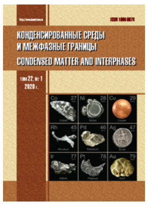

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Spectral analysis of heat fluctuations in KI transient premelting states

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Abstract
Nonequlibrium fluctuations, which are of nonlinear Brownian noise by type, occur in different systems near the phase transition points. As a rule, such nonequlibrium processes are the precursors of materials fracture and degradation. Observation of the transient premelting states near the melting point T_m and anomalous temperature behaviour of some physical parameters indicate changes in the structure and properties of a solid body as it approaches the melting point. As a rule, the changes are nonlinearly dependent on heating rate. It is necessary to calculate the index of the shape of the fluctuation spectrum to characterise the state of complex dynamic systems. The index has information about the processes in the system and the interrelations between different subsystems. Changes in the spectral characteristics of fluctuation processes may indicate the state of the system and also help us to develop the methods to predict its evolution. The aim of this study is parametrisation of heat fluctuations in the premelting states of KI ionic crystals and the study of the dependence of spectral parameters on kinetic modes of heating.
Wavelet-analysis has been used to determine the spectral characteristics of thermal fluctuations in the KI premelting states in various kinetic modes. Wavelet-analysis combines the capabilities of classical spectral Fourier-analysis with the capabilities of a local study of various fluctuation and oscillating processes in frequency and time domains. It makes it possible to determine the features of the processes at various times and scales of the evolution of the system.
Wavelet transform of oscillating processes allowed obtaining information about the dynamics of the development of complex systems under various nonequilibrium conditions. It was shown that heat fluctuations in the KI premelting states are nonlinear Brownian noise with the coefficient of selfsimilarity of $\beta \sim 2$. Using the Hurst parameter, the type of fluctuation process was defined. It was shown that in dynamic heating modes (v = 5, 10 K/min) the fluctuation process is characterised by oscillating nature of evolution of the "stable-unstable" type (the property of antipersistency). In quasistatic modes (v = 1 K/min) the initial tendency of the evolution of the system is maintained (the property of persistence).

Keywords: potassium iodide, premelting, melting point, fluctuation, wavelet-analysis, index of selfsimilarity, nonlinear Brownian noise, Hurst parameter, structural reconstruction.

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1. Introduction

Fluctuation processes with $1/f^{\beta}$ spectrum (β – the index of the shape of the spectrum) occur in different physical, chemical, and biological systems [1–4]. The study of such processes is one of the most important issues in material science. In the context of deformation and fracture of materials and various phase transitions far from thermodynamic equilibrium, unstable dynamic states arise. They are the precursors of structural changes in the system [5–9].

The study of fluctuation processes at critical points in order to obtain new materials and systems with unique properties is of great practical importance. In this case, new technological approaches are required, which are based on the concept of nonlinear phenomena, when the choice of a specific development path of the system at a critical point can be carried out under the influence of a small control action.

Dynamic methods of analysis can be effectively used in the study of the precursors of various phase transitions [10,11]. An analysis of the evolution of complex excited systems with determination of the low-frequency spectral dependences of dynamic variables allows us to come closer to understanding of the features of the formation of spatio-temporal structures during such evolution.

To characterise the state of complex fluctuating systems, spectral parameters are introduced that carry information about the dynamic processes taking place in the system and the interrelations of various subsystems. A change in these spectral parameters at different hierarchy levels indicates a change in the state of the system. Based on this information, it is possible to develop methods for predicting the evolution of complex dynamic systems.

The aim of this work is to study, using the wavelet-analysis method, the spectral characteristics of fluctuation processes of KI premelting phases in various kinetic heating modes.

2. Experimental

Previously, our studies of the melting of substances with various types of chemical bonds showed that the fluctuation transient states occur near the melting point in certain temperature-time intervals [12, 13]. It is particularly interesting to observe thermal fluctuations (fluctuations in the dissipation heat) in the vicinity of a first-order phase transition in this context, since the presence of such processes cannot be unambiguously associated with the existence of a continuous relaxation time spectrum in the system.

