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Optical and structure characteristics of vacuum-deposited layers

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We report results of a complex study of growth rates, refractive indexes, and structure of real cryocrystals of nitrous oxide as well as light and heavy water. The corresponding experimental setup and the relevant experimental procedures are described. We demonstrate possibilities of the available experiment-and-computing complex for the purposes of studying growth kinetics, thermal properties, and structure-morphologic characteristics of real cryocrystal quench-condensed deposits. A structure transformation from the low-temperature highly amorphized state to the *Pa*3 structure has been observed at a temperature near 40 K in nitrogen monoxide. The spectrum of spontaneous luminescence bursts of freshly prepared N_2O samples has been measured. It consists of two main bands in the red and blue domains of the visible spectral range. Existence of three structural modifications of vacuum condensed water deposits has been confirmed and their temperature boundaries of existence revised. Our results on heavy water cryocondensates allowed us to infer ultrapolymorphism in this solid.

Introduction

Traditionally, the main objective of an experimental investigation on a cryocrystal is to obtain information on its properties in the state with the exactly known and maximally stable structure. Therefore, much effort is spent to fight and to get rid of the various unstable or metastable states, which inevitably form in the cryocrystal samples prepared in situ. At the very least, when such states are short-lived, they are disregarded. However, of late the demands of many application, research, and industrial tasks have invoked a necessity to study the cryocrystals in their metastable states, whose very instability is controlled by the conditions under which the samples are prepared. Of course, as usual, the relevant fundamental physical facets turned out to be of considerable interest in their own right.

At present, the field of research of thermal and structure properties of cryocrystals versus the preparation procedure parameters (in particular, the depositioh temperature) is still expanding. The work is mostly of application character, related to the processes of heat and mass transfer in space conditions and in various cryogenic apparatuses. For instance, what is of acute importance for space station applications is to study the process of gas condensation on surfaces cooled down to liquid-helium temperature, or specifically, on cooled radiation detectors, on the elements of optical communication systems, such as photo sensors, mirrors etc. The solid gas films that condense on these surfaces considerably affect their operational characteristics. One of the way to study these phenomena is to reproduce space environment in a laboratory testing setup.

The most important factor that controls the structural and morphologic state of a condensate is the deposition temperature. In this connection, of special importance is to investigate into the temperature dependence of the structure-morphologic characteristics of real cryocrystals. Regretfully, examples of such direct structure studies are scarce. Usually the information about structure or/and morphology of vacuum-deposited as-prepared layers is inferred indirectly from various physical characteristics such as:

– optical characteristics (reflectance, refractive index, optical density) in the infrared and visible ranges (see, e.g., [1–3]);

– thermal characteristics (heat capacity, thermal conductance, density, condensation index). The basic results concerning these topics for cryocrystals can be found in Refs. 4–6;

– various properties of cryocrystal condensates as cryopumps [7,8].

Obviously, when based on indirect data, information concerning the temperature-controlled structure-morphologic variations in real cryocrystals is only of qualitative character and cannot constitute a basis for unambiguous conclusions about specific structure transitions. However, considering the long time needed to prepare and the complexity of the procedures involved in direct structure studies, a quite reasonable way of obtaining express preliminary information about cryocrystals seems to be the investigation of the variations with temperature of their structure-controlled characteristics. Some of them might very well be those listed above. An ultimate aim of this kind could have been the determination of special points and the corresponding recommendations for more detailed structure studies.

Notwithstanding the bare fact that the studies carried out in the Cryophysics Laboratory of the Kazak State University during the last 10 or 15 years were at the start predominantly of applied character, the methods employed to obtain information of the kind specified turned out to be quite acceptable, when the direction of the investigations has been gradually changed towards the fundamental physics of cryocrystals, in particular, real cryocrystals. This concerns the data on deposition rates, densities, refractive index, and reflectivity of cryocrystals as functions of the condensation temperature. Interpretation of these data allows us to make conclusions as to the variations of both structure and morphology in the layers under study.

Apparatus

Obviously, obtaining a reliable dependence of the above properties on the preparation conditions requires a complex investigation of these properties within a single series of experiments. This explains the design of the experimental installation, which is essentially a multi-purpose vacuum spectrometer. A diagram of this installation is shown in Fig. 1.

