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Fast switching times of KD_2PO_4-KH_2AsO_4 ferroelectric domains monitored by ESR

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The domain switching experiments involving As-doped KD_2PO_4 ferroelectric crystals described in a previous publication in this journal were extended to higher electric field strengths with the aid of a new pulsed-field method for monitoring the switching process. Studies were carried out at 109 K using electric field strengths of 6.7, 10.0, and 13.7 kV/cm, and the ESR spectra of radiation-induced free radicals were used to monitor the domain switching. It was found that at short times after the application of the electric field the fractional polarization $g(t)$ that remained unswitched varied exponentially with the time, $g(t) \sim e^{-bt}$, while at intermediate times it followed a power law $g(t) \sim t^{-a}$, where a and b are parameters which depend upon the electric field strength and the temperature. Values were given for the electric field dependence of these parameters at 109 K, and that of a was compared with the value determined in the previous work at 82 K.

I. INTRODUCTION

In the ferroelectric state uniaxial single crystals such as those of the potassium dihydrogen phosphate (KDP) type possess two types of domains of oppositely directed polarization.[1] These domains have been studied by optical and displacement current methods,[2,3] and more recently by recording the electron-spin-resonance (ESR) spectra of radiation-induced free radicals in these samples.[4–11]

In earlier works we reported ESR studies of hysteresis effects[9] in several KDP-type ferroelectrics and of domain switching[10,11] in arsenic-doped KD_2PO_4. The most recent work[11] summarizes the way domains become formed and polarized, the preparation of the samples, and the ESR techniques that were used to study the domain switching. The techniques used in the earlier article permitted data to be obtained for times as short as 100 ms after the switching of the electric field. Unfortunately, they could not be used at high electric field strengths. The present paper describes a method for obtaining data at times as short as 0.1 ms after the switching and at high electric field strengths that could not be studied previously.

In Sec. II we will review the main results obtained from earlier switching experiments.[11] In Sec. III we will describe a new pulse technique that we have developed to measure fast switching times and in Sec. IV we compare the results obtained using this pulse technique with those obtained using the continuous method that was employed previously. An intermediate switching time was selected for this comparison. In Sec. V we present data which show that the measured switching times do not depend upon the pulse width. The results given in this section also demonstrate that the pulse technique is capable of determining switching times that are 3 orders of magnitude faster than those measurable by previous ESR methods.

II. DOMAIN SWITCHING

As we explained in the previous work[11] on KD_2PO_4 single crystals doped with 5 mole % KH_2AsO_4 the two domain types polarized in opposite directions give the respective time-dependent ESR signal amplitudes I_1 and I_2, and when a crystal is switched from one polarization (I_1) to a reversed polarization (I_2), the function $g(t)$

$$g(t)=I_1/(I_1+I_2) \tag{1}$$

is proportional to the fractional polarization that remains unswitched. Figure 1 shows typical spectra with the amplitudes I_1 and I_2 indicated. It was found that at a short time t after the application of an electric field pulse the fractional polarization $g(t)$ that remained unswitched varied exponentially with the time

$$g(t) \sim e^{-bt} , \tag{2}$$

while at intermediate times it followed a power law

$$g(t) \sim t^{-a} \tag{3}$$

and at still longer times the decay become more gradual. These results were found for electric field strengths sufficiently low so that the application of the field did not disturb the resonant cavity.

When the experiments were carried out at high electric field strengths the polarization process was accompanied by an initial disturbance which momentarily mismatched the cavity followed by a rapid reversal of the polarization. The spectrometer had to be retuned before spectra could be recorded, and by the time the retuning had been accomplished the polarization reversal was virtually complete. The higher the electric field strength the more pronounced the disturbance and the more rapid the occurrence of the polarization reversal. A new experimental approach is required for these high electric field strengths.