Along with the traditional spectral analysis methods, the method of wavelet-analysis [14–17] of nonequilibrium oscillating processes is applied to study the dynamics of complex systems to determine their interrelations and certain possible development paths under various external influences.

A wavelet transform is one of the methods of analysis and processing of nonstationary (in time) or heterogeneous (in space) signals of different types. Such an analysis is used when it is necessary to obtain not only a simple enumeration of the characteristic frequencies of the studied fluctuation signal, but also to obtain information at certain local points at which these frequencies appear.

For the spectral analysis of fluctuations of the dissipation heat and parameterisation of the KI premelting phases in various kinetic modes, the obtained database was used. It includes the records of the readings of the differential thermocouple in the dynamic mode at heating rates $v = 5$, 10 K/min and in the quasistatic mode ($v = 1$ K/min). The constant recording sample speed is 1 s. The length of the record in the files ranged from 500 to 1500 samples.

DTA-curves of KI premelting in different kinetic modes are shown in Fig. 1. As can be seen from the above figure, on the DTA-curves in dynamic and quasistatic modes, the dynamic states arising at the premelting stage have clear temperature boundaries.

The premelting effects are characterised by the system of experimentally defined nonequilibrium thermodynamic parameters: the temperature of the beginning and end of the premelting effect ($T'_{pre\text{-}m}$, $T''_{pre\text{-}m}$), the premelting temperature range ($\delta T_{pre\text{-}m}$), the premelting dissipation temperature ($\Delta Q_{pre\text{-}m}$) [12]. Each heating mode has its own values of thermodynamic parameters of the transient states. Depending on the heating mode, different states are formed which characterise the premelting effects. Thus, in contrast with

