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Numerical Simulation of Energy Relaxation Processes in a ZnMoO₄ Single Crystal

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Abstract—We present the results of our experimental investigation and numerical simulation of excitationenergy relaxation processes in zinc molybdate crystals. We show that our kinetic model of the energy relaxation makes it possible to describe basic features of experimental results. Using this model, we estimate the trap concentration in $ZnMoO_4$ upon irradiation of the crystal by VUV synchrotron radiation and X-ray radiation. We conclude that prolonged phosphorescence of $ZnMoO_4$ that is observed after irradiation of the crystal by X-ray radiation can be caused by the occurrence of additional traps with a low activation energy.

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INTRODUCTION

Recently, crystals based on MoO₄ complexes have attracted attention as a possible material for cryogenic phonon-scintillation detectors [1]. Simultaneous recording of photon and phonon responses of the detector increases its resolving power, which makes it possible to use such a detector for recording rare events, e.g., neutrinoless double beta decay. Zinc molybdate ZnMoO₄ may be of interest for use in cryogenic detectors, since the isotope ¹⁰⁰Mo is one of the most probable sources of neutrinoless double beta decay [2, 3]. The absence of heavy elements in the crystal ensures achieving a low radioactive background, which is a necessary condition for application of cryogenic phonon-scintillation detectors. The first results that demonstrate the potential of ZnMoO₄ as a cryogenic detector were recently reported in [4].

The table summarizes data on certain physical properties and the crystal structure of zinc molybdate. At T = 10 K, the luminescence of zinc molybdate upon interband excitation is a broad elementary band with an intensity maximum at 2.0 eV. It is known that molybdate compounds are capable of luminescing without introducing activator ions. Therefore, the observed luminescence band is the intrinsic luminescence of zinc molybdate and, as was shown in studies of different molybdates, is caused by the luminescence

of an exciton that is self-trapped at the MoO_4^{2-} complex [6–9].

It has been found previously that the band gap of $ZnMoO_4$ contains traps [1, 4, 6]. The light yield of the scintillator substantially depends on the occurrence of traps in the crystal. Upon energy relaxation of an absorbed high-energy quantum, numerous low-

energy electron-hole pairs are created. During thermalization of these pairs, traps can form a channel of energy relaxation of the absorbed high-energy quantum, which competes with the intrinsic luminescence and prevents the formation of excitons at low temperatures. As a result, the occurrence of traps gives rise to prolonged components in the luminescence decay kinetics and causes a decrease in the total luminescence light yield of the scintillator. Therefore, to improve the scintillation properties of ZnMoO₄, it is important to elucidate the nature of traps and the character of the influence of traps on energy transfer processes to luminescence centers in this compound.

The objective of this work was to study excitationenergy relaxation processes in the $ZnMoO_4$ crystal in the presence of traps of several types. This investigation was performed based on experimental results and on their numerical simulation. Results were obtained using X-ray radiation and VUV synchrotron radiation as luminescence excitation sources.

Crystal structure and physical properties of ZnMoO₄

Melting temperature, °C	986
Density, g/cm^3 [5]	4.37
Space group [5]	P-1
Type of crystal lattice [5]	α -ZnMoO ₄
Refractive index	1.98
Band gap width, eV [6]	4.3

EXPERIMENTAL

Samples of the ZnMoO₄ single crystal under study were grown by the Czochralski method from platinum crucibles in the air atmosphere at the Prokhorov General Physics Institute of the Russian Academy of Sciences [10]. Luminescence spectra and thermoluminescence curves, i.e., temperature dependences of the intensity of thermostimulated luminescence, were measured. Experiments with the X-ray excitation were performed on a setup of the laboratory of luminescent materials at the Claude Bernard University (Lyon, France). As a source of X-ray radiation (24 keV), an XRG 3000 INEL X-ray tube was used. Details of the experimental setup were described in [11]. Experiments with VUV synchrotron radiation were carried out on the Superlumi setup (DESY, Germany) [12].

Mathematical simulation of experimental results and visualization of the numerical solution were performed using the Mathematica 7.2 computer algebra system.

