Some peculiarities of first order phase transitions

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Abstract. The paper presents evidence of the existence of infrared characteristic radiation accompanying phase transitions of the first order, especially crystallization. Experimental results of the author and other researchers concerning crystallization from the melt of some infrared transparent substances (alkali halides, sapphire) and nontransparent ones (tellurium, ice, copper) as well as condensation of water vapor, are presented. The author has critically analyzed these experimental data in terms of correspondence to theoretical models. The last ones are based on the assumption that a particle, during transition from a higher energetic level (vapor or melt) to the lower energetic level (crystal), emits one or more photons equal to the latent energy of the transition, or part of the energy. Based on the experimental data, the author proposes a model explaining the appearance of a window of transparency for the characteristic radiation in the substances when first order phase transitions take place. It is possible to imagine several applications of this phenomenon in different fields, for instance, new types of crystallization process regulation; crystallization stimulated by the characteristic radiation; an infra-red laser based on the condensation of water vapor, or crystallization of lithium fluoride or sapphire. Formation of hailstorm clouds in the atmosphere should be accompanied by intensive characteristic infrared radiation that could be detected for process characterization and meteorological warnings. Detection of water in the atmospheres of other planets can also be realized by this technique. This radiation might explain the red color of Jupiter as well as the orange color of its satellite Io.

1. Definition of the Scope of Discussion

Between the years 1979 – 84, three papers were published presenting a rather unusual experimental finding: The appearance of characteristic infrared radiation accompanying crystallization from the melt of some infrared transparent substances (alkali halides, sapphire) [1–3]. These results were not obtained casually. They were preceded by a long search for the radiation of crystallization on the basis of the assumption that during crystallization a particle transitioning from a higher energetic level (vapor or melt) to the lower energetic level (crystal) must emit one or more photons equal to the latent energy of the phase transition, or part of the energy. Now, there are experimental evidence of radiation accompanying phase transitions of the first order and its theoretical basis. This paper seeks to review the up-to-date situation as well as to analyze the author’s model explaining the mechanism of transparency window appearance for the characteristic radiation in the substances when first order phase transitions take place.

2. Macroscopic Heat Balance Analysis on the Crystallization Boundary

Let us analyze melt crystallization, for instance, water freezing. A great number of papers describing calculations of the temperature fields in the crystallization–melt system exist. They are known as the group of Stefan’s problems with a movable crystal – melt...
boundary. There is liberation of the latent energy of crystallization on this boundary. Therefore, the boundary is a heat source. As a rule, the heat–balance condition on the crystallization front is presented in the following way [4]

\[-\mu_s G_s(h) + \mu_l G_l(h) = \zeta V_c. \tag{1}\]

Here $\mu_s$ and $\mu_l$ denote the thermal conductivities of solid and liquid phases, respectively, $h$ is the crystallization front position, $G_s(h)$ and $G_l(h)$ are the temperature gradients in the solid and liquid phases at the crystallization front respectively; $\zeta$ denotes the latent melting heat of a material unit volume, $V_c$ is the crystallization rate. It follows from Eq. (1) that the latent heat of the phase transition is removed from the crystallization boundary by a thermal conduction process in the solid as well as in the liquid phase (if the liquid phase is supercooled).

If a crystal or a melt (or both of them) of crystallizing substance are transparent in some range of the wavelengths, for instance sapphire [5], it is considered that the latent heat of the phase transition may be removed from the crystallization boundary by radiation as well as by thermal conductivity. The equation of thermal conductivity will not be changed in this case, but radiance flow availability can be, for instance, equalized by introducing the effective thermal-conductivity coefficient, proportional to $T^3$ [6]. It is important to determine more accurately, that in this it bears in mind the Plank’s equilibrium radiation corresponding to the temperature in the analyzing system. Let us title this approach as a macroscopic one.

3. NEW APPROACH TO THE LATENT ENERGY LIBERATION

In 1964 the author tried to use a microscopic approach to the latent energy liberation. From this point of view, crystallization from the melt or vapor phase can be described as transitions of particles from a higher energy level, in the melt or vapor, to the lower one, in the solid. The first level can be treated as an excited level in relation to the second one. The gap between these two levels corresponds to the latent energy of crystallization per atom. In the macroscopic description of the crystallization process mentioned above, it was postulated that each act of particle transition from the melt to the solid produces one or more phonons. This process contributes to the Planck’s radiation by the particle’s increased motion, and hence, to temperature.

