloy melting. This indicates a partial irreversibility of the melting processes. However, the temperature dependence of the attenuation coincides closely with those observed in the full cycle.

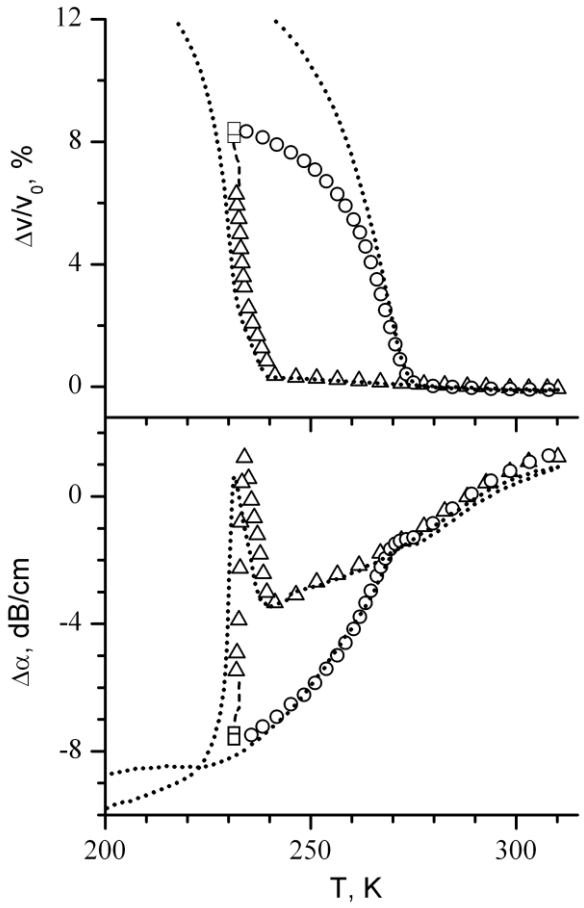


**Figure 5:** Temperature dependences of ultrasound velocity and attenuation at a partial cooling-heating cycle. Open triangles correspond to cooling, open circles – to heating. Dashed line and open squares correspond, respectively, to the stages 1 and 2 of the temperature stabilization period (see the text for details). Dotted line represents a part of the full cooling-heating cycle shown in Fig.1.

The phase diagram of the bulk In-Ga system is of the eutectic type with the solidus temperature of ~289 K and the eutectic composition of 14.2 at.%In [22,23]. Upon sufficiently slow cooling a mixture of two components is formed. The first of them is a solid solution consisting mainly of indium and having the structure of the pure indium. The second consists almost entirely of gallium (the content of indium is less than 0.3 at.% [22]) and has the structure of α-Ga. For brevity, below they will be referred to simply as In and α-Ga, respectively.

At sufficiently fast cooling of the bulk alloy a metastable solid solution with structure of β-Ga can be formed instead of α-Ga. In this case the phase diagram of In-Ga system is also of the eutectic type with the solidus temperature of ~244.5 K and the eutectic composition of 6.2 at.% In [22,23]. It should be noted that upon cooling of microscopic gallium droplets in various dispersive media (see [24-27] and references therein), of the mixtures of gallium with fullerenes [28] and of gallium confined within nanopores [29-32] several other metastable phases can arise.

As it was already pointed out above, the melting and the solidification of an eutectic alloy, even for bulk samples, occur not at definite temperature but in the temperature range between the liquidus and the solidus. For In-Ga alloys in pores the width and position of this interval is determined by type of the polymorph phases, by the thermodynamic size effects and by interactions of the alloy with the pore walls. For the alloy under study, the freezing begins at 239 K and ends at ~155 K. The melting starts at 188K and terminates at 276 K. For the bulk alloy of the same composition the melting range is 289–298 K in the case of α-Ga formation and 244.5-248 K in the case of β-Ga formation. Taking into account the anomaly on the temperature dependence of the ultrasound velocity at ~223 K it may be supposed that upon cooling both α- and β-Ga are formed but fraction of the β-Ga is very small. Conceivably, the part of the alloy which crystallized with the β-Ga formation melts in the temperature range 188-219K while that with α-Ga – in the temperature range 228-276K. To definitely prove or disprove this conjecture XRD studies in the same temperature change modes are required.