RESULTS AND DISCUSSION

Luminescence and Thermostimulated Luminescence of ZnMoO₄ upon X-ray Excitation

Experimental data on the excitation of luminescence by an X-ray radiation source, are presented in Fig. 1a. A sample of ZnMoO₄ was cooled to a temperature of T = 26 K and was X-ray irradiated for 510 s. At a time moment of $t_0 = 510$ s, the excitation was terminated and phosphorescence of the sample was observed. At t = 900 s, the sample began to be heated at a constant rate of 0.169 K/s. During heating, a peak of thermostimulated luminescence (TSL) of a nonelementary form with an intensity maximum at a temperature of T = 65 K was observed. We note that the intensity of the TSL peak is high, approximately four times higher than the intensity of the stationary luminescence. The inset of the figure shows that the spectral composition of the luminescence in the TSL peak corresponds to the spectrum of the intrinsic luminescence upon excitation by the X-ray source.

The profile of the TSL peak can be approximated using a model that assumes that charge carriers thermally released from traps are more likely to be bound to form an exciton than to be captured again by a trap (the so-called first-order kinetics) [13]. In the approximation of the first-order kinetics, the elementary TSL peak can be described by the following formula:

$$I_{\text{lum}}(t) = n(0)\omega_0 \exp\left[-\frac{E_A}{k_B T(t)} - \frac{\omega_0 k_B T^2(t)}{E_A T'(t)}e^{-E_A/k_B T(t)}\right].$$
(1)

Here, n(0) is the concentration of filled traps in the crystal immediately after the termination of the excitation, E_A is the depth of traps, ω_0 is the frequency factor of traps, k_B is the Boltzmann constant, T is the temperature, and T is the rate of linear heating.

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Fig. 1. Luminescence and thermoluminescence of $ZnMoO_4$ upon excitation by (a) X-ray radiation and (b) VUV radiation. Curves in the inset in (a): (1) spectral composition of the TSL peak, and (2) spectrum of stationary luminescence excited by an X-ray source.

In accordance with this model, we approximated the TSL spectrum assuming that there exist traps of two types in the crystal. As can be seen from Fig. 2a, the approximating curve describes the experimental results well. We calculated the following parameters of traps: the activation energies of traps of these two types were determined to be 50 and 69 meV; their frequency factors were estimated to be 180 and 615 s⁻¹, respectively; and the concentration ratio of traps of the two types proved to be $n_{t1}(0)/n_{t2}(0) = 2$. We note that the obtained values of the frequency factors are unusually small. It is known that the frequency factor of a trap should not exceed the frequency of optical phonons, 10^{14} s⁻¹; therefore, commonly, the frequency factors of traps are $10^{11}-10^{13}$ s⁻¹ [14–16].

The frequency factors of traps can also be obtained from the formula

$$\omega = \left(\alpha E/kT_m^2\right) \exp\left(E/kT_m\right). \tag{2}$$

Here, α is the rate of heating, *E* is the depth of the trap, and T_m is the temperature that corresponds to the maximum of the TSL peak. Formula (2) for the frequency factor of the trap, as well as formula (1), was



Fig. 2. Approximation of the TSL peak under the assumption of occurrence of traps of two types: (a) upon excitation by an X-ray source ($E_{\text{exc}} = 24 \text{ keV}$) and (b) upon excitation by VUV radiation ($E_{\text{exc}} = 13.8 \text{ eV}$).

obtained in the approximation of the first-order kinetics and was used for determining frequency factors, e.g., in [17]. Frequency factors obtained using formula (2) (230 s⁻¹ for traps of the first type and 692 s⁻¹ for traps of the second type) are consistent with corresponding values obtained by formula (1).

It should be noted that small frequency factors of traps were already previously observed for lead tungstate $(\sim 10^3 \text{ s}^{-1})$ [18] and cadmium tungstate $(\sim 10^4 \text{ s}^{-1})$ [17]. The luminescent properties of these compounds are similar to the properties of ZnMoO₄. In particular, the nature of intrinsic luminescence centers in all these compounds is related to radiative transitions at the oxyanion complex. These small frequency factors of traps in CdWO₄ and PbWO₄ were explained by a spatial correlation between traps and luminescence centers, which leads to temperature tunneling of charge carriers from traps to luminescence centers. In other words, under the action of temperature vibrations of lattice ions, there is a probability for a charge carrier to escape a trap, and, missing the valence band, if the carrier is a hole, or the conduction band, if the carrier is an electron, directly reach the complex

 MoO_4^{2-} ; bind into an exciton; and be relaxed emitting luminescence quanta. It seems that a similar tunneling process also takes place in zinc molybdate upon charge carrier transfer from traps to luminescence centers.