But the author suggested that the act of transition of the particle from the exited level in the melt, solution, or vapor, to the lower one in the solid can produce one or more photons. The energy of the photon principally has to be equal to the full latent energy of crystallization per atom, if one photon is produced, or to part of this energy, if more than one photon is produced. Probably, it could be a little higher for some particles if they, in addition, are activated, or the lower level is reduced with respect to the main level by super–cooling or some other effects. The lower energetic level may be divided with the main level corresponding to the ideal crystal structure and other levels corresponding to different defects formed during crystallization. But in any case, the sets of photons have to form a characteristic spectrum for the crystallizing substance.

Consider, for instance, the crystallization of snow or hail formation from water in atmosphere. In this case, the crystallization process takes place on the surfaces of the snow or hail particles, and the characteristic radiation can easily go out to the environment. Snow or hail formation in the atmosphere can occur in two different ways: firstly, water drops formation from the water vapor with subsequent crystallization of the water drops; secondly, direct formation of the particles by the direct condensation of the water vapor. Hail stones are probably formed by the first way, and snow particles by the second. The first path includes two first order phase transitions, and each of them can give the corresponding characteristic spectrum.

On the basis of this description we can conclude that the characteristic spectrum of the first order phase transition could give the following information:
1. If the phase transition occurs or not.
2. Peculiarities of the phase transition, for instance defect formation.
3. The speed of the phase transition.

4. HISTORY OF THE QUESTION

In 1966, on the basis of these assumptions, the author began experiments at the Physical and Technical Institute of the USSR Academy of Sciences. They were continued in the Leningrad State Optical Institute from 1972 to 1973, in the Solid State Physics Institute of the USSR Academy of Sciences from 1973 to 1983 with few interruptions, and at the Massachusetts Institute of Technology (USA) in 1978. Since 1959, the author’s main activity has been ‘shaped crystal growth from the
melt. As a hypothesis arrived at during these experiments, it was natural to attempt to verify this hypothesis by crystallization from the melts and fluxes. Practically for all substances, the characteristic radiation corresponds to the infrared (IR) range of the spectrum. Thus, the first problem was to find substances transparent to the characteristic radiation at the crystallization temperature. The second problem was that it was necessary to record a rather weak radiation against a significant background; and the third, it was necessary to eliminate numerous parasitic radiations. Here are two typical examples:

- During crystallization of gallium arsenide from flux, the appearance of the first crystals was accompanied by a power flash. But it was found that the crystals reflected the light by their singular faces.
- During crystallization of some salts from melts it was found that fast cooling caused crystal cracking and surfaces of the formed fractures reflected the light in the recording system.

These are the reasons why the first positive results were not obtained until 1970. The results were unusual from the point of view of many specialists in the field of optics. They rejected a high temperature luminescence possibility in favor of the phonon path of energy removal. We had to look for more experimental evidence that the phase transition was the source of the radiation. In 1977 the first results were accepted for publication. The main

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Fig. 1. a) Open air environment: b) Argon environment: Thermogram (II) and radiation spectra (I) of crystallizing LiF: 1 - Spectrum of superheating melt; 2, 3, 4 - Spectra of crystallizing melt; 5 - Spectrum of crystallized substance. (replotted from [2]).
II. EXPERIMENTAL RESULTS FOR ALKALI HALIDES AND SAPPHIRE

