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Selective infrared absorption and refraction of symmetrical two-layered molecular nanofilms

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We have supplemented the already formulated microscopic theory of optical properties of very ultrathin molecular films (quantum nanofilms), *i.e.*, quasi 2D systems parallel to *XY* planes bounded by two surfaces. The exposure of nanofilms to the external electromagnetic fields has resulted in the creation of excitons, but different than bulk ones in one direction perpendicular to surfaces. The analysis of the dielectric response of the system to perturbation of an external electromagnetic field shows that optical properties of these crystalline nanosystems for low exciton concentration of Frenkel's excitons strongly depend on boundary parameters and the thickness of the film. In addition, the dynamical absorption and the refraction coefficient show a very narrow and discrete dependence of external electromagnetic field frequency, which is the consequence of both resonance and quantum size effects. Influences of boundary conditions on optical characteristics (through the analyses of dynamical absorption and refraction indices) of these nanostructures were specially and in details explored. The emission and the luminescence spectrum of the whole film have been analyzed and the results compared to experimental data show very good behavior and very good coordination.

Keywords: nano-film, excitons, Green's functions, permittivity, absorption, refraction.

1. Introduction

This paper presents the results of further researches into dielectric properties of symmetrical molecular crystalline nanofilms, whose properties were investigated and presented in earlier works [1–3].

In our previous works we investigated and presented frequent dependences and specific characteristics of relative permittivity of the ultrathin film as a result of

quantum size effects and conformation properties of the observed sample with different boundary parameters. Further researches primarily refer to the discovery of the above mentioned effects on refraction and absorption of infrared electromagnetic radiation for the interval of frequencies in which bulk samples are complete absorbents.

Symmetrical nanofilms are particularly important because specific properties which are the result of boundary perturbation parameters come from physical conditions as well as from technical and technological procedures used in the production of such films.

We will examine here an ideal ultrathin film with a simple cubic crystalline structure, produced in/upon a substrate or matrix, using a suitable technological doping method. The term "ideal" is used here in the sense of the absence of disturbances in the internal crystalline structures (such as defects, impurities or similar) and not in the sense of spatial infinity or the absence of disturbances in translational invariance of relevant energy parameters in the system. Dimensions of the film are such that it is infinite in XY planes and has a finite thickness L in z-directions. Therefore, this film has two infinite boundary surfaces parallel with XY-planes, namely for: $z = 0$ and $z = L$ [3, 4].

Using a specially adjusted method (Green's functions) for these very discrete crystalline structures [1] and supported by the research of changes of dynamic permittivity with perturbable ultrathin two-layered molecular crystalline films [2], we continued in this work with the research of optical properties of these structures. We determined the indices of absorption and refraction in layers and for the whole film, keeping up with the research from the previous work [3, 4] in which we found out that the presence of boundaries and changes in boundary parameters will lead to the presence of discrete absorption and a possibility for a selective absorption of a single line of incoming electromagnetic radiation.

2. Model and theoretical calculations

We carried out the above mentioned research starting with the standard expression for effective exciton Hamiltonian [5], in Bose [6] and nearest neighbor approximations:

$$H = \sum_{\mathbf{n}} \Delta_{\mathbf{n}} B_{\mathbf{n}}^{+} B_{\mathbf{n}} + \sum_{\mathbf{n},\,\boldsymbol{\lambda}} X_{\mathbf{n}\boldsymbol{\lambda}} B_{\mathbf{n}}^{+} B_{\mathbf{n}+\boldsymbol{\lambda}} \tag{1}$$

along with the two boundary parameters: $d \in [-0.2; +0.2]$, $x \in [-0.99; +2.0]$ and for two-layer film $n_z = 0, 1, 2$:

$$\Delta_{\mathbf{n}} \equiv \Delta\left[1 + d(\delta_{nz,\,0} + \delta_{nz,\,N})\right] \tag{2a}$$

$$X_{\mathbf{n},\,\mathbf{n}+\boldsymbol{\lambda}} \equiv X\left[1 + x(\delta_{nz,\,0} + \delta_{nz,\,N-1})\right] \tag{2b}$$

$$X_{\mathbf{n},\,\mathbf{n}-\boldsymbol{\lambda}} \equiv X\left[1 + x(\delta_{nz,\,1} + \delta_{nz,\,N})\right] \tag{2c}$$

The method of Green's functions [1] has been used in the research, adjusted to structures with the interrupted symmetry [7][1].

