Double magnesium donors as a potential active medium in the terahertz range

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Experimental results on the observation of terahertz luminescence under optical excitation of silicon doped with neutral helium-like magnesium donors under photoionization conditions under uniaxial stress are presented. Possible options for creating stimulated radiation sources based on Si:Mg under optical excitation are considered. The possibility of obtaining inversion at the lowest odd level and significant gain coefficients is difficult due to the rather short relaxation time of the $2p_0$ level. The possibility of using an alternative inversion mechanism presupposes knowledge of relaxation routes. The mechanism of stimulated Raman scattering is theoretically considered and it is shown that terahertz stimulated radiation with optical excitation of double magnesium donors in silicon can be achieved using the mechanism of electronic-type Raman scattering.

Keywords: silicon, helium-like donor, photoluminescence, stimulated Raman scattering.

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1. Introduction

The development of stimulated radiation sources in the terahertz frequency range is dictated by the importance of this range for use in solving various scientific problems in the field of physics, chemistry, biology, civil safety [1,2]. In this connection, impurity centers in semiconductors are of particular interest, since the energies of impurity transitions correspond to the specified spectrum. In addition, donors in materials such as germanium and silicon are also interesting from the point of view of creating new quantum devices, and the presence of laser systems in the range of donor transitions would make it possible to obtain a tool for manipulating orbital states [3,4]. At this stage, laser generation was obtained by optical excitation of group V donors in silicon [5]. Despite noticeable differences in the energy of occurrence of various donors (antimony — 43 meV, bismuth — 71 meV), there is practically no difference in the energies of working transitions, due to the fact that the energies of excited states in semiconductors practically do not depend on the chemical nature of the impurity. Uniaxial deformation does not lead to a significant restructuring of the stimulated radiation spectrum, since it practically does not affect the binding energy of the excited levels relative to the corresponding valleys of the conduction band. On the contrary, the use of the effect of stimulated Raman scattering (SRS) of light in silicon doped with small donors makes it possible to adjust the radiation frequency within sufficiently wide limits, which have the potential to expand using uniaxial deformation of the crystal [6].

2. Double donors in silicon

Double helium-like donors in silicon (magnesium — Mg_0, sulfur — S_0, selenium — Se_0, tellurium — Te_0) have a whole a number of differences from such hydrogen-like donors as phosphorus, antimony, arsenic, bismuth, which can give some additional advantages [7,8]. Firstly, there are two systems of levels in such donors that differ in the permutation symmetry of the total wave function and the spin (para- and orthostates) [9]. Secondly, the occurrence energies of the split states 1s exceed those for hydrogen-like donors [10]. Thirdly, the spectroscopy results indicate a deepening of the state $2s(A_1)$ relative to the state $2p_0$ [9,10]. Fourth, it was shown that the state $1s(T_2)$ is Raman active for neutral selenium in silicon [11]. A diagram of the levels of magnesium donor in silicon depending on uniaxial compression deformation in the direction of [100] is shown in Figure 1. These factors hold out a hope of an expansion of the frequency range of radiation during optical excitation of donors in silicon. However, there are no data on relaxation times at this stage, with the exception of magnesium, for which it was shown that the characteristic lifetimes $2p_0$ and $2p_\pm$ turned out to be ~ 10 and ~ 30 ps, respectively, which limits the possibility of obtaining an inversion and a reasonable gain, but is not an obstacle for the SRS.

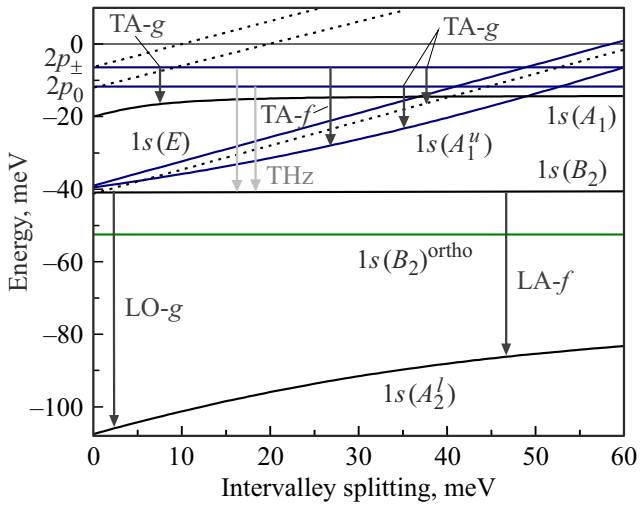

Figure 1. Energy levels of the helium-like Mg donor in silicon at uniaxial stress along the crystallographic direction [001]. The down arrows indicate possible resonances with interline phonons LO-g, LA-f, TA-f, TA-g. The upper components of the levels $1s(T_2)$ are not specified-ortho, para.

