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A Relationship between Thermal Diffusivity and Finite Deformation in Polymers[1]

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The thermal diffusivity of elastomers (i.e., rubber-like materials) can change substantially with elastic finite deformation. Initially isotropic elastomers may be thermally anisotropic when deformed. Data from several experimental studies demonstrate significant changes in the thermal conductivity or diffusivity tensor with finite deformation. Formulating the thermal diffusivity tensor and deformation in terms of the reference configuration may aid in the development of constitutive relations by use of material symmetry. Illustrated here is a relationship between the diffusivity and deformation of representative materials during uniaxial and equibiaxial deformation. Each component of the diffusivity tensor appears to be related to the deformation in the direction of the component only.

KEY WORDS: biaxial tests; constitutive equations; elastomers; thermal diffusivity; thermoelasticity; thermophysical properties.

1. INTRODUCTION

Elastomers are often subjected to substantial deformation and temperature gradients during use. The increased reliance on computer modeling of material performance, in lieu of measurements, necessitates improved constitutive relations of elastomers for a wide range of boundary conditions. Specifically, thermomechanical modeling of the response of elastomers requires constitutive models that account for both the mechanical and

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temperature dependence of the thermophysical properties of these materials. Although the effects of the temperature level on the value of the thermal diffusivity have been relatively well studied [1, 2], the effect of deformation on the value of the thermal diffusivity tensor has been less explored. That is, few studies have examined the influence of deformation on the thermal response of elastomers, and, there is no widely accepted relation to describe the changes in thermophysical properties with respect to finite deformation.

Measurements have demonstrated that there can be significant changes in the thermal conductivity or diffusivity tensors of elastomers subject to finite deformation. Venerus et al. [3] used forced Rayleigh scattering (FRS) to measure the thermal diffusivity of silicone rubber subject to uniaxial stretching. In FRS, a transient optical grating is formed in the material by a diffraction pattern that results from absorption of intersecting laser beams, which have been split from a single source [4]. The rate of decay of the efficiency of diffraction is a function of one of the components of the thermal diffusivity, depending on the relative orientation of the lasers to the specimen. Multiple experiments are required in order to measure multiple components of the diffusivity. Venerus et al. [3] report that for initially isotropic silicone rubber, the component of the thermal diffusivity tensor in the direction of a uniaxial stretching α_{11} increases by 10% for a stretch of ratio of $\lambda_1 = 2$, where λ_1 equals the current length l divided by an undeformed length L. The component of the diffusivity orthogonal to the stretching α_{33} decreased by 5%. Figure 1 shows these variations in α_{11} and α_{33} for stretching in the 1-direction. Motivated by the stress-optic rule, Venerus et al. describe their results using a stress-thermal rule [5], that is,

$$(\alpha_{11} - \alpha_{33})/\alpha_{\text{eq}} = c(t_{11} - t_{33}), \tag{1}$$

where c is a material parameter, t_{11} and t_{33} are the components of the Cauchy stress in the direction of stretch and orthogonal to it, respectively, and the diffusivities are in the stretched state except α_{eq}, which is the thermal diffusivity of the unstretched elastomer. Equation (1) correlates the difference between these orthogonal components of the diffusivity tensor with the difference in the Cauchy stress components in the two directions for this case of uniaxial stretching. The magnitude of each component is not uniquely described, however. Because the change in each component of the diffusivity appears linear with respect to stretch ratio, this suggests that the stress is also linearly correlated with stretch, which typically occurs over only limited ranges of stretches in most elastomers.

Measurements during homogeneous multiaxial deformations are needed to formulate constitutive models for multiaxial behavior [6]. Thus,