By solving the system of non-homogeneous differential equations, Green's functions were determined. On the basis of standard definition (linear response of the system on external perturbation of electromagnetic field [5, 8]) of relative permittivity with Green's functions:

$$\varepsilon_{nz}^{-1}(\omega) = 1 - 2\pi i S\Big[G_{nz}(\omega) + G_{nz}(-\omega)\Big] \tag{3}$$

we have found the expression for the dependence of film relative permittivity on the frequency of external electromagnetic field:

$$\varepsilon_{nz}(\omega) = \left\{1 + \frac{2\hbar S}{|X|}\sum_{v=1}^{N+1} g_{nz}^{v}\,\frac{\Delta/|X| + F_{xy} - \rho_v}{\hbar\omega/|X| - \left(\Delta/|X| + F_{xy} - \rho_v\right)^2}\right\}^{-1} \tag{4}$$

All values in this expression have been defined in our previous work [3].

3. Absorption and refraction in ultrathin molecular film

The refraction n and absorption κ indices are usually defined in the literature [9] by the permittivity term $\sqrt{\varepsilon} = n + i\kappa$. Introducing the complex frequency $\omega \to \omega + iv$ in expression for permittivity (4), we get complex permittivity $\varepsilon = \varepsilon' + i\varepsilon''$. Based on this, we can find the expression for absorption and refraction indices in the following form:

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[1] Theoretical analysis has been provided by Green's functions:

$$G_{\mathbf{nm}}(t) = \langle\langle B_{\mathbf{n}}(t)|B_{\mathbf{m}}^{+}(0)\rangle\rangle \equiv \Theta(t)\langle[B_{\mathbf{n}}(t), B_{\mathbf{m}}^{+}(0)]\rangle$$

with the following equation of motion:

$$i\hbar\frac{\mathrm{d}}{\mathrm{d}t}G_{\mathbf{nm}}(t) = i\hbar\delta(t)\langle[B_{\mathbf{n}}(t), B_{\mathbf{m}}^{+}(0)]\rangle + \Theta(t)\langle[[B_{\mathbf{n}}(t), H], B_{\mathbf{m}}^{+}(0)]\rangle$$

Having in mind the Hamiltonian (1), boundary conditions (2), and Green's equation of motion, we can derive the system of $(N+1)$ non-homogenous algebraic-differential equations for Green's functions (for details, see in [3, 7]):

$$G_{nz,\,mz}\Big[\rho - \frac{\Delta}{|X|}d(\delta_{nz,\,0} + \delta_{nz,\,N})\Big] + G_{nz+1,\,mz}\Big[1 + x(\delta_{nz,\,0} + \delta_{nz,\,N})\Big] +$$

$$+ G_{nz+1,\,mz}\Big[1 + x(\delta_{nz,\,1} + \delta_{nz,\,N})\Big] = \frac{i\hbar}{2\pi|X|}\delta_{nz,\,mz}$$

where $\rho = \dfrac{\hbar\omega - \Delta}{|X|} + F_{xy}$, and $F_{xy} \equiv 2\Big[\cos(ak_x) + \cos(ak_y)\Big]$.

$$\kappa_{nz}(\omega) = \sqrt{\frac{\varepsilon'}{2}\sqrt{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2}-1} \tag{5}$$

$$n_{nz}(\omega) = \sqrt{\frac{\varepsilon'}{2}\sqrt{1+\left(\frac{\varepsilon''}{\varepsilon'}\right)^2}+1} \tag{6}$$

From these expressions and expression (4) one can see that dynamical absorption and refraction indices as well as relative permittivity depend on the position of a film--layer n_z and on the perturbation at and within an ultrathin film.

By numerical calculations, we have analyzed the absorption index behavior on plane position and on values of boundary parameters, and calculated that. The number of resonant peaks directly depends on the film width, *i.e.*, on the number of layers N (there $N = 2$). General rule is that the number of resonance peaks decreases inside layers of the film, although with the influence of perturbation parameters d and x this rule can be broken and in that case the number of peaks is $(N + 1)$, with the possibility of some resonance peaks fading.