Magnesium has significant differences in the position of the ground state from the other most well-known deep donors, which are represented by elements of group VI. The donors formed by the introduction of sulfur, selenium and tellurium have a very large chemical shift, which raises the question of the possibility of inversion in such media due to the relaxation features of deep levels [12]. The mechanism of stimulated Raman scattering (SRS) for these donors has not been well studied, since the relaxation times for deep donors are unknown. It is also possible to mention thermodonors [13], which, as a rule, form several families of donors in silicon, differing in ionization energy, which complicates the analysis of the possibility of creating active media.

The aim of this work was to obtain initial experimental data on photoluminescence under excitation of neutral magnesium in silicon. The choice of magnesium is due to the ionization energies of the ground state of 107.5 meV, which is close to the energy of the radiation quantum of the CO_2-laser (117 meV) used for the study of V group donors, which made it possible to use the experimental solutions obtained, in particular the filtration system.

3. Experiment

The samples for the study were obtained by diffusion doping of monocrystalline silicon with magnesium [14], had a concentration of donors $\sim 3 \cdot 10^{15}$ cm^{-3}, which is a record value, were cut in the form of a rectangular parallelepiped, had characteristic dimensions $1 \times 5 \times 7$ mm^3 with polishing of all faces. The samples were placed in a cryogenic insert in a helium Dewar vessel, allowing optical pumping of the samples and applying uniaxial stress (Figure 2).

A CO_2-laser (wavelength 10.6 micron, 117 meV) with a modulated Q-factor (pulse duration 300 ns, repetition rate 300 Hz, average power ~ 0.5 W) was used as an excitation source. The filter in the form of a crystal sapphire and the detector itself were located outside the direction of propagation of the radiation beam from the CO_2-laser to reduce the impact of pumping radiation on the Ge : Ga detector. A TEA CO_2-laser with a peak power of up to 100 kW with a pulse duration of 100 ns and a repetition frequency of 5 Hz was used as a more powerful radiation source.

Figure 3, *a* shows the result of measuring the dependence of the spontaneous radiation signal on the intensity of pumping by CO_2-laser radiation (wavelength 10.6 micron) for several values of applied stress along the crystallographic direction [001]. As can be seen from the above results, the dependences have a character close to linear for the range of excitation intensities up to 4 kW/cm^2. An increase in the luminescence signal is observed at the same time with an increase in the stress value.

Figure 3, *b* shows the dependence of the spontaneous emission signal as a function of the applied stress along the direction [001] at a fixed intensity (4 kW/cm^2). There are several characteristic sections according to the figure: the initial section (0–1 kbar) with no change, a moderate growth section (1–4 kbar) and a faster signal increase section (4.2–4.8 kbar) with a change in the rate of rise (4.8–5.2 kbar).

The radiation signal was measured using a powerful TEA CO_2-laser to excite Si : Mg. The dependence of the photoluminescence signal has the form of a superlinear dependence in the range up to 100 kW/cm^2 (Figure 4)

The modulation of the absorption of background radiation with an intensity of 4 kW/cm^2 was measured for studying the absorption capacity of Si : Mg in the terahertz range as a function of stress (Figure 5). The background radiation frequencies recorded by the detector correspond to a temperature of 300 K and are additionally limited by the band of the impurity receiver Ge : Ga and the filter used (crystal sapphire), which corresponds to the terahertz range. The figure shows that there is a slight increase of absorption at low stress, which changes to a decrease up to 2 kbar and practical absence of any change of the signal in the range from 2 to 4 kbar.

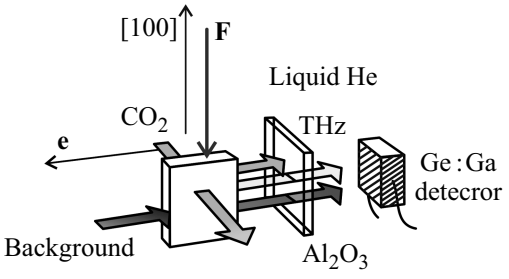

Figure 2. Diagram of an experimental setup for the observation of Si : Mg photoluminescence under optical excitation under conditions of uniaxial crystal compression stress.