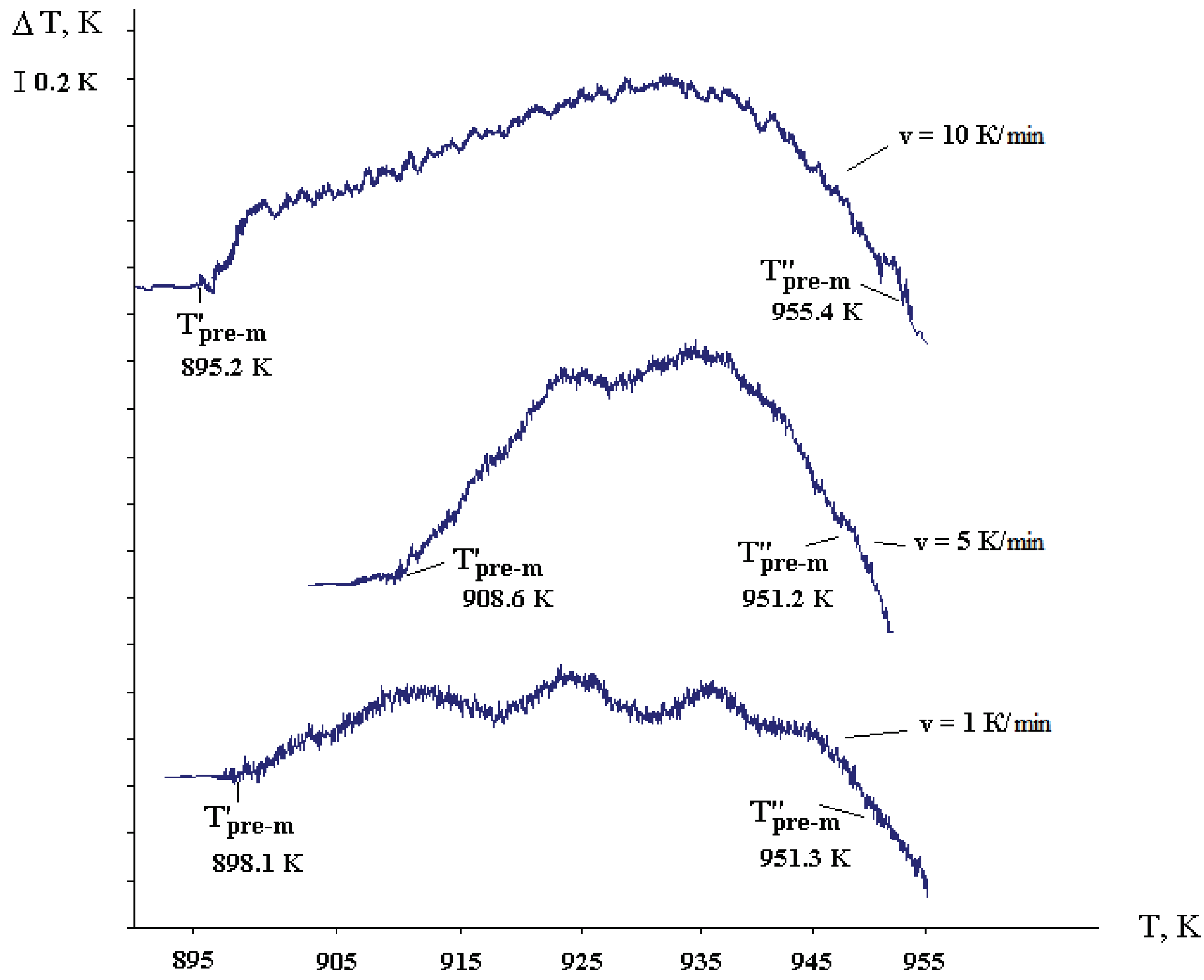

Fig. 1. DTA-curve of the KI premelting effect in different kinetic modes

the dynamic heating mode (v = 5, 10 K/min), the amplitude of the heating impulse of KI premelting in the quasistatic heating mode (v = 1 K/min) decreases, and the thermal fluctuations become oscillating.

The spectral analysis of fluctuation processes of KI premelting was carried out in the MatLab software using the continuous wavelet transform method with the basis function Symlet8. The continuous wavelet transform allows for a more explicit and clear interpretation of the results of the signal analysis, and information about changes in characteristic frequencies of fluctuation processes and their interaction is easier to analyse. Moreover, when studying the fluctuation process, it is possible to consider the group of phases of this process corresponding to various independent spectral components.

3. Results and discussion

The wavelet-diagram of the KI premelting effect in the dynamic mode at a heating rate of 5 K/min is shown in Fig. 2. Time τ (or the shift parameter b) is plotted along the abscissa and the wavelet time scale a. Dark areas of the diagram correspond to the positive values of the $W(a,b)$ coefficients and its bright areas correspond to the negative values. The $W(a,b)$ value ranges are marked with different intensities of colour. The hierarchical arch structure of local extrema of the $W(a,b)$ coefficients, reproduced at different scales, is clearly visible in the given wavelet-diagram. It demonstrates a scaled self-similarity of dissipation heat fluctuations of KI premelting.

A scalogram is used to define the self-similarity coefficient β or the index of the shape of the spectrum. It is given as a mean square of wavelet coefficients $E_w \sim W^2(a,b)$ with a given scale

