

NONLINEAR OPTICAL PHENOMENA

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Cascaded second-harmonic generation, summation of the wave vectors of the bulk defect-deformation waves, and generation of multimode micro- and nanostructures by laser irradiation of solids

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***Abstract*. We consider for the first time three-wave interactions of bulk quasi-static defect-deformation (DD) waves (generation of the second DD harmonic and summation of the wave vectors), similar to three-wave interactions in nonlinear optics and acoustics, leading to cascaded broadening of the spectrum of spatial DD harmonics. Based on the theory developed, we interpret the recently observed effect of laser-induced generation of the bulk periodic structure of silver nanoparticles with a discrete spatial spectrum, extending from micro- to nanometres.**

Keywords: *bulk defect-deformation waves, harmonic generation and wave-vector mixing, laser-induced micro- and nanostructures.*

1. Introduction

Emel'yanov and Seval'nev [1] have shown that there are quasi-static counterparts of classic dynamic nonlinear optical [2] and acoustic [3] wave effects [second harmonic generation (SHG) and frequency summation], which involve waves of new types – the quasi-static surface (zero frequency) defect-deformation (DD) waves excited by laser irradiation of solids. These effects include SHG of a surface relief: $2q = q_1 + q_2$ ($q_1 = q_2 = q$), where q_i are the wavenumbers of surface relief gratings, and wave-vector mixing of surface DD gratings ($q_3 = q_1 \pm q_2$). In this paper we show that similar three-wave DD interactions, for which the DD anharmonicity is responsible, also take place in the bulk of solids. We have established that in the presence of one seed bulk DD harmonic with a micron period, the cascaded SHG and wave-vector mixing of DD harmonics lead to generation of a bulk multimode DD structure with a spectrum of spatial harmonics, which extends from micro- to nanometres. Based on these results, we have interpreted the laser-induced generation in a polymer matrix of the layered structure of Ag nanoparticles with a discrete spatial spectrum, occupying the region from ~ 530 to $30-15$ nm [4].

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2. Equation for the Fourier amplitudes of the concentration field of mobile laser-induced defects

Suppose that in the bulk of a solid exposed to laser radiation, mobile point defects ('inclusions') with the concentration N_d are generated. The plane $z = 0$ coincides with the free surface of the sample, the z axis being directed perpendicular to the surface inside the sample. We consider a one-dimensional case where all variables depend only on the coordinate z.

The diffusion equation for N_d in this case has the form

$$\frac{\partial N_\mathrm{d}}{\partial t} = D_\mathrm{d}\,\frac{\partial^2 N_\mathrm{d}}{\partial z^2} - \frac{D_\mathrm{d}\theta_\mathrm{d}}{k_\mathrm{B}T}\,\frac{\partial}{\partial z}\left(N_\mathrm{d}\,\frac{\partial \xi}{\partial z}\right), \tag{1}$$

where $\theta_\mathrm{d} = \Omega_\mathrm{d}K$ is the deformation potential of the defect; Ω_d is the change in the medium volume during the formation of a defect; K is the elasticity modulus; $\xi = x(z,t) = \partial u_z/\partial z$ is the deformation in the bulk; $\boldsymbol{u} = \boldsymbol{u}(z,t)$ is the vector of the medium displacement; D_d is the coefficient of bulk diffusion of defects; T is the temperature. The second term in the right-hand side of (1) takes into account the strain-induced drift of defects interacting with the deformation. Equation (1) corresponds to the energy of the DD interaction $H = -\theta_\mathrm{d}\xi$.

The equation for the medium strain corresponding to the same interaction energy has the form

$$\frac{\partial \xi}{\partial t} = c^2\,\frac{\partial^2 \xi}{\partial z^2} - \frac{\theta_\mathrm{d}}{\rho}\,\frac{\partial^2 N_\mathrm{d}}{\partial z^2}, \tag{2}$$

where c is the longitudinal sound velocity; ρ is the medium density.

