Phonon anharmonicity of rutile SnO$_2$ studied by Raman spectrometry and first principles calculations of the kinematics of phonon-phonon interactions

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Raman spectra of rutile tin dioxide (SnO$_2$) were measured at temperatures from 83 to 873 K. The pure anharmonicity from phonon-phonon interactions was found to be large and comparable to the quasiharmonicity. First-principles calculations of phonon dispersions were used to assess the kinematics of three-phonon and four-phonon processes. These kinematics were used to generate Raman peak widths and shifts, which were fit to measured data to obtain the cubic and quartic components of the anharmonicity for each Raman mode. The $B_{2g}$ mode had a large quartic component, consistent with the symmetry of its atom displacements. The broadening of the $B_{2g}$ mode with temperature showed an unusual concave-downwards curvature. This curvature is caused by a change with temperature in the number of down-conversion decay channels, originating with the wide band gap in the phonon dispersions.

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I. INTRODUCTION

Rutile tin dioxide (SnO$_2$) is the most common and stable oxide of tin found in nature. Owing to the wide variety of its applications for optoelectronics, heterogeneous catalysis, and gas sensors, rutile SnO$_2$ has been the subject of much recent research.$^1$ Lattice dynamics, phase transitions, and nanostructures of SnO$_2$ have been studied by measurements of optical phonons with Raman, Brillouin, or infrared spectroscopy$^{2–6}$ and by computation with force field models or density functional theory.$^{7–11}$ Rutile SnO$_2$ is tetragonal with the space group $P4/nmm$. The modes of symmetry $B_{1g}$, $E_g$, $A_{1g}$, and $B_{2g}$ are Raman active (Fig. 1) and comprise motions of oxygen anions with respect to stationary tin cations, either perpendicular to the $c$ axis (modes $B_{1g}$, $A_{1g}$, and $B_{2g}$) or along the $c$ axis (mode $E_g$).

Nonharmonic effects are known to be important for understanding the thermodynamic stability and the thermal transport properties of materials at elevated temperatures, but the anharmonic lattice dynamics of rutile SnO$_2$ is largely unknown. Perhaps the most complete experimental results are from Peercy and Morosin’s work in 1973.$^3$ They reported frequency shifts of Raman modes with temperature and pressure, although the temperature range was below 480 K and no phonon broadening information was reported. The linewidth broadening of the $A_{1g}$ mode was measured to 973 K by Sato and Asari and compared well with results from shell model calculations.$^8$ Their results suggest that the anharmonicity of SnO$_2$ is large.

In our recent study on rutile TiO$_2$, the pure anharmonicity gave shifts of Raman peaks that were as large as from quasiharmonicity.$^{12}$ In that study we developed a rigorous method of simultaneously fitting Raman peak widths and shifts with calculations from the kinematics of phonon-phonon interactions. The effects of cubic and quartic anharmonicity were separated, and these anharmonic effects were found to be dominated by phonon kinematics. This previous work on TiO$_2$ used kinematics calculated with a shell model, but in the present study on rutile SnO$_2$, inconsistencies in the different shell model parameters from the literature motivated the use of $ab$ initio methods to calculate phonon dispersions. The analysis and comparison of our present results on rutile SnO$_2$ with previous results on TiO$_2$ provide a better understanding of the anharmonic phonon dynamics in both.

Here we report high-resolution measurements of Raman spectra at temperatures from 83 to 873 K. Both phonon frequency shifts and broadenings are reported. The quasi-harmonic effects from thermal expansion were separated from the anharmonic effects of phonon-phonon interactions by comparing the temperature dependence to the pressure dependence of the Raman peaks. The data fitting method used $ab$ initio calculations of two-phonon kinematic functionals to identify the effects of cubic and quartic anharmonicity. The peak broadening originates with cubic anharmonicity, but the peak shifts depend on both cubic and quartic effects. The phonon-phonon kinematics explains an unusual feature in the temperature dependence of the broadening of the $B_{2g}$ mode of rutile SnO$_2$. The large difference in masses of Sn and O atoms causes a gap in the phonon density of states (DOS) that produces a peak in the two-phonon DOS (TDOS). The thermal shift moves the frequency of the $B_{2g}$ mode away from this peak in the TDOS and reduces the number of channels available for three-phonon processes, giving a concave-downwards curvature to the thermal broadening of the $B_{2g}$ peak. The symmetrical $B_{2g}$ mode was found to have a relatively large quartic anharmonicity.

