JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 16, No. 3-4, March - April 2014, p. 457 - 462

# Estimation of essential dielectric parameters in ferroelectric state of TGS crystal

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The ferroelectric parameters of pure TGS crystal were estimated using the frequency dependence of permittivity components and approximate related Debye equations. The experimental components of permittivity were presented on semi-log frequency dependence on seven orders of magnitude in the ferroelectric range (43 $^{o}$C). The three relaxation maxima of the imaginary components of permittivity allowed estimating the related values of the real components and of the three associated relaxation times. The extreme values of the real component of permittivity on the abscissa scale and the associated relaxation times were estimated according to the approximated Debye equations. The calculated values of the radius and α parameters of arcs Cole-Cole scarcely agree with the values estimated from the direct experimental (ε” vs. ε’) analysis.

(Received February 12, 2014; accepted March 13, 2014)

*Keywords:* Ferroelectric crystals, Triglycine sulphate, Dielectric spectroscopy, Permittivity relaxation

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## 1. Introduction

Triglycine sulphate crystal (TGS for short) has been intensively studied both as fundamental properties [1-4] and technological applications [5]. Crystal growth conditions of TGS and ferroelectric properties we have earlier presented [6-8]. Relaxation phenomena [3, 4] and other specific properties [9-11] were studied. Essential mechanisms of relaxation we have recently presented [12-15]. There are three relaxation times, two of them around $10^{-3}$ sec and $10^{-7}$ sec being fundamental. The third one around $10^{-5}$ sec (the middle relaxation) seems to be an interaction of the previous ones with the lattice vibrations [12]. The frequency displacement and the intensity variation of $\varepsilon''_{max}$-the maxima of the three relaxations in the ferro phase, down the Curie point (~49 $^{o}$C), we have presented in ref. [12]. The middle frequency relaxation (around $10^4$ Hz, i.e. $\tau \approx 10^{-5}$ sec), which was “born” near the higher relaxation maxima at Tc, “travel” to the lower frequency relaxation, by the temperature decrease. Down to about room temperature it disappears. We have chosen to study the ferroelectric parameters at 43 $^{o}$C, where the middle relaxation maximum is somewhere half-way in-between.

We shall use some approximate formulas from ref. [16, 17]. Data similar to ref. [18] shall be used in order to check the validity of the mentioned formulas.

## 2. Experimental

Details about the crystal growth, sample preparation and dielectric measurements were presented in ref. [12]. In short, pure TGS crystal was grown from solutions in a thermostated oven by slow solvent evaporation. Growth was realized in paraelectric phase at 54 $^{o}$C in order to avoid the lattice defects and mechanical tension which appear in crystals grown in ferroelectric phase.

Measurements were realized with the dielectric spectrometer [12] on the frequency range 1 Hz to 10 MHz down to 65 $^{o}$C, taking 5 point measurements equidistant in log scale, on every frequency decade.

## 3. Method of analysis

The Debye equations were used [16] in order to get the following formulas:

$$\omega\,\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega^2\tau}{1+\omega^2\tau^2} = (\varepsilon_s - \varepsilon'(\omega))/\tau \quad (1)$$

$$\varepsilon''(\omega)/\omega = \frac{(\varepsilon_s - \varepsilon_\infty)\tau}{1+\omega^2\tau^2} = \tau(\varepsilon'(\omega) - \varepsilon_\infty) \quad (2)$$

The significance of parameters used: ε’(ω), ε”(ω) – real and imaginary component of permittivity, $\boldsymbol{\varepsilon_\infty}$, $\varepsilon_{st}$ – the extreme values of ε’(ω) on the abscissa scale, τ - the relaxation time.