The system of equations (1) is closed and describes the DD instability in the bulk with mobile defects. We will use below the spatial Fourier transforms in the form

$$N_\mathrm{d}(z,t) = \sum_q N(q)\exp[\mathrm{i}qz + \lambda(q)t], \tag{3a}$$

$$\xi(z,t) = \sum_q \xi(q)\exp[\mathrm{i}qz + \lambda(q)t]. \tag{3b}$$

Expression (3) specifies the bulk DD structure as a superposition of one-dimensional DD gratings (quasi-static waves), consisting of coupled gratings of the concentration

of defects and the strain whose amplitudes increase in time with the growth rate $\lambda(q)$.

Assuming that the strain is adiabatically adjusted to the defect subsystem ($\partial^2\xi/\partial t^2 = 0$), we obtain from expressions (1), (2) for the Fourier amplitudes of the defect concentration the equation

$$\frac{\partial N(q)}{\partial t} = \lambda(q)N(q) + \frac{D_\mathrm{d}}{n_\mathrm{cr}}\sum_{q'\neq 0} qq' N(q')N(q-q'), \tag{4}$$

where the critical concentration of defects $n_\mathrm{cr} = \rho c^2 k_\mathrm{b} T/\theta_\mathrm{d}^2$ is introduced. The growth rate has the form

$$\lambda(q) = D_\mathrm{d} q^2(\varepsilon - 1),$$

where $\varepsilon = N_{\mathrm{d}0}/n_\mathrm{cr}$ is the control parameter of the DD instability, which is determined by the spatially uniform concentration of the defects $N_{\mathrm{d}0} \equiv N(q=0)$.

3. Equations for bulk three-wave interactions of DD gratings

We will consider the interaction of three DD gratings with wave vectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, directed along the z axis. In particular, as the wave vector $\boldsymbol{q}_1$ use can be made of the wave vector of the seed DD grating (see Sections 4 and 5). The equations for the Fourier amplitudes of the interacting DD gratings follow from (4) and have the form

$$\begin{aligned}
\frac{\partial N(q_1)}{\partial t} &= \lambda(q_1)N(q_1) - \frac{D_\mathrm{d} q_1 q_2}{n_\mathrm{cr}} N(q_1+q_2)N(-q_2),\\
\frac{\partial N(q_2)}{\partial t} &= \lambda(q_2)N(q_2) - \frac{D_\mathrm{d} q_1 q_2}{n_\mathrm{cr}} N(q_1+q_2)N(-q_1),\\
\frac{\partial N(q_1+q_2)}{\partial t} &= \lambda(q_1+q_2)N(q_1+q_2)\\
&\quad + \frac{D_\mathrm{d}(q_1+q_2)^2}{n_\mathrm{cr}} N(q_1)N(q_2).
\end{aligned} \tag{5}$$

Passing in (5) to real variables $N(q_j) = n(q_j)\exp[\mathrm{i}\varphi(q_j)]$, where $q_j = q_1, q_2, q_1+q_2$, we obtain a system of three equation for the real amplitudes $n(q_j)$:

$$\begin{aligned}
\frac{\partial n(q_1)}{\partial t} &= \lambda(q_1)n(q_1) - \frac{D_\mathrm{d} q_1 q_2}{n_\mathrm{cr}} n(q_1+q_2)n(-q_2)\cos\Phi,\\
\frac{\partial n(q_2)}{\partial t} &= \lambda(q_2)n(q_2) - \frac{D_\mathrm{d} q_1 q_2}{n_\mathrm{cr}} n(q_1+q_2)n(-q_1)\cos\Phi,\\
\frac{\partial n(q_1+q_2)}{\partial t} &= \lambda(q_1+q_2)n(q_1+q_2)\\
&\quad + \frac{D_\mathrm{d}(q_1+q_2)^2}{n_\mathrm{cr}} n(q_1)n(q_2)\cos\Phi,
\end{aligned} \tag{6}$$

and the equation for the phase difference $\Phi = \varphi(q_1+q_2) - \varphi(q_1) - \varphi(q_2)$:

$$\frac{\partial\Phi}{\partial t} = -\frac{D_\mathrm{d}}{n_\mathrm{cr}}\left[(q_1+q_2)^2\frac{n(q_1)n(q_2)}{n(q_1+q_2)} - q_1 q_2\frac{n(-q_2)n(q_1+q_2)}{n(q_1)} - q_1 q_2\frac{n(-q_1)n(q_1+q_2)}{n(q_2)}\right]\sin\Phi. \tag{7}$$

