Tracking the continuous spin-flop transition in Ni$_3$TeO$_6$ by infrared spectroscopy

Michael O. Yokosuk, Sergey Artyukhin, Amal al-Wahish, Xueyun Wang, Junjie Yang, Zhiqiang Li, Sang-Wook Cheong, David Vanderbilt, and Janice L. Musfeldt

1Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA
2Department of Physics and Astronomy and the Rutgers Center for Emergent Materials, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08854, USA
3Laboratory for Pohang Emergent Materials and Max Plank POSTECH Center for Complex Phase Materials, Pohang University of Science and Technology, Pohang 790-784, Korea
4National High Magnetic Field Laboratory, Tallahassee, Florida 32310, USA
5Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA

(Received 26 July 2015; published 8 October 2015)

Easy axis antiferromagnets usually exhibit a first-order spin-flop transition when the magnetic field is applied along the easy axis. Recently a colossal magnetoelectric effect was discovered in Ni$_3$TeO$_6$, suggesting a continuous spin-flop transition across a narrow phase in this material [Oh et al., Nat. Commun. 5, 3201 (2014)]. Additional evidence is, however, desirable to verify this mechanism. Here we measure the infrared vibrational properties of Ni$_3$TeO$_6$ in high magnetic fields and demonstrate that the phonon anomalies are consistent with a second-order mechanism.

DOI: 10.1103/PhysRevB.92.144305 PACS number(s): 75.80.+q, 75.30.Kz, 78.30.Am, 75.50.Ee

I. INTRODUCTION

Ni$_3$TeO$_6$ sports the largest magnetoelectric effect seen to date in a single-phase material [1] and the second-largest magnetically induced polarization change [2]. This system has a polar R3 structure [3,4], insulating behavior [5], and is pyroelectric [1] (Fig. 1). The polarization direction is set by the sequence of Ni and Te ions along the c axis in the rhombohedral unit cell. Ni ions have the outer shell electronic configuration $t^2_2e^6_s^2$ and spin $S = 1$, whereas Te is nonmagnetic [1,4]. This system thus provides an opportunity to examine (i) magnetoelastic and magnetoelastic coupling when magnetic order develops in a polar lattice and (ii) how transition metal centers mix with nonmagnetic ions that have large spin-orbit coupling. The complex magnetism also provides a framework that motivates the search for new high field phases. Antiferromagnetic ordering sets in at $T_N = 53$ K, with Ni spins along the hexagonal c axis having $\uparrow\uparrow\uparrow\downarrow\downarrow\uparrow$ ordering in the doubled rhombohedral unit cell (AFM-I) [4]. At a 9 T magnetic field applied along the hexagonal c axis, the spins flop into the ab plane (AFM-II phase). While most antiferromagnets show a first-order spin-flop transition when the magnetic field is applied along the easy axis [6–8], Ni$_3$TeO$_6$ displays a sequence of two second-order transitions near 9 T limiting a narrow intermediate phase, across which the antiferromagnetic order parameter rotates by a 90° angle [2]. Heisenberg exchange striction in this polar material couples spin canting to the polarization change, giving rise to a colossal magnetoelectric effect in the intermediate phase [1].

Considering the foundational role of Heisenberg exchange striction in generating spin-lattice coupling, the complex magnetism, and the enormous field-induced polarization changes, direct measurements of the elementary excitations are important for understanding Ni$_3$TeO$_6$ and other members of this promising family of compounds [9–15]. Here, we employ infrared vibrational spectroscopy to reveal the lattice dynamics of Ni$_3$TeO$_6$ over a broad range of temperature and magnetic field. Our measurements uncover frequency shifts in the phonons across $T_N$ and through the field-driven spin-flop transition, demonstrating that the lattice is sensitive to changes in the microscopic spin arrangement. Corroborating the measurements with $ab$ initio calculations, we assign infrared absorption peaks, identify phonons that have the largest spin-phonon coupling, and trace the microscopic origin of this coupling. Unexpectedly, spin-lattice coupling in Ni$_3$TeO$_6$ involves modes in the ab plane in addition to those along the c axis. Both act to modify superexchange. Trends in these features are consistent with the peculiar second-order character of the spin-flop transition. Our measurements also reveal signatures of a previously unknown transition between 30 and 35 T that merits additional investigation.

