

## Local Activation of Crystals by $\gamma$ -Rays and Self-Organization Processes

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**Abstract**—It was shown that irradiation of the crystals with high-energy (up to 55 MeV)  $\gamma$ -rays leads to the prolonged self-organization of atomic displacements. A tiny portion (at about  $10^{-9}$  of the sample volume) of the initially excited atoms organize the entire crystal volume with respect to the time and the space.

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### INTRODUCTION

The investigations of the self-organization processes in condensed matter presume their initial activation by some external effect. It can be electric or magnetic impact, pressure, temperature jumps, etc. This activation uniformly affects all atoms in a material volume adding elements of chaos to the atomic and magnetic structures and leading to their subsequent ordering in time and space. As can be seen, the bulk effect is quite effective in the case of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  metal crystal subjected to an electric impact where pronounced variations in the occupancy parameters of two structurally nonequivalent positions of Fe atoms were observed [1]. The period of variations was  $\sim 30$  days, and they ceased after  $\sim 150$  days. At the same time the bulk effect does not allow us to estimate the lower limit of the possibilities of matter to emerge from the chaotic state (in particular, the lowest number of atoms that must be excited to make this phenomenon manifest itself).

Therefore it is of great interest to investigate the sample responses to irradiation with high-energy elementary particles with a rather small capture cross section. The number of excited atoms can also be limited by the intensity of the particle flux and the irradiated area on the sample surface. A strong response of a system to such local perturbation can be a good argument in favour of the expected synergetic character of the process.

In this work we present the results of our study of  $\gamma$ -irradiation on metal ( $\text{Nd}_2\text{Fe}_{14}\text{B}$ ) and nonmetal (multiferroic  $\text{BiFeO}_3$ ) crystals.

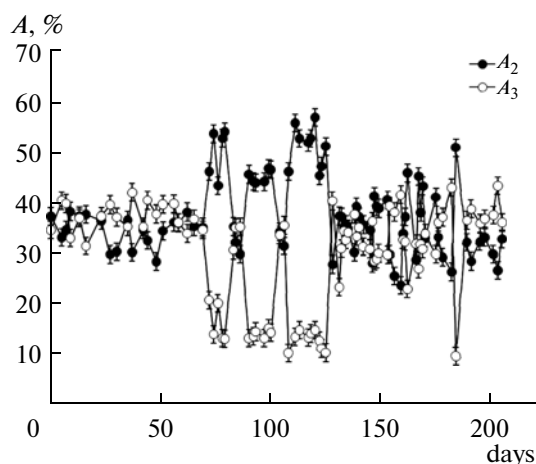
### EXPERIMENTAL PART

#### *Investigation of Local $\gamma$ -Activation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ Crystal*

$\text{Nd}_2\text{Fe}_{14}\text{B}$  sample prepared by sintering was a grinded powder uniformly distributed in a plexiglass

cell 20 mm in diameter without glue to form a layer of approximately 0.3 mm thick. The sample was irradiated directly in the cell by a pulse of bremsstrahlung  $\gamma$ -rays with upper boundary of 6 MeV in the commercial electron accelerator (Moscow State University Institute of Nuclear Physics). The radiation was generated by means of deceleration of electrons in a tungsten plate of 0.2 mm thick. The length of irradiation in the first series of experiments was 1 h and the absorbed dose was 655 Gy. Just after the radiation impact only narrow strip of 2 mm wide with an axis coinciding with the diameter of the sample was irradiated and the rest of the sample volume was not irradiated. It means that only at about  $\sim 10^{-9}$  of the sample volume was initially excited by irradiation. However, the entire volume becomes excited over time. Transmission Mössbauer spectroscopy with  $^{57}\text{Co}$  in a Pd matrix source was used in our experiments. Each spectrum was recorded for 8–10 h. We monitored the state of the sample for several hundred days at  $T = 293$  K.