II. EXPERIMENTAL PROCEDURES

Measurements were performed on both powder and single-crystal samples of rutile SnO$_2$. The powder sample was prepared from commercial SnO$_2$ powder (Alfa Aesar, Ward Hill, MA) with a grain size of 10 $\mu$m. The powder was compressed into pellets of 1-mm thickness using a pressure of 50 MPa at ambient temperature. Raman spectra were acquired before and after compression into a pellet and were found to be identical. A sample of single-crystal cassiterite of high optical quality was provided by the Mineral Museum of the Division of Geological and Planetary Sciences at the California Institute of Technology. The sample was cut and polished to a thickness of approximately 0.3 mm. Samples were mounted on the silver...
block of a Linkam thermal stage that provided excellent heat transfer and temperature stability for both heating and cooling. The sample chamber was sealed and purged with nitrogen gas flow. A temperature controller drove a 200-W power supply for heating. For low-temperature measurements, the stage was equipped with a coolant pump that injected liquid nitrogen directly into the silver block. Samples of powder pellets were measured at temperatures from 83 to 833 K, and the single-crystal sample was measured from 83 to 873 K. Each temperature was held stable for 10 min before the spectrum was taken. The temperature precision was within 1 K.

Raman spectra were measured with a Renishaw micro-Raman system with an Olympus LMPlanFI microscope lens. The spectrometer was configured in backscattering geometry, minimizing issues with the thickness of the sample. A depolarized solid-state laser operated at a wavelength of 514.5 nm excited the sample with the low incident power of 10 mW to avoid additional thermal heating. The laser spot size was 12 μm in diameter. To test for heating effects this spot size was varied, but no changes were found. Each Raman spectrum was accumulated in 10 measurements with 10-s exposure times.

III. RESULTS

Representative Raman spectra of powder samples are shown in Fig. 2. Three of the four Raman-active modes, $E_g$, $A_{1g}$, and $B_{2g}$, have enough intensity for extracting quantitative information on phonon frequencies and linewidths. The $B_{1g}$ mode was too weak to obtain quantitative information (its intensity is about three orders of magnitude lower than that of the $A_{1g}$ mode). The single-crystal sample showed very similar spectra, but the $E_g$ mode was weaker, primarily because of orientation effects. Three weak abnormal Raman bands reported previously were also observed at 503, 545, and 692 cm$^{-1}$ for both powder and single-crystal samples.

After background subtraction, each peak in each spectrum was fitted to a Lorentzian function to obtain a centroid and full width at half-maximum (FWHM). FWHM data from the experiment were corrected for the finite resolution of the spectrometer. At room temperature, the Raman peak frequencies were 475 cm$^{-1}$ for $E_g$, 633 cm$^{-1}$ for $A_{1g}$, 774 cm$^{-1}$ for $B_{2g}$. The mode frequencies at 83 K, $\omega$(83 K), were 476, 636, and 778 cm$^{-1}$. Figure 3 presents the results on peak shifts and widths versus temperature. Here the peak shift $\Delta\omega$ is defined as $\omega(T) - \omega$(83 K). We find good agreement with the frequency shift data reported by Peercy and Morosin at temperatures below 480 K. We also find good agreement with the linewidth broadening data of the $A_{1g}$ mode reported by Sato and Asari to 900 K.

With increasing temperature, the $A_{1g}$ and $B_{2g}$ modes undergo large shifts to lower frequencies and significant linewidth broadenings, but the $E_g$ mode undergoes less shift and broadening. At high temperatures, above 500 K, the broadening of the $B_{2g}$ mode shows an unusual concave-downwards curvature, while the other two modes broaden linearly. At low temperatures, the $B_{2g}$ mode has a much larger linewidth than the other two modes. The linewidth of the $B_{2g}$ mode extrapolated to 0 K is approximately 8 cm$^{-1}$, whereas the linewidths of the $E_g$ and $A_{1g}$ modes extrapolate to less than 2 cm$^{-1}$.

