PHYSICAL REVIEW A **67**, 041804(R) (2003)

Nonlinear optics in the angstrom regime: Hard-x-ray frequency doubling in perfect crystals

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(Received 8 July 2002; published 25 April 2003)

Based on the dynamical diffraction theory, we demonstrate the important role of the multiple scattering effects in an x-ray frequency doubling in crystals, generally leading to a generation of two coupled second-harmonic waves propagating in the forward and scattering direction. The possibility to phase match the process is shown for the Laue and Bragg geometry. Modeling of a frequency-doubling experiment suggests that the harmonic signal should be measurable for x-ray pumping with picosecond pulses of mJ energy.

DOI: 10.1103/PhysRevA.67.041804 PACS number(s): 42.65.Ky

Since the discovery of x rays, the foremost application of this radiation has been to reveal the inner structure of objects not transparent to visible light by exploiting linear properties of x-ray photons [1]. So far, nonlinear optical phenomena with x rays (XNLO) have been studied in much less detail compared to nonlinear processes in the IR, visible, and UV regions. The recent years have been marked by an increasing interest in this field of research, which is strongly motivated, on one hand, by the development of soft-x-ray lasers [2] and coherent higher-order harmonic sources (HHG) [3], and, on the other hand, by advances in the hard-x-ray generation technique based on laser-plasma interactions [4,5]. In addition, x-ray sources employing laser field scattering by relativistic electrons [6] and self-amplification of spontaneous emission in free electron lasers (FEL) have been demonstrated [7,8]. Very recently, low-order XUV-nonlinear processes (two-photon absorption and laser-assisted ionization) have been observed [9] and gave rise to unique spectroscopic studies in the soft-x-ray region [10]. These advances bring up the question: what kind of nonlinear effects might be expected for even shorter, angstrom wavelengths? The question is particularly interesting in the context of recently proposed hard-x-ray FEL facilities [8]. These systems could potentially generate x-ray fields with an intensity sufficient to observe strong field interactions in the vacuum, and, thus, there are good grounds to believe that lowest-order XNLO phenomena with hard x rays will be explored even in the near future.

Second-harmonic generation (SHG) is one of the best-understood nonlinear effect in optics and a study of this process in the angstrom regime, e.g., on the natural scale of atomic and molecular structure of matter, is of great interest both from a fundamental and practical viewpoint. Note that one of the lowest-order XNLO processes—three wave decay of x rays—has already been observed [11,12]. It results from the beatings of the vacuum field fluctuations with the input x-ray field, and, unlike the SHG process, falls in the category of spontaneous nonlinear effects. What is special about XNLO in the hard-x-ray region is the nature of nonlinearity responsible for frequency conversion. In traditional nonlinear optics, the radiation wavelength is much greater than the characteristic atomic spatial scale and the response of a crystal to the field is insensitive to the microscopic structure. In these conditions, the presence of inversion asymmetry in the crystal is necessary for the SHG process to occur. The situation is different when the crystal is exposed to hard-x-ray radiation. The local response now depends on the coordinates of atoms in the lattice, and therefore the medium no longer can be considered as a homogeneous one. The spatial inhomogeneity of the response in the x-ray region makes possible the observation of the second-order processes even in centrosymmetric media, much as SHG occurs in plasma [13]. Moreover, one may expect that periodicity of the crystal can essentially modify the interaction. Such effects as Bragg reflection, the pendulumlike behavior of the coupled waves [1], well known from linear x-ray diffraction, can also be involved in nonlinear interaction, leading to new physical features. Although different XNLO processes were discussed (parametric conversion [12], x-ray modulation by optical field [14], nonlinear absorption [15,16]), the role of the dynamical effects has not been addressed so far.

In this paper we discuss the physical aspects of the SHG process with hard-x-ray radiation and formulate the optimum conditions for experimental observation of this phenomenon in crystals. Based on the dynamical theory approach, we demonstrate the important role of multiple scattering effects in x-ray SHG, leading generally to a generation of two coupled harmonic waves propagating in the forward and scattering direction. The possibility to synchronize the process in the Laue and Bragg geometry is shown. Modeling of SHG in a LiF crystal suggests that in the picosecond (ps) regime x-ray frequency doubling should be measurable starting from pump intensities of the order of 1 $\mathrm{TW/cm^2}$. The results are of great importance both for the understanding of fundamental properties of x-ray diffraction and for practical realization of nonlinear interaction schemes in the Angström regime.