III. PULSED SWITCHING TECHNIQUE

In order to monitor the kinetics of the polarization reversal at high electric field strengths a technique was developed which employs the repeated application of pulses with the desired electric field amplitude each of which remains on for a sufficiently short length of time so

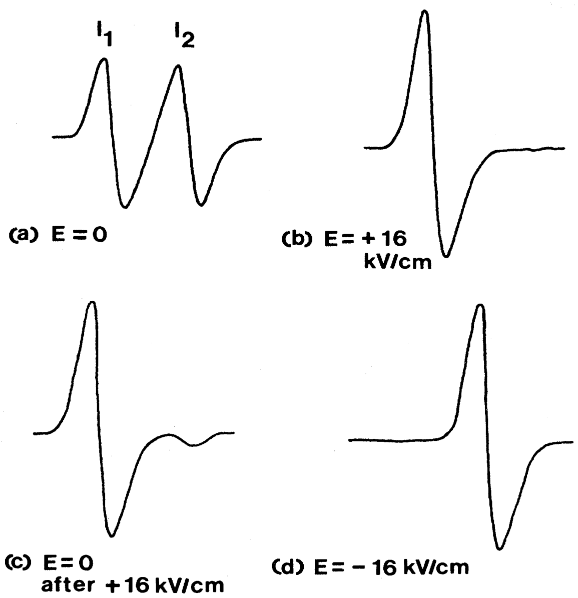

FIG. 1. Effect of an applied electric field on the split lowest-field hyperfine component of the AsO_4^{4-} radical in deuterated potassium dihydrogen phosphate—potassium dihydrogen arsenate (DKDP-KDA) at 82 K showing (a) an equal intensity doublet for an initially unpolarized crystal, (b) the presence of a single low-field line I_1 after polarization in the $+c$ direction, (c) growth of a weak I_2 line on the right-hand side spectrum when the electric field is returned to zero, and (d) disappearance of the line I_1 and appearance of the strong line I_2 when the crystal is polarized in the opposite ($-c$) direction. ($\vec{H}\perp c$; $\vec{H}\,||\,\hat{X}$ or $\hat{Y}$; $\vec{E}\,||\,c$).

that only a small fraction of the polarization is switched, the cavity is not appreciably mismatched. As a result, the crystal is switched in steps by a series of identical short duration electric field pulses.

Consider the switching to be carried out by a sequence of pulses of width t_w and spacing t_0 as indicated on Fig. 2 with the duty cycle

$$t_w/(t_0+t_w) \ll 1 \tag{4}$$

as indicated on Fig. 2. The number of pulses N that have been applied in a time t is

$$N = t/(t_0+t_w) \tag{5}$$

and the integrated time t_N that the electric field has been applied to the sample by the pulses during the total time is given by

$$t_N = Nt_w \tag{6}$$

$$= t\left[\frac{t_w}{t_0+t_w}\right]. \tag{7}$$

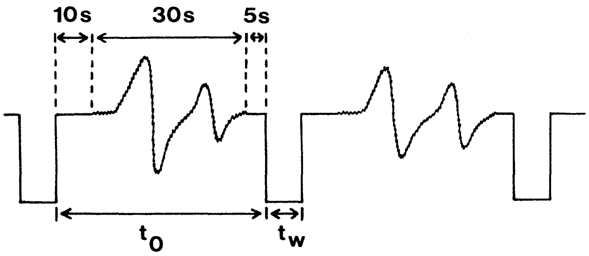

FIG. 2. Pulse method for measuring polarization reversal using successive pulses of variable width t_w. The spectrum is recorded between each pair of pulses as indicated.

The time dependence of the fractional polarization $g(t)$ that remained unswitched at various times t was determined by scanning through the spectrum during the intervals t_0 between the pulses when the polarization state of the crystal was stable. A 30-s interval was required to scan through a spectrum, and to minimize interference effects while the spectrum was being recorded; we waited 10 s after the pulse before we started the recording of the spectrum as indicated on Fig. 2. The total time between pulses $t_0 = 45$ s was kept constant and the pulse width t_w was varied for the different experiments. Figure 3 illustrates qualitatively the pulse sequences, how the relative amplitudes I_1 and I_2 change, and how $g(t)$ decreases while the successive pulses are applied.

