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# High-throughput study of the static dielectric constant at high temperatures in oxide and fluoride cubic perovskites

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Using finite-temperature phonon calculations and the Lyddane-Sachs-Teller relations, we calculate *ab initio* the static dielectric constants of 78 semiconducting oxides and fluorides with cubic perovskite structures at 1000 K. We first compare our method with experimental measurements, and we find that it succeeds in describing the temperature dependence and the relative ordering of the static dielectric constant  $\epsilon_{DC}$  in the series of oxides BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, KTaO<sub>3</sub>. We show that the effects of anharmonicity on the ion-clamped dielectric constant, on Born charges, and on phonon lifetimes, can be neglected in the framework of our high-throughput study. Based on the high-temperature phonon spectra, we find that the dispersion of  $\epsilon_{DC}$  is one order of magnitude larger among oxides than fluorides at 1000 K. We display the correlograms of the dielectric constants with simple structural descriptors, and we point out that  $\epsilon_{DC}$  is actually well correlated with the infinite-frequency dielectric constant  $\epsilon_{\infty}$ , even in those materials with phase transitions in which  $\epsilon_{DC}$  is strongly temperature dependent.

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## I. INTRODUCTION

Capacitors for emerging power electronics—including those in avionics and automotive systems—must operate in specific temperature ranges, often outside ambient conditions. Perovskite materials have been widely used as ceramic dielectrics in capacitors, exhibiting different capacitances as a function of temperature. For example, BaTiO<sub>3</sub> has been used for ambient-condition applications since it has a Curie point close to room temperature, yielding high static dielectric constants. However, at higher temperatures, its lattice properties change, and capacitance drops. To optimize ceramic dielectrics for custom temperature ranges, it would be useful to perform high-throughput searches at finite temperatures. The static dielectric constant can be computed from first principles, e.g., using density-functional perturbation theory (DFPT) [1]. Such calculations have already been performed in a high-throughput fashion for a large number of materials [2,3]. Still, the approach is limited to ground-state properties, irrelevant for strongly anharmonic materials like perovskites, whose phonon spectrum and crystal structure vary significantly with temperature. In previous studies, this temperature dependence has been obtained via the electro-optic coefficients, which link the polarization with the refractive index [4–8]. The polarization can then be computed by using effective Hamiltonians [8,9] or with molecular dynamics [10,11].

Here, we use finite-temperature lattice dynamics calculations to compute the static dielectric constant of 78 oxide

and fluoride cubic perovskites at high temperature, directly from the temperature-dependent phonon spectra. Our high-throughput methodology is particularly interesting for the search of new materials that could operate under specific conditions. In particular, with the recent development of sensors and electronics designed to operate close to the engine of airplanes or vehicles, the industry would benefit from compounds that are more adapted to high-temperature conditions, especially for use in capacitors [12].

We first describe the method, which is based on the Lyddane-Sachs-Teller (LST) relations [13,14] combined with temperature-dependent lattice dynamics calculations [15], and demonstrate its reliability by computing the dielectric constants of BaTiO<sub>3</sub>, SrTiO<sub>3</sub>, and KTaO<sub>3</sub>. We also evaluate the impact of the modifications of the Born charges and of the electronic dielectric constant due to thermal effects on the value of the static dielectric constant, as well as the effect of lifetime broadening, in the case of SrTiO<sub>3</sub>. In a second part, we build on the high-throughput finite-temperature phonon spectra that we obtained in our previous work [16] to study the dielectric constant of oxide and fluoride cubic perovskites at high temperature. We find that oxides present a larger diversity of values, and that the ion-clamped value of the dielectric constant is unexpectedly well correlated with the high-temperature dielectric properties.