Below we will be interested in the case when at the initial time $t=0$, the nonzero $n(q_2, t=0)$ and $n(q_1, t=0)$ ($q_1 = q_2 = q$) are given, and $n(q_1+q_2, t=0) = 0$. Then, the first positive term in square brackets in (7) is much larger of the other two negative terms [for $t=0$ fluctuation plays the role of $n(q_1+q_2, t=0)$ in the denominator of the first term in (7)]. Therefore, equation (7) describes the relaxation of the phases $\Phi \to 0$ over time. Comparison of equations (7) and (6) shows that the ratio of the characteristic relaxation time of the phases to the characteristic time of transfer of defects from one DD grating to another has the form

$$\frac{\tau_\mathrm{phase}}{\tau_0} \sim \frac{n(q_1+q_2)}{n(q_1)} = \frac{n(2q)}{n(q)} \ll 1.$$

Therefore, when considering nonlinear transformations of the DD gratings in (6) we can put $\Phi = 0$.

4. Generation of even DD harmonics in the bulk

Let the volume initially contain a spatially uniform concentration of mobile defects $n_{\mathrm{d}0} \equiv n(q=0) = \mathrm{const}$, and in addition, one seed stationary DD grating with the wavenumber q, given by expression (3), where $\lambda(q) = 0$ (see Section 6). We will show that in the process of summation of two identical wavenumbers $2Mq = Mq + Mq$ ($M = 1, 2, 3, \ldots$), a DD grating with the wavenumber $2Mq$ is generated in the bulk. This process corresponds to SHG in a nonlinear optical crystal, when the exact phase-matching condition is fulfilled [2]. In addition to this process, the process of summation of the wavenumbers $2Mq = (2M-1)q + q$ ($M = 2, 3, 4, \ldots$) is also possible. Due to the cascaded repetition of these processes, there occurs cascaded generation of the spectrum of DD gratings with the wavenumbers $2Mq$ ($M = 1, 2, 3, \ldots$).

Consider the process of cascaded generation of even DD harmonics at the initial stage, when we can neglect the back effect of the generated harmonics on the generation process and assume $n(q) = \mathrm{const}$. For this case, the last of the three equations in (6) with the $\Phi = 0$ yields the equation for the real Fourier amplitude of the DD gratings with the wavenumber $2Mq$ ($M = 1, 2, 3, \ldots$):

$$\begin{aligned}
\frac{\partial n(2Mq)}{\partial t} &= \lambda(2Mq)n(2Mq) + \frac{\lambda(2Mq)}{n_\mathrm{cr}(\varepsilon-1)}\\
&\quad\times\left[n^2(Mq) + 2n((2M-1)q)n(q)(1-\delta_{1M})\right],
\end{aligned} \tag{8}$$

where the growth rate $\lambda(2Mq) = D_\mathrm{d}(2Mq)^2(\varepsilon-1)$ ($M = 1, 2, 3, \ldots$); δ_{1M} is the Kronecker delta.

The solution of equation (8) with the initial condition $n(2Mq,\ t=0) = 0$ has the form

$$\begin{aligned}
n(2Mq, t) &= \frac{\lambda(2Mq)}{n_\mathrm{cr}(\varepsilon-1)}\int_0^t \Big[n^2(Mq, t')\\
&\quad + 2n\big((2M-1)q, t'\big)n(q)(1-\delta_{1M})\Big]\exp\big[\lambda(2Mq)(t-t')\big]\mathrm{d}t',
\end{aligned} \tag{9}$$

where $M = 1, 2, 3, \ldots$.

