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Dependence of the anisotropy parameter of drag thermo-emf on the impurity concentration in the *n*-type germanium and silicon crystals

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Abstract. Features of the concentration dependences of the anisotropy parameter of thermo-emf of electron-phonon drag *M* in germanium and silicon crystals of *n*-type conductivity were found in a wide range of charge carrier concentrations. Insensitivity of the anisotropy parameter *M* to the presence of impurities in the germanium crystals up to the concentrations of ~ 10^{15} cm^{-3} was found, whereas in silicon with increasing the doping level the monotonic decrease in this parameter was observed. The significantly lower absolute values of the parameter *M* were obtained for the silicon crystals as compared with the corresponding values of this parameter for the germanium ones. The physical nature of the identified effects was explained.

Keywords: germanium, silicon, thermoelectromotive force (thermo-emf), tenso-thermo-emf, anisotropy parameter of thermo-emf, anisotropy parameter of mobility, charge carrier concentration.

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1. Introduction

Investigations of semiconductors under extreme conditions (in the strong quantizing magnetic and electric fields, at very low temperatures, at high pressures) make it possible to obtain the important information concerning their properties and characteristics [1]. The studies under conditions of the strong uniaxial deformation are of particular interest, since these experiments allow changing (relatively easy and in a wide range) the essential characteristics of semiconductor crystals [2-5]. For example, the many-valley *n*-Ge and *n*-Si crystals can be converted into one- and two-valley states by application of uniaxial compression, which can provide a real opportunity to measure such characteristics as the deformation potentials, the anisotropy parameters, *etc* [6-10].

However, it should be noted that under study of semiconductors in conditions of strong deformation the galvanomagnetic measurements became widespread [11-13], while the experimental works devoted to the study of thermoelectric and thermomagnetic phenomena under these conditions appear quite rare [14, 15]. The studies, especially at low temperatures in the region of drag effect of electrons by phonons, can provide information not only concerning the structure of the energy spectrum of carriers and the character of their scattering but also about the phonon-phonon interaction mechanism. In addition, these studies will make it possible to determine a number of important characteristics and parameters of crystals, namely: the anisotropy parameter of thermo-emf, the effective masses of charge carriers, the impurity concentration, the relaxation time of the phonon-phonon interaction and others.

The anisotropy parameter of drag thermo-emf of electrons by phonons

$$M = \alpha_{\parallel}^{ph} \Big/ \alpha_{\perp}^{ph} \qquad (1)$$

is one of the most important parameters of the kinetics theory for electronic processes in the many-valley semiconductors, along with the anisotropy parameter of mobility $K = \mu_{\perp}/\mu_{\parallel}$ [14, 16, 17]. Here, $\alpha_{\parallel}^{ph}$, $\alpha_{\perp}^{ph}$ are the phonon components of drag thermo-emf along and across the long axis of isoenergetic ellipsoid, respectively; $\mu_{\parallel}$, $\mu_{\perp}$ are the mobilities of charge carriers along and across the long axis of this ellipsoid, respectively.

In contrast to the values of the anisotropy parameter of mobility K that describes the electronic subsystem, the anisotropy parameter of thermo-emf M characterizes the phonon subsystem in a certain way. This parameter is found from the thermoelectric measurements, whereas the parameter K is found from the experimental data on tensoresistance.

The value of parameter M for *n*-Ge was found by various authors and even with using of the different techniques, but mainly for the conditions of phonon scattering (see, *e.g.*, [18, 19]). In consideration of differences in the values of M, which are available in the individual papers, we can assume that the most probable value of this parameter is equal to 9 ± 1 for the sufficiently pure *n*-Ge crystals. With account that germanium and silicon doped with impurities over a wide range of concentrations are used in the electronic engineering, it is also necessary to know the value of parameter M in the mixed scattering region, when we calculate the thermoelectric and thermomagnetic effects in these crystals by using the anisotropic scattering theory.

The aim of this study was to investigate the anisotropy parameter of drag thermo-emf M of electrons by phonons in germanium and silicon of *n*-type conductivity over a wide range of concentrations, which includes both mixed and predominantly phonon scattering.

