Annotation

for dissertation for the degree "Doctor of Philosophy» (Phd),
specialty 6D072300 - Technical Physics

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Research of polymorphic and polyamorphous transformations in water and ethanol cryovacuum condensates and their weak solutions in nitrogen cryomatrix

Relevance of the research

The establishment of thr unique relationship between the conditions of formation and the properties of the solid phase id one of the important problems in modern condensed matter physics. Its decision will contribute to a major breakthrough in the creation of materials with desired properties. Like any scientific and technological problem, this approach involves the need to solve a wide range of fundamental issues. The basis of success in this direction is a performance of the comprehensive model tests when the test substance is not only important from a practical point of view, but in itself has interesting physical and chemical properties. Hydrogen bond substances, in which interactions due to the presence of intermolecular hydrogen bonding are important besides the van der Waals forces, can be fully attributed to these objects. Water (heavy water) and ethanol are the most prominent representatives of such substances.

The solid phase of water, perhaps, has a variety of structural modifications of the solid phase - polymorphs more than any other solid. This structural diversity of the solid phase of water is largely due to the emergence of specific interactions between its molecules in the condensed state. Today we know 13 (some say 14) crystalline modifications of ice. All they occupy certain areas of the phase diagram. Changes in the symmetry structure of ice occurre at phase transitions, which are accompanied by changes in the angular and linear dimensions of the lattice, sometimes coordination number changes too. Solid ethanol also has unique properties, showing amorphous, crystalline and liquid properties at narrow range of temperatures.

Current status of the research of water ice and ethanol polyamorphous and polymorphic states implies a huge array of experimental and computational and theoretical data, often in a specific conflict with each other. Common is clear recognition of the fact that the properties of the resulting ice is rigidly dependent on the conditions of their formation and existence, such as substrate temperature and morphology, rate of condensation and heating of the samples, the state of vapor - directional condensation or growth of a spatially homogeneous gas phase, film thickness. However, much less attention is paid to the study of the formation and properties of the crystalline and amorphous states of water and ethanol produced from the gas phase. It is known that condensation at low temperatures leads to the formation of amorphous solid water and amorphous ethanol with a

very large surface area, which plays a crucial role in the mass transfer process in the Universe.

An objective, thus, may be formulated as a detailed study of the formation and properties of cryovacuum condensates of molecules, which are bounded by hydrogen bond, on water and ethanol example. The study of thermally structural phase transitions in water and ethanol cryocondensates for the purpose of determination of temperature ranges of the test substances different structural states existence is an important part of the research.

A significant part of the investigations in this study is focused on the study of water and ethanol, which are immobilized in cryomatrixes in the process of co-condensation, in particular, in nitrogen cryomatrix. Thus studying of molecules of ethanol or water in a matrix wasn't set as the purpose, and research of substance molecules clustering processes was supposed during a co-condensation with matrix gas. Also we discussed the question of what occurred with water and ethanol, immobilized at low temperatures in the nitrogen matrix, after the nitrogen evaporates at process of temperature increase. What are the properties of a new phase, which forms on a substrate.

Object of the research are thin films of cryovacuum condensates of water, heavy water and ethanol, which formed in the temperature range from T = 12 K to T = 180 K at condensation pressures of the order of 10^{-5} Torr.

To achieve this goal the following tasks were solved:

1. To study the influence of the condensation temperature in the range from T = 12 to T = 180 K, on the formation and properties of water, heavy water and ethanol cryocondensates;
2. To study the effect of water and ethanol concentration in nitrogen cryomatrix on structural-phase transitions parameters;
3. To study the effect of cryomatrix temperature on the relaxation processes of structural ethanol elements in nitrogen cryomatrix;
4. To investigate the processes of formation and properties of water heavy water and ethanol nano-objects in nitrogen cryomatrix;
5. To study the relaxation processes near the temperature of structural phase transitions.

The subjects of the research are:

1. Thermally structural and phase transformations in cryocondensed water, heavy water and ethanol film;
2. Water, heavy water and ethanol nanoobjects in nitrogen and argon cryomatrix.