Initially [1,2] the investigation of IR emission spectra during crystallization was performed on an apparatus consisting of a resistance furnace, in which a platinum or alundum crucible without a lid was placed, and a one-beam IR spectrophotometer with a remote globar. The standard spectrometer was modified for the recording of rapid processes. The radiation from the melt-crystallizing substance system was directed to the spectrophotometer by a metal mirror. Crystallization led to formation of a polycrystalline bar within a period ranging from a few tens of seconds to an hour, depending on the type of cooling. During crystallization of some substances (LiF, NaCl, NaBr, NaI, KCl, KBr, KI, PbCl₂), the recorded curves exhibited not only thermal radiation, but also additional peaks corresponding to the wavelength λ ≈ 2 - 5 µm. Fig. 1a from [2] presents a set of five consequent spectra in relative units recorded during LiF cooling. The curve of the melt temperature change during the experiment is presented in the same figure. The less inclined part of the curve corresponds to the crystallization of the melt. We can conclude that the appearance of the peak precedes the start of crystallization in the melt. The peak does not disappear immediately after visual completion of crystallization. The time taken for it to disappear depends on the rate of crystallization and ranges from a few seconds to a period of two to five minutes. The value of peak 3 is higher than that of peak 2 in spite of the decreasing system temperature and the resultant decrease in the background radiation. The decreasing temperature is accompanied by an increase of the crystallization rate, so the intensity of the characteristic radiation increases with the crystallization rate.

In [1] the energy corresponding to the spectrum was found to be higher than the latent energy of crystallization and this fact was explained by the hypotheses of Jackson and Chalmers [7]. Their model postulates that crystallization is an activated process with energy of activation equal to that of self-diffusion or viscous flow.

In [2] the experiments were mainly carried out with LiF because of its low hygroscopicity (Later LiF was found to be the most acceptable for the experiments because of its low melt viscosity). The spectra structures and peak positions from [2] shown in Fig. 1a are similar to those from [1]. They are rather complicated because of the bands of adsorption of atmospheric water vapor (3.4 µm), atmospheric CO₂ (3.95 µm and 4.35 µm) and are bonded with crystallographic LiF structure OH groups (2.7 µm). Later, in [2] the parasitic bands were eliminated to allow more precise determina-
Fig. 3. Radiation spectra of sapphire: Differential spectrum of radiation flare (dashed curve). 1. Emission spectrum of cooled sapphire, first heated to the temperature less than 2050 °C. 2. Emission spectrum of crystallizing melt. (replotted from [3]).

tion of the peak wavelengths. For this, the experiments were carried out in atmospheres of Ar or N₂. The results are presented in Fig. 1b. The second step in improving detection of the pure characteristic spectrum consisted of using a two-beam spectrometer with compensation of the heat radiation of a crucible and LiF melt. This allowed the peak positions to be determined more accurately and sometime to resolve its fine structures. The resulting LiF peak presented in Fig. 2 can be interpreted as a superposition of the four peaks with \( \lambda_1 = 2.80 \mu \text{m}, \lambda_2 = 3.45 \mu \text{m}, \lambda_3 = 4.05 \mu \text{m}, \lambda_4 = 4.35 \mu \text{m} \). The position of the last peak corresponds exactly to the latent energy of crystallization. In spite of our efforts, we could not resolve the fine structure of crystallization radiation for other investigated alkali halides. Only the main peaks corresponding to the latent heats of phase transitions were detected. So, in this manner we could relatively easily observe the crystallization radiation of low-viscosity melts, which are transparent in the near IR region. For more viscous melts, such as KCl, it was difficult to observe and even more to separate pure crystallization radiations.

In [3] we described our experiments concerning recording of the characteristic spectra during sapphire \( (\text{Al}_2\text{O}_3) \) crystallization from the melt. As was mentioned above, sapphire is transparent over a wide range of the spectrum from infra-red to ultra-violet. The substance is interesting on account of its low entropy of fusion (2.2), corresponding to slight structure differences between the crystal and the melt — in contrast with semiconductors and alkali halide crystals. We measured the emission spectra of solid, liquid, and crystallizing sapphire in the spectral region from 0.7 to 2.5 \( \mu \text{m} \) at the temperatures between 2100 °C and 1600 °C. Heating and melting were effected in a vacuum with the aid of a high-frequency apparatus fitted with optical windows of fluorite or fused quartz. Other details of the apparatus are given in [3].

The main result is presented in Fig. 3. From the spectrum of crystallizing melt 2, we subtracted the emission spectrum of crystalline sapphire, first heated to the temperature less than the melting temperature 2050 °C. Thus, the crystallization of sapphire from the melt is accompanied by the appearance of a band of IR radiation (additional to the thermal radiation) at a wavelength of 1.1 mm, corresponding to the heat of fusion of sapphire 26 kcal/mol.
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Fig. 4. Relative intensity of the phase transition luminescence from water; $I_{\text{w}}$, intensity from the boiling water; $I_{\text{bb}}$, intensity from the black body. (replotted from [9]).