2. Theoretical information

Germanium and silicon are characterized by isotropism of the kinetic coefficients in the natural (*i.e.*, mechanically relaxed) state due to cubic symmetry of these crystals. Consequently, the kinetic phenomena in these crystals (including thermo-emf) are described by the scalar quantities under the named conditions. In particular, thermo-emf coefficient (Seebeck coefficient) also is a scalar on the macrolevel (*i.e.*, on the level of crystal). The situation changes in the uniaxially elastically deformed Ge and Si crystals, and the Seebeck coefficient becomes a tensor quantity [20].

On the example of *n*-Ge many-valley semiconductor, let us consider the method for determination of the anisotropy parameter for thermo-emf in the area of electron-phonon drag by using the results of measuring the diagonal components of thermo-emf tensor.

In a general case, the experimentally measured values of the coefficient of differential thermo-emf α can be represented as a sum of the electronic (diffusion) α^{e} and phonon α^{ph} components [21]:

$$\alpha = \alpha^{e} + \alpha^{ph}. \qquad (2)$$

Taking into account that, in the elastically deformed along the crystallographic direction [111] *n*-Ge, the thermo-emf can be represented as a second-rank tensor in the laboratory system of coordinates (associated with the axes of the isoenergetic ellipsoid, located on the deformation axis) [17]

$$\hat{\alpha} = \begin{vmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{22} & 0 \\ 0 & 0 & \alpha_{33} \end{vmatrix}, \qquad (3)$$

where $\alpha_{11} = \alpha_{22}$ and α_{33} are the diagonal terms of the thermo-emf tensor, then $\alpha_{11} = \alpha_{11}^{e} + \alpha_{11}^{ph}$ and $\alpha_{33} = \alpha_{33}^{e} + \alpha_{33}^{ph}$.

It is noted that under the uniaxial elastic deformation of *n*-Ge along [111] the energy minimum, oriented in this direction, is shifted down along the energy scale, while the remaining three minima are shifted upwards. Let us denote the concentration of charge carriers in the minimum, which is lowered, by N_1 and the concentration of charge carriers in any from three minima, which is raised, by N_2.

It can be shown [22] that, at the arbitrary in magnitude mechanical load X on the *n*-Ge crystal, the following expression will take place under the condition of $\vec{X} \parallel \vec{J} \parallel [111]$ (J – current):

$$\alpha_{33} - \alpha_{33}^{e} = \alpha_{\perp}^{ph} \cdot \frac{M + \gamma \dfrac{8K + M}{3}}{1 + \gamma \dfrac{8K + 1}{3}}, \qquad (4)$$

where $\gamma = \dfrac{N_2}{N_1} = e^{-\frac{4}{9}\frac{\Xi_u S_{44}}{kT} X} = e^{-0.120 \frac{X}{T}}$ is the ratio of the carrier concentrations in ellipsoids for arbitrary values of the mechanical stress X and temperature T; Ξ_u is the constant of the shear deformation potential; S_{44} is the compliance coefficient (for *n*-Ge $S_{44} = 1.46 \cdot 10^{-11}$ Pa^{-1}). The anisotropy parameter of electron mobility K within the separate isoenergetic ellipsoid is given by the expression

$$K = \frac{\mu_\perp}{\mu_\parallel} = \frac{3}{2}\frac{\rho_\infty}{\rho_0} - \frac{1}{2}, \qquad (5)$$

where ρ_0 and $\rho_\infty = \lim\limits_{X\to\infty} \rho(X)$ are the resistivity of undeformed (at $X = 0$) and uniaxially elastically deformed (at $X \to \infty$) crystal, respectively [ρ_∞ corresponds to the saturation region of the function $\rho = \rho(X)$].