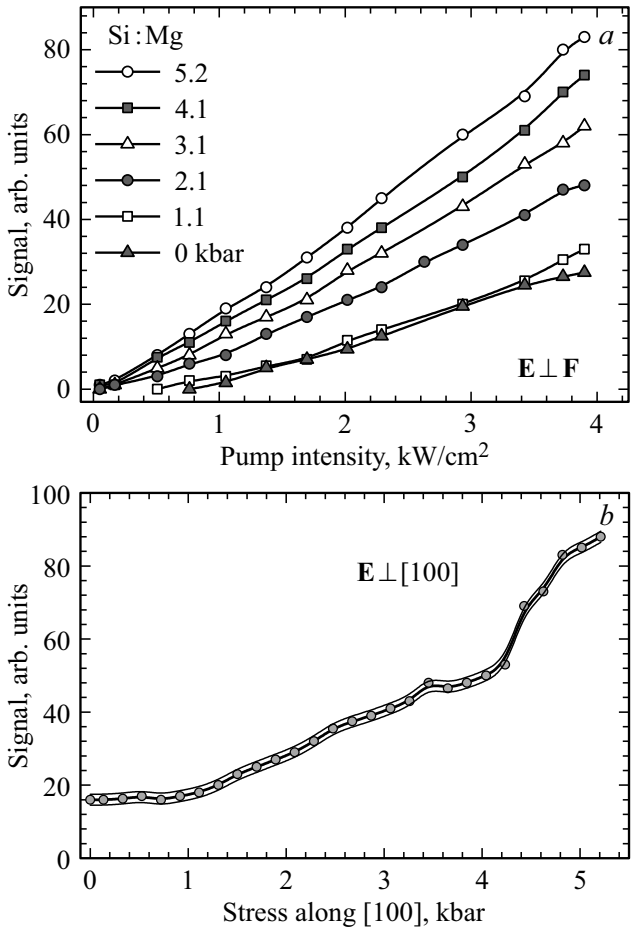

Figure 3. *a* — dependence of the spontaneous emission signal on the excitation intensity for several values of uniaxial stress along the crystallographic direction [001]. *b* — dependence of the intensity of spontaneous radiation Si : Mg on the value of uniaxial stress along the crystallographic direction [001]. The excitation intensity is 4 kW/cm^2.

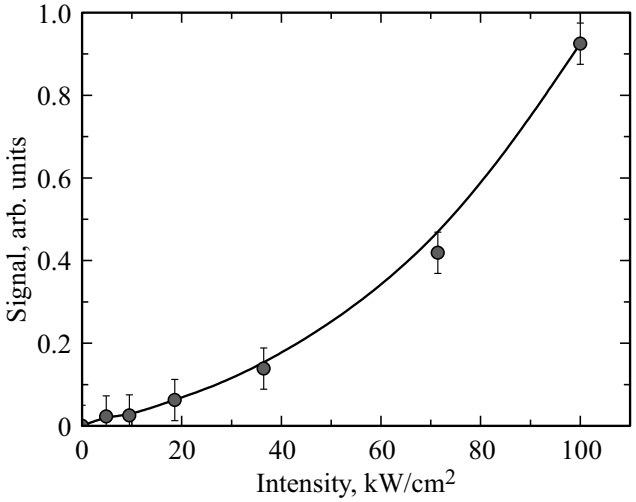

Figure 4. The dependence of the spontaneous emission signal on the excitation intensity at uniaxial stress 4 kbar along the crystallographic direction [001].

