Acoustic effect of crystallization and melting of matter

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A phenomenon is observed which consists in the crystallization and melting of matter, accompanied by the appearance of elastic pulses in the liquid; the pulses lie in a broad frequency range (0.5–2000 kHz) and have characteristic first spikes of height 1–250 μV, depending on the nature of the material. The maximum sound-signal repetition rate is related to the degree of supercooling. The phenomenon is known as the acoustic crystallization effect.

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As is well known, existing representations of the crystallization of liquids indicate that the growth of crystals takes place basically by means of three different mechanisms: by formation of two-dimensional embryos and their growth along the faces; by a dislocation mechanism, when the particles are joined to steps formed by exposure of screw dislocations; by disordered joining of particles to the surface of a growing crystal, when the front of crystallization moves normal to itself.[1]

The elementary processes of crystallization from the melt and the melting of material take place stochastically. It can be assumed that in this case, the abrupt deposition (or disappearance) of macrolayers and macroregions on the growing or melting surfaces will be accompanied by the generation of pressure pulses into the medium surrounding the crystal. This effect should be amplified with increasing difference between the densities of the crystal and the melt and with increasing temperature gradient on the crystallization front. These pressure pulses create oscillations of the medium which can propagate in the form of sound waves. We succeeded in detecting acoustic waves in the crystallization and melting of water, benzene, sodium hyposulfite, salol, oleic acid, tertiary butyl alcohol and a number of other materials.

A block diagram of the experimental setup for verifying the presence of the acoustic effect is shown in Fig. 1. The apparatus consists of a liquid thermostat in which the crystallization cell 2 is placed, a selective amplifier 6, oscilloscope 7 and movie camera 8. A cooling element 3 in the form of a small metal tube with freon is placed in the thermostat along with an electric heater 4 made of a nichrome coil set in a glass tube. As a cryoliquid, we used denatured alcohol, stirred by the stirrer 5. The thermostat allowed us to maintain the temperature in the interval -35 to $+45^\circ$C with an accuracy of $\pm 0.2^\circ$C. The temperature in the thermostat was controlled with the help of three chromel-aluminum thermocouples, placed at the points a. The dimensions of the thermostat were $500 \times 500 \times 500$ mm^3.

The crystallization cell was made of clear plastic and had the shape of a cylinder of diameter 60 mm and height 100 mm. The wall thickness was 2 mm. A differential thermocouple b was placed in the cell for determination of the temperature gradient during crystallization.

The crystallization front moves parallel to the surface of the cell, advancing toward its axis, in the middle of which was placed a lead titanium zirconate transducer 1 with a sensitivity of 14 μ V/bar. The latter had the shape of a cylinder of height 10 mm and external and internal diameters of 9 and 6 mm, respectively. The transducer records the acoustic signals that arise in the process of crystal growth or melting. From it, the signals are fed to a U2-6 selective amplifier; then the amplified signals are recorded by an S1-15 oscilloscope with an S1-15/5 preamplifier. The oscillograms of the acoustic signals are photographed by a "Krasnogorsk" movie camera at a rate of 16 frames/sec.

Measures were built into the apparatus to remove all possible sources of extraneous noise which could serve as sources of acoustic signals. In particular, special studies were undertaken with the aim of making clear whether there is an acoustic effect as a result of elastic signals generated in the possible cracking of crystals in their growth process. Evidently this is not a cause of the observed signals, since the latter appear both in crystallization and in the melting of the materials, when such "soft" crystals as benzene, oleic acid etc. are formed or disappear.

Moreover, to test the assumption that the acoustic effects of crystallization may result from formation of discharges that are generated as a result of the accummulation of charges on the faces of the crystal, we carried out the following experiment. Grounded cylindrical grids of fine copper wires were placed in the crystallization cell parallel to the axis of the camera between the crystallization front and the transducer, where they could pick off charges stored on the faces of the crystal. The experiment showed that the acoustic effect is reliably observed during both melting and crystallization on passage of either a crystallization front or the melting front across the grid.

Finally, we carried out an additional experiment with the purpose of eliminating thermoelastic oscillations of the solid phase due to thermoplastic deformation as a factor affecting the observed phenomenon of formation of acoustic oscillations of the medium in the process of crystallization or melting. For this purpose, we carried out melting in an inert medium.