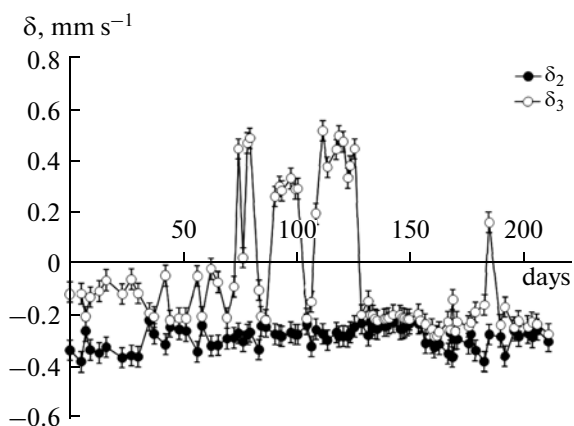
Unperturbed sample was studied in the course of 69 days prior to irradiation. Following the results, which were obtained for  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , [1] our spectra were processed using a model of four Zeeman sextets with the following variable parameters: hyperfine field ( $H_{\text{hf}}$ ), isomeric shift ( $\delta$ ), quadrupole splitting ( $Q$ ), linewidth  $\Gamma$ , and relative weight  $A$  of a partial sextet. This model corresponds to six structurally nonequivalent positions of Fe atoms in a tetragonal  $\text{Nd}_2\text{Fe}_{14}\text{B}$  cell ( $a = 8.8$  Å,  $c = 12.19$  Å) [2]:  $16K_1$ ,  $16K_2$ ,  $8j_1$ ,  $8j_2$ ,  $4e$ , and  $4c$ , where the first numbers correspond to the numbers of Fe atoms in a certain position (total number of atoms in the cell is 68; cell contains 56 Fe atoms). The  $H_1$  field corresponds to the  $j_2$  position;  $H_2$  corresponds to the  $K_2$  position;  $H_3$  corresponds to the sum of three positions ( $K_1 + j_1 + e$ ) whose Mössbauer parameters are quite close; and  $H_4$  corresponds to the  $c$  position.



**Fig. 1.** Time dependence of parameters  $A_2$  and  $A_3$  in the first series of experiments with irradiation.

There are 2.4 stoichiometric vacancies per cell in the sample. The spectra processing revealed that the parameters of the unperturbed sample changed significantly over time (up to 69 days). For example, Fig. 1 shows the behavior of the parameters  $A_2$  and  $A_3$  (occupancies of the second and third sextets are  $H_2 \sim 290$  kOe and  $H_3 \sim 285$  kOe, respectively). It can be seen that their average values ( $\sim 35\%$ ) are almost identical.

However, the situation changes radically after  $\gamma$  irradiation. In this case oscillations composed of three characteristic waves with durations of 15–20 days and peak-to-peak differences  $\Delta = A_2 - A_3$  of up to  $\sim 48\%$  clearly manifest themselves in the time interval from 69 to 128 days (Fig. 1). It should be noted that the weight of the second sextet dominates strongly over the weight of the third ( $A_2 \gg A_3$ ). The isomeric shifts  $\delta_2$  and  $\delta_3$  behave in a manner similar to  $A_2$  and  $A_3$  with just one difference: videlicet only parameter  $\delta_3$  oscillates



**Fig. 2.** Time dependence of parameters  $\delta_2$  and  $\delta_3$  in the first series of experiments with irradiation.

(Fig. 2). A characteristic spike that occurred on the 184th day is presented in Figs. 1 and 2.

We can obviously conclude on the basis of our experiments that the system synchronously responds to  $\gamma$ -irradiation and as a whole over the entire atomic ensemble.

Once relaxation in the sample finished, the second series of experiments was fulfilled, notable the sample was subjected to radiation again with higher dose (1300 Gy). The irradiation response of the system was extremely strong and in many respects similar to the one observed in the first series of experiments. However, we revealed the following distinctions:

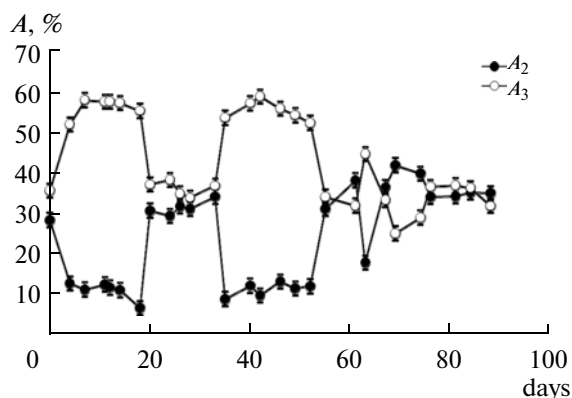
(i) Two (rather than three) oscillation waves separated by a gap of at about 13 days were observed in the parameters of hyperfine interactions.