IV. CALCULATIONS

A. First-principles lattice dynamics

Phonon dispersion calculations over the whole Brillouin zone were performed with the QuantumEspresso package, within the framework of ab initio density functional perturbation theory. Vanderbilt ultrasoft pseudopotentials with the local density approximation (LDA) and nonlinear core
considering the frequency dependence of three-phonon and four-phonon processes. The dashed curve was calculated without fittings with a full calculation of the kinematics of three-phonon single-crystal samples, respectively. Solid curves are the theoretical results. Filled and open symbols represent experimental data from powder and decay channels, at elevated temperatures.

(b) breadths as FWHMs of the Raman modes \( \Delta \omega \).

FIG. 3. Temperature dependence of (a) frequency shifts and (b) breadths as FWHMs of the Raman modes \( E_g, A_{1g}, \) and \( B_{2g} \). Filled and open symbols represent experimental data from powder and single-crystal samples, respectively. Solid curves are the theoretical results. Filled and open symbols represent experimental data from powder and decay channels, at elevated temperatures.

corrections were used. The LO / TO splitting was corrected by adding a nonanalytical part into the dynamical matrix. The calculated dispersion curves are shown in Fig. 4(a), and mode frequencies at the \( \Gamma \) point are reported in Table I. Calculations of the phonon DOS with a uniform 16 \times 16 \times 16 sampling grid were also performed, as shown in Fig. 4(b). Our calculations are in good agreement with prior experimental and theoretical results. A band gap of width 100 cm\(^{-1}\), centered around 400 cm\(^{-1}\), is evident in Fig. 4. Above the gap, phonon modes are dominated by the motions of oxygen atoms.

B. The kinematic functionals \( D^\omega(\Omega) \) and \( P^\omega(\Omega) \)

In anharmonic phonon perturbation theory, the phonon linewidth is related to the TDOS, \( D(\Omega) \), which is defined as

\[
D(\Omega) = \sum_{\tilde{q}_1, \tilde{q}_2} D(\Omega, \omega_1, \omega_2)
\]

\[
= \frac{1}{N} \sum_{\tilde{q}_{1,2}} \sum_{\tilde{q}_{1,2}} \Delta(\tilde{q}_1 + \tilde{q}_2)[(n_1 + n_2 + 1)\delta(\Omega - \omega_1 - \omega_2)
+ 2(n_1 - n_2)\delta(\Omega + \omega_1 - \omega_2)],
\]

where \( \Omega \) is the frequency of the initial phonon, and phonon modes \( (\tilde{q}_i, j) \) have quasiharmonic frequencies \( \omega_i \) and occupancies \( n_i \). The first and second terms in brackets are from down-conversion and up-conversion phonon processes, respectively.

FIG. 4. (Color online) (a) Calculated phonon dispersion along high-symmetry directions of rutile SnO\(_2\). \( \Gamma \) (0,0,0), \( \chi \) (0.5,0,0), \( M \) (0.5,0.5,0), \( Z \) (0,0.0,5), \( R \) (0.5,0.5,0.5), and \( A \) (0.5,0.5,0.5). At the \( \Gamma \) point, the frequencies from Table I are presented as upward-pointing triangles (Raman) and downward-pointing triangles (infrared). At the \( X, M, Z, R, \) and \( A \) points, the mode frequencies from Ref. 9 (all doubly degenerate) are presented as squares. (b) Total phonon DOS (black curve) and oxygen-projected DOS [shaded (green) area].