Initiation of the acoustic effect during the melting of

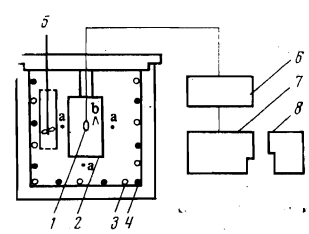

FIG. 1. Block diagram of apparatus for study of the acoustic effect of crystallization and melting of material: 1–lead titanium zirconate signal transducer; 2–crystallization cell; 3–tubes for Freon-22; 4–heating coil; 5–mixer, 6–U2-6 selective amplifier; 7–S1-15 oscilloscope; 8–"Krasnogorsk" movie camera.

ice in a neutral medium was verified on the same apparatus (Fig. 1). The experimental method was as follows: a preformed sample of ice in the form of a hollow cylinder, is lowered into the cell 2, which is filled with an inert liquid (kerosene) at a temperature 20–30° below the melting temperature of ice. The entire system is temperature-stabilized until identical temperatures of the ice and the neutral liquid are established. Then the temperature of the inert liquid is increased so that various temperature gradients from 0 to 20 deg/cm are created between the ice sample and the liquid. While the ice temperature is below 0°C, the transducer at the center of the cell shows only the presence of background noise on the screen of the oscilloscope; consequently, thermoplastic deformations of the ice in the experiment evidently have no significance for the generation of acoustic signals in the medium. When the temperature of the inert liquid is somewhat above the melting point of the ice, the transducer detects acoustic oscillations, which propagate in the kerosene as a result of abrupt disappearance of macrolayers or macroregions on the melting surface of the ice. The acoustic signals observed on the screen of the oscilloscope are of the same shape as those in the water in the melting of ice in the experiments described above, but with a smaller characteristic height of the first spike. The repetition rate of the pulses was $\nu \sim 7$–8 pulses/min. The characteristic heights of the first spikes I vary from 10 to 50 μ V. The total duration of the positive and negative first spikes at the zero level was $\tau\Sigma \sim 5$–10 μsec.[2]

As a result of these experiments, we came to the aforementioned conclusion as to the possible reason for the acoustic signals. Until the first small crystals appear on the walls of the cell, the oscillograms show only background (the horizontal line in Fig. 2). With the appearance of the small crystals, intermittent signals appear on the screen of the oscilloscope in the form of distorted damped sinusoids. Similar signals are observed as long as the process of crystallization is under way. If the growth of the crystals ceases, then the oscillogram again indicates the background.

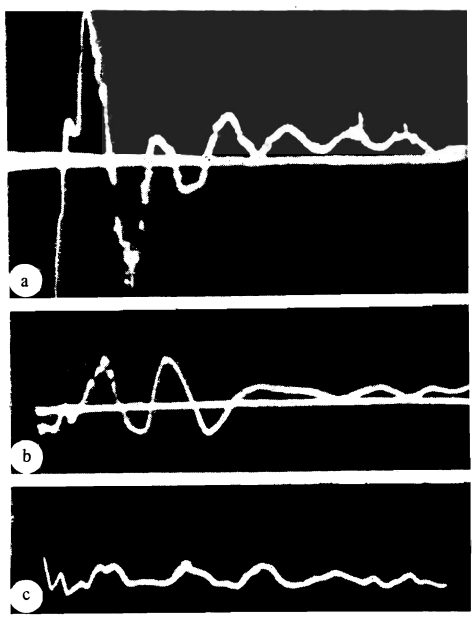

FIG. 2. Acoustic signals accompanying the crystallization processes of (a) water, (b) hyposulfite, and (c) benzene.

The oscilloscope also records the presence of signals during melting of the crystal. The signals observed during the melting of the crystals have the wame form (Fig. 3).

Experiments on the observation of the acoustic effect of crystallization were carried out at different rates of growth (melting) of crystals from 0.1 to 1.3 mm/min and at temperature gradients from 2 to 15 deg/cm.