II. METHODS

Ni$_3$TeO$_6$ single crystals were grown by flux techniques as described previously [1]. Reflectance measurements were performed using a series of spectrometers in the ab plane and

FIG. 1. (Color online) (a) Temperature dependence of the electric polarization P$_E$ (H$_c$) showing the magnetically induced polarization change below the 53 K Néel transition [1]. (b) Magnetization curves at different temperatures [1]. (c) Schematic phase diagram of Ni$_3$TeO$_6$ for $H \parallel c$ showing the 9 T spin flop and the possibility of an unexplored transition between 30 and 35 T.
along the c axis between 5 and 300 K. A Kramers-Kronig analysis was used to obtain the optical constants. Magneto-infrared experiments employed a polycrystalline sample in either a polyethylene or KBr matrix and a resistive magnet at the National High Magnetic Field Laboratory (100–3000 cm\(^{-1}\); 4.2 K; 0–35 T). The absorption \(\alpha(\omega)\) was calculated as \(\alpha(\omega) = -\frac{1}{h}\ln[T(\omega)];\) where \(T(\omega)\) is the measured transmittance, \(h\) is the loading, and \(d\) is the effective thickness. Absorption differences were also calculated in order to highlight small field-induced changes. Here, \(\Delta\alpha = \alpha(\omega,H) - \alpha(\omega,H = 0)\). Standard peak fitting techniques were employed as appropriate.

Phonon frequencies were computed using the frozen-phonon method as implemented in PHONOPY and VASP software packages [16–21]. Calculations used generalized gradient approximation within projector-augmented wave formalism, and Ni p electrons were treated as valence, a plane-wave cutoff of 500 eV, a \(4 \times 4 \times 4\) \(\Gamma\)-centered \(k\)-point grid, and up-up-down spin ordering in a \(1 \times 1 \times 1\) rhombohedral unit cell. Using a \(1 \times 1 \times 2\) unit cell where spin exchanges are not frustrated is computationally more expensive, and magnetic field-induced phonon frequency shifts are much smaller than the frequencies themselves, so that a \(1 \times 1 \times 1\) rhombohedral unit cell seems appropriate for phonon assignment purposes.

### III. RESULTS AND DISCUSSION

Figure 2(a) displays the polarized infrared absorption of Ni\(_3\)TeO\(_6\) at 300 K. A symmetry analysis predicts nine \(E\) symmetry optical phonons in the \(ab\) plane and nine optical modes of \(A\) symmetry polarized along \(c\) \((\Gamma_0 = 9E + 9A)\). In the polar \(R3\) structure [3,4], the optical modes are both infrared and Raman active [22]. All are present in the infrared response of Ni\(_3\)TeO\(_6\) save one, and that mode is observed clearly in the Raman spectrum. The vibrational features are assigned according to our lattice dynamics calculations. A comparison of the theoretically predicted and experimentally observed mode frequencies is shown in Table I along with a description of the displacement patterns. For instance, the phonon at 310 cm\(^{-1}\) corresponds to Ni\(_I\) displacing opposite to Te in the \(ab\) plane in a symmetric stretch with Ni\(_{II}\) and Ni\(_{III}\) remaining at rest. By contrast, the 597 and 666 cm\(^{-1}\) modes are octahedral stretching modes, differentiated by the cluster...
TABLE I. Phonon frequencies obtained from DFT calculations ($U = 8$ eV), experimental mode frequencies, mode symmetries, spin-lattice coupling constants (the $\lambda$'s in the text), and displacement patterns. The mode description in the final column encodes shifts of the three Ni ions and the Te center in the sequence $\text{Ni}^{\text{I}}$-$\text{Ni}^{\text{II}}$-$\text{Ni}^{\text{III}}$-$\text{Te}$. $u/d$ = shifts up/down along the $c$ axis; $l/r$ = motion to the left/right in the $ab$ plane; “-” indicates almost no displacement; octahedral distortions (compression/extension along certain axis/in plane) and rotations are also indicated.

