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**Structural and spectroscopic properties of the polar antiferromagnet Ni$_2$MnTeO$_6$**

Maria Retuerto, Stella Skiadopoulou, Fedir Borodavka, Christelle Kadlec, Filip Kadlec, Jan Prokleška, Zheng Deng, Jose A. Alonso, Maria T. Fernandez-Diaz, Felix O. Saouma, Joon I. Jang, Dominik Legut, Stanislav Kamba, and Martha Greenblatt

Phys. Rev. B **97**, 144418 — Published 23 April 2018

DOI: [10.1103/PhysRevB.97.144418](https://doi.org/10.1103/PhysRevB.97.144418)
We present a structural and spectroscopic study of a new compound Ni$_2$MnTeO$_6$, closely related to the polar antiferromagnet Ni$_3$TeO$_6$ known to show a colossal magnetoelectric effect and pronounced elementary magnetoelectric excitations. For the first time, we prepared single crystals and polycrystalline samples of Ni$_2$MnTeO$_6$ showing the same polar structure as Ni$_3$TeO$_6$ from room temperature down to 4 K with the R3 space group symmetry. Magnetic and dielectric measurements have indicated an antiferromagnetic phase transition at $T_N \approx 70$ K, almost 20 K higher than that of Ni$_3$TeO$_6$. Extensive infrared, Raman and THz spectroscopy experiments were employed for investigating lattice and spin excitations, revealing all phonons predicted by the factor group analysis. THz spectra below $T_N$ reveal one new excitation, which is strongly influenced by external magnetic field, thus assigned to a magnon.

In pursuit of multiferroic compounds with crystal structure other than that of the perovskites, the corundum-related (Al$_2$O$_3$) family A$_2$BB'O$_6$ scores a success among the magnetic systems, and lately, due to the colossal magnetoelectric effect in the polar antiferromagnet Ni$_3$TeO$_6$, the multiferroic community.

In the above structural formula, A is usually a small diamagnetic, or paramagnetic divalent cation, B a divalent or trivalent transition metal cation, and B' a pentavalent or hexavalent transition metal or a diamagnetic cation (e.g., Sb, Te).

During the 80s, a few studies on corundum- and cryolite-related (a-Na$_3$AlF$_6$) compounds suggested ferroelectric (FE) properties for a series of M$_3$TeO$_6$ compounds, with M corresponding to paramagnetic cations, and the reported Curie temperatures around 500 K. However, no evidence of non-centrosymmetric structure for any of the above compounds at room temperature was reported ever since, except for Ni$_3$TeO$_6$. Thus, Mg$_3$TeO$_6$ and Mn$_3$TeO$_6$ crystallize in the rhombohedral $R\bar{3}$ space group, Cd$_3$TeO$_6$ and Ca$_3$TeO$_6$ in the monoclinic $P2_1/n$, Co$_3$TeO$_6$ in the monoclinic $C2/c$, and Cu$_3$TeO$_6$ in the cubic $Ia\bar{3}$ space groups. To date, Ni$_3$TeO$_6$ and (Mn$_{0.2}$Ni$_{0.8}$)$_3$TeO$_6$ are the only reported compounds without inversion symmetry. The Ni$_{3-x}$Mn$_x$TeO$_6$ system shows the $R\bar{3}$ space group at room temperature, and, interestingly, it displays an antiferromagnetic (AFM) transition temperature of $T_N=67$ K, higher than that in Ni$_3$TeO$_6$. A further increase in $T_N$ upon increasing $x$ was suggested by Mathieu et al. in view of an expected stabilization of the $R\bar{3}$ space group.
Aiming at enhancing the critical temperature, \( \text{Ni}_2\text{MnTeO}_6 \) was synthesized, for the first time, in the form of single crystals and ceramics; their magnetic and dielectric properties were studied, together with lattice and spin dynamics. Since \( \text{Ni}_3\text{TeO}_6 \) exhibits a strong magnetoelectric coupling which activates electromagnons in THz and Raman spectra,\(^{15} \) we wanted to check for the presence of such spin excitations also in \( \text{Ni}_2\text{MnTeO}_6 \). The increase in \( T_N \) predicted by Mathieu et al.\(^{8} \) was confirmed, since \( \text{Ni}_2\text{MnTeO}_6 \) exhibits an AFM transition at \( T_N \approx 70 \) K. In addition, the THz spectra unveil a spin excitation below \( T_N \).