Eq. (2) shows that the phonon components of thermo-emf without pressure ($X = 0$) α_0^{ph} and in saturation ($X \to \infty$) α_∞^{ph} are equal to the experimentally measured values of thermo-emf (α_0 and α_∞) without electronic component (α_4^e and α_1^e – for the case of the non-deformed and strongly deformed crystal, respectively):

$$\alpha_0^{ph} = \alpha_0 - \alpha_4^e,$$

$$\alpha_\infty^{ph} = \alpha_\infty - \alpha_1^e \equiv \alpha_\parallel^{ph}. \qquad (6)$$

The electronic (diffusion) component of thermo-emf α_N^e can be determined by the Pisarenko formula [23]:

$$\alpha_N^e = \frac{k}{e}\left[2 + \ln\frac{2\left(2\pi m^* kT\right)^{3/2}}{n_0 h^3}\right], \qquad (7)$$

where n_0 is the charge carrier concentration; e – electron charge; k – Boltzmann constant; T – temperature; h – Planck constant; $m^* = N^{3/2}\sqrt[3]{m_\parallel m_\perp^2}$ – effective mass of the density of states; N – number of the isoenergetic ellipsoids, particularly, for *n*-Ge $N = \begin{cases} 4 & \text{at } X = 0, \\ 1 & \text{at } X \geq 0.6\ \text{GPa and } T = 77\ \text{K} \end{cases}$. Since the electronic component of thermo-emf α^e is essentially independent of the mechanical load X, then $\alpha_4^e \approx \alpha_1^e \approx \alpha^e$.

Using the directly measured values of α_∞, one can obtain, according to Eq. (6), the value of the longitudinal phonon component $\alpha_\parallel^{ph} = \alpha_\infty - \alpha_1^e$. And using Eq. (1), one can find the transverse phonon component:

$$\alpha_\perp^{ph} = \alpha_\parallel^{ph} \big/ M. \qquad (8)$$

It follows from Eqs (6) and (8) that

$$\alpha_\infty - \alpha^e = \alpha_\parallel^{ph} = \alpha_\perp^{ph} \cdot M. \qquad (9)$$

In the absence of uniaxial mechanical load ($X = 0$) on the investigated sample, one can obtain from Eq. (4) (if removing the indices 33) the following expression:

$$\alpha_0^{ph} = \alpha_0 - \alpha^e = \alpha_\perp^{ph} \cdot \frac{2K + M}{2K + 1}. \qquad (10)$$

Equation (10) binds (through the anisotropy parameters K and M) the phonon thermo-emf of the whole crystal (at $X = 0$) with one of the components of phonon thermo-emf in a single isoenergetic ellipsoid $\alpha_\perp^{ph}$.

Thus, we have a system of two equations (9) and (10) with two unknown quantities ($\alpha_\perp^{ph}$ and M). Excluding the value of $\alpha_\perp^{ph}$ from this system, the expression for determining the anisotropy parameter of thermo-emf in germanium crystals can be obtained:

$$M = \frac{2K}{(2K+1)\dfrac{\alpha_0 - \alpha^e}{\alpha_\infty - \alpha^e} - 1} = \frac{2K}{(2K+1)\dfrac{\alpha_0^{ph}}{\alpha_\infty^{ph}} - 1}. \qquad (11)$$

Usage of a system of two equations (9) and (10) when transferring to the study of *n*-Si (instead of *n*-Ge) is related with deformation of this crystal in the [100] direction (at conditions $\vec{X} \parallel \vec{J} \parallel [100]$) instead of the experimental conditions $\vec{X} \parallel \vec{J} \parallel [111]$ that are used in the study of *n*-Ge.

3. Experimental results and discussion

Measurements of the thermo-emf and tenso-thermo-emf were carried out at the temperature of 85 K on the single *n*-Ge and *n*-Si crystals within the range of the concentrations $1.9\cdot10^{12}\ldots4.6\cdot10^{17}$ cm^{-3}, and measurements of the Hall parameters and tensoresistance were carried out at $T = 77$ K. At the beginning, the resistivity ρ_0 and thermo-emf α_0 were measured without pressure, then the *n*-Ge and *n*-Si samples were converted into the one- and two-valley state, respectively, and the values of ρ_∞ and α_∞ were measured. The mechanical load of $X = 0.8$ GPa was applied to the investigated samples (in order to convert them into the one- and two-valley state): in conditions of $\vec{X} \parallel \vec{J}$, $\nabla T \parallel [111]$ for *n*-Ge; at $\vec{X} \parallel \vec{J}$, $\nabla T \parallel [100]$ for *n*-Si.

The typical view of the tensoresistance ρ_X/ρ_0 and tenso-thermo-emf α_X/α_0 dependences on the mechanical load X is presented in Fig. 1 for one of the studied silicon samples.