First we represent both component of permittivity vs. frequency as in Fig. 1. The components appear about at the same scale, but the imaginary component is 5 times smaller (right hand side ordinate scale). Thus, there are three maxima L, M, and H corresponding to the three relaxation processes to be analyzed. The ε” accurate maxima values and the corresponding frequencies were

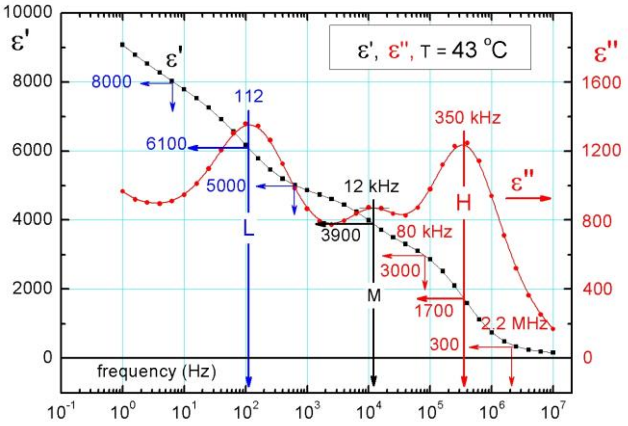

*Fig. 1. The frequency dependence of real ε' and imaginary ε" (right side) component of permittivity. The frequencies corresponding to ε" maxima: L-low, M-middle and H-high, have been used to estimate directly τ- the relaxation times (see table).*

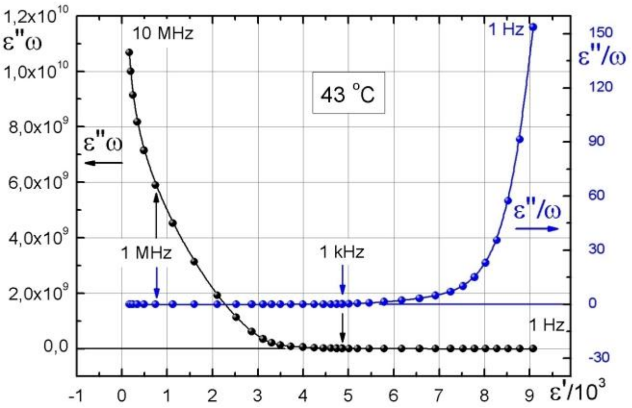

*Fig. 2. The linear dependence of functions ε"ω and ε"/ω (right side) versus ε', according to equations (1) and (2) on the whole frequencies range.*

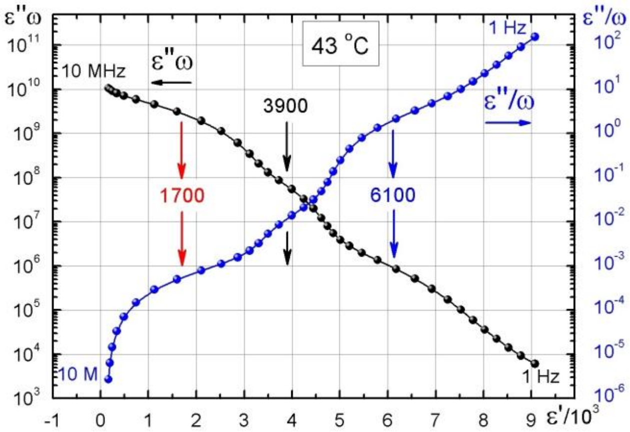

*Fig. 3. The semi-log dependence of the same functions as in Fig.2. The ε' values 1700, 3900, 6100 corresponding to ε" maxima in Fig. 1 shows the regions where application of equations (1) and (2) has to be searched.*

registered as $\varepsilon''_{max}$ in the table. The values of ε' at the same frequencies were also registered as $\varepsilon'_{max}$ and the range of interest for the three relaxation, on both coordinate were marked in Fig. 1.

The relaxation time τ* in the table, corresponding to the mentioned relaxation processes were registered, using the $\varepsilon''_{max}$ condition: $\omega_{max}\ \tau_{relax} = 1$, i.e. $\tau_{relax} = 1/2\pi\nu_{max}$ . Other values of relaxation times in the table (parentheses) were estimated according to equations (1) and (2).

In order to explore the possibility to apply the mentioned formalism, we have drawn in Fig. 2 the linear dependence of ε" ω and ε"/ω versus ε' according to equations (1) and (2). There are seven order of magnitude variations of both functions, which shall to be analyzed only on narrow intervals.

We have redrawn the same dependences in Fig. 3 on a semi-log scale and we have mentioned the ε' values 1700, 3900 and 6100 according to the narrow sections where the equations (1) and (2) might be valid. However, this graphic is not directly useful and we have to search further on the narrow intervals in the linear dependence.

