Report

on the thesis by **Nefedov Denis Yurievich**

titled "**NMR of Ga-In and Ga-In-Sn alloys under nanoconfinement**"

for the degree of Candidate of Physical and Mathematical Sciences,

Scientific specialty 1.3.8. - Condensed matter physics

Understanding the specific physical properties of nanostructured materials are of great importance for modern fundamental physics and applications. In particular, low-dimensional systems of metals and metallic alloys are extremely interesting for new areas of applied physics and techniques such as soft electronics, biorobotics, micro and nanoelectronics, and fabrication of sensors. Both Ga-In and Ga-In-Sn alloys are now considered as very prospective alloys due to their low melting temperatures, very good electronic and mechanical characteristics, and non-toxicity. Many features of nanostructured metallic alloys are expected to differ remarkably from those of the relevant bulk alloys. For instance, we can guess that phase diagrams, crystalline symmetry, and atomic mobility of metallic nanoalloys are strongly affected. However, these problems are still poorly studied. NMR is a very powerful tool to investigate the low-dimensional materials of different physical nature and is useful especially for nanostructures of metals and metallic alloys owing to high sensitivity of the NMR line shifts and spin relaxation to any changes in the local properties. The thesis focuses on the impact of nanostructuring obtained via introducing the Ga-In and Ga-In-Sn alloys into nanoporous matrices on the phase diagrams of these alloys, namely on the structural transformation in melts (so called, the liquid-liquid transition), emergence of another structure of gallium-rich segregates, and shift of the eutectic point and on mobility of ions in melts. We can conclude that the topic of the thesis is crucial at present for modern pure and applied physics.

In introduction, the author of the thesis poses the problems and discusses their importance. Also, the main necessary experiments are described.

First chapter of the thesis offers a short review of NMR features, which are important for better understanding the further content of the thesis. The Knight shift of NMR lines, lineshapes and relaxation in metallic materials are discussed.

Second chapter presents results of NMR experiments on the Ga-In alloy under nanoconfinement. For the first time the liquid-liquid transition in the supercooled Ga-In nanoalloy was found and justified due to thorough monitoring the temperature variations of the Knight shift and spin-lattice relaxation rate. The lower-temperature liquid structure appeared as an additional component of NMR lines with larger Knight shift in the partly frozen alloy. It was also shown that different liquid structures have different spin relaxation rates.

Third chapter presents findings, which demonstrate the emergence upon the alloy continuous crystallization of the segregates with symmetry of β-Ga. The simulation of the NMR lineshape allowed evaluating the quadrupole shift within a temperature range of β-Ga existence. This was compared to studies of bulk β-Ga by Nuclear quadrupole resonance. The stabilization of nanostructured β-Ga was confirmed while in bulk this structure is metastable. The detailed treatment of spin relaxation and separation of the magnetic and quadrupole contributions to relaxation gave values of correlation time of ionic mobility and activation energy in the solid segregates with β-Ga symmetry.

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Fourth chapter discusses the important phenomenon of slowing the ionic mobility in the ternary Ga-In-Sn liquid alloy. Theoretical interpretation of spin relaxation using the models valid for viscous liquids demonstrated a drastic acceleration of quadrupole relaxation for the liquid alloy under nanoconfinement caused by increasing the correlation time of ionic mobility. The phenomenon of the pronounced slowdown of the ionic mobility under nanoconfinement was first obtained for gallium and indium melts. The thesis proved that this effect extends also on the confined liquid Ga-In-Sn alloy.

Fifth chapter presents results of studies of the gallium dynamic shift in the Ga-In-Sn alloy embedded into two porous glasses with pores of 7 and 25 nm in diameter. It was shown that due to strong slowdown of ionic mobility in the glass with finer pores, the Knight shifts for two gallium isotopes are different. The findings in this chapter are compared with those in Chapter 4 and their full consistency was demonstrated, which evidenced the validity of the approaches used in the thesis.

All results presented in the thesis are unique. They are very significant for greater knowledge of the physics of two important for applications gallium alloys, which becomes quite complicated upon nanostructuring. The unambiguous findings of the liquid-liquid phase transition and the stabilization of β-Ga in the nanostructured binary alloy, of the remarkable slowdown of ionic mobility in the nanostructured triple alloy are very important for future uses of these alloys. The results of the thesis are presented in 6 publications in the high quality journals and were reported at conferences. The thesis is written clear and well structured.

Based on the high quality of research contents and writing skill, I claim that the thesis titled "NMR of Ga-In and Ga-In-Sn alloys under nanoconfinement" by Nefedov Denis Yurievich deserves to be awarded the degree of Candidate of Physical and Mathematical Sciences.

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