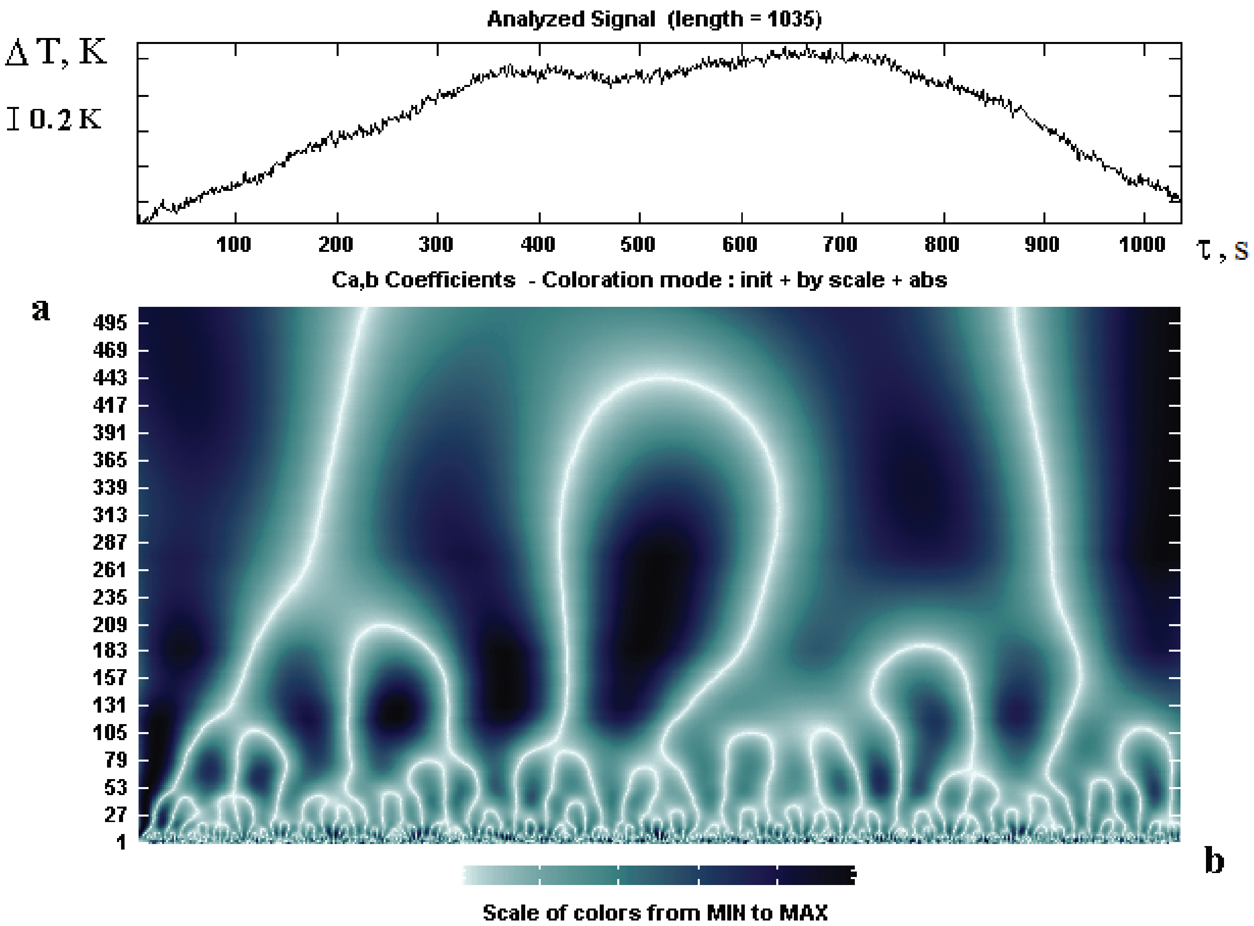

Fig. 2. DTA-curve of dissipation heat fluctuation and wavelet-diagram of the KI premelting effect (dynamic mode, v = 5 K/min)

a. The scalogram represents the same information as the Fourier power spectral density that is the function of frequency, i.e., it corresponds to the smoothed power spectrum of the Fourier transform. The self-similarity coefficient β is defined as the angle of the dependence of lg E_w on lg a (Fig. 3) and it indicates the degree of correlation of the frequency components of the fluctuation signal.

Scalogram analysis of the thermal fluctuations of KI premelting in the dynamic mode (v = 5, 10 K/min) showed that the coefficient is β ~ 2, and in the quasistatic mode (v = 1 K/min) the self-similarity coefficient slightly decreases. The values of the self-similarity coefficients β and frequency intervals of dissipation heat fluctuations in transient states of KI premelting in different kinetic modes are provided in the Table. 1.

This kind of wavelet transform pattern and the value of the self-similarity coefficient indicate that the fluctuation processes in KI premelting states are nonlinear Brownian noise ($1/f^2$ type noise), i.e., they are a random process with independent increments.