## 3. Results

Equation (1) has been used in Fig. 4 to find τ the relaxation time and $\varepsilon_s$ the extreme value of ε' (at lower frequencies), corresponding to the abscissa scale of arcs Cole-Cole (C-C) as in Fig. 6. In the first line of the table we have registered data estimated from Fig. 1 (and Fig. 2) and in the second line were registered characteristic data of C-C representation from Fig. 6. Data have been collected for the three relaxation processes at Low, Middle and High ranges of frequencies in the table.

It was quite difficult to choose the experimental points where the linear dependence predicted by eq. (1) to be checked. However the frequency values of ε" maxima and the related ε' guiding values found in Fig. 1 were very useful. There where narrow intervals where the appropriate data could be found.

In a similar way, equation (2) has been used in Fig. 5 to find again the relaxation time from the slope of the linear dependence of ε"/ω vs. ε' and the data were registered in the table (column τ, the second figure in parentheses). The other extreme parameter $\varepsilon_\infty < \varepsilon_s$ (related to much higher frequencies) where found by extrapolation $\varepsilon' \rightarrow 0$ in eq. (2). All the data are presented in the table. Fig. 6 shows the C-C representation which shall be considered as standard, to compare all the dielectric parameters we have previously found. We note that at frequencies smaller than 100 Hz there are important losses due to conduction and possibly space charge.

The formulas for calculation of the radius R and of the α parameters, corresponding to arcs C-C, have been presented in appendix and data estimation is presented in the table.

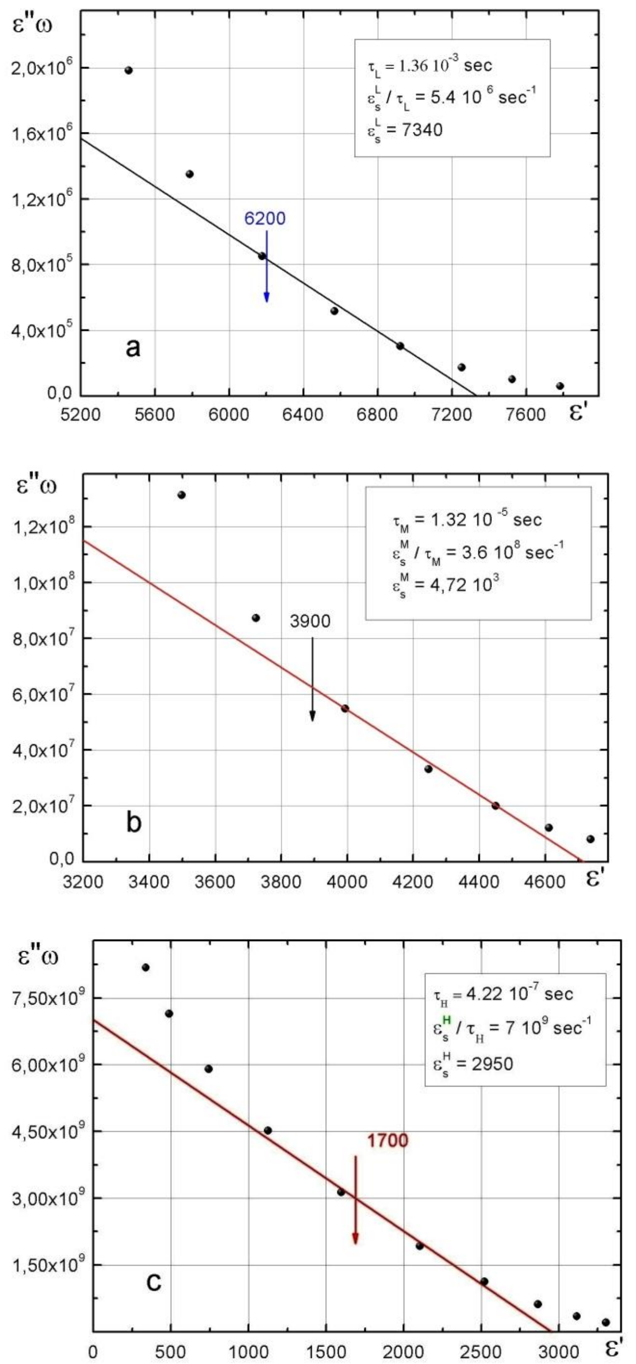

*Fig. 4. The application of eq. (1) in the frequency ranges: a/ L-low, b/ M-middle and c/ H-high, mentioned in Fig. 1 and in Fig. 3. The corresponding relaxation times estimated from the slope (first figures in the parentheses) and the extreme values $\varepsilon_s$ were collected in the table.*

