ABSTRACT

of the dissertation for the degree of Philosophy Doctor (PhD) in specialty "6D072300 - Technical Physics"

SHINBAYEVA AINURA KADYRZHANOVNA

«THE EFFECT OF POLYMORPHIC TRANSFORMATIONS ON THE OPTICAL CHARACTERISTICS OF ORGANIC MOLECULES CRYOVACUUM CONDENSATES»

Relevance of research. One of the important problems of modern condensed matter physics is the study of polymorphic transformations, which are mainly accompanied by the formation of metastable states. The stability of these states is largely determined by the thermodynamic intensive parameters of phase formation and the physical and chemical properties of the substance's molecules.

From a fundamental point of view, cryocrystals are interesting for many reasons. One of them is the simplicity of the crystal structure of the arrangement of molecules in the lattice close to the theoretical model. Cryocrystals include crystals of solidified inert gases, in which the Van der Waals forces bind atoms and molecular cryocrystals (N_2, CO, CH_4, etc.) rather than molecules.

Thus, considering intramolecular phenomena leads to the fact that the transition from single molecules to a gaseous environ to condensed matter also changes the optical characteristics along this path. At the same time, a clear control of the external parameters of cryoprecipitation and the purity of the gas phase allows one to obtain and study isolated forms of polymorphic species of these substances.

The fact that it is possible to precisely control cryoprecipitation conditions, such as the condensation temperature and the rate of cryocrystal formation, makes it possible to establish an unambiguous correlation between the properties of cryocondensates and the conditions for their formation. This, in turn, allows one to experimentally verify various theoretical models of the processes of formation and modification of condensed objects with a disordered structure. However, often low activation energies between the various structural states of thin films of cryocondensates limit the use of analytical methods that can exert comparable external influences on the test sample and, thereby, stimulate changes in the structure of cryofilms. This can lead to an erroneous interpretation of the results obtained in the temperature ranges of the existence of polymorphic states of the studied objects. Therefore, the methods of low-energy optical characterization of samples are the most suitable way to study the properties of a substance at low temperatures. As a rule, in practice, by the optical method, determining changes in the electromagnetic wave after interaction with an object that has a combination of structural properties, most often solve a direct problem. In this case, the main thing is to solve the inverse problem - to determine the structural-phase properties of the cryocondensate based on these changes, i.e. experimental data obtained by the optical method. Comparing the changes in the values of the fundamental characteristic absorption bands in the

spectra of the studied object with its polymorphic states, which are formed in accordance with the conditions of their condensation, we can judge the structural-phase properties of these states and their influence on the optical characteristics.

The aim of the dissertation investigation

The main purpose of the dissertation work is revealing the effect of polymorphic transformations on the optical characteristics of cryovacuum condensates of methane, methanol and freon 134a, as well as determining the temperature boundaries of the existence of their structural-phase states.

The implementation of the **goal** envisaged the solution of the following tasks:

1. To study the influence of the deposition temperature on the vibrational spectra of cryocondensates of freon 134a and methanol;
2. To determine the temperature limits of the existence of various structural-phase states of cryovacuum condensates of freon 134a and methanol;
3. To study the effect of changes in sample temperature on the vibrational spectra of Freon 134a and methanol molecules;
4. To study the dependence of the density and refractive index of cryovacuum condensates in various structural states on the cryoprecipitation temperature;
5. To reveal the effect of inert gas impurities on the optical properties of methane curvacuum condensates.

The object of the study is thin films of cryovacuum condensates of organic molecules formed on a cooled substrate in the temperature range from 16 to 130 K and pressures from 10^{-5} to 10^{-2} Torr, leading to a change in the reflectance of the substrate in the IR range of the spectrum and laser wavelength $\lambda = 403$ nm.

The subject of research is the thermophysical and optical properties of the cryocondensed phases of organic substances.

Methodological base of the study

To achieve the goal of research, the following experimental methods were used:

laser-interferometric method for measuring the condensation rate, thickness and refractive index of cryocondensed thin films of methane, freon 134a, methanol and ethanol;

IR spectrometric method for the analysis of polymorphic transformations in cryocondensates of methane, freon 134a, methanol;

thermal desorption method for determining the parameters of structural-phase transformations in the studied samples.