The vertical view of the installation is shown in Fig. 2. The progress of the gas-solid interface during cryodeposition leads to changes in the interference pattern formed by the laser beams reflected from the substrate and from the progressing interface. Carrying out measurements of this kind for two different laser beam incidence angles makes it possible to close the relevant set

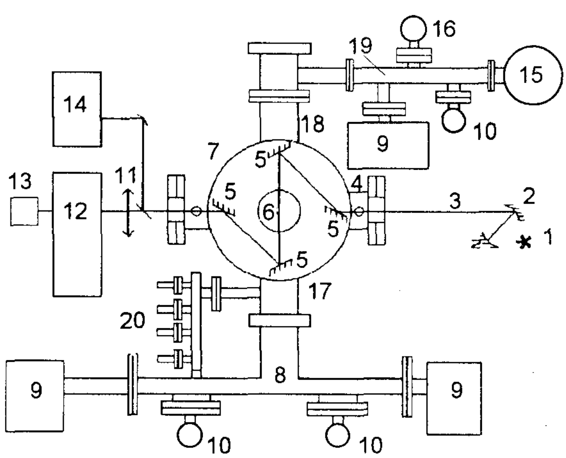

Fig. 1. Experimental setup (top view): *1* radiation source; *2* parabolic mirror; *3* radiation path; *4* chamber window; *5* mirror reflectors; *6* deposition surface; *7* chamber wall; *8* vacuum system; *9* magneto-discharge NORD pumps; *10* zeolite cryopumps; *11* condenser; *12* monochromator; *13* optical pickup; *14* gate chamber; *15, 16* mass spectrometer; *17, 18* connecting ducts; *19* mass spectrometer unit; *20* filling system.

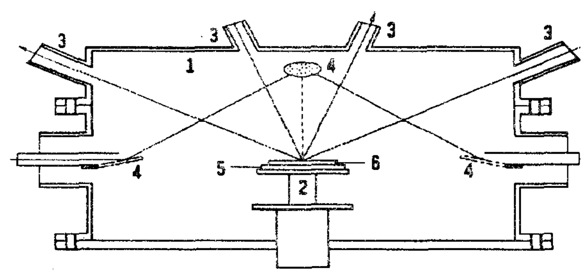

Fig. 2. Working chamber (vertical section); *1* chamber walls; *2* micro-cryogenic machine; *3* to lasers of interferometer; *4* light guides; *5* cryostat; *6* substrate.

of equations and to evaluate the linear growth rate V and the refractive index n of the cryocondensate. The working parameters of the installation are as follows: gas pressure in the chamber $10^{-6}-10^{-5}$ Pa; substrate temperature 10–200 K; wavelength range 0.2 to 20.0 mcm.

To record on line the dynamically varying visible-range spectral characteristics of the layers being condensed as well as to investigate into the spontaneous optical emission during condensation of nitrogen monoxide layers, which has been found earlier [9], we have manufactured a special auxiliary device (Fig. 3) to supplement the above-described complex. This device, operating on the basis of a multi-channel analyzer of optical spectra, allows studies to be carried out in the range of wavelengths 360–380 nm with a time resolution of 50 mcs.

The basic module of this installation is an optical bench with 1024 pickups per 24 mm of its length. A

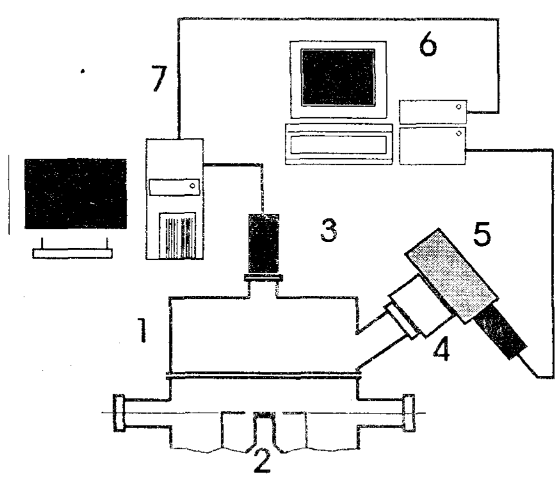

Fig. 3. Multi-channel analyzer of optical spectra: *1* vacuum chamber; *2* column of microcryogenic machine with sample; *3* photomultiplier; *4* quartz objective; *5* analyzer chamber; *6* eight-digit computer to control analyzer; *7* IBM PC.

two-stage image brightness amplifier ensures pickup sensitivity in every channel at a level of 1 photon/count. The relevant software enables recording spectra of pulsed-periodic processes, triggered from the analyzer itself with frequencies of 5 and 10 Hz, as well as spectra of continuous and quasi-continuous sources in the on-line and accumulation regimes of observation during time intervals from 10 ms to tens of seconds.