The linear display of scalograms revealed the difference in the intensity of dissipation processes of KI premelting in different kinetic modes (Fig. 4). Based on this analysis, it can be seen that with a decrease in the heating rate during the transition from dynamic to quasistatic mode, the intensity of thermal fluctuations decreases. A decrease in the intensity of thermal fluctuations in the KI premelting states in the quasistatic

Table 1. Fluctuation of dissipation heat parameters of transient processes during the melting of KI

v, K/min	β	$\Delta f_{pre\text{-}m}$, Hz	H
1	1.9	0.007–0.03	0.58
5	2.2	0.01–0.07	0.42
10	2.1	0.02–0.18	0.4

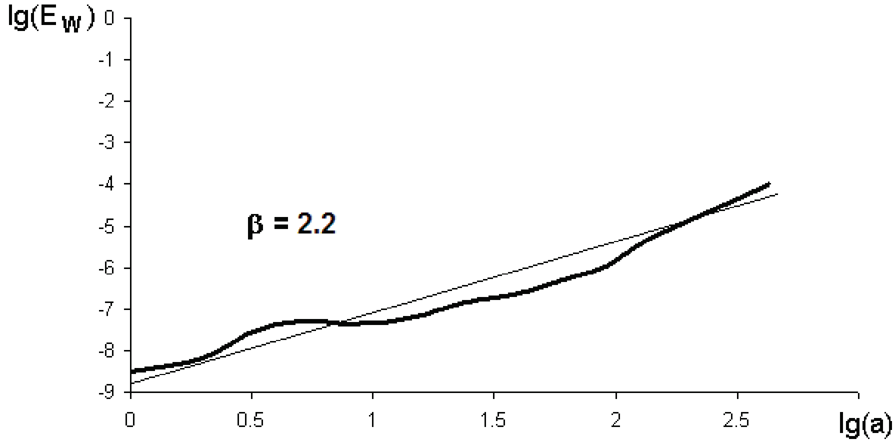

Fig. 3. Scalogram of the KI premelting effect (dynamic mode, v = 5 K/min)

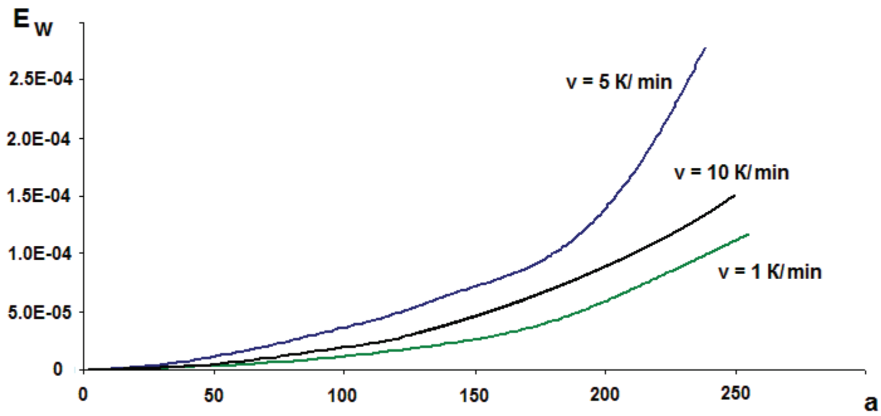

Fig. 4. Evolution of heat fluctuation intensity of the KI premelting effect in different kinetic modes

mode leads to a weakening of correlations in the system, which is also indicated by a decrease in the self-similarity coefficient β.

When analysing complex fluctuation signals, it is possible to evaluate the degree of their randomness using such a stochastic characteristic as the Hurst parameter (H) [18, 19]. The Hurst parameter is the measure of the tendency of the process towards trend (in contrast to the usual Brownian motion). A value of $H > 0.5$ indicates that the dynamics of the process in the past, heading in a certain direction, and is likely to continue its development in the same direction. If $H < 0.5$, the process is predicted to change its direction, while in the case of $H = 0.5$ it indicates uncertainty.

