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Defect – deformation theory of the formation of a nanoparticle ensemble with a bimodal size distribution on solids under cw laser irradiation

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***Abstract*. This paper presents a defect – deformation (DD) theory of the formation of a nanoparticle ensemble under cw laser irradiation. A formula is derived for a bimodal nanoparticle size distribution function expressed through a bimodal growth rate of laser-induced DD surface gratings.**

Keywords: *cw laser exposure, solid state, defect – deformation theory, bimodal nanoparticle ensemble.*

This communication presents defect – deformation (DD) theory of the formation of a bimodal nanoparticle ensemble under cw laser irradiation. Antipov et al. [1] compared predictions of this theory to their experimental data on the formation of a bimodal nanoparticle ensemble on PbTe film under cw laser irradiation.

Let the $z = 0$ plane coincide with a free sample surface (exposed to laser radiation) and the z axis be directed to the bulk of the medium. Laser irradiation produces mobile point defects in a surface layer of thickness h. Their concentration is $n_{\rm d}(x, y, z, t) \equiv N_{\rm d}(x, y, t)f(z)$, where $N_{\rm d}(x, y, t)$ is the defect concentration at $z = 0$; the function $f(z)$ will be defined below [see Eqn (3)]; and d = v (vacancies) or i (interstitials). The defect flux on the surface is given by

$$\boldsymbol{j}_{\rm d}(\boldsymbol{r}) = -D_{\rm d}\nabla N_{\rm d} + N_{\rm d}\frac{D_{\rm d}}{k_{\rm B}T}\theta_{\rm d}\nabla\xi_f\Big|_{z=0}.$$

Here, $\boldsymbol{r} = (x, y)$; $D_{\rm d}$ is the surface diffusion coefficient; $\nabla \equiv \boldsymbol{e}_x\partial/\partial x + \boldsymbol{e}_y\partial/\partial y$; $\boldsymbol{e}_x$ and $\boldsymbol{e}_y$ are unit vectors along the x and y axes, respectively; $\theta_{\rm d} = \Omega_{\rm d}K$ is the deformation potential of the defects; $\Omega_{\rm d}$ is the volume change upon the formation of one defect; K is the elastic modulus; $\xi_{\rm f} = \xi_{\rm f}(x, y, z, t) = {\rm div}\boldsymbol{u}_{\rm f}$ is the strain in the layer; $\boldsymbol{u}_{\rm f} = \boldsymbol{u}_{\rm f}(x, y, z, t)$ is the displacement vector in the layer; $k_{\rm B}$ is the Boltzmann constant; and T is the absolute temperature. Considering the layer as a surface film, we express the strain in the layer, $\xi_{\rm f}$, through the bending coordinate $\zeta = \zeta(x, y, t)$ (z-axis displacement of the points in the middle plane of the film):

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$$\xi_{\rm f} = -v(z - h/2)\Delta\left(1 + l^2\Delta + L^4\Delta^2\right)\zeta, \qquad (1)$$

where $v = (1 - 2\sigma_{\rm P})/(1 - \sigma_{\rm P})$; $\sigma_{\rm P}$ is Poisson's coefficient; $\Delta = \partial^2/\partial x^2 + \partial^2/\partial y^2$; and the scale parameters have the form

$$l^2 = \frac{f_1^2}{24}\frac{\sigma_{\rm P}}{1 - \sigma_{\rm P}}h^2, \quad L^4 = \frac{f_2^4}{1920}\left(\frac{\sigma_{\rm P}}{1 - \sigma_{\rm P}}\right)^2 h^4.$$

The linear, sign-alternating variation of the strain in the film with z, represented by (1), is characteristic of Lamb waves in plates [2].

