A method of measuring transmittance of radiation from the film of ice 0 in the IR wave band deposited on a dielectric plate

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Abstract. A method of measuring transmittance of radiation from the film of ice 0 in the infrared wave band is described. Ice 0 is formed from supercooled water at the temperature below −23°C. This ice is ferroelectric and forms a highly conductive layer of the nanometric order of thickness at the boundary with dielectric. The complexity of the experiment consisted in the necessity of using low intensities of the probing signal and considering radiation of the cooled parts of the installation. In order to obtain a thin film of ice, the method of depositing water vapor on a substrate cooled in nitrogen was used. The method rules out formation of condensate in cooling. Deposition of water vapor is possible only in heating, when delivery of cold nitrogen vapor into the chamber with the sample is excluded. To ensure exposure of the film to IR radiation, two sources of infrared radiation were considered: a halogen lamp with a broad radiation spectrum (on the surface of heated glass) and a CO2 laser with the radiation wavelength of 10.6 µm. In the first case, spectral measurements are possible when filters are used. In the installation based on a CO2 laser, an intense signal is emitted, requiring consideration of sample heating. Components of the installation have been elaborated and investigated, on which transmittance of radiation from the film of ice 0 is planned to be measured.

1. Introduction
In computer simulation of the structure of water molecule clusters under different conditions (temperature, pressure), in [1–3], a new metastable crystalline modification of ice, ice 0, was discovered. According to [1], this ice is a transitional form between liquid water and crystalline ice forms Ih and Ic. The view of the crystalline lattice of ice 0 is shown in figure 1.

However, this ice is formed only from supercooled water at the air temperature below −23°C. A cell of the crystalline structure of ice 0 contains 12 molecules of water. Its view is shown in figure 2. In [2], in which stability of ice 0 was investigated, its main state was defined as ferroelectric.
Experimentally, ice 0 was first discovered in [4], in which supercooling of water was achieved in nanometric pores of silicate materials. The conclusion regarding formation of ice 0 was made on the basis of theoretically predicted properties of this ice, namely, manifestation of the ferroelectric state and the value of the temperature of phase transition. It was demonstrated in the further work [5] that ice 0 deposited onto a dielectric plate caused strong attenuation of the electromagnetic waves of the visible band of the spectrum. That occurs because at the interface between ferroelectric ice 0 and dielectric, there appears a nanometric layer having high conductivity. In the case of insular films, additional absorption emerges there in them in the optical range due to appearance of surface plasmons. Both effects result in the fact that ice 0 at the interface with dielectric should create attenuation caused by absorption and scatter of electromagnetic radiation in the broad range of the wavelengths.

To ensure further studies of the spectral characteristics of absorption of electromagnetic radiation by 0, we set an aim in the given work to measure transmittance of radiation through a dielectric plate with ice 0 deposited on it in the infrared band.
2. The experimental technique
To investigate film of ice $\theta$ in the infrared band, an installation was established, in which radiation was generated by a strong halogen lamp, whereas reception was exercised by an IR radiometer. To generate a probing beam and to maintain constant temperature of the radiating element, the lamp was placed into a metal case with a cylindrical tube serving as a radiation exit. The filament of the lamp was positioned opposite the tube to enable maximum intensity of thermal radiation coming out of it. The configuration of the installation is shown in figure 3.

![Figure 3. Configuration of an installation for irradiating samples in the IR-band. 1 – a thermostat; 2 – a sample; 3 – a radiation source (a halogen lamp); 4 – an IR radiometer; 5 – a Dewar flask with liquid nitrogen; 6 – stabilized current to feed the resistor evaporator; 7 – a thermocouple; 8 – a data collection system.](image)

Radiation from the lamp (3), limited by the exit tube, passed through holes in thermostat (1), then through thermostat (2), which was a plate of a sodium chloride crystal. Part of the radiation which passed through the sample was registered with an IR radiometer (4) and was recorded with the Agilent data collection and commutation system (8). In the experiment, the sample was cooled with cold nitrogen vapor received from the Dewar flask (5) when heating liquid nitrogen to the boiling point (−196°C). Nitrogen was heated with a resistor evaporator fed from a stabilized module (6). The temperature of the sample was measured with thermocouple (7) with accuracy of 1°C.

