

Liquid-liquid phase transition in the nanoconfined Ga-In-Sn eutectic alloy

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Introduction

The study of properties of gallium and gallium alloys in bulk and in nanocomposites are of great interest for modern applied physics [1, 2]. Structural transformations and size effects in such systems attract the increasing attention of investigators. In this regard, liquid-liquid phase transition (LLPT) in gallium alloys is of special interest due to the ability of gallium to be supercooled. Embedding such liquids in nanoporous matrices allows alloys to be supercooled to temperatures much lower than the melting temperatures, which raises expectations that LLPT can be found in liquids under nanoconfinement.

The present study has been carried out by using NMR technique, which is a powerful instrument for obtaining information about the internal structure of metallic liquids and solids. The ⁷¹Ga and ¹¹⁵In NMR measurements were performed for a ternary eutectic Ga-In-Sn alloy, embedded into porous alumina, with a view to study LLPT.

Experiment

The ternary eutectic Ga-In-Sn alloy with a composition of 75 at.% Ga, 17 at. % In and 8 at.% Sn was embedded into porous alumina with mean diameter of pores 11 nm under pressure up to 10 kbar. At room temperature, the confined alloy was in the melted state, which is in agreement with its phase diagram [3].

Studies were carried out using a Bruker Avance 400 NMR pulse spectrometer at magnetic field 9.4 T within a temperature range from 200 to 300 K. We observed NMR signals for the ⁷¹Ga and ¹¹⁵In isotopes. The NMR spectra were obtained as Fourier transforms of free-induction decays after 90° pulses. The Knight shift for gallium and indium isotopes was referenced to NMR signals from a GaAs single crystal and a In(NO₃)₃ molar solution respectively.

Results

The relative ⁷¹Ga and ¹¹⁵In NMR signal intensity from liquid alloy during the cooling-heating cycle is presented in Fig. 1. One can see two phase transition steps of gallium under both freezing and melting which demonstrates the complex structure of solid Ga-In-Sn.

The Fig. 2 shows the evolution of the ⁷¹Ga NMR spectrum. It can be seen that spectrum at the temperature 257K demonstrates two lines. One can conclude from the width of the lines that these components correspond to a liquid phase. The relative integral intensity of the high-frequency component increases, whereas the relative integral intensity of the low-frequency component decreases upon cooling. The last one disappears at the temperature 249 K.

NMR studies revealed changes in behavior of the ternary Ga-In-Sn alloy in comparison with the bulk alloy. It has been found that the splitting of ⁷¹Ga NMR lines in two components is followed by the gradual transformation of low-frequency signal into the high-frequency one upon cooling. The NMR measurements proved that the line splitting occurs due to LLPT under nanoconfinement within a temperature range where the coexistence of two spectral components is seen.

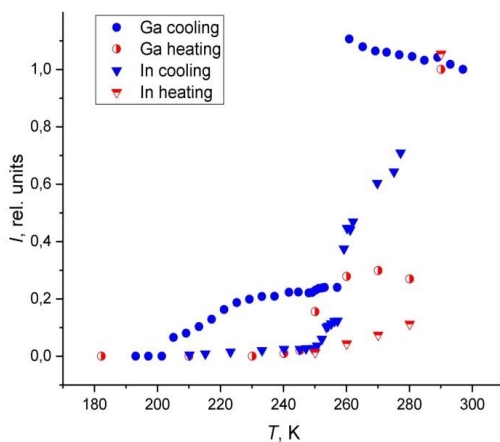


Figure 1. The temperature dependencies of the ^{71}Ga and ^{115}In signal relative integral intensities for the full freezing-melting cycle

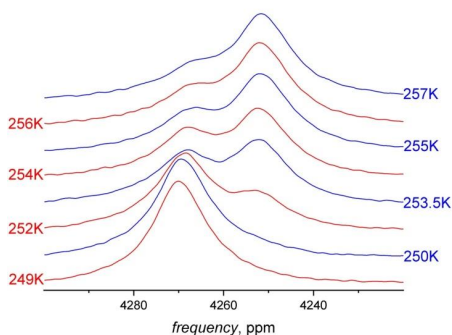


Figure 2. The evolution of the ^{71}Ga NMR spectrum

References

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