<table>
<thead>
<tr>
<th>Theoretical frequencies (cm$^{-1}$)</th>
<th>Experimental frequencies (cm$^{-1}$)</th>
<th>Mode symmetries</th>
<th>Coupling constants (cm$^{-1}$)</th>
<th>Mode displacement patterns</th>
</tr>
</thead>
<tbody>
<tr>
<td>167</td>
<td>171</td>
<td>A</td>
<td>–</td>
<td>uudd</td>
</tr>
<tr>
<td>205</td>
<td>214</td>
<td>A</td>
<td>–</td>
<td>uudd</td>
</tr>
<tr>
<td>209</td>
<td>217</td>
<td>E</td>
<td>–</td>
<td>lrl</td>
</tr>
<tr>
<td>217</td>
<td>228</td>
<td>E</td>
<td>–</td>
<td>lrl</td>
</tr>
<tr>
<td>264</td>
<td>278</td>
<td>A</td>
<td>–</td>
<td>-ddu</td>
</tr>
<tr>
<td>265</td>
<td>278</td>
<td>E</td>
<td>–</td>
<td>llrr, oct rot around $a(b)$</td>
</tr>
<tr>
<td>297</td>
<td>310</td>
<td>E</td>
<td>0.4</td>
<td>l--r, oct rot</td>
</tr>
<tr>
<td>343</td>
<td>360</td>
<td>E</td>
<td>–</td>
<td>oct compression $ab$</td>
</tr>
<tr>
<td>353</td>
<td>370</td>
<td>A</td>
<td>–</td>
<td>udud oct compr $c$</td>
</tr>
<tr>
<td>399</td>
<td>–</td>
<td>A</td>
<td>–</td>
<td>oct twist</td>
</tr>
<tr>
<td>425</td>
<td>456</td>
<td>E</td>
<td>–</td>
<td>oct compr $ab$+twist</td>
</tr>
<tr>
<td>426</td>
<td>451</td>
<td>A</td>
<td>–</td>
<td>d-dd+oct twist</td>
</tr>
<tr>
<td>488</td>
<td>513</td>
<td>E</td>
<td>–</td>
<td>oct twist $ab$</td>
</tr>
<tr>
<td>512</td>
<td>541</td>
<td>A</td>
<td>–</td>
<td>oct contr $c$+rot $c$</td>
</tr>
<tr>
<td>562</td>
<td>597</td>
<td>E</td>
<td>0.3</td>
<td>oct contr $a(b)$</td>
</tr>
<tr>
<td>601</td>
<td>649</td>
<td>A</td>
<td>–</td>
<td>oct axial stretching</td>
</tr>
<tr>
<td>622</td>
<td>666</td>
<td>E</td>
<td>3.7</td>
<td>oct contr $a + b(a - b)$</td>
</tr>
<tr>
<td>653</td>
<td>692</td>
<td>A</td>
<td>–</td>
<td>oct asymmetric stretching</td>
</tr>
</tbody>
</table>

of oxygens that move with respect to the nickel centers (in- vs out-of-phase oxygen shifts between consecutive planes).

The optical absorption measurements on Ni$_3$TeO$_6$ provide microscopic information on the elementary excitations of the lattice. Frequency shifts of these excitations are sensitive probes of structural dynamics, and spin-phonon coupling communicates information on magnetic phase transitions to the structural degrees of freedom. Therefore by tracking the phonon frequencies across the Néel and spin-flop transitions, we can shed light on the mechanism of spin-lattice coupling.