(ii) The amplitude of oscillations of parameter  $\Delta$  was larger (by as much as  $\sim 52\%$ ). It turned out to be in antiphase with the one observed in Fig. 1, i.e.,  $A_2$  decreased and  $A_3$  increased upon irradiation (Fig. 3). There was also a peak about 70th day.

(iii) The oscillations of isomeric shifts were also in antiphase with the data which is given in Fig. 2.  $\delta_2$  oscillated while  $\delta_3$  remained constant and vice versa.

### Result Discussion

Analyzing received results, we should especially note the rapid (several days) response of the system to irradiation (Figs. 1–3). This is extremely important therefore, such response apparently indicates some inherent property of specifically metal systems. This property is likely to be fast diffusion or, more exactly, the displacement of some atoms to stoichiometric unoccupied sites in the atomic structure. Which are these atoms?



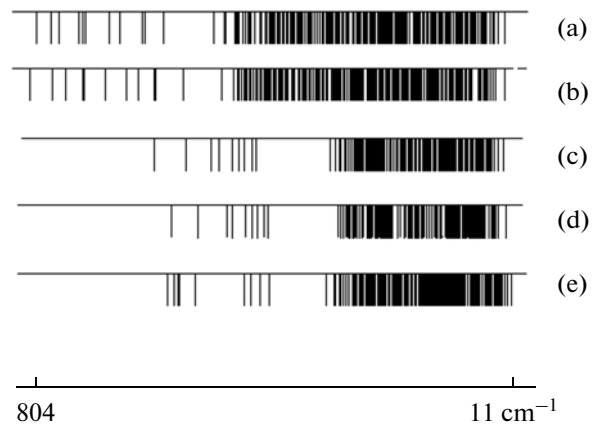
**Fig. 3.** Time dependence of parameters  $A_2$  and  $A_3$  in the second series of experiments with irradiation.

To answer this question we calculated the IR vibrational spectrum of the  $\text{Nd}_2\text{Fe}_{14}\text{B}$  structure. The technique for quantum-chemical calculations of IR spectra which was applied to solve this problem was described in [3]. The first step was to calculate the IR spectrum of the initial structure without vacancies, using the atomic coordinates [2]. The result is shown in Fig. 4a. The dark bands and lines correspond to the actual vibrational frequencies. The lowest vibrational frequencies (the right side of the spectrum) inhaled in B atoms and an ensemble of B atom surrounded by Fe atoms. Then we simulated a situation with one or two Fe vacancies inhaled in the sample and with three and four Fe vacancies indicated the knockout of Fe atoms from irradiated cell (Figs. 4b–4e). The presence of vacancies affects the shape of the spectra considerably. From Fig. 1a to Fig. 1e the bands of different frequencies are combined in the region of the continuous spectrum. In addition, these bands shift to the low vibrational frequencies (region of B atom frequencies). Figures 4a (a line spectrum) and 4e (wide bands of the continuous spectrum) differ especially strongly. We determined the signification as the following:

(i)  $\gamma$ -ray excitation induces the motion of light B atoms through vacancies. As it is indicated by the considerable narrowing of the spectrum in Fig. 4e in the direction of low frequencies, B atoms initiate the process of cell irradiation.

(ii) The bond energies of atoms in different positions differ only slightly in the situation shown in Fig. 4e. For example,  $(K_1 + j_1 + e)$  is easily transformed into the  $K_2$  position via migration small variations in the distances between atoms and bond angles are the required conditions provided by the excitation of the lattice after its irradiated by  $\gamma$ -photons. B atoms moving to unoccupied voids initiate the process, which results to strong upset of the electronic balance and distorts on the local atomic structure. A wave of  $(K_1 + j_1 + e) \rightarrow K_2$  transformation thus propagates through the entire sample. As follows from the invariable behavior of isomeric shift  $\delta_2$  (Fig. 2) it is noteworthy that the  $K_2$  positions are crystallographically stable. There is only the low number of these positions that changes. The waves of structural reorganization transfers the excitation from areas inside of each crystal to the entire volume of the sample, which is larger by a factor of  $10^9$ , therefore, a certain time is necessary to make an order in it.

