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Lattice, elastic, polarization, and electrostrictive properties of BaTiO₃ from first-principles

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Predicting the domain structures and properties in both bulk single crystal and thin film ferroelectrics using the phase-field approach requires the knowledge of fundamental mechanical, electrical, and electromechanical coupling properties of a single-domain state. In this work, the elastic properties and structural parameters of cubic single crystals as well as tetragonal, orthorhombic, and rhombohedral BaTiO₃ single domain states are obtained using first-principles calculations under the local density approximation. The calculated lattice constants, bulk modulus, and elastic constants are in good agreement with experiments for both the cubic paraelectric phase and the low-temperature ferroelectric phases. Spontaneous polarizations for all three ferroelectric phases and the electrostrictive coefficients of cubic BaTiO₃ are also computed using the Berry's phase approach, and the results agree well with existing experimentally measured values. © *2010 American Institute of Physics.* [doi:10.1063/1.3462441]

I. INTRODUCTION

BaTiO₃ is a well known classic ferroelectric that has a wide range of applications from dielectric capacitors to nonlinear optic devices.[1] At high temperatures, BaTiO₃ is paraelectric with a cubic structure. When the temperature decreases to below 125 °C, paraelectric cubic BaTiO₃ transforms to a ferroelectric tetragonal phase. Between 125 and 8 °C, the ferroelectric BaTiO₃ in tetragonal structure is stable. In the range of 8–(−71) °C, its stable structure is orthorhombic. Finally, below −71 °C, BaTiO₃ is a rhombohedral ferroelectric.[2] The structures and properties of BaTiO₃ have been extensively studied for more than half a century after the discovery of piezoelectricity and ferroelectricity in this system.

The strain effect on phase transition and domain structures in thin films in BaTiO₃ is largely determined by the elastic constants and electrostrictive coefficients.[3,4] Despite the extensive interest in this material, surprisingly, there are only a scarce of data available for the elastic properties,[5,6] and electrostrictive coefficients. As a matter of fact, due to the difficulty of obtaining the single crystal rhombohedral BaTiO₃, there are no experimental data available on its elastic constants. In this work, we calculated the electrostrictive coefficients of the cubic phase by using the first-principle method under the Berry's phase approach.[7] We also calculated the elastic constants, bulk modulus, and lattice constants of the BaTiO₃ in different phases, including the cubic phase, tetragonal phase, orthorhombic phase, and rhombohedral phase, by using the first-principle method.

II. METHODS

All calculations were performed using the ABINIT package in GNU General Publication License (GPL)[8,9] with the local density approximation (LDA) and projector-augmented-wave (PAW) potentials.[10,11] The calculations were carried out using a plane-wave energy cutoff of 50 hartree. A $6 \times 6 \times 6$ **k**-point mesh was used to yield convergence. BaTiO₃ has the classical pervoskite structure of ABO₃ (Fig. 1). The unit cell contains five atoms for the cubic, tetragonal, and rhombohedral BaTiO₃, and ten atoms or two formula units for orthorhombic one.

Using the method of density-function perturbation theory,[12–15] many response properties of materials in which electronic correlations are not too strong can be computed directly without the need for multiple ground-state calculations.[16,17] Three kinds of perturbations, including strain, electric-field, and atomic-displacement were added to the ABINIT package recently,[18] and hence the elastic constants, piezoelectric coefficients, dielectric constants, Born effective charges can be obtained by treating different perturbations. In this paper, the elastic constants are computed directly by treating strain as a perturbation. It is well known that LDA usually underestimates the equilibrium lattice constants compared with experimental data.[19] Therefore, the initial structural relaxation was carried out by constraining the cell volume at the experimental lattice parameters.
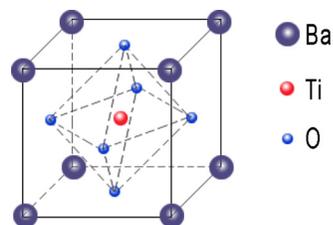
FIG. 1. (Color online) The crystal structure of cubic BaTiO₃. The relative atom positions of Ba and Ti in the unit cell are (0 0 0) and (0.5 0.5 0.5), respectively. And the O atoms take up the relative positions of (0.5 0.5 0), (0.5 0 0.5), and (0 0.5 0.5).