The terms with $l \sim h$ and $L \sim h$ in (1) were obtained by generalising standard thin plate bending theory, which uses the Kirchhoff approximation [2] and gives only the first term on the right-hand side of (1) ($l = L = 0$). The correction factors $f_1 > 1$ and $f_2 > 1$ are treated as fitting parameters. Using the formulas for $\boldsymbol{j}_{\rm d}(\boldsymbol{r})$ and $\xi_{\rm f}$ in the continuity equation, we obtain the following equation of surface diffusion and drift:

$$\frac{\partial N_{\rm d}}{\partial t} = D_{\rm d}\Delta N_{\rm d} - \gamma_{\rm d}N_{\rm d} - \frac{vhD_{\rm d}\theta_{\rm d}}{2k_{\rm B}T}$$

$$\times{\rm div}\left[N_{\rm d}\nabla\left(\Delta\zeta + l^2\Delta^2\zeta + L^4\Delta^3\zeta\right)\right],$$

where $\gamma_{\rm d}^{-1}$ is the defect lifetime. Taking into account the dependence of the surface defect diffusion coefficient in the drift term on surface strain,

$$D_{\rm d} = D_{\rm d}^0\exp[-(E_{\rm d} - \theta_{\rm ad}\xi_f)/k_{\rm B}T]$$

$$\approx D_{\rm d0}[1 + (\theta_{\rm ad}\xi_f/k_{\rm B}T)] \approx D_{\rm d0}[1 + (vh\theta_{\rm ad}/2k_{\rm B}T)\Delta\zeta],$$

where $D_{\rm d0}$ is the diffusion coefficient with an initial activation energy $E_{\rm d}$, and $\theta_{\rm ad} > 0$ is the activation deformation potential, we obtain the nonlinear equation

$$\frac{\partial N_{\rm d}}{\partial t} = D_{\rm d0}\Delta N_{\rm d} - \gamma_{\rm d}N_{\rm d} - \frac{vhD_{\rm d0}\theta_{\rm d}}{2k_{\rm B}T}$$

$$\times{\rm div}\left[N_{\rm d}\nabla\left(\Delta\zeta + l^2\Delta^2\zeta + L^4\Delta^3\zeta\right)\right]$$

$$-\frac{v^2h^2D_{\rm d0}\theta_{\rm d}\theta_{\rm ad}}{4(k_{\rm B}T)^2}\Delta\zeta{\rm div}\left[N_{\rm d}\nabla\left(\Delta\zeta + l^2\Delta^2\zeta + L^4\Delta^3\zeta\right)\right]. \qquad (2)$$

The equation for ζ can be obtained by generalising the equation of thin plate bending [2]:

$$\frac{\partial^2\zeta}{\partial t^2} + l_0^2 c^2 \Delta^2 \zeta - \frac{\sigma_{||}}{\rho_f}\Delta\zeta$$

$$= \frac{\sigma_\perp}{\rho_f h} - \sum_d \left[\frac{\theta_d}{\rho_f h}\int_0^h \frac{\partial n_d}{\partial z} dz + \frac{v\theta_d}{\rho_f h}\int_0^h \left(z - \frac{h}{2}\right)\Delta n_d dz \right]. \quad (3)$$

Here, $c^2 = E_f/\rho_f(1-\sigma_P^2)$; $l_0^2 = h^2/12$; ρ_f and E_f are, respectively, the density and Young's modulus of the film; $\sigma_{||}$ is the tangential stress in the defect-enriched film; and $\sigma_\perp$ is the normal stress acting on the film from the substrate. Since $h < \Lambda$, where Λ is a characteristic lateral length scale for the forming DD surface structure, the defect density n_d rapidly adjusts to the z-axis strain distribution:

$$n_d(x,y,z,t) = \frac{2}{h}\left(\frac{h}{2} - z\right) N_d(x,y,t).$$

Surface film bending gives rise to a displacement of the medium in the substrate, $\boldsymbol{u} = \boldsymbol{u}(x,y,z,t)$, which satisfies the equation $\partial^2\boldsymbol{u}/\partial t^2 = c_t^2\Delta\boldsymbol{u} + (c_l^2 - c_t^2)\ \times\mathrm{grad}\,\mathrm{div}\boldsymbol{u}$, where c_l and c_t are, respectively, the longitudinal and transverse sound velocities in the substrate. Let us establish three boundary conditions at the film-substrate interface. The z-axis displacement is continuous, that is, $u_z(z=h) = \zeta$. The normal stress in the substrate at the interface determines the normal stress in the film, $\sigma_\perp(x,y)$:

$$\left[\frac{\partial u_z}{\partial z} + (1-2\beta_s)\left(\frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y}\right)\right]_{z=h} = \frac{\sigma_\perp(x,y)}{\rho_s c_l^2},$$

where ρ_s is the density of the medium in the substrate and $\beta_s = c_t^2/c_l^2$. There is no tangential stress:

$$\left[\frac{\partial u_{x_\alpha}}{\partial z} + \frac{\partial u_z}{\partial u_{x_\alpha}}\right)\Bigg]_{z=h} = 0; \quad x_\alpha = \{x,y\}.$$