Research methods. To achieve the research objectives, the following experimental methods were used:

Laser interferometric method for measuring the condensation rate, the thickness and refractive index of thin films of solid solutions of nitrogen and ethanol;

IR spectrometry analysis of the processes of structural and phase transformations in cryovacuum condensed water, heavy water and ethanol, as well as their weak solid solutions in nitrogen and argon;

Thermodesorption method for determining the parameters of structural phase transitions in the samples.

Scientific novelty

1. Thermally stimulated transformations in thin films of cryovacuum condensed water studied. In the interval of temperatures between 16K to 160K found of amorphous states of cryovacuum condensed: hda-amorphys ice with a high density (16K-40K), lda-amorphys ice with low density (40-140K), ra-amorphys ice with the content of the metastable cubic phase (140-160KDetermine the value of the glass transition temperature for water condensates cryovacuum, $T_g = 137 \pm 2$ K.

2. Thermally stimulated transformations in thin films of cryovacuum condensed ethanol studied. The existence of different states of ethanol: ASE-amorphous solid ethanol (16K-80K); SG-structural glass (80K-98K); SCL-super cooled liquid ethanol (98K-104K); PC plastic crystal (106K-130K). Determine the value of the glass transition temperature for vacuum cryocondensated ethanol. Its value is $Tg = 97 \pm 2$ K.

3. The method of isolation cryomatrix shown that during kriokondensation both water and ethanol cryomatrix nitrogen form nanoscale objects of different composition. Based on a comparing with quantum-chemical calculations of other authors suggest that nano-objects are clusters of water and ethanol in the form of dimers, trimers, quatromers, pentamers, hexamers, and polymers.

4. Based on the data obtained by cryomatrix insulation method is assumed that during cryo condensation pure components of water and ethanol at an intermediate stage in the process adsorb layer formation of clusters having a short-range order, similar to the liquid state water or ethanol. This explains the fact that the values of glass transition temperature Tg cryocondensates water and ethanol coincide with the corresponding values for the samples obtained by other authors directly from the liquid phase by the method of ultrafast cooling.

The provisions for the thesis defense

1 Depending on the temperature cryoprecipitated cryovacuum condensates of water exist in various crystalline and amorphous states: hda-amorphous ice high density, lda-low density amorphous ice, ra-amorphous ice with a content of metastable cubic phase, Ic-cubic ice; Ih-hexagonal ice. During the heating occurs successive transformations less stable states in a more stable state. In the vicinity of the temperature T = 137 K structural transformations are carried out through an intermediate metastable liquid phase-SCL.

2 Depending on the temperature and the thermodynamic cryoprecipitated prehistory cryovacuum ethanol condensates form various amorphous and crystalline states: ASE- amorphous solid ethanol; SG-structural glass; PC-plastic crystal; MS-monoclinic crystal; SCL-super cooled liquid ethanol. Moving away from the glassy state to a plastic crystal is carried out in the vicinity of T = 97 K via an intermediate metastable liquid phase ethanol.

3 Process of cryocondensation pure components of water and ethanol at an intermediate stage in adsorb layer accompanied by the formation of clusters having a short-range order, similar to the liquid state water or ethanol. Thus argues that the phase transition gas-solid through intermediate metastable liquid state. This explains the fact that the values of glass transition temperature Tg cryocondensates water and ethanol coincide with the corresponding values for the samples obtained by other authors directly from the liquid phase by the method of ultrafast cooling.

Publications. Total on the dissertation topic 23 publications are published in collaboration, of which 3 articles are published in journals, which are recommended by the Committee for Control of Education and Science of RK; 7 articles are published in foreign journals with non-zero impact factor, that is the part of the ThomsonReuters and Scopus database; 13 abstracts and papers are in the proceedings of international conferences.

Structure and scope of the thesis. The work consists of an introduction, three chapters, conclusion and list of references. It is stated on 134 pages, contains 69 pictures and a list of references of the 99 items.