The main provisions to be defended:

1. The high-density amorphous state of methanol cryocondensate exists in the range 16–40 K. At T = 40 K, the sample passes into a low-density amorphous state, in the range from 60 K to 80 K, into an amorphous form equivalent to the glassy state obtained during ultrafast cooling from the liquid phase.
2. The cryocondensates of Freon 134a in the range 16–60 K are in an amorphous state with varying degrees of amorphization, and at 72 K occurs transition from the amorphous glassy state to the supercooled liquid phase with its subsequent crystallization to the state of a plastic crystal, after which the subsequent transition to a crystalline state with a monoclinic lattice in the temperature range 78–80 K;

3. Based on the change in optical characteristics, the glass transition temperatures of the cryocondensates of methanol and Freon 134a were determined Tg = 102.6 K and T_g = 72 K, respectively;

4. The phase transition from the orientationally disordered α phase to the partially ordered β phase and vice versa in methane cryocondensates changes the nature of the interaction of radiation with methane molecules, which leads to a change in the refractive index and density of the samples, and their dependence on temperature undergoes a break in the vicinity of the phase temperature transition;

5. The presence of a 5% impurity of argon or nitrogen in methane cryocondensates violates the reversibility of the α-β transition, demonstrating the relationship between the concentration of components and the position of the absorption band of deformation vibrations.

The scientific novelty of the thesis is that by the methods of low-temperature optical studies, the relationship between polymorphic transformations and optical characteristics in the cryovacuum condensates of methane, freon 134a and methanol is revealed. At the same time, the following new results were obtained:

1. During the condensation of organic molecules from the gas phase, an amorphous film of varying degrees of density is formed depending on the condensation temperature;

2. For the first time, based on the registration of changes in optical characteristics, the glass transition temperatures of cryocondensates of methanol and freon 134a were determined;

3. The splitting of the absorption band of the Freon 134a molecule corresponding to vibrations of the ν_{15} mode, which is related to the symmetry type A`, was experimentally discovered.

4. Based on optical methods, the dependence of the density and refractive index of cryovacuum condensates of methane on the deposition temperature is determined, which is associated with the formation of various polymorphic states;

5. The optical characteristics of cryovacuum condensates of methane mixtures with inert gases were measured, and the presence of the α-β transition depends on the concentration of impurities.

Scientific and practical significance of the study

The results of this study, the development and justification of experimental methods, allow one to obtain fundamental results in classical low-temperature solid state physics, in particular, to identify the relationship between the conditions of condensation of the solid phase and the properties of the resulting films, which are unique objects of study of the mechanisms of structural-phase transformations in solid states.

The results of this thesis can be the basis for a larger work on creating a verification database of the optical characteristics of carbon-containing substances for the study of astrophysical and astrometric measurements of near and far space.

In the course of the work, a method of IR spectroscopy was developed, based on the analysis of thermostimulated changes in the vibrational spectra of thin films in the frequency ranges of characteristic vibrations of molecules at a fixed frequency.

The results of the work were used by “Regtormed” LLP to develop a technical solution for creating a system for the separation of drug components.

The obtained research results are of practical importance in the development of modern cryogenic technologies, requiring knowledge of the thermophysical and optical characteristics of the working surfaces of cryogenic-vacuum technological equipment, during the operation of which the formation of cryocondensed layers is carried out.

Personal contribution of the author

The personal contribution of the author to the works carried out in collaboration is the main for all stages of the work and consists in choosing a fundamental scientific problem and ways to solve it, directly performing the bulk of experimental and theoretical research, writing and editing articles and abstracts.