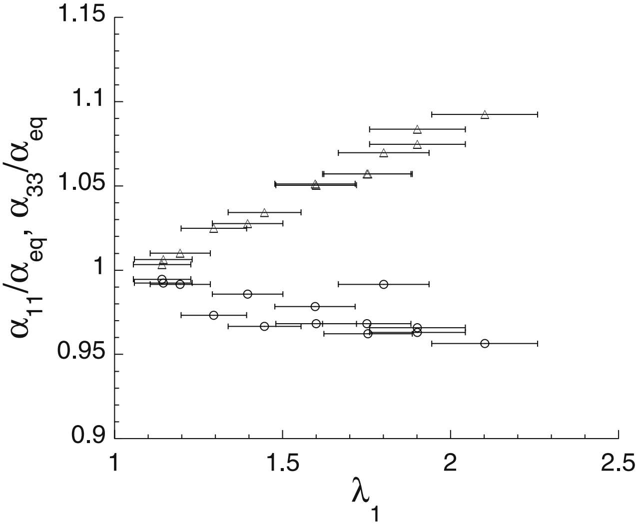

Fig. 1. Diffusivity of silicone rubber subject to uniaxial stretching [3]. Triangles are α_{11}, parallel to the stretch λ_1 and the circles are α_{33}, orthogonal to λ_1. The error bars represent ±7.5% uncertainty in the stretch measurement.

LeGall and Wright [7] measured the three orthogonal components of the diffusivity tensor during biaxial stretching of polyurethane, natural gum rubber (NGR), and neoprene rubber. The deformation was homogeneous in the central region of the specimen where the diffusivity was measured. These results showed an increased diffusivity in the direction of stretch and a decreased value in the orthogonal direction, similar to the uniaxial results. LeGall and Wright did not provide a correlation of their data.

Here, an alternative correlation of diffusivity, based on methods of finite elasticity, is presented. This relationship relies on transferring the thermal diffusivities that are measured in the deformed state to the undeformed reference configuration of the material. The results are then correlated in terms of the deformation via the right Cauchy–Green deformation tensor, instead of the extra stress, as done in Eq. (1). In this manner, a simple relation between the components of the diffusivity tensor and the deformation is observed for several elastomers.

2. BACKGROUND

Theory reveals that two constitutive functions are required to describe the reversible finite strain thermomechanical response of elastomers [8]. These may be the Helmholtz free energy ψ and the spatial heat flux vector

$\mathbf{q}$. Theory further shows that $\psi=\hat{\psi}(\mathbf{F},T)$ and $\mathbf{q}=\hat{\mathbf{q}}(\mathbf{F},T,\nabla T)$, where $\mathbf{F}=\partial\mathbf{x}/\partial\mathbf{X}$ is the deformation gradient tensor, T is the temperature, $\nabla T(=\partial T/\partial\mathbf{x})$ is the temperature gradient, $\mathbf{X}$ is the position vector of a material particle in the reference configuration, and $\mathbf{x}$ is the position vector of a material particle in the current configuration (see Fig. 2). Material frame indifference allows ψ to be written as $\psi=\psi(\mathbf{C},T)$, where $\mathbf{C}=\mathbf{F}^T\mathbf{F}$ is the right Cauchy–Green deformation tensor. Stress–strain–temperature relations result from derivatives of ψ with respect to $\mathbf{C}$. For example, the Cauchy (or true) stress tensor $\mathbf{t}$ may be calculated by

$$\mathbf{t}=\frac{2}{J}\mathbf{F}\frac{\partial\psi(\mathbf{C},T)}{\partial\mathbf{C}}\mathbf{F}^T, \tag{2}$$

where $J=\det\mathbf{F}$, which equals one for an incompressible material.

A number of models for ψ, such as the Mooney–Rivlin and Ogden models, have been proposed and describe the mechanical response for various boundary conditions or levels of deformation [9]. Most studies of elastomer mechanics have focused on isothermal deformations, with less attention being devoted to the effects of temperature on ψ. Some exceptions include Ogden [10] proposing a method for finding ψ as a function of biaxial stretches and temperature, and Humphrey and Rajagopal [11] showing that in-plane biaxial tests allow measurement of thermoelastic response functions (e.g., $\partial\psi/\partial I_C$, where $I_C=\mathrm{tr}\mathbf{C}$) similar to the isothermal