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TABLE I. The relaxed structures, bulk modulus, and the spontaneous polarization of BaTiO$_3$ of the cubic, tetragonal, orthorhombic, and rhombohedral phases in our work, compared with the experimental data and prior theoretical results in the literature.

Phase	Source	Lattice constants a (Å)				Bulk modulus B_0 (GPa)
Cubic	Our work	4.000				172
	Expt.	4.000 (Ref. 22)				162 (Ref. 22)
	Theory	4.030, (Ref. 23) 4.006, (Ref. 24), 3.943 (Ref. 25)				175, (Ref. 23) 168, (Ref. 24), 189 (Ref. 25)
		a (Å)	c (Å)	P_s (μC/cm^2)		B (GPa)
Tetragonal	Our work	3.966	4.035	29.0		147
	Expt.	3.992 (Ref. 26)	4.036 (Ref. 26)	26 (Ref. 27)		
	Theory	3.943 (Ref. 28)	3.994 (Ref. 28)	22.9 (Ref. 28)		98.6 (Ref. 24)
		a (Å)	b (Å)	c (Å)	P_s (μC/cm^2)	B (GPa)
Orthorhombic	Our work	5.704	3.963	5.683	33.0	135
	Expt.	5.682 (Ref. 29)	3.990 (Ref. 29)	5.669 (Ref. 29)		97.54 (Ref. 24)
		a (Å)	θ	P_s (μC/cm^2)		B (GPa)
Rhombohedral	Our work	4.000	89°56′	35.0		126
	Expt.	3.998 (Ref. 30)	89°52.5′ (Ref. 30)	34 ± 7 (Ref. 30)		
	Expt.	4.000 (Ref. 31)	89°54′ (Ref. 31)	34 ± 7 (Ref. 31)		
	Theory	4.000 (Ref. 21)	89°51′ (Ref. 21)			103.5 (Ref. 24)

To obtain the electrostrictive coefficients of cubic BaTiO$_3$, we calculated polarizations of one unit cell under different strains. Given that $\varepsilon_i(\vec{P})$ represents strain functions related with polarizations, where $i = 1, 2, 3, 4, 5, 6$ label the six strains in Voigt notation. Expend $\varepsilon_i(\vec{P})$ around zero polarization we get the following expression:

$$\varepsilon_i(\vec{P}) = \varepsilon_i(0) + \frac{\partial \varepsilon_i}{\partial P_j} P_j + \frac{1}{2!} \frac{\partial^2 \varepsilon_i}{\partial P_\alpha \partial P_\beta} P_\alpha P_\beta + \cdots. \quad (1)$$

The first item gives strain at zero polarization and it should be zero for cubic phase. The second item represents converse piezoelectric effect and it should be zero as well for center-symmetry cubic phase. And the third item reflects the electrostrictive response. Neglecting the higher order items, formula (2) is obtained.

$$\varepsilon_i = \frac{\partial^2 \varepsilon_i}{\partial P_\alpha \partial P_\beta} P_\alpha P_\beta = Q_{i\alpha\beta} P_\alpha P_\beta, \quad (2)$$

where $Q_{i\alpha\beta}$ represents the electrostrictive coefficients. Similar to elastic constants tensors, the electrostrictive coefficient tensor of cubic BaTiO$_3$ has only three independent components because of its symmetry, i.e., Q_{11}, Q_{12}, and Q_{44}. Therefore, the electrostrictive response of cubic BaTiO$_3$ can be described as follows:

$$\varepsilon_1 = Q_{11}P_1^2 + Q_{12}(P_2^2 + P_3^2), \quad (3)$$

$$\varepsilon_2 = Q_{11}P_2^2 + Q_{12}(P_1^2 + P_3^2), \quad (4)$$

$$\varepsilon_3 = Q_{11}P_3^2 + Q_{12}(P_1^2 + P_2^2), \quad (5)$$

$$\varepsilon_4 = Q_{44}P_2P_3, \quad (6)$$

$$\varepsilon_5 = Q_{44}P_1P_3, \quad (7)$$

$$\varepsilon_6 = Q_{44}P_1P_2. \quad (8)$$

In our calculation, strains and polarizations were controlled by moving Ti atom, and other degrees of freedom (including both atomic positions and cell shape) are optimized, while keeping the cell volume fixed at the equilibrium quantity of cubic phase. The polarizations were computed from the optimized geometric structure using the Berry's phase approach.[7]