I. Experimental details

Polycrystalline \( \text{Ni}_2\text{MnTeO}_6 \) was prepared from stoichiometric amounts of analytical grade \( \text{NiO} \), \( \text{TeO}_2 \), and \( \text{MnCO}_3 \). The mixture was heated in a tubular furnace under oxygen flux at 800°C with intermediate grindings between 700 and 800°C. Single crystals were prepared by the flux method in the following steps: \( \text{Ni}_2\text{MnTeO}_6 \): \( \text{V}_2\text{O}_5 \): \( \text{TeO}_2 \): \( \text{NaCl} \): \( \text{KCl} \) in a molar ratio of 1:5:10:10:5 was kept for two days at 800°C and then cooled down to 600°C during three days. Plate-shaped green crystals with lateral dimensions of less than 1 mm were obtained. The structure and purity of the single crystals were determined by powder X-ray diffraction (XRD) (Cu \( K_α \), \( λ = 1.5406 \) Å) and energy dispersive spectroscopy (EDS, X-ray microanalyzer JXA-733 Superprobe). For structural refinements, powder neutron diffraction (PND) was performed. PND was collected at the Institute Laue-Langevin, Grenoble. The data at room temperature were collected in the D2B High Resolution instrument (\( λ = 1.5940 \) Å). For the determination of the magnetic structure between 5 and 100 K we used the D20 (\( λ = 2.410 \) Å) instrument. Diffraction data analysis by Rietveld refinement\(^ {22} \) was performed with the Fullprof software\(^ {23} \). The structure of the single crystals was determined by single-crystal X-ray data collected on a Bruker Smart APEX CCD diffractometer with graphite-monochromatized Mo \( K_α \) radiation (\( λ = 0.71073 \) Å) at 100 K. Magnetic measurements of the single crystals were performed on a Quantum Design SQUID system, whereas those of polycrystalline samples utilized the ACMS and VSM options (extraction and vibrating sample magnetometers) of the PPMS apparatus (Quantum Design) in fields up to 14 T and temperatures down to 2 K.

Near-normal incidence IR reflectivity spectra of the \( \text{Ni}_2\text{MnTeO}_6 \) ceramics were measured by a Fourier-transform IR spectrometer Bruker IFS 113v in the frequency range of 20-3000 cm\(^{-1} \) (0.6 – 90 THz) at room temperature; for the low-temperature measurements, an Optistat optical cryostat (Oxford Instruments) with polyethylene windows was used; their transparence reduced the spectral range to 20-650 cm\(^{-1} \). A pyroelectric deuterated triglycine sulfate detector was used for the room-temperature measurements, whereas a He-cooled (\( T = 1.6 \) K) Si bolometer was used for the low-temperature measurements down to 7 K.

THz measurements from 3 to 60 cm\(^{-1} \) (0.09 – 1.8 THz) were performed in the transmission geometry with a custom-made time-domain terahertz spectrometer. Here, a femtosecond Ti:sapphire laser oscillator (Coherent, Mira) produces a train of femtosecond pulses, which generate linearly polarized broadband THz pulses radiated by a photoconducting switch TeraSED (Giga-Optics). A gated detection scheme based on electrooptic sampling with a 1 mm thick [110] ZnTe crystal as a sensor allows one to measure the time profile of the electric field of the transmitted THz pulse. An Oxford Instruments Optistat optical cryostat with mylar windows was used for low-temperature measurements. THz experiments in an external magnetic field \( H_{\text{ext}} \leq 7 \) T were performed with an Oxford Instruments Spectromag cryostat in the Voigt configuration, where the electric component of the THz radiation \( E_{\text{THz}} \) was set parallel and perpendicular to \( H_{\text{ext}} \).