To get insight into the physics of SHG with hard x rays, we consider a propagation of an x-ray electromagnetic wave $\mathbf{E}(\mathbf{r},t)$ in an ideal crystal far from the absorption edge. Because of the large mass of the nuclei, x-ray interactions with the ionic core can be neglected [1], and we come to the problem of the scattering of a high-frequency field by quasi-free atomic electrons. Assuming the medium nonmagnetic, propagation of an x-ray wave $\mathbf{E}(\mathbf{r},t)$ is described by

$$\mathrm{rot}\,\mathrm{rot}\;\mathbf{E}+c^{-2}\partial^2\mathbf{E}/\partial^2 t=-4\pi c^{-2}\;\partial\mathbf{J}(\mathbf{E})/\partial t. \qquad (1)$$

To solve Eq. (1) one needs to know the relation between the current $\mathbf{J}$ and the field $\mathbf{E}$, which can generally be determined by calculating the expectation value of the Schrödinger current [1]. Due to the essentially classical character of the electron-field interaction assumed (no resonance with quantum transitions, the energy of the x-ray photon $\hbar\omega_X$ is much less than the Compton energy $\hbar\omega_c = m_e c^2$) the current $\mathbf{J}(\mathbf{r},t)$ in Eq. (1) can be treated as a classical current induced by the field $\mathbf{E}(\mathbf{r},t)$ in a medium with the charge density $\rho(\mathbf{r},t)$ [12,13]. The problem can be reduced to the interaction of electromagnetic wave with a cold collisionless plasma with "frozen" ions, and $\mathbf{J}(\mathbf{E})$ is determined from the Lorentz equation for the electronic liquid with "zero" pressure [17]. Assuming the x-ray field in the form of a plane wave $\mathbf{E}(\mathbf{r},t) = \mathbf{e}E_1 \exp(i\mathbf{k}_1\cdot\mathbf{r}\text{-}i\omega t)$ ($\mathbf{e}$ is a unit polarization vector, $|\mathbf{k}_1| = \omega/c$), the lowest-order nonlinear current $\mathbf{J}_2 \propto \exp[i(2\mathbf{k}_1\cdot\mathbf{r}\text{-}2\omega t)]$ giving rise to the SHG process is calculated to be

$$\mathbf{J}_2(\mathbf{r},t) = i[\rho_0(\mathbf{r})e^2/2m_e^2\omega^3][(\mathbf{E},\boldsymbol{\nabla})\mathbf{E} + i(\omega/c)\mathbf{E}\times\mathbf{H}] + i(e^2/m_e^2\omega^3)[\boldsymbol{\nabla}\rho_0(\mathbf{r}),\mathbf{E}]\mathbf{E}, \tag{2}$$

where $\rho_0(\mathbf{r})$ is the nonperturbed electron charge density. The three terms in Eq. (2) arise from the nonlinear displacement, nonlinear Lorentz force, and spatially inhomogeneous density $\rho_0(\mathbf{r})$, respectively. According to Eq. (2), in a homogeneous medium $[\nabla\rho_0(\mathbf{r}) = 0]$ no SHG is observed in the far field since the electric field vector induced by $\mathbf{J}_2$ is parallel to the wave vector of the current. Due to the spatial periodicity of the crystal, $\rho_0(\mathbf{r})$ can be expanded in a Fourier series in terms of reciprocal-lattice vectors $\mathbf{g}_m$ of the crystal: $\rho_0(\mathbf{r}) = \Sigma_m \rho_m \exp(i\mathbf{g}_m\cdot\mathbf{r})$, where ρ_m is the corresponding Fourier component. By substituting the expansion into Eq. (2), we find that the nonlinear current is described by a superposition of spatial harmonics:

$$\mathbf{J}_2(\mathbf{r},t) = -(e^2/2m_e^2\omega^3)E_1^2(\mathbf{r},t)\sum_m \rho_m \times[\mathbf{k}_1 + 2(\mathbf{g}_m,\mathbf{e})\mathbf{e}]e^{i(2\mathbf{k}_1+\mathbf{g}_m)\mathbf{r} - i2\omega t}. \tag{3}$$