## II. AB INITIO CALCULATIONS OF THE STATIC DIELECTRIC CONSTANT AT FINITE TEMPERATURE

The ionic contribution to the relative permittivity can be obtained from the generalized LST relations [14]. The crystal

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is isotropic in cubic perovskites, leading to

$$\frac{\epsilon_{DC}}{\epsilon_{\infty}} = \prod_j \left( \frac{\omega_{Lj}}{\omega_{Tj}} \right)^2, \quad (1)$$

with  $\epsilon_{DC}$  the static dielectric constant,  $\epsilon_{\infty}$  the ion-clamped dielectric constant, and  $\omega_L$  and  $\omega_T$  the long-wavelength longitudinal and transverse optical frequencies. The splitting between longitudinal (LO) and transverse (TO) modes, along with  $\epsilon_{\infty}$ , can be obtained from DFPT as implemented for instance in VASP [17]. To obtain effective second-order interatomic force constants at finite temperature including anharmonic effects, we use the method presented in Ref. [15], which uses a regression analysis of forces from density-functional theory coupled with a harmonic model of the quantum canonical ensemble. This is done in an iterative way to achieve self-consistency of the phonon spectrum. The value of  $\epsilon_{\infty}$  is taken from ground-state calculations (see discussion below). LO-TO splitting is obtained from the nonanalytical correction for  $q \rightarrow 0$  using ground-state Born charges, as implemented in PHONOPY [18,19]. In practice, we adiabatically turn on the nonanalytical correction in order to track the different pairs of modes that are relevant in Eq. (1).

We first perform the calculations for a series of three oxides, BaTiO<sub>3</sub> (at 400, 700, and 1000 K), SrTiO<sub>3</sub> (at 300, 500, and 1000 K), and KTaO<sub>3</sub> (at 100, 500, and 1000 K, including also spin-orbit coupling), using the PBEsol functional, a  $4 \times 4 \times 4$  supercell, and a  $30 \times 30 \times 30$  phonon wave-vector grid. For other temperatures, we simply interpolate the force constants linearly: under the approximation that the eigenvectors are unchanged, the soft mode would then follow a Curie law,

$$\omega^2 = A(T - T_c). \quad (2)$$

This interpolation also allows us to estimate the Curie temperature of those compounds. We obtain for BaTiO<sub>3</sub>:  $T_c \approx 270$  K, for SrTiO<sub>3</sub>:  $T_c \approx 140$  K, and for KTaO<sub>3</sub>:  $T_c \approx 80$  K. This difference of about 100 K compared with the experimental values corresponds to very tiny energy scales (less than 10 meV) and is comparable to what has been found in other studies [20].

Our results for the static dielectric constant are displayed in Fig. 1 and compared with the experimental data from Rupprecht and Bell [21]. As expected from the transition temperatures, there is a shift of the curve of about 150 K for BaTiO<sub>3</sub> compared with the experiment, and a difference in the temperature dependence, reflecting the limitations of the method. Notably, this kind of calculation can be sensitive to the choice of the exchange and correlation functional, already for the ground-state properties [2]. Nevertheless, the order of magnitude and the respective ordering of the values are correct.

The Born charges and electronic dielectric constant  $\epsilon_{\infty}$  are also modified by temperature, due to thermal expansion and to ionic displacements [8,22]. Furthermore, the LST relations can be generalized to account, for instance, for the effect of lifetime broadening [23,24]. We now evaluate the impact of those effects on the value of the static dielectric constant, in the case of SrTiO<sub>3</sub>. Table I shows the computed thermal average of the Born charges and of  $\epsilon_{\infty}$  on three different

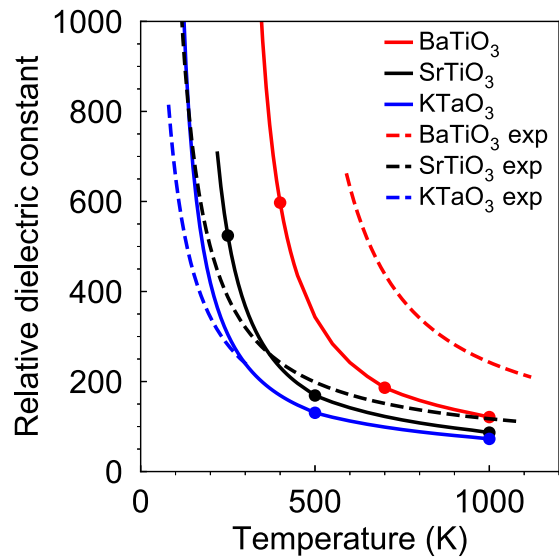


FIG. 1. A comparison between the static dielectric constants of BaTiO<sub>3</sub> (red), SrTiO<sub>3</sub> (black), and KTaO<sub>3</sub> (blue), as calculated *ab initio* (dots, the value at 100 K for KTaO<sub>3</sub> is 1794, out of scale) and using a linear interpolation of the interatomic force constants for other temperatures (full lines), and the fitted expressions  $\epsilon = \epsilon_L + C/(T - T_c)$  obtained from experimental measurements in Rupprecht and Bell [21] (dashed lines).