4. Discussion of results

At this stage, it is not possible to measure the luminescence spectrum of Si : Mg due to the relatively weak signal. Nevertheless, it is possible to limit the number of transitions using data on the spectrum of states, the filter bandwidth and the sensitivity band of the detector (10−40 meV), transitions from the states $2p_0$ and $2p_\pm$ to the states $1s(T_2)$ and $1s(E)$. Moreover, we are talking about both transitions within a subsystem with spin 0 and a subsystem with spin 1. The possibility of obtaining a stimulated effect is largely determined by the relaxation times of potential working levels. Relaxation times of $2p$ levels are known, which turned out to be ~ 10 ps for $2p_0$ and 30 ps for $2p_\pm$ [15] for a non-deformed silicon crystal. Such times are relatively short to obtain population inversion and sufficient gain at transitions $2p_0-1s(E, T_2)$. A longer relaxation time $2p_\pm$ leaves the possibility of obtaining an inversion, which is realized in the case of Si : Bi, where the level $2p_\pm$ has a similar relaxation time [16]. However, in the case of bismuth, it is known that the main relaxation channel $2p_0$ is the transition to the ground state with the emission of an optical phonon [3], which contributes to a small population of states $1s(E, T_2)$. Since at this stage there is not enough experimental material and theoretical analysis concerning relaxation transitions for electrons at the $2p_0$ level, as well as relaxation times $1s(E, T_2)$, the question remains open about the possibility of creating an inversion at the transitions $2p_\pm - 1s(T_2)$ and $2p_\pm - 1s(E)$. For donor levels, the presence or absence of resonances with intervalley phonons is of great importance, such as LO-g (63 meV), TO-f (59 meV), LA-f (46 meV), TA-f (20 meV), LA-g (18 meV), TA-g (10 meV). At this stage, there are no final data on the binding energy of the states $1s(E)$ and $2s(A_1)$, which somewhat complicates the interpretation of the experimental data described above and the theoretical analysis for comparison with the experimental values of relaxation times. In addition, there is no data in publications on the effect of uniaxial deformation on relaxation times in Si : Mg for values > 1 kbar. Thus, due to the rather short relaxation times, the linear nature of the dependence on the excitation intensity at medium intensities (units of kW/cm^2) is quite natural (Figure 3, *a*). Some deviation from the linear law (Figure 4) when using intensities up to 100 kW/cm^2 signals the existence of gain. Nevertheless, stimulated radiation was not obtained in the presented experiments. The result of measuring the dependence of the output radiation signal on the stress value, shown in Figure 3, *b*, should be interpreted from the point of view of interaction with intervalley phonons. A similar interpretation is possible to some extent when considering the energy gaps between the levels of $2p$ and the lowest $1s$ states. Qualitatively, it can be concluded at this stage that it is possible to detect stress ranges at which interactions with phonons TA-f, LA-g, TA-g are disabled (Figure 1).

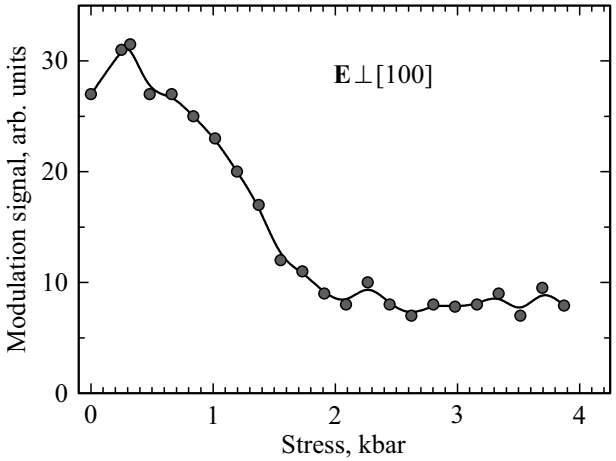

Figure 5. Dependence of the modulation signal the background depends on the value of uniaxial stress along the crystallographic direction [001]. The excitation intensity is $4\,\mathrm{kW/cm^2}$.

The measurement of the modulation of the absorption of background radiation clearly indicates the occurrence of absorption in the medium under the impact of pumping. Interpretation by way of analogy with donors of V group where negatively charged donors are the factor determining losses, is impossible in this case, since we are talking about a helium-like center in which the third electron will have to have a very low bond energy. Negatively charged Mg donors (and also S, Se, Te) are not experimentally observed at temperatures of 4.2 K. However, the orthostates subsystem is an obvious candidate for the role of a nonequilibrium absorber. Currently, there is no adequate model describing the reasons for the decrease in the population of orthostates at uniaxial stress (Figure 5). The main channel of settlement of orthostates assumes, due to weak spin-orbital coupling, ionization of the donor and electron capture on a neighboring once ionized magnesium atom, with the corresponding direction of electron spin. Therefore, from the point of view of eliminating this channel, it is preferable to use the energy of excitation quanta smaller than the ionization energy, i. e. resonant pumping. In this case, it becomes possible to consider the effect of stimulated Raman scattering.