A. Spin-lattice coupling across the Néel transition

The frequency vs temperature plots in Figs. 2(b)–2(f) summarize the elastic properties of Ni$_3$TeO$_6$ across the 53 K paramagnetic (PM) $\rightarrow$ AFM-I transition. Three $ab$-plane modes at 310, 597, and 666 cm$^{-1}$ are sensitive to the Néel transition, an indication that lattice behavior is coupled to the magnetic structure. From the displacement patterns in Fig. 3, we see that all three modes involve ionic shifts within the $ab$ plane along with octahedral stretching or bending. Softening of the 666 cm$^{-1}$ stretching mode below $T_N$ is perhaps the clearest change, with a frequency shift of $\approx 3.7$ cm$^{-1}$. If this were a simple binary spin system, then using $\delta\omega = (S_i \cdot S_j)$ and assuming a limiting low-temperature value of the spin-spin correlation function of $S^2 = 1$ would lead to a spin-lattice coupling constant of the 666 cm$^{-1}$ mode of approximately $3.7$ cm$^{-1}$ [23–25]. The coupling constants of the 310 and 597 cm$^{-1}$ modes, 0.4 and 0.3 cm$^{-1}$, respectively, are estimated in a similar manner (Table I). These spin-lattice coupling constants compare well with those in ferromagnetic CrSiTe$_3$ but are smaller than what is observed in SrMnO$_3$ [26,27]. By contrast, spin-lattice coupling in $\alpha$-RuCl$_3$ manifests primarily as a linewidth effect [28]. A mean-field analysis of relative slopes of the frequency vs temperature data near $T_N$, including an explicit treatment of the multiple sublattices, reveals similar results as discussed below.

The other vibrational modes in Ni$_3$TeO$_6$ are insensitive to the magnetic ordering transition, with the peak position vs temperature data following a sigmoidal Boltzmann curve that captures anharmonicity effects and the temperature dependence of short-range magnetic interactions [26]. Two examples of this behavior are shown in Figs. 2(b) and 2(c). Clearly the $c$-directed 171 and 214 cm$^{-1}$ shearing displacements do not display spin-lattice coupling. The rigidity of these (and other) $c$-directed modes is somewhat unexpected since the macroscopic polarization develops in this direction. The local lattice distortions in the $ab$ plane induced by the magnetic ordering, and the manner in which the displacements modify the superexchange interactions between the magnetic centers and break inversion symmetry, clearly play a much more important role.

A generic Hamiltonian for a phonon mode with a coordinate $q$, mass $m$, and frequency $\omega$ is given by

$$H = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} + \sum_{ij} \left( \alpha_{ij} + \frac{q^2}{2} \gamma_{ij} \right) \mathbf{S}_i \cdot \mathbf{S}_j + \frac{\beta q^4}{4},$$

(1)

where the first two terms are the kinetic and potential energy in the paramagnetic state, the term with $\alpha_{ij}$ describes the force on $q$ due to Heisenberg exchange striction, and the term with $\gamma_{ij}$ is the spin-dependent part of the mode stiffness [29]. As a result of magnetic ordering, the mode frequency will shift for two reasons: (i) the stiffness will change due to the $\gamma_{ij}$ term and the force described by the $\alpha_{ij}$ term will shift the equilibrium position to $q_0$, and (ii) the anharmonic effects (term with $\beta$) will further shift the frequency. One can obtain the frequency shift by substituting $q = q_0 + \delta q$, and completing the full square in
\[ \delta \omega \text{ we obtain for the phonon frequency shift to the linear order in small } \alpha_{ij} \text{ and } \gamma_{ij}: \]
\[ \delta \omega = \frac{1}{2m} \left( \Gamma + \frac{3 \beta A}{2 \omega_0^2} \right), \]
where we denote
\[ A = \sum_{ij} \alpha_{ij} \vec{S}_i \cdot \vec{S}_j, \]
\[ \Gamma = \sum_{ij} \gamma_{ij} \vec{S}_i \cdot \vec{S}_j. \]

Above the Néel temperature \( \vec{S} = 0 \), while below the ordered magnetic moments grow with some critical exponent \( S \sim (T_N - T)^{\nu} \). That leads to \( A \sim \Gamma \sim (T_N - T)^{2\nu} \).