6. WATER PHASE TRANSITIONS

Here we present some experiments concerned with the infrared radiation appearance during water phase transitions. In [8], an infrared line scan photo camera has been developed that scans an object simultaneously with three separate spectral regions and produces an image of the object as a color photograph. The three spectral regions are 0.5-1.0 µm, 3.9-5.5 µm and 8-14 µm. Each of the infrared spectral regions is rendered in one of the primary colors: blue, green and red respectively. As a result, the color of objects in a picture indicates their temperature and also their reflective and emissive properties. The pictures presented in [8] allow conclude that the authors found the infrared sources of the range 8-14 mm radiations in the atmosphere that can be concerned neither with temperature radiation nor with reflective radiation. These sources were the bottom sides of cumulus clouds with the temperature −5 ºC and the rising warm air saturated with water vapor.

In [9] experiments were carried out in an installation including a vessel with boiling water, a cooled glass surface for the vapor condensation, and a sensitive system of the infrared radiation recording. The authors of [9] observed an anomalous increase in the infrared radiation intensity from the boundary between the glass surface and condensed vapor. The intensity was increased with the condensation rate increasing. At the range 1-4 µm the integral intensity was four times more than the Plank’s radiation. Two main emission bands were seen at 2.10 µm and 1.54 µm wavelengths (Fig. 4). The intensity of both bands exceeded the background radiation by a factor of ten.

In [10], at observation of sonaro-luminescence, the author used a spectrometer with a thermocouple detector and a Lead Sulphide Photometer. The peak of emission with wavelength 1.05 µm was detected. In [11] characteristic radiation was recorded during water vapor condensation and water crystallization in a closed chamber. The temperature was decreased by adiabatic expansion. The radiation was led out from the chamber through Ge window. Systems of filters as well as of mirrors were used to cut desirable ranges from the full spectrum. Radiation was detected by a bolometer. This technique allowed authors to confirm that they recorded the characteristic radiation with a maximum in the range 4-8 µm for the first process and in the range of 28-40 µm for the second process. The radiation intensity exceeded the background Plank’s intensity many times for the same temperature.

Now, one can find infrared images of the Earth from Space. The following information from NASA (March 23, 2002 [12]) is interesting to us: The orbiting GOES 8 satellite’s multi-channel imager pro-
Fig. 5 What alien planet's bizarre landscape lurks below these fiery-looking clouds? It is only Planet Earth, of course — as seen on the Water Vapor Channel. Hourly images, like this one (shown in false color), are brought to you by the orbiting GOES 8 satellite's multi-channel imager. This instrument can produce images at the infrared wavelength of 6.7 µm, recording radiation emitted by water vapor in the upper troposphere. Bright regions correspond to high concentrations of water vapor while dark spots are relatively dry areas. Atmospheric water vapor is produced by evaporation from the oceans. Convected upward in the tropical zones, it affects the climate by contributing substantially to the greenhouse effect. (replotted from [12]).

produces images of upper troposphere at the infrared wavelength of 6.7 µm (Fig. 5). Bright regions correspond to high concentrations of water vapor while dark spots are relatively dry areas.

7. EXPERIMENTAL RESULTS FOR Te AND Cu

A differential technique of radiation recording has been used to study the crystallization of Te [13]. Ten grams of tellurium were sealed under a vacuum into a quartz ampoule. A similar quartz ampoule was filled with a powder of graphite and metal shaving. Both ampoules were inserted into a furnace. The temperature in the ampoules was measured by thermocouples. Radiation beams from the ampoules' bottom in the optical range 2-4 µm (the transparency window of the system) were collected on two PMT. The difference of electric signals was detected by the oscilloscope. So the detecting system allowed recording very fast processes. The crystallization has begun with an undercooling of ~100 °C. Very intensive radiation impulses of 1.5 ms duration have been recorded at the very beginning of each of the 20 experiments.

Luminescence has been recorded while copper wires have been exploded by a high electric current [14,15]. A luminescence band with peak intensity near 1.5 µm was interpreted as the crystallization emission of liquid metal particles. The bands at 0.70 µm, 0.80 µm, 0.85 µm have not been identified [15].