IV. COMPARISON OF CONTINUOUS AND PULSED SWITCHING TECHNIQUES

The continuous-field switching method used in the previous work and the pulsed one used in the present investi-

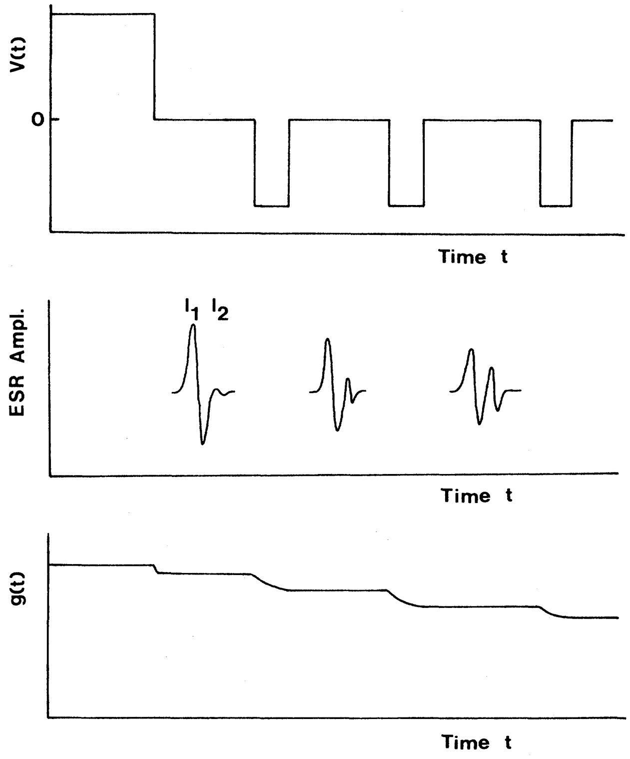

FIG. 3. Illustration of the pulse sequences, how the relative amplitudes I_1 and I_2 change, and how $g(t)$ decreases as successive pulses are applied. The relative amplitude changes between successive spectra are exaggerated for illustrative purposes.

gation were compared by recording data both ways at the relatively low electric field strength of 6.0 kV/cm and the relatively low temperature of 88 K. These conditions were convenient for the use of the continuous method of repeatedly scanning through spectra at 40-s intervals. The pulsed-field spectra were recorded using pulse widths t_w of 40 s so that each successive spectrum in both cases was recorded after the sample had experienced an additional 40 s of the applied electric field. All other conditions were kept the same for the two sets of measurements, and the results are presented on Fig. 4 which is a log-log plot of $g(t)$ versus the total time that the electric field had been applied to the sample. Both the pulsed-field and the continuous-field data lie along straight lines on this log-log plot indicating that the power law of Eq. (3) was satisfied.

We see from Fig. 4 that the pulsed data lie on a line which is above that corresponding to the continuous-field measurements. To ascertain the origin of this result some experiments were carried out in which $g(t)$ was measured immediately before and immediately after turning off the electric field during the switching process. During these experiments $g(t)$ was continuously decreasing while the field was on, and upon removal of the field $g(t)$ exhibited a slight increase in magnitude before reaching a constant value which persisted as long as the field remained off. However, quantitative measurements of this back-relaxation effect of $g(t)$ were not made. The back relaxation after the removal of the polarizing electric field is evident at all stages of the reversal shown in Fig. 4. Most of the backswitching occurs at a rapid rate and appears to be similar to the backswitching effects observed by other methods in $BaTiO_3$ single crystals and ceramics (and related materials) after the removal of the poling field.[12-14] Nevertheless, it explains why the pulsed data fall on a line that lies above the continuous-field data of Fig. 4. In other words, this back-relaxation effect of $g(t)$ causes the effective duration t_w of the pulse to be slightly less than the actual value of t_w. The slope of the line which fits the pulsed-field data is 0.85 times that of the continuous line, so the exponent a_p of Eq. (3) for the pulsed switching is 85% of the exponent a_c for the continuous switching process

$$a_p = 0.85 a_c \; . \tag{8}$$

This factor 0.85 may depend somewhat on the temperature and the electric field strength. Nevertheless, this result shows that the pulsed technique gives results similar to the continuous one and it permits us to use the pulsed method to study the switching process at high electric field strengths where the switching time is short.