Let us consider the microscopic mechanism of the propagation of these waves. Let  $X$  be the distance by which a group of B atoms with mass  $m$  shifts collectively and simultaneously. Displacement occurs through unoccupied positions, both initial and those



**Fig. 4.** IR spectra calculated for  $\text{Nd}_2\text{Fe}_{14}\text{B}$  vacancies (a) 0, (b) 1, (c) 2, (d) 3, and (e) 4.

formed upon irradiation. The  $X$  vibrations can then be described by the equation

$$m d^2 X / dt^2 = -kX + f_0, \quad (1)$$

where  $k$  (constant) is the coefficient of the vibrational system rigidity and  $f_0$  is the force impeding the atomic displacement, which is of both an electrostatic and a magnetoelastic character. It is in fact the force of internal friction associated with the upsetting of the thermodynamic equilibrium upon perturbations in electric balance created by a moving atomic ensemble. This force turns opposite to the direction of atomic motion, i.e., it is  $-f_0$  for atomic displacement along the  $x$  axis to the right and  $+f_0$  for atomic displacement to the left. Parameter  $f_0$  is independent of velocity  $dX/dt$  and is determined only by the structural and magnetic features of the crystal. The stepwise shape of the function  $f_0(x)$  makes (1) exceptionally nonlinear. Introducing the designations  $k/m = \omega_0^2$  and  $f_0/k = a$  and substituting the variables  $X_1 = X - a$  and  $X_2 = X + a$ , we arrive at the following system of equations:

$$\begin{aligned} d^2 X / dt^2 + \omega_0^2 X_1 &= 0 \\ \text{for leftward motion along the } x \text{ axis,} \end{aligned} \quad (2)$$

$$\begin{aligned} d^2 X / dt^2 + \omega_0^2 X_2 &= 0 \\ \text{for rightward motion along the } x \text{ axis.} \end{aligned} \quad (3)$$

The points of equilibrium in (2) and (3) are shifted, respectively, by  $(+a)$  and  $(-a)$  with respect to point  $x = 0$ . In the interval  $(+a) - (-a)$  the system can be stable at any point, since  $kX < f_0$ . Equations (2) and (3) describe oscillations that are close to harmonic and tend toward suppression rather than damping after a certain number of cycles. The parameter  $a$  lies in the nanometer range.

Having introduced the designation  $dX/dt = y$  and integrated (2) and (3), we can present dependence  $y(x)$  in the phase plane as a phase diagram (Fig. 5). The

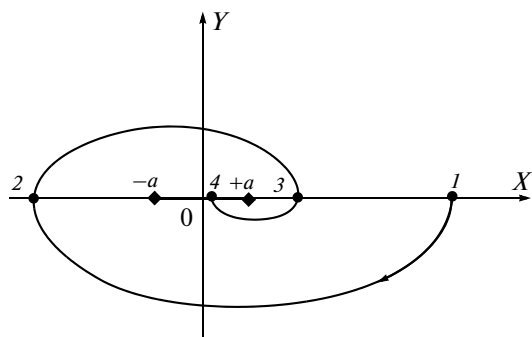


Fig. 5. Phase diagram of atomic displacements in  $\text{Nd}_2\text{Fe}_{14}\text{B}$  crystal upon  $\gamma$ -ray irradiation.

phase trajectories are sets of semi-ellipses whose centers are shifted to the right and to the left along the  $x$  axis by distance  $a$ . At initial point  $I$ , the system is strongly perturbed and  $y = 0$  due to the retarding action of force  $-f_0$ . The system then returns to equilibrium, i.e., to motion in the lower half-plane from point  $I$  to point  $2$  along an elliptical trajectory centered on point  $+a$ . At point  $2$  ( $y = 0$ ), motion stops due to the action of  $+f_0$ . Motion then occurs along an ellipse (from point  $2$  to point  $3$ ) centered on point  $-a$ . The first oscillation period ends at point  $3$  and the second period begins, but the latter is quickly interrupted because point  $4$  falls inside the dead zone. Figure 5 is arbitrarily plotted based on the assumption of one oscillation period. Far to the right shifting point  $I$  would ensure both a second and a third period. The proposed model allows us to explain a great deal:

(i) The mechanism of oscillation suppression is obvious: there is the fall of the system in the interval  $(-a, +a)$ .