To visualize the obtained results and to compare them with the results of the acoustic studies of melting and crystallization of In-Ga alloy of the same composition in LPG [12] and in the syntetic opal matrices [13], corresponding melting intervals as a function of the inverse pore diameter are plotted in Fig.6.

It may be seen that for the part of alloy that crystallized with formation of α-Ga the above conjecture implies a reasonable agreement with linear dependence of the low temperature limit of the melting temperature interval on the inverse pore size. (Remember that the linear dependence of melting temperature for single-component systems is predicted by thermodynamic models of the size effects, see [2-5] and references therein).

At the same time, according to the [12, 13] the In-Ga alloy of the same composition in the pores of the synthetic opal matrices and of the porous glass with the pore size of 18 nm crystallized with formation of only α-Ga. In [12] it was supposed that at freezing of an alloy of the composition 6 at.% In–94 at.% Ga in the pores of LPG a small fraction of β-Ga formed. For alloys with higher contents of indium both α- and β-phases of gallium formed and the stabilization of β-phase metastable in bulk occurs both in the opals and in LPG. So, if the above conjecture is valid, it implies that *ceteris paribus* decreasing of the pore size promotes the appearance and stabilization of β-Ga and diminishes the indium concentration limit above which the stabilization of this phase occurs.

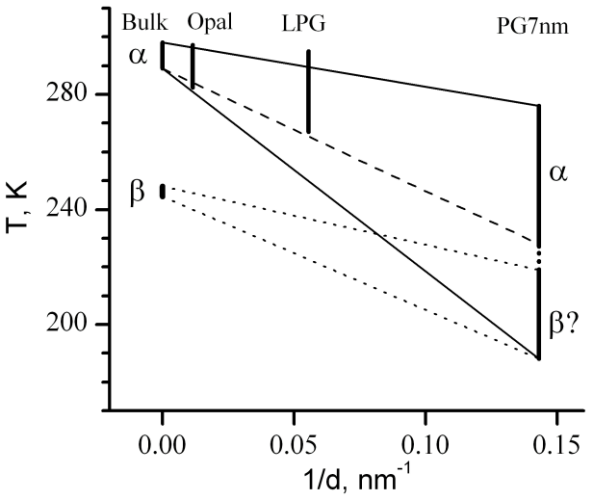


**Figure 6:** Temperature intervals of melting for the bulk indium-gallium alloy of composition 4 at.% In–96 at.% Ga [22,23] and for the nanostructured alloys of the same composition embedded into synthetic opal matrices [13] and into porous glasses with the average pore size of 18 nm (LPG) [12] and of 7 nm (PG7nm). For the opals the inverse size of the octahedral pores is used. The dashed (respectively, thin dotted) line(s) connect(s) low temperature limit (respectively, both limits) of the melting intervals for the studied alloy under the conjecture of formation of the both phases in the pores and limit(s) of melting interval for corresponding phases in the bulk case.

## CONCLUSION

The present acoustic studies of the indium-gallium alloy embedded into the porous glass matrix with the pore size of 7 nm revealed a pronounced temperature hysteresis between heating and cooling branches of the temperature dependence of the ultrasound velocity which corresponds to melting and crystallization of the alloy in the pores. Temperature

dependence of the ultrasound attenuation has a complicated character. Main part of the alloy crystallizes with formation of α-Ga. The interval of melting for this part of the alloy was widened and shifted to lower temperatures relative to the bulk alloy of the same composition. An anomaly was observed upon heating near ~223K on the temperature dependences of both the velocity and the attenuation which can be explained by formation in pores of a small fraction of β-Ga. The obtained results show once again that ultrasonic methods are very suitable for studies of the phase transitions in the nanostructured materials.