<table>
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<tr>
<th>Mode</th>
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<th>Calc. from Ref. 28</th>
<th>Experimental</th>
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<tr>
<td>( B_{1u} )</td>
<td>147</td>
<td>138</td>
<td>140</td>
<td>–</td>
</tr>
<tr>
<td>( E_{2g}^{\text{(TO)}} )</td>
<td>223</td>
<td>200</td>
<td>236</td>
<td>244</td>
</tr>
<tr>
<td>( E_{1u}^{\text{(LO)}} )</td>
<td>269</td>
<td>252</td>
<td>268</td>
<td>276</td>
</tr>
<tr>
<td>( E_{2u}^{\text{(TO)}} )</td>
<td>285</td>
<td>270</td>
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<td>( E_{1u}^{\text{(LO)}} )</td>
<td>335</td>
<td>307</td>
<td>377</td>
<td>366</td>
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<tr>
<td>( A_{2g} )</td>
<td>360</td>
<td>320</td>
<td>398</td>
<td>–</td>
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<tr>
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<td>457</td>
<td>512</td>
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<td>( B_{3g} )</td>
<td>564</td>
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<td>505</td>
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<td>584</td>
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<td>( A_{3u} )</td>
<td>633</td>
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<td>636</td>
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<tr>
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<td>670</td>
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<td>687</td>
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<td>( E_{3u}^{\text{(LO)}} )</td>
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<td>712</td>
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<td>( B_{3g} )</td>
<td>765</td>
<td>734</td>
<td>752</td>
<td>778</td>
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</tbody>
</table>

\( ^a \)First-principles LDA calculation from Borges et al.\(^1\)

\( ^b \)Force-field calculation from Katiyar et al.\(^2\)

\( ^c \)Data for infrared active modes at 100 K are from Katiyar et al.\(^2\)

\( ^d \)Data for Raman-active modes at 83 K are from the present measurements.
The two-phonon kinematical functional $P(\Omega)$ for the anharmonic frequency shift is

$$P(\Omega) = \sum_{\vec{q}_1,\vec{q}_2,\vec{q}} \sum_{\omega_1,\omega_2} P(\Omega,\omega_1,\omega_2)$$

$$= \frac{1}{N} \sum_{\vec{q}_1,\vec{q}_2,\vec{q}} \sum_{\omega_1,\omega_2} \Delta(\vec{q}_1 + \vec{q}_2)\rho \left[ \frac{n_1 + n_2 + 1}{\Omega + \omega_1 + \omega_2} - \frac{n_1 + n_2 + 1}{\Omega - \omega_1 - \omega_2} + \frac{n_1 - n_2}{\Omega - \omega_1 + \omega_2} - \frac{n_1 - n_2}{\Omega + \omega_1 - \omega_2} \right], \quad (2)$$

where $\rho$ denotes the Cauchy principal part. The two-phonon spectra, $D(\Omega)$ and $P(\Omega)$, depend on temperature through the phonon occupancy factor, $n$. Both $D(\Omega)$ and $P(\Omega)$ were calculated at various temperatures from the first-principles lattice dynamics calculations described in the previous subsection, sampling modes $\{\vec{q}_j\}$ with a $16 \times 16 \times 16$ $q$-point grid over the first Brillouin zone for good convergence.

V. ANALYSIS

A. Separating anharmonicity from quasiharmonicity

Both quasiharmonicity and pure anharmonicity contribute to the nonharmonic lattice dynamics of rutile SnO$_2$. In the quasiharmonic model, phonon modes behave harmonically with infinite lifetimes, but their frequencies are altered by the effects of volume on the interatomic potential. Pure anharmonicity originates with phonon-phonon interactions, which increase with temperature. Pure anharmonicity contributes to shifts in phonon frequencies, but also causes phonon damping and lifetime broadening of phonon peaks. The large peak broadenings in SnO$_2$ show that there are large effects from pure anharmonicity.