III. RESULTS

The lattice constants and bulk modulus of BaTiO$_3$ in cubic, tetragonal, orthorhombic, and rhombohedral phases are calculated, and the results are summarized in Table I. Experimental data and prior theoretical results by others are included for comparison. All unit cells are relaxed in the calculation. The approximate bulk moduli are obtained from the relationship with elastic constants according to formula (12) cited from Ref. 20. From Table I we can see that our results are in good agreement with the corresponding experimental data. As mentioned in the introduction, there are no experimental data on the bulk modulus and elastic constants for the rhombohedral phase, and hence only previous theoretic calculation by Wu *et al.*[21] was given for comparison.

To calculate all the independent elastic constants of different phases, three calculation steps were carried out by LDA in each phase. First, relaxation at constant-volume

TABLE II. The calculated elastic constants of BaTiO$_3$ of the cubic, tetragonal, orthorhombic, and rhombohedral phases in our work, compared with the experimental data in the given references.

Phase	Source	Elastic constants (GPa)								
Cubic		C_{11}		C_{12}		C_{44}				
	Our work	305		106		128				
	Expt. (Ref. 30)	255		82		108				
Tetragonal		C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}			
	Our work	300	109	90	149	124	128			
	Expt. (Ref. 32)	275	179	152	165	54.4	113			
	Expt. (Ref. 33)	222	134	111	151	61.1	134			
Orthorhombic		C_{11}	C_{22}	C_{33}	C_{44}	C_{55}	C_{66}	C_{12}	C_{13}	C_{23}
	Our work	150	312	150	135	118	134	100	102	100
	Expt. (Ref. 34)	218	270	218	84.0	33.1	73.5	154	109	154
Rhombohedral		C_{11}	C_{12}	C_{13}	C_{14}	C_{33}	C_{44}	C_{65}	C_{66}	
	Our work	276	79	41	45	263	47	45	98	
	Theory (Ref. 31)	277	79	41	45	264	48	45	99	

adopted from the experimental structure was performed to get the equilibrium states, including the atomic positions and cell shape. Second, response function calculations were carried out to get the first derivatives of occupied wave functions with respect to perturbations of strain, atomic displacement, and electric field. Then the computed occupied wave functions were used to calculate the second derivative response-function tensors.[21] And finally, ANADDB utility was used to analyze the second derivative database from the second step to get the elastic constants. Both elastic constants in clamped-ions and relaxed-ions cases could be obtained from the final step. And only the relaxed-ions elastic constants, which are physically meaningful, of different phases are summarized in Table II. The results are compared with the experimental values and previous theoretical data from the corresponding reference. Our calculation results are in good agreement with the experimental data.

In the calculation of electrostrictive coefficients, we first calculated the optimized structures and spontaneous polarization P_s by LDA+PAW for the four phases. The calculated results are listed in Table I. Comparisons with the experimental data and other theoretical calculations are also given in the same table. And the calculated electrostrictive coefficients and their comparisons with experimental data are listed in Table III.

IV. DISCUSSION

We discuss the mechanical stability conditions of the cubic, tetragonal, orthorhombic, and rhombohedral symmetries, so as to further validate our calculated results.

TABLE III. Our calculated electrostrictive coefficients of cubic BaTiO$_3$, compared with the experimental data from given references.