To obtain integrated characteristics, we have designed a special input card as well as the relevant program for reading signal from a wide-band photoamplifier into an IBM-compatible computer during the entire period of existence of the emission, with a resolution below 50 mcs. The available analog digitizer allows reading out signals with a quantum of 7 mcs. These parameters enable sufficiently accurate description of the shape of the burst signals and their subsequent analysis. On the whole, the above-described complex allows studying the growth kinetics of real cryocrystals as well as various properties of quench condensed layers. In this paper we report the results obtained in studies of the growth rate and refractive indexes of various cryocrystals versus the deposition temperature as well as the corresponding correlating data on IR reflectivity of thin layers.

Results

Nitrogen monoxide. One of the bright examples that justify the above approaches to the investigation into the properties of real cryocrystals is the results, presented below, which have been obtained in the process of accumulation of the data pertaining to the laws of formation and the properties of the nitrogen monoxide cryocrystals. Initially planned and performed measurements of growth rates and refractive indexes of N_2O condensates gave indications that there is a temperature range where the behavior of the quantities studied reveals certain irregularities (Fig. 4). In addition, the measured IR reflectances of nitrogen monoxide films deposited on a metal mirror also exhibited appreciable shifts of the absorption bands in the range that embraces the resonance molecular frequencies [10]. By measuring the reflectance at a fixed frequency during warmup of a 5 mcm thick layer condensed on $T = 10$ K (Fig. 4), we were able to determine the transition temperature more accurately. As one can see, the irregularities in the behavior of the growth rate and the reflectance are well correlated with the variations of the film's spectral characteristics, so that this combined information gives us ground to infer a structure-morphologic transformation in the nitrogen monoxide cryocrystal around $T = 40$ K. More detailed measurements of reflectivity spectra at different frequencies (Fig. 5) corroborated the above assumption of a transformation present and served as a stimulus to carry out direct structure studies at more or less known experimental parameters. The relevant electron diffraction studies have been performed in cooperation with the Verkin Low Temperature Physics Institute in Kharkov. We have found [11] that around 40 K a structure transformation occurs from a strongly amorphous phase (existing at T from 10 to 40 K) to the well known $Pa3$ structure inherent in bulk N_2O (at temperatures above 40 K).

The results obtained for N_2O could have looked rather unexpected, if not for the bulk of experimental data that have been obtained during the last years and that give indications that solid nitrogen monoxide is not so simple a substance as it might seem. In particular, what we have in mind is the earlier found effect of spontaneous optical emission (cryoemission)

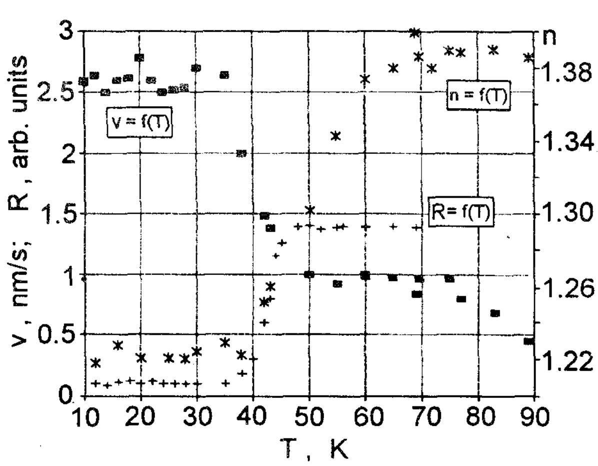

Fig. 4. The growth rate v (■), and the refractive index n (*) of a nitrogen monoxide cryocondensate versus the condensation temperature at a gas pressure of $P = 10^{-5}$ Torr. R (+) is the reflectivity (in arbitrary units) of the film at a frequency of 590 cm^{-1} during warmup. For details of the procedure of measuring growth rates v and refractive indexes n see Sec. Apparatus.