V. VARIABLE-PULSE-WIDTH STUDIES

To check the effect of pulse width on the back-relaxation effect, a series of switching measurements was carried out at 6.7 kV/cm and 109 K where the switching time was 2 orders of magnitude shorter than for the case discussed in the preceding section. Pulses of 10, 50, and 100 ms were used, and the results are presented on Fig. 5 which plots $\log_{10} g(t)$ versus the number of pulses. The 10-ms data fit a straight line because they lie in the short-time exponential region, while most of the 50- and 100-ms points are in the power-law region. This is shown by replotting these data as a function of the integrated time t_N defined by Eq. (6), and the results appear on Fig. 6. We see from the figure that the 50- and 100-ms data plus the longest time 10-ms points fit the same straight line on the

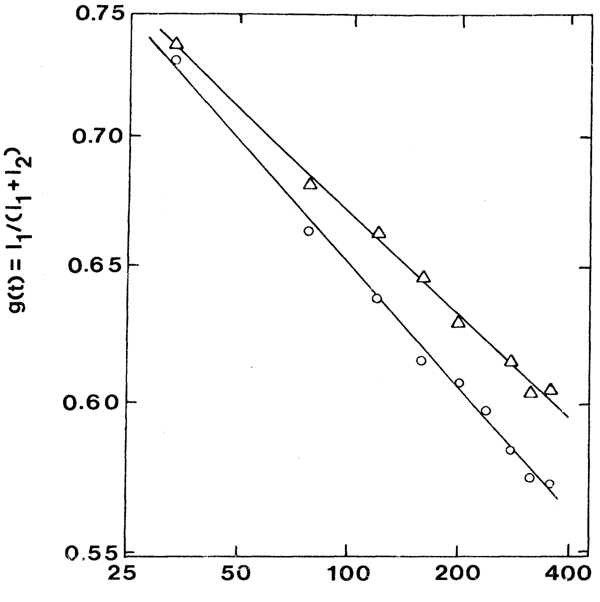

FIG. 4. Power-law decay curves for pulsed-field switching (△) and continuous-field switching (○) showing $\log_{10} g(t)$ vs $\log t$ ($E = 6.0$ kV/cm, $T = 88$ K).

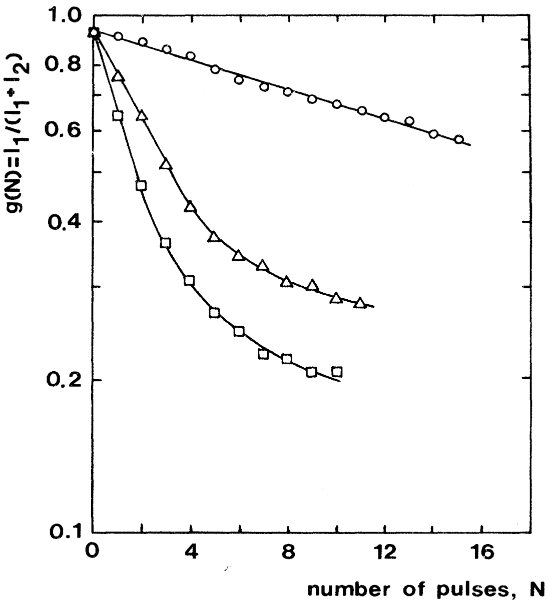

FIG. 5. Plot of $\log_{10} g(t)$ vs number of pulses using pulse widths of 10 ms (○), 50 ms (△), and 10 ms (□) for $E = 6.7$ kV/cm and $T = 109$ K.

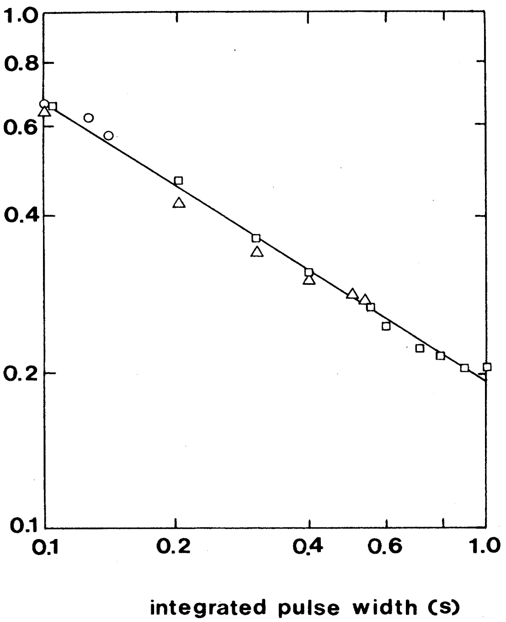

FIG. 6. Plot of $\log_{10} g(t)$ vs log of integrated pulse width using pulse widths of 50 ms (△) and 100 ms (□) for $E = 6.7$ kV/cm and $T = 109$ K.

