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Infrared laser based on the principle of melt crystallization or vapor condensation. Why not?

Vitali A. Tatartchenko *

Saint-Gobain Crystals, France, 23 Rue Louis Pouey, Apt. 353, 92800 Puteaux, France

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ABSTRACT

The paper discusses a possibility of new effects in quantum electronics: amplification of certain frequency infrared beams in supersaturated vapors or super-cooled melts as well as design of infrared lasers based on a new type of pumping. The basis of these effects is the existence of characteristic infrared radiation accompanying phase transitions of the first order, especially crystallization and condensation. Experimental results of the author and other researchers concerning characteristic infrared emission detection during crystallization from the melt of some substances (alkali halides, sapphire, tellurium, ice, etc.) are presented, as well as condensation of water vapor. The author has critically analyzed these experimental data in terms of correspondence to the theoretical models. The last ones are based on the assumption that the particle (atom, molecule or cluster), during transition from higher energetic level (vapor or melt) to the lower energetic level (crystal), emits one or more photons depending on the latent energy of the transition. Based on the experimental data, the author postulates a transparency window appearance for the characteristic radiation in the substances where first-order phase transitions take place.

1. Introduction: definition of the scope of discussion

Between the years 1979–1984, a rather unusual for that time experimental finding was published: The appearance of characteristic infrared radiation accompanying crystallization from the melt of some alkali halides, lead chloride, and sapphire [1–3]. These results were not casually obtained but were preceded by a long search for the radiation of crystallization on the basis of a new approach to liberation of the first-order phase transition's latent energy. First-order phase transitions (in our case-crystallization from the melt or vapor phase as well as condensation from vapor phase) can be described as transitions of particles (atoms, molecules, or clusters) from an excited energy level in the melt or vapor to the lower one in the solid or liquid. The gap between these two levels corresponds to the latent energy of crystallization or condensation per the particle. In the widespread description of the crystallization and condensation processes, it is 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 temperature. But in 1964, the author suggested that the act of transition 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 lowered with respect to 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.

On the basis of these assumptions, the author began experiments. The first positive results supported this assumption were obtained in 1970. The results were unusual from the point of view of most specialists in the field of optics, which rejected the suggestion of a high-temperature luminescence in favor of the phonon path of energy removal. But more and more experimental evidence that phase transitions were the source of the radiation, had been obtained and in 1977 first results were accepted for publication [1]. The main results were published in the years 1979–1984 [1–3].

Now numerous experimental and theoretical evidences of radiation accompanying phase transitions of the first-order exist. Partly these results were mentioned in [4–7]. This paper, especially, seeks to review the up-to-date situation from a point of view of the possibility of amplifying the characteristic radiation in a supersaturated medium, as well as the design of infrared lasers with a new type of pumping.

* Tel.: +33 1 47 78 98 76.
E-mail address: vitali.tatartchenko@orange.fr

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2. Experimental results

In [1–3], during crystallization of some alkali halides (LiF, NaCl, NaBr, NaI, KCl, KBr, KI), sapphire (Al_2O_3), and $PbCl_2$, radiation in IR range was detected. The recorded curves exhibited not only thermal radiation, but also characteristic peaks in the range of the wavelengths $\lambda \approx 1$–$5\,\mu m$ corresponding to the radiation of latent energy of crystallization. For instance, for sapphire (Al_2O_3), $\lambda = 1.1\,\mu m$ (the heat of fusion is equal to 108 kJ/mol); for KBr, $\lambda = 4.5\,\mu m$ (the heat of fusion is equal to 25.4 kJ/mol). Besides, for the LiF peak, a fine structure was found. It can be interpreted as a superposition of the four peaks with $\lambda_1 = 2.80\,\mu m$; $\lambda_2 = 3.45\,\mu m$; $\lambda_3 = 4.05\,\mu m$; $\lambda_4 = 4.35\,\mu m$. The position of the last peak exactly corresponds to the latent energy of crystallization (the heat of fusion is equal to 26.9 kJ/mol).

The authors of [8] found the infrared sources in the range 8–14 μm radiations in the atmosphere that can be concerned neither with temperature radiation nor reflective one. These sources were the bottom sides of cumulus clouds and the rising warm air saturated with water vapor.