	Q_{11} (m^4 C^{-2})	Q_{12} (m^4 C^{-2})	Q_{44} (m^4 C^{-2})
Expt. (Ref. 35)	0.1	−0.034	0.029
Expt. (Ref. 36)	0.11	−0.0452	0.0289
Our work	0.115	−0.033	0.041

The requirement of the mechanical stability in a cubic crystal leads to the following restrictions on the elastic constants:[23,37]

$$(C_{11} - C_{12}) > 0, \quad C_{11} > 0, \quad C_{44} > 0, \quad (C_{11} + 2C_{12}) > 0. \tag{9}$$

These conditions also lead to a restriction on the magnitude of the bulk modulus B,[23,37] i.e.,

$$C_{12} < B < C_{11}. \tag{10}$$

From Table II we can see that the calculated elastic constants of cubic BaTiO$_3$ in our work obey these mechanical stability conditions, including the fact that B must be larger than C_{12} and smaller than C_{11}.

In a tetragonal symmetry, the requirement that the crystal be stable against any homogenous elastic deformation places restrictions on the elastic constants, just as in the cubic case. For tetragonal crystals these mechanical stability restrictions are as follows:[23]

$$(C_{11} - C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0,$$

$$C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0,$$

$$(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0. \tag{11}$$

The elastic constants of our calculation in Table II satisfy all the conditions in formula (12). Particularly, C_{12} is smaller than C_{11}, and C_{13} is smaller than the average of C_{11} and C_{33}. The stability conditions again lead to restriction on the magnitude of B under zero-strain condition. We use a relationship between the bulk modulus and the elastic constants in the tetragonal phase from Ref. 20, that is:

$$B_0 = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}]. \tag{12}$$

As C_{22} equals C_{11}, C_{23} equals C_{13} in the tetragonal phase, so B_0 becomes:

$$B_0 = \frac{1}{9}(2C_{11} + 2C_{12} + 4C_{13} + C_{33}). \tag{13}$$

Combining conditions (11) and formula (13), $(1/3)(C_{12} + 2C_{13}) < B_0 < (1/3)(C_{11} + 2C_{33})$ can be easily obtained.[20] It implies that bulk modulus must be larger than the weighted average of C_{12} and C_{13}. In our work, under zero-strain condition, according to formula (13), B_0 equals 147 GPa, $(1/3)(2C_{11} + C_{33})$ equals 249 GPa, and $(1/3)(C_{12} + 2C_{13})$ equals 96 GPa, thus the condition $(1/3)(C_{12} + 2C_{13}) < B_0 < (1/3)(C_{11} + 2C_{33})$ is satisfied.

Considering the mechanical stability at zero stress in the orthorhombic phase, the elastic constants must satisfy the following conditions:[38,39]

$$(C_{11} + C_{22} - 2C_{12}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0,$$

$$(C_{22} + C_{33} - 2C_{23}) > 0,$$

$$C_{11} > 0, \quad C_{22} > 0, \quad C_{33} > 0, \quad C_{44} > 0,$$

$$C_{55} > 0, \quad C_{66} > 0,$$

$$(C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0 \tag{14}$$

And the restrictions on the magnitude of B_0 is given as follow:[38,39]

$$\frac{1}{3}(C_{12} + C_{13} + C_{23}) < B_0 < \frac{1}{3}(C_{11} + C_{22} + C_{33}). \tag{15}$$

From Table II we can see that the elastic constants satisfy all the stability conditions, and we can get $(1/3)(C_{12} + C_{13} + C_{23}) = 101$, $(1/3)(C_{11} + C_{22} + C_{33}) = 204$, $B_0 = 135$. It is easy to find that the formula (15) is agreed well.

The mechanical stability conditions of rhombohedral phase require its elastic constant tensors to meet the following expressions:

$$C_{11} + C_{12} > 0, \quad C_{33} > 0, \quad (C_{11} + C_{12})C_{33} > 2C_{13}^2,$$

$$C_{11} - C_{12} > 0, \quad C_{44} > 0, \quad (C_{11} - C_{12})C_{44} > 2C_{14}^2. \tag{16}$$

We can see that all the elastic constants in Table II satisfy all the mechanical stability conditions very well. We evaluated the bulk modulus B_0 according to the following derivation.