Subsequently we have carried on with the research of the same structures and investigated the influence of boundary parameters on absorption and refractive properties of these structures $n_{nz}(\omega)$, and showed results in Figs. 1–3[2] for different values of perturbation parameters: $x = -0.75, 0.0, 0.75$ and $d = -0.1, 0.0, 0.1$.

Since the emission and absorption spectra can be experimentally recorded but only for the whole film, we have determined these optical characteristics (indices of absorption and refraction) not only for the particular layers but for the whole film as well and in the normal direction on boundary surface of the film where the changes of these values occur in relation to their bulk values.

Comparing to resonant lines of permittivity, we can observe that there are less absorption peaks, *i.e.*, that there are dominant frequencies which will be absorbed truly. Actually there is a dominant peak on boundary planes, but with the half of these cases that peak is narrow for lower values of the parameter x, and in the other half its width is larger (x of a bit higher value).

[2]The influence of a change in the parameter x is shown in all pictures: when the transfer of excitons in border layers is about half the value comparing to the bulk $x = -0.75$, when there is no change of transfer – ideal film $x = 0$, and for about two times higher border transfer $x = 0.75$. On each of these three figure, the influences of the changes in the value of the parameter d are shown (ranging from the case when this parameter is lowered for 10% through the case when the value of the parameter d is unchanged comparing with the bulk case, to the cases when this parameter is increased for 10% in the node of a border area of the film), while the values of parameter x are fixed. Each figure has four columns with six graphs which show positions of absorption and refraction peaks on a border plane of the film, while right side next columns show positions of absorption and refraction peaks in the internal plane of the film. On each figure, ordinate has relative values of absorption index (comparing with bulk values), while abscise has non-dimensional values of frequencies of external electromagnetic field (defined in [3, 7]). The last two columns show the sum of absorption and refraction spectra for the whole film.

For the whole film, the absorption spectra possess one more expressive peak out of the three possible peaks in a narrow zone, except when $d = -d$, then we have two peaks symmetrical around a central narrow zone. The place of a peak and the zone depends on values d: when $d > 0$, then the peak is on sides (on higher frequencies), but when $d < 0$, then it is the opposite way. The specific case is when $d = 0$, then there appears only one (a little wider) absorption peak on certain frequency. In that case the positions of zones and peaks in certain layers are congruous.

