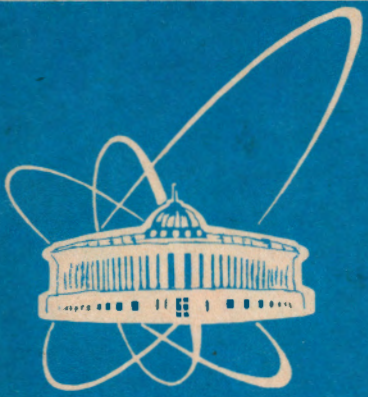

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FREEZING AND MELTING OF MERCURY IN POROUS GLASS

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1. INTRODUCTION

The physical properties of finite systems, especially of ultra-small particles, have been under extensive experimental and theoretical consideration for a long time. In recent years special attention has been paid to the investigation of substances confined in the nanometer pores of porous matrices.

Such of systems are interesting because confined materials can form either a system of isolated particles or some interconnected fractal cluster system with a specific nanostructure determined by the porous structure of the matrix, surface tension, wetting and other characteristics of the material and its interface with the matrix. One of the most interesting topics is the influence of the restricted geometry on phase transformation. Particularly, the effect of such restricted geometry on melting and freezing transformations were studied for a number of systems, such as cryogenic fluids [?] water [?, ?] and indium metal [?] in porous glasses using several experimental techniques including calorimetry, ultrasound measurements, X-ray and neutron diffraction, etc.

At the same time there is no direct experimental data about structural changes at the melting-freezing transition for metals within porous glasses, although this transition for metallic systems is very interesting since no metals wet the porous glass. Therefore, in some sense, they are more independent of the matrix than the wetting liquids. In the present paper we report the results of the neutron scattering study of freezing and melting transitions in metallic mercury embedded in porous glass, together with its calorimetric study.

2. EXPERIMENT

Porous silica glass has a well defined pore structure with a relatively narrow pore size distribution. Our samples had effective pore diameters of 7 nm with 80% of the pore diameters lying within ± 0.5 nm of the average diameter, as determined by mercury intrusion porosimetry. In fact, the process of mercury intrusion porosimetry was the process used to prepare our sample. After filling (when the maximum pressure of the liquid mercury was about 10 Kbars) the samples were kept at normal pressure and room temperature without any substantial weight loss. The neutron scattering measurements were repeated on the same sample several times at intervals of several months and the results were undistinguishable, verifying that the samples were stable at normal conditions.

All neutron scattering measurements were carried out at the DN-2 time-of-flight diffractometer installed at the IBR-2 pulsed reactor in Dubna. The sample was rod-shaped 4x4x20 mm in size and was placed in a specially made sample holder attached to the cold finger of a closed cycle helium refrigerator. The Hg content was about 23 vol%. The sample holder was made from copper and covered with 1 mm of Cd to remove spurious peaks. Such design provided a sample temperature inhomogeneity of less than 1K. He^3 detector with soller slit collimator and large vertical divergence was used. Such a configuration results in complete suppression of the scattering from the cryostat. At room temperature, no peaks were observed in the diffractogram. The calorimetric measurements were performed with use of ac technique [?], with a constantan electric heater and a Cu-constantan thermocouple mounted to the sample (for the calorimetric study we used a small part of the sample used for the neutron diffraction measurements).

3. RESULTS

As already mentioned, no peaks were observed in the diffraction pattern at room temperature (Fig.1a) and the amount of Hg in the sample was too small to study $S(Q)$ for liquid Hg. At low temperatures Bragg peaks appeared (Fig.1b), corresponding to the trigonal structure of bulk mercury. The peaks were essentially wider than the experimental resolution as can be easily seen in Fig.2b where the temperature dependence of the width of the (210) with $d_{hkl} \approx 1.37\AA$ peak for Hg in glass and the width of the Bragg peak with nearly the same d for a standard Al_2O_3 sample are shown.

In the first approximation one can consider Hg in glass as a conglomerate of small unconnected particles. In this case it is possible to attribute the observed widening to the final size effect. The experimental results after resolution deconvolution correspond to a particle size of about 7 nm in reasonable agreement with the porosimetry results. In principle an analysis of the line shapes of the Bragg peaks should enable us to get valuable information about the existence and nanostructure of the fractal cluster mentioned above. But in the present experiment both resolution and detector statistics were too low for such an analysis. In the future we are going to perform separate line shape measurements.

We have analyzed the temperature dependence of the intensity and the width of the observed Bragg peaks. The sample was heated (or cooled) to the required temperature and kept at this temperature for 20 min to provide temperature homogeneity. Measurement at each temperature took 3 hr to reach satisfactory statistics. So in the hysteresis region, the effective cooling/heating rate was about 0.5deg/hour and the obtained results could be considered as static, neglecting the kinetics of the transition. In Figs. 2 and 3a the temperature dependence of the integrated intensity of (210) peak is shown. When sample is heated from 80K, the intensity first stays nearly temperature independent. Then at 150K, it starts decreasing and at 222K almost instantly drops and disappears. Upon cooling, the diffraction peaks reappear only at 206K. One should mention that the width of the Bragg peaks does not depend on temperature, within statistical errors. This fact does not allow us to explain the broadening of the freezing and melting transitions by the dispersion of the pores sizes.

The neutron results are in quite good agreement with the calorimetric data as one can see from Fig.3a, where the relative values of heat capacity during the melting and freezing transitions are shown. The main features of these data are the broadening of the transition, the existence of the large thermal hysteresis between melting and freezing and the essentially different behavior on heating and cooling (the heat capacity peak for melting is much stronger than for freezing). We may denote that such behavior of the heat capacity is similar to that of melting and freezing of liquid Ne, Ar, O_2 in porous glass [?]. This similarity seems interesting because really we have a different situation here with liquid-matrix interaction (Ne, Ar and O_2 do wet the porous glass and Hg does not).