(ii) The reason for the reduction in the number of oscillation waves in the second series of experiments is an increase in the relative weight of the dead zone due to possible softening of the lattice under intense irradiation ( $a = f_0/k$ ).

(iii) The single peak in the oscillations (Figs. 1–3) is obviously due to random fluctuations at the edge of the dead zone.

(iv) The discontinuity between oscillation periods (Fig. 3) for  $\sim 13$  days is also a result of random fluctuations in which point  $+a$  approaches to point  $3$  (Fig. 5).

(v) The antiphase state of the parameters in the second series of experiments is likely due to initial point  $I$  being to the left of the equilibrium point (in the area where the structure is compressed rather than expanded). Arising later expansion wave leads to an opposite change in the parameters, apparently initiated by the higher dose of radiation.

Arising simultaneously at a very few crystal described above nanooscillations induce similar processes among their immediate neighbors, which in

turn transfer them to their neighbors, and so on. Thus synchronous transformation wave is formed that permeates the entire crystal volume after several days.

#### Investigation of Local $\gamma$ -Activation of $\text{BiFeO}_3$ Crystal

It has been shown in previous studies [4] that self-organization similar to the familiar Belousov–Zhabotinsky chemical reaction, which occurs in crystals.  $\text{Tb}$ ,  $\text{Tb}_2\text{Fe}_2$ ,  $\text{SmFe}_{11}\text{Ti}$ , and  $\text{Nd}_2\text{Fe}_{14}\text{B}$  crystals were examined in our experiments, as well as amorphous alloy  $\text{Fe}_{34}\text{Si}_{13}\text{Cu}_1\text{Nb}_3$  (all of these samples reveal the metallic properties). Different activation techniques, namely, electric impact, magnetic impact,  $\gamma$ -ray irradiation, and external pressure were applied. The self-oscillating processes under observation had durations of 15–20 days and lasted up to one year. They were essentially vibrations of atomic and magnetic structures upon a single external pulse. So far, the class of nonmetals (insulators and semiconductors) has been beyond the scope of this field of research. The aim of our study was to fill in this gap through investigations of  $\text{BiFeO}_3$  insulator activated by  $\gamma$ -ray irradiation.  $\text{BiFeO}_3$  compound is a multiferroic one, i.e., a material is simultaneously characterized by electric dipole and spin magnetic orderings. It has a rhombohedrally distorted perovskite-type structure with a bimolecular unit cell in which  $\text{Fe}^{3+}$  and  $\text{Bi}^{3+}$  ions are shifted along a threefold axis so as to induce electric polarization ( $T_c \sim 810\text{--}830^\circ\text{C}$ ) [5]. The parameters of the  $\text{BiFeO}_3$  rhombohedral unit cell are  $a = 3.96 \text{ \AA}$  and  $\alpha = 89^\circ 28'$  the parameters of a hexagonal system are  $a_{\text{hex}} = 5.587 \text{ \AA}$  and  $c_{\text{hex}} = 13.876 \text{ \AA}$  at 293 K. The compound is antiferromagnetic ( $T_N = 352\text{--}370^\circ\text{C}$ ). Its structure is a magnetic cycloidal spiral with the period of  $\lambda = 620 \pm 20 \text{ \AA}$ . The magnetic moments of  $\text{Fe}^{3+}$  ions rotate in a plane oriented perpendicular to the hexagonal basal plane.

The  $\text{BiFeO}_3$  sample was prepared by sintering  $\text{Fe}$  up to 90% enriched in  $^{57}\text{Fe}$ . Placed in a plexiglass cell powder sample was irradiated by a bremsstrahlung  $\gamma$ -radiation with an upper energy of 55 MeV in the electron accelerator (Moscow State University Institute of Nuclear Physics). The length of irradiation was 1 h and the absorbed dose was 100 Gy. The Mössbauer source was  $^{57}\text{Co}$  in  $\text{Rh}$ . The spectra were recorded for 8–10 h. The measurements were performed at 293 K.