It is worth noting that we also considered the possibility of approximating TSL curves using a model of the second-order kinetics. This model assumes that charge carriers that escaped a trap are more likely to be captured by the trap again than to be bound into an exciton. However, this model did not ensure good approximation of the experimental TSL peak and yielded considerably different frequency factors of traps, namely, 10^{18} and 10^{-1} s⁻¹. In our opinion, there is no reasonable physical explanation for this difference, and, therefore, this approximation model is definitely erroneous.

Luminescence and Thermostimulated Luminescence of ZnMoO₄ upon VUV Excitation

Experimental data on the excitation of luminescence by the synchrotron radiation are presented in Fig. 1b. A sample under study was cooled to 7 K and irradiated for 510 s by VUV radiation at a wavelength of 90 nm ($E_{\text{exc}} = 13.8 \text{ eV}$). As the excitation was terminated, no phosphorescence of the sample was observed, which differs from the result obtained upon X-ray excitation. The absence of phosphorescence may be related to the fact that the initial temperature from which the heating began was 7 K rather than 26 K as in the experiment with the X-ray source. Then, the crystal was heated at a constant rate of 0.163 K/s and a TSL peak with a maximum at 62 K was observed. The intensity of the TSL peak was seven times lower than the intensity of the stationary luminescence, which also appreciably differs from the experiment with the X-ray excitation. The shape of the TSL peak is nonelementary and is a superposition of two elementary peaks that can be described by formula (1) under the assumption that there exist two types of traps. The depths of traps were determined to be 40 and 67 meV; their frequency factors were calculated to be 34 and 777 s^{-1} , respectively; and the concentration ratio of traps was found to be $n_{t1}(0)/n_{c2}(0) = 4$ (Fig. 2b). A small low-temperature peak at 35-40 K is hardly distinguishable and was not taken into account upon approximation; however, it is quite likely that this peak corresponds to the contribution of shallow traps, depletion of which at 26 K in the experiment with the X-ray source leads to phosphorescence. The occurrence of the low-temperature peak in the range of 30 K is also confirmed by the results of investigations performed in [1].

We also note that, despite the fact that the profiles of the TSL peaks obtained after the VUV and X-ray irradiations were the same, the parameters of traps obtained from the approximation proved to be somewhat different. This difference can be associated with

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a small shift of the TSL peak in the VUV experiment (to 62 K) compared to its position in the X-ray experiment (65 K). The relative concentrations of filled traps are also different. Indeed, upon X-ray excitation, the relative concentration of filled deep traps (67-69 meV) is higher than upon excitation by the VUV radiation.

Kinetic Model of Energy Relaxation in the Crystal

To simulate our experimental results, we used a kinetic model of the energy relaxation in the crystal. Processes that are described by the model are schematically shown in Fig. 3. We will assume that traps capture free holes from the valence band. Indeed, it was shown in [17, 19] that low-temperature TSL peaks (T < 75 K), which are characterized by low-frequency factors, are associated with the thermal release of selftrapped holes. Nevertheless, we note that, for the model presented in this work, the character of the trap (electron or hole) does not affect the calculation results. The model assumes that, under the action of excitation radiation, separated electron-hole pairs can be produced in the crystal (process 1) and excitons can be directly created (process 2). During migration of separated charge carriers over the crystal, traps can capture holes (process 3) with their subsequent thermal release (process 4); furthermore, secondary excitons that can also be formed as free electrons are bound with free holes (process 5). Excitons can relax either radiatively (process 6) or nonradiatively as a result of intracenter temperature quenching (process 7).