As $(C_{11} + C_{12})C_{33} > 2C_{13}^2$, $C_{11} + C_{12} > 0$ in stability conditions (16), we can get:

$$C_{33} > \frac{2C_{13}^2}{C_{11} + C_{12}} > 0. \tag{17}$$

Substituting $0 < C_{11} + C_{12} < 2C_{11}$ into (17) we obtain:

$$C_{33} > \frac{C_{13}^2}{C_{11}} > 0. \tag{18}$$

As we know, for positive C_{11} and C_{33}, there must be:

$$C_{11} + C_{33} \geq 2\sqrt{C_{11} \cdot C_{33}}. \tag{19}$$

Substituting formula (18) into formula (19) we can educe:

$$C_{11} + C_{33} \geq 2\sqrt{C_{11}C_{33}} > 2\sqrt{C_{11}\frac{C_{13}^2}{C_{11}}} = 2\sqrt{C_{13}^2} = 2|C_{13}|$$

$$\geq 2C_{13}. \tag{20}$$

Simplifying inequality (20) we obtain:

$$C_{11} + C_{33} > 2C_{13}. \tag{21}$$

Substituting $C_{22} = C_{11}$, $C_{23} = C_{13}$ into Eq. (13), we obtain the bulk modulus B_0 of the rhombohedral phase:

$$B_0 = \frac{1}{9}(2C_{11} + 2C_{12} + 4C_{13} + C_{33}). \tag{22}$$

Using the same analysis method in the tetragonal phase, we can easily evaluate the magnitude of B_0, that is:

$$\frac{1}{3}(C_{12} + 2C_{13}) < B_0 < \frac{1}{3}(C_{11} + 2C_{33}). \tag{23}$$

This indicates that the bulk modulus must be larger than the weighted average of c_{12} and c_{13}, and smaller than the weighted average of C_{11} and C_{33}. From our calculated result of the bulk modulus and elastic constants in Tables I and II we can obtain $(1/3)(C_{12} + 2C_{13}) = 54$, $(1/3)(C_{11} + 2C_{33}) = 267$, $B_0 = 126$, satisfy formula (23) very well.

Actually, only six independent elastic constant components exist in rhombohedral phase, since $C_{56} = C_{14}$, $C_{66} = (1/2)(C_{11} - C_{12})$. In order to cross-check the calculation result, C_{56} and C_{66} were also obtained and given in Table III, and they agree with each other very well.

To obtain the electrostrictive coefficients of the cubic phase, the strain and polarization behaviors may be calculated by first principles. First principles calculation about the polarization and strains could be performed by Berry's phase approach.[40,41] Spontaneous polarization variation with different strains were calculated with first principles by Fu and Cohen and Ederer and Spaldin in Refs. 40 and 6. Fu and Cohen calculated the strains variation with polarization rotation induced by an external electric field, and they concluded that the polarization rotation alone can result in the giant piezoelectric response. Claude *et al.* calculated the effect of epitaxial strain on the spontaneous polarization of the ferroelectrics $BaTiO_3$, $PbTiO_3$, $LiNbO_3$, and the multiferroic material $BiFeO_3$. They showed that the epitaxial strain dependence of the polarization varies considerably for the different systems and consequently some of the piezoelectric coefficients were obtained. In our calculation of electrostrictive coefficients, strains, and polarizations were controlled by moving Ti atom, and other degrees of freedom (including both atomic positions and cell shape) are optimized, while keeping the cell volume at the equilibrium value for cubic phase. Polarization was computed from the optimized geometric structure using the Berry's phase approach.[7] Q_{11}, Q_{12}, and Q_{44} are given in Figs. 2–4, respectively. To obtain Q_{11}, Ti atom was moved along z direction. Then after structure optimization and Berry's phase calculation, ε_3, P_1, P_2, and P_3 were obtained with $P_1 = P_2 = 0$. According to formula (11), $\varepsilon_3 = Q_{11}P_3^2$ was obtained. Q_{12} and Q_{44} were obtained using
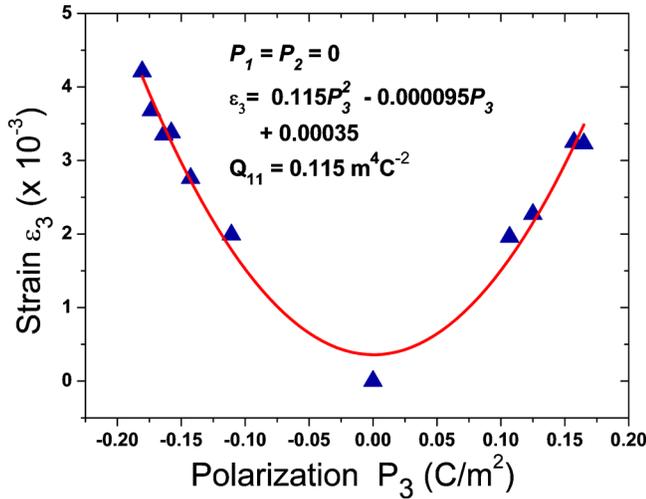
FIG. 2. (Color online) The relationship between strains ε_3 and polarization P_3. It is computed from the optimized structures when Ti ion of the unit cell is moved along [001] and [00$\bar{1}$] directions to small distances.