The IR reflectivity and THz complex permittivity spectra were fitted assuming a sum of \( N \) independent damped harmonic oscillators, expressed as:\(^ {24} \)

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{N} \Delta \varepsilon_f \omega_{\text{TOj}}^2 \omega_j^2 + i \omega_j \gamma_j \]

(1)

where \( \Delta \varepsilon_f \) is the dielectric strength of the \( j \)-th mode, \( \omega_{\text{TOj}} \) the frequencies of the \( j \)-th transverse optical (TO) phonons, and \( \gamma_j \) are the corresponding damping constants. \( \varepsilon_\infty \) is the high-frequency (electronic) contribution to the permittivity, determined from the room-temperature frequency-independent reflectivity tail above the phonon frequencies. The reflectivity \( R(\omega) \) is related to the complex dielectric function \( \varepsilon^*(\omega) \) by:

\[
R(\omega) = \left| \frac{\sqrt{\varepsilon^* + 1}}{\sqrt{\varepsilon^* - 1}} \right|^2
\]

(2)
For Raman studies of single crystals, a Renishaw RM 1000 Micro-Raman spectrometer with Bragg filters was used, equipped with an Oxford Instruments Microstat continuous-flow optical He cryostat. The experiments were performed in the backscattering geometry in the 5–1800 cm⁻¹ range. An Ar⁺-ion laser operating at 514.5 nm was used. The spectra were carefully fitted with a sum of independent damped harmonic oscillators multiplied by the corresponding Stokes temperature factor.²⁵

Spin-polarized density functional theory calculations were conducted, implementing the projector-augmented-wave formalism to describe the electron-ion interactions, and the generalized gradient approximation parametrized by Pedrew, Burke, and Ernzerhof (GGA-PBE) for the exchange-correlation potential.²⁶,²⁷ To account for the correct AFM order, the unit cell was doubled along c-axis and sampled by 5x5x2 grid. The lattice dynamics calculations were used within the Phonopy code, employing calculated Hellman Feynman forces, and using 2x2x2 supercell with 60 displacements of 0.01 Å. Additional on-site Coulomb repulsion interactions were considered concurrently, within the rotationally invariant form of the GGA+U approach,²⁸ where the localized 3d electrons experience a spin- and orbital-dependent potential (U) and the exchange interaction J, while the other orbitals are delocalized and treated by the conventional GGA approximation.

![Figure 1](image1.png)

**Figure 1** PND pattern of Ni₂MnTeO₆. The lower row of Bragg reflections (green lines) represents an impurity of Mn₂TeO₆ amounting to 3%. Left inset: photograph of the Ni₂MnTeO₆ single crystals. Right inset: schematic representation of the crystal structure, cyan: NiO₆ octahedra, purple: MnO₆ octahedra, and grey: TeO₆ octahedra. The displacements of the atoms from the octahedral center can be seen.

**Figure 2** (a) Thermal evolution of the PND pattern of polycrystalline Ni₂MnTeO₆, showing the peaks related to the AFM transition at ~70 K. (b) Temperature dependence of the unit cell volume and magnetic moments per magnetic cation. (c) Prominent magnetic transition at 73 K, as seen by the evolution of the PND peak. (d) Schematic representation of the AFM configuration (the magnetic unit cell is larger) (purple: Mn, cyan: Ni).