To describe these processes, we proposed a system of kinetic equations for the concentration of excitons n_{ex} , free holes n_h , free excitons n_e , and filled traps n_t ,

$$\frac{\partial n_{\text{ex}}(t)}{\partial t} = -n_{\text{ex}}(t) / \tau_{\text{rad}} - \omega_{q} e^{-E_{q}/kT(t)} n_{\text{ex}}(t) + \beta_{e-h} n_{e}(t) n_{h}(t) + I(t) r_{\text{ex}}, \frac{\partial n_{h}(t)}{\partial t} = \omega_{t} e^{-E_{t}/kT(t)} n_{t}(t) - \beta_{h-t} n_{h}(t) [n_{t0} - n_{t}(t)] - \beta_{e-h} n_{e}(t) n_{h}(t) + I(t) (1 - r_{\text{ex}}), \frac{\partial n_{e}(t)}{\partial t} = -\beta_{e-h} n_{h}(t) n_{e}(t) + I(t) (1 - r_{\text{ex}}), \frac{\partial n_{t}(t)}{\partial t} = -\omega_{t} e^{-E_{t}/kT(t)} n_{t}(t) + \beta_{h-t} n_{h}(t) [n_{t0} - n_{t}(t)].$$
(3)

Changes in the density of low-energy electronic excitations in the sample I(t) and changes in the temperature of the sample T(t) can be described as follows:

$$I(t) = \begin{cases} I_0, & t < t_0, \\ 0, & t \ge t_0, \end{cases}$$
$$k T(t) = \begin{cases} k T_0, & t < t_{T0}, \\ k T_0 + \alpha(t - t_{T0}), & t \ge t_{T0}. \end{cases}$$

Here, k is the Boltzmann constant and α is the rate of the linear heating of the sample.



Fig. 3. Processes described by a kinetic model of the energy relaxation in a crystal: (1) creation of separated electron—hole pairs, (2) direct creation of excitons, (3) capture of holes by traps, (4) thermal release of holes from traps, (5) formation of secondary excitons, (6) radiative relaxation of excitons, and (7) nonradiative relaxation of excitons.

The first equation of system (3) describes the variation with time of the concentration of excitons. The first term of the right-hand side, $-n_{\rm ex}(t)/\tau_{\rm rad}$ characterizes the process of radiative relaxation of excitons. In this case, the exciton lifetime τ_{rad} was taken to be 10^{-5} s, which is consistent with the experimental results by order of magnitude [6, 20]. The second term $-\omega_{d}e^{-Eq/kT(t)}n_{ex}(t)$ describes the nonradiative decay of the exciton under the action of temperature, (the intracenter temperature quenching). We obtained the values of the coefficient $\omega_q = 5500 \text{ s}^{-1}$ and activation energy $E_q = 0.117 \text{ eV}$ of the luminescence temperature quenching process previously from approximation of the temperature dependence of the luminescence intensity using the Mott formula [6]. The third term of the equation $+\beta_{e-h}n_e(t)n_h(t)$ describes the process of formation of secondary excitons from free excitons and holes. The last term in the right-hand side describes the process of direct formation of excitons under the action of the excitation radiation on the crystal.

The second equation of the system describes the variation with time of the concentration of free holes in the valence band. The first term $\omega_r e^{-Et/kT(t)}n_r(t)$ in the right-hand side of this equation describes the appearance of holes due to their release from traps. The term $-\beta_{h-t}n_h(t)[n_{t0} - n_t(t)]$ describes the process of the hole capture by the trap. The higher the concentration of free holes in the valence band and the higher the concentration of free traps, the higher the probability of this process. The third term of the equation $-\beta_{e-h}n_e(t)n_h(t)$ describes the process of formation of secondary excitons from free excitons and holes. The last term of this equation $I(t)(1 - r_{ex})$ describes the variation in the concentration of free holes due to the

creation of electron-hole pairs under the action of the excitation radiation.

The third equation of the system describes the variation in the concentration of free excitons in the conduction band. The processes that this equation describes are similar to those described by the third and fourth terms of the second equation of the system.