Using the Fourier expansions

$$N_d(\boldsymbol{r},t) = \sum_{\boldsymbol{q}} N_d(\boldsymbol{q})\exp(i\boldsymbol{q}\boldsymbol{r} + \lambda_q t),$$

$$\zeta(\boldsymbol{r},t) = \sum_{\boldsymbol{q}} \zeta_{\boldsymbol{q}}\exp(i\boldsymbol{q}\boldsymbol{r} + \lambda_q t), \quad (4)$$

$$\sigma_\perp = \sigma_\perp(\boldsymbol{r},t) = \sum_{\boldsymbol{q}} \sigma_\perp(q)\exp(i\boldsymbol{q}\boldsymbol{r} + \lambda_q t),$$

the displacement vector in the substrate can be written as a superposition of quasi-Rayleigh waves, which are a quasi-static (zero frequency, $\omega_q = 0$) analogue of a Rayleigh dynamic surface wave [2]:

$$u_{lx_\alpha} = -i\sum_q q_{x_\alpha} R(q)\exp(i\boldsymbol{q}\boldsymbol{r} - k_l z + \lambda_q t),$$

$$u_{lz} = \sum_q k_l R(q)\exp(i\boldsymbol{q}\boldsymbol{r} - k_l z + \lambda_q t),$$

$$u_{tz_\alpha} = -i\sum_q \frac{q_{x_\alpha}}{q} k_t Q(t)\exp(i\boldsymbol{q}\boldsymbol{r} - k_t z + \lambda_q t), \quad (5)$$

$$u_{tz} = \sum_q qQ(t)\exp(i\boldsymbol{q}\boldsymbol{r} - k_t z + \lambda_q t).$$

Here, $k_{l,t}^2 = q^2 + \lambda_q{}^2/c_{l,t}$, $R(q)$ and $Q(t)$ are Fourier amplitudes.

Formulas (4) define a superpositional DD structure composed of coupled two-dimensional (2D) surface DD gratings of defect density and surface relief. Each DD grating with a wave vector $\boldsymbol{q}$ can be thought of as a quasi-static Lamb wave with a wavelength $\Lambda = 2\pi/q$, which is maintained by a self-consistent point defect distribution. Each quasi-Lamb wave $\boldsymbol{q}$ is related to a quasi-Rayleigh wave with the same wave vector $\boldsymbol{q}$ from superposition (5).

Solving the boundary value problem in a Fourier representation with the constraint $\lambda_q^2/c_{l,t}^2 q^2 \ll 1$, we find $\sigma_\perp(q) = \zeta_q 2q(\beta_s - 1)\rho_s c_t^2$. Using this relation in the equation for ζ, taking into account that $\partial^2\zeta/\partial t^2 = 0$ in the adiabatic approximation and calculating the integrals, we obtain a linear relation between the bending coordinate and surface defect density: $\zeta_{\boldsymbol{q}}(t) = \sum_d \eta_d(\boldsymbol{q})N_{\boldsymbol{q}}(t)$, where the DD coupling coefficient is given by

$$\eta_d(\boldsymbol{q}) = -\frac{2\theta_d(1 + vl_0{}^2q^2)}{\sigma_{||}hq^2[1 + l_{||}q^2 + 2(1-\beta_s)\mu_s/\sigma_{||}qh]}.$$

Here, we use the following expression for the shear modulus: $\mu_s = \rho_s c_t^2$. The characteristic scale parameter is $l_{||} = h(\rho_f c^2/12\sigma_{||})^{1/2} \sim h$. For simplicity, in what follows we will take into account the contribution of only one defect species.

