A comparative Raman study between PrMnO$_3$, NdMnO$_3$, TbMnO$_3$ and DyMnO$_3$

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In this paper, we present a detailed Raman study of the non-multiferroic compounds PrMnO$_3$ and NdMnO$_3$ and the multiferroic compounds TbMnO$_3$ and DyMnO$_3$ as a function of temperature and magnetic field. All studied systems show anomalous phonon shifts close to the Néel transition $T_N$. In PrMnO$_3$ and NdMnO$_3$, the frequency softenings are partly attributed to an orbital-spin-phonon coupling whereas in TbMnO$_3$ and DyMnO$_3$, the relatively weak frequency shifts are rather attributed to an expansion of the Mn—O bond lengths. On the other hand, the frequencies of TbMnO$_3$ phonons are shifted as a function of magnetic field, while those of PrMnO$_3$ remain unaffected. These frequency shifts are interpreted in terms of local oxygen rearrangements under magnetic field that could play an important role in the multiferroicity of TbMnO$_3$ and DyMnO$_3$.

In the last decade, the study of the perovskite manganites RMnO$_3$ (R = lanthanides, Y and Bi) have attracted a considerable interest because of their fascinating properties such as colossal magnetoelectric and magnetocaloric effects$^{1,2}$. Their physical properties are determined by a delicate interplay of charge, spin, orbital, and lattice degrees of freedom$^{3–5}$. The study of the coupling between the lattice and the magnetic properties of these compounds represents an interesting starting point to understand the microscopic parameters controlling their magnetoelectric effects at low temperature. The RMnO$_3$ with larger ionic radius (R = La, Pr, Nd, … and Dy) compounds crystallise in the orthorhombic structure with a space group Pbnm, whereas the compounds with smaller ionic radius (R = Dy, Ho, Er and Y) can be obtained either in the orthorhombic or the hexagonal structure with a space group P6$_3$cm$^{6,7}$. In the orthorhombic compounds the Mn ion has the $t_{2g}$ electronic configuration. The $e_g$ orbital degeneracy is lifted by the Jahn-Teller distortion$^{5,8}$. These compounds exhibit an orbital ordering at high temperature $T_{OO} \sim$ 780 – 1500 K$^9$–$^{11}$. Below $T_{OO}$, the orbital degree of freedom is spontaneously frozen by the real-space $C$–type ordering of the $e_g$ orbitals accompanied by the development of a static Jahn-Teller lattice distortion of the MnO$_6$ octahedra$^{12,13}$. Many previous works have suggested a strong coupling between the spin and the orbital degrees of freedom in the RMnO$_3$ systems$^{9,10,12–14}$. Murakami et al.$^9$ have reported an experimental evidence of the orbital ordering in LaMnO$_3$ by measuring the (3,0,0) reflection intensity of resonant x-ray scattering$^8$. They have found that its integrated intensity, which is related to the order parameter of the orbital ordering, becomes constant below the magnetic ordering temperature $T_N \approx$ 140 K and decreases above it, which suggests that the spin and the orbital orders are intercoupled. The orbital ordering temperature in RMnO$_3$ is significantly enhanced by increasing the GdFeO$_3$-type lattice distortion with decreasing the ionic radius of R (r$_R$)$^{15,16}$. These lattice distortions increase the orbital ordering frustration and provoke a change of the lattice parameters as shown by x-ray and neutron diffraction measurements$^{15,16}$ with a sharp fall in the ordering temperature of the Mn spins$^1$. For example, PrMnO$_3$ (NdMnO$_3$) exhibits an A-type antiferromagnetic magnetic structure at $T_N \approx$ 100 K ($T_N \approx$ 80 K) in which the spins are aligned ferromagnetically in the basal plane ($xz$) and antiferromagnetically along the perpendicular direction ($y$)$^{7,16}$. In more distorted compounds (R = Dy, Tb and Gd) the spin structure becomes sinusoidally modulated in the $ab$–plane below 39–43 K and spirally modulated below 18–17 K$^{10}$. This last transition coincides with the appearance of a spontaneous electric polarization $P_s$ parallel to the $c$–axis$^{1,20}$. In these spin–spiral systems the magnetic field is able to flip their electric polarization from $c$ to $a$–axis.