## ACKNOWLEDGMENTS

This work was partially supported by Saint-Petersburg State University.

## REFERENCES

[1] Pawlow P. On the melting temperature of the corns of salol// Z. Phys. Chem. 1910. V. 74, P. 562 ().

[2] Christenson H.K. Confinement effects on freezing and melting. // J. Phys.: Condens. Matter. 2001. V. 13. No. 11. P. R95-R133.

[3] Alba-Simionesco C., Coasne B., Dosseh G., Dudziak G., Gubbins K.E., Radhakrishnan R., Sliwinska-Bartkowlak M. Effects of confinement on freezing and melting. // J. Phys.: Condens. Matter. 2006. V. 18. P. R15.

[4] Caupin F. Melting and freezing of embedded nanoclusters // Phys. Rev. B. 2008. V. 77. P. 184108.

[5] Nagaev E.L. Small metal particles. // UFN. 1992. V. 162. No. 9. P. 49 (in Russian).

[6] Charnaya E.V., Tien C., Lee M.K., Kumzerov Yu.A. NMR studies of metallic tin confined within porous matrices. // Phys. Rev. B. 2007. V. 75. No. 14. P. 144101.

[7] Petrov O.V., Furó I. NMR cryoporometry: Principles, applications and potential. // Progr. in Nuclear Magnetic Resonance Spectroscopy. 2009. V. 54. No. 2. P. 97.

[8] Xu Q., Sharp I.D., Yuan C.W. и др. Large melting-point hysteresis of Ge nanocrystals embedded in $SiO_2$. // Phys. Rev. Lett. 2006. V. 97. No. 15. P. 155701.

[9] Charnaya E.V., Tien C., Lee M.K., Kumzerov Yu.A. Superconductivity and structure of gallium under nanoconfinement. // J. Phys.: Condens. Matter. 2009. V. 21. P. 455304.

[10] Lee M.K., Tien C., Charnaya E.V., Sheu H.-S., Kumzerov Yu.A. Structural variations in nanosized confined gallium. // Phys. Lett. A. 2010. V. 374. No. 13-14. P. 1570.

[11] A.L. Pirozerskii, E.V. Charnaya, E.N. Latysheva, A.I. Nedbai, Yu.A. Kumzerov, and A.S. Bugaev. Acoustic studies of melting and crystallization of indium-gallium alloy in porous glass. // Acoustical Physics. 2011. V. 57, No. 5, P. 637–641.

[12] E.N. Latysheva, A.L. Pirozerskii, E.V. Charnaya, Y.A. Kumzerov, A.V. Fokin, A.I. Nedbai, A.S. Bugaev. Polymorphism of Ga-In alloys in nanoconfinement conditions // Physics of the Solid State. 2015. V. 57. No. 1, P. 131-135.

[13] A.L. Pirozerskii, E.V. Charnaya, M.K. Lee, L.J. Chang, A.I. Nedbai, Yu.A. Kumzerov, A.V. Fokin, M.I. Samoilovich, E.L. Lebedeva, A.S. Bugaev. Acoustic and NMR investigations of melting and crystallization of indium–gallium alloys in pores of synthetic opal matrices. //Acoustical Phisics. 2016. V. 62, Is. 3. P.. 306–312.

[14] Borisov B.F., Charnaya E.V., Baryshnikov S.V., Pirozerskii A.L., Bugaev A.S., Tien C., Lee M.K., Michel D. Ferroelastic phase transition in LiCsSO4 embedded into molecular sieves // Phys. Lett. A. 2010. V. 375. № 2. P. 183-186

[15] Charnaya E.V. Acoustic studies of phase transitions in crystals and nanocomposites // Acoustical Physics. 2008. V. 54, Is. 6. P. 802-813

[16] Borisov B.F., Charnaya E.V., Gartvik A.V., Tien C., Kumzerov Yu.A., Lavrentev V.K Peculiarities of gallium crystallization in confined Geometry. // Physics of the Solid State. 2004. V. 46, Is. 12. P. 2286-2291

[17] Charnaya E.V., Plotnikov P.G., Michel D., Tien C., Borisov B.F., Sorina I.G., Martynova E.I.. Acoustic studies of melting and freezing for mercury embedded into Vycor glass // Physica B. 2001. V. 299. No.1-2. P. 56.