The SHG process is now possible because the polarization vector and the wave vector of the spatial harmonics are generally nonparallel. Accumulation of the SHG field will occur when all unit cells of the crystal radiate in phase. This is the case when for some reciprocal vectors, $\mathbf{g}_m = \mathbf{g}$, wave vector $(2\mathbf{k}_1 + \mathbf{g})$ is close to the wave vector of the second-harmonic field $\mathbf{k}_2$, or when the momentum conservation condition, $2\mathbf{k}_1 + \mathbf{g} \approx \mathbf{k}_2$, is fulfilled (Fig. 1). Note that the phase-matching mechanism here is similar to quasi-phase-matching in nonlinear optics [18].

The important moment (which has not been addressed so far) is that the SHG proces is accompanied by the process of energy exchange with a second- (coupled) harmonic field. This is because the momentum conservation law (Fig. 1) implies that the harmonic propagates under the condition of Bragg scattering. As a result of rescattering of the harmonic with wave vector $\mathbf{k}_{2,g}$ on the reciprocal vector $(-\mathbf{g})$, a harmonic field with $\mathbf{k}_{2,0} = (\mathbf{k}_{2,g} - \mathbf{g})$ will be generated in the pump propagation direction. Owing to the coupling of the harmonics, specific phenomena such as Bragg reflection and

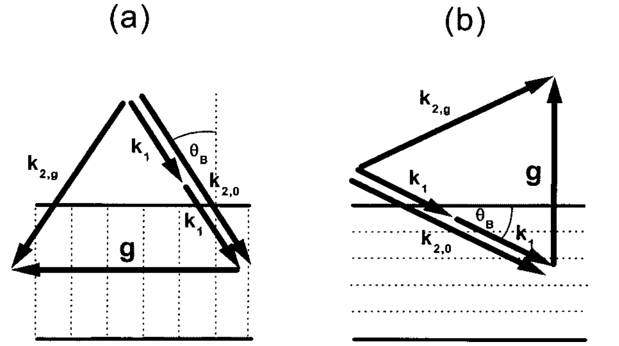

FIG. 1. Schematic of x-ray SHG in the Laue (a) and Bragg (b) geometry.

the pendulumlike behavior of the coupled waves [1] may be expected. This can strongly limit the penetration depth of the harmonic into the crystal, change phase velocity of the waves, leading to saturation of the conversion efficiency.

Below we will focus on the analysis of these effects and consider propagation of the harmonic wave $\mathbf{E}_{2,g}$ generated by the current (3) and the coupled wave $\mathbf{E}_{2,0}$ which arises as a result of the dynamic scattering. Assuming conversion to the harmonics small (which allows using the given pump field approximation) and considering a quasistationary interaction regime, from Eq. (1) we get the following equations for the "slow" harmonic amplitudes:

$$\frac{\lambda_2}{\pi}\gamma_g\frac{dE_{2,g}}{dz} = i[\chi_0(2\omega) - \cos(2\theta_B)\chi_0'(\omega)]E_{2,g} + i\chi_g(2\omega)E_{2,0} + i[2\sin(2\theta_B)\Delta\theta_B]E_{2,g} + \chi_{NL}(2\omega)E_1^2, \tag{4a}$$

$$\frac{\lambda_2}{\pi}\gamma_0\frac{dE_{2,0}}{dz} = i[\chi_0(2\omega) - \chi_0'(\omega)]E_{2,0} + i\chi_{-g}(2\omega)E_{2,g}. \tag{4b}$$