Fourier transforming Eqn (2) and using expressions for $\zeta_q(t)$, we obtain an equation for the Fourier amplitude of surface defect density, $N_q \equiv N_d(q,t)$ with allowance for the DD wave self-action effect:

$$\frac{\partial N_{\boldsymbol{q}}}{\partial t} = \lambda_q N_{\boldsymbol{q}} + D_{d0}\frac{1}{N_{cr}}$$

$$\times \sum_{\boldsymbol{q}_1 \neq \boldsymbol{q}} (\boldsymbol{q}\boldsymbol{q}_1)\frac{(1 + vl_0^2 q_1^2)}{[1 + l_{||}^2 q_1^2 + 2(1-\beta_s)\mu_s/\sigma_{||}hq_1]} N_{\boldsymbol{q}_1} N_{\boldsymbol{q}-\boldsymbol{q}_1} \quad (6)$$

$$-D_{d0}\frac{2}{N_{cr}^2}\frac{\theta_{ad}}{\theta_d}\frac{q^2(1 + vl_0^2q^2)^2}{[1 + l_{||}^2q^2 + 2(1-\beta_s)\mu_s/\sigma_{||}hq]^2}|N_{\boldsymbol{q}}|^2 N_{\boldsymbol{q}}.$$

Here, $l = L = 0$ in the nonlinear terms, and the growth rate is given by

$$\lambda_q = -\gamma_d + D_{d0}q^2$$

$$\times \left[\varepsilon\frac{(1 + vl_0^2q^2)(1 - l^2q^2 + L_d^4q^4)}{1 + l_{||}^2q^2 + 2(1-\beta_s)\mu_s/\sigma_{||}hq}\Theta(q_c - q) - 1\right], \quad (7)$$

where $\varepsilon = N_{d0}/N_{cr}$, $N_{d0} = N_d(q=0)$ is a control parameter, with $N_{cr} = \sigma_{||}k_B T/v\theta_d^2$ (critical defect density). Because (7) contains a Θ function [$\Theta(q_c - q) = 0$ for $q > q_c$ and $\Theta(q_c - q) = 1$ for $q < q_c$], λ_q is zero for the limiting bending mode with $q = q_c = \pi/h$. When the defect density exceeds the critical level ($\varepsilon > 1$), the growth rate has a maximum at $\Lambda = \Lambda_m = 2\pi/q_m = 2\pi h(\rho_f c^2/12\sigma_{||})^{1/2}[(N_{d0}/N_{cr})^{1/2} - 1]^{-1/2}$ in a long-wavelength region (L peak). At high values of the control parameter ε, a second, shorter wavelength maximum (S peak) emerges at $\Lambda = \Lambda_c = 2\pi/q_c = 2h$.

Figure 1 shows the bimodal growth rate of a DD grating, $\lambda_q = \lambda_q(\Lambda)$, where $\Lambda = 2\pi/q$, calculated by formula (7) with $\varepsilon = 57$ and $h = 0.5\times10^{-5}$ cm, $\sigma_P = 0.35$, $\sigma_{||} = 6\times10^9$ erg cm^{-3}, $D_{d0} = 10^{-8}$ cm^2 s^{-1}, $\rho_f c^2 = 10^{12}$ erg cm^{-3}, $\mu_s = 8\times10^{10}$ erg cm^{-3}, $\beta_s = 0.8$, $\gamma_d = D_d R^{-2}$, and $R = 5\times10^{-6}$ cm. The scale parameters, $l = 7.489\times10^{-7}$ cm and

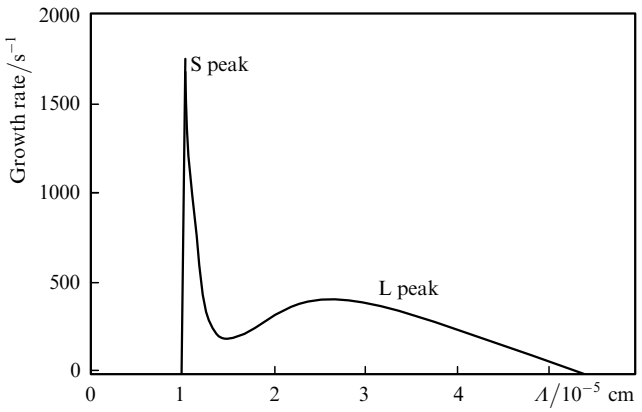

Figure 1. Bimodal growth rate of a DD grating as a function of its period. The growth rate was calculated by formula (7) with $\varepsilon = 57$ and the values of the other parameters specified in text. The cutoff grating period is $\Lambda = 2h$, which corresponds to the limiting bending mode with $q = q_c = \pi/h$.