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Raman scattering spectroscopy is a powerful tool to investigate the driving force of the interplay of charge, spin, orbital and lattice degrees of freedom\textsuperscript{21–25}. The Raman spectra of R\textsubscript{Mn}O\textsubscript{3} orthorhombic compounds have been previously studied\textsuperscript{21,22,26}. In particular, they have explained the frequency softening of the 490 cm\textsuperscript{-1} and 600 cm\textsuperscript{-1} modes below \( T_N \) in terms of spin-phonon coupling caused by the phonon modulation of the superexchange integral\textsuperscript{21,22,26}. Recently, Xu et al\textsuperscript{27} have attributed the softening behavior of the two excitations at 490 cm\textsuperscript{-1} and 610 cm\textsuperscript{-1} of LaMnO\textsubscript{3} to an orbital-spin-phonon (OSP) coupling rather than limited to a spin-phonon coupling only. The verification of the suggested theoretical models requires more studies of the effects of magnetic and orbital orderings on the phonon frequencies in the R\textsubscript{Mn}O\textsubscript{3} compounds.

In this paper, we investigate the Raman-active phonons in PrMnO\textsubscript{3}, NdMnO\textsubscript{3}, TbMnO\textsubscript{3} and DyMnO\textsubscript{3} compounds as a function of temperature and magnetic field. The objectives are (i) to study and compare the Raman spectra of PrMnO\textsubscript{3}, NdMnO\textsubscript{3}, TbMnO\textsubscript{3} and DyMnO\textsubscript{3} at low temperature.

#### Results and Discussion

Based on group-theory, the orthorhombic R\textsubscript{Mn}O\textsubscript{3} (space group Pbnm) has twenty-four Raman-active modes (\( 7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g} \))\textsuperscript{28}. The R\textsubscript{Mn}O\textsubscript{3} unit cell contains two MnO\textsubscript{6} octahedra along the \( y \)-direction with two apical O2 and four equatorial O1 oxygen ions at the summits. The Mn–O2 bond is along the \( y \)-axis while the Mn–O1 bonds are in the \( xz \) plane (ab–plane).

Figure 1 shows the polarized Raman spectra of R\textsubscript{Mn}O\textsubscript{3} (\( R = \text{Pr, Nd, Tb and Dy} \)) in the \( xx \) (\( aa \)) and \( xz \) (\( ab \)) configurations at \( T = 5\, \text{K} \). The typical phonons associated with the orthorhombic R\textsubscript{Mn}O\textsubscript{3} manganites are observed\textsuperscript{21,22}. For both configurations, six \( A_g \) and six \( B_{1g} \) Raman-active phonons are detected. The selection rules are well respected and the phonon linewidths are close to 3–7 cm\textsuperscript{-1} attesting the high crystalline quality of the samples. With decreasing temperature, no additional modes appear indicating a structural phase stability of the R\textsubscript{Mn}O\textsubscript{3} compounds. The frequencies of the \( A_g \) and \( B_{1g} \) Raman active phonons of PrMnO\textsubscript{3}, NdMnO\textsubscript{3}, TbMnO\textsubscript{3} and DyMnO\textsubscript{3} are reported in Table 1. Their vibrational characters are assigned in agreement with previous Raman measurements\textsuperscript{29}. With decreasing the ionic radius of R (\( R_{\text{Tb}} > R_{\text{Nd}} > R_{\text{Pr}} > R_{\text{Dy}} \)) most phonon frequencies shift towards higher values. Simultaneously, there is a transfer of intensity between the two high-frequency \( A_g \) phonons close to 500 cm\textsuperscript{-1} due to lattice distortions induced by the ionic radius size that mixes the symmetry characters of some phonon excitations\textsuperscript{21,22}. Here we focus on the microscopic mechanisms and the theoretical models required to explain the phonon frequency shifts and how they differ in the multiferroic TbMnO\textsubscript{3} and DyMnO\textsubscript{3} compounds as compared to the non-multiferroic compounds PrMnO\textsubscript{3} and NdMnO\textsubscript{3}.

