

Influence of symmetry-resolved phonon dynamics on the temperature-dependent electric field gradients in solids

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The temperature-dependent electric field gradient (EFG) tensor at a probe nucleus reflects the combined effects of local symmetry, bonding, and lattice dynamics. However, determining the primary atomic distortions responsible for this response can be difficult. Here, we combine electron-gamma ($e\text{-}\gamma$) time-differential perturbed angular correlation (TDPAC) measurements on ^{181}Ta probes produced by the $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ decay at substitutional Ti sites in rutile TiO_2 with symmetry-resolved local frozen-phonon density functional theory (LFP-DFT) calculations. Atomic displacements of the TiO_6 octahedron are decomposed into site-symmetry-adapted local modes, and their contributions to the EFG are thermally weighted via Boltzmann averaging. We find that, in pristine rutile TiO_2 , the temperature evolution of the EFG shape is primarily governed by two orthogonal B_{1g} equatorial-oxygen shear distortions. For Ta substituting the Ti site, the same shear sector remains active but preserves a finite in-plane anisotropy, resulting in a comparatively weak temperature dependence of the asymmetry parameter η . Measurements between 30 and 470 K, together with earlier high-temperature gamma-gamma ($\gamma\text{-}\gamma$) data, show weak low-temperature curvature and high-temperature quasilinearity of the principal EFG component $V_{33}(T)$, while $\eta(T)$ remains comparatively robust. The calculations reproduce these qualitative trends and provide a microscopic, symmetry-based interpretation of the thermal evolution of hyperfine tensors in solids.

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I. INTRODUCTION

Temperature-dependent electric field gradients (EFGs) measured at probe nuclei serve as a sensitive local indicator of symmetry, bonding, and lattice dynamics in solids [1–4]. Although the temperature dependence of the largest principal EFG component V_{33} and the asymmetry parameter η can often be phenomenologically reproduced, it is usually less obvious which local lattice distortions are primarily responsible for the observed behaviors.

In practice, finite-temperature EFGs are typically understood in terms of thermal expansion, harmonic vibrational averaging, or more general phonon-based models [5–7]. Although these approaches can capture general trends, they often do not clarify the local origins of the response because they do not specify which symmetry-related distortions primarily drive the observed changes in $V_{33}(T)$ and $\eta(T)$.

To address this attribution challenge, we employ a symmetry-resolved, local frozen-phonon density functional theory (LFP-DFT) method [8,9]. In this approach, atomic displacements of the probe-centered coordination octahedron are decomposed into site-symmetry-adapted local modes, with their EFG responses thermally weighted. Since the EFG is primarily influenced by the immediate electronic surroundings of the probe, this local perspective offers a physically meaningful way to identify the distortions that most significantly affect the measured thermal response while remaining clearer than a comprehensive vibrational average across all phonon branches.

Rutile TiO_2 serves as a valuable test case because its D_{2h} site symmetry [10,11] at the cation site constrains the

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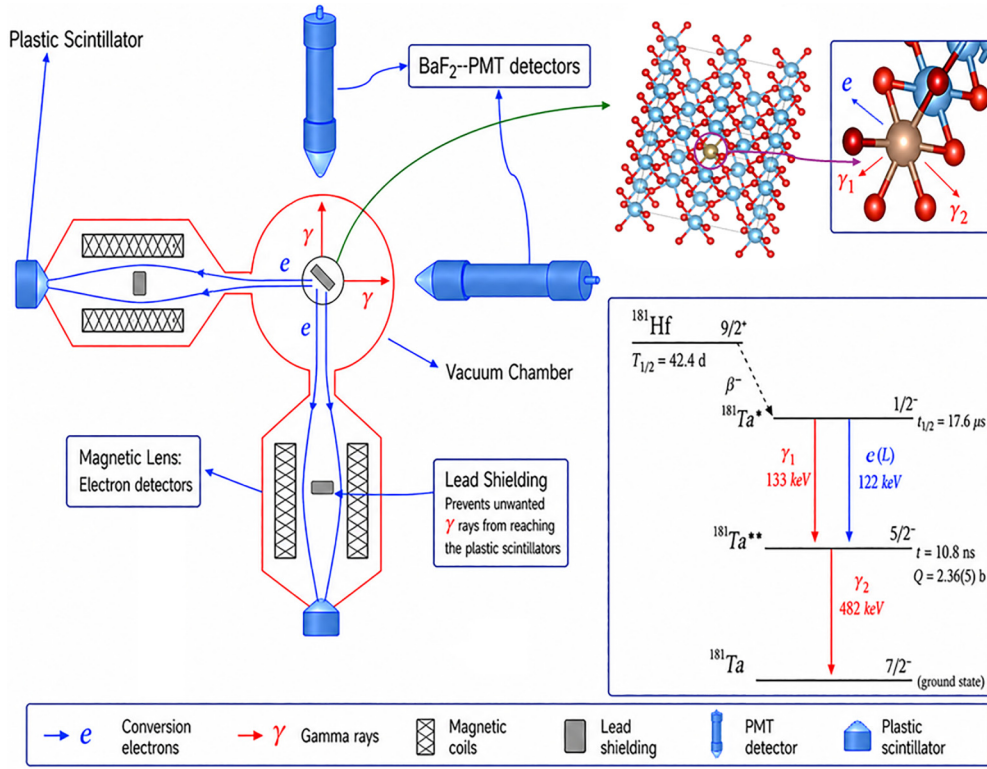


FIG. 1. Schematic overview of the $e\text{-}\gamma$ TDPAC experiment and the local probe environment in rutile TiO_2 . The left panel shows the experimental geometry, where conversion electrons are guided by Siegbahn-type magnetic lenses to plastic scintillators, while coincident γ -rays are detected by BaF_2 -PMT detectors. Lead shielding suppresses unwanted γ -ray background at the electron detectors. The upper-right panel shows the rutile TiO_2 lattice and the local TaO_6 coordination octahedron formed when ^{181}Ta substitutes for Ti at a cation site. The lower-right panel shows the relevant $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ decay scheme [15], including the conversion-electron and γ_1 - γ_2 cascade used for the TDPAC measurement. Figure adapted and redrawn from Refs. [4, 16–18].

EFG principal-axis structure: one principal axis aligns with the crystallographic c axis. Consequently, the temperature dependence primarily reflects how thermal distortions affect in-plane anisotropy. This characteristic makes rutile particularly suitable for linking symmetry-specific distortions to observed EFG trends.

For ^{181}Ta substituting at the Ti site, previous gamma-gamma ($\gamma\text{-}\gamma$) time-differential perturbed angular correlation (TDPAC) studies highlighted an almost linear increase in the EFG at high temperatures [12, 13]. In this work, we extend the temperature range downward, using electron-gamma ($e\text{-}\gamma$) TDPAC measurements from 30 to 470 K, which reveal a subtle curvature in $V_{33}(T)$ at low temperatures, while $\eta(T)$ remains relatively stable. This expanded temperature range offers a rigorous test for microscopic interpretations of the EFG response.

We find that in pristine rutile TiO_2 , the temperature evolution of the EFG shape is primarily governed by two orthogonal local equatorial-oxygen shear distortions that transform as B_{1g} [10, 11]. At the Ta-substitutional site, the same shear sector remains active, but a finite in-plane anisotropy persists across the thermally relevant displacement range, resulting in the much weaker temperature dependence of η .

This framework is intended as a symmetry-guided local analysis rather than offering a comprehensive finite-temperature lattice-dynamical treatment. It employs a mode-separable local estimator to pinpoint the key distortions

influencing the observed EFG changes; however, residual mode coupling, extra phonon branches, thermal expansion, and temperature-dependent electronic screening may still cause some quantitative discrepancies, particularly at higher temperatures.

In sum, this study demonstrates that a symmetry-resolved local frozen-phonon analysis can clearly link temperature-dependent hyperfine observables to specific microscopic distortions, providing a useful interpretive framework for EFG measurements in oxides and similar solids.

II. EXPERIMENTAL METHODS: $e\text{-}\gamma$ TDPAC

Commercially obtained single-crystal rutile TiO_2 ($10 \times 10 \times 1 \text{ mm}^3$, Crystals GmbH) was implanted with ^{181}Hf ions at the Bonn Isotope Separator (BONIS) at an implantation energy of 80 keV and an incidence angle of 10° [14]. The ^{181}Hf parent isotope, produced by thermal-neutron activation of HfO_2 in the V4 position of ILL's high-flux reactor, decays by β^- emission to ^{181}Ta . After implantation, the samples were annealed in air at 873 K for 5 h to repair implantation damage and promote substitutional incorporation of $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ into Ti lattice sites [12, 13, 17, 18], as illustrated in the upper-right panel of Fig. 1.

We observed $e\text{-}\gamma$ coincidences in the ^{181}Ta cascade, where a 122-keV conversion-electron transition is followed by a

482-keV γ -ray through the $I = 5/2^+$ intermediate state ($\tau = 10.8$ ns), as illustrated in the lower-right panel of Fig. 1.