The last equation of the system describes the variation in the concentration of holes in traps due to their capture and temperature release. In modeling, we assumed that there exist several types of hole traps in the crystal, which differ in their activation energy and relative concentration. For this purpose, we added equations to the system that described the dependence of the concentration of holes captured by traps of the given type (similarly to the last equation of the system) and, as a result, the system contained either four or six equations (with allowance for traps of two or three types, respectively) rather than four equations. The parameters of traps, which are the activation energy and the frequency factor, as well as the ratio of the limiting concentrations of traps, were obtained from the approximation of the experimental TSL spectra using formula (1). The model did not consider the possibility of a hole transiting from a deep trap to a shallow one without escaping to the valence band.

The bimolecular coefficients β_{e-h} and β_{h-t} that determine the probability for an electron and a hole to be bound into an exciton and the probability for a hole to be captured by a trap, respectively, are described in the diffusion approximation as follows:

$$\beta_{e-h} = 4\pi (D_e + D_h) R_{e-h}, \quad \beta_{h-t} = 4\pi D_h R_{h-t},$$

where R_{ij} are the radii of the capture sphere and D_e and D_h are the coefficients of diffusion of excitons and holes over the crystal. The diffusion coefficients $D_e =$ $a^2 v_e/3$ and $D_h = a^2 v_h/3$ are expressed in terms of the distance a between neighboring MoO₄ complexes, through which the hop diffusion occurs, and via the diffusion frequency factors v_e and v_h of excitons and holes, respectively. In accordance with the results of the X-ray diffraction analysis of ZnMoO₄ [21], the distance a was assumed to be 0.5×10^{-7} cm. The frequency factors v_e and v_h were taken to be 3×10^{13} s⁻¹, which is of the same order of magnitude as the experimentally determined phonon frequencies of zinc molybdate [22]. The radius of the capture sphere of the electron and hole R_{e-h} was assumed to be 10^{-7} cm, while the radius of the capture sphere of the electron by the trap was $R_{e-t} = 10^{-8}$ cm. These values of the capture sphere radii are consistent with the approximation of the model of the first-order kinetics that was used to describe TSL curves.

The parameter r_{ex} characterizes the probability of direct creation of excitons under the action of the excitation radiation and can be estimated from the excitation spectrum. The excitation spectrum of zinc

molybdate at a temperature of 10 K was reported in [6]. If we assume that, at the excitation energy of 4.24 eV (the first peak in the excitation spectrum), only excitons are created, rather than separated electrons and holes, the ratio of the excitation intensity at the energy of 13.8 eV to the intensity of the first peak yields the upper estimate $r_{\rm ex} < 0.28$. In this work, we used the value of 0.2 for this parameter. To model experiments with the X-ray excitation source, the parameter $r_{\rm ex}$ was taken to be 0.02 in view of the fact that the probability for a high-energy exciton and hole to be bound into an exciton decreases with increasing excitation energy.

The density of low-energy electronic excitations I_0 can also be estimated. In experiments with the X-ray excitation source, the photon flux incident on the sample was 6.5×10^7 mm⁻² s⁻¹. Taking into account that the penetration depth of the radiation with the energy of 24 keV into the zinc molybdate crystal, the density of which is 4.37 g/cm³ (table), is 81 μ m, the density of absorbed photons is 0.8×10^{12} cm⁻³ s⁻¹. We can also estimate the number of low-energy electronhole pairs created by one quantum of the excitation radiation with the energy of 24 keV, which turned out to be 1.86×10^3 . This estimate takes into account that, to create one electron-hole pair upon high-energy excitation, the energy of about triple band-gap width E_g is required (the value of E_g is given in the table) [23]. As a result, the density of low-energy electronic exci-tations is $I_0 = 1.5 \times 10^{15} \text{ cm}^{-3} \text{ s}^{-1}$.

In the case of the excitation by the synchrotron VUV radiation, $I_0 = 3.2 \times 10^{18} \text{ cm}^{-3} \text{ s}^{-1}$. Here, we took into account the photon flux of the Superlumi setup, which is equal to $3 \times 10^{10} \text{ mm}^{-2} \text{ s}^{-1}$; the characteristic penetration depth of 13.8–eV photons into the sample with a thickness of 0.01 µm; and the fact that, on the average, the energy of 13.8 eV suffices to create 1.07 low-energy electron—hole pairs.