8. EXPERIMENTAL RESULTS DISCUSSION

Experimental evidence of the phenomenon under investigation is relatively uncommon. The phenomenon does not follow from general phase-transition conceptions and is not usually considered in the analysis of transition kinetics. A new theory of this phenomenon has to be developed. To be accepted it has to answer three main questions:
1. Why does the radiation accompanying the phase transition exist?
2. What is the energetic spectrum of the radiation?
3. Which part of the latent energy of phase transition is radiated?

The following sections discuss these questions in turn.

8.1. Radiation existence

Let us consider an excited particle near a phase transition boundary. For phase transition radiation to occur, the probability of excitation energy being converted to light emission by this particle at phase transition must be equal to, or greater than the probability of the excitation energy being converted to heat. It has been generally thought that this probability is negligibly small. An example of probability estimation is given in [16]: For a free molecule in the excited state, its optical lifetime (the longitudinal relaxation time) is equal to \( t_1 = 10^{-7} - 10^{-8} \). For transitions in the near-infrared range at the temperature \( T \approx 1000K \), the non-radiative multi-phonon relaxation time in solids is \( t_2 \leq 10^{-9} \) s. Then the probability of light emission \( p \sim t_2/t_1 \ll 1 \), thus non-radiative phase transitions occur. For a radiative phase transition with \( p \sim 1 \), the time \( t_1 \) of the optical
transition between the melt and the crystal ground states has to be less than, or comparable to the non-radiative relaxation time $t_r$. We believe that this may occur only in a large number of particles, such as nuclear fission reactions, where a critical mass, depending on the system geometry, is needed for the reaction's realization. Similarly, laser radiation depends on population density.

The feasibility of radiative phase transition in an ensemble of particles was treated in terms of quantum electrodynamics (QED) by M. Perelman [17-28]. The model predicted some new effects such as characteristic phase radiation corresponding to transition energy, and stimulated phase transitions. Let us briefly discuss it.

Let us consider a substance near a three phase point. In the solid phase, atoms are at the lowest-lying level and interact through an exchange by virtual photons (more precisely, two-photon) [29]. With an increase of a substance temperature, there is an accumulation of the photons that are able to promote virtually, i.e. temporarily, separate atoms onto the higher level. But to remain on this level, some threshold intensity of photon radiation (depending on a temperature) is necessary. Therefore, a new type of interaction corresponding to liquid or gas phases appears. Thus, in the condensed phases, potentially, there are photons determining opportunities of transitions in phases with other internal energies. In the more common thermodynamic language, the energy of the ensemble of these photons should correspond to the latent heat of the first kind phase transitions.

To develop and justify the theory, the following has been undertaken:

1. The van der Waals forces, as one has been shown in the frame of quantum electrodynamics (QED) [29], are effectively described by photon exchanges. In [17,18], these forces were reduced to the short-range near field.
2. Thresholds of interaction changing in monochromatic laser fields have been determined [19-21]. At this stage, it was shown that temporal parameters of interaction durations can be revealed in the canonical QED theory, and they do not need to be complimentary [22,23].
3. It has been shown that, determined by the rules of QED and taking into account the durations of processes, such temperature thresholds exist for thermal radiation and they don't change the forces and types of interaction [24-26].
4. It has been shown that just the electron-photon interactions, taking into account their duration, describe the basic features of phase transitions [28]. Here, in the frame of QED, the full set of critical indexes of all thermodynamic parameters is designed, which was not possible with other theories. Also, on this basis, the empirical Trouton rule was deduced. Connecting the latent heat with the temperature of vapor condensation, the rule has been used in physical chemistry without any proof for more than a hundred years [30].
5. The latent heat of transition has to escape outside upon back transition from the higher levels onto the lower ones, for example, at vapor condensation or liquid crystallization. In the frame of the theory under consideration, such allocation is possible only by photons' emission of characteristic frequencies for given substance and conditions [24–27].
6. Number and frequencies of formed photons should correspond to newly established bonds of the particle included into a condensate. For atoms and simple molecules, the radiation of two oppositely polarized photons of identical frequencies, corresponding to half of the allocated latent energy per atom/simple molecule, is most probable. Such conclusion corresponds, firstly, to the invariance of spatial parity of joined particles, and secondly to the most intensive electro-dipole interaction. The dipole can either exist in a particle initially, or can be temporarily generated in it and/or in a condensed cluster. Therefore, truly neutral particles (atoms of noble gases, molecules $\text{CO}_2$, etc.) are characterized by the lower temperatures of transitions. As photons' emissions demand certain time, the speed limit of condensation and/or crystallization can be established.