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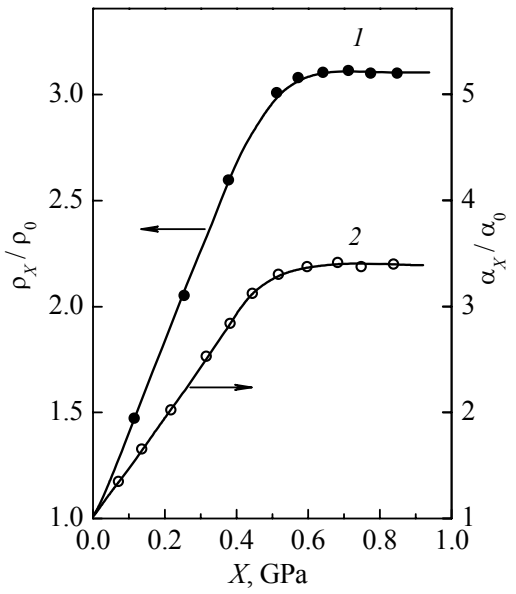

Fig. 1. Typical view of the dependences of tensoresistance ρ_X/ρ_0 (*1*) and tenso-thermo-emf α_X/α_0 (*2*) on the mechanical load X for *n*-Si.

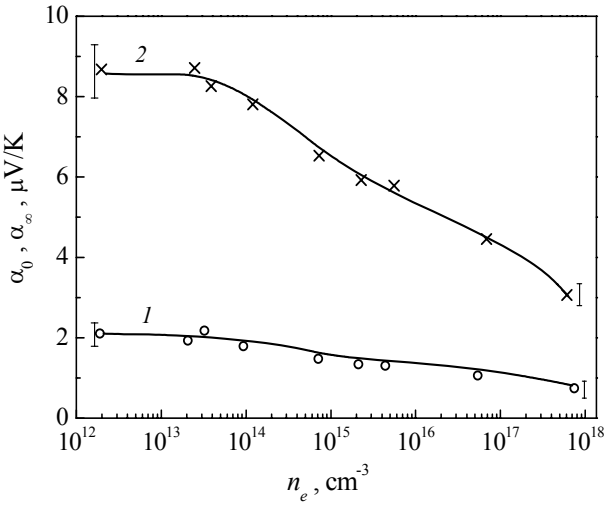

Fig. 2. Concentration dependence of thermo-emf (at T = 85 K) for *n*-Ge crystals: *1* – undeformed (four-valley); *2* – deformed (one-valley) in conditions of X = 0.8 GPa, $\vec{X} \parallel \vec{J}$, $\nabla T \parallel [111]$.

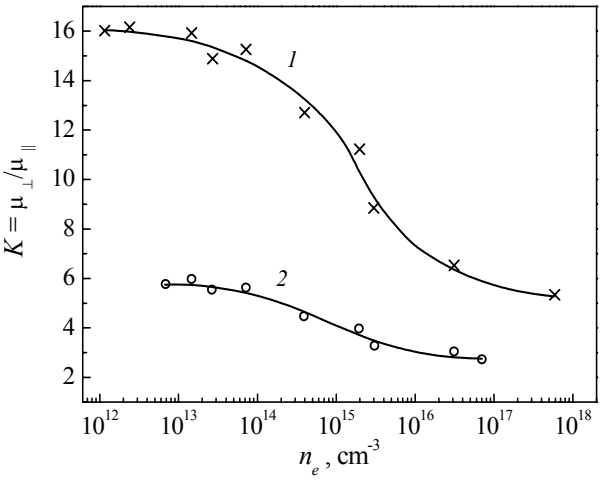

Fig. 3. Concentration dependence (at T = 77 K) of the anisotropy parameter of mobility $K = \mu_\perp/\mu_\parallel$ in crystals: *1* – *n*-Ge; *2* – *n*-Si.

In order to not significantly affect on the average sample temperature, which is given by the ambient temperature, the temperature gradient on the sample must be set, possibly, by the insignificant temperature drop $\Delta T = T_2 - T_1$. This temperature drop in the working conditions will not exceed of 5 degree/cm. In these experiments, the one-dimensionality of the heat flow must be provided, reducing the lateral heat loss from the studied samples to the possible minimum and supporting the high-quality lateral thermal insulation.