The e- γ TDPAC spectra were recorded from 30 K to 470 K using a coplanar setup with four detectors: two magnetic-lens electron spectrometers and two BaF₂ γ detectors [19,20]. The electron arms employ Siegbahn-type magnetic lenses that focus the 122-keV conversion electrons onto fast plastic scintillators, while the γ -ray arms use BaF₂ detectors for fast timing. The sample was mounted in the Raghavan geometry, with its long axis oriented at 45° relative to the detector arrangement as shown in the left panel of Fig. 1 [21]. Low-temperature data were collected in a helium-flow cryostat, whereas higher-temperature data were collected in a resistively heated setup. The finite time resolution was accounted for using a Gaussian response function with a FWHM of 0.7 ns.

The measured coincidence spectra were reduced to the time-dependent count-rate ratio $R(t)$ using the standard combination of 180° and 90° detector-pair count rates,

$$R(t) = 2 \frac{N(180^\circ, t) - N(90^\circ, t)}{N(180^\circ, t) + 2N(90^\circ, t)}, \quad (1)$$

where $N(180^\circ, t)$ and $N(90^\circ, t)$ denote the averaged coincidence spectra for the detector pairs at 180° and 90°, respectively. This construction removes the exponential decay of the intermediate state and isolates the hyperfine modulation.

The resulting $R(t)$ spectra were fitted with the standard static quadrupole interaction formalism for the $I = 5/2^+$ intermediate state. For the present single-crystal geometry, the fit model can be written as a sum of three cosine components:

$$R(t) = A_{22}^{\text{expt}} \left(\xi_0(\eta, \theta, \varphi) + \sum_{i=1}^3 \xi_i(\eta, \theta, \varphi) \cos(\omega_i t) \exp(-\delta_L \omega_i t) \right), \quad (2)$$

where $A_{22}^{\text{expt}} = -0.3077$ is the effective e- γ anisotropy, the coefficients $\xi_i(\eta, \theta, \varphi)$ depend on the crystal orientation relative to the detector geometry, encoded in θ and φ .

For the $I = 5/2^+$ state, the three perturbation frequencies ω_i are conventionally expressed in terms of the quadrupole frequency ω_Q ,

$$\omega_Q = \frac{eQ|V_{33}|}{4I(2I-1)\hbar}, \quad (3)$$

using the literature quadrupole moment $Q = +2.36(5)$ b [22] of the intermediate state of ^{181}Ta . Throughout this work, the principal EFG components are reported in the PAC convention $|V_{33}| \geq |V_{22}| \geq |V_{11}|$, so that

$$\eta = \frac{|V_{22}| - |V_{11}|}{|V_{33}|} \in [0, 1] \quad (4)$$

The raw spectra $N(180^\circ, t)$ and $N(90^\circ, t)$ were processed with InterludeTM [23] to obtain $R(t)$, and the resulting spectra were fitted with Gfit19, a modified version of the NNfit suite [24–26], with a well-defined substitutional Ta site. In the analysis, a minor additive constant was included to account for setup-dependent offsets, which measure the deviation of the rutile TiO₂ sample from the setup center. A multiplicative

TABLE I. Experimental e- γ TDPAC results for rutile $^{181}\text{Ta}(\text{TiO}_2)$ over 39–474 K. Temperatures are rounded to the nearest Kelvin, and η values to two decimal places. Typical fitted uncertainties in η are 0.002–0.005; uncertainties in $|V_{33}|$ are shown in parentheses.

Measurement temperature (Kelvins)	Asymmetry parameter η	$ V_{33} $ (V/Å ²)
39	0.54	138.3(3)
60	0.55	138.7(1)
70	0.54	138.9(1)
102	0.55	139.6(1)
139	0.54	140.3(1)
180	0.55	140.8(1)
220	0.55	141.3(1)
260	0.54	141.8(1)
296	0.55	142.2(2)
296	0.54	142.1(1)
348	0.55	142.8(1)
397	0.55	143.1(1)
428	0.55	143.3(1)
474	0.55	143.5(1)

factor was allowed to account for minor deviations from nominal anisotropy.

A pedagogical overview of the appropriate formalism and its implementation for the present setup is available in Ref. [18]. The conventions for the single-crystal perturbation function, the static quadrupole Hamiltonian, the construction of $N(90^\circ, t)$ and $N(180^\circ, t)$, and the extraction of V_{33} and η are summarized in Sec. I of the Supplemental Material (SM) [27]; see also Refs. [1–4, 15–18, 22, 28–31].

III. EXPERIMENTAL RESULTS: e- γ TDPAC

Figure 2 shows representative e- γ TDPAC spectra and their cosine Fourier transforms at temperatures sampled across the experimental range. The oscillatory cosine signatures are clearly resolved throughout the dataset and the FFT peaks shift systematically with temperature, reflecting changes in the quadrupole interaction at the Ta site. The narrow line broadening and stable fit parameters across the series are consistent with a single dominant substitutional Ta environment in rutile TiO₂.

The fitted temperature dependences of the principal EFG component $V_{33}(T)$ and the asymmetry parameter are shown in Fig. 3, and the corresponding numerical values are listed in Table I. Over the range 30–470 K, the present e- γ data show a weak but clear concave-down low-temperature evolution of $V_{33}(T)$, in contrast to the approximately linear high-temperature behavior reported previously from γ - γ measurements above 600 K. By comparison, $\eta(T)$ remains nearly constant, with only a weak linear temperature dependence over the same interval. Extending the measurements to lower temperatures shows that the widely cited quasi-linear $|V_{33}(T)|$ behavior applies only to the higher-temperature portion of the broader temperature evolution.

To contextualize these measurements, Table II compares the temperature dependences derived from the current

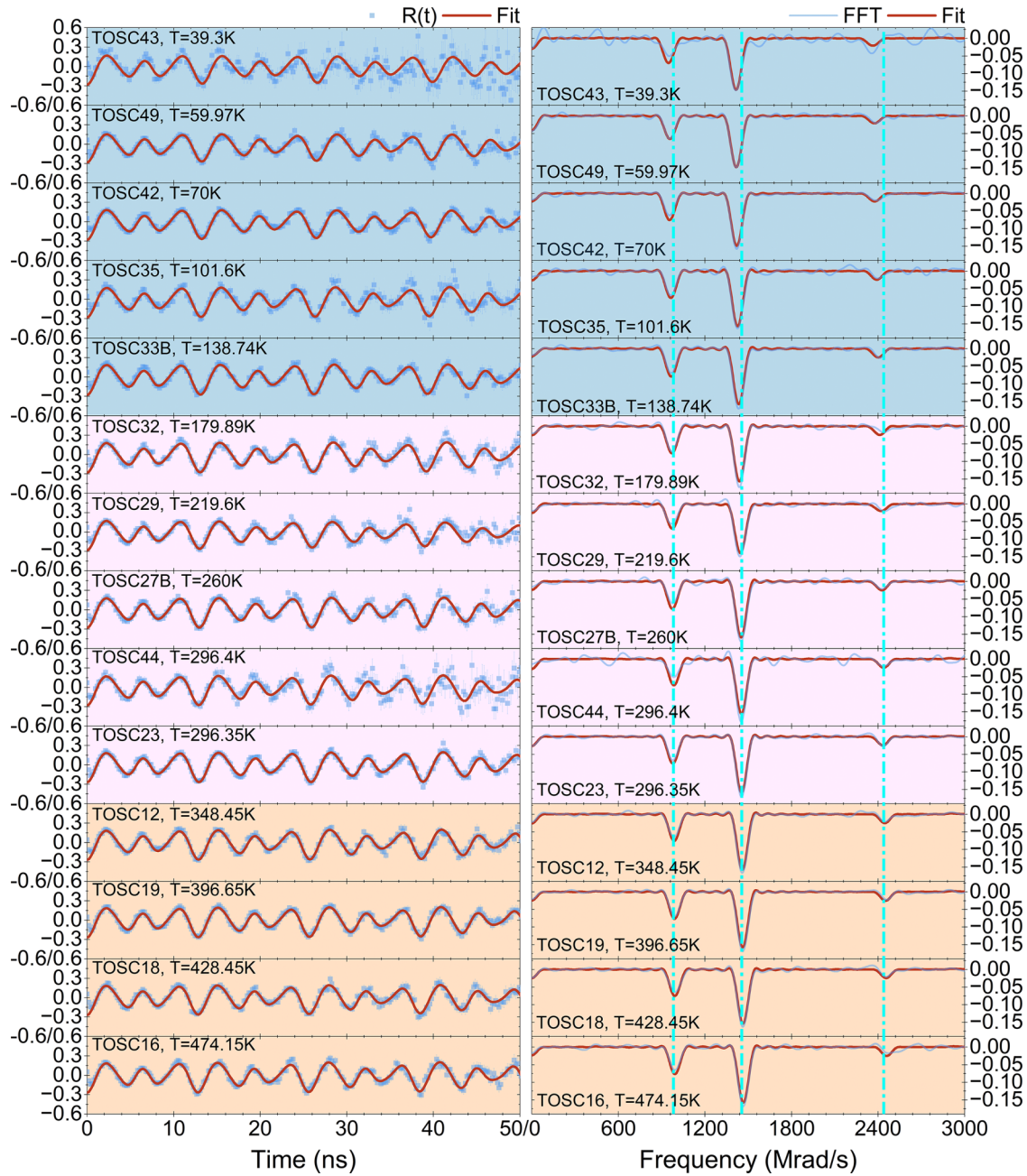


FIG. 2. (Left) Time-dependent count-rate ratio $R(t)$, and (right) corresponding cosine FFT spectra for 14 representative e- γ TDPAC measurements of $^{181}\text{Ta}(\text{TiO}_2)$, arranged in the order of increasing temperature. Vertical cyan lines mark the three characteristic frequencies observed at room temperature (TOSC23). Reproduced from Ref. [18].

low-temperature e- γ data with previous high-temperature γ - γ results [12] and selected theoretical values from literature [13]. Notably, the measurements indicate that the Ta-site EFG does not exhibit a strictly linear temperature dependence across the entire accessible range: $|V_{33}(T)|$ shows a subtle curvature at low temperatures, while $\eta(T)$ remains only weakly temperature-dependent.