4. DISCUSSION

Neutron measurement gives us additional data about the amount of the solid phase and about the size of the solid particles that could not be obtained by macroscopic methods. From these data we can affirm that some assumptions [?] about the nature of the hysteresis are not valid, at least in our case, and this is our main result. In [1] it was

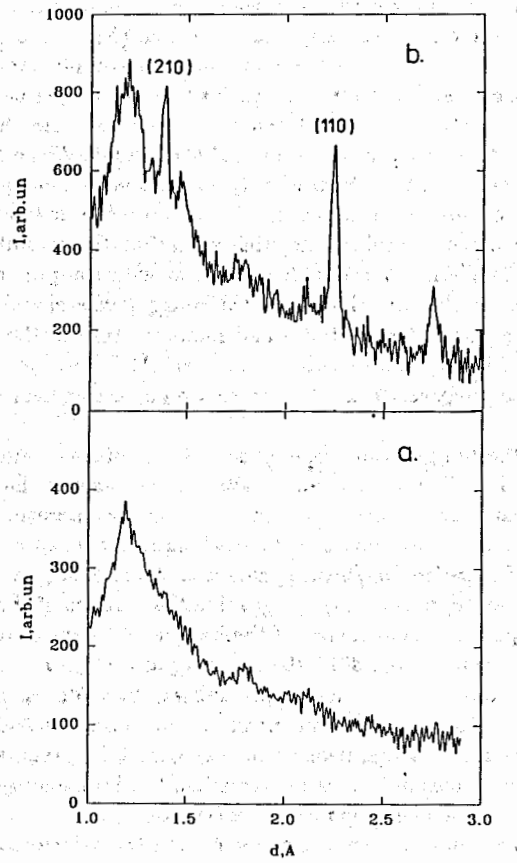

Figure 1: Diffraction pattern for Hg in porous glass, a - room temperature, b - 80K.

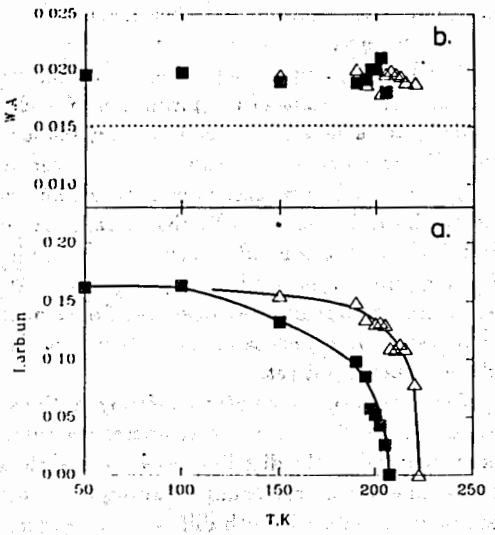

Figure 2: Temperature dependencies of a - (210) Bragg peak integrated intensity and b - (210) peak linewidth (the instrument resolution is shown by the dotted line, determined from the diffractogram of standard Al_2O_3): ■ - at cooling; △ - at heating.

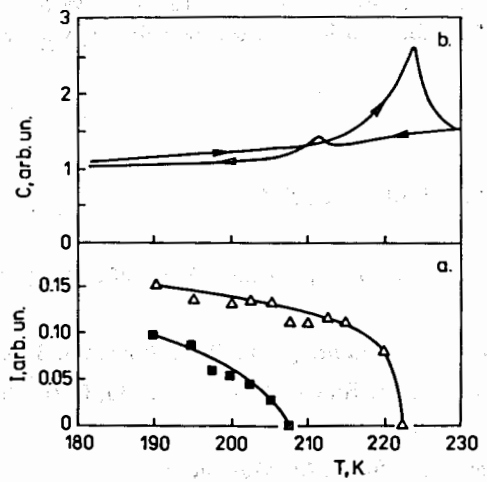

Figure 3: Part of the temperature dependencies of the integrated intensity of the (210) Bragg peak - a, and relative heat capacity - b.

assumed, that the solid phase within the porous glass, after nucleation, can expand along the pore forming cylindrical frozen regions or solid clusters could appear independently in neighboring pores but with further cooling they touch and stick together forming a coherent cluster of larger size. Some proof of the formation of such relatively large solid particles were obtained [?] by neutron scattering measurements for oxygen and deuterium in porous glasses. It was shown that there exists a frozen region 40-70 nm in size that is essentially larger than the pore size. Our data demonstrate (see Fig.2b) that the width of the Bragg peaks and, consequently, the average size of solid clusters, is practically temperature independent and nearly exactly corresponds to the average pore size (about 7nm). So there are no phase expansion processes. At the same time the large hysteresis between melting and freezing is observed. So probably in the case of wetting liquids the growth of the frozen regions is not the only reason for such hysteresis and its origin is not completely understood yet.

The same could be said about the broadening of the melting and freezing transitions. From the porosimetry data and from the fact of the temperature independence of the neutron line widths, we can estimate that the distribution of sizes of the frozen particles is quite narrow and could not explain such broadening (if we supposed that there are the particles with different sizes and consequently with different melting and freezing temperature). The estimation of fluctuation broadening for the first order melting/freezing transition [?] gives, for the 70 nm particles, a value of only about 0.1K and therefore the fluctuations also are not the reason for the observed broadening.

Finally, it is interesting to mention that the experimental data for the temperature dependencies of the Bragg peak integrated intensities (and respectively, the amount of the solid phase in porous glass) follow $(T_F - T)^{0.5}$ with $T_F = 206K$ for freezing and $(T_M - T)^{0.25}$ with $T_M = 222K$ for melting, and so, look like typical order parameter temperature dependencies.

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