Fig. 2 shows the experimentally determined concentration dependences of the α_0 and α_∞ values for *n*-Ge samples. Fig. 3 presents the values of the anisotropy parameter of mobility K for the silicon and germanium crystals obtained using the measurement results of tensoresistance in the saturation region (ρ_∞) and the magnitude of this resistance without the mechanical load (ρ_0) as well as Eq. (5). Thermo-emf in the undeformed (α_0) and deformed (α_∞) states, the value of the parameter K and the value of the electronic component of thermo-emf (α^e) calculated using Eq. (7) made it possible to calculate for each of the samples of silicon and germanium the value of the anisotropy parameter of drag thermo-emf $M = \alpha_\parallel^{ph}/\alpha_\perp^{ph} = f(n_e)$ by Eq. (11) under the assumption that $n_e \equiv N_d$ (Fig. 4).

As it follows from Fig. 4, the value of the parameter M for *n*-Ge (curve *1*) remains constant [unlike that in *n*-Si (Fig. 4, curve *2*)] in the fairly wide concentration range ($1.9\cdot10^{12} \le n_e \le 10^{15}$ cm^{-3}) and equals approximately 9.8, which agrees well with the known data for this parameter in the area of the predominant phonon scattering. As opposed to the anisotropy parameter of mobility K, which is formed by combination of the electron scattering mechanisms related with crystal lattice vibrations and impurity centers, the phonon component of thermo-emf (more precisely, its anisotropy, *i.e.*, the ratio $M = \alpha_\parallel^{ph}/\alpha_\perp^{ph}$) is almost independent from the concentration $n_e \equiv N_d$ [in any case, in the investigated limits $1.9\cdot10^{12}\ldots10^{15}$ cm^{-3}] and is completely determined by the vibrations of the atoms in the lattice sites.

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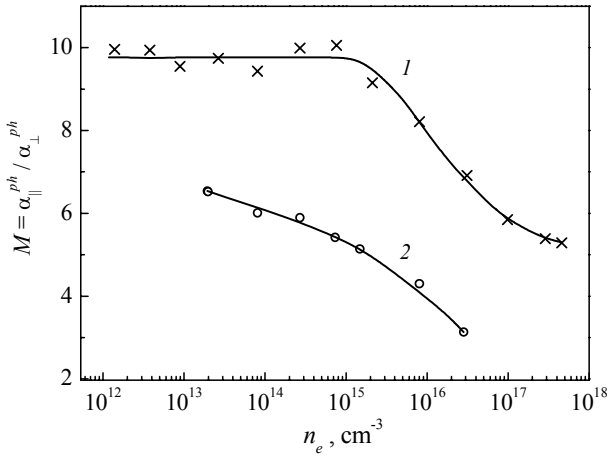

Fig. 4. Concentration dependence (at $T = 85$ K) of the anisotropy parameter of drag thermo-emf $M = \alpha_{\parallel}^{ph} / \alpha_{\perp}^{ph}$ in crystals: *1* – *n*-Ge; *2* – *n*-Si.

The further growth of the doping level ($n_e \equiv N_d \geq 10^{15}$ cm^{-3}) in germanium crystals leads to a sharp decrease of the parameter *M*. The revealed effect is associated with an increase in the efficiency of the scattering of both electrons (which are captured by the phonons) on the impurity ions, and phonons on the conduction electrons in the field of ionized impurity. Insensitivity of the parameter *M* to the presence of impurities in *n*-Ge (within the concentration range 10^{12}…10^{15} cm^{-3}) is probably caused by the features of the phonon subsystem in this material.

It is necessary to draw attention to the different character of the effect of increasing the dopant concentration on the electron and phonon subsystems in *n*-Ge and *n*-Si. While changes in the anisotropy parameter of mobility *K* in *n*-Ge and *n*-Si with increase of the concentration are qualitatively similar (Fig. 3), the changes in the anisotropy parameter of drag thermo-emf *M* differ significantly (Fig. 4). In *n*-Si crystals, both the parameter *M*, and the parameter *K* are decreased within the range of charge carrier concentrations $10^{12} \leq n_e \leq 2 \cdot 10^{15}$ cm^{-3} with an increase of the contribution of impurity scattering, whereas in *n*-Ge crystals only the parameter *K* is reduced, while the parameter *M* is almost constant.