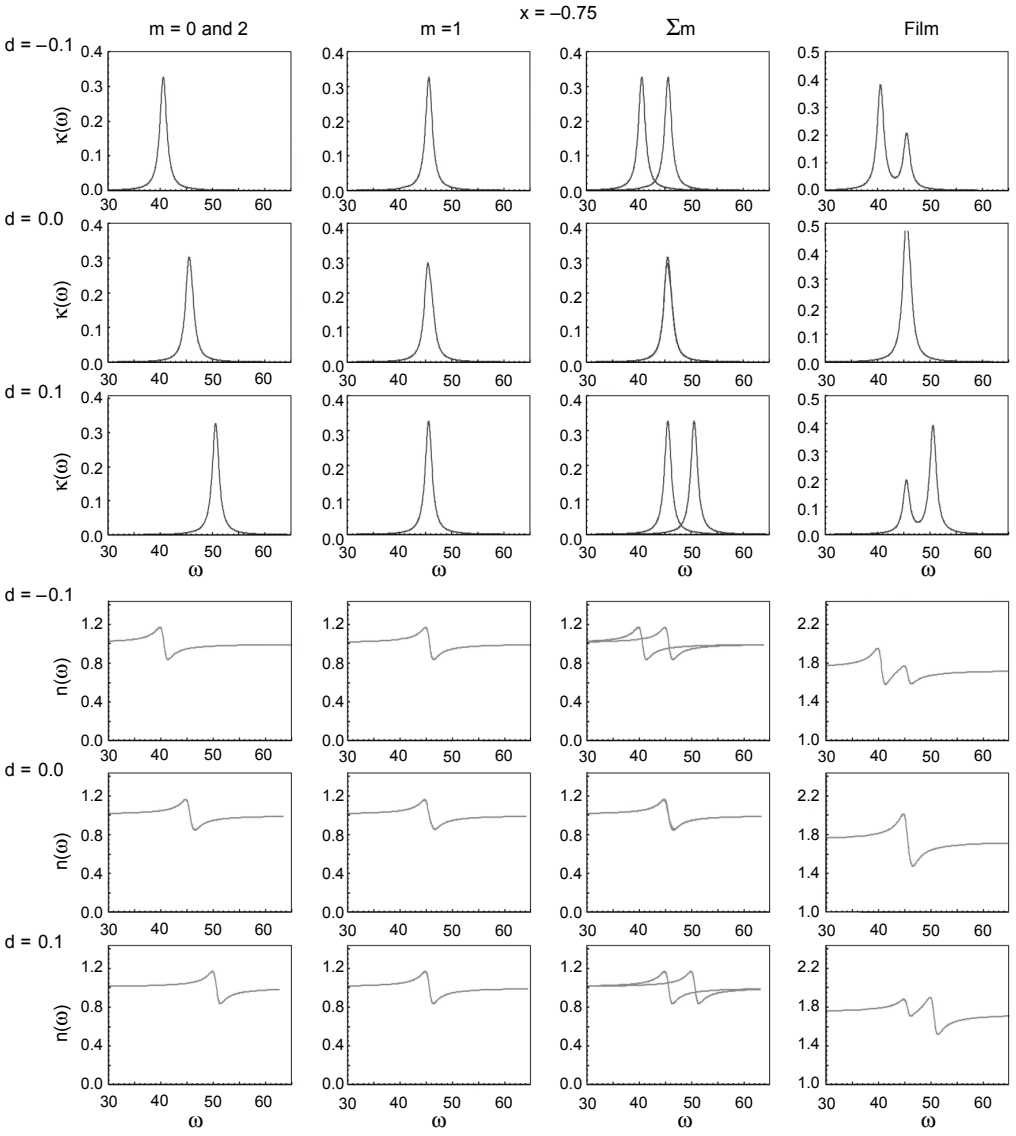

Fig. 1. Relative dynamical absorption and refraction indices of symmetrical perturbed two-layered film (see text for explanation).

In the down parts of all pictures, the dependence of the refraction index on reduced frequency of an external electromagnetic field is given. From all those given charts, we can see that slight growth of refraction breaks at points of change of absorption characteristics. At the point where the index of absorption increases – the index of refraction decreases, at the point where the index of absorption alternates abruptly (increase/decrease) there are the peaks of refraction index. This is in accordance with the assumption of Kramer's theory, but there the effects only appear at the beginning