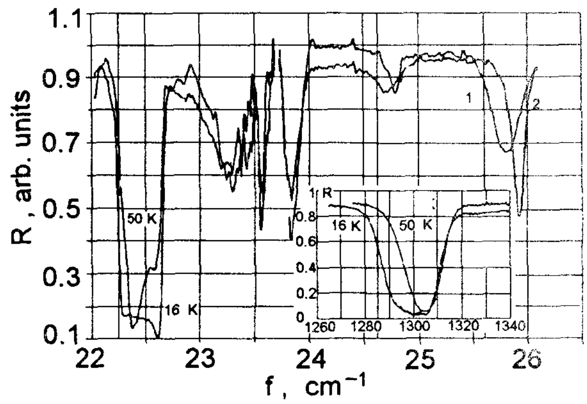

Fig. 5. Variations of the IR reflectance spectrum of a 2.5 mcm thick nitrogen monoxide condensate during warmup.

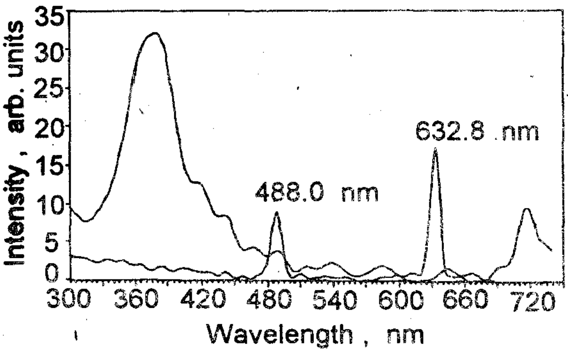

Fig. 6. The spectrum of the spontaneous cryoemission of a growing nitrogen monoxide film; $T = 30$ K; the vertical scale is the analyzer signal intensity.

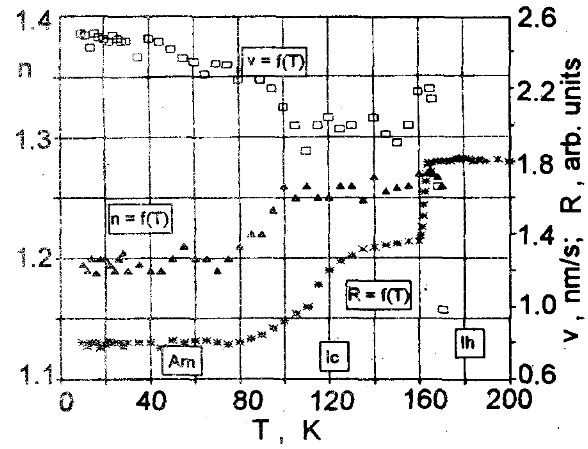

Fig. 7. The growth rate v (□) and the refractive index n (▲) of cryocondensed water versus the condensation temperature. R (*) is the reflectivity of the film at a frequency of 700 cm^{-1} during warmup.

that accompanies the process of cryocondensation of nitrogen monoxide from the gas phase at substrate temperatures below 130 K [9]. The principal experimental objective of further investigation of this phenomenon was to determine the spectrum of a spontaneous emission burst of duration less than 50 ms. This problem has been solved with the aid of the above-described device (multi-channel analyzer of optical spectra). The spectrum of a cryoemission burst of nitrogen monoxide deposited at $T = 60$ K is shown in Fig. 6. As one can see, the spectrum consists essentially of two lines, the brighter one at the blue side and the other in the wavelength range 800 to 860 nm. For comparison we plotted the reference spectra of the helium-neon laser and the interferrometric filter. Of course, in order to understand the mechanism of this phenomenon, further investigations are needed, but even the now available information permits the conclusion to be drawn that the effect under consideration is of origin different from tribololuminescence. This can primarily be inferred from the absence of a wide set of frequencies in the spectrum and its high energy release.