configurations of our  $4 \times 4 \times 4$  supercell with a  $2 \times 2 \times 2$  grid. We observed that  $\epsilon_{\infty}$  is decreased by anharmonic effects, in agreement with Ref. [8], whereas thermal expansion actually increases  $\epsilon_{\infty}$ . If we now include these effects into  $\epsilon_{DC}$  using the corresponding nonanalytical correction, we find that, at 1000 K,  $\epsilon_{DC}$  is corrected to 76.6 instead of 86.5. The main correction comes from the difference in the splitting of the highest optical mode due to the thermally averaged Born charges. For the generalized LST relations, we evaluate the expression of Barker [23]:

$$\frac{\epsilon_{DC}}{\epsilon_{\infty}} = \prod_j \left( \frac{|\omega_{Lj}|}{\omega_{Tj}} \right)^2, \quad (3)$$

where  $\omega_L = \text{Re}\omega_L - i\gamma/2$ . We use the previously calculated value as the real part, and  $\gamma$  is evaluated from the lifetime of the corresponding phonon mode computed at the  $\Gamma$  point with almaBTE [25] on a  $15 \times 15 \times 15$  phonon wave-vector grid, using the temperature-dependent second- and third-order force constants. Table II shows the real and imaginary parts for all LO modes in SrTiO<sub>3</sub>. This translates into a correction of the static dielectric constant from 86.5 to 87.0 at 1000 K. Thus those two effects account for a modification of about 10% of  $\epsilon_{DC}$ , which is similar to the potential error in the estimation of

TABLE I. Thermal average of  $\epsilon_{\infty}$  and of the Born effective charges in SrTiO<sub>3</sub> at 1000 K.

	$\epsilon_{\infty}$	$Z_{\text{Sr}}^*$	$Z_{\text{Ti}}^*$	$Z_{\text{O}_{\perp}}^*$	$Z_{\text{O}_{\parallel}}^*$
Ground state	6.36	2.55	7.35	-2.04	-5.82
1000 K	6.27	2.54	6.76	-1.94	-5.41

TABLE II. Real part (rad/ps), lifetime (ps) and imaginary part (rad/ps) of the LO modes in SrTiO<sub>3</sub> at 1000 K.

	Re $\omega_{L_1}$	$\tau_{L_1}$	Im $\omega_{L_1}$	Re $\omega_{L_2}$	$\tau_{L_2}$	Im $\omega_{L_2}$	Re $\omega_{L_3}$	$\tau_{L_3}$	Im $\omega_{L_3}$
1000 K	32.4	0.30	1.7	84.2	0.11	4.4	145.2	0.15	3.4

the phonon frequencies and of the transition temperature, in particular if we compare between different functionals. This picture might be different close to displacive phase transitions, where lifetimes can typically become shorter and ionic fluctuations more important. Since we are here mostly interested in high-temperature properties and in global trends over the whole family of fluoride and oxide cubic perovskites, we choose to neglect those effects in the rest of the article.

### III. HIGH-THROUGHPUT RESULTS

We now apply the same methodology to the set of 92 oxide and fluoride perovskites that we identified as mechanically stable at 1000 K in our previous work [16]. Because of the reduced precision (notably, a smaller  $2 \times 2 \times 2$  supercell) and of the high-throughput methodology, the absolute values are expected to be less accurate. Still, the general trends can give useful physical insight. We recomputed the phonon spectra of all compounds using the latest version of our code, which has been made public recently [26]. We also used the PBEsol functional that is more adapted to most of these compounds, except from those including Fe that were then found to be metals and excluded from our set. Spin-orbit coupling was also taken into account for all compounds containing atoms heavier than Hf. This gave us a new total of 78 oxide and fluoride perovskites mechanically stable in the cubic phase at 1000 K.