Evaluation of the Hurst parameter of heat fluctuations of the KI premelting states in the dynamic heating modes provides the values of $H < 0.5$ (Table 1). This indicates a system which is more prone to reconstructions when its development tendency changes. Such fluctuation signals are characterized by a lack of stability (antipersistency). Their growth in the past means a decrease in the future, and a tendency to decrease in the past makes an increase in the future likely. Evaluation of the Hurst parameter in the dynamic heating mode gives the value of $H \sim 0.58$. This value of H indicates that this time dependence has a stable tendency to change (persistence). In other words, the presence of $1/f^2$ type fluctuations in the system indicate structural changes in it. In such cases, as a rule, an oscillatory change of the "stability-instability-stability" type occurs.

If far from a critical point, the system will be quite stable, and the fluctuations will not have a noticeable effect on its behaviour. But if the system is near a critical point (phase transition point T_m), then an intensification of fluctuations will be a consequence of its sensitivity to small changes in the initial conditions. The intensification of fluctuations may lead to the formation of the ordered or so-called dissipative structures. This important phenomenon is known as ordering through fluctuations [20]. When the system approaches a phase transition point T_m, characteristic features appear that are the precursors of nonlinear instabilities.

4. Conclusions

Therefore, the wavelet transform allows us to identify a complex hierarchy of scales in the process of energy redistribution of the fluctuation process. The energy represented by a large-scale "plateau" is redistributed between several "ridges" in a certain range of scales. Energy maxima can also be found between them. A similar process is observed with smaller scales. Therefore, a certain combination of ordering and chaos in the case of nonlinear Brownian noise, revealed during wavelet processing, reflects the presence of correlations in the system with a fluctuating dynamic variable.

Based on the wavelet-analysis, it was found that the transient fluctuation processes of KI premelting in various kinetic modes are nonlinear Brownian noise and are characterized by such features as the frequency interval, self-similarity coefficient of thermal fluctuations of the premelting, and Hurst parameter. In quasistatic modes, at heating rates of $v \sim 1$ K/min, states with a weaker correlation arise in the KI premelting states. The fluctuation process in this case is characterized by a long-term memory effect with a tendency to follow trends. With dynamic modes of thermal fluctuations in the KI premelting states the correlations in the system intensify, and the resulting reconstructions in the system lead to a qualitative change in the structure. As a result, it is possible to not only describe the behaviour of the investigated fluctuation process, but also to predict its dynamics. In this case, it becomes possible to get an idea of the properties of fluctuating systems and distinguish noise (random process) from a certain determinisitic behaviour.

Conflict of interests

The author declares that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Bityutskaya L. A., Selezvev G. D. Thermal flicker noise in dissipative processes of pre-melting of crystalline materials. *Physics of the Solid State*. 1999;41(9): 1537–1540. DOI: https://doi.org/10.1134/1.1131018

2. Gerashchenko O. V., Matveev V. A., Pleshanov N. K., Bairamukov V. Yu. Electrical resistance and 1/*f* fluctuations in thin titanium films. *Physics of the Solid State*. 2014;56(7): 1443–1448. DOI: https://doi.org/10.1134/S1063783414070130

3. Klochikhin V. L., Lakeev S. G., Timashev S. F. Flicker-noise in chemical kinetics (Microscopic kinetics and fluctuations in stationary chemical processes). *Russian Journal of Physical Chemistry A*. 1999;73(2): 172–178. Available at: https://elibrary.ru/item.asp?id=13313799

4. Pavlov A. N., Hramov A. E., Koronovskii A. A., Sitnikova E. Yu, Makarov V. A., Ovchinnikov A. A. Wavelet analysis in neurodynamics. *Phys. Usp*. 2012;55: 845–875. DOI: https://doi.org/10.3367/UFNe.0182.201209a.0905

5. Kosopov G. D., Bardyug D. Yu. Analysis of ice premelting in water-containing disperse media *Technical Physics Letters*. 2007;33(7): 622–624. DOI: https://doi.org/10.1134/S1063785007070243

6. Shibkov A. A. Gasanov M. F., Zolotov A. E., Zheltov M. A., Denisov A. A., Koltsov R. Yu., Kochegarov S. S. Elektrokhimicheskaya emissiya pri deformirovanii i razrushenii

alyuminii-magnievogo splava v vodnoi srede [Electrochemical emission at deformation and fracture of aluminium-magnesium alloy in water medium]. *Technical Physics*. 2020;90(1): 85–93. DOI: https://doi.org/10.21883/JTF.2020.01.48666.151-19 (In Russ.)