$L = 1.885 \times 10^{-6}$ cm, were calculated with fitting parameters $f_1 = 1$ and $f_2 = 3.4$. At $k_B T = 0.05$ eV and $\theta_d = 10^2$ eV, the critical defect density is $N_{cr} = 4 \times 10^{16}$ cm^{-3}.

According to numerical simulations of the nonlinear regime of the DD surface instability [3], three-wave interactions of DD waves on an isotropic surface lead to the formation and angular ordering of equilateral triangles (triads) of DD grating wave vectors. The triads are formed by wave vectors related to both the longer (L) and shorter (S) wavelength peaks (Fig. 1). Similar triads are formed on a (111) crystalline surface (see Ref. [1]). Each DD triad from superposition (4) with a period $\Lambda = 2\pi/q$ and wave number q within the S or L peak will be thought of as a 2D hexagonal supercrystal whose regular sites are occupied by nanoparticle nuclei (accumulations of interstitials), by analogy with atoms that occupy regular lattice sites in a crystal (Fig. 2). The surface concentration of 'supervacancies' (vacant sites), n_{sv}, in a hexagonal supercrystal with a lattice parameter Λ is given by a standard thermodynamic formula. Therefore, the nanoparticle (nanodot) size distribution function can be written in the form

$$n_{dot}(\Lambda) = \alpha\Lambda^{-2} - n_{sv}(\Lambda) = \alpha\Lambda^{-2} \times [1 - \exp(-E_{sv}(\Lambda)/k_B T)] \approx \alpha\Lambda^{-2}(E_{sv}(\Lambda)/k_B T), \quad (8)$$

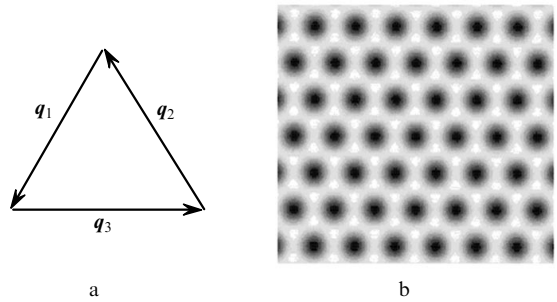

Figure 2. (a) Spatial match between three DD gratings with wave vectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$ and $\boldsymbol{q}_3$ ($|\boldsymbol{q}_1| = |\boldsymbol{q}_2| = |\boldsymbol{q}_3| = q$) (triad) and (b) superpositional hexagonal DD structure defined by $\cos \boldsymbol{q}_1\boldsymbol{r} + \cos \boldsymbol{q}_2\boldsymbol{r} + \cos \boldsymbol{q}_3\boldsymbol{r}$: a 2D supercrystal corresponding to a triad with a wave number q. The dark areas are zones where interstitials (nanoparticle nuclei) are concentrated.

where E_{sv} is the binding energy of a nucleus in a regular superlattice site (energy of supervacancy formation); $\alpha\Lambda^{-2}$ is the surface density of cells in the superlattice; and α is a proportionality coefficient which takes into account the shape of a regular hexagonal cell. To find E_{sv}, we use the following expression for the DD interaction energy in a bent layer of thickness h:

$$W = -\int_S d\boldsymbol{r} \int_0^h dz\, \theta_d n_{d1}(\boldsymbol{r}, z)\xi(\boldsymbol{r}, z) = -S\int_0^h dz \sum_{\boldsymbol{q}} \theta_d n_{dq}(z)\xi_{-q}(z),$$

where S is the surface area of the layer. The energy of supervacancy formation on a regular site of a hexagonal supercrystal (Fig. 2) with a period $\Lambda = 2\pi/q$ then takes the form

$$E_{sv}(q) = -3\frac{\Lambda^2}{S\alpha} S\int_0^h dz \theta_d n_d(q, z)\xi_{-q}(z) = \frac{\Lambda^2}{\alpha}\frac{h v \theta_d^2}{\sigma_{||}} \times \frac{1 + v l_0^2 q^2}{[1 + l_{||}^2 q^2 + 2(1 - \beta_s)\mu_s/(\sigma_{||} q h)]} |N_d(q)|^2.$$