Upon approximation, the limiting concentration of empty traps in the crystal prior to its excitation n_{n0} (for each type of traps) was selected such that the experimentally obtained intensity ratio between the TSL peak and the stationary luminescence would be retained.

RESULTS OF SIMULATION

By numerical solving system of equations (3), we obtained curves of the time dependence of the luminescence intensity, which can be compared with experimental dependences in the entire time range of measurements.

The simulated time dependence of the luminescence intensity obtained in the experiment with the VUV excitation is presented in Fig. 4a. Upon simulation, it was assumed that there exist traps of two types in the crystal, the parameters of which were obtained

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from the approximation of the experimental TSL spectrum using formula (1). The limiting concentrations of traps (the number of filled traps per 1 cm³ of the crystal at the moment of the termination of excitation) were $n_{t1} = 6.4 \times 10^{19}$ cm⁻³ for traps of the first type and $n_{t2} = 1.6 \times 10^{19}$ cm⁻³ for traps of the second type. As a result, the simulated dependence agrees rather well with the obtained experimental data. This means that, upon simulation, we took into account the basic physical processes that affect the relaxation of excitations upon VUV excitation.

Figure 4b presents the result of simulation of the time dependence of the intensity of luminescence excited by the X-ray source. Qualitatively, the simulated spectrum repeats basic features of the obtained experimental results. However, in the course of the simulation, it was assumed that there exist traps of three types in the crystal. The parameters of two of them were obtained from the approximation of the experimental TSL spectrum using formula (1). The parameters of traps of the third type were selected such that it could be possible to describe the phosphorescence. The frequency factor of traps of the third type was $\omega_{t3} = 100 \text{ s}^{-1}$, and their activation energy was $E_{t3} =$ 0.02 eV. The limiting concentrations of traps of the first, second, and third types were $n_{t1} = 4 \times 10^{18}$, $n_{t2} = 2 \times 10^{18}$, and $n_{t3} = 4 \times 10^{18}$ cm⁻³, respectively. Therefore, our theoretical model predicts the occurrence of shallow traps (20 meV) in the crystal, with their concentration being rather high. It seems that the phosphorescence observed for 400 s after the termination of the excitation at a constant temperature of 26 K, to which the sample was cooled, is caused by a gradual depletion of shallow traps.

We note that, in both cases, the simulated concentrations of filled traps proved to be physically reasonable. Indeed, for an average concentration of atoms of 10^{23} cm⁻³, we find that the relative concentration of filled traps was about 0.08% in the experiment with the VUV synchrotron excitation and 0.01% in the experiment with the X-ray excitation source. The concentration of filled traps in the experiment with the synchrotron excitation was higher because the photon flux of the Superlumi setup was almost three orders of magnitude higher than that of the setup with the X-ray excitation source. If, upon simulation, we assume that the photon fluxes in both experiments are the same, the concentration of traps created by the X-ray radiation becomes considerably higher than the concentration created under the action of the VUV radiation. It is likely that this is related to the destructive action of Xray radiation on the crystal. The nature of hole traps in the zinc molybdate crystal is not yet known with certainty. However, there are several works in the literature in which such traps were observed. In [24], selftrapping of holes at low temperatures was observed in zinc tungstate, and, in [19], in cadmium tungstate. In these works, the nature of hole traps was investigated

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Fig. 4. Theoretical calculation of stationary luminescence and TSL peak: (a) upon excitation by VUV radiation and (b) upon excitation by an X-ray excitation source.

by the method of electron paramagnetic resonance (EPR). The authors of these two works arrived at the conclusion that, at low temperatures (below 75 K), holes are self-trapped at one of two possible states of oxygen. The EPR method showed that, at temperatures below 50 K, the self-trapped hole experiences temperature hop diffusion between two neighboring equivalent states of oxygen, An increase in the temperature to 50 K causes a partial destruction of this trap, and, at a temperature of 75 K, the trap is completely destroyed. Here, it should be noted that zinc and cadmium tungstates belong to a structural type of the tungstate such that it is characterized by two different positions of oxygen atoms in the crystal structure. In zinc molybdate, the crystal structure is somewhat different and is characterized by five different positions of the oxygen ion. It is likely that it is this fact that leads to the appearance of traps of three types with different depths, which is manifested in the nonelementary character of the TSL peak.