[18] Dereppe J.M., Borisov B.F., Charnaya E.V., Shelyapin A.V., Nassar M.M., Kumzerov Yu.A. Acoustic study of the melting and solidification of gallium incorporated in an opal matrix. // Physics of the Solid State. 2000. V. 42, Is. 1. P. 193-196

[19] Borisov B.F., Charnaya E.V., Loeser T., Michel D., Tient C., Wur C.S., Kumzerov Yu.A Nuclear magnetic resonance, resistance and acoustic studies of the melting-freezing phase

[20] A.L. Pirozerski, E.V. Charnaya, S.V.Baryshnikov, B.F. Borisov, V.M.Mikushev, E.L. Lebedeva, A.S. Khomutova, M.V.Dolgova. Acoustic studies of the ferroelastic phase transition in $LiCsSO_4$/MCM-41 nanocomposite using longitudinal ultrasonic waves.

// International Journal of Applied Engineering Research. 2016. V.11. N.5. P. 3309-3313

[21] M. B. Gitis, I. G. Mikhailov, and V. A. Shutilov. Measurements of the temperature dependence of the sound velocity in solid samples of small sizes. //Akust. Zh. 1969. V.15. P.28. (In Russian).

[22] Anderson T.J., Ansara I. The Ga-In (gallium-indium) system // J. Phase Equil. 1991. V. 12. № 1. P. 64-72..

[23] T. J. Anderson, I. Ansara. // Journal of Phase Equilibria, 1992, 13, 181.

[24] R.D. Heyding, W. Keeney, S.L. Segel. Metastable phases in gallium dispersions. // Journal of Physics and Chemistry of Solids. 1973. V. 34. P. 133-136

[25] L.Bosio, A.Defrain, H.Curien and A.Rimsky. Structure crystalline du gallium β. // Acta Crystallographica. 1969. B 25. P.995

[26] L. Bosio, A. Rimsky, M. Dupont and H. Curien. Structure crystalline du Ga γ. // Acta Crystallographica 1972. B 28. P. 1974-1975

[27] L. Bosio, A. Rimsky, M. Dupont and H. Curien. Structure crystalline du Ga δ. // Acta Crystallographica 1973. B 29. P. 367-368

[28] D. Teske and J.E. Drumheller. Phases of gallium nucleated by small particles. // J. Phys.: Condens. Matter. 1999. V.11. P.4935-4940.

[29] E.V. Charnaya, C. Tien, K.J. Lin and Yu. A. Kumzerov. X-ray and resistance studies of the melting and freezing phase transitions for gallium in an opal // J. Phys.: Condens. Matter. 1998. V. 10 P.7273-7282.

[30] I.G. Sorina, E.V. Charnaya, L.A. Smirnov, Yu.A. Kumzerov and C.Tien. Structural features of solid gallium in microporous glass// Physics of the Solid State. 1998. V.40. Is. 8. P. 1407-1408.

[31] E.V. Charnaya, C. Tien, K.J. Lin, C.S. Wur and Yu.A. Kumzerov Superconductivity of gallium in various confined geometries. // Phys. Rev. B. 1998, V.58., P. 467-472

[32] E.V. Charnaya, C. Tien, K.J. Lin and Yu.A. Kumzerov. X-ray studies of the melting and freezing phase transitions for gallium in a porous glass // Phys.Rev. B. 1998. V.58. P. 11089-11092.