To separate the peak shifts caused by pure anharmonicity from the shifts caused by quasiharmonicity, we treat the mode frequency $\omega_j = \omega_j(V,T)$ as a function of volume and temperature

$$\left( \frac{\partial \ln \omega_j}{\partial T} \right)_P = \frac{\beta}{\kappa} \left( \frac{\partial \ln \omega_j}{\partial P} \right)_T + \left( \frac{\partial \ln \omega_j}{\partial T} \right)_V, \quad (3)$$

where $j$ is the phonon mode index, $\beta$ is the volume thermal expansivity, and $\kappa$ is the isothermal compressibility. This is a general method to separate phonon quasiharmonicity from phonon anharmonicity and is not unique for rutile structures, for example. The left-hand side gives the directly measurable temperature-dependent isobaric frequency shift, including both quasiharmonic and pure anharmonic behavior. The first term on the right-hand side, the isothermal frequency shift as a function of pressure, is the quasiharmonic contribution, which is also measurable. By defining a mode Gr"uneisen parameter as the proportionality of the relative change of the mode frequency to the relative change of volume, i.e., $\gamma_j = -\partial(\ln \omega_j)/(\partial(\ln V))$, the quasiharmonic term can be written as $\gamma_j \beta$. The second term on the right-hand side of Eq. (3) is the frequency shift from the pure anharmonicity, which depends on temperature and not volume. From the difference between the isobaric and the isothermal frequency shifts, the pure anharmonicity can be determined experimentally.

To obtain the quasiharmonic contributions to the peak shifts, we used the mode Gr"uneisen parameters $\gamma_j$ reported recently by Hellwig et al. from Raman measurements at pressures to 14 GPa, which agreed well with earlier high-pressure measurements to 4 GPa. These results suggest that Peercy and Morosin overestimated the quasiharmonic contributions to their data, for which the pressure was only 0.4 GPa.

We also performed first-principles calculations of the mode Gr"uneisen parameters by optimizing the enthalpy function to 10 GPa. Our calculated $\gamma_j$ values were in good agreement with the experimental results of Hellwig et al., and both are listed in Table II. Since the $\gamma_j$ are very weakly dependent on temperature, as is the thermal expansion above 400 K, the $\gamma_j$ values were assumed to be constants when assessing the volume-dependent quasiharmonic contribution. The last two columns in Table II separate the measured isobaric temperature derivatives into the pure volume and pure temperature contributions as in Eq. (3). These last columns in Table II are the frequency shifts from quasiharmonicity and pure anharmonicity at temperatures above 400 K.

By comparing the last two columns in Table II, we see that, like rutile TiO$_2$, the pure anharmonic contribution is comparable to the quasiharmonic contribution above 400 K. Nevertheless, the total anharmonicity of SnO$_2$ is considerably smaller than that of TiO$_2$. For modes $A_{1g}$ and $B_{2g}$ in SnO$_2$, the pure anharmonic contribution is larger than the quasiharmonic one, while the $E_g$ mode is more quasiharmonic. The relative magnitudes of pure anharmonicities of the three modes derived from the frequency shift data are consistent with the relative magnitudes of linewidth broadenings of the modes as shown in Fig. 3(b).

### Table II. Frequencies of the three Raman modes, mode Gr"uneisen parameters, and logarithmic pressure and temperature derivatives of frequency.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$\omega(300 \text{ K})$ (cm$^{-1}$)</th>
<th>$\gamma_j$</th>
<th>$(\frac{\partial \ln \omega}{\partial T})_P$ (10$^{-5}$ K$^{-1}$)</th>
<th>$(\frac{\Delta \ln \omega}{\partial T})_P$ (10$^{-5}$ K$^{-1}$)</th>
<th>$-\gamma_j \beta^4$ (10$^{-5}$ K$^{-1}$)</th>
<th>$(\frac{\Delta \ln \omega}{\partial T})_V$ (10$^{-5}$ K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_g$</td>
<td>475</td>
<td>1.45</td>
<td>1.48</td>
<td>-2.6</td>
<td>-1.7</td>
<td>-0.9</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>633</td>
<td>1.65</td>
<td>1.81</td>
<td>-4.2</td>
<td>-1.9</td>
<td>-2.3</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>774</td>
<td>1.49</td>
<td>1.71</td>
<td>-4.6</td>
<td>-1.7</td>
<td>-2.9</td>
</tr>
</tbody>
</table>