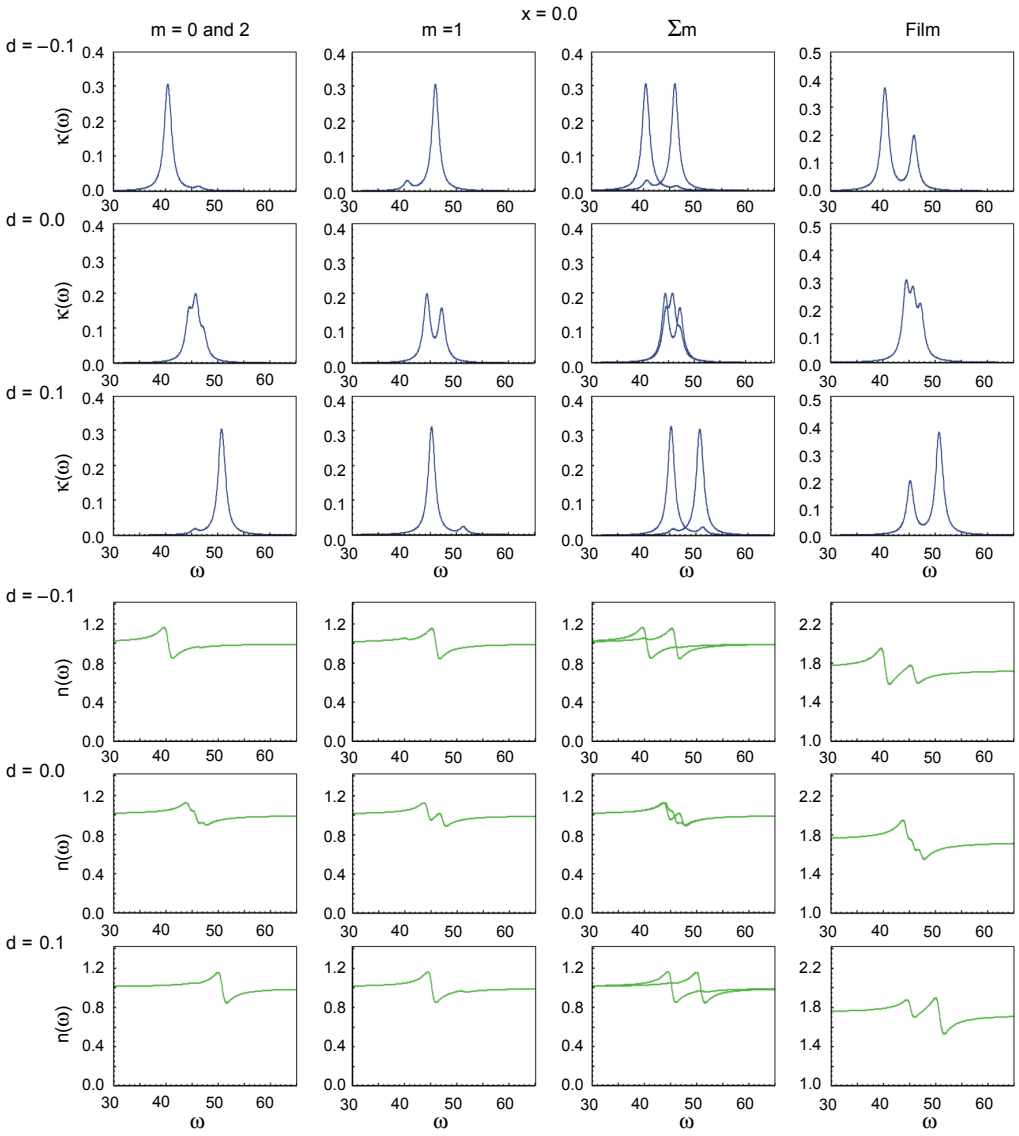

Fig. 2. Relative dynamical absorption and refraction indices of symmetrical perturbed two-layered film (see text for explanation).