Water and heavy water. Not belonging to the classical molecular cryocrystals, these two substances are interesting from both applicational and fundamental-research considerations. Water is, naturally, a more thoroughly studied object, so that when planning the investigations of the influence of the deposition temperature and of the thermocycling regimes on the structure-morphologic characteristics of H_2O condensates, we pursued, among other, the aim of developing suitable procedures. Vacuum-condensed water layers are known [12,13] to have three structural modifications, which depend on the temperature range, where a condensate is formed and is maintained to exist. According to the previously available conflicting information, below 80–120 K water condenses as an amorphous phase (Am). The range from 100 to 150 K corresponded to a mixture of a cubic modification (Ic) and the amorphous phase. At temperatures above 130 or 150 K, only a hexagonal lattice (Ih) was observed. Thus, detailed studies of growth rates and refractive indexes of water cryocondensates versus the deposition temperature in a combination with their IR reflectivity spectra had two objectives. First, testing our standard procedures on a substance with known structure-morphologic behavior. Second, a more accurate determination of the boundaries of existence of the phases of cryocondensed water layers.

Measured growth rates v and refractive indexes n of thin quench-condensed water layers as a function of the deposition temperature are plotted in Fig. 7. These results suggest certain singularities in the behavior of the properties under study, which could be easily interpreted as being due to some structural transformations in the layers. The same plot shows reflectances (in arbitrary units) of the system «mirror substrate — condensate layer» at a frequency of 700 cm^{-1} during warmup of a 2.5 mcm thick water layer deposited at $T = 16$ K. Correlation between all the data shown in Fig. 7 is self-evident, which allows the following conclusions to be made. The temperature range 16 to 90 K is the domain where water condensates exist in amorphous state. The gradual build-up of the reflectance R within the range from 90 to 160 K and the correlated variations of the growth rate and the refractive index can be explained by a coexistence of the amorphous and cubic phases of the H_2O layer with a gradual transformation of the amorphous component into the cubic phase. The abrupt increase of R in the range 160–162 K is a manifestation of the transition to the hexagonal crystalline modification. Like in the case with nitrogen monoxide, detailed spectral characterization indicates

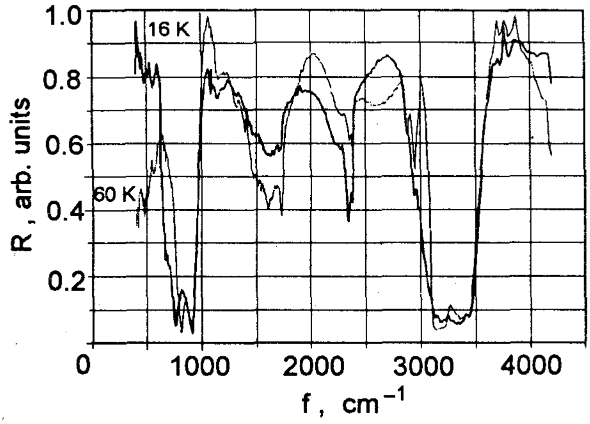

Fig. 8. IR reflectivity spectra of H_2O cryocondensates at two condensation temperatures.

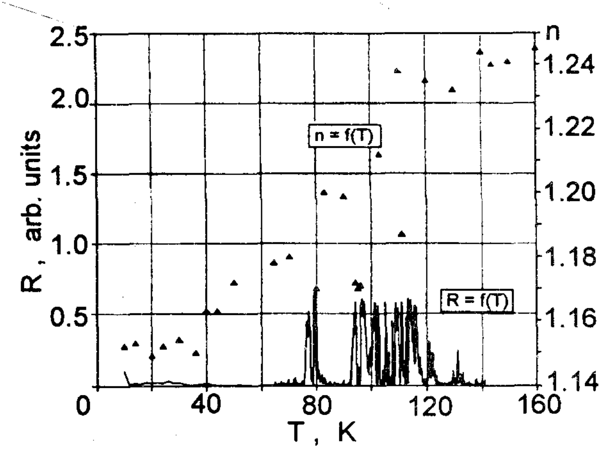

Fig. 10. Temperature dependence of the refractive index of D_2O against the variation of R (at $f = 2890$ cm^{-1}) during warmup.

that virtually all vibration modes has responded to this structure change (Fig. 8).

The drop in growth rate at 175 K can be undoubtedly explained as being due to the closeness of the saturation temperature and pressure. Thus, our studies not only confirmed the presence of the three states in water cryocondensates but delineated more accurately the temperature boundaries of their existence.