*Thermal expansion data from Peercy and Morosin.\textsuperscript{3}

\textsuperscript{a}Gr"uneisen parameters data from Hellwig et al.\textsuperscript{4}

\textsuperscript{b}From the present first-principles calculations.
B. Cubic and quartic anharmonicity

Anharmonicity tensors describe the coupling strengths for phonon-phonon interactions, but a prerequisite is that the phonons in these processes satisfy the kinematical conditions of conservation of energy and momentum. An anharmonicity tensor element for an s-phonon process is

\[ V(j; q_{1j}; \ldots; q_{s-1j}; j_{s-1}) = \frac{1}{2s!} \left( \frac{\hbar}{2N} \right)^s N \Delta(q_1 + \ldots + q_{s-1}) \times \{ \omega_{j0} \omega_{j1} \ldots \omega_{j(s-1)} \}^2 C(j; q_{1j}; \ldots; q_{s-1j}; j_{s-1}), \]

where \( \Delta(q_1 + \ldots + q_{s-1}) \) enforces momentum conservation and the \( C(\cdot) \)'s, elements of the s-phonon anharmonic tensor, are expected to be slowly varying functions of their arguments. The cubic anharmonicity tensor has been calculated by first-principles methods, but to our knowledge, the quartic anharmonicity tensor has never been fully calculated from first principles.

Nevertheless, if the anharmonicity tensor or its average does not vary significantly for different phonon processes, the coupling factor and the kinematic factor are approximately separable in Eq. (4). The separation of the anharmonic coupling and the kinematics has been used with success in many studies including our recent report on rutile TiO\(_2\). We consider the term \( C(j; q_{1j}; \ldots; q_{s-1j}; j_{s-1}) \) to be a constant of the Raman mode \( j \) and use it as a fitting parameter. Although \( C(j; q_{1j}; q_{1j}; j_1) \) and \( C(j; q_{1j}; q_{1j}; j_2) \) change with \( j_1 \) and \( j_2 \), an average over modes, \( \langle C(j; q_{1j}; q_{1j}; j_2) / \sum_{j_1, j_2} \rangle \), is needed for the fitting, where 1, 2 under the summation symbol represent \( q_{1j} \) and \( q_{1j} \).

The best fits for the shifts and broadenings are shown in Fig. 3, and the fitting parameters are listed in Table III. Figure 6 also shows contributions to the shift from the quasiharmonic and pure anharmonicity (dashed curves).

With a single parameter \( |C_{j}^{(3)}|^2 \) for each mode, good fittings to the broadenings are obtained as shown in Fig. 3(b), indicating significant cubic anharmonicity for these Raman-active modes. Moreover, our fittings also successfully reproduced the unusual concave curvature of the \( B_{2g} \) mode at high temperatures. The \( |C_{j}^{(3)}|^2 \) values do not vary much among different modes, suggesting that the assumption of slowly varying properties of \( C(\cdot) \) values is reasonable.

Starting with the same cubic fitting parameters used for the broadenings, the frequency shifts of these modes are fit well by adding the quasiharmonic and quartic anharmonic effects.

\[
\begin{align*}
\Gamma^{(3)}(j; \Omega) &= \frac{\pi \hbar}{64} \omega_{j0} |C_j^{(3)}|^2 \sum_{q_{1j}, q_{2j}} \omega_{j1} \omega_{j2} D(\Omega, \omega_{j1}, \omega_{j2}) \\
&= \omega_{j0} |C_j^{(3)}|^2 D^{(\Omega)}(\omega_{j1}, \omega_{j2}), \tag{6a} \\
\Delta^{(3)}(j; \Omega) &= -\frac{\hbar}{64} \omega_{j0} |C_j^{(3)}|^2 \sum_{q_{1j}, q_{2j}} \omega_{j1} \omega_{j2} P(\Omega, \omega_{j1}, \omega_{j2}) \\
&= \omega_{j0} |C_j^{(3)}|^2 P^{(\Omega)}, \tag{6b} \\
\Delta^{(3)}(j) &= -\frac{\hbar}{16N} \omega_{j0} |C_j^{(3)}|^2 \sum_{q_{2j}} \omega_{j2} (q_{2j}) (n_{q_{2j}} + \frac{1}{2}), \tag{6c} \\
\Delta^{(4)}(j) &= \frac{\hbar}{8N} \omega_{j0} |C_j^{(4)}|^2 \sum_{q_{1j}} \omega_{j1} (q_{1j}) (n_{q_{1j}} + \frac{1}{2}), \tag{6d}
\end{align*}
\]