Since various literature sources use different nuclear quadrupole moments Q for the intermediate state of ^{181}Ta , the reported $|V_{33}(T)|$ values are generally not directly comparable and are related by $|V_{33}| \propto 1/Q$.

We note that, for a well-defined substitutional ^{181}Ta site in bulk rutile single-crystal TiO_2 , no data are available in the

intermediate temperature range. Consequently, it is unclear how the low-temperature concave-down behavior transitions into the high-temperature linear regime. Related temperature-dependent $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ TDPAC data for thin-film and non-single-crystal TiO_2 are compared in Sec. II of the SM [27] (see also [12,32–38]).

Earlier interpretations of the Ta-site EFG in rutile TiO_2 were generally not framed in terms of specific, symmetry-resolved local phonon distortions but instead emphasized probe chemistry, directional bonding, impurity electronic structure, or broader temperature-dependent lattice effects [39]. This motivated the present DFT analysis, which asks whether the measured temperature dependence can be traced

TABLE II. Comparison of experimental trends and theoretical EFG values for rutile $^{181}\text{Ta}(\text{TiO}_2)$. Values are quoted as reported. Because the cited studies adopt different nuclear quadrupole moments Q for the intermediate state of ^{181}Ta , the reported $|V_{33}(T)|$ values are not directly comparable without rescaling, with $|V_{33}| \propto Q^{-1}$.

	Q (b)	η	$ V_{33} $ ($\text{V}/\text{\AA}^2$)
Adams and Catchen, γ - γ fit (T) [12]	2.51	$0.57(1) + (1.1(5) \times 10^{-5}) \times T$	$133.0(6) + (3.6(6) \times 10^{-3}) \times T$
Darriba <i>et al.</i> , Expt. [13]	2.36(5) [22]	0.56(1)	133(1)
Darriba <i>et al.</i> , DFT-LDA [13]		Neutral: 0.65 Charged: 0.63	Neutral: 130 Charged: 125
Darriba <i>et al.</i> , DFT-GGA [13]		Neutral: 0.86 Charged: 0.88	Neutral: 124 Charged: 119
Darriba <i>et al.</i> , DFT-WC-GGA [13]		Neutral: 0.83 Charged: 0.80	Neutral: 123 Charged: 120
Das <i>et al.</i> , Expt. [32]	2.51	0.56(1)	137(1)
Banerjee <i>et al.</i> , Expt. [33]	2.51	0.51(1)	133.5(2)
Our work, e- γ fit (T)	2.36(5) [22]	$0.5423(9) + (1.3(3) \times 10^{-5}) \times T$	$137.2(6) + (2.07(5) \times 10^{-2}) \times T$ $+ (-1.8(1) \times 10^{-5}) \times T^2$

microscopically to local vibrational distortions of the TaO_6 octahedron.

IV. THEORETICAL METHODS

A. Ground-state DFT

All first-principles calculations were performed within Kohn–Sham DFT [40] using the projector-augmented-wave (PAW) method as implemented in VASP [41,42]. Since pristine rutile TiO_2 is nonmagnetic, all calculations were carried out without spin polarization. Relativistic effects were treated at the scalar level (mass-velocity and Darwin terms). To assess the sensitivity of the EFG to the exchange-correlation treatment, we employed both the PBE and HSE06 functionals [43,44].

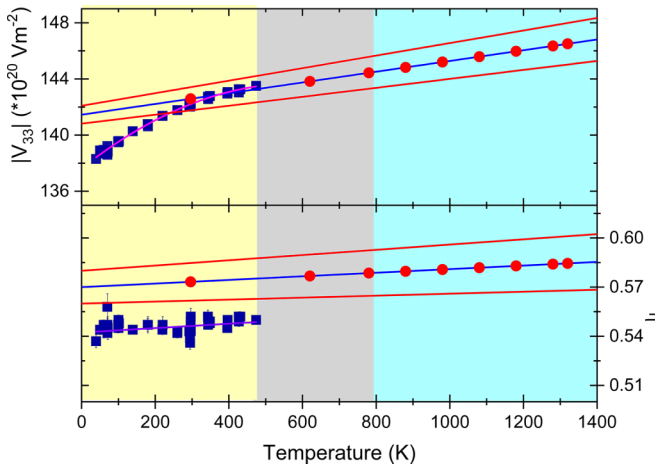


FIG. 3. Temperature dependence of (top) V_{33} , and (bottom) η at the Ta-substitutional site in rutile TiO_2 . Blue squares, present e- γ TDPAC data for $^{181}\text{Ta}(\text{TiO}_2)$; red circles, earlier γ - γ TDPAC data. The magenta and violet lines denote the fitted e- γ trends for V_{33} and η , respectively. The blue lines show the fitted γ - γ trends, and the red lines their uncertainty bounds. Adapted from Ref. [18], with the corrected high-temperature gradient and the literature EFG values rescaled to $Q = 2.36$ b.

To ensure the quantitative reliability of the EFGs (following Ref. [45]), we used the recommended settings and PAW datasets (details are given in Table III) that include Ti and Ta semicore s and p states [46].

To model pristine rutile TiO_2 in a $1 \times 1 \times 1$ single cell, initial structural parameters were taken from Refs. [45,47] and were based on experimental values: $a = b = 4.586$ Å, $c = 2.952$ Å, with internal parameter $x = 0.3048$. The plane-wave cutoff was set to 520 eV, and PREC = Accurate was used to ensure dense FFT and augmentation grids. Structural relaxations allowed both lattice vectors and internal coordinates to vary until convergence, using an electronic threshold of 10^{-9} eV and a residual-force threshold of 10^{-6} eV Å $^{-1}$. Brillouin-zone sampling for the primitive rutile cell used Monkhorst–Pack meshes of $15 \times 15 \times 15$ for PBE and $6 \times 6 \times 9$ for HSE06, both including the Γ point. We then used the converged lattice vectors and internal coordinates to create a $2 \times 2 \times 3$ supercell.

Table IV presents the lattice parameters and bond lengths of the horizontal and vertical Ti–O bonds within the primitive rutile TiO_2 cell, obtained from the PBE and HSE06 workflows. For comparison, we include calculations from Ref. [48] as well as experimental results, including one study reporting on the lattice parameters [47] and another reporting the band gap [49].

In pristine rutile, PBE slightly overestimates the lattice constants and underestimates the band gap, whereas HSE06 yields lattice parameters and an electronic band gap close to experiment. The calculated EFG parameters at the Ti and O sites are consistent with previous all-electron benchmarks [45].

For Ta-substituted rutile, a $2 \times 2 \times 3$ supercell was constructed from the converged rutile TiO_2 structure, and one Ti

TABLE III. The utilized PAW potentials.

Potential name	Number of valence electrons	Valence electron configuration	Cutoff energy (eV)
O	6	$2s^2 2p^4$	400.00
Ti_sv	12	$3s^2 3p^6 3d^3 4s^1$	274.61
Ta_sv_GW	13	$5s^2 5p^6 5d^5$	286.01

TABLE IV. Lattice parameters and bond lengths of converged $1 \times 1 \times 1$ pristine rutile TiO_2 against Ref. [48] and the neutron diffraction experiment of Ref. [47].