Since the frequency shift away from normal temperature trends due to anharmonicity and short-range magnetic interactions is related to the square of the order parameter, plots of \( \delta \omega \) vs temperature provide insight into the nature of the ordering transition. The 666 cm\(^{-1}\) \( \text{NiO}_6 \) stretching mode is most revealing in this regard. To test the predictions outlined above, we fit the experimental frequency shift \( \delta \omega \) as \( \alpha (T_c - T)^{2\nu} \).

The results for all three of the \( ab \)-plane phonons that engage in spin-lattice coupling through \( T_N \) are shown in Fig. 2(g). We immediately observe the linear \( \delta \omega \) vs temperature relationships and exponents of \( 2\nu \) that are very close to 1.0. This is consistent with expectations for a continuous second-order transition. The coupling is strongest for the 666 cm\(^{-1}\) mode with \( \alpha = 8 \times 10^{-2} \text{ cm}^{-1}/\text{K} \). The 310 and 597 cm\(^{-1}\) modes have \( \alpha \)’s of \( 8 \times 10^{-5} \) and \( 6 \times 10^{-3} \text{ cm}^{-1}/\text{K} \), respectively [30]. When one multiplies by an appropriate temperature scale such as \( T_N \), these \( \alpha \)’s are in good agreement with the aforementioned \( \lambda \)’s.

As we can see from the size of the coupling constants, the 666 cm\(^{-1}\) mode dominates spin-lattice coupling through the 53 K Néel transition. This mode compresses the octahedra in the \( ab \) plane with out-of-phase motion between consecutive planes [31]. The latter is essentially an antiphase accordion-like pattern that modulates superexchange between \( \text{Ni}^2 \) and \( \text{Ni}^{\text{II}} \) in the \( c \) direction. This aspect of the interplane motion reinforces the development of the remarkable low-temperature polarization.

A Kramers-Kronig analysis of the measured reflectance also provides the frequency dependent dielectric response of \( \text{Ni}_3\text{TeO}_6 \), which we can extrapolate to zero frequency for comparison with the permittivities reported in Ref. [1]. Just above \( T_N \), we find \( \epsilon_1(0) = 7.6 \) in the \( ab \) plane, typical of a magnetic oxide, whereas \( \epsilon_1(0) = 6.5 \) at 4.2 K. The difference is 1.1. The noise level is larger in the \( c \) direction. Here, we find that \( \epsilon_1 \) is approximately 17.2 near \( T_N \) and about 16 at 4.2 K, giving \( \Delta \epsilon_1 = 1.2 \) within our sensitivity. These values of \( \epsilon_1 \) are in reasonable agreement with the size and temperature dependence of the dielectric constant reported previously [1], suggesting that there will be limited dispersion between the THz and MHz regimes.

B. Spin-lattice coupling through the field-driven spin-flop transition

We can more deeply examine the role of Heisenberg exchange striction in generating spin-lattice interactions by investigating the magnetic field-driven AFM-I \( \rightarrow \) AFM-II spin-flop transition. Analogous to the temperature-driven PM \( \rightarrow \) AFM-I transition that was modeled as \( A \sim \Gamma \sim (T_c - T)^{2\nu} \) in Fig. 2(g), the magnetization is predicted to grow from zero as \( (H - H_c)^{2\nu} \) at a second-order spin-flop transition. Therefore \( A \) and \( \Gamma \) acquire analogous contributions, growing as \( (H - H_c)^{2\nu} \). This according to Eq. (2) leads to \( \delta \omega \sim (H - H_c)^{2\nu} \), and a cusp in \( \delta \omega(H) \) should be observed. In the case of a first-order phase transition, magnetization should emerge in a jumplike fashion, and therefore a sudden jump is expected in \( \delta \omega \). Furthermore, the jump must be hysteretic. This scenario describes a traditional spin-flop transition such as that found in hematite [6,32,33]. A second-order transition will be different in that field-induced frequency shifts and linewidth modifications should be continuous. We test these ideas against the behavior of several representative phonons below.