In Eqs. (4a) and (4b) the coordinate z is directed along the atomic planes in the Laue case and perpendicular to the planes in the Bragg geometry. The parameters γ_0 and γ_g take the values $\{\cos\theta_B;\cos\theta_B\}$ for the Laue and $\{\sin\theta_B; -\sin\theta_B\}$ for the Bragg case, where θ_B is the Bragg angle $(2\sin\theta_B = |\mathbf{g}|/|\mathbf{k}_2|)$; $\chi_m(\omega) = (4\pi e\rho_m/m_e\omega^2)$, $(m = 0,\pm g)$ is the Fourier component of the linear susceptibility associated with Fourier expansion of $\rho_0(\mathbf{r})$. The component $\chi_0 = \chi_0' + i\chi_0''$ describes refraction and absorption in a balk medium, while χ_g describes coupling between the harmonics due to the dynamical scattering. Absorption of the pump field is included by assuming an exponential decrease of $E_1(z)$. $\chi_{NL}(2\omega) = -(\pi e^2\rho_g/m_e^2\omega^3 c)\Phi(\theta_B)$ is the nonlinear susceptibility, where the factor $\Phi(\theta_B)$ equals $\sin(2\theta_B)$ or $\sin(2\theta_B)[1-4\cos(2\theta_B)]$ for the pump with σ and π polarization, respectively. The third term on the right-hand side of Eq. (4a) accounts for a small deviation $\Delta\theta_B = (\theta - \theta_B)$ of the pump incidence angle from the vacuum Bragg angle. Note, for $E_1 = 0$ and $\chi_0(\omega) = 0$ Eqs. (4) turn into the Takagi-Taupin equations [1].

As follows from Eq. (4a), effective conversion requires that the contributions to the harmonic phase due to the difference between the polarizabilities $\chi_0(\omega)$ and $\chi_0(2\omega)$ and the dynamical scattering (χ_g) be small. Actually, both factors are significant and lead to a rapid saturation of conversion. It turns out, however, that the SHG process can be synchronized by properly choosing the Bragg detuning $\Delta\theta_B$. To show this we will neglect for simplicity absorption of the pump and harmonic field. Then solutions to Eqs. (4) are described by a sum of two fundamental waves with spatial frequencies K_1 and K_2 which depend on the polarizabilities of the crystal, the coupling parameter, and the Bragg detuning. The condition of synchronous propagation then consists of the requirement that one of the spatial frequencies be zero. This is the case when the Bragg detuning takes the value

$$\Delta\theta_B = (|\chi_g|^2 - \Delta\chi_1\Delta\chi_2)/[2\sin(2\theta_B)\Delta\chi_1], \tag{5}$$

where $\Delta\chi_1 = \chi_0'(2\omega) - \chi_0'(\omega)$ and $\Delta\chi_2 = \chi_0'(2\omega) - \cos(2\theta_B)\chi_0'(\omega)$. The optimum detuning has the same form (5) for both geometries. This is explained by the fact that physically the synchronism condition depends only on the intrinsic properties of the crystal, but not on the boundary conditions. In particular, in the optimized Laue geometry, dependence of the harmonic fields on the dimensionless length $L = \pi(z/\lambda_2\gamma)$ is given by

$$E_{2,g}(L) = \chi_{\rm NL}E_1^2\frac{\Delta\chi_1}{|\chi_g|^2+|\Delta\chi_1|^2}\left\{\frac{i|\chi_g|^2}{|\chi_g|^2+|\Delta\chi_1|^2}\times\left[1-\exp\left(i\frac{|\chi_g|^2+|\Delta\chi_1|^2}{\Delta\chi_1}L\right)\right]+\Delta\chi_1 L\right\}, \tag{6a}$$

$$E_{2,0}(L) = \chi_{\rm NL}E_1^2\frac{\chi_g\Delta\chi_1}{|\chi_g|^2+|\Delta\chi_1|^2}\left\{\frac{i\Delta\chi_1}{|\chi_g|^2+|\Delta\chi_1|^2}\times\left[1-\exp\left(i\frac{|\chi_g|^2+|\Delta\chi_1|^2}{\Delta\chi_1}L\right)\right]+L\right\}. \tag{6b}$$

Equations (6) show that, in addition to the term describing spatial oscillations at frequency $K_L = (|\chi_g|^2 + |\Delta\chi_1|^2)/\Delta\chi_1$, the fields contain a phase-matched term increasing linear with L. Thus, for $L \gg (1/K_L)$ the generated harmonics will grow nearly linear with the crystal length. Equation (6) also shows that the asymptotic ratio of harmonic intensities is proportional to $|\chi_g|^2/|\Delta\chi_1|^2$ and provides direct information about the optical constants of the crystal.