similar method. Table III shows our calculation results, and results are compared with experimental data. We can see that our results agree well with the experiment.

V. SUMMARY

In summary, we calculated the elastic properties of BaTiO$_3$ in the cubic, tetragonal, orthorhombic, and rhombohedral phases. We obtained the lattice constants, bulk modulus, elastic constants of BaTiO$_3$, and they agree well with the experimental data for four phases, especially for the relaxed structure parameters. Spontaneous polarizations for three ferroelectric phases were computed as well and the calculated data agree well with those of experiments. We calculated the electrostrictive coefficients of cubic BaTiO$_3$ based on polarization variations with strains by first principles. The information obtained from this work is useful for predicting the strain effect on ferroelectric phase transitions and domain structures and properties of ferroelectric thin films.
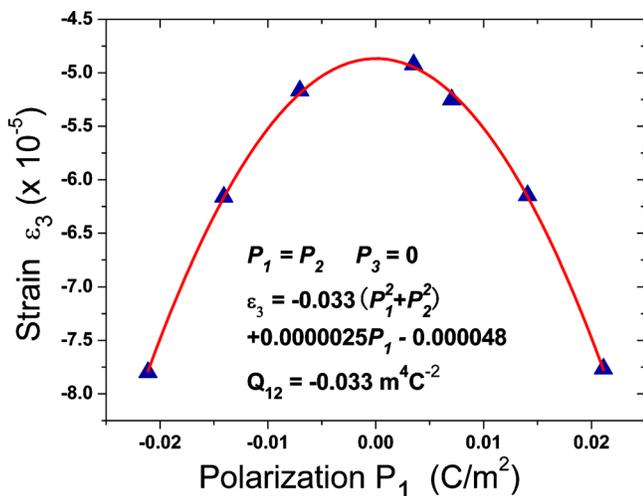
FIG. 3. (Color online) The relationship between strains ε_3 and polarization P_1. It is computed from the optimized structures when Ti ion of the unit cell is moved along [110] and [$\bar{1}\bar{1}$0] directions to small distances.
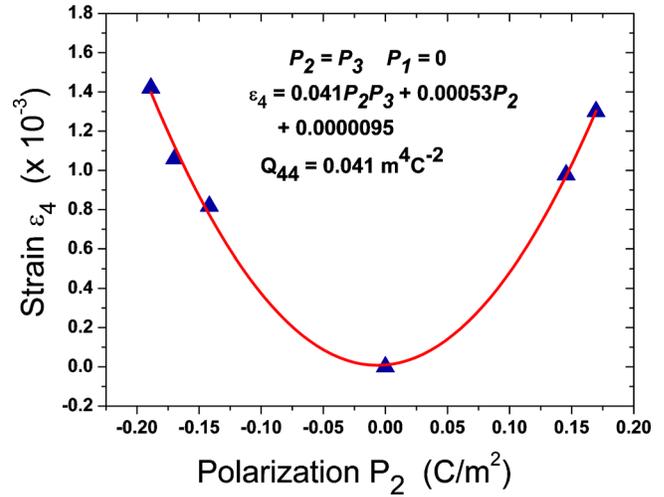
FIG. 4. (Color online) The relationship between strains ε_4 and polarization P_2. It is computed from the optimized structures when shear strains ε_4 are applied on the unit cell.

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