	Lattice parameters (Å)	Horizontal Ti-O _{xy} bonds (Å)	Vertical Ti-O _z bonds (Å)	Band gap (eV)
This work, PBE	$a = b = 4.65$, $c = 2.97$, $x = 0.305$	1.96	2.00	1.80
This work, HSE06	$a = b = 4.58$, $c = 2.95$, $x = 0.305$	1.94	1.98	2.8
Ref. [48], PBE	$a = b = 4.66$, $c = 2.99$, $x = 0.305$	1.97	2.01	2.0
Ref. [48], HSE06	$a = b = 4.59$, $c = 2.95$, $x = 0.305$	1.95	1.98	3.1
Ref. [47], Expt. 15 K	$a = b = 4.58666(4)$, $c = 2.95407(3)$, $x = 0.30469(6)$	1.9459(3)	1.9764(4)	3.0 [49]

atom was replaced by Ta. The system is in the ionized-donor configuration by removing one electron from the supercell. The resulting net charge was treated using the standard homogeneous compensating background required for charged periodic calculations. This choice is consistent with prior first-principles work, which showed that the Ta-site EFG is only weakly sensitive to the selected charge state (see Table II and Ref. [13]). The defect supercell was relaxed using the same plane-wave cutoff, with convergence thresholds of 10^{-8} eV for the electronic self-consistency and 10^{-5} eV Å⁻¹ for the ionic forces. Monkhorst–Pack meshes of $4 \times 4 \times 4$ for PBE and $2 \times 2 \times 2$ for HSE06 were used for the supercell calculations, both including the Γ point.

After electronic and ionic relaxations, single-point self-consistent calculations were performed at fixed geometry to obtain the converged charge density and wave functions, from which the EFG tensors were evaluated using LEFG = .TRUE., with the principal components (V_{33} , V_{22} , V_{11}) and asymmetry parameters η extracted for each atom in the principal axis frame (PAS), which is obtained via a rotation from the crystallographic frame.

For the target quantities of this work, namely lattice parameters and EFGs, additional tests showed that increasing the plane-wave cutoff from 520 to 600 eV, refining the k-point mesh, and, for the Ta-defect case, enlarging the supercell changed the results by less than 1–2%. Therefore, we consider the reported values to be numerically well converged.

Table V presents the ground-state EFG tensors for the primitive rutile TiO_2 structure, calculated using the current PBE and HSE06 workflows. These results are compared with CP-PAW calculations using experimental lattice parameters and internal coordinates of $x = 0.305/0.3025$ [45], along with NMR-derived Ti- and O-site EFGs [50]. The consistency in EFG magnitude provides a reliable pristine reference for the subsequent symmetry-resolved LFP analysis.

Table VI summarizes the ground-state Ta-site EFG tensor and relaxed Ta-O bond lengths obtained with the present PBE and HSE06 workflows. Earlier experimental and theoretical

Ta-site EFG values, including those of Ref. [13], are listed in Table II. Both functionals reproduce the expected order of magnitude of the Ta-site EFG. HSE06 gives larger $|V_{33}| = |V_{zz}|$ and η , along with slightly shorter Ta-O bonds than PBE. The Ta-O bond lengths differ by no more than 0.023 Å between the two functionals, indicating that the local structural relaxation around Ta is similar in both workflows.

Compared with the experimental Ta-site $|V_{33}|$ values of approximately 133–138 V/Å² listed in Table II, PBE produces a similar ground-state magnitude ($|V_{33}| = 141$ V/Å²). In contrast, HSE06 overestimates the magnitude ($|V_{33}| = 161$ V/Å²), but it stays within the correct EFG scale.

B. Symmetry-resolved LFP-DFT

Finite-temperature EFGs were computed using symmetry-resolved LFP-DFT [8,9]. From well-converged $2 \times 2 \times 3$ supercells of pristine and Ta-substituted rutile TiO_2 , we define a seven-atom Ti/TaO₆ coordination octahedron centered on the representative cation site and work in a D_{2h} -constrained local description. Specifically, atomic displacements and EFG responses are decomposed into the set of local, site-symmetry-adapted displacement coordinates $\{y_j\}_{j=\{1,\dots,21\}}$ spanning the $3N = 21$ degrees of freedom. These coordinates form an orthonormal symmetry-adapted basis for the octahedron and are not obtained from a full phonon calculation of the supercell.

The motivation for this local description is that the EFG is primarily a near-field observable, determined by the electronic charge density near the probe nucleus. Thus, an octahedron-based representation is a natural approach for identifying which local distortions most strongly influence the hyperfine tensor. In this work, the goal is to decompose the measured EFG response into local distortions of the Ti/TaO₆ environment that are distinct by symmetry.

The central assumption of the LFP formalism is mode separability. In a symmetry-adapted coordinate basis $\vec{y} = (y_1, y_2, \dots, y_{21})^T$ with $\hat{e}_j$ denoting the unit vector along

TABLE V. Benchmark of the Ti EFG components of our work against Ref. [45] and the NMR experiment of Ref. [50].

Workflow	Diagonalized EFG for Ti site ($\text{V}/\text{\AA}^2$)	Asymmetry parameter η for Ti	Diagonalized EFG for O site ($\text{V}/\text{\AA}^2$)	Asymmetry parameter η for O
This work, Converged Parameters, PBE	$V_{xx} = 18.8$ $V_{yy} = 3.68$ $V_{zz} = -22.5$,	0.67	$V_{xx} = -22.1$, $V_{yy} = -1.95$, $V_{zz} = 24.1$	0.84
This work, Converged Parameters, HSE06	$V_{xx} = 18.2$, $V_{yy} = 7.45$, $V_{zz} = -25.6$	0.42	$V_{xx} = -27.5$, $V_{yy} = -1.79$, $V_{zz} = 29.3$	0.88
Ref. [45], Expt. Lattice, $x = 0.305$, PBE	$V_{xx} = 13.1$, $V_{yy} = 7.5$, $V_{zz} = -20.6$	0.27	$V_{xx} = -20.6$, $V_{yy} = -0.80$, $V_{zz} = 21.4$	0.93
Ref. [45], Expt. Lattice, $x = 0.3025$, PBE	$V_{xx} = 10.8$, $V_{yy} = 1.7$, $V_{zz} = -12.5$	0.73	$V_{xx} = 22.3$, $V_{yy} = 0.90$, $V_{zz} = -23.2$	0.92
Ref. [50], Expt. Lattice, $x = 0.305$, NMR	$V_{xx} = 13.4$, $V_{yy} = 8.6$, $V_{zz} = -22.0$	0.22	$V_{xx} = 22.2$, $V_{yy} = 1.60$, $V_{zz} = -23.8$	0.87

coordinate y_j , we neglect mixed mode coupling terms in the multivariate dependence of the EFG on $\vec{y}$ and approximate the EFG tensor $\vec{V}$ as a sum of independently computed one-dimensional responses [8,9],

$$\vec{V}(\vec{y}) \approx \vec{V}(\vec{0}) + \sum_{j=1}^{21} \Delta \vec{V}^{(j)}(y_j), \quad (5)$$

where $\vec{V}(\vec{0})$ is the static (0 K) value, and $\Delta \vec{V}^{(j)}(y_j) \equiv \vec{V}(y_j \hat{e}_j) - \vec{V}(\vec{0})$ is the one-dimensional tensor response caused by displacement along mode j .

Under the D_{2h} -projected local description, the principal-axis frame of the EFG is pinned to the chosen local frame, so mode-resolved principal components are well defined along each 1D trajectory. Accordingly, for each mode j and displacement amplitude y , we diagonalize $\vec{V}(y_j \hat{e}_j)$, order the eigenvalues in the PAC convention, and define the mode-resolved principal-component shift,

$$\Delta V_{ii}^{(j)}(y \hat{e}_j) = V_{ii}^{(j)}(y \hat{e}_j) - V_{ii}^{(j)}(\vec{0}). \quad (6)$$

For each mode j , we define the one-dimensional mode energy profile $E_j(y) \equiv E(y \hat{e}_j) - E(\vec{0})$, from which the

partition function and the normalized Boltzmann weight follow [51]

$$Z_j(T) = \int_{\mathbb{R}} \exp\left(-\frac{E_j(y)}{k_B T}\right) dy, \quad (7)$$

$$P_{T,j}(y) = \frac{1}{Z_j(T)} \exp\left(-\frac{E_j(y)}{k_B T}\right), \quad (8)$$

with k_B as the Boltzmann constant. The corresponding single-mode thermal contribution to the EFG component is then [51]

$$\langle \Delta V_{ii} \rangle_{T,j} = \int_{\mathbb{R}} [\Delta V_{ii}^{(j)}(y \hat{e}_j) * P_{T,j}(y)] dy. \quad (9)$$

Rather than evaluating the full multi-mode thermodynamic expectation value, we combine the mode-separable local-mode treatment [8,9] with the canonical Boltzmann weighting [51], and define a symmetry-selected, mode-resolved subspace estimator for a chosen set of symmetry-adapted coordinates Ξ ,

$$\langle V_{ii} \rangle_T = V_{ii}(\vec{0}) + \frac{1}{|\Xi|} \sum_{j \in \Xi} \langle \Delta V_{ii} \rangle_{T,j}. \quad (10)$$

This definition averages the one-dimensional thermal responses over an orthogonal basis spanning Ξ , thereby avoiding bias toward any basis direction within the selected

TABLE VI. Ground-state benchmark of the Ta-site EFG tensor and local Ta–O bond lengths in substitutional Ta-doped rutile TiO_2 .