In order to model a real experimental situation, we performed a numerical study of the SHG process for several crystals using the model (4). We found that a LiF crystal exhibits promising characteristics. Its photoabsorption length is one order of magnitude larger than the characteristic scattering (extinction) lengths at the pump and harmonic frequencies [1]. This suggests that the dynamical effects should play a central role in the SHG process. Below we discuss the results for LiF pumped with $\lambda_X = 3.1$ Å ($I_X = 1$ TW/cm^2) at incidence angle close to $\theta_B = 22.6°$, reflection (002). In Figs. 2 and 3 we show calculated intensities of the harmonics as a function the crystal thickness L and the Bragg detuning $\Delta\theta_B$. First, the computer modeling shows that in both interaction geometries second-harmonic radiation is generated for an angle of incidence slightly deflected from the Bragg angle and concentrated within angular detunings as small as only one arcsecond. Intensity of the harmonic radiation first grows monotonically but then shows saturation due to photoabsorption in the crystal. In the Laue geometry (Fig. 2), the harmonic intensities show a well-pronounced maximum near $L \approx 100$ μm followed by a slow decrease. In the Bragg case, dynamics of saturation is different for the wave propagating in the forward and scattering direction (Fig. 3). Intensity of the reflected harmonic tends to the constant value which does not depend on the crystal thickness, while the coupled harmonic field, after achieving maximum at $L \approx 40$ μm, monotonically decreases with the thickness. In Fig. 4 the intensity of the reflected harmonic is shown with a spatial resolution much higher than that used in Figs. 2 and 3. One can see the characteristic spatial modulation of the intensity due to the contribution into the harmonic fields of the ‘‘nonsynchronized’’ oscillating term.

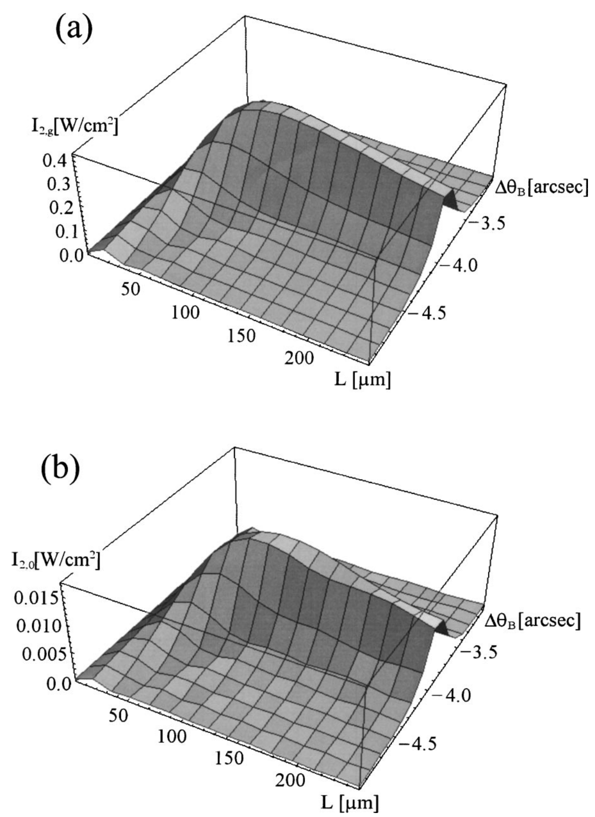

FIG. 2. Laue geometry: SHG in LiF(002) ($\theta_B = 22.6°$) in the scattering (a) and forward (b) directions vs the Bragg detuning $\Delta\theta_B$ and crystal thickness L for $\lambda_X = 3.1$ Å, $I_X = 10^{12}$ W/cm^2.

Now let us formulate requirements on the parameters of the pump field on the assumption that one photon of the harmonic field can be detected. According to the numerical results, in the optimum regime divergency of the pump x-ray beam should be as small as only a few arcseconds, and for a beam with a radius $\sim 10^{-2}$ cm this is close to the diffraction limit. Taking the pump intensity $I_P \approx 1$ TW/cm^2, we find that