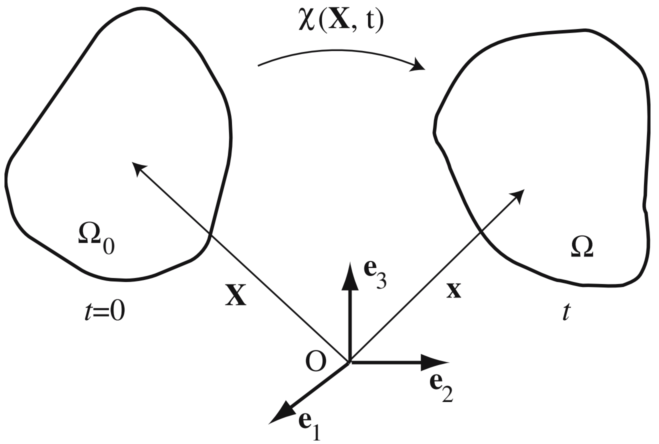

Fig. 2. Illustration of the reference configuration Ω_0, the current configuration Ω, and the motion of a continuum body $\chi(\mathbf{X},t)$. Coordinates are shown for the reference configuration $\mathbf{X}$ and current configuration $\mathbf{x}$.

results of Rivlin and Saunders [12]. Wineman and Min [13] have demonstrated the importance of temperature on the mechanical response of elastomers in studies of the development of a secondary molecular network resulting from microstructural changes due to elevated temperature and deformation. This new network results in a changed mechanical response.

Alternatively, most conduction heat transfer analyses neglect the influence of finite strain on the heat flux vector. Rather, most reports assume Fourier conduction $\mathbf{q}(\mathbf{x}, T) = -k(T)\nabla T$, where $\mathbf{q}(\mathbf{x}, T)$ is the spatial heat flux, ∇T $(= \partial T/\partial \mathbf{x})$ is the spatial gradient of temperature, and $k(T)$ is the scalar (i.e., isotropic) spatial thermal conductivity [1]. If anisotropy is considered, then the heat flux may be written in the current configuration as Duhamel conduction [9] with $\mathbf{q}(\mathbf{x}, T) = -\mathbf{k}(\mathbf{F}, T)\nabla T$, where $\mathbf{k}(\mathbf{F}, T)$ is the spatial thermal conductivity tensor. For materials subject to small deformation, models of thermal response that are formulated in either the current or reference configuration will yield similar results. Elastomers, however, are often subject to large multiaxial deformation, and models of the thermal response of materials subject to large deformation must include changes to both the geometry and the material properties, such as the thermal conductivity. Moreover, the thermal conductivity of polymers, and specifically elastomers, can change isotropy as a result of large strain [3, 14].

Finite strain constitutive relations are often formulated in terms of the referential thermal conductivity $\mathbf{K}(\mathbf{C}, T)$, to take advantage of material symmetry. Using Nanson's formula [9], the heat flux in the reference and current configurations is related by $\mathbf{q} = (1/J)\mathbf{F}\mathbf{q}_0$, where $\mathbf{q}_0$ is the heat flux vector in the reference configuration. Conduction in the reference configuration may be written as $\mathbf{q}_0(\mathbf{x}, T) = -\mathbf{K}(\mathbf{C}, T)\nabla_0 T(\mathbf{X}, T)$, where $\nabla_0 T$ $(= \partial T/\partial \mathbf{X})$ is the referential temperature gradient. One can thus determine $\mathbf{K}(\mathbf{C}, T)$ from the measurable $\mathbf{k}(\mathbf{F}, T)$ via $\mathbf{k}(\mathbf{F}, T) = (1/J)\mathbf{F}\mathbf{K}(\mathbf{C}, T)\mathbf{F}^T$. Substituting Duhamel's equation into the referential conservation of energy equation yields, neglecting the stress power and heat sources,

$$\partial T(\mathbf{X}, t)/\partial t = \nabla_0 \cdot (\boldsymbol{\alpha}_0(\mathbf{C}, T) \cdot \nabla_0 T(\mathbf{X}, t)), \tag{3}$$

where $\boldsymbol{\alpha}_0(\mathbf{C}, T)$ $(= \mathbf{K}(\mathbf{C}, T)/\rho_0 c_F(\mathbf{C}, T))$ is the referential thermal diffusivity tensor, in which ρ_0 is the referential mass density and c_F is the referential constant deformation specific heat. Because elastomers are here assumed to be incompressible and c_F is insensitive to deformation [3], either the thermal diffusivity tensor or the thermal conductivity tensor may be used to characterize changes in thermophysical response due to deformation. The thermal diffusivity is more easily measured by noncontact methods, which is beneficial for measurement of $\boldsymbol{\alpha}$ in materials subject to finite deformation.