### II. Results and discussion

#### A. Structural Characterization

Based on the room-temperature PND (Figure 1) and XRD characterization, we determined that the structure of Ni₂MnTeO₆ is analogous to that of Ni₃TeO₆ (rhombohedral, space group R3 (No. 146), Z = 3), which can be viewed as a A₂BB’O₆-type corundum derivative. The structure contains two crystallographically distinct Ni atoms at the A-sites, denoted here as Ni¹ and Ni², ordered Mn and Te on both B sites, and two independent oxygen atoms (for details see Tables S1 and S2 in Supplemental Information).²⁹ XRD on single crystals revealed slightly different lattice parameters, which can be explained by a small difference between Ni/Mn ratios in crystals and ceramics. The structure is formed by layers of edge-sharing TeO₆ and Ni¹O₆ octahedra in the ab plane; these layers alternate with those containing edge-sharing MnO₆ and Ni²O₆ octahedra. The layers are connected along the c axis by face-
sharing dimers of TeO$_6$/Ni$^{II}$O$_6$ and MnO$_6$/Ni$^{II}$O$_6$ (see Inset of Figure 1). The non-centrosymmetry of Ni$_2$MnTeO$_6$ structure was supported by SHG measurements (Supplemental Information, Figure S2).29

Due to electrostatic repulsion, the cations inside the face-sharing octahedra are displaced from their centers along the $c$ direction, moving closer to the octahedral vacancies and farther away from the other cation in the dimer. This gives rise to three long and three short octahedral separations. This effect is more pronounced in Ni$_2$MnTeO$_6$ than in Ni$_3$TeO$_6$,30 and it is analogous to that in the isostructural Mn$_2$FeWO$_6$.

B. Magnetic Structure

In order to determine the magnetic structure, PND at low temperatures was measured. The temperature dependences of the diffraction pattern, unit cell volume and magnetic moments are shown in Figure 2(a), (b). The magnetic transition is clearly observed at $T_N \approx 70$ K (Figure 2(c)), nearly 20 K higher than in Ni$_3$TeO$_6$. The magnetic structure (Figure 2(d)) is AFM, characterized by a propagation vector $\mathbf{k} = (0 0 3/2)$, and it consists of spins ferromagnetically ordered in adjacent $ab$-planes, pairwise alternately pointing parallel and antiparallel along the $c$ direction.

The magnetic moments at Ni, Ni$^{II}$ and Mn sites at 5 K were refined as 2.1(2) $\mu_B$/f.u. for Ni and 3.7(3) $\mu_B$/f.u. for Mn. The moments at the Ni positions are slightly larger than those expected for the Ni$^{II}$ spin state $S=1$, which can be explained by the disorder with Mn$^{II}$, expected to exhibit a spin state of $S=5/2$. And the same with Mn moments, that are slightly smaller than expected due to the partial disorder.

Employing first-principles calculations, we have determined the structural geometry with the AFM order as depicted in Figure 2(d). The calculated hexagonal lattice parameters of $a=5.21386\,\text{Å}$ and $c=14.17241\,\text{Å}$, correspond to a less than 1% higher volume value than the experimental one (see Table S1 in Supplemental Information).29 Within the GGA+U approach, the $U_{\text{eff}}=U-J$ is only meaningful, where $U_{\text{eff}}=7 \text{ eV}$ for both Ni and Mn sites, yield the Ni and Mn magnetic moments: 1.8 $\mu_B$ and 4.8 $\mu_B$, respectively. These values lie close to the previously reported experimental ones for Ni (2 $\mu_B$) and Mn (3-6 $\mu_B$), in the Ni$_3$TeO$_6$ and Mn$_3$TeO$_6$ compounds, respectively.