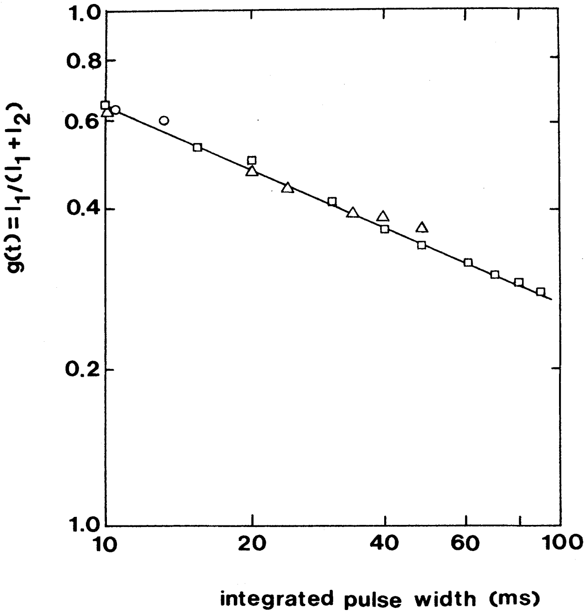

FIG. 8. Plot of $\log_{10} g(t)$ vs the integrated pulse width using widths of 1 ms (○), 5 ms (△), and 10 ms (□) for $E = 10$ kV/cm at $T = 109$ K.

log-log plot. This indicates that the back-relaxation effect differs very little for the switching conditions of these two pulses. The 10-ms data of Fig. 5 correspond to integrated times that are too short to plot on Fig. 6.

Data for the even higher electric field strengths of 10.0 and 13.3 kV/cm at the same temperature of 109 K are presented in Figs. 7—9. Under these conditions the switching times are, respectively, 4 and 5 orders of magnitude shorter than those determined in the preceding section. The 10-ms data obtained at 10 kV/cm lie on a straight line on the semilogarithmic plot of Fig. 7 because they are in the exponential region. The corresponding 5- and 10-ms data plus the two longest 1-ms points provide a good fit to a straight line when replotted on a log-log scale using integrated times for the abscissa, as indicated on Fig. 8. This means that they are in the power-law region of Eq. (3). The 13.3-kV/cm data obtained with 0.1- and 0.5-ms data plus the first three 5-ms points are linear on Fig. 9 indicative of the short-time exponential law. Since

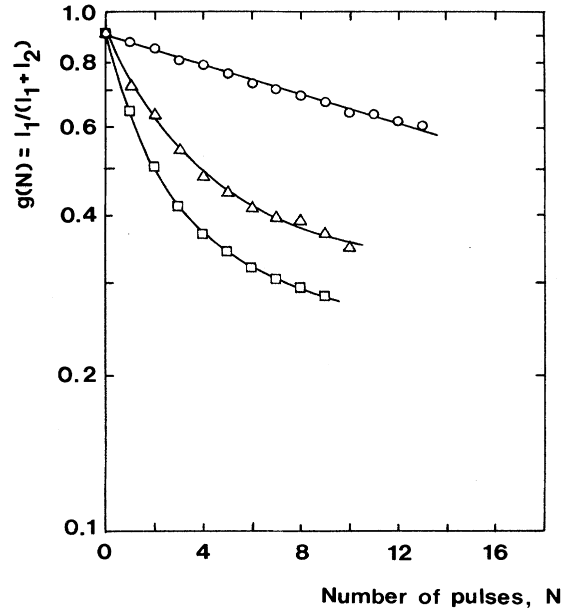

FIG. 7. Plot of $\log_{10} g(t)$ vs number of pulses using pulse widths of 1 ms (○), 5 ms (△), and 10 ms (□) for $E = 10$ kV/cm and $T = 109$ K.