Figure 4(a) displays the magnetoinfrared response of \( \text{Ni}_3\text{TeO}_6 \), \( \Delta \alpha = [\alpha(H = 20 \text{ T}) - \alpha(H = 0 \text{ T})] \), along with the linear absorption for comparison. Several phonons are
FIG. 4. (Color online) (a) Polarized infrared absorption spectrum, the polycrystal response, and the absorption difference spectrum at 20 T. The latter highlights the changes in the elastic properties between the AFM-I and AFM-II phases and is defined as $\Delta \alpha = \alpha(\omega, H) - \alpha(\omega, H = 0)$. (b)–(d) Close-up view of the field-induced absorption difference spectrum in the vicinity of the 310 cm$^{-1}$ mode through the 9 T spin-flop transition along with the field-induced frequency shift and linewidth changes. The curves in (b) are offset for clarity, and the dotted arrow is a 20 cm$^{-1}$ scale bar. The vertical line in (c) and (d) indicates the 9 T critical field. (e), (f) Close-up view of the field-induced absorption difference spectra in the vicinity of the most collective vibrational modes along with a contour plot revealing the subtle frequency shifts through the spin-flop transition. The curves in (e) are offset for clarity, and a 20 cm$^{-1}$ scale bar is included. (g) Waterfall plot in the vicinity of the 451 and 456 cm$^{-1}$ modes providing evidence for an unexplored transition between 30 and 35 T. Each curve in the waterfall plot is offset for clarity, and a scale bar is 20 cm$^{-1}$. All data was taken at 4.2 K.

Sensitive to changes in the microscopic spin pattern across the 9 T transition. The absorption difference spectrum reveals a number of small, sharp structures below 280 cm$^{-1}$ along with larger derivative-like features that correspond to modifications of the 310, 597, and 666 cm$^{-1}$ modes. While the latter correspond to changes in the familiar $E$ symmetry vibrational modes (polarized in the $ab$ plane), the structures below 280 cm$^{-1}$ arise from both $ab$-plane and $c$-polarized structures with $E$ and $A$ symmetries, respectively (Table I). No spectral hysteresis is observed, consistent with expectations for a nonhysteretic transition.

Figure 4(b) shows a close-up view of the field-induced absorption difference in the vicinity of the 310 cm$^{-1}$ mode. A clear derivative-like structure develops above 9 T in the $\Delta \alpha$ spectrum. Driving through the spin-flop transition modifies both frequency and linewidth—different from the trends across the 53 K Néel transition. The field-induced frequency shift and change in linewidth extracted from an analysis of the 310 cm$^{-1}$ feature are shown in Figs. 4(c) and 4(d). We find that $\delta \omega$ is rigid in the AFM-I phase, whereas it softens with increasing field in AFM-II. The latter trend is fit as $\delta \omega \sim (H - H_c)^{2\nu}$. Although the number of points in the vicinity of $H_c$ is not enough to precisely determine the critical exponent, there is no characteristic first-order jump. The 597 and 666 cm$^{-1}$ modes display similar behavior, although the error bars are larger. Likewise, the linewidth is relatively constant in the AFM-I phase, whereas it narrows with increasing field in AFM-II. A fit to $\delta \Gamma \sim (H - H_c)^{2\nu}$ again yields a reasonable match (within error bars), in line with expectations for a continuous phase transition.