Using this relation and (8), we find the size distribution of nanoparticle nuclei:

$$n_{dot}(q) = \frac{h}{N_{cr}} \times \frac{1 + v l_0^2 q^2}{[1 + l_{||}^2 q^2 + 2(1 - \beta_s)\mu_s/(\sigma_{||} q h)]} |N_d(q)|^2, \quad (9)$$

where the spectral function of defect density fluctuations, $|N_d(q)|^2$, can be found by solving the steady-state ($\partial N_q/\partial t = 0$) equation (6) with the quadratic term (which maintains a constant number of defects in the triad) neglected:

$$|N_{\boldsymbol{q}}|^2 = N_{cr}^2 \frac{\lambda_q}{D_{d0} q^2}\frac{\theta_d}{2\theta_{ad}} \times \frac{[1 + l_{||}^2 q^2 + 2(1 - \beta_s)\mu_s/(\sigma_{||} h q)]^2}{(1 + v l_0^2 q^2)^2}. \quad (10)$$

The nucleus size, $\Lambda = 2\pi/q$, determines the nanoparticle size in the laser-induced ensemble. Substituting (10) into (9), we obtain the steady-state nanoparticle size distribution function in the form

$$n_{dot}(q) = C\left\{\frac{[1 + l_{||}^2 q^2 + 2(1 - \beta_s)\mu_s/(\sigma_{||} h q)]}{(1 + v l_0^2 q^2)}\right\}\left(\frac{\lambda_q}{D_{d0} q^2}\right), \quad (11)$$

where $C = N_{cr} h \theta_d / 2\theta_{ad}$ and the growth rate λ_q is given by (7). The wave number q is related to the nanoparticle size Λ by $q = 2\pi/\Lambda$. Since λ_q is bimodal at sufficiently high ε values (Fig. 1), the size distribution function (11) is also bimodal at such ε values (Fig. 3). As shown by Antipov et al. [1], the distribution function (11), shown in Fig. 3, adequately represents the experimentally determined bimodal size distribution for a nanoparticle ensemble produced

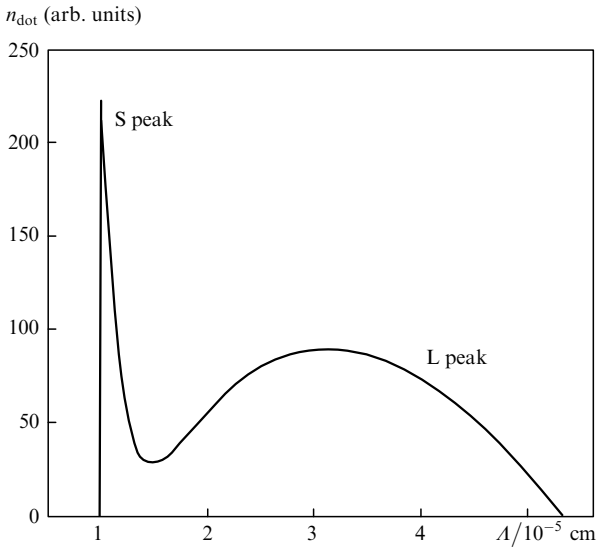

Figure 3. Normalised bimodal nanoparticle size distribution function calculated with the parameters used in growth rate calculation (Fig. 1). For comparison with the experimentally determined normalised size distribution in Ref. [1], C in (11) is treated as a normalisation factor and is taken to be 5.

by cw laser irradiation of a PbTe semiconductor film [1, Fig. 5].

In conclusion, note that this work is the first to examine a bimodal growth rate of DD instability (Fig. 1), which results in a bimodal nanoparticle size distribution function (Fig. 3). This is due to the fact that the present layer bending strain calculation ξ_f [Eqn (1)] has gone beyond the commonly used Kirchhoff approximation [2]. In the Kirchhoff approximation, only the first term on the right-hand side of (1) is retained ($l = L = 0$). As a result, both the growth rate (Fig. 1) and nanoparticle size distribution function (Fig. 3) have only one, longer wavelength (L) maximum.

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