where \( D^{(\Omega)}(\omega_{j1}, \omega_{j2}) \) and \( P^{(\Omega)} \) are functionals of \( D(\Omega, \omega_{j1}, \omega_{j2}) \) and \( P(\Omega, \omega_{j1}, \omega_{j2}) \) weighted by the kinematics of anharmonic phonon coupling. Figure 5 shows representative results for \( D^{(\Omega)}(\Omega) \) and \( P^{(\Omega)}(\Omega) \) at 0 and 800 K. The down-conversion and up-conversion subspectra are also shown.

The \( \Delta^{(3)} \) is an additional local-order cubic term that corresponds to instantaneous three-phonon processes. It is nonzero for crystals having atoms without inversion symmetry, as in the case of oxygen atom motions in the \( A_{1g} \) mode. It is much smaller than other contributions, however, owing to symmetry restrictions.

| TABLE III. Fitting parameters for the temperature-dependent Raman modes (units: \( 10^{16} \text{erg}^{-1} \)) |
|-----------------|---------|---------|
| \( |C_{j}^{(3)}|^2 \) | 0.87 | 1.6 | 1.0 |
| \( -C_{j}^{(4)} \) | 1.0 | 2.6 | 7.3 |
As shown in Fig. 6, the quartic contribution $\Delta^{(4)}$ is generally of the same order as the cubic contribution $\Delta^{(3)}$, consistent with the fact that $\Delta^{(4)}$ and $\Delta^{(3)}$ are both leading-order terms for the anharmonic frequency shifts. For the $E_g$ and $A_{1g}$ modes, the pure anharmonicity is mainly from the cubic terms, but for the $B_{2g}$ mode, the quartic anharmonicity is dominant and is as large as the quasiharmonic part.

VI. DISCUSSION

We can understand why the $B_{2g}$ mode has a relatively larger quartic anharmonicity than the $A_{1g}$ mode from the differences in how the O atoms move towards the Sn atoms. Using a unit cell with four O atoms and two Sn atoms, as shown in Fig. 1, the $A_{1g}$ mode has all four O atoms moving directly into one Sn atom in one-half of the cycle but moving between two Sn atoms during the other half of the cycle. The $B_{2g}$ mode has two O atoms moving into a Sn atom and two O atoms moving between two Sn atoms in both halves of the vibrational cycle, making for a potential that is an even function of the phonon coordinate. Table III reports a larger quartic contribution for the $B_{2g}$ than for the $A_{1g}$ mode. (The $E_g$ mode does not have similar atom motions for comparison.)

The TDOS function $D^\text{QW}(\Omega)$ in Fig. 5 shows large variations with $\Omega$, which explains a trend in the thermal broadening in Fig. 3(b). Owing to the high frequency of the $B_{2g}$ mode, at the temperatures used in this study its phonon-phonon anharmonicity comes mostly from down-conversion processes, as shown in Fig. 5. Ignoring the small up-conversion contribution, at high temperatures\textsuperscript{24}

$$D^\text{QW}(\Omega, T) \propto T \sum_{q_1,j_1} \sum_{q_2,j_2} \delta(\Omega - \omega_1 - \omega_2) \equiv T D_{01}(\Omega),$$

where $D_{01}(\Omega)$ is the number of two-phonon down-conversion channels. Usually the line broadening is linear in $T$ because $D_{01}(\Omega)$ does not vary much with temperature. However, the $B_{2g}$ mode at 774 cm\textsuperscript{-1} lies on a steep gradient of $D^\text{QW}(\Omega, T)$ in Fig. 5. Because the $B_{2g}$ mode undergoes a significant shift of frequency with temperature, it moves down the gradient of $D^\text{QW}(\Omega, T)$, and its broadening is less than linear in $T$. The temperature dependence of the broadening of the $B_{2g}$ mode has an unusual concave-downwards shape. For comparison, the dashed line in Fig. 3 was calculated without considering the frequency dependence of $D_{01}(\Omega)$ at elevated temperatures, and it deviates substantially from the experimental trend.