Workflow	Diagonalized EFG for Ta site ($\text{V}/\text{\AA}^2$)	Asymmetry parameter η for Ta	Horizontal Ta–O _{xy} bonds ($\text{\AA}$)	Vertical Ta–O _z bonds ($\text{\AA}$)
This work, PBE	$V_{xx} = 105$, $V_{yy} = 36$, $V_{zz} = -141$	0.495	1.9812	1.9997
This work, HSE06	$V_{xx} = 132$, $V_{yy} = 29$, $V_{zz} = -161$	0.640	1.9616	1.9771

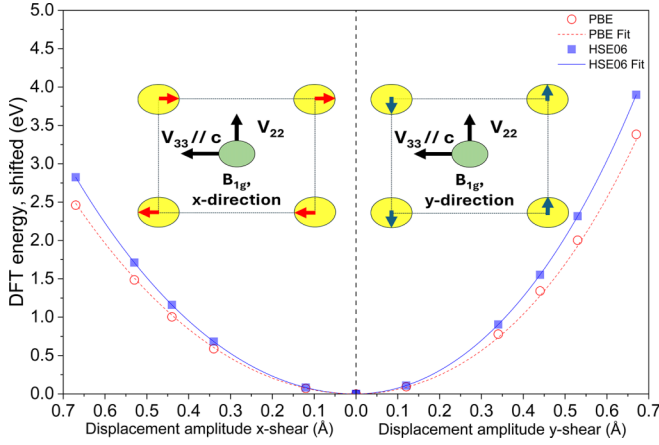


FIG. 4. Total-energy change $\Delta E(y)$ for displacements of amplitude $|y|$ along the two orthonormal basis vectors of the local B_{1g} equatorial-oxygen shear of a TiO_6 octahedron in a rutile $2 \times 2 \times 3$ supercell. The left (right) branch plots the shear, polarized along the local x (y) direction. Insets indicate oxygen displacements and the EFG axes, with $V_{33} \parallel c$. Symbols: PBE (open circles) and HSE06 (solid squares). Curves are least-squares fit to an even quartic, as described in Sec. VII of the SM [27], and are referenced to the relaxed minimum at $y = 0$.

subspace. Accordingly, Eq. (10) is a symmetry-informed subspace estimator, rather than the full multidimensional partition-function average over all modes.

This approximation is justified by symmetry considerations. In the local D_{2h} frame, the diagonal EFG components transform as A_g , meaning bilinear cross-terms between different symmetry sectors cannot affect the diagonal EFG. Consequently, bilinear couplings between sectors vanish, and the first intersector corrections only appear at higher orders. While residual symmetry-allowed couplings can modify quantitative details, they do not undermine the use of a symmetry-resolved, approximately mode-separable subspace estimator for the EFG response. The group-theoretical explanation is provided in Sec. III of the SM [27]; see also Refs. [10,11,13,21,45,52–57].

For the dominant in-plane B_{1g} sector $\Xi_{B_{1g}} = \text{span}\{\hat{e}_{B_{1g}}^{(1)}, \hat{e}_{B_{1g}}^{(2)}\}$, Eq. (10) reduces to

$$\langle V_{ii} \rangle_T = V_{ii}(\vec{0}) + \frac{1}{2}(\langle \Delta V_{ii} \rangle_{T,B_{1g,1}} + \langle \Delta V_{ii} \rangle_{T,B_{1g,2}}). \quad (11)$$

We verified that the B_{1g} plane is near-isotropic over the Boltzmann-weighted region (Fig. 4), so Eq. (11) is insensitive to the orthonormal choice within the subspace.

Details of the derivation, as well as an independent consistency check based on a $1 \times 1 \times 2$ supercell phonon calculation and its projection onto the local octahedron coordinates, are provided in Sec. IV of the SM [27]; see also Refs. [8–11,51,55–65].

While the thermal average is formally over all y , large $|y|$ contributions are strongly suppressed because the Boltzmann weight $\exp(-E_j(y)/k_B T)$ rapidly decays as $E_j(y)$ increases with $|y|$.

All D_{2h} vibrational irreducible representations are one-dimensional, so each site-symmetry-adapted coordinate carries an unambiguous symmetry label [57,66]. Among the 21

local coordinates of the Ti/TaO_6 octahedron, we find that the two orthogonal in-plane B_{1g} shears of the four equatorial O atoms are sufficient to reproduce the NMR-observed temperature dependence of the Ti-site EFG in pristine rutile TiO_2 . Other symmetry-allowed coordinates do not drive the EFG trajectory to a V_{22} – V_{11} degeneracy over the displacement range that contributes appreciably to the thermal averages in the temperature window studied.

For Ta substitution, translational symmetry is locally broken, and a full defect-supercell phonon spectrum would require substantially larger cells, which are computationally expensive. The present LFP treatment, in contrast, retains a consistent local description by projecting both pristine and Ta-substituted systems onto the same D_{2h} -projected Ti/TaO_6 octahedron basis around the probe site. Because the EFG is dominated by the near-field charge distribution, this local, symmetry-resolved approach captures the vibrational contributions most relevant to the hyperfine tensor without computing the full defect-supercell phonon spectrum.

We would like to emphasize that the host D_{2h} site symmetry admits a B_{1g} shear trajectory that reaches the in-plane degeneracy condition $V_{22} = V_{11}$ within the thermally sampled (accessible) window. Ta-substitution introduces a static in-plane anisotropy that removes the accessible approach to the $V_{22} = V_{11}$ locus within the B_{1g} plane. The discriminant surface is displaced such that the thermally sampled distribution encounters only a finite splitting preserving eigenvalue ordering.

Residual mode coupling or defect-induced relaxation can be viewed as renormalizing this in-plane splitting and the location of the $V_{22} = V_{11}$ locus. The qualitative distinction is whether thermal sampling can reach a gap closing (so that $V_{22} = V_{11}$ interchange contributes to the average) or whether a finite splitting persists over the entire Boltzmann-weighted window (so the principal-component ordering remains fixed).

V. THEORETICAL RESULTS: LFP-DFT

A. Pristine rutile

Figure 4 shows the mode energy profile $\Delta E(y)$ along the two orthogonal local B_{1g} equatorial-O shear coordinates of a TiO_6 octahedron. Over the sampled range, $\Delta E(y)$ is nearly harmonic, with only weak quartic hardening, and the two orthogonal shear directions have nearly identical curvature. This near-isotropy within the in-plane B_{1g} sector motivates treating the two orthogonal B_{1g} coordinates on an equal footing in the finite-temperature averaging. HSE06 yields a slightly stiffer curvature than PBE, consistent with its modified Ti–O bonding response under shear distortion.

As shown in Fig. 5, the largest EFG principal component along the crystallographic c axis remains well defined, while the two in-plane principal components respond strongly to the B_{1g} shear. Displacement along either orthogonal B_{1g} shear direction interchanges the roles of the in-plane components (V_{11} and V_{22}), reflecting the symmetry of an equatorial-O shear distortion. A key feature is the occurrence of a symmetry-enabled eigenvalue crossing, $V_{22}(y) = V_{11}(y)$, along thermally accessible displacements in the B_{1g} sector. Although the formal thermal average is over all y , large- $|y|$ contributions are exponentially suppressed by the Boltzmann factor

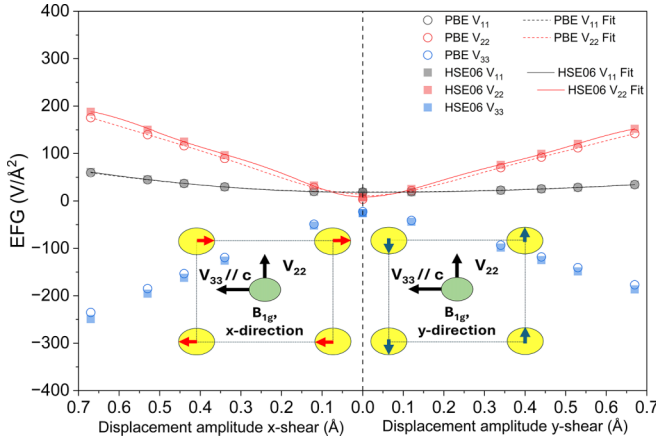


FIG. 5. Principal components of the EFG tensor V_{11} , V_{22} , and V_{33} at the Ti site in a rutile $2 \times 2 \times 3$ supercell as a function of the shear amplitude $|y|$ along the two orthonormal basis vectors of the local B_{1g} equatorial-oxygen shear. The left (right) branch corresponds to the shear, polarized along the local x (y) direction. The insets indicate the distortion and EFG axes, with $V_{33} \parallel c$. Symbols: PBE (circles) and HSE06 (squares). Curves are even-quartic fits used for thermal averaging, as described in Sec. VII of the SM [27]. Displacements along either basis direction interchange the in-plane components V_{11} and V_{22} .