We also need to mention other attempts of theoretical estimation of the radiation under consideration. In [16], the feasibility of radiative phase transition was considered in terms of the theory of super-radiation. The phenomenon of super-radiation is that a system of excited particles undergoes optical transition to a lower level due to their interaction with each other through the common radiation field, the transition time being much shorter than the radiative decay time of an individual particle. The quasi-classical approach, which corresponds to the experimental results, can be employed in super-radiation estimations [31]. Let us remind, that in the quasi-classical approach, an atomic system is described in terms of quantum mechanics whereas the Maxwell's equations are used for electromagnetic field description.
In [32], the possibility of radiation is estimated for phase transitions in solids accompanied by motion of charges from one equilibrium position to another. A ferroelectric transition of the first type is an example of these phase transitions. In this case, the sample polarization changes from some fixed value to zero during the transition. The radiation has to be located in the range of $\lambda \sim 1$ cm.

Thus, our brief review of the new theoretical approach to the phase transitions of the first order and the experimental results prove the existence of the characteristic radiation under consideration. But another interesting fact has to be mentioned. If the condensed substance is formed with characteristic radiation, there should be features in its absorption spectrum on the frequencies corresponding to characteristic radiation. Such features, corresponding more often to half of the energy of transition per particle, have been known for a long time [33–35], however any interpretation of this phenomenon has not been given earlier.

As was indicated above, in our experiments with alkali halides and sapphire, the time of the peak’s appearance does not always coincide with the time at which the crystallization process is recorded. In Refs. 2 and 3 we suggested that formation of clusters in the melt can be accompanied by additional radiation. The estimation in [16] shows that for the simplest case of cubic crystal, in an ensemble including more than $10^5$ particles, radiative phase transition can be realized. It confirms our assumption. Moreover, if bonds of various strengths in a crystal are broken or formed during the phase transition, the phase transition occurs smoothly (sometimes with peculiarities) in some temperature interval. This temperature interval can be determined by infrared spectroscopy. For instance, this technique was used in [36] for determination of the temperature interval of cyclohexane phase transition. It was not a crystallization process, but it is interesting as another example of radiation accompanying phase transition. A cyclohexane crystal is transformed at $T=186$K from a plastic (high-temperature) to an anisotropic (low-temperature) modification. The phase transition at this temperature is accompanied by radiation of the radio frequency $55$ cm$^{-1}$. The optical energy emitted by a crystal is part of the electromagnetic component of the polariton energy. (The polariton energy is equal to the energy of a transverse electromagnetic wave with a small admixture of the mechanical vibration energy of a dipole). The emission appears at the temperature of about $T=190$K, grows to its maximum value at the temperature of $T=186$K and smoothly decreases down to the temperature of $T=183$K.

### 8.2. Energetic spectrum of radiation

As was mentioned above, we found the energetic spectrum of LiF to consist of four bands: $\lambda_1 = 2.80$ $\mu$m, $\lambda_2 = 3.45$ $\mu$m, $\lambda_3 = 4.05$ $\mu$m, $\lambda_4 = 4.35$ $\mu$m. With an error of 7% the energies of the peak set can be expressed as

$$E_{\lambda,n} = 2\pi q \left( L \cdot \frac{n^2}{Z} \right)^{1/2}$$

Here $q$ is the latent heat of phase transition for one particle (for LiF it is equal 6.47 kcal/mol); $z$ is a coordination number (for LiF $z=6$); $(L,n)=0,1,2,\ldots,z$. The $\lambda_1$ corresponds to ($L,n) = (1,3)$; $\lambda_2$ to ($L,n) = (1,2)$; $\lambda_3$ to ($L,n) = (1,1)$ $\lambda_4$ to ($L,n) = (1,0)$. This formula follows from the phase transitions theory developed in [17–29].