5. Generation of odd DD harmonics in the bulk

Summation of the wavenumbers leading to the appearance of DD gratings with the wavenumbers $(2M+1)q$ $(M=1,2,3,\ldots)$ is described at the initial stage by an equation following from the last equation in (6) at $\Phi=0$:

$$\frac{\partial n((2M+1)q)}{\partial t}=\lambda((2M+1)q)n((2M+1)q)$$
$$+\frac{2\lambda((2M+1)q)}{n_{\rm cr}(\varepsilon-1)}\,n(2Mq)n(q), \qquad (10)$$

where $\lambda((2M+1)q)=D_{\rm d}[(2M+1)q]^2(\varepsilon-1)$.

The solution of equation (10) with the initial condition $n((2M+1)q,t=0)=0$ has the form

$$n((2M+1)q,t)=\frac{2\lambda((2M+1)q)}{n_{\rm cr}(\varepsilon-1)}$$
$$\times\int_0^t n\big(2Mq,t'\big)n(q)\exp\big[\lambda((2M+1)q)\big(t-t'\big)\big]{\rm d}t'. \qquad (11)$$

6. Discussion of the results and their comparison with the experiment

For a graphic illustration of the results, we consider the generation of the three lowest harmonics with wavenumbers $2q$, $3q$ and $4q$. We pass to dimensionless variables $n_{2M}=n(2Mq)(n_{\rm cr}/n^2(q))$ and $n_{2M+1}=n((2M+1)q)\times[n_{\rm cr}/n^2(q)]$ $(M=1,2,3,\ldots)$ and the dimensionless time $T=\lambda(2q)t$. Putting $M=1$, we obtain from (9) the dimensionless amplitude of the second DD harmonic

$$n_2(T)=\frac{1}{\varepsilon-1}\int_0^T\exp\big(T-T'\big){\rm d}T'. \qquad (12)$$

At $M=1$, we find from (11) the dimensionless amplitude of the third DD harmonic

$$n_3(T)=\frac{9b}{2(\varepsilon-1)}\int_0^T\exp\left[\frac{9\big(T-T'\big)}{4}\right]n_2\big(T'\big){\rm d}T', \qquad (13)$$

where $b=n(q)/n_{\rm cr}$.

At $M=2$, we find from (9) the dimensionless amplitude of the fourth DD harmonic

$$n_4(T)=\frac{4b^2}{\varepsilon-1}\int_0^T\exp\big[4\big(T-T'\big)\big]$$
$$\times\left[n_2^2\big(T'\big)+\frac{2}{b}\,n_3\big(T'\big)\right]{\rm d}T'. \qquad (14)$$

In this case, the dimensionless amplitude n_1 of the seed (steady-state) harmonic with the wavenumber q is equal to $1/b$.

Figure 1 shows the time dependences of the amplitudes of the second, third and fourth DD harmonics in the constant amplitude approximation of the first seed harmonic. One can see that there takes place a successive switching on of the generation of DD harmonics when their wavenumbers increase.

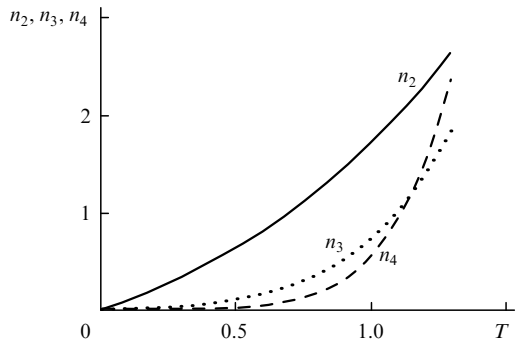

Figure 1. Dependences of the dimensionless amplitudes of the second (n_2), third (n_3) and fourth (n_4) DD harmonics on the dimensionless time T, constructed with Eqns (12)–(14) at $b=10^{-1}$, $\varepsilon=2$. The amplitude of the seed first harmonic is $n_1=10$.