5. Stimulated Raman scattering cross section

Theoretically, the cross section of the SRS was described within the framework of the 2nd order of perturbation theory [17,18], wherein the Raman sum was limited to fourteen terms corresponding to electrodipole transitions with the most noticeable values of matrix elements. The factoring in of the decay of electronic states with phonon emission was taken into account by adding to the energy of the state of the imaginary part corresponding to the relaxation rate, the inhomogeneous broadening of the impurity lines of the — real part, over which averaging was subsequently performed, considering that this addition is a random variable with a Gaussian distribution. The relaxation rates of all states considered in the Raman sum were assumed to be 0.1MeV, which is close to the theoretical estimates [19] and experimental data on relaxation times [15]. The section of the SRS and the matrix element of the combinational transition are given by the formulas:

$$\sigma_\delta = 4\pi^2 |M|^2 \frac{\omega'}{ch^3} \frac{I_\omega}{\Gamma}, \tag{1}$$

$$M = \sum_m \frac{d^*_{2m} d_{m1}}{\omega_{m1} + i\delta_m + \delta - \omega} + \frac{d_{2m} d^*_{m1}}{\omega_{m1} + i(\delta_m - \delta') + \delta + \omega'}, \tag{2}$$

where I_ω — intensity of excitation radiation $\left(n = V\frac{I_\omega}{\hbar\omega c}\right)$, d_{m2}, d_{m1} — matrix elements of electrodipole transitions, ω — radiation frequency excitation, ω' — frequency of Stokes radiation, ω_{m1} — frequency of transition from ground state to state m, Γ — half-width of the Stokes transition line, δ_m — level width m, determined by the lifetime of the state m or the duration of the excitation pulse, δ' — the width of the upper level of the transition, determined by the lifetime of this state or the duration of the excitation pulse, δ — the energy spread of the ground state, obeying the normal distribution law.

Figure 6 shows the cross section of the stimulated Raman scattering as a function of the excitation quantum. As expected, the maximum cross section is achieved in resonance with the impurity absorption lines.

The SRS effect can also be obtained outside resonances with levels $2p_0$ and $2p_\pm$ as has been shown for donors of the V group [5]. The difference in the output intensity for the resonant and non-resonant cases depends, in particular, on the value of the relaxation time of the final electronic level in the SRS process. As a rule, the concentration of magnesium in silicon can be brought to the values of

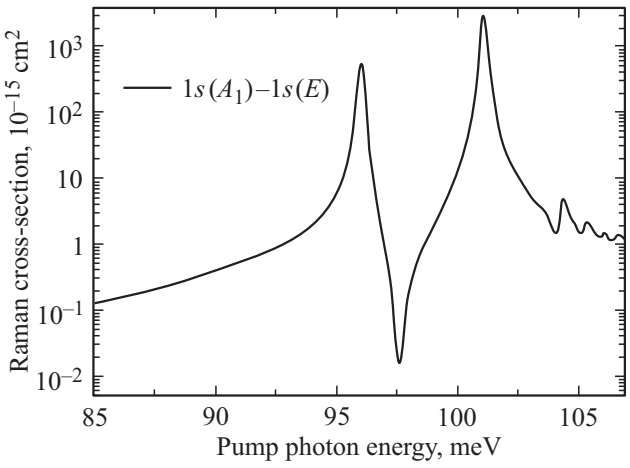

Figure 6. Dependence of the SRS cross section at the transition $1s(A_1) \to 1s(E)$ on the excitation quantum energy at $\delta = \delta' = \delta_m = 0.1\,\mathrm{meV}$, $\Gamma = 0.2\,\mathrm{meV}$, $I = 0.2\,\mathrm{MW/cm^2}$. SRS quantum energy $\hbar\omega' = \hbar\omega - 67.5\,\mathrm{meV}$.

$\geq 10^{15}\,\mathrm{cm}^{-3}$, therefore, with characteristic losses in the silicon crystal in the terahertz region of the spectrum $\leq 0.1\,\mathrm{cm}^{-1}$, one can hope for obtaining the desired effect under cryogenic temperatures at which donors will not be ionized.