The authors of [9] observed an anomalous increase in the infrared radiation intensity from the boundary the glass surface-condensed vapor. In the range 1–4 μm, the integral intensity was found to be four times more than Plank's radiation. Two main emission bands were seen at 2.10 and 1.54 μm wavelengths. The intensity of both bands exceeded the background radiation by a factor of ten. Probably, a third band with a wavelength of 3.2 μm, not mentioned by the authors, could be detected on the curve from [9].

In [10] the characteristic radiation was recorded during water vapor condensation and water crystallization in a closed chamber. After passing through a system of filters, the radiation was detected by a bolometer. This technique allowed the authors to confirm that they recorded the characteristic radiation with a maximum in the range 4–8 μm for the vapor condensation and in the range 28–40 μm for the water freezing.

When observing sonaro-luminescence, the author of [11] detected the peak emission at a wavelength of 1.05 μm. A second peak at 0.9 μm, not mentioned by the author, could be seen in the curve from [11]. In the analysis of infrared images of the Earth from the Space, the wavelength range 6.7–6.9 μm is used for clouds registration [12].

In case of the water vapor discharge laser, the main emission bands are ~119 and 220 μm. On the other hand, as was mentioned in [13], few complementary bands have been recorded in its emission spectrum. Four of them, 11.83, 38.1–39.7, 57.8, and 79 μm, which have not been identified, are interesting for us.

A differential technique of radiation recording has been used to study the crystallization of Te [14]. The detection system allowed the recording of very fast processes in the infrared range 2–4 μm (the transparency window of the system). Te crystallization began with an undercooling of ~100 °C. Very intense radiation impulses of 1.5 ms duration have been recorded at the very beginning of each of the 20 crystallizations in the study.

Luminescence has been recorded while copper wires have been exploded by a high electric current [15,16]. A luminescence band with peak intensity near 1.5 μm was interpreted as the crystallization emission of liquid metal particles. Bands at 0.70, 0.80, and 0.85 μm have not been identified [16].

3. Theoretical basis of characteristic radiation existence

Evidence of the phenomenon under investigation does not follow from general phase-transition conceptions. Indeed, 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. Here is an example of the probability estimation from [17]: for a free molecule in the excited state, its optical life-time (the longitudinal relaxation time) is equal to $t_1 = 10^{-7}$–10^{-8} s. For transitions in the near-infrared range at the temperature $T \approx 1000$ K, the non-radiative multi-phonon relaxation time in solids is $t_2 \leqslant 10^{-9}$ s. Then, the probability of light emission $p \sim t_2/t_1 \ll 1$ and non-radiative phase transitions have to be realized. 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_2.

It is important to emphasize that the previous estimation was accomplished for a free molecule in the excited state. We believe that in a large number of particles the situation will be completely different and that radiative phase transition would occur. A similar situation exists for nuclear fission reactions, where a critical mass depending on the system geometry is needed for the reaction realization. Similarly, laser radiation depends on population density.

In [17], 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.

Much earlier, for the first time, the feasibility of radiative phase transition in an ensemble of particles was treated in terms of quantum electrodynamics (QED) in [18] and later in few papers, [6,19]. The model predicts some new effects such as characteristic phase radiation corresponding to transition energy, and stimulated phase transitions.

4. Energetic spectrum of radiation

Let us consider the main points of the last two papers [6,19]. When the particle (atom, molecule, or cluster) enters into a new phase, it radiates the latent heat of transition for this particle as one or several quanta. It has to be mentioned that some of these quanta can be thermalized before they leave the substance.

The following opportunities for the ranges of radiation follow from [6,19]:

A. If radiation has one-photon character;

$$\hbar\omega_1 = \Lambda/N_A, \text{ that corresponds to } \lambda_1 = 120/\Lambda; \tag{1}$$

Here, $\hbar\omega_1$ is the energy of emitted photon; λ_1 the length of the one-photon radiation wave in μm; N_A the Avogadro number; the latent energy of phase transition Λ is expressed in kJ/mole (it has to be mentioned that latent heat of condensation as well as the latent heat of crystallization are not constant; they both change with pressure and other extensive parameters).

B. The n-photon transition with equal frequencies;

$$\hbar\omega_n = \Lambda/nN_A \text{ or } \lambda_n = 120n/\Lambda. \tag{2}$$

Here, n is the number of new formed bonds in the condensate liberating the bond energy via radiation. It can be less than or equal to the coordination number m: $n = 1, 2, 3, \ldots, m$. The singularities of the spectra of the condensate media can describe the number of the new bonds, i.e. their