As noted above, in [2] we used a more accurate technique with respect to [1] and determined more precise band positions for all alkali halides investigated. We now believe that our interpretation of the process as described in [1] probably has to be corrected. We suggested that the energy of radiation is the latent energy of phase transition plus the activation energy. But the majority of particles lose the energy of activation for transition of a potential barrier. Thus, the liberated energy mainly has to be equal to the latent energy of phase transition. Nevertheless, we don’t exclude that some particles can liberate the energy that is equal to the sum of the latent energy and the additional kinetic energy that is the most probable for the excited particles in a gas phase.

Let us discuss the water phase transitions. If we suggest that each molecular transition from one phase to another produces one photon, the characteristic radiation has to have the following parameters:

1. For water condensation (for instance, drop formation from the vapor – cloud formation in the atmosphere), the main peak has to correspond to $\lambda_1 = 2.90$ $\mu$m;
2. For water crystallization (water drops freezing – hail formation in the atmosphere): $\lambda_2 = 19.62$ $\mu$m;
3. For crystallization from vapor phase (snow particle formation): $\lambda_4 = 2.53$ $\mu$m.

In [27], for two photons produced, taking into account Doppler’s broadening of the characteristic radiation, the following ranges for $\lambda_1$ and $\lambda_4$ were estimated: $\lambda_1 = 5.2 - 6.4$ $\mu$m and $\lambda_4 = 34 - 42$ $\mu$m.
Hence the experimental results from [11,12] correspond to [27] estimation. The increased intensity of radiation was found in these ranges. In [8], near λ, range radiation was recorded.

In [9,10] the positions of the peaks correspond to emitted energy that exceeds the phase transition energy. Our opinion is that these results are explained, firstly, by higher harmonics radiation with respect to the formula above and, secondly, by the particular conditions of the water vapor condensation in [9]. The condensed water forms a thin film on a glass surface. We suggest that water molecules have more adhesion to the glass surface than to each other, and as a result, the lower energetic level of phase transition is located deeper than the level in larger volumes of water. Superheated vapor on the cooled glass surface was also present in this experiment. Therefore, a complimentary reason could be vapor superheating and, as a result, raising of the upper energetic level. Both of these effects can increase the photon energy.

The latent energy of Cu melt crystallization is 304 kJ/mol. One of the unidentified characteristic radiation. The latent energy of Te melt crystallization is 17.5 kJ/mol. For one photon characteristic emission, this energy corresponds to λ₁ = 6.8 μm. The radiation recorded in [12] corresponds to the second harmonic. The transparency window of the system, 2-4 μm, doesn’t allow the observation of lower harmonics.

The latent energy of Cu melt crystallization is 13 kJ/mol. For one photon characteristic emission, the wavelength would be λ₁ = 9.2 μm. The 1.5 mm radiation detected in [14,15] corresponds to the sixth harmonic. The system of recording used, did not allow detection of lower harmonics. At the same time, some non-identified bands 0.70 μm, 0.80 μm, 0.85 μm could be higher harmonics. We also don’t exclude that condensation of the metal vapor after the wire explosion could produce the characteristic radiation. The latent energy of Cu vapor condensation is 304 kJ/mol. One of the unidentified bands may correspond to the two photon characteristic emission at λ₁ = 0.80 μm.

8.3. Which part of the latent energy of phase transition is radiated?

In [10] the recorded energy is estimated as 3 – 5% of full phase transition energy. The problem of characteristic radiation yield has not been solved in the frame of the theories mentioned above. It is evident that the yield, first of all, depends on the transparency of both phases. But here the transparency problem is a very specific one. Indeed, our system contains the main level and the exited one. For the supersaturated phase, the exited level is a filled one. Thus, it can work as an amplifier for the characteristic radiation and, consequently, to be transparent for it. This is the only explanation for the detection of the characteristic radiation of phase transitions for water, ice, Te and Cu. All these substances are non-transparent for infrared radiation. Practically, homogeneity and geometry of a system under consideration have to be very important.