We list the stable compounds and their static dielectric constants at 1000 K,  $\epsilon_{1000}$ —and when they are also mechanically stable at 300 K,  $\epsilon_{300}$ —in Table III. We highlight in blue 35

perovskites that have been reported experimentally in the ideal cubic structure, and in red nine compounds that are reported only in a nonperovskite form (see references in Ref. [16]). On top of the list of the reliable materials, we see that niobates and, in particular, KNbO<sub>3</sub> appear to be the most promising compounds for high-temperature applications, along with PbTiO<sub>3</sub>. These compounds are actually already used on an industrial scale for this property.

Figure 2 illustrates the distribution of compounds as a function of the dielectric constant, both for the ion-clamped (with electronic contribution only) and for the static one at 1000 K, based on logspline density estimation as implemented in R [27]. As can be seen already in Table III, the effect of the lattice screening is sometimes much stronger in oxides and, as a consequence, there is a larger dispersion of the values of the static dielectric constant than for the fluorides. We also remark that the high-frequency dielectric properties reflect the fact that oxygen is more polarizable than fluorine, and this stronger polarizability might be linked to the stronger reaction of the lattice.

We delve into the question by computing the Spearman correlograms of the static dielectric constant at 1000 K  $\epsilon_{DC}$  with  $\epsilon_{\infty}$ , and with several simple descriptors of the cubic perovskite structure  $ABX_3$ : the masses of atoms  $A$  and  $B$ , their position in the periodic table, their electronegativity and Pettifor scales, their ionic radii, the lattice parameter of the compound and its electronic band gap. This is shown in Fig. 3, for fluorides and for oxides separately. We indeed find that there is a strong correlation between the high-frequency and the static dielectric constants, which was not obvious since the transition temperature plays a crucial role, even if  $\epsilon_{\infty}$  is a factor in Eq. (1). We note that we have obtained similar correlograms when we computed the dielectric constants using the phonon spectra with a different exchange-correlation functional from our previous work [16].

Interestingly, the ionic radius of atom  $A$  and the electronic band gap have significant negative correlation with the static

TABLE III. List of the calculated relative static dielectric constants of cubic perovskites that were found to be mechanically stable at 1000 and 300 K. We highlight in blue the compounds that are experimentally reported in the ideal cubic perovskite structure, and in red those that are reported only in nonperovskite structures (same as in Ref. [16]).