Evidently, in order to have possibly complete information about the role of the molecular shape and structure in the formation of the properties of the solid phase, it would be very desirable to carry out coordinated investigations, similarly as for H_2O, for any other molecule of nonlinear shape. The most appropriate candidate in this respect is heavy water (D_2O), for which we have also done growth rate and refractive index measurements versus deposition temperature. The pressure in the chamber was constant and equal to 10^{-5} Torr.

Results of these studies are shown in Fig. 9; inspection leads to rather unexpected inferences. As one can see, against the general rather monotone behavior with temperature of both quantities, $v(T)$ and $n(T)$, there is a deposition temperature interval, where the scatter of experimental data becomes unusually wide, without any plausible considerations of experimental or procedural character to account for this phenomenon. A conclusion suggests itself that this is most likely related to some structure transformations in solid D_2O. Quite natural in this connection is the next step, viz. to use IR spectroscopy in the range of the resonance molecular frequencies. By analogy with water and nitrogen monoxide condensates, we measured variations of the reflectivity with temperature at a fixed frequency. A D_2O layer with thickness $d = 2.5$ mcm was quench condensed on substrate at a temperature of 10 K and then slowly warmed up. During the warmup, we recorded vari-

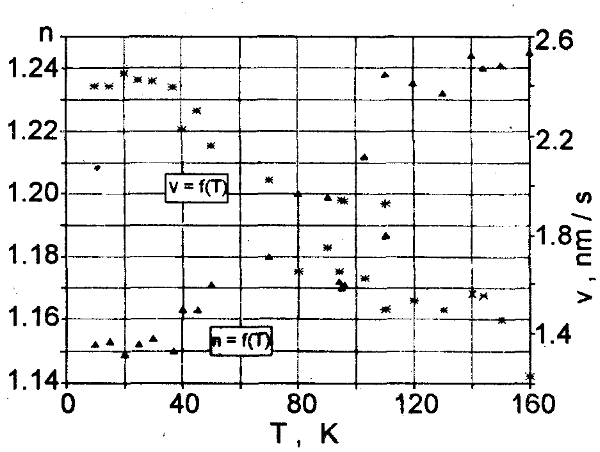

Fig. 9. The growth rate v and the refractive index n of a heavy water cryocondensate versus the condensation temperature. The gas pressure is 10^{-5} Torr.

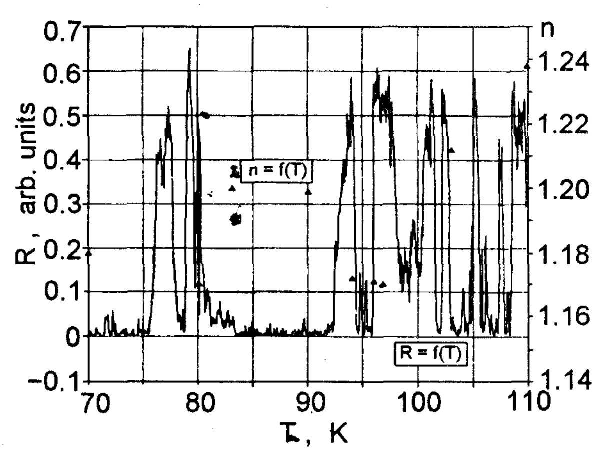

Fig. 11. A fragment of the temperature dependence of the refractive index n of D_2O in comparison with the variation of the film reflectivity R at $f = 2890$ cm^{-1} during warmup.

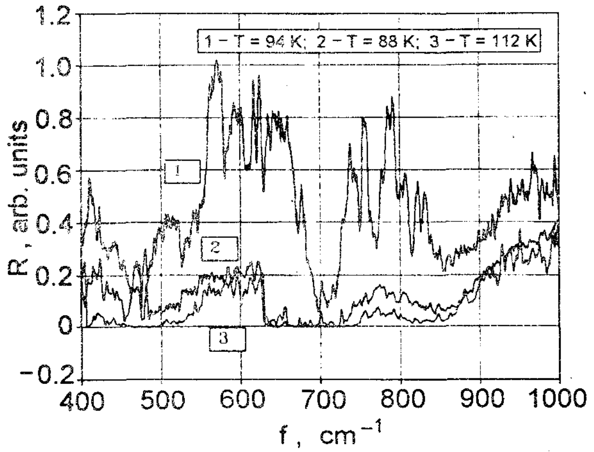

Fig. 12. The spectral reflectance of a heavy water condensate at different temperatures.

ations of the reflectivity at 2890 cm^{-1} as a function of temperature. The measured values, together with the relevant refractive index data, are represented in Fig. 10. A correlation of the data is easily discernible, the abrupt upsurges of the n values are in correspondence with the sharp changes in the layer reflectance, R. A more detailed comparison within a narrower temperature range is depicted in Fig. 11.