The obtained results are valid only at the initial stage of the cascaded SHG and summation of the wavenumbers. At later stages, it is necessary to solve numerically the complete systems of equations (6) in the same way as was done in [1] for the case of surface DD gratings and take into account the depletion of the pump, i.e., to remove the restriction $n_{\rm d0}\equiv n(q=0)=$ const. In addition, system (6) for large t should additionally take into account the stabilising effect of the elastic anharmonicity of the medium. However, the results obtained here already suggest that the resulting bulk DD structure is indeed given by (3), the summation being performed over values of the wavenumbers that are multiples of natural numbers: q, $2q$, $3q$, $4q$, etc., where q is the wavenumber of the seed DD grating. Note that all these DD harmonics in the studied nonequilibrium (metastable) medium with laser-induced nonequilibrium defects are unstable [$\lambda(2Mq)>0$ and $\lambda(2Mq+1)>0$], when the threshold ($\varepsilon>1$) is exceeded: their amplitudes $n(2Mq)$ and $n((2M+1)q)$ grow over time due to pumping the defects in the harmonics from a spatially uniform concentration $N_{\rm d0}$ of the defects [our analysis is valid if $n(2Mq)$, $n((2M+1)q)<N_{\rm d0}$]. The growth rate increases with increasing harmonic number (Fig. 1). The exception is the seed (by assumption – steady-state) fundamental harmonic with the wavenumber q.

The instability of DD harmonics and an increase in their growth rate with increasing harmonic number qualitatively distinguish the studied effect of three-wave DD interactions from the cascaded SHG and summation of frequencies in nonlinear optics [2], where all the generated harmonics are stable and their amplitudes decrease sharply with increasing harmonic number. Note that the above process of generation of a broad spectrum of DD harmonics is also possible (but with a lower efficiency) for $\varepsilon<1$. In this case, the amplitudes of all the harmonics, except (by assumption) the first one, first increase and then decay over time. The time decay of the harmonics is caused by the spatial diffusion of defects that erase the DD gratings. In the case of $\varepsilon>1$, the strain-induced drift flux of the defects in equation (1) exceeds the diffusion flux, and the harmonic amplitudes, on the contrary, increase in time.

The physical mechanism for the generation of harmonics in the DD system consists in the spatial redistribution of defects under the action of the self-consistent strain grating on the initial defect grating. For example, in the case of SHG, the defect grating with a wavenumber q is affected by

a strain grating with the same wavenumber q, but phase-shifted by $\pi/2$. This leads to the appearance of a grating of the defect fluxes with the wavenumber $2q$, which serves as a source in the equation for the concentration field of defects (1) [or, in the Fourier transform, in equation (4)]. Thus, the nonlinear (quadratic) flux of defects in the case of the second DD harmonic is similar to the quadratic polarisation (or current) in the case of generation of the second optical harmonic.

In [4], laser-induced decomposition of molecules with silver atoms, introduced previously in the polymer film, lead to the formation of periodic layered structures of silver nanoparticles (nanoclusters) with layers parallel to the exposed surface of the film. When using incoherent radiation, the structure was not formed. The authors of [4] made in this connection a hypothesis that the interference of coherent incident and reflected waves is responsible for the formation of a periodic structure of nanoparticles; this interference forms a standing wave in the bulk of the film and leads to a spatially periodic modulation of the photolysis (pyrolysis) rate, and hence to modulation of the concentration of Ag atoms and nanoparticles. According to [4], the period of the interference pattern is $\Lambda = \lambda/(2n) \sim 200$ nm ($\lambda = 532$ nm, $n \sim 1.35$ is the refractive index). The wavelet analysis of the structure performed in [4] reveals the existence of not one harmonic but of a broad spectrum of harmonics extending from $\Lambda \sim 30$ nm to $\Lambda \sim 530$ nm (Fig. 2a), which contains also one harmonic with the period $\Lambda \sim 260$ nm, close to the evaluation period of the interference pattern (Fig. 2a). The origin of the remaining spatial frequencies in the spectrum remains unclear.