C. Magnetic and dielectric properties

The temperature dependence of the magnetic susceptibility measurements for Ni$_2$MnTeO$_6$ single crystal is displayed in Figure 3(a), for two orientations of the magnetic field: $H_{\text{ext}} \parallel c$ and $H_{\text{ext}} \perp c$. The AFM transition occurs at ca. 67 K, and it is markedly stronger in the susceptibility along $c$, as expected from the magnetic structure (Figure 2). The discrepancy between the values of the Néel temperature, 73 K from PND data and 67 K from the magnetic measurements, can be ascribed to the different experimental techniques, and to the use of different samples (polycrystalline in the former and single crystalline in the latter case) with slightly different Ni/Mn ratios. Figure 3(b) shows the temperature dependence of permittivity in the ceramics measured at 1 MHz. Since the magnetic structure was shown to be collinear with the $c$ axis, the decrease in $\chi$ observed below $T_N$ for $H_{\text{ext}} \perp c$ is probably an artifact of a partial sample misalignment. The dielectric anomaly appearing at 67 K, at the AFM transition, indicates an interplay between the magnetic and polar characters (i.e. change in the electric polarization) of the phase transition. An additional dielectric anomaly is clearly seen at 23 K. This temperature corresponds to a phase transition in Mn$_3$TeO$_6$ which is AFM and probably FE. The Mn$_3$TeO$_6$ secondary phase, amounting to ca. 3%, is observed by PND (Figure 1). According to literature, Mn$_3$TeO$_6$ should conserve the non-centrosymmetric rhombohedral $R3$ space group down to 5 K. However, Zhao et al.33 reported a FE phase transition a few K below the AFM one, at around 21 K. The FE distortion is so small that it was not detected in previously published PND studies,6 and Ivanov et al.34 attempted to perform
Figure 3 (a) Temperature dependence of magnetic susceptibility of the Ni$_2$MnTeO$_6$ single crystal at 0.1 T with two distinct orientations: $H_{\text{ext}}$ $\parallel$ c and $H_{\text{ext}}$ $\perp$ c; the anomaly appears at ~67 K. (b) Temperature dependence of the permittivity of Ni$_2$MnTeO$_6$ ceramics, recorded at 1 MHz; the anomaly occurring around 67 K is due to the spin-order-induced FE transition, whereas the one anomaly at 23 K is probably due to a FE phase transition in the secondary phase of Mn$_3$TeO$_6$. (c), (d): magnetic-field dependences of magnetization in the single crystal and ceramics, respectively. In the single crystal, a spin-flop transition occurs at ~4.5 T, which is not observed in the ceramics. Inset of (d): low-magnetic-field hysteretic behavior in the ceramics, most probably due to the Mn$_3$TeO$_6$ secondary phase.
a more detailed structural analysis in order to explain this intriguing behavior, however, with no success. Note that for most of spin-order induced FEs, the FE distortions were not resolved in diffraction experiments, but only in dielectric measurements, because the FE distortions are usually very small.\(^3\)

Figure 4 presents the temperature dependences of magnetization for the polycrystalline Ni\(_2\)MnTeO\(_6\) at various values of applied magnetic field. For any value of \(H\), the magnetic transition takes place at \(\sim 70\) K, in agreement with the PND results. A noteworthy anomaly at \(23\) K suggests another magnetic transition (Figure 4(b)). We observed this anomaly in the PND but not in the single crystal susceptibility measurements (Supplemental Information, Figure S3). As mentioned above, the magnetic transition at \(23\) K corresponds to Mn\(_3\)TeO\(_6\) in the polycrystalline sample. Another possible explanation for the \(23\) K feature might be linked to impurities from the grain boundaries, which can contribute to the total magnetization. The magnetic structure of Ni\(_2\)MnTeO\(_6\) ceramics changes above \(0.4\) T (a double hysteresis loop is seen - Figure 4(c)), and therefore the low-temperature anomaly in \(M(T)\) (Figure 4(a)) disappears at higher fields.
Since pure Ni$_3$TeO$_6$ exhibits a colossal static magnetoelectric coupling at the spin-flop transition near 8 T and a similar spin-flop transition occurs in Ni$_2$MnTeO$_6$ 4 T lower, pyrocurrent and capacitance measurements of Ni$_2$MnTeO$_6$ crystals at external magnetic field are required. Unfortunately, the small size of our crystals did not allow such experiments. Growth of larger single crystals required for these experiments (more than 1 mm in diameter) is in progress.