The spectrum of the sample before irradiation was fairly simple. It was a sextet of lines with a weak quadrupole shift, i.e., a shift of four internal lines. The spectra were processed according to model 1 of a sextet with the following parameters: hyperfine field ( $H_{\text{hf}}$ ), isomeric shift ( $\delta$ ), quadrupole splitting ( $Q$ ), and linewidth  $\Gamma$ . For the  $\text{BiFeO}_3$  structure, where the number of nonequivalent positions of  $\text{Fe}$  atoms is rather large, these parameters were averaged; nevertheless, their physical content was not reduced at all, as was

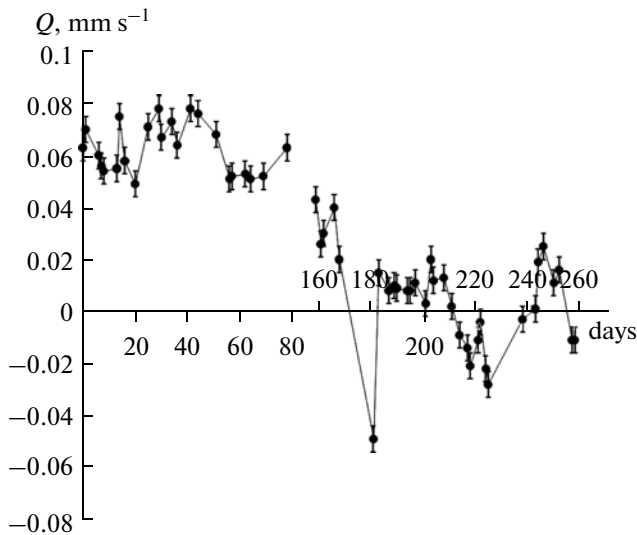


Fig. 6. Time dependence of the quadrupole-splitting parameter  $Q$  in  $\text{BiFeO}_3$  crystal upon  $\gamma$ -ray irradiation.

confirmed by the narrow spread of the parameters:  $\Gamma \approx 0.5 \text{ mm s}^{-1}$ ; i.e., they were only twice as high as the conventional value. The state of the sample after irradiation was monitored for  $\sim 8$  months. Sample behavior strongly differed from one obtained in above case of metal  $\text{Nd}_2\text{Fe}_{14}\text{B}$ . For example, Fig. 6 shows the time dependence of quadrupole splitting. Point  $t = 0$  days corresponds to the initial state of the sample. We have to note that:

(i) An oscillating and not quite regular process begins immediately after irradiation at an average level of  $\sim 0.06 \text{ mm s}^{-1}$ .

(ii) There is a dramatic change in parameter  $Q$  after six months ( $\sim 180$  days): it falls almost to zero, i.e., quadrupole splitting ceases.

Parameter  $H_{\text{hf}}$  exhibits oscillating behavior similar to that one observed in the initial stage (Fig. 6), parameter  $\delta$  is stable at the level of  $\sim 0.31 \text{ mm s}^{-1}$ , and parameter  $\Gamma$  is also stable at a level of  $\sim 0.5 \text{ mm s}^{-1}$ . Thus, the catastrophe behavior is inherent only in the case of parameter  $Q$ .

## RESULT DISCUSSION

The most important feature of the results presented in Fig. 6 is that the strongest changes in parameter  $Q$  occur after an immense delay in time ( $\sim 180$  days) with respect to irradiation. Parameter  $Q$  is associated with the symmetry of the local environment of isolated Mössbauer atoms. If the symmetry is cubic, as in the case of an ideal perovskite,  $Q \rightarrow 0$ . However, it is exactly the situation that is observed in Fig. 6. It is therefore of interest to determine what kind of process in the atomic structure could correspond to this situation.