The absorption difference spectrum in Fig. 4(a) also reveals a great deal of low frequency fine structure. These features are indicated by arrows. The majority correspond to changes in the 171, 214, 217, 228, and 278 cm$^{-1}$ fundamentals, although the 158 cm$^{-1}$ structure, for example, is new. Figure 4(e) shows a close-up view of how these features change with magnetic field, and Fig. 4(f) diagrams the development of the magneto-infrared contrast in a more graphical way.
out the extent to which applied field modifies a particular feature. The zero-field phonon frequencies are indicated with horizontal dotted lines for comparison. All of these modes involve displacements of the Ni and Te centers that alter the magnetic exchange pathway between the Ni centers. Remembering that polarization is along c, these shifts of the magnetic centers along with the movement of Te ions and oxygen octahedra contribute to altering the magnetic exchange pathway and furthermore the polarization. The intermediate phase, across which the antiferromagnetic order parameter rotates continuously by 90°, is narrow, and present measurements do not resolve it.

The magneto-infrared spectra also reveal the possibility of an additional, as yet unexplored, transition between 30 and 35 T. Figure 4(g) displays the strongest evidence for this crossover, although the absorption difference curves in Fig. 4(e) show additional fine structure developing in this regime as well. These changes correlate well with a slope change in the high field magnetization [2], which presumably corresponds to a canting of the spin. Alternately, the high field transition may be related to elongation of the unit cell. In this scenario, zone folding will activate zone boundary modes—in addition to narrowing the 451 and 456 cm$^{-1}$ features. For illustrative purposes, we include this transition in the schematic phase diagram of Fig. 1(c). Spin-lattice interactions between NiI and NiII as well as the development of the elastic properties of Ni$_3$TeO$_6$ across the Neél and spin-flop transitions. Our analysis unexpectedly reveals that the 660 cm$^{-1}$ in-plane octahedral stretching mode is most sensitive to the 53 K magnetic ordering transition, a finding that we discuss in terms of modified superexchange interactions between NiI and NiII as well as the development of the sizable polarization. At the same time, magneto-infrared spectroscopies demonstrate the gradual evolution of a number of modes across the 9 T spin-flop transition, consistent with a continuous second-order mechanism and quite distinct from expectations for a first-order process. We also provide evidence for a previously unexplored transition between 30 and 35 T. These findings reveal another aspect of magnetoelectric coupling and are important for understanding the development of large, controllable responses in Ni$_3$TeO$_6$ and other multifunctional materials.

IV. CONCLUSION

Summarizing, vibrational property measurements were brought together with complementary first-principles lattice dynamics calculations and a mean-field analysis to uncover the elastic properties of Ni$_3$TeO$_6$ across the Neél and spin-flop transitions. Our analysis unexpectedly reveals that the 660 cm$^{-1}$ in-plane octahedral stretching mode is most sensitive to the 53 K magnetic ordering transition, a finding that we discuss in terms of modified superexchange interactions between NiI and NiII as well as the development of the sizable polarization. At the same time, magneto-infrared spectroscopies demonstrate the gradual evolution of a number of modes across the 9 T spin-flop transition, consistent with a continuous second-order mechanism and quite distinct from expectations for a first-order process. We also provide evidence for a previously unexplored transition between 30 and 35 T. These findings reveal another aspect of magnetoelectric coupling and are important for understanding the development of large, controllable responses in Ni$_3$TeO$_6$ and other multifunctional materials.

ACKNOWLEDGMENTS

Research at the University of Tennessee and Rutgers University was supported by the NSF-DMREF program under DMR-1233118 and DMR-1233349. D.V. and S.A. also acknowledge the partial support through the ONR Grant No. N00014-12-1-1035. Work at Postech is funded by the Max Planck POSTECH/KOREA Research Initiative Program 2011-0031558 through NRF of Korea funded by MEST. A portion of this work was performed at the National High Magnetic Field Laboratory, which is supported by the National Science Foundation Cooperative Agreement DMR-1157490, the State of Florida, and the US Department of Energy.


[29] We assume a phonon irrep for which $q^3$ terms vanish by symmetry.

[30] Examination of the displacement patterns in Fig. 3 reveals that all three modes either shift the NiI center or modify the environment around NiI and NiII. The magnetic interaction between these centers is strong because the octahedra share edges.

[31] This is different from the 597 cm\(^{-1}\) mode which also modulates the octahedra and has an in-phase relationship between consecutive layers.