**D. Spin and lattice excitations**

The IR reflectivity spectra of the Ni$_2$MnTeO$_6$ ceramics for selected temperatures from 10 to 300 K are shown in Figure 5(a), together with the fitted complex permittivity (Figure 5(b,c)). As predicted by the factor-group analysis for the $R3$ structure, nine $E(x,y,x^2-y^2,xy,xz,yz)$ and nine $A(x^2+y^2,z^2,z)$ modes are expected, both IR and Raman active, analogously to the Ni$_3$TeO$_6$ case.$^{15,36}$ All 18 modes are clearly visible in the IR spectra up to 300 K. Similarly to Ni$_3$TeO$_6$, the phonon eigenfrequencies are practically unaffected by temperature changes, since the $R3$ space group is preserved at all investigated temperatures. The damping of the modes slightly decreases upon cooling, as expected. A few of the mode frequencies lie close to the values of those reported for Ni$_3$TeO$_6$,$^{15,36}$ most of them corresponding to the vibrations of the TeO$_6$ octahedra.$^{37}$ The eigenfrequency values of the measured IR-active modes at 10 K, together with the respective damping and dielectric strength, are presented in Table 1. For comparison, the previously published Ni$_3$TeO$_6$ IR modes at 7 K by Skiadopoulou et al.$^{15}$ are also listed. The possible structural distortion at the AFM (and FE) transition at 67 K suggested by the anomaly in the permittivity data (Figure 3(b)) should have only a negligible effect on the IR spectra.

In Figure 5(b) and (c), permittivity $\epsilon'(\omega)$ and extinction coefficient $k(\omega)$ spectra are displayed, respectively. Here we plot $k(\omega)$ spectra because we are not sure whether the excitation seen below 10 cm$^{-1}$ contributes to permittivity or magnetic permeability. These spectra were extracted by fitting the IR reflectivity spectra of Figure 5(a) and complex THz spectra (Figure 6) by damped harmonic oscillators (Eqs. (1) and (2)). The static permittivity obtained from the fits amounts to $\sim$10, close to the value of $\sim$11 reported in the radio-frequency range for Ni$_3$TeO$_6$ by Oh et al.$^{12}$ The permittivity of our ceramics at 1 MHz (Figure 3(b)) even exceeds 20, but it is probably enhanced by a contribution of interlayer barriers...
on grain boundaries, which are responsible for a Maxwell-Wagner contribution to the permittivity, dominant especially above 100 K.

The highly dense ceramics allowed micro-Raman studies with the possibility of focusing at a single grain, since the laser spot diameter (∼4 μm) was much smaller than the typical grain size of 30 μm (confirmed by Scanning Electron Microscopy micrographs – see Figure S1 in Supplemental Information). The spectra were collected in the back-scattering geometry, in both parallel and crossed polarizations, at temperatures from 4 to 300 K. Here, only the crossed polarized spectra are presented, since no significant differences between the two polarizations were observed, except for different intensity magnitudes. A plot of the Raman spectra at selected temperatures from 4 to 300 K is shown in Figure 5(d). The Raman mode frequencies at 4 K are presented in Table 1 in comparison with the IR modes at 10 K. The polycrystalline nature of the samples is not suitable for a symmetry analysis of the observed modes. All Raman modes which are not IR active correspond most probably to longitudinal optical modes (similarly as in Ni3TeO6 – see Ref. 15). As for the IR spectra, no substantial changes were observed on cooling, apart from splitting of the mode at around 600 cm⁻¹ and an expected decrease in damping. Such splitting originates mainly from the decrease in damping and a possible small frequency shift of the order of 1 cm⁻¹, due to thermal contraction. No new modes due to a possible change of crystal symmetry, or due to appearance of spin excitations, activate below T_N. This absence of newly-activated phonons in Raman and IR spectra below T_N supports the fact that the crystal symmetry is the same in the paramagnetic and ferromagnetic phases, belonging to the polar R3 space group.