## 4. Discussions

We have tried to check the validity of equations (1) and (2) derived from Debye equations for dielectric parameters of TGS. The carefully drawn arcs C-C (Fig. 6) was considered as standard model, to compare our data with. The data corresponding to this representation was presented in the table as the second line on every frequency range (Low, Middle, and High).

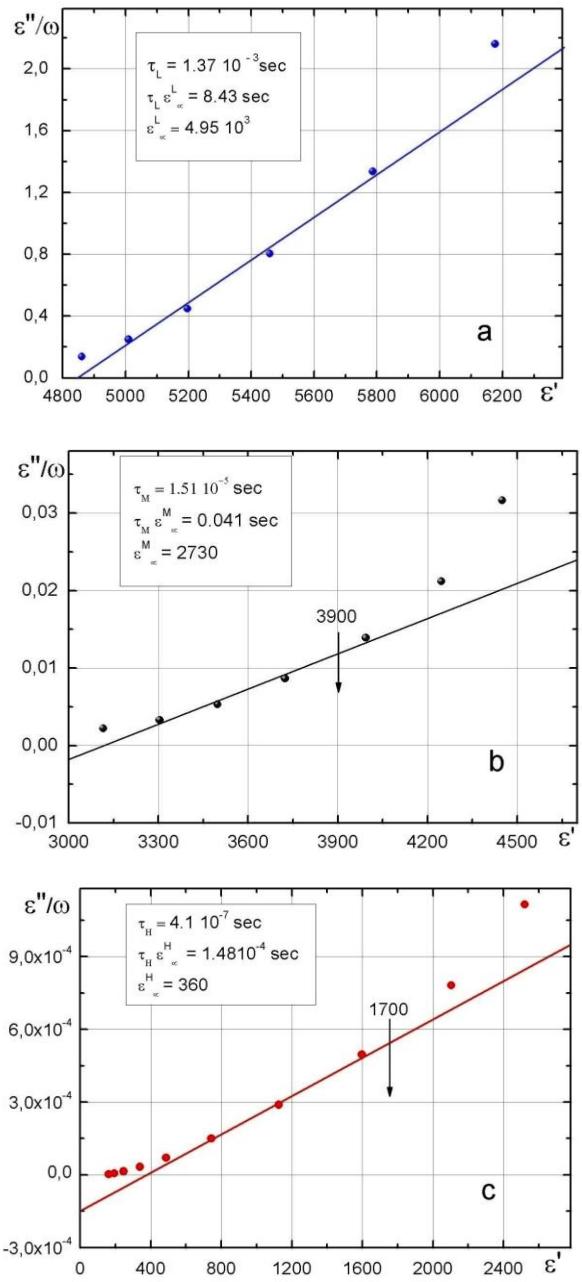

*Fig. 5. The application of eq. (2) in the frequency ranges as in Fig. 4. The corresponding relaxation times estimated (second figures in the parentheses) and the $\varepsilon_\infty$ values were also collected in the table.*

The relative errors of the first two lines for every frequency range are presented as a third line in table for the three ranges of frequency. Errors larger than 10% were underlined. We shall further analyze the estimated errors on the columns of the table.

The basic parameters ε'$_{max}$ and ε"$_{max}$ determined from Fig. 1 versus C-C diagrams still have considerable errors, particularly larger for High frequency range, which is difficult to motivate. The Middle one error in all columns can be motivated on the account of less extended arc C-C, which is "covered" more or less by the neighbor arcs C-C, High and Low.