In principle, one could have conjectured that cryocondensates of heavy water possess several structural modifications. But then the amazing thing would be the large number of presumably observed structure-morphologic transformations in quite a broad temperature range as well as very narrow domains of existence of different states: indeed, we would be dealing with more than 15 transitions within the range from 70 to 130 K. Spectral measurements within various frequency ranges are also suggestive of globality of the changes occurring in the D_2O crystal (Fig. 12). It is now high time to turn to direct structure studies within the known temperature intervals, which are to give clear answers to the questions put.

Conclusions

1. We have demonstrated a possibility of employing the available experimental complex for the investigation of growth kinetics, thermal properties, and structure-morphologic characteristics of real cryocrystals.

2. A structural transition has been found in the nitrogen monoxide cryocrystal, which occurs near 40 K and consists in a transformation from the low-temperature amorphous phase into the modification with the $Pa3$ lattice.

3. We have recorded the spectrum of cryocondensation emission bursts of freshly grown nitrogen monoxide layers. It has been established that the spectrum comprises two main bands in the blue and red regions of the visible spectral range.

4. We have confirmed existence of the three structural modifications of vacuum deposited water layers and corrected the boundaries of the respective domains of existence.

5. The results of studies on heavy water layers gives ground to assume ultrapolymorphism to exist in the solid of this substance.

Acknowledgement

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1. J. Kruger and W. Ambs, *J. Opt. Soc. Amer.* **48**, 1195 (1959).
2. B. E. Wood, A. M. Smith, J. A. Roux, and B. A. Seiber, *AIAA Journ.* **9**, 1836 (1971).
3. K. Tempelmeyer and D. Mills, *J. Appl. Phys.* **39**, 2068 (1968).
4. V. P. Koverda, N. M. Bogdanov, and V. P. Skripov, *J. Non-Cryst. Sol.* **57**, 203 (1983).
5. L. Levenson, *J. Vac. Sci. Tech.* **8**, 629 (1972).
6. C. Bryson, V. Cazcarra, M. Chouarain, and L. Levenson, *J. Vac. Sci. Tech.* **9**, 557 (1971).
7. V. B. Yuferov, *Effect of Growth Conditions on the Adsorptive Properties of Condensed Gases*, in: Atom Science and Technology: Low-Temperature Adsorption and Cryogenic Vacuum [in Russian] **1**, 41 (1973).
8. V. B. Yuferov, *Fiz. Nizk. Temp.* **19**, 579 (1993) [*Low Temp. Phys.* **19**, 413 (1993)].
9. D. N. Garipogly and A. S. Drobyshev, *Fiz. Nizk. Temp.* **16**, 936 (1990) [*Sov. J. Low Temp. Phys.* **16**, 227 (1990)].
10. A. S. Drobyshev and D. N. Garipogly, *Fiz. Nizk. Temp.* **20**, 600 (1994) [*Low Temp. Phys.* **20**, 475 (1994)].
11. A. S. Drobyshev, N. V. Krainyukova, and M. A. Strzhemechny, *Proceedings of Symposium on Low Temperature Physics*, Dubna (1994), part 2, p. 94; N. V. Krainyukova, M. A. Strzhemechny, A. S. Drobyshev, *Fiz. Nizk. Temp.* 22 (1996) (to appear)
12. J. Bertie and E. Whalley, *J. Chem. Phys.* **40**, 1637 (1964).
13. A. S. Drobyshev, N. V. Atapina, D. N. Garipogly, S. L. Maksimov, and E. A. Samyshkin, *Fiz. Nizk. Temp.* **19**, 567 (1993) [*Low Temp. Phys.* **19**, 404 (1993)].