$\exp(-E_j(y)/k_B T)$, since the energy $E(y)$ increases rapidly with $|y|$. Consequently, eigenvalue intersections that occur only at very large displacements in other symmetry channels do not affect the finite-temperature average in the temperature window studied. In contrast, the B_{1g} equatorial-O shears reach $V_{22} = V_{11}$ already at small $|y|$, making this sector dominant in controlling the observed $\eta(T)$ behavior.

Figure 6 illustrates the temperature dependence of (top) the principal EFG component $V_{33} \parallel c$ and (bottom) the asymmetry parameter η at the Ti-site, obtained from LFP-DFT

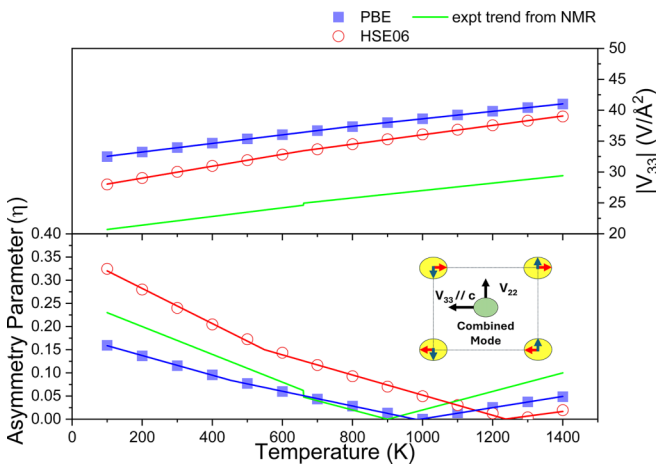


FIG. 6. Temperature dependence of (top) the principal EFG component V_{33} and (bottom) the asymmetry parameter η at the Ti site, obtained from LFP-DFT thermal averaging over the dominant B_{1g} shear subspace using PBE (blue squares) and HSE06 (red circles). Lime curves indicate the experimental trends extracted from NMR [50]. (Inset) Schematic of the in-plane equatorial O-shear (combined B_{1g} mode) that governs the evolution of $V_{33}(T)$ and $\eta(T)$.

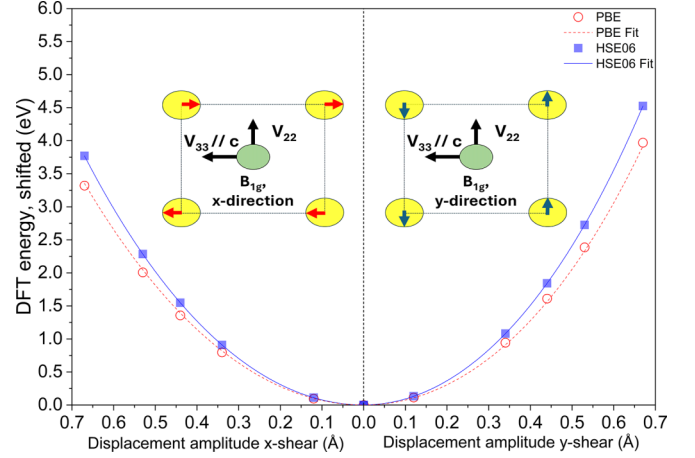


FIG. 7. Total-energy change $\Delta E(y)$ for displacements of amplitude $|y|$ along the two orthonormal basis vectors of the local B_{1g} equatorial-oxygen shear of a TaO_6 octahedron in the rutile $2 \times 2 \times 3$ supercell. The left (right) branch plots the shear polarized along the local x (y) direction. Insets indicate oxygen displacements and the EFG axes, with $V_{33} \parallel c$. Symbols: PBE (open circles) and HSE06 (solid squares). Curves are least-squares fit to an even quartic, as described in Sec. VII of the SM [27], and are referenced to the relaxed minimum at $y = 0$.

thermal averaging restricted to the two orthogonal B_{1g} modes [Eq. (11) in Sec. IV B]. Results are shown for PBE (blue squares) and HSE06 (red circles), together with the experimental trend from NMR (lime curve) [50]. Both functions reproduce (within the symmetry-selected subspace estimator) the overall increase in $|V_{33}|$ with increasing temperature and capture the qualitative evolution of $\eta(T)$.

The nontrivial $\eta(T)$ behavior follows from B_{1g} -driven $V_{22} - V_{11}$ crossings identified in Fig. 5: As thermal sampling accesses displacements on both sides of the degeneracy, the in-plane principal components interchange and the principal-axis frame effectively reorients, producing the observed temperature dependence of $\eta(T)$. HSE06 yields systematically larger η than PBE over the low-intermediate temperature range, consistent with its modified bonding response to the shear distortion.

B. Ta-substituted rutile

Figure 7 shows the mode energy profile $\Delta E(y)$ along the two orthogonal local B_{1g} equatorial-O shear coordinates of a TaO_6 octahedron. Over the sampled range, $\Delta E(y)$ remains predominantly harmonic with only weak quartic hardening, and the two orthogonal shear directions exhibit comparable curvature. This indicates that the near-isotropy of the in-plane B_{1g} sector is largely retained after Ta substitution, so the two orthogonal B_{1g} coordinates can again be treated on an equal footing in the finite-temperature averaging. As in the pristine case, HSE06 yields a slightly stiffer curvature than PBE, consistent with its modified Ta-O bonding response under shear distortion.

As shown in Fig. 8, the largest EFG principal component along the crystallographic c axis remains well defined, while the two in-plane principal components respond strongly to

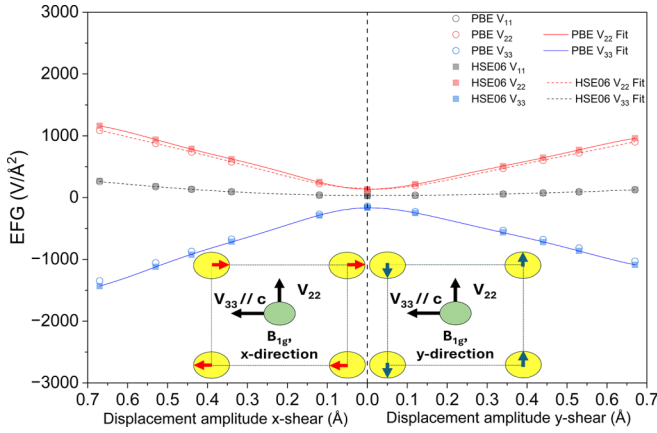


FIG. 8. Principal components of the EFG tensor V_{11} , V_{22} , and V_{33} at the Ta-substituted Ti site in the rutile $2 \times 2 \times 3$ supercell as a function of the shear amplitude $|y|$ along the two orthonormal basis vectors of the local B_{1g} equatorial-oxygen shear. The left (right) branch corresponds to the shear polarized along the local x (y) direction. The insets indicate the distortion and EFG axes, with $V_{33} \parallel c$. Symbols: PBE (circles) and HSE06 (squares). Curves are even-quartic fits used for thermal averaging, as described in Sec. VII of the SM [27].

the B_{1g} shear. As in the pristine case, the equatorial-O shear strongly modulates V_{11} and V_{22} . However, the crucial difference is that Ta substitution completely lifts the host-like in-plane degeneracy. The $V_{22}(y) = V_{11}(y)$ crossing reached within the thermally accessible B_{1g} window of pristine rutile is removed, so that a finite in-plane splitting persists along both orthogonal B_{1g} trajectories. Therefore, the same B_{1g} sector modulates a finite anisotropy rather than driving an accessible in-plane eigenvalue crossing, thereby preserving a robust, nonzero η .

Figure 9 compares the B_{1g} -restricted LFP-DFT thermal averages for substitutional Ta in rutile TiO_2 with the present low-temperature $e-\gamma$ data and the earlier high-temperature $\gamma-\gamma$ measurements (see Fig. 3), with Table VII providing the B_{1g} -restricted LFP-DFT-calculated $V_{33}(T)$ and $\eta(T)$ for both PBE and HSE06. Within this symmetry-selected treatment, both PBE and HSE06 yield monotonic $|V_{33}(T)|$ and a smooth, weakly temperature-dependent $\eta(T)$, consistent with the absence of a $V_{22} = V_{11}$ crossing in the thermally sampled B_{1g} window discussed above.