To obtain film of ice deposited on the sample plate, a method described in [5] was used. The sample was cooled by intensive outsting of air from the thermostat with nitrogen vapor. Water vapor was removed from the chamber; thus, condensate was not formed on the cooled sample. When the evaporator is turned off, the flow of nitrogen stops, and water vapor penetrates into the thermostat from the environment. When vapor is deposited on the cold sample (−60…−23°C), supercooled water and ice $\theta$ are formed, as the temperature of water is much lower than the temperature of its phase transition to this kind of ice. At the interface of ice $\theta$ and the sample material, a nanometric conductive layer emerges, which causes intense absorption and scatter of the signal. The IR radiometer registers the drop of the feed-through power. As ice $\theta$ is further heated at temperatures above −23°C, it should turn into ice modification Ih or Ic or become evaporated. This transition is also registered in the radiation receiver by significant rise of the signal intensity. Conformity of the measured temperature with the theoretical value of the temperature of the water – ice $\theta$ phase transition testifies to formation of this crystalline modification of ice in the film.
3. The first experiments

Using the technique described, we conducted the first experiment. The results of measuring the intensity which was fed through the sample, depending on temperature at cooling of the NaCl plate, followed by its heating, are shown in figure 4.

![Figure 4](image)

**Figure 4.** The results of measuring the intensity of infrared radiation (in relative units) in irradiating a NaCl plate in a cooling cycle followed by heating. Arrows indicate the direction of change of the temperature in the cooling–heating process.

The experiment showed that radiation from the halogen lamp had lower intensity compared with the interfering signal, depending on the temperature of the sample itself and of the thermostat chamber. The increment related to switching on of the lamp was ~0.05 relative units; the change of the signal related to cooling of the sample and the thermostat walls was 1.1 relative units. That is, the signal change due to the temperature of the installation components exceeded the useful signal from the irradiator approximately 20 times.

4. Modifications in the measurement configuration

As the intensity of the useful signal proved to be low, and it was difficult to register its change in the course of the experiment, the installation was upgraded. The configuration of the upgraded installation is shown in figure 5.

First, the radiation source was replaced for a more powerful one having a narrow beam. A CO₂ laser (3) was chosen, having a wavelength of 10.6 μm, referring to the thermal infrared band. However, the laser power turned out to be high; therefore, it had to be reduced, not to melt down the sample and not to damage the sensitive receiver. For this purpose, an attenuator was installed between the laser and the thermostat, which consisted of two metal mirrors (9) and a plate of a NaCl monocrystal on non-transparent absorbing material (thermal paste) with a radiator (10). Adjusting the tilting angle of the mirrors, we were able to decrease the radiation reflected from the salt crystal surface to the required value of about 1% of the laser power. The remaining radiation, after passing through the plate, was absorbed by the thermal paste and scattered by the radiator, which was blown over by a fan.
Figure 5. The configuration of irradiating the sample in the IR band on the basis of a CO$_2$ laser. 1 – a thermostat; 2 – a sample; 3 – a radiation source (a CO$_2$ laser); 4 – an IR radiometer; 5 – a Dewar flask with liquid nitrogen; 6 – a stabilized power unit of the resistor evaporator; 7 – a thermocouple; 8 – a data collection system; 9 – mirrors; 10 – a NaCl plate with an absorbing substrate and a radiator; 11 – a metal screen.

To reduce the impact of the thermostat walls’ temperature on the signal registered by the radiometer, a metal screen with a tube was installed between them (11). The temperature of the metal screen did not affect the intensity of the emitted signal, while the tube narrowed down the beam of the probing signal. Due to the upgraded installation, we were able to achieve significant intensification of the useful signal that passed through the sample, compared with the parasitic signals caused by changes in the temperature of the constructive parts of the installation.

5. Conclusions
The first experiments conducted have shown that a halogen lamp without additional focusing of the beam emits a weak useful signal, 20 times less than signal increment related to change of the temperature of constructive elements of the measurement chamber. An upgraded installation based on a CO$_2$ laser allowed us to obtain a probing signal which was 80 times more intensive than that from the halogen lamp. The metal screen added reduced the impact of the chamber temperature on the total signal. It is expected that the upgraded installation will make it possible to obtain a good ratio between the probing radiation and the parasitic signals over the entire range of the sample temperatures.

Acknowledgments
The study has been conducted with the support of the Russian Foundation for Basic Research (project № 20-05-00563)

References
[1] Russo J, Romano F and Tanaka H 2014 Nature materials 13 733–93
[2] Quigley D, Alfe D and Slater B 2014 J. Chem. Phys. 141 161102
[3] Slater B and Quigley D 2014 Nature Materials 13 670–1
[4] Bordonskiy G S and Orlov A O 2017 JETP Letters 105 492–6
[5] Bordonskiy G S, Gurulev A A and Orlov A O 2020 JETP Letters 111 278–81