3. RESULTS

Consider the relationship of α_{11} with respect to λ_1 and α_{33} with respect to λ_3. Assuming material incompressibility ($J = \lambda_1\lambda_2\lambda_3 = 1$), the deformation gradient tensor for uniaxial stretching is

$$\mathbf{F} = \begin{bmatrix} \lambda & 0 & 0 \\ 0 & \lambda^{-1/2} & 0 \\ 0 & 0 & \lambda^{-1/2} \end{bmatrix} \tag{4}$$

and, thus, $\lambda_3 = 1/\sqrt{\lambda_1}$. Figure 3 shows that the data from Fig. 1 can be correlated with a single power law correlation in terms of α_{ii} and λ_i, or with separate linear correlations, that is, a single trend for α_{11} in terms of λ_1, and another for α_{33} in terms of λ_3. Estimating the parameters using a least-squares method, each of these correlations has approximately the same quality of fit.

To take advantage of possible symmetry conditions for initially isotropic materials, the values of $\boldsymbol{\alpha}$ should be transformed to $\boldsymbol{\alpha}_0$, i.e., the thermal diffusivity in the reference configuration, and the deformation should

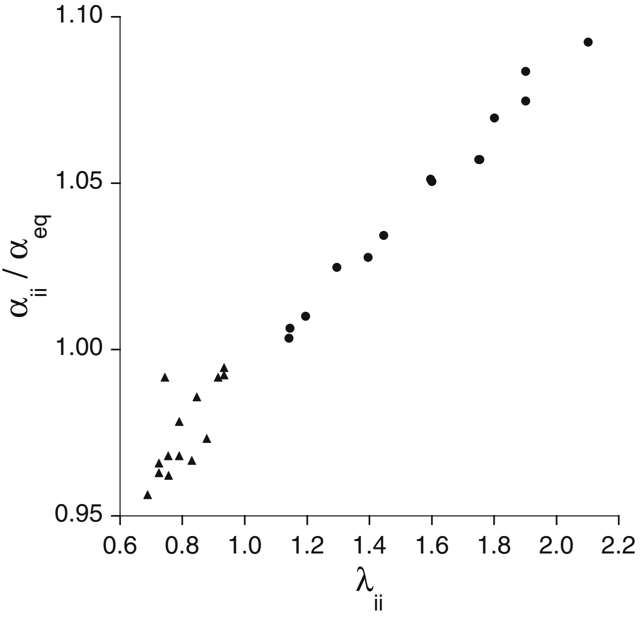

Fig. 3. Silicone rubber uniaxial loading data of Fig. 1 replotted as α_{11} vs. λ_{11} (circles) and α_{33} vs. λ_{33} (triangles). The orthogonal stretch λ_{33} was calculated assuming incompressibility.

be described using **C**. Figure 4 shows the relationship between $\boldsymbol{\alpha}_0$ and **C** for the silicone rubber data from Fig. 1. The only nonzero components of $\boldsymbol{\alpha}_0$ are $\alpha_{0,11} = \alpha_{11}\lambda^{-2}$, $\alpha_{0,22} = \alpha_{22}\lambda$, and $\alpha_{0,33} = \alpha_{33}\lambda$. Here, the material is assumed to be transversely isotropic, with $\alpha_{33} = \alpha_{22}$, consistent with Venerus et al. reporting only a single component of $\boldsymbol{\alpha}$ in the orthogonal direction. A least-squares fit of these data shows that both the stretched and orthogonal directions apparently follow the same trend. This trend is described well by

$$\frac{\alpha_{ii}}{\alpha_{\mathrm{eq}}} = aC_{ii}^{b} \qquad i = 1, 2, 3 \qquad \text{(not summed)}, \tag{5}$$

where a and b are dimensionless material parameters. Values of a and b are listed in Table I.