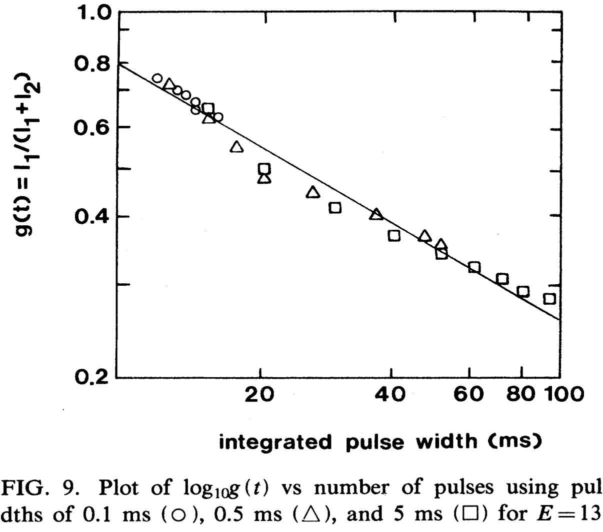

FIG. 9. Plot of $\log_{10} g(t)$ vs number of pulses using pulse widths of 0.1 ms (○), 0.5 ms (△), and 5 ms (□) for $E = 13.3$ kV/cm and $T = 109$ K.

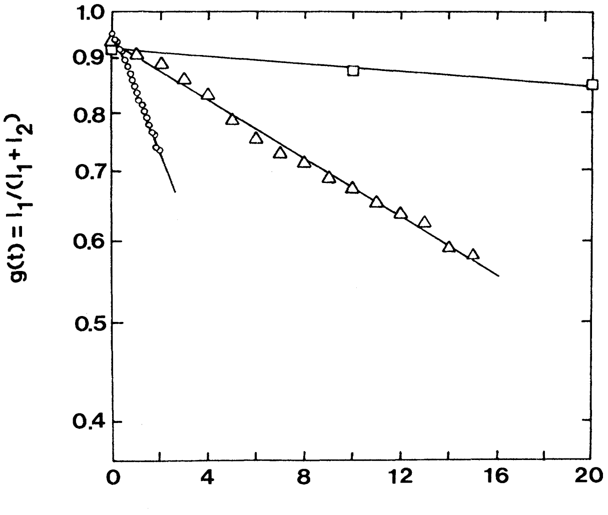

FIG. 10. Plot of $\log_{10}g(t)$ vs the integrated pulse width for the cases 6.7 kV/cm and 10 ms (□); 10.0 kV/cm and 1 ms (△) and 13.3 kV/cm and 0.1 ms (○), respectively, at $T=109$ K.

the switching time decreased as the electric field increased the pulse lengths had to be correspondingly decreased at higher electric field values. In order to cover both the short-time exponential and longer-time power-law regions three different pulse widths were employed for each case, as indicated in Figs. 5, 7, and 9.

As we mentioned previously, the shortest pulse-length data shown on the semilogarithmic plots of Figs. 5, 7, and 9 are linear, indicative of an exponential process corresponding to Eq. (2). These are compared on Fig. 10 by replotting them as a function of the integrated time defined by Eq. (6). The slopes of these lines give the values of b in Eq. (2) and when these slopes were plotted on a semilogarithmic graph against $1/E$ they fit a fairly good straight line with the slope γ,

$$\gamma \cong 50 \text{ kV/cm} . \tag{9}$$

Now we can rewrite b of Eq. (2) using γ as

$$b(E) \sim e^{-\gamma/E} . \tag{10}$$

Since only three points were used to determine this line this electric field dependence of b should be considered only a tentative suggestion. An expression of this type for the decay constant has been derived by other workers by assuming that most of the switching results are from a nucleation process.[1] It is, nevertheless, an interesting relation in view of the temperature $[a \sim \exp(-\beta/T)]$ and electric field $[a \sim \exp(\alpha E)]$ dependences found for the power-law exponent a of Eq. (3) in the previous work.

VI. CONCLUSIONS

We have developed a technique to measure ferroelectric domain switching times that are 3 orders of magnitude shorter than those measurable by earlier ESR techniques. The results were compared with the values obtained by the continuous method with good agreement. In addition, cavity disturbances were overcome and now measurements can be carried out for higher electric field strengths where the switching times are much shorter.

Our experiments show that for the highest field that we can apply, $E \cong 13.3$ kV/cm, the polarization function $g(t)$ follows an exponential law for short times, and up to 10 kV/cm it follows a power law at intermediate times. The power-law behavior may arise from a distribution of barriers[15] instead of a single barrier which produces an exponential decay.

ACKNOWLEDGMENT

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