Let us consider a supersaturated phase which is unstable and is ready to be crystallized. A crystallization scheme, taking in to account the phase transition radiation (PTR), can be presented as follows:

- In the supersaturated phase, a transparency window for PTR opens. Thus, for PTR recording during explosive crystallization of supersaturated phase, one doesn’t need to use IR transparent substances, as we thought earlier. IR transparent substances only decrease the absorption of PTR by the grown crystal and the nonsupercooled melt.
- It is possible to understand the existence of the transparency window. Let us consider the described above experiment of Te crystallization. Crystallization began when the supercooling had reached 100 °C. Before, the PTR photons, which exist in the Plank’s radiation, were partly absorbed with excitation of the system. When the supersaturation had reached 100 °C, a threshold for avalanche photon emission has been exceeded by PTR photons in Plank’s radiation. The avalanche initiated the explosive crystallization.
- This scheme can explain deep supercooling of small drops. The threshold of PTR photon emission is higher when a drop is smaller.
- In the crystal growth process, a narrow zone PTR transparency is parallel to the interface. It has to change the Eq.(1) for the heat balance on the interface.

9. CONCLUSION

On the basis of the experimental and theoretical data, we can conclude the following:

- Characteristic radiation corresponding to the first order phase transitions exists.
- A transparency window for the characteristic radiation exists in the supersaturated (suprcooled) phase.
10. PERSPECTIVES

There are a number of experimental and theoretical aspects still to be investigated. But even now we can imagine perspectives of this phenomenon’s application:

• According to the principles of QED the presence of described spontaneous transitions should lead to an opportunity of stimulation of such transitions, for example crystallization, by irradiation of the substance, close to the temperature of crystallization, at a resonant frequency corresponding to the particular path of reaction. Such opportunities, which until now have not been investigated experimentally, should stimulate new effects. For instance, fog formation may be observed as a result of atmosphere irradiation by the characteristic radiation. Sometimes, the crystallizing system would have to be protected against the characteristic radiation to decrease the probability of parasitic nucleation.

• Infrared lasers could be made on the basis of phase transitions (We have the evidence for the vapor water condensation, the crystallizing of lithium fluoride, sapphire, Te and metals).

• Formation of hail in storm clouds in the atmosphere has to be accompanied by intensive characteristic infrared radiation, which could be used for prediction and warning of damaging hail falls.

• A program could also be suggested to use this effect in the study of climate problems. Atmospheric radiation is one of the key subjects of the atmospheric sciences, linking the fields of chemistry, aerosol and cloud physics, and thermodynamics to global climate and climate change. The Atmospheric Radiation Measurement (ARM) Program was created to help resolve scientific uncertainties related to global climate change, with a specific focus on the crucial role of clouds and their influence on radiative feedback processes in the atmosphere [37]. But in spite of the huge scale of the program, including 50 countries, attentive analysis of the program shows that it could be improved. A measurement of intensity of characteristic radiation accompanying water vapor condensation with clouds formation, as well as water drops crystallization with hail and snow clouds formation, could provide significant information concerning cloud formation, as well as the energy balance in atmosphere. We could also use these radiation measurements to know if there is water in the atmosphere of other planets, for instance Mars’ atmosphere.

But preliminary precise investigations of the radiation accompanying water phase transitions in laboratories have to be carried out. On the basis of our experience, we could recommend the use of two-beam IR spectrometers for recording. It could be reasonable to manipulate with humid and dry air in two identical chambers connected to different beams of the spectrophotometer. As for natural experiments, it would probably be reasonable to carry them out on cumulus clouds. Generated most commonly through either thermal convection or frontal lifting, these clouds can grow to heights in excess of 12,000 meters, releasing incredible amounts of energy through the condensation of water vapor within the cloud itself and clouds with vertical development, 500–6,000 m (temperature change –3 °C – 40 °C). The apparatus for radiation recording can be delivered in the zone of cloud formation by balloons or aircraft.

• This radiation may explain Jupiter’s red spot’s color, as well as the orange color of its satellite Io. It is well known that Jupiter emits more energy than it receives from the Sun. Circulation in Jupiter’s atmosphere lifts the heated ammonium and water vapors which are condensed and solidified in the upper part of the atmosphere. Characteristic infrared radiation of these processes may be the reason for the emission in the red range of Jupiter’s radiation.

• A similar process could be realized for the cooling of the Earth: provocation of upper clouds by the characteristic radiation and, as a result, a heat radiation in the space environment.

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REFERENCES


Some peculiarities of first order phase transitions