In addition, the data comparison for the *n*-Ge and *n*-Si samples, presented in Figs 3 and 4, indicates the much higher (in absolute magnitude) values of the *M* and *K* parameters, which are characteristic for the *n*-Ge single crystals as compared with the corresponding values for *n*-Si. In the first place, this is related with the higher anisotropy of the effective mass of the charge carriers in *n*-Ge, than in *n*-Si ($m_{\parallel} / m_{\perp} = 1.58/0.082 \cong 19.3$ for *n*-Ge and $m_{\parallel} / m_{\perp} = 0.91/0.191 \cong 4.75$ for *n*-Si), which causes the appearance of substantially different scattering conditions in the *n*-Ge and *n*-Si crystals. This is also related with a significant difference in the arrangement of the isoenergetic ellipsoids relative to the crystal axes in germanium and silicon (Fig. 5).

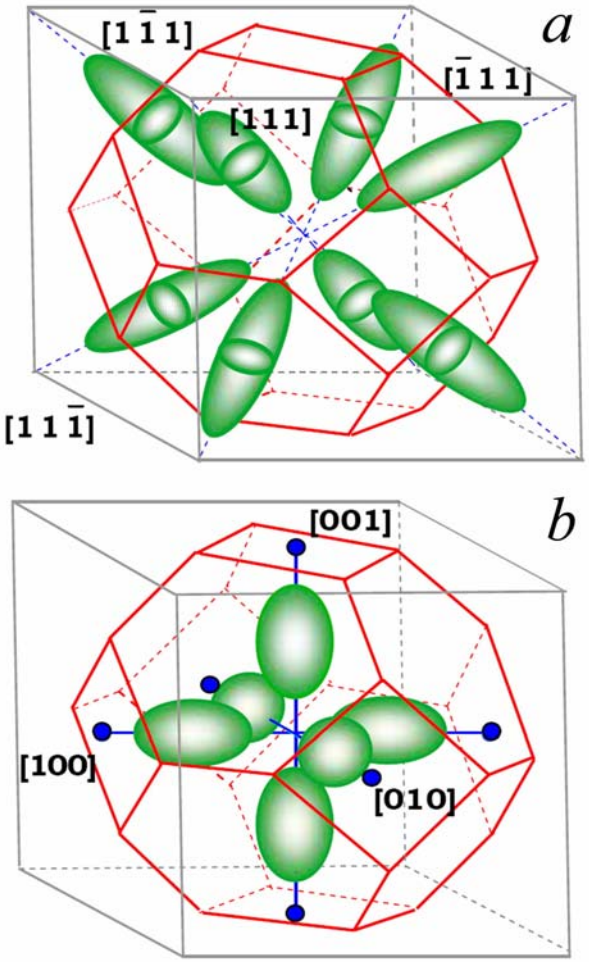

Fig. 5. Reciprocal arrangement of the isoenergetic ellipsoids in the conduction band of germanium (*a*), silicon (*b*) [24].

4. Conclusions

1. In the many-valley *n*-Ge and *n*-Si crystals, the relationship of the thermo-emf in undeformed (α_0) and strongly deformed (α_∞) states with the transverse phonon component ($\alpha_{\perp}^{ph}$) and with the anisotropy parameter of drag thermo-emf *M* was ascertained. The relationship of the drag thermo-emf in undeformed crystal (α_0) with the anisotropy parameter of mobility *K* within the individual isoenergetic ellipsoid was revealed, too.
2. It was found that the anisotropy parameter of drag thermo-emf *M* is changed monotonically in *n*-Si with an increase of the charge carrier concentration (n_e), whereas in *n*-Ge this parameter is decreased sharply for the concentrations above 10^{15} cm^{-3}.
3. It is shown that the *n*-Si single crystals are characterized by significantly smaller (in absolute magnitude) values of the anisotropy parameter *M* as compared with the corresponding values for *n*-Ge. This fact is explained by lower anisotropy of the electron effective mass and, consequently, the substantially different scattering of electrons.

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