The unusual temperature dependence of the linewidth of the $B_{2g}$ mode comes from the sharp peak in $D^\text{QW}(\Omega, T)$ centered at 800 cm\textsuperscript{-1}. This feature in the TDOS originates with the phonon DOS of SnO\textsubscript{2} shown in Fig. 4, which has a band gap between 360 and 450 cm\textsuperscript{-1} associated with the mass difference between Sn and O atoms. The shape of the TDOS can be understood as the convolution of the phonon DOS with itself. With two approximately equal regions above and below the gap, the result is a peak at 800 cm\textsuperscript{-1}, with steep slopes on both sides. For comparison, although the TDOS of rutile TiO\textsubscript{2} is shaped as a broad peak,\textsuperscript{12} it does not have the sharp features shown in Fig. 5(a) because the mass difference between Ti and O atoms does not cause a band gap in the phonon DOS of TiO\textsubscript{2}.

Especially with more up-conversion processes at higher temperatures, there is another peak in the SnO\textsubscript{2} TDOS, at 400 cm\textsuperscript{-1}. The up-conversion channels are primarily from the pairs of sharp peaks in the phonon DOS at 100 and 500, 200 and 600, and 350 and 750 cm\textsuperscript{-1}. Although the $E_g$ mode at 475 cm\textsuperscript{-1} is on the slope of this peak in the TDOS, the $E_g$ mode does not show anomalous broadening with temperature because it undergoes only a small thermal shift in frequency.

In the low-temperature limit, up-conversion processes are prohibited because $n \to 0$. The peak linewidth extrapolated to 0 K is determined entirely by down-conversion processes, quantified by the down-conversion TDOS.\textsuperscript{24} The $B_{2g}$ mode has a significant broadening because its frequency is near a peak in the down-conversion TDOS, as shown in Fig. 5. On the other hand, the $E_g$ and $A_{1g}$ modes are not broadened at low temperatures because their frequencies are at low values of the TDOS. The phonon-phonon kinematics accounts for the significant difference in linewidths between the $B_{2g}$ and the other two Raman modes at low temperatures.

VII. CONCLUSIONS

Raman spectra were measured on rutile SnO\textsubscript{2} at temperatures from 83 to 873 K, and large anharmonic shifts and broadenings were found for the three measurable Raman
peaks. Individual assessments of the cubic and quartic contributions to the anharmonicity were performed by calculating the kinematics of three-phonon and four-phonon processes with ab initio methods and varying the anharmonic coupling parameters to fit the peak shifts and broadenings simultaneously. The quartic anharmonicity of the $B_{2g}$ mode was found to be large, unlike the $E_g$ and $A_{1g}$ modes, for which cubic anharmonicity is dominant. The quartic behavior of the $B_{2g}$ mode can be understood from the symmetry of the oxygen atom displacements.

The phonon DOS of SnO$_2$ has a band gap around 400 cm$^{-1}$ owing to the mass difference of Sn and O atoms, with a similar structure above and below the gap. This causes a sharp peak in the TDOS at 800 cm$^{-1}$. The frequency of the $B_{2g}$ mode is on the slope of this peak in the TDOS, and its frequency shift with temperature reduces the number of down-conversion channels for its broadening. The thermal broadening of the $B_{2g}$ mode consequently shows an anomalous concave-downwards curvature. At 0 K, the large TDOS around 800 cm$^{-1}$ explains the large linewidth of the $B_{2g}$ mode. The anharmonic peak shifts and broadenings were well accounted for by the kinematics of phonon-phonon interactions, suggesting that, on average, the anharmonicity tensors for rutile SnO$_2$ are not rich in structure.

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