CONCLUSIONS

We presented the results of our experimental investigations into the stationary excited luminescence and thermoluminescence of zinc molybdate using VUV and X-ray excitation sources. We showed that there exist two types of traps in the crystal. Using a model of the first-order kinetics, the parameters of traps were determined. Based on the obtained parameters, we concluded that the traps are of the hole type and that the transfer of charge carriers to luminescence centers is of the tunnel character. We proposed a kinetic model of the energy relaxation in the crystal, using which we qualitatively simulated basic features of the experimental results. We showed that, under the action of Xray radiation on the crystal, the specific concentration of filled traps is considerably higher than that under the VUV irradiation. Based on the results of simulation, we assumed that the X-ray excited phosphorescence is explained by the occurrence of shallow traps.

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REFERENCES

- L. L. Nagornaya, F. A. Danevich, A. M. Dubovik, et al., IEEE Tran. Nucl. Sci. 56 (4), 2513 (2009).
- A. N. Annenkov, O. A. Buzanov, F. A. Danevich, et al., Nucl. Instr. Meth. Phys. Res. A. 584, 334 (2008).
- 3. S. Pirro, S. Capelli, M. Pavan, et al., Phys. Atom. Nucl. **69**, 2109 (2006).
- 4. L. Gironi, C. Arnaboldi, J. Beeman, et al., J. Instr. JINST 5, 11007 (2010).

- 5. S. C. Abrahams, J. Chem. Phys. 46, 2052 (1967).
- D. Spassky, A. Vasil'ev, I. Kamenskikh, et al., Phys. Status Solidi A 206 (7), 1579 (2009).
- 7. E. G. Reut, Izv. Akad. Nauk SSSR 49, 2032 (1985).
- 8. V. B. Mikhailik, H. Kraus, D. Wahl, and M. S. Mykhaylyk, Phys. Stat. Sol. b **242** (2), 17 (2005).
- N. Saito, N. Sonoyama, and T. Sakata, Bull. Chem. Soc. Jpn. 69, 2191 (1996).
- L. Ivleva, I. Voronina, L. Berezovskaya, et al., Crystallogr. Rep. 53 (6), 1087 (2008).
- I. Kamenskikh, C. Pedrini, A. Vasil'ev, et al., J. Lum. 129, 1509 (2009).
- 12. G. Zimmerer, Rad. Meas. 42, 859 (2007).
- V. V. Mikhailin and A. N. Vasil'ev, *Introduction to Spectroscopy of Solids* (Izd. Mosk. Gos. Univ., Moscow, 1987) [in Russian].
- 14. R. K. Bull, Nucl. Tracks Rad. Meas. 11, 105 (1986).
- A. M. Gurvich, Introduction to Physical Chemistry of Crystal Phosphors (Vysshaya Shkola, Moscow, 1971) [in Russian].
- J. J. Brophy and R. J. Robinson, Phys. Rev. 118, 959 (1960).
- 17. A. Vedda, F. Moretti, M. Fasoli, et al., Phys. Rev. 80, 045104 (2009).
- M. Martini, F. Meinardi, G. Spinolo, et al., Phys. Rev. 60 (7), 4653 (1999).
- V. Laguta, M. Nikl, J. Rosa, et al., J. Appl. Phys. 104, 103525 (2008).
- V. Mikhailik, H. Kraus, D. Wahl, et al., Nucl. Instr. Meth. Phys. Res. A 562, 513 (2006).
- 21. W. Reichelt, T. Weber, T. Soehnel, and S. Daebritz, Ref. Zeit. Anorg. Allgem. Chem. **626**, 2020 (2000).
- 22. Z. Liu, L. Dong, W. Ji, and Y. Chen, J. Chem. Soc., Faraday Trans. 94 (8), 1137 (1998).
- 23. M. Nikl, Meas. Sci. Technol. 17, 37 (2006).
- A. Kotlov, V. Nagirnyi, M. Kirm, et al., Rad. Meas. 38, 715 (2004).

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