*Table. The main dielectric parameters of the three relaxation proceses at 43 °C in TGS.*

| frequency range | $\varepsilon'_{max}$ | $\varepsilon''_{max}$ | $\varepsilon_\infty$ (eq. (2)) | $\varepsilon_s$ (eq. (1)) | R calc(1) (exp) | $\alpha$(2) calc(exp) | $\tau$(3) (eq. (1) / eq. (2)) | reference |
|---|---|---|---|---|---|---|---|---|
| **LOW** | 6040 | 1380 | 4950 (?) | 7340 | 1250 | ----- | $1.42\ 10^{-3}$ ($1.36$ / $1.37\ 10^{-3}$) | this paper |
| | 5730 | 1380 | 4211 | 7250 | 1530 (1530) | 5.5° (5.3°) | $1.42\ 10^{-3}$ | Cole-Cole(4) |
| | 5 % | 0 % | 17 % | 1.2 % | - 18 % | 4 % | 0 % (- 4.3 % / - 3.5 %) | relative error |
| **MIDDLE** | 3880 | 870 | 2730 (?) | 4720 | 990 | 7.6° (?) | $1.33\ 10^{5}$ ($1.32$ / $1.51\ 10^{-5}$) | this paper |
| | 3620 | 830 | 2320 | 4920 | 1440 (1430) | 25.1° (25°) | $1.59\ 10^{-5}$ | Cole-Cole(4) |
| | 7 % | 5 % | 17 % | -4 % | - 31 % | 0.5 % | - 16 % (- 17 % / - 5.0 %) | relative error |
| **HIGH** | 1770 | 1240 | 360 (?) | 2950 | 1300 | 2.8° (?) | $4.55\ 10^{-7}$ ($4.22$ / $4.1\ 10^{-7}$) | this paper |
| | 1640 | 1160 | 96 | 3185 | 1608 (1608) | 16,2° (16,2°) | $4.41\ 10^{-7}$ | Cole-Cole(4) |
| | 7% | 6.4% | ----- | - 7 % | - 19 % | 0 % | 3.1 % (- 4.3 % / - 7.0 %) | relative error |

(1) R - arc radius estimated according to eq. (6.a) from appendix

(2) Error of $\alpha$ along the column was estimated as the ratio between calculated by eq. (A.1) and found from Fig. 6.

(3) From Fig. 1 – see text

(4) Cole-Cole estimation of experimental data.

Our estimated errors (the third line in every frequency range) larger than 10% were underlined in the table.

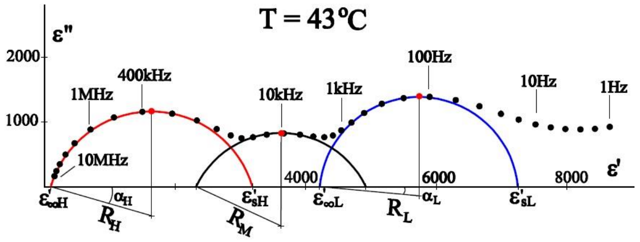

*Fig. 6. The arcs C-C drawing of the three relaxation phenomena. From this precisely drawn graphic we have estimated all dielectric parameters (the second line in table) for low, middle and higher frequencies. These data were considered the reference standard data. Error figures are given in the third line for the three frequency ranges.*

The error of low frequency $\boldsymbol{\varepsilon}_s$ derived from eq. (1) appears in the reasonable limits, except High frequency range (-7%). On the other hand the errors of the parameter $\varepsilon_\infty$ estimated from eq. (2) is considerable higher (17% ) for Low and Middle ranges and unexpectedly erroneous for High range.

The relaxation time $\tau$ estimated by several procedures is in reasonable agreement, except the middle one range, the motivation already pointed out.

The radius R of arcs C-C calculated, (see appendix) have much higher negative errors (-20/-30%) versus estimated values from Fig. 6. The value of the calculated radius R is larger than $(\varepsilon_s$-$\boldsymbol{\varepsilon}_\infty)/2$, suggesting indeed a sort of C-C behavior. The most inappropriate values have been estimated (see appendix) for $\alpha$, the C-C parameter in the table. However, the relative errors between calculated (eq.5.a - appendix) and estimated from Fig. 6 are almost negligible except for Low frequencies where conduction is an important disturbing parameter.

## 5. Conclusions

The dependence $\varepsilon''(\omega)$ allowed to estimate for $\varepsilon''_{max}$ the relaxation time and the associate $\varepsilon'_{max}$ with reasonable precision.