Testing the studies

According to the results of the dissertation, 17 works were published, there are:

Seven articles in international journals of the Thomson Reuters base:

1. A. Shinbayeva et al. Structure transformations in thin films of CF3-CFH2 cryodeposites. Is there a glass transition and what is the value of Tg? // Applied Surface Science. – 2018. – Vol. 446. – P. 196–200. (IF-5.155)

2. А. Шинбаева и др. ИК исследования термостимулированных структурно-фазовых трансформаций в криовакуумных конденсатах фреона 134a // Low Temperature Physics/Fizika Nizkikh Temperatur. – 2018. – Vol. 44 (8). P. 1062–1072. (IF-0.825)

3. А. Шинбаева и др. ИК спектрометрические исследования криовакуумных конденсатов метанола // Low Temperature Physics/Fizika Nizkikh Temperatur. – 2019. – Vol. 45 (4). P. 511-522. (IF-0. 825)

4. A. Shinbayeva et al. IR studies of the spin–nuclear conversion in the vicinity of *α-β-* transition in cryodeposited methane films. // J Low Temp Phys. – 2017. – Vol.187 (5). – P. 742–748. (IF-1.491)

5. A. Shinbayeva et al. Polarizability of methane deposits. // J Low Temp Phys. – 2017. – Vol.187(5). – P. 749–756. (IF-1.300)

6. A. Shinbayeva et al. Refractive indices and density of cryovacuum deposited thin films of methane in the vicinity of the α-β-transition temperature. // Low Temperature Physics/Fizika Nizkikh Temperatur. – 2017. – Vol. 43 (6). P. 909–913. (IF-0. 825)

7. A. Shinbayeva at al. Refractive indices vs deposition temperature of thin films of ethanol, methane and nitrous oxide in the vicinity of their phase transition temperatures. // Low Temperature Physics/Fizika Nizkikh Temperatur. – 2017. – Vol. 43 (10). – P. 1521–1524 (IF-0. 825)

Four articles recommended by the Committee for Supervision of Education and Science:

1. Шинбаева А. К. и др. ИК-спектрометрические исследования стеклоперехода фреона CF3-CFH2 // Вестник КазНУ им Аль – Фараби. Серия физическая. – 2018. – №1(64). – С. 39 – 47.

2. Шинбаева А. К. и др. ИК-спектрометрический метод регистрации структурно-фазовых превращений в тонких пленках криовакуумных конденсатов // Вестник КазНУ им Аль – Фараби. Серия физическая. – 2018. – №1(64). – С. 48 – 53.

3. Шинбаева А. К. и др. Коэффициенты преломления, плотность и поляризуемость криовакуумных конденсатов метана // Вестник КазНУ им Аль – Фараби. Серия физическая. – 2017. – №1(60). – С. 28 – 37.

4. Шинбаева А. К. и др. Плотность тонких пленок криовакуумных конденсатов метана // Вестник КазНУ им Аль – Фараби. Серия физическая. – 2017. – №3(62). – С. 10 – 16.

Материалы диссертационной работы докладывались на следующих международных конференциях:

1. A. Shinbayeva et al. Structure transformations in thin films of CF3-CFH2 cryodeposites. Is there a glass transition and what is the value of Tg? //15th International Conference on the Physics of Non-Crystalline Solids & 14th European Society of Glass Conference, Saint-Malo, France. – 2018. – P.133-134.

2. International Conference on Strongly Correlated Electron Systems (SCES), Prague, Czech Republic, 2017

3. A. Shinbayeva et al. 8th International Discussion Meeting on Relaxations in Complex Systems, Wisla, Poland. – 2017. – P.447

4. 12th International Conference on Surfaces, Coatings and Nanostructured Materials (NANOSMAT), Paris, France, 2017.

5. 9th International Scientific Conference «Modern Achievements of Physics and Fundamental Physical Education», Almaty, Kazakhstan, 2016.

6. Шинбаева А. К. и др. ИК-спектрометрические исследования криовакуумных конденсатов метана и тетрахлорометана // V международная научная конференция «Современные проблемы физики конденсированного состояния, нанотехнологии и наноматериалов (Сарсембиновские чтения), Алматы, Казахстан, 2018.

Volume and structure of the dissertation

The dissertation contains a list of notation and abbreviations, introduction, the main part of five sections, conclusion, list of references and four appendices. The dissertation is 123 pages of typewritten text, including 52 drawings, and 143 references.