	$\epsilon_{1000}$	$\epsilon_{300}$		$\epsilon_{1000}$	$\epsilon_{300}$		$\epsilon_{1000}$	$\epsilon_{300}$		$\epsilon_{1000}$	$\epsilon_{300}$		$\epsilon_{1000}$	$\epsilon_{300}$
TiNbO <sub>3</sub>	190	2954	BeScF <sub>3</sub>	58	105	InCdF <sub>3</sub>	22	114	TlHgF <sub>3</sub>	17	33	RbSrF <sub>3</sub>	8	
PbTiO <sub>3</sub>	190		AgTaO <sub>3</sub>	57		ZnInF <sub>3</sub>	22	32	TlCdF <sub>3</sub>	16	32	CsZnF <sub>3</sub>	8	9
GaTaO <sub>3</sub>	155		PbSiO <sub>3</sub>	51	61	ZnScF <sub>3</sub>	22	30	ZnYF <sub>3</sub>	15	18	CsSrF <sub>3</sub>	8	12
KNbO <sub>3</sub>	122	835	CdSbF <sub>3</sub>	42		InMgF <sub>3</sub>	20	33	TlZnF <sub>3</sub>	15	18	KCaF <sub>3</sub>	8	12
NaNbO <sub>3</sub>	116		TlSnF <sub>3</sub>	35	136	ZnAlF <sub>3</sub>	20	23	NaBeF <sub>3</sub>	14	25	BaSiO <sub>3</sub>	8	
SnSiO <sub>3</sub>	116	443	BaZrO <sub>3</sub>	34	45	ZnBiF <sub>3</sub>	20	23	KPbF <sub>3</sub>	14		KCdF <sub>3</sub>	8	
AgNbO <sub>3</sub>	115		SrHfO <sub>3</sub>	31		HgScF <sub>3</sub>	19	23	HgYF <sub>3</sub>	13	15	RbZnF <sub>3</sub>	7	8
PbHfO <sub>3</sub>	111		RbSnF <sub>3</sub>	30	217	PdYF <sub>3</sub>	19		RbPbF <sub>3</sub>	13	16	RbCaF <sub>3</sub>	7	10
BaTiO <sub>3</sub>	105	612	GaZnF <sub>3</sub>	29	95	TlPbF <sub>3</sub>	18		TlMgF <sub>3</sub>	13	15	CsCaF <sub>3</sub>	7	8
BeAlF <sub>3</sub>	99	64	BeYF <sub>3</sub>	28	37	SrSiO <sub>3</sub>	18	19	BaLiF <sub>3</sub>	12	13	KZnF <sub>3</sub>	7	8
AlMgF <sub>3</sub>	97		BaHfO <sub>3</sub>	27	34	CdYF <sub>3</sub>	18	25	AgZnF <sub>3</sub>	10	11	CsCdF <sub>3</sub>	7	8
TlTaO <sub>3</sub>	95	465	KSnF <sub>3</sub>	26		HgBiF <sub>3</sub>	18	24	CsBaF <sub>3</sub>	10		RbCdF <sub>3</sub>	7	9
SrTiO <sub>3</sub>	81	221	GaMgF <sub>3</sub>	26	76	CaSiO <sub>3</sub>	18		RbHgF <sub>3</sub>	9	12	KMgF <sub>3</sub>	6	6
RbTaO <sub>3</sub>	78	249	XeBiF <sub>3</sub>	24	121	HgInF <sub>3</sub>	18	24	KHgF <sub>3</sub>	9		RbMgF <sub>3</sub>	6	6
AlZnF <sub>3</sub>	63		CdBiF <sub>3</sub>	24	47	XeScF <sub>3</sub>	17	30	CsHgF <sub>3</sub>	9	11			
NaTaO <sub>3</sub>	58		InZnF <sub>3</sub>	23	46	TlCaF <sub>3</sub>	17	39	AgMgF <sub>3</sub>	9	16			

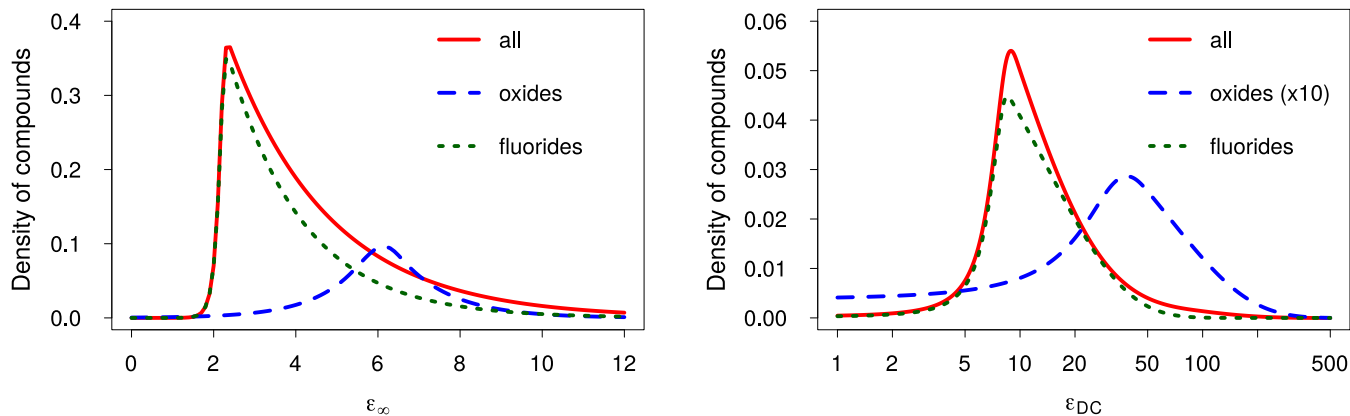


FIG. 2. Distribution of compounds as a function of the static dielectric constant including only the electronic contribution ( $\epsilon_\infty$ , left) and also the lattice contribution at 1000 K ( $\epsilon_{DC}$ , right). The red curve corresponds to the distribution for all mechanically stable compounds. The green curve corresponds to the distribution for fluorides only. The blue curve corresponds to the distribution for oxides only (the scale has been multiplied by 10 on the right graph).