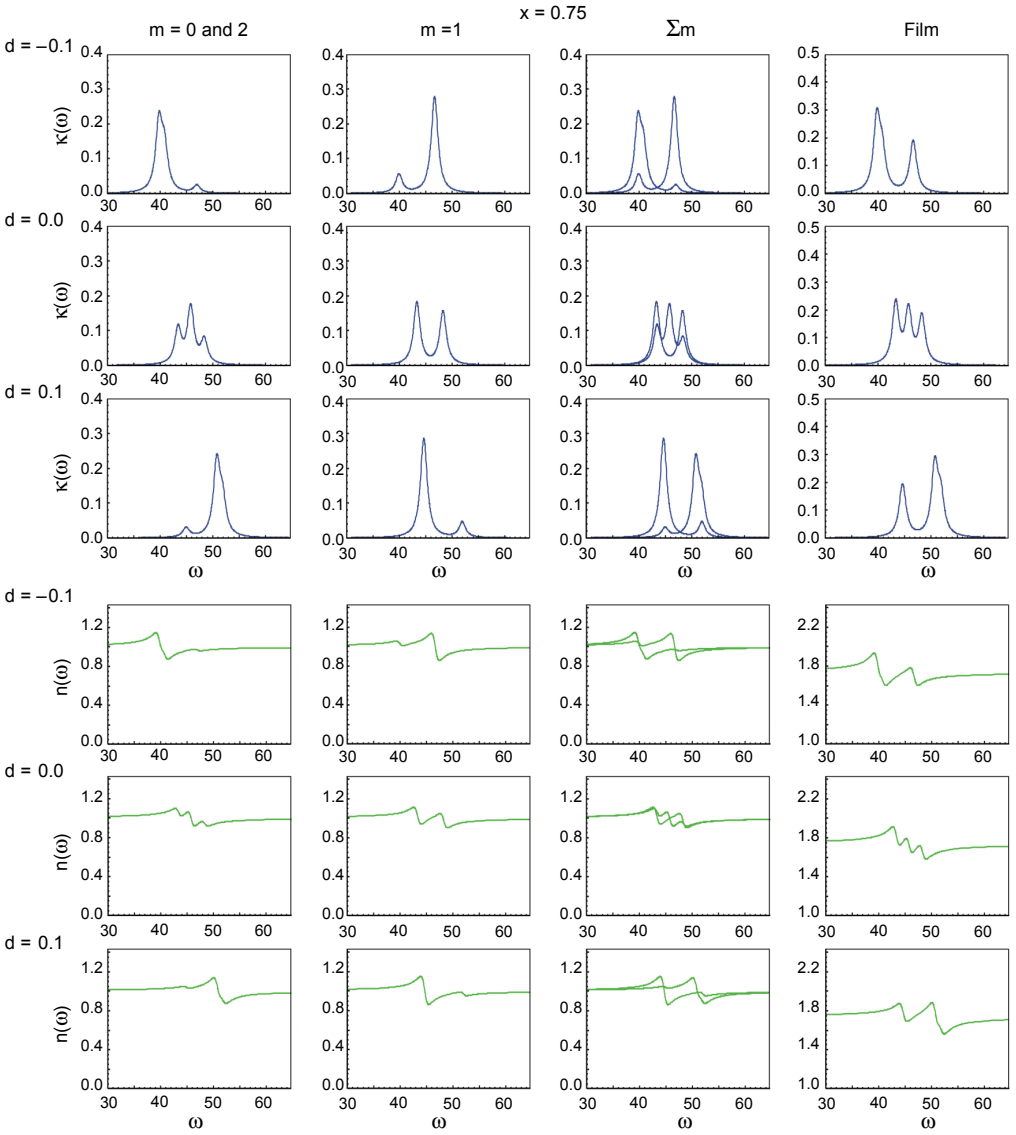

Fig. 3. Relative dynamical absorption and refraction indices of symmetrical perturbed two-layered film (see text for explanation).

and at the end of absorption zone, and here they are discrete and do not describe wider continual zone, but quantum and very selective narrow zone change.

In the area of frequency where absorption peaks and narrow absorption zone appear, there comes the decrease in refraction indices values. The interval of decreasing frequency of refraction index and the appearance of absorption peaks are identical. For certain layers, the decrease is not a monotonous function of frequency, but there appears a certain number of extremes which is equal to the number of absorption

peaks. The same thing rules for the whole film and overlaps with the conclusions about the positions of peaks and narrow zone.

4. Conclusions

Optical, *i.e.*, absorption and refraction properties of these nanostructures demonstrate very narrow or discrete characteristics, where relative dielectric permittivity dependence on external electromagnetic field indicates the existence of discrete resonant lines, whose number is, in general, equal to the number of atomic layers in nanostructure.

Characteristic resonant peaks appear in the dependence of the absorption index of an ultrathin film on the frequency of external electro-magnetic field. The peaks' widths increase with the increase in exciton spectral weights and there is a possibility to manage film dielectric response with a suitable selection of boundaries perturbation parameters. All peaks fall into infrared region and respond to the absorption of corresponding external electromagnetic frequencies. It means that discrete and selective absorption appears. There is apparently a different distribution of these peaks with the position and number of crystallographic plains parallel to boundary surfaces of the film, and the greatest symmetry belongs to the middle (inner) crystallographic plain. Due to spatial symmetry of boundary conditions of the observed model structure of the ultrathin film, absorption peaks occur with symmetrical and mirror-symmetric distribution more prominent on plains which are more remote from the middle one.

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Consequently with space symmetry of the observed ultrathin film model, we get symmetrical situation for peaks distribution.

These results may be better explained by experimental facts regarding resonating optical/luminescence peaks in similar molecular layered nanostructures. In papers [10–12], this was evidenced in perylene chemical compounds and explained by resonating effects at specific unoccupied levels. These effects are manifested by narrow optic absorption and refraction in close infrared band. Very good agreement in resonating absorption may be attributed to and explained by the presence of boundary conditions and quantum size effects for nano-sized samples. Relative small differences in profile of absorption lines appear because we observed only electron line spectra in our work, disregarding oscillatory and rotational contributions.

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