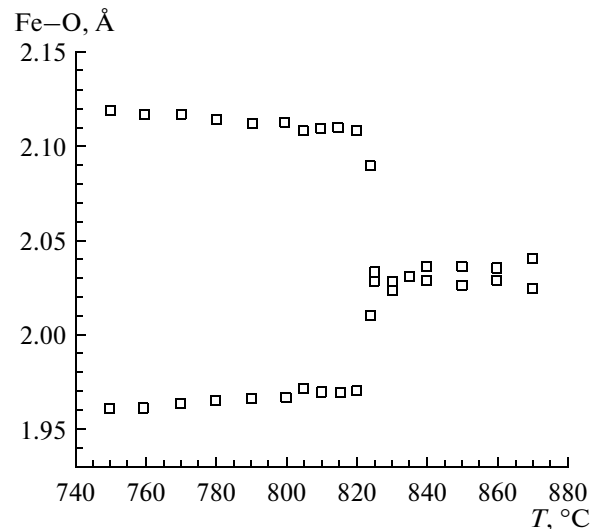
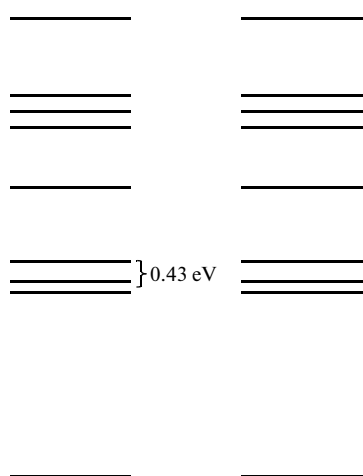


Fig. 7. Evolution of Fe–O bond length in  $\text{BiFeO}_3$ , indicating the loss of  $\text{Fe}^{3+}$  polar displacement in an  $\text{FeO}_6$  octahedron above the Curie point [5].

High-energy  $\gamma$  rays interact with individual atoms, thus forming regions of local heating in the sample in which the temperature can be as high as several thousands of degrees Kelvin [6]. This heat rapidly dissipates, but the existence of local regions in a crystal with temperatures above  $T_c \sim 820^\circ\text{C}$  can lead to irreversible consequences in the material. The perturbed nonequilibrium atomic crystal structure that is energetically more advantageous than the initial structure can arise. Let us outline its possible features. We refer to the data on phase transitions in  $\text{BiFeO}_3$ . The transition from the ferroelectric to the paraelectric phase at  $820^\circ\text{C}$  was analyzed in details via neutron diffraction in [5]. The final state was found to be the orthorhombic phase with lattice parameters  $a = 5.61 \text{ \AA}$ ,  $b = 5.64 \text{ \AA}$ , and  $c = 7.97 \text{ \AA}$ . Most remarkably, the local environment of the Fe atom in the  $\text{FeO}_6$  octahedron turned to cubic one during the transition and the Fe–O bond lengths become almost equal (as in an ideal perovskite).

This is seen clearly in Fig. 7 (taken from [5]). It is logical to assume that it is this cubic transformation ( $Q \rightarrow 0$ ) that we observe in Fig. 6, but after an immense time delay rather than immediately after irradiation. It takes 0–180 days to prepare for this dramatic change. The oscillation waves of parameter  $Q$  reveal that the system immediately tends to implement this process, but the initial dominant structure strongly hinders it. Only the slow induction of structural transformation creates the necessary conditions for the bulk effect. We may state that the interval of 0–180 days is the bifurcation state of a system initiated by  $\gamma$ -ray irradiation. At time of 180 days the system finally decides in favour of a structure of another type. A structural state similar to the one presented in Fig. 6 at time above 180 days



**Fig. 8.** Calculated structure of the  $\text{BiFeO}_3$  electron levels in an orthorhombic lattice. The spectra correspond to different orientations of electron spins. The band gap is indicated by the bracket.

exists at room temperature. It is nonequilibrium state as well as the state in the interval of 0–180 days and tends to return to the initial rhombohedral structure for which  $Q$  lies in the range of negative values [4].

We calculated the electron spectrum of the  $\text{BiFeO}_3$  orthorhombic phase in semiempirical approach with PM3 parametrization using an iterative approach based on the data of [5]. The results are given in Fig. 8. Here the Fermi gap is 0.43 eV. According to [7], this

value for the initial structure is 1.13 eV, indicating that quite a long time is needed to achieve equilibrium.

## CONCLUSIONS

Our investigation suggests that the local activation of crystals by  $\gamma$ -ray irradiation is a promising physical tool for solving the problem of self-organization in crystals. A tiny portion of initially activated atoms transfer their effect throughout the volume of a material and order it in time and space.

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