LeGall and Wright [7] used a variation of the flash method [15] to measure simultaneously the three principal components of $\boldsymbol{\alpha}$ of room-temperature vulcanizing (RTV) polyurethane that was subject to homogeneous equibiaxial deformation, that is, both in-plane directions are stretched equally. This pulse system involves a minimum of contact with

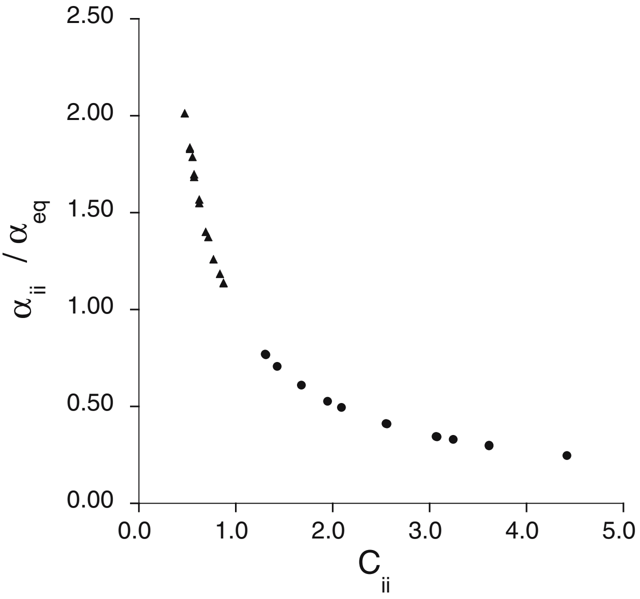

Fig. 4. Silicone rubber uniaxial loading data from Fig. 1 plotted in the reference configuration as $\alpha_{0,11}$ vs. C_{11} (circles) and α_{33} vs. C_{33} (triangles).

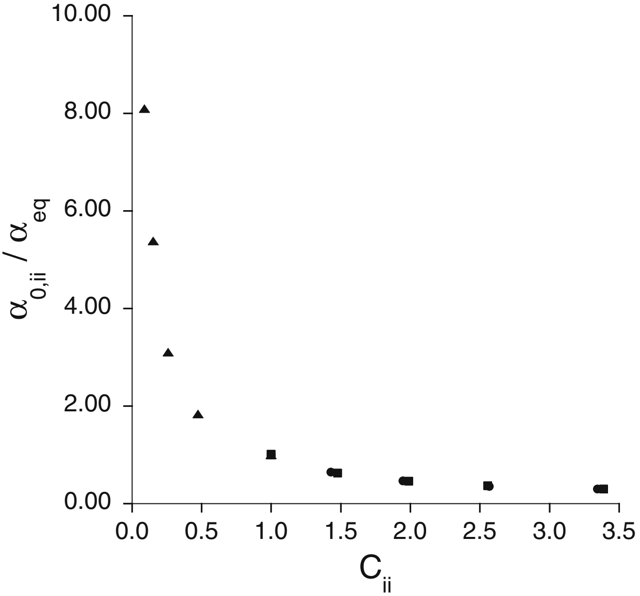

Fig. 5. Diffusivity of biaxially stretched polyurethane RTV rubber, in terms of the reference configuration. In-plane components are $\alpha_{0,11}/\alpha_{\mathrm{eq}}$ vs. C_{11} (circles), $\alpha_{0,22}/\alpha_{\mathrm{eq}}$ vs. C_{22} (squares), and $\alpha_{0,33}/\alpha_{\mathrm{eq}}$ vs. C_{33} (triangles).

Table I. Coefficients for Eq. (5); Fit of $\alpha/\alpha_{\mathrm{eq}}$ for Initially Isotropic Elastomers Subject to Uniaxial or Biaxial Stretching

Material	Loading	a	b	r^2	T	Ref
Silicone rubber	Uniaxial	0.998	−0.945	0.990	25°C	[3]
PU RTV (preconditioning 1)	Biaxial	0.929	−0.926	0.998	20°C	[7]
PU RTV (preconditioning 2)	Biaxial	0.931	−0.946	0.998		
PU RTV (preconditioning 3)	Biaxial	0.897	−0.929	0.998		

the specimen, which is required for measuring the thermal diffusivity of materials undergoing finite stretching. For in-plane stretch ratios of λ_1 and λ_2, the out-of-plane stretch ratio will be $\lambda_3 = 1/(\lambda_1\lambda_2)$, for an incompressible material. The deformation gradient tensor for equibiaxial stretch is

$$\mathbf{F} = \begin{bmatrix} \lambda_1 & 0 & 0 \\ 0 & \lambda_2 & 0 \\ 0 & 0 & \lambda_1^{-1}\lambda_2^{-1} \end{bmatrix}. \tag{6}$$