7. Feychuk P., Bityutskaya L., Mashkina E., Shcherbak L. Heat processes oscillations in the molten and solid CdTe. *J. Cryst. Growth*. 2005;275 (1–2): e1827–e1833. DOI: https://doi.org/10.1016/j.jcrysgro.2004.11.256

8. Umeno Y., Shimada T., Kitamura T. Dislocation nucleation in a thin Cu film from molecular dynamics simulations: Instability activation by thermal fluctuations. *Phys. Rev. B*. 2010;82(10): 104108/1–104108/11. DOI: https://doi.org/10.1103/PhysRevB.82.104108

9. Urakaev F. Kh., Massalimov I. A. Energy fluctuations and particle emission in a crack mouth. *Physics of the Solid State*. 2005;47(9): 1675–1680. DOI: https://doi.org/10.1134/1.2045350

10. Koverda V. P., Terekhov V. N. Scaling of 1/*f* noise in nonequilibrium phase transitions. *Technical Physics*. 2004; 49(9):1104–1109. DOI: https://doi.org/10.1134/1.1800229

11. Zhigalskii G. P. Fluktuacii i shumi v elektronnyh tverdotel'nyh priborah [Fluctuation and noises in electronic solid state devices]. Moscow: Fizmatlit Publ.; 2012. 512 p. (in Russ.)

12. Bityutskaya L. A., Mashkina E. S. System of kinetic parameters of the transition processes under melting of crystalline substances. *Phase Transition*. 2000;71: 317–330. DOI: https://doi.org/10.1080/01411590008209312

13. Mashkina E. S. An anion influence on transient states during ionic crystals melting. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2011;13(3): 309–314. Available at: http://www.kcmf.vsu.ru/resources/t_13_3_2011_010.pdf (In Russ.)

14. Astaf'eva N. M. Wavelet analysis: basic theory and some applications. *Phys. Usp.* 1996;39(11): 1085–1108. DOI: https://doi.org/10.1070/PU1996v039n11ABEH000177

15. Dremin I. M., Ivanov O. V., Nechitailo V. A. Wavelets and their uses. *Phys. Usp.* 2001;44(5): 447–478. DOI: https://doi.org/10.1070/PU2001v044n05ABEH000918

16. Arby P., Goncalves P., Vehel J. L. *Scaling, fractals and wavelets*. London: John Wiley & Sons; 2009. 464 p.

17. Smolentsev N. K. *Osnovi teorii waveletov. Waveleti v MATLAB* [Fundamentals of wavelet theory. Wavelets in MATLAB]. Moscow: DMK Press; 2014. 628 p. (In Russ.)

18. Hurst H. E., Black R. P., Simaika Y. M. *Long-term storage: An experimental study*. London: Constable; 1965. 145 p.

19. Chen B. B., Imashev S. A. Evaluation of Hurst parameter on energetic spectrum based on wavelet transform. *Vestnik KRSU*. 2007;7(8): 65–75. Available at: https://www.elibrary.ru/item.asp?id=13519890 (In Russ., abstract in Eng.)

20. Zulpukarov M.-G. M., Malinetsky G. G., Podlazov A. V. Bifurcation theory inverse problem in a noisy dynamical system. Example solution. *Izvestiya VUZ. Applied Nonlinear Dynamics*. 2005;13(5–6): 3–23. Available at: file:///C:/Users/%D0%BF%D0%BE% D0%BB%D1%8C%D0%B7%D0%BE%D0%B2%D0%B0%D1%82%D0%B5%D0%BB%D1%8C/Downloads/2005no5-6p003.pdf (In Russ., abstract in Eng.)

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