Lattice dynamics calculations, based on the computed Hellman Feynman forces, yield all expected 18 IR- and Raman-active phonon modes. The computed values are in good agreement with the experimental ones obtained by IR and Raman spectroscopies (see Table 1).

Time-domain THz transmission measurements were performed for the Ni₂MnTeO₆ ceramics (thickness 1.9 mm), at temperatures from 4 to 300 K. Figure 6 shows the THz spectra for selected temperatures. Upon cooling, a gradual decrease in the real part of the index of refraction occurs. The increase in n with frequency comes from the phonon contribution, and the value of n~3.2 is in agreement with the static permittivity value obtained from the IR spectra. A new low-frequency excitation at ∼6 cm⁻¹ appears at 60 K, below the AFM transition of ∼70 K, and upon cooling it sharpens and shifts to 8 cm⁻¹ at 4 K. Note that the signal is rather noisy below 8 cm⁻¹, since it is close to the border of the accessible frequency region. The emergence of the new excitation below the magnetic transition, in combination with the fact that all 18 phonons predicted by the factor-group analysis are resolved in the IR and Raman spectra, suggest that this new excitation is of magnetic origin. The broader feature, also notable at higher frequencies (∼40 cm⁻¹) in the k(ω) spectra, and equally emerging below T_N, is possibly due to multimagnon absorption. However, it may also correspond to a single-magnon excitation, since a similar feature at 32 cm⁻¹ was observed in Ni₃TeO₆; the high value of damping could be attributed to the chemical disorder of Mn in the lattice (PND revealed Mn in B-sites of A₂B₂O₆ with an occupancy rate of 93%, whereas 7% of B-sites are occupied by Ni – see Table S1 in Supplemental Information).

We measured THz spectra also in an external magnetic field of up to 7 T in the Voigt configuration, with H_ext parallel and perpendicular to the electric vector E₀ of the THz beam. Here, we present only the spectra with H_ext ⊥ E₀ (Figure 7), where the magnetic-field effect upon the spin excitation was more pronounced (yet qualitatively the same). At 30 K (Figure 7(left)), the magnetic mode below 10 cm⁻¹ shifts down and sharpens with increasing magnetic field. At 5 K (Figure 7(right)), a conspicuous sharpening up to 4 T takes place, followed by decrease in its intensity upon increasing H_ext up to 7 T.
Table 1 Frequencies of the IR-active modes in the Ni$_2$MnTeO$_6$ ceramics at 10 K and Raman-active modes at 4 K, as obtained by fits of IR reflectivity with $\varepsilon_\infty = 3.9$. The low-frequency mode in the first line was identified in the THz spectra as a magnon. The first column corresponds to the IR mode frequencies of Ni$_2$TeO$_6$ ceramics at 7 K from Skiadopoulos et al. The damping constants and dielectric strengths of the IR-active modes are also listed. The modes observed as weak in Raman spectra are marked by w in subscript. All Raman modes which are not IR active correspond to longitudinal optic modes. The theoretical frequencies obtained by first-principles calculations are also included, together with the assigned symmetry for each mode in the parentheses.

<table>
<thead>
<tr>
<th>Ni$_3$TeO$_6$</th>
<th>Ni$_2$MnTeO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IR 7 K</td>
<td>Calculations</td>
</tr>
<tr>
<td>$\omega_{10}$ (cm$^{-1}$)</td>
<td>$\omega$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>16.2</td>
<td>168.0 (A)</td>
</tr>
<tr>
<td>32.4</td>
<td>195.4 (E)</td>
</tr>
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<td>219.3</td>
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<td>454.2</td>
<td>507.7 (E)</td>
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</table>
Such behavior might be related to the spin-flop transition occurring at around 4.5 T (Figure 3(c)) or to the frequency limit of our experimental setup. Nevertheless, at 5 K a clear magnon frequency softening is exhibited with increasing $H_{\text{ext}}$, from 8 cm$^{-1}$ at 0 T to 6 cm$^{-1}$ at 7 T.