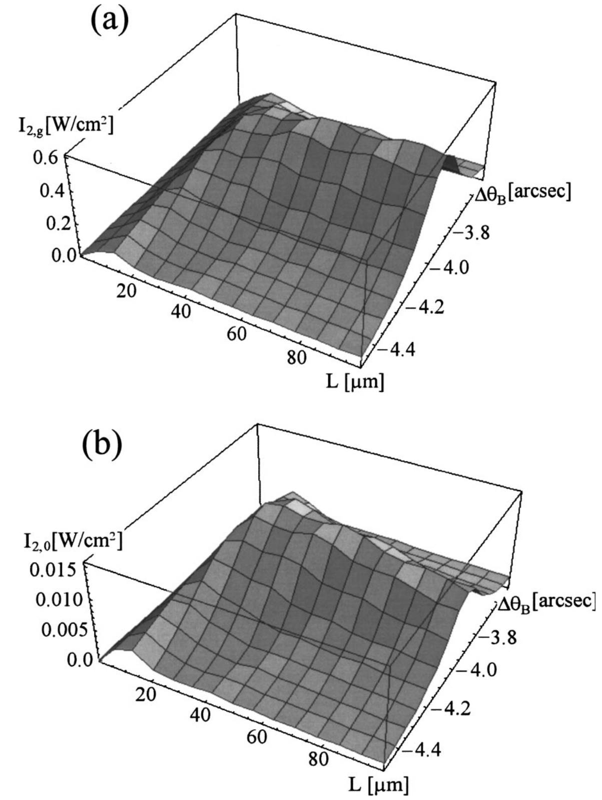

FIG. 3. Bragg geometry: SHG in LiF(002) ($\theta_B = 22.6°$) in the scattering (a) and forward (b) directions vs the Bragg detuning $\Delta\theta_B$ and crystal thickness L for $\lambda_X = 3.1$ Å, $I_X = 10^{12}$ W/cm^2.

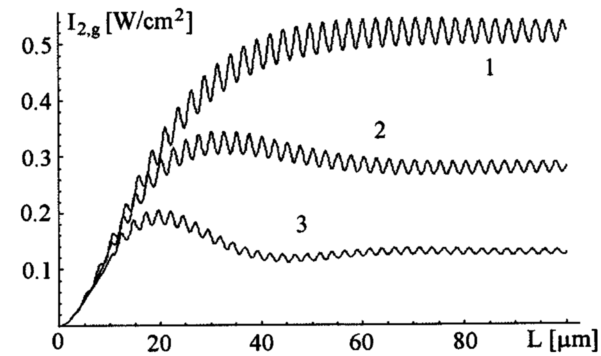

FIG. 4. Bragg geometry: the reflected harmonic [Fig. 3(a)] shown with higher spatial resolution. 1, $\Delta\theta_B = -4$ arcsec; 2, -3.8 arcsec; 3, -3.6 arcsec.

to produce more than one SHG photon one needs an x-ray pump pulse with energy $E_p \approx 1.5$ mJ, which corresponds to the number of x-ray photons $N_{ph} \approx 10^{12}$. The available sources of hard x rays (for example, laser-plasma sources [4,5]) can deliver a comparable number of photons in the ps regime, but can hardly provide the required extremely high brightness. On the other hand, the requirements on brightness and energy of the pump could be fulfilled for radiation produced by future FELs [7,8]. These systems are expected to generate a diffraction-limited radiation in the angstrom region with peak power about 10 GW and an energy per pulse of few mJ, which would result in a SHG efficiency comparable to that of the available soft-x-ray sources [3]. In focused beams, pump intensities as high as 10^{30} W/cm^2 should be achievable [8]. Assuming that far above the highest K-absorption edge the mechanism of nonlinearity based on the free electron response remains valid up to relativistic intensity $I_{Rel} = 3\pi m_e^2 c^5 / 2e^2 \lambda x^2 \sim 10^{26}$ W/cm^2, we find from Eq. (6) that SHG with an efficiency of several percents might be expected. Fundamentally, the use of centrosymmetric materials (like LiF) in such XNLO experiments would provide direct evidence of the electronic nature of nonlinearity in the angstrom region.

In conclusion, we have discussed the SHG process with hard x rays and formulated the optimum conditions for experimental observation of this phenomenon in crystals. We note that the approach can be extended to higher-order XNLO processes. Indeed, far from the absorption edge, the linear susceptibility is a monotonous function of frequency, and the phases of the fields cannot be matched unless operating near the Bragg condition. This suggests that the main features established for the SHG process (generation of two coupled harmonics, the possibility to synchronize the process by finely tuning the Bragg angle) will also be valid for a generation of higher-order harmonics of x rays.

The authors gratefully acknowledge helpful discussions with Dr. C. Rose-Petruck.

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