At the qualitative level, the calculations capture the key contrast with pristine rutile: the same B_{1g} shear sector remains active, but it now modulates a finite preexisting in-plane anisotropy rather than driving an accessible eigenvalue crossing. As a result, $\eta(T)$ remains comparatively robust, in agreement with experiment. Quantitatively, however, the calculated low-temperature curvature of $|V_{33}(T)|$ is weaker than observed in the $e-\gamma$ data by a factor of 5 to 8, indicating

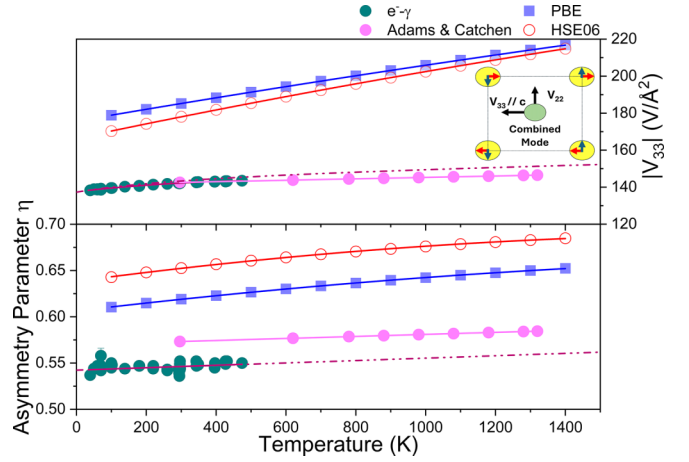


FIG. 9. Temperature dependence of (top) the principal EFG component V_{33} and (bottom) the asymmetry parameter η at the Ta-substitutional site in rutile TiO_2 , obtained from LFP-DFT thermal averaging over the dominant B_{1g} shear subspace using PBE (blue squares) and HSE06 (red circles). The calculations are compared with the present $e-\gamma$ measurements (green circles) and prior $\gamma-\gamma$ data (pink circles) [12]. The dashed-dotted curve is a Padé-type interpolation used to guide the eye for $V_{33}(T)$, as described in Secs. V–VI of the SM [27]. (Inset) Schematic of the in-plane equatorial O-shear (combined B_{1g} mode) used in the LFP analysis. The literature EFG values plotted in Figs. 3 and 9 are rescaled to $Q = 2.36$ b. The PBE and HSE06 fits were performed over 100–1400 K; their intercepts are regression parameters and do not represent physical $T = 0$ values.

that the minimal B_{1g} -restricted LFP treatment does not fully account for all contributions to the Ta-site thermal response. This underestimation leads to a weaker T-flattening of $|V_{33}(T)|$ than observed experimentally.

Considering the LFP-DFT results, and in preparation for the discussion, we parameterize the full experimental $|V_{33}(T)|$ evolution across the combined low- and high-temperature datasets using a Padé-(1,1) form with an added linear term [67]

$$|V_{33}(T)| = V_0 + \frac{a \times T}{1 + b \times T} + (c \times T), \quad (12)$$

with the numerical values $V_0 = 137.27847 \text{ V } \text{\AA}^{-2}$, $a = 0.02815864 \text{ V } \text{\AA}^{-2} \text{ K}^{-1}$, $b = 0.002376326 \text{ K}^{-1}$, and $c = 0.0038 \text{ V } \text{\AA}^{-2} \text{ K}^{-1}$. Here, V_0 , a , and b were obtained by fitting $V_0 + aT/(1 + bT)$ to the $e-\gamma$ data, whereas cT is an independently fixed linear contribution based on the high-temperature gradient reported by Adams and Catchen, rescaled from $Q = 2.51$ b to $Q = 2.36$ b [see the dash-dotted curve in Fig. 9].

This interpolation is convenient for summarizing the crossover from low-temperature concavity to high-temperature quasi-linearity, but it should be viewed as

TABLE VII. Fits for B_{1g} -restricted LFP-DFT calculated $V_{33}(T)$ and $\eta(T)$, for both PBE and HSE06, in Fig. 9.

	η	$ V_{33} \text{ (V/}\text{\AA}^2\text{)}$
PBE	$0.6063(1) + (4.47(3) \times 10^{-5}) \times T + (-8.55(2) \times 10^{-10}) \times T^2$	$175.70(1) + (3.238(4) \times 10^{-2}) \times T + (-2.17(3) \times 10^{-6}) \times T^2$
HSE06	$0.6384(2) + (5.02(7) \times 10^{-5}) \times T + (-1.24(5) \times 10^{-10}) \times T^2$	$166.43(3) + (3.97(1) \times 10^{-2}) \times T + (-3.69(7) \times 10^{-6}) \times T^2$

an empirical parameterization rather than as part of the microscopic LFP model itself, as discussed in Sec. V of the SM [27]; see also Refs. [51,60,64,65,67,68].

VI. COMBINED DISCUSSION

Before discussing the combined temperature evolution, we note that the comparison between the present e- γ data and the earlier γ - γ measurements could, in principle, be affected by differences in the electronic configuration of the probe immediately after the first transition [16,28]. In γ - γ TDPAC, the first transition leaves the electronic shell of the probe unchanged, whereas in e- γ TDPAC, the conversion-electron emission creates an electronic vacancy [16–18,28].

However, for rutile TiO₂, our earlier room-temperature study found the e- γ and γ - γ spectra to be effectively indistinguishable, consistent with electronic recombination on a timescale much shorter than the ~ 10 ns lifetime of the intermediate ¹⁸¹Ta state [17,18]. Therefore, we attribute the difference between the present e- γ data and the earlier γ - γ results primarily to the different temperature ranges covered, rather than to differences in the electronic state of the probe immediately after the first transition [see Fig. 2].

In the Ti and Ta cases discussed here, the largest principal EFG axis remains aligned with the crystallographic c direction [13]. By contrast, Cd substitution rotates this axis away from c , yielding a qualitatively different hyperfine response [69]. This mainly reflects the larger size and bond-length mismatch of Cd at the Ti site, while the impurity state near the Fermi level accounts for the stronger charge-state sensitivity of the Cd EFG and relaxation pattern via APW+lo DFT calculations [13,69].

For the ground-state Ta-substitutional defect in rutile TiO₂, HSE06 relaxation yields two distinct Ta-O bond lengths: four equatorial Ta-O_{xy} ≈ 1.96 Å and two apical Ta-O_z ≈ 1.98 Å, consistent with the larger ionic radius of Ta [13]. The corresponding PBE values are approximately 1.98 and 2.00 Å, respectively. Thus, the Ta-O bond lengths differ by no more than 0.023 Å between PBE and HSE06, indicating that both functionals produce similar local relaxations around the Ta impurity. Therefore, the remaining difference in the calculated EFG is unlikely to arise primarily from large structural differences, but rather from the functional dependence of the Ta-O valence charge distribution, especially regarding the O-2p contribution to this bond. The calculated partial density of states (pDOS), shown in Sec. VIII of the SM [27] is consistent with earlier work [13]: Ta introduces shallow-donor character without mid-gap states, while O-2p states dominate the valence band, and Ti/Ta- d states contribute near the conduction-band edge.

Within the LFP-DFT framework, the Ta-site EFG retains a fixed ordering of principal components over the thermally sampled B_{1g} shear displacements, in contrast to pristine TiO₂, where the same symmetry channel reaches $V_{22} = V_{11}$ and yields principal-component interchange. The absence of a $V_{22} = V_{11}$ crossing at the Ta site implies robust in-plane anisotropy through the relevant vibrational window, yielding a smooth, weakly temperature-dependent $\eta(T)$. This is consistent with the more rigid local Ta-O response inferred from the ground-state relaxation and pDOS analysis presented in

Sec. VIII of the SM [27], in agreement with earlier work [13]. At the Ti site, by contrast, the B_{1g} shear trajectory drives V_{22} toward V_{11} and reaches an in-plane degeneracy within the thermally sampled displacement range, producing the stronger $\eta(T)$ evolution.

The weak low-temperature concavity of $|V_{33}(T)|$ reflects the fact that thermal sampling of the dominant B_{1g} shear mode is not strictly harmonic. The LFP energy profile is well described by a harmonic-quartic potential with weak hardening (Fig. 7), so within a self-consistent harmonic approximation (SCHA) [64,65,68], the renormalized curvature $K_{\text{eff}}(T)$ increases with temperature and $\langle u^2 \rangle_T$ grows sublinearly (approaching $\langle u^2 \rangle_T \propto \sqrt{T}$ in the classical quartic-dominated limit). Over the experimentally accessed range, this behavior can be conveniently parameterized in Padé form [67]. For the B_{1g} mode at the D_{2h} Ti/Ta site, the distortions at u and $-u$ are symmetry-equivalent. Hence, the EFG expansion contains only even powers of u . To leading order [56,64,65,68,70]

$$|V_{33}(T)| = |V_0| + \alpha \langle u^2 \rangle_T + \mathcal{O}(\langle u^4 \rangle_T), \quad \alpha > 0, \quad (13)$$

which naturally yields concave-down $|V_{33}(T)|$. The derivation of this even-amplitude expansion in Eq. (13) and the associated Padé-like temperature dependence of the EFG are given in Sec. VI of the SM [27]; see also Refs. [8,9,56,60,64,65,67,68,70].