Using the results of this paper, we may give the following interpretation of the effect of formation of a broad discrete spectrum of spatial harmonics of a silver concentration field observed in [4]. In the laser photolysis (pyrolysis) there appear silver atoms, which play the role of mobile microscopic inclusions (defects) in the polymer matrix. The seed DD harmonic is the DD structure with an interference period $\Lambda_1 \sim 200$ nm. Generation of the second DD harmonic leads to the formation of structures with a period $\Lambda_2 \sim 100$ nm, close to the period of 90 nm of the most intense harmonic in the experimental spectrum [4]. Cascaded generation of the second DD harmonic and summation of spatial frequencies result in the transformation of the vectors of DD gratings up, i.e., in the formation of DD structures with periods Λ_3, Λ_4, Λ_5, etc., which explains the presence of a high-frequency part of the spectrum ($\Lambda_i <$ 200 nm) in Fig. 2a. The formation of a low-frequency part of the spectrum ($\Lambda_i > 200$ nm) should then be attributed to the decay of DD harmonics and generation of difference spatial frequencies. This interpretation is confirmed by a similar form of wavelet transforms of the experimental (Fig. 2a) and theoretical [Eqn (3) and Fig. 2b] concentration fields of defects.

The characteristic formation time of a structure with a period $\Lambda_2 = 100$ nm by the SHG, as seen from formula (12) and Fig. 1, is estimated as $\lambda^{-1}(2q)$, where the growth rate is determined in (8). Therefore, for this structure to have time to be formed during the irradiation time $t_{ir} = 5$ min [4], the diffusion coefficient of the Ag atom in the polymer matrix must satisfy the condition $D_{Ag} > \Lambda_2^2/[4\pi^2 t_{ir}^2(\varepsilon - 1)] \sim 8 \times 10^{-15}$ cm^2 s^{-1} at $\varepsilon = 2$. This condition is met with a safety margin in polymers (see, for example, [5]). The stability of the produced periodic structure can be achieved through the formation of immobile nanoparticles (nanoclusters) of silver in places where silver atoms aggregate.

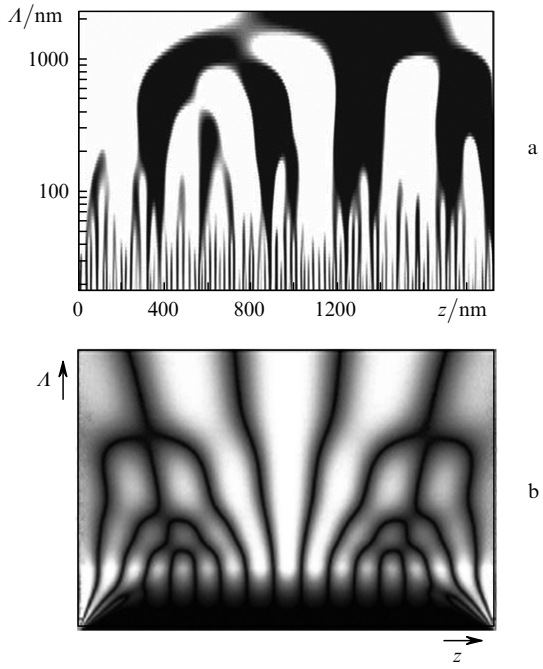

Figure 2. Wavelet transforms of experimental (a) and theoretical (b) [expression (3a)] concentration fields of defects. Dark areas in Fig. 2a, taken from [4], correspond to an increased concentration of Ag atoms and nanoclusters, and bright areas in Fig. 2b – to a high concentration of defects. Expression (3a) takes into account the first four harmonics: $N_d(z) = \cos z + \cos(2z) + \cos(3z) + \cos(4z)$.

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