dielectric constant. This has indeed been observed empirically based on experimental data [28]. Since the stability of the cubic phase is known to be intimately linked with geometric factors [29], it is likely that the ionic radius of atom  $A$  influences both the electronic polarizability of the compound and its transition temperature. A consequence of this finding is that, if one wishes only to know the order of the static dielectric constant between perovskites in the same cubic phase, the high-frequency limit is actually a sufficiently good indication. This is valid for instance for the series studied above,  $\text{BaTiO}_3$ ,  $\text{SrTiO}_3$ , and  $\text{KTaO}_3$ . It also explains the good Spearman correlation that was found in Ref. [2] between calculated values using DFPT at the ground state and experimental measurements at room temperature, despite the occasional strong discrepancies in the order of magnitude for perovskite compounds.

#### IV. CONCLUSION

In conclusion, we have shown that the temperature dependence of the static dielectric constant can be calculated from first principles with reasonable agreement with experiment over a large temperature range, simply taking into account the temperature dependence of the phonon spectrum and ground-state properties. In particular, we have evaluated quantitatively the effects of anharmonicity on the ion-clamped dielectric constant and Born charges, as well as the inclusion of lifetime effects in the generalized Lyddane-Sachs-Teller relations. Then, we have conducted a high-throughput study of the high-temperature static dielectric constant in oxide and fluoride cubic perovskites. We observed that the rank of the static dielectric constant at high temperature is already well described by the ion-clamped value, and mostly linked to the ionic radius of atom  $A$  of the perovskite  $ABX_3$ .

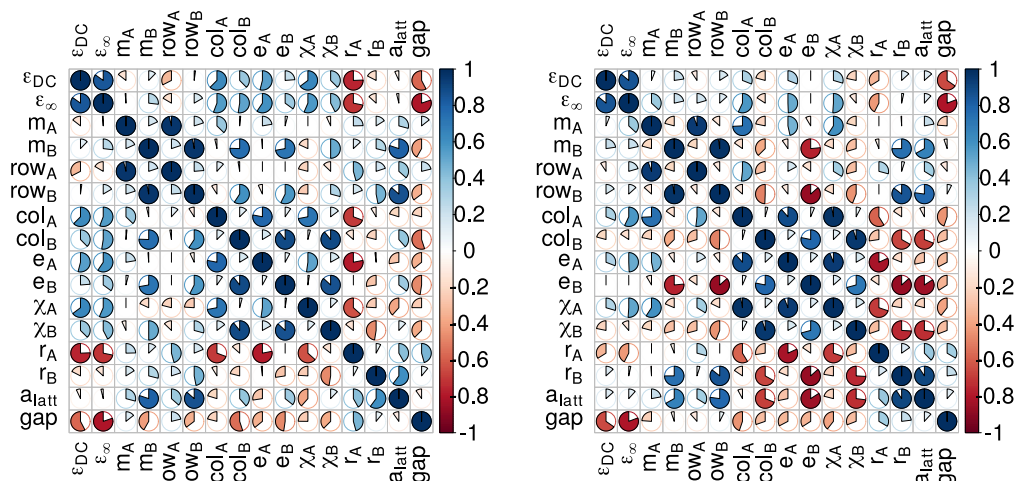


FIG. 3. Spearman correlograms between the static dielectric constant at 1000 K  $\epsilon_{DC}$ , the infinite frequency (static electronic) dielectric constant  $\epsilon_\infty$ , the masses  $m_A$  and  $m_B$  of atoms at sites  $A$  and  $B$  of the perovskite  $ABX_3$ , their position in the periodic table, their electronegativity  $e_A$ ,  $e_B$ , their Pettifor scale  $\chi_A$ ,  $\chi_B$ , their ionic radius  $r_A$ ,  $r_B$ , the lattice parameter of the compound  $a_{\text{latt}}$  and its electronic band gap, for mechanically stable fluorides (left) and oxides (right).

These findings bring coherence to the puzzling correlations between ground-state calculations and temperature-dependent experimental measurements that have been found in previous high-throughput studies of the dielectric constant. We hope that our study will motivate a high-throughput computational search of dielectric materials for specific applications in harsh temperature conditions.

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