We conclude with an additional remark. Previous studies on Cd impurities in rutile TiO₂, such as Ref. [69], and to a lesser extent, the Ta calculations in Ref. [13], used a quasistatic lattice-expansion method in which temperature effects are modeled through the thermal expansion of the host lattice, with local impurity environments re-relaxed at each lattice setting. For Cd, this method already captures a dip-and-rise $\eta(T)$ behavior, suggesting that the temperature-dependent EFG response mainly results from static-like anisotropic relaxations of the surrounding oxygen octahedron. Yet, our current Ti-site findings demonstrate that such behavior is not solely caused by impurity-induced local relaxations. In pure rutile, it mainly involves a symmetry-driven local B_{1g} shear mode, leading to a thermally accessible $V_{22} = V_{11}$ crossing. This shows that the dip-and-rise pattern is more closely related to whether thermal sampling can access in-plane degeneracy of the EFG tensor, rather than quasistatic lattice expansion alone. So, while the quasistatic approach may partially capture the effects of underlying distortion physics when impurity relaxations dominate, it does not identify the microscopic mechanism driving the response.

Overall, the comparison between experiment and simulation indicates that the LFP-DFT approach effectively captures the qualitative trend of the temperature dependence of the EFG, although it shows some quantitative discrepancies in the Ta-substituted case. For pristine rutile TiO₂, the B_{1g} -focused calculation reproduces the experimental increase in $|V_{33}(T)|$ and the typical evolution of $\eta(T)$, supporting the view that the equatorial-oxygen shear is the main local distortion. In substitutional Ta, the computed ground-state EFG scale appears reasonable: PBE yields $|V_{33}| = 141$ V/Å², close to the experimental values around 133–138 V/Å², while HSE06 overestimates the magnitude but stays within the correct scale. Finite-temperature calculations for Ta also reproduce the experimentally observed stability of $\eta(T)$, con-

sistent with the absence of a thermally accessible $V_{22} = V_{11}$ crossing. Nonetheless, the weaker curvature of $|V_{33}(T)|$ compared to low-temperature e- γ data suggests that additional factors (such as other vibrational modes, thermal expansion, or changes in electronic screening) may influence the results beyond the minimal B_{1g} -restricted local model.

VII. LIMITATIONS

The present LFP-DFT framework is intended as a symmetry-guided local analysis of the finite-temperature EFG response, rather than as a comprehensive finite-temperature lattice-dynamical treatment. Its main purpose is to identify which local, symmetry-resolved distortions dominate the observed evolution of $V_{33}(T)$ and $\eta(T)$, rather than to provide a fully converged multidimensional anharmonic average across all phonon branches.

The method fundamentally relies on mode separability. In practice, the LFP approach analyzes one-dimensional mode trajectories and combines them through the symmetry-selected subspace estimator. This approach presumes that mixed-mode couplings remain small within the displacement range that significantly contributes to thermal activity. Symmetry reduces bilinear intersector couplings in the local D_{2h} symmetry description, but does not completely remove all higher-order or same-sector couplings. As a result, residual symmetry-allowed mixing and defect-related relaxation could slightly modify quantitative details, such as the exact positions of near-degeneracies, while still preserving the core identification of the primary B_{1g} shear sector.

The current method focuses on a symmetry-selected local subspace. While this is physically justified for understanding the microscopic basis of the $\eta(T)$ evolution, it is a simplification relative to averaging over all vibrational states. Notably, symmetry-inequivalent modes that do not directly lead to a $V_{22} = V_{11}$ approach can still collectively affect the finite-temperature EFG response. Consequently, identifying the B_{1g} sector as the main contributor highlights the primary microscopic mechanism behind the observed behavior, without suggesting that other vibrational contributions are negligible.

All EFG responses are calculated within static displaced-structure DFT using PBE and HSE06 functionals at the electronic-structure level. Quantitative differences in absolute EFG magnitude and curvature may result from typical exchange-correlation limitations and the lack of explicit many-body screening and electron-phonon renormalization beyond this static approach. Relativistic effects are considered at the scalar-relativistic level, with spin-orbit coupling not included.

The $V_{33}(T)$ values from experiments are also affected by the uncertainty in the nuclear quadrupole moment Q for the intermediate state of ^{181}Ta . However, the uncertainties reported for $V_{33}(T)$ in this study do not account for this systematic error and reflect only the fitting uncertainty. Meanwhile, $\eta(T)$, which is a ratio of principal components, is not influenced by Q . Although DFT-calculated EFGs are independent of this convention, when comparing simulated and experimental absolute $|V_{33}(T)|$ values, it is important to consider the uncertainty and how the results depend on the Q convention.

These limitations are most evident in the Ta-substituted case. Although the B_{1g} -restricted LFP-DFT approach captures the qualitative difference between pristine and Ta-substituted rutile and reflects the smooth, weakly temperature-dependent $\eta(T)$, it underestimates the low-temperature concavity of $|V_{33}(T)|$ by roughly a factor of 5 to 8. This suggests that the simple local B_{1g} model does not fully account for all factors affecting the Ta-site thermal response, especially those related to additional phonon modes, thermal expansion, and other background effects, such as temperature-dependent electronic screening outside the considered subspace.

Finally, the Padé-like interpolation summarizing the entire experimental $|V_{33}(T)|$ evolution should be seen as an empirical fitting approach rather than an element of the microscopic LFP model itself. Specifically, the supplementary linear $c \times T$ term acts as a phenomenological high-temperature background component, not something derived directly from the quartic-oscillator SCHA alone.

We emphasize again that, within this scope, the primary benefit of the current framework is to identify the dominant symmetry-resolved local distortions that control the observed evolution of the EFG and to explain why the Ti and Ta cases exhibit qualitatively different $\eta(T)$ behaviors.

VIII. CONCLUSIONS

In this study, we examined the temperature-dependent EFG at the substitutional $^{181}\text{Hf} \rightarrow ^{181}\text{Ta}$ site in single-crystal rutile TiO_2 , using e- γ TDPAC across temperatures from 30 to 470 K. The results reveal a subtle but noticeable concave-down variation of $|V_{33}(T)|$ at lower temperatures, while $\eta(T)$ remains nearly unchanged. Combining these findings with previous high-temperature γ - γ TDPAC data, it appears that the EFG at the Ta site does not follow a simple linear temperature trend throughout the entire range but instead evolves from low-temperature curvature toward nearly linear behavior at higher temperatures.

Comparison with LFP-DFT reveals that the calculations capture the main qualitative experimental trends, although some quantitative discrepancies remain in the Ta-substituted case. The calculated ground-state Ta-site EFG scale appears reasonable: PBE predicts $|V_{33}| = 141 \text{ V}/\text{\AA}^2$, which is close to the experimental range of about 133–138 $\text{V}/\text{\AA}^2$, while HSE06 tends to overestimate the magnitude but still provides a correct EFG scale. In the finite-temperature analysis, the B_{1g} -restricted LFP approach captures the steady increase of $|V_{33}(T)|$ and the stability of $\eta(T)$, though it underestimates the low-temperature curvature of $|V_{33}(T)|$. This suggests that factors beyond the minimal B_{1g} -restricted model are important for accurately describing the thermal response at the Ta site.

In pristine rutile TiO_2 , the local D_{2h} site symmetry aligns one principal EFG axis with the crystallographic c direction. Within this framework, symmetry-resolved LFP-DFT analysis reveals two orthogonal B_{1g} equatorial-oxygen shear modes as the dominant symmetry-resolved local distortions influencing the temperature dependence of $|V_{33}(T)|$ and $\eta(T)$. This sector alone facilitates the system's approach to a thermally accessible crossing of V_{22} and V_{11} , offering a microscopic explanation for the characteristic change of $\eta(T)$.

At the Ta-substitutional site, the same B_{1g} shear sector remains active, but the host-like in-plane degeneracy is lifted, so that a finite splitting persists over the thermally sampled displacement range. As a result, the principal-component ordering remains fixed, and $\eta(T)$ stays comparatively robust. The qualitative contrast between pristine and Ta-substituted rutile therefore arises from whether thermal sampling can access the in-plane EFG degeneracy within the active B_{1g} shear sector.

Within this scope, the main value of the current framework is to isolate the main symmetry-resolved local distortions that influence the observed EFG evolution and to explain why Ti and Ta show qualitatively different $\eta(T)$ behaviors. A natural next step for testing this symmetry-based approach would be to apply it to different impurity cases, such as Cd in rutile TiO_2 , where the largest principal EFG axis is known to rotate away from the crystallographic c direction, indicating a different microscopic regime.

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DATA AVAILABILITY

The mode-resolved LFP-DFT dataset (PBE) for all 21 site-symmetric modes [mode energy profile $E(y)$, principal EFG components $V_{11}(y)$, $V_{22}(y)$, $V_{33}(y)$, and the derived thermal-averaged observables] is available in an open repository [71].

Additional supporting data for the coupled B_{1g} shear-plane analysis discussed in the Supplemental Material, including the symmetry constrained polynomial-fit coefficients, residual analysis, and goodness-of-fit measures, are available in a separate open repository [72].

The processed $e\text{-}\gamma$ TDPAC datasets used in this work, including the time spectra, extracted EFG parameters with uncertainties, and fit settings, are provided in an open repository [73].

The materials used to prepare the figures in the main text and SM are available in a separate open repository [74].

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