The linear dependence of $\omega\varepsilon''(\omega)$ and $\varepsilon''(\omega)/\omega$ versus $\varepsilon'$, in the Debye approximation were used to evaluate parameters $\varepsilon_s$ , $\varepsilon_\infty$ and the relaxation times for Low, Middle and High frequencies ranges and the radius R and $\alpha$ the Cole-Cole parameters. Estimated errors shows $\varepsilon'_{max}$ , $\varepsilon''_{max}$ , $\varepsilon_s$ and the relaxation times $\tau$ could be reasonable estimated. The errors estimated for $\varepsilon_\infty$ and R (the radius of arcs C-C) are very high (20/30%), while the $\alpha$ - C-C estimated parameters shows, as expected, unacceptable higher relative errors.

The mentioned Debye approximation can be used to find several dielectric parameters only for very small $\alpha$ - C-C parameters. This approximation is doubtful to be used for two or three relaxation processes on the usual $1\div10^7$ Hz frequencies range. The "conduction" effect might introduce important errors on the frequencies range smaller than $10^2$ Hz.

## Acknowledgements

One of the author (R. BACŞEI) acknowledge the support offered by the sectorial operational program human resources development (sop HRD), financed from the European social found and by the Romanian government under the contract number sop HRD/107/1.5/S/82514.

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## APENDIX

The frequency dependence of the components ε’ and ε” of the complex dielectric were directly estimated from experimental data.

The $\varepsilon''_{max}$ value and the corresponding $\nu_{max}$ frequency (related to the relaxation time $\tau=1/2\pi\nu_{max}$) were estimated from the graphic ε”(ν). The parameters $\varepsilon_\infty$ and $\varepsilon_s$ the extreme values of ε’ were estimated as previously shown.

At this stage the Cole-Cole (C-C) representation would be practically fixed.

However, we need the arc radius and the α parameter to compare with the directly Cole-Cole representation.

In the Fig. 1.A, the angle corresponding to α parameter is (π/2) α

From this figure we find the angle α as:

$$\alpha = \pi/2 - 2\beta \tag{1.a}$$

and

$$tg\ \beta = \frac{2\,\varepsilon''_{\max}}{\left(\varepsilon_S - \varepsilon_\infty\right)} \tag{2.a}$$

The radius of the arc C-C is:

$$R = \frac{\varepsilon''_{\max}}{1-\sin\alpha} = \frac{\varepsilon''_{\max}}{1-\cos 2\beta} \tag{3.a}$$

and

$$\sin^2\beta = \left[1+\frac{1}{tg^2\beta}\right]^{-1} \tag{4.a}$$

From eq. (1) we have: $\sin\alpha = \cos 2\beta = 1 - 2\sin^2\beta$

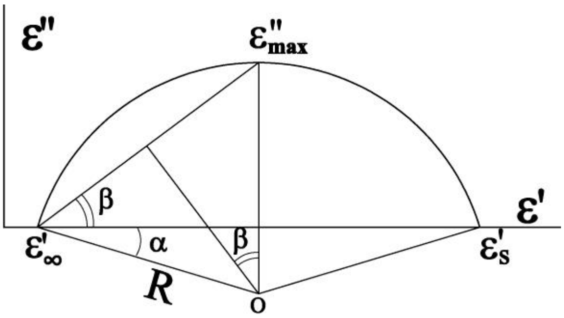

*Fig. 1.A. The arc C-C used for calculation of radius R and α-Cole-Cole parameters, using the data $\varepsilon_s$ , $\varepsilon_\infty$ and $\varepsilon''_{max}$ previously estimated.*

and find:

$$\sin\alpha = 1 - 2\left[1+\left(\frac{\varepsilon_s - \varepsilon_\infty}{2\,\varepsilon''_{\max}}\right)^2\right]^{-1} \tag{5.a}$$

$$R = \frac{\varepsilon''_{\max}}{2}\left[1+\left(\frac{\varepsilon_S - \varepsilon_\infty}{2\,\varepsilon''_{\max}}\right)^2\right] \tag{6.a}$$

These parameters were calculated based on $\varepsilon''_{\max}$ and $\left(\varepsilon_S - \varepsilon_\infty\right)$ values previously estimated and all the data are presented in table.

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