By again transferring $\boldsymbol{\alpha}$ to the reference configuration, and plotting the components of $\boldsymbol{\alpha}_0$ against the corresponding components of $\mathbf{C}$, there appears to be a single relationship for the polyurethane RTV (Fig. 5). A least-squares fit of these data suggests a similar trend as in the uniaxial data. The coefficients for the three specimens are listed in Table I; LeGall and Wright [7] cite the three specimens separately because each had undergone a different mechanical preconditioning protocol. Preconditioning of elastomeric specimens is required to obtain repeatable thermoelastic results due to the Mullins effect [16].

4. DISCUSSION

The isotropic thermal diffusivity of undeformed silicone and polyurethane rubbers becomes anisotropic when these elastomers undergo reversible finite strain. The results for uniaxial stretching [3] and biaxial stretching [7] imply that $\boldsymbol{\alpha}$ is transversely isotropic after homogeneous deformation. Figure 3 suggests that a single correlation, nearly linear in stretch, may describe the change in diffusivity during uniaxial deformation, both in the stretching direction and orthogonal to it.

While constitutive relations for thermal diffusivity that include the influence of finite deformation could be developed using a number of coordinate frames, relating $\boldsymbol{\alpha}$ to $\boldsymbol{\alpha}_0$ and comparing it with $\mathbf{C}$, i.e., in the reference configuration, can aid in the development of the constitutive relations because of the material symmetry. The ability of Eq. (5) to correlate the diffusivity data is expected, given the relationship between $\boldsymbol{\alpha}_0$ and $\mathbf{C}$. That is, if $\boldsymbol{\alpha}$ were constant with stretch, then in the reference configuration, $\boldsymbol{\alpha}_0 \propto \mathbf{C}^{-1}$. This is revealed in Table I, where b is almost -1, the deviation being the result of the actual change in diffusivity. The scatter in the measurements is revealed by the value of a, which is essentially 1 for the uniaxial data, but deviates from 1 by as much as 10% for the biaxial data. Thus, while care must be exercised to avoid obscuring the small variations in $\boldsymbol{\alpha}$ with deformation, both components of $\boldsymbol{\alpha}$ may be correlated in the reference configuration.

Figure 3 and Eq. (5) further suggest that components of diffusivity are described by the deformation in the direction corresponding to that component. Deformation orthogonal to the uniaxial stretch or in the out-of-plane direction for the biaxial stretch case was computed assuming that rubber-like materials are volume preserving on deformation. This assumption has been well-justified based on measurements that have shown that volume changes are of the order of 10^{-4} or less [16]. Based on the assumption of incompressibility, the components of $\mathbf{F}$ are related by $J = 1$ and only one component of $\mathbf{F}$ is needed to characterize the deformation

Table II. Coefficients for Eq. (5) for α_0/α_{eq} of Initially Anisotropic Elastomers Subject to Equibiaxial Loading

Material	Loading	a	b	r^2	T	Ref.
NGR	Biaxial	0.9273	−0.9783	0.9943	20°C	[7]
Neoprene	Biaxial	0.9378	−0.9331	0.9948	20°C	[7]

for the uniaxial and equibiaxial cases. This suggests that the off-axis terms are unlikely to contribute to changes in $\boldsymbol{\alpha}_0$ for initially isotropic materials.

LeGall and Wright [7] also measured the principal components of $\boldsymbol{\alpha}$ of NGR and neoprene that were anisotropic in the undeformed state due to manufacturing. The in-plane components of $\boldsymbol{\alpha}_0$ were 5 and 6% higher than the out-of-plane coefficient for the NGR and neoprene, respectively. Materials with initial anisotropy violate the assumptions leading to Eq. (5). Nevertheless, the response of these materials, shown by the values of a and b for the NGR and neoprene listed in Table II, is similar to those listed in Table I.

A simple relation between finite deformation and the change in diffusivity of elastomers has been presented. Clearly, further study is required to clarify the relationship between $\boldsymbol{\alpha}$ and deformation for elastomers and other polymers. Both molecular weight [17] and cross-linking [13] have influence on the thermomechanical response of elastomers. Their role in the thermophysical constitutive behavior needs to be examined.

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