6. Conclusion

In conclusion, it can be noted that the paper presents the results of measuring terahertz photoluminescence when Si : Mg is pumped when excited by CO_2-laser radiation under conditions of $T = 4.2\,\mathrm{K}$ and uniaxial deformation of the crystal. The obtained dependences on the excitation intensity indicate the absence of amplification at moderate intensities and weak amplification at intensities $\sim 100\,\mathrm{kW/cm}^2$. It was experimentally shown that the losses in the terahertz range are maximal at low stress values and decrease several times at a stress of 2 kbar, while the losses are caused by the existence of a subsystem of orthostates. A variant of resonant excitation was considered, and a theoretical estimate of the cross section of stimulated Raman scattering was made, which hold out a hope of a stimulated effect in the terahertz frequency domain.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] M.S. Rider, V. Giannini. Nanophotonics, **10**, 3497 (2021).
[2] P. Chevalier, A. Amirzhan, F. Wang, M. Piccardo, S.G. Johnson, F. Capasso, H.O. Everitt. Science, **366**, 856 (2019).
[3] L.M.K. Vandersypen, M.A. Eriksson. Phys. Today, **72**, 38 (2019).
[4] J. C. McCallum, B.C. Johnson, T. Botzem, Appl. Phys. Rev., **8**, 031314 (2021).
[5] S.G. Pavlov, R.Kh. Zhukavin, V.N. Shastin, H.-W. Hübers. Phys. Status Solidi B, **250**, 9 (2013).
[6] R.H. Zhukavin, K.A. Kovalevsky, S.G. Pavlov, N. Deßmann, A. Pohl, V.V. Tsyplenkov, N.V. Abrosimov, H. Riemann, H.W. Hübers, V.N. Shastin. FTP, **54**, 816 (2020). (in Russian).
[7] S. Kudryashov, A. Nastulyavichus, G. Krasin, K. Khamidullin, K. Boldyrev, D. Kirilenko, A. Yachmenev, D. Ponomarev, G. Komandin, S. Lebedev, D. Prikhod'ko, M. Kovalev. Opt. Laser Techn., **158**, 108873 (2023).
[8] D.D. Awschalom, R. Hanson, J. Wrachtrup, B.B. Zhou. Nature Photonics, **12**, 516 (2018).
[9] K. Bergman, G. Grossmann, H.G. Grimmeiss. Phys. Rev. Lett., **56**, 2827 (1986).
[10] A. K. Ramdas, S. Rodriguez. Rep. Progr. Phys., **44**, 1297 (1981).
[11] A. DeAbreu, C. Bowness, R.J.S. Abraham, A. Medvedova, K.J. Morse, H. Riemann, N. V. Abrosimov, P. Becker, H.-J. Pohl, M.L.W. Thewalt, S. Simmons. Phys. Rev. Appl., **11**, 044036 (2019).
[12] N.A. Bekin. Semiconductors, **54**, 1112 (2020).
[13] P. Wagner, J. Hage. Appl. Phys. A, **49**, 123 (1989).
[14] Yu.A. Astrov, L.M. Portsel, V.B. Shuman, A.N. Lodygin, N.V. Abrosimov. Phys. Status Solidi A, **219**, 2200463 (2022).
[15] N. Dessmann, S.G. Pavlov, A. Pohl, V.B. Shuman, L.M. Portsel, A.N. Lodygin, Yu.A. Astrov, N.V. Abrosimov, B. Redlich, H.-W. Hübers. Phys. Rev. B, **106**, 195205 (2022).
[16] N. Stavrias, K. Saeedi, B. Redlich, P.T. Greenland, H. Riemann, N.V. Abrosimov, M.L.W. Thewalt, C.R. Pidgeon, B.N. Murdin. Phys. Rev. B, **96**, 155204 (2017).
[17] V.B. Berestetsky, E.M. Lifshitz, L.P. Pitaevsky. *Teoreticheskaya fizika*. Vol. IV. *Kvantovaya elektrodinamik* (M., Nauka, 1989) p. 255. (in Russian).
[18] I.R. Shen. *Printsipy nelineinoi optiki* (Nauka, M., 1989) p. 148. (in Russian).
[19] S.G. Pavlov, L.M. Portsel, V.B. Shuman, A.N. Lodygin, Yu.A. Astrov, N.V. Abrosimov, S.A. Lynch, V.V. Tsyplenkov, H.W.Hübers. Phys. Rev. Mater., **5**, 114607 (2021).

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