The acoustic signals are characterized by a rather broad range of frequencies, from 0.5 to 2000 kHz and characteristic first-spike heights of 5–1000 μV. The repetition rate of the signals depends on the value of the supercooling, increasing with increasing temperature gradient, as is seen from the table. Here the ranges of frequencies in which the most characteristic signals lie also change. For example, in the case of water at $\Delta T/\Delta x \sim 2$–8 deg/cm, the acoustic signals are observed basically at frequencies of 0.5–60 kHz, although there are individual signals with frequencies as high as ~1000 kHz; at temperature gradients of 10–15 deg/cm, signals whose frequencies lie in the range from 100 to 2000 kHz predominate. The characteristic heights of the first spikes change from signal to signal, but are not observed to depend on the value of the temperature gradient.

The acoustic effect was reliably observed both in the crystallization of water, benzene, sodium hyposulfite, salol and other materials, and also during their melting. The acoustic signals observed during the crystallization of benzene are low frequency in most cases (below

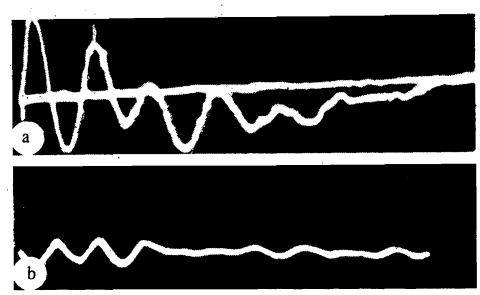

FIG. 3. Acoustic signals accompanying the melting processes of (a) ice and (b) benzene.

Some statistical data for the study of the acoustic effect of crystallization and melting of materials.

Material	t_{melt} °C	$\Delta T/\Delta x$, deg/cm	ν pulses/min	$\tau\Sigma$, μsec	I, μV
		Crystallization			
Distilled water	0	2–4	10	25–100	25–70
		4–8	20	10–50	50–100
		8–12	40–50	2–20	70–150
		12–15	60–70	~1	100–350
					sometimes to 1000
Sodium hyposulfite	+25	20–25	80–90	2–20	100–400
					sometimes to 1000
Benzene	–6	8–10	30–35	500–1000	50–200
		10–13	45–50	~10	100–200
Salol	+43	20–25	100–200	2–20	from 50 to 20000
Oleic acid	–30	15–17	15	5–10	25–150
Tertiary butyl alcohol	–25	17–20	2–3	5–500	10–30
Acetic acid	–18	12	8–10	20–50	10–100
Diphenylamine	+54	11	70–80	1–25	5–20
Benzoic anhydride	+42	20–25	100–150	3–25	2–20
Decane	–30	16–20	3–4	10–25	10–500
		Melting			
Distilled water	0	8–10	15	~10	17–100
Benzene	–6	8–10	10–14	200–500	20–25
		10–13	20	100	30

1 kHz). During melting of benzene, the signals are much less frequent than during the melting of ice (at the same temperature gradient). It was observed that the characteristic heights of the first spikes of the signals, their repetition rates, and the total durations of the first positive and negative spikes at the zero level are, at a given supercooling, directly connected with the discontinuity of the specific volume in the first-order phase transition as a consequence of the solidification or melting of the material, as is seen from the table, where some statistical data from study of the acoustic effect of crystallization are given. At a given supercooling, the repetition rates of the signals and the characteristic heights of their first spikes increase with increasing density discontinuity, and the total durations of the first positive and negative spikes at zero level fall off.

Thus, we observed a new physical phenomenon—the appearance of acoustic oscillations in a medium in which directional motion of a crystallization or melting front takes place. The acoustic oscillations have a complicated composition; the frequencies and characteristic heights of the first spikes lie in the ranges 0.5—2000 kHz and 1—250 μV, respectively. The frequency ranges in which the acoustic effect is observed depend on the temperature gradient or the rate of displacement of the crystallization (melting) front.

It is well known that there are various ways to affect the process of crystallization. One of them is exposure of the solidifying or supercooled melt to ultrasound. The latter accelerates the crystallization process, affecting the freezing temperature and the structure of the solid phase. The effectiveness of the action of the external ultrasonic field on the crystallization process should evidently be connected with the characteristic frequency of the acoustic noises of the natural process of crystallization. This hypothesis is being checked by us at the present time and further study of the acoustic effect is being continued.

[1]W. Hilling and D. Turnbull, Elementary Processes of Crystal Growth (Russian translation, IIL, 1959).
[2]V. I. Tikhonov, Vybrosy sluchaĭnnykh protsessov (Emissions of Random Processes) Nauka Press, 1970, p. 8.

Translated by R. T. Beyer
141