Liquid-liquid phase transition in metallic melts

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Introduction

Structural transformations in liquids pose severe challenges to condensed matter physics. Conclusive theoretical and experimental evidences of a phase transition between different structures in liquids (liquid-liquid phase transition (LLPT)) were obtained for water and few other liquids. However, the nature of LLPT is poorly understood and even its occurrence in many substances is in doubt. It was suggested that LLPT at ambient pressure takes place under strong supercooling. Therefore, LLPT in bulk is disguised by crystallization or vitrification processes. In contrast, liquids confined to nanoporous matrices are easy to supercool to temperatures much lower than the melting temperatures. This raises expectations that LLPT can be found in liquids under nanoconfinement.

Generally, they tried to reveal LLPT using various experimental techniques. Among them, neutron scattering and x-ray diffraction provided the most convincing evidences due to their sensitivity to the short-range order. However, solidification often masks the alterations in neutron and x-ray patterns induced by LLPT.

Here we review our recent results on LLPT in metallic melts using NMR [1-3]. It should be emphasized that applications of NMR to LLPT were not reported until these studies. Up to now only one other publication was devoted to LLPT investigations by NMR [4], as far as we know.

Experimental

For metallic substances NMR acts as a powerful experimental technique, which gives valuable information about the structure of metallic liquids through measurements of the shift in the resonance frequency, the Knight shift, and the nuclear spin-lattice relaxation rate caused by coupling with conduction electrons. Moreover, NMR allows studying properties of metallic melts confined to nanoporous templates, in which liquid metals and alloys can be strongly supercooled much below their melting temperatures. The nanostructured Ga metal, ternary Ga-In-Sn and binary Ga-In alloys were obtained by embedding the melts into opal matrices, porous glasses and porous alumina under pressure up to 10 kbar in Ioffe Institute RAS.

Studies were carried out using NMR Bruker Avance 400, Avance 500, and Avance 750 pulse spectrometers within a broad temperature range. We observed the variations with temperature of the Knight shift, integral intensity of the NMR lines, and relaxation rate for the isotopes ^{69}Ga, ^{71}Ga, and ^{115}In in the melts. At each target temperature the samples were stabilized for about 20 min. The rate of changing temperature did not excide 0.5 K/min to prevent the temperature overshoots. Note that at ambient conditions the confined gallium and gallium alloys were totally in the liquid state in agreement with their phase diagrams and the general reduction of the melting temperatures under nanoconfinement.

Results and discussion

At room and higher temperatures the NMR spectra for both gallium isotopes and indium in confined melts consisted of a single quite narrow Lorentzian line. Upon cooling and partial freezing the lines first moved to high frequency and then split into two signals at lower temperatures. Upon further cooling only one signal survived. Signals from solid gallium and gallium alloys were not observed because of strong broadening the NMR lines due to the Knight shift anisotropy and quadrupole coupling.

The evolution of the NMR spectra for the ^{71}Ga isotope observed at cooling from room temperature is illustrated in Fig. 1 for the Ga-In alloy under nanoconfinement.

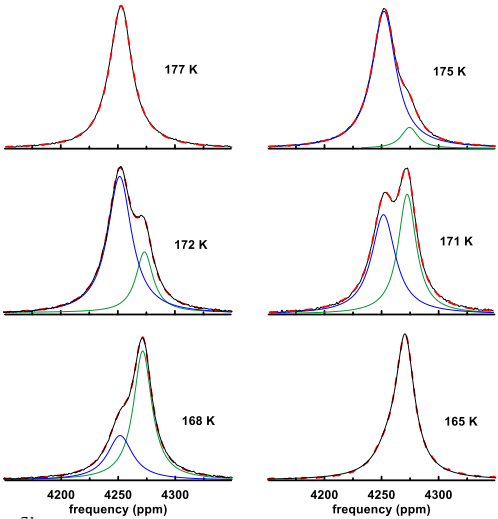

Figure 1. ^{71}Ga NMR lines in the binary Ga-In alloy confined to opal.

From the NMR spectra the Knight shift dependences on temperature were found. The emergence of a second ^{71}Ga NMR signals and the coexistence of two signals within some temperature ranges prove unambiguously the appearance of a new liquid state at supercooling and segregation of liquids into two parts.

NMR studies showed that LLPT is characterized by a large thermal hysteresis. The transition upon cooling is associated with the step-like change in the Knight shift which corresponds to the step-like changes in the structure of confined liquid. While at warming the phase transition is continuous in agreement with gradual changes in the Knight shift. This thermal asymmetry can arise in the case when the upper limit of the hysteresis loop coincides to the critical point of the boundary line between two liquid phases.

Acknowledgements

This work is supported by RSF (grant 21-72-20038). Part of measurements was carried out using the equipment of "Center for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics, SPbGU.

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