Finally, the very small size of the single crystals did not allow for performing spectroscopic studies based on the orientation of the crystal structure. For example, directional dichroism might reveal the character of the spin excitation observed in the THz spectra and identify whether it corresponds to a pure magnon or electromagnon, as in Ni$_3$TeO$_6$. Unfortunately, since the magnetic excitation lies below 8 cm$^{-1}$, more precise transmission measurements with a spectrometer based on backward-wave oscillator sources$^{39}$ and a crystal with diameter at least 10 mm would be required. In addition, using single crystals, one can avoid possible impurities often present at grain boundaries of polycrystalline samples, thus the anomaly seen at 23 K could be absent or better resolved. Last but not least, capacitance and pyrocurrent measurements of Ni$_2$MnTeO$_6$ single crystals in external magnetic field could shed more light on the magnetoelectric properties of Ni$_2$MnTeO$_6$, since the very similar compound Ni$_3$TeO$_6$ presents a colossal magnetoelectric effect at the spin-flop transition occurring near 8 T.

**Figure 7** Real and imaginary part of index of refraction from the THz measurements of Ni$_2$MnTeO$_6$ ceramics, at external magnetic field in Voigt configuration $H_{\text{ext}} \perp E^\omega$, for 30 K (left) and 5 K (right) as measured.
III. Conclusions

Single crystals and polycrystalline ceramic samples of the new compound Ni$_2$MnTeO$_6$ were synthesized for the first time. The Mn-substitution of Ni in Ni$_3$TeO$_6$ leads to an increase in the AFM transition temperature by 20 K, thus reaching ~70 K, whereas the compound preserves the polar $R3$ space group. At the same time, an anomaly is also seen in the low-frequency permittivity spectrum. Another anomaly observed at 23 K is likely due to a Mn$_3$TeO$_6$ impurity phase. A spin-flop transition is triggered by an external magnetic field above 5 T, i.e. $\sim$3 T lower than that of Ni$_3$TeO$_6$. Since in Ni$_3$TeO$_6$ a colossal magnetoelectric effect close to the spin-flop transition is known to exist, a strong static magnetoelectric coupling in Ni$_2$MnTeO$_6$ might appear at a lower magnetic field. To that aim growth of larger single crystals suitable for magnetoelectric studies is in progress.

The high-quality dense ceramic samples revealed all expected IR and Raman active modes of the $R3$ symmetry. A magnetic-field-tunable spin excitation at $\sim$8 cm$^{-1}$ is clearly seen in the THz spectra below $T_N$. Such a low frequency of the magnon does not allow for measuring also its Raman spectra, leaving the question open whether the magnon bears a magnetoelectric character. THz measurement of directional dichroism could reveal the character of the spin excitation (magnon or electromagnon). However, single crystals with more than 3 mm in diameter are required for such an experiment and these are not yet available.

Acknowledgements

The work of MG, MR and ZD was supported by the NSF-DMR-1507252 grant. MR also acknowledges the Juan de la Cierva program of the Spanish Ministry of Economy and Competitiveness for a grant FPDI-2013-17582. The work of SK, SS, FB, CK and FK was supported by European Union funding under the 7th Framework Programme (Project NOTEDEV), by the Czech Science Foundation (Projects 15-08389S and 18-09265S) and MŠMT KONTAKT II project LH15122. EDS characterization of ceramics performed by K. Jurek is highly appreciated. JAA thanks the financial support of the Spanish Ministry of Science and Innovation to the project MAT2013-41099-R. DL and SS acknowledge the European Regional Development Fund in the IT4Innovations national supercomputing centre-Path to Exascale (Project number CZ.02.1.01/0.0/0.0/16_013/0001791) within the Operational Programme Research, Development and Education, and DL acknowledges also the project No. 17-27790S of Czech Science Foundations and Mobility grant No. 8×17046.

29 Supplemental Information (n.d.).