Figures 2 and 3 respectively show the temperature dependences of the \( A_g \) and \( B_{1g} \) phonon frequencies for PrMnO\textsubscript{3} (a), NdMnO\textsubscript{3} (b) TbMnO\textsubscript{3} (c) and DyMnO\textsubscript{3} (d). Between 300 K and \( T^* \), the temperature evolutions of the different R\textsubscript{Mn}O\textsubscript{3} phonon frequencies are very similar: they harden with decreasing temperature. This frequency hardening is due to the anharmonic effect (dashed line) which can be simulated by the following formula: 
\[
\omega(T) = \omega_0 - C\left(1 + \frac{x}{2s^2-1}\right),
\]
where \( x = \frac{\hbar \omega}{K_B T} \), \( \omega_0 \) and \( C \) are adjustable parameters. For PrMnO\textsubscript{3} (NdMnO\textsubscript{3}), the frequencies of the most detected modes soften significantly below \( T_N \sim 100\, \text{K} \) (\( T_N \sim 80\, \text{K} \)). Remarkably, the fre-
The frequency shift of the Raman active modes 27. The frequency shift of the spin-phonon coupling mode and have developed a theoretical model that takes into account the contribution of the orbital ordering. The total frequency shift \( \Delta \omega \) is written as a function of the effective force constant of orbital-spin-phonon (second term).

\[
(\Delta \omega)_{\text{sp-phon}} \approx -\frac{2}{\mu} \sum_{ij} \left( \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} - \frac{1}{2} \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} \right) \frac{(M(T))^2}{4\mu_B}
\]

where \( J_{ij} \) are the exchange constants in the equatorial plane and along the apical axis respectively and \( u_{ij} \) is the displacement vector from the equilibrium positions of the \( k^{th} \) \( O^{2-} \) ion. Xue et al.27 have revised the spin-phonon coupling model and have developed a theoretical model that takes into account the contribution of the orbital ordering. The total frequency shift \( \Delta \omega_{\text{sp}}(T) \) is written as a function of the effective force constant of the spin-phonon coupling (first term) and the effective force constant of orbital-spin-phonon (second term).

\[
\Delta \omega_{\text{sp}}(T) \approx \frac{1}{2\mu_B} \sum_{i} \left( \frac{\partial^2 J_{i}}{\partial u_{i}^2} S_i + \frac{4}{3} \frac{\partial^2 J_{i}}{\partial u_{i}^2} S_i S_j \right)
\]

where \( \tau, \tau_j \) are the orbital correlation operators and \( S_i, S_j \) are the spin correlation functions for the \( i \) and \( j \) \( Mn^{3+} \) ions. Using the multivariable Taylor expansion and the spin correlation functions for the \( i \) and \( j \) \( Mn^{3+} \) ions we can establish the expression of the frequency softening of some Raman active modes 27. The frequency shift \( \Delta \omega(T) \) of the in-phase stretching mode at \( \sim 600\, \text{cm}^{-1} \) becomes

\[
\Delta \omega_{\text{in}}(T) \approx \frac{m}{2} \left( \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} - 4 \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} \right) \frac{(M(T))^2}{4\mu_B} + 4 \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} \delta S_{ij}
\]

and the \( \Delta \omega(T) \) of the out-of-phase bending mode at \( \sim 490\, \text{cm}^{-1} \):

\[
\Delta \omega_{\text{out}}(T) \approx \frac{m}{2} \left( \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} - 4 \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} \right) \frac{(M(T))^2}{4\mu_B} + 4 \frac{\partial^2 J_{ij}}{\partial u_{ij}^2} \delta S_{ij}
\]

Table 1. Frequencies (cm\(^{-1}\)) of the Raman-active modes in PrMnO\(_3\), NdMnO\(_3\), TbMnO\(_3\), and DyMnO\(_3\) at 5 K.

| Modes            | Atomic displacements | PrMnO\(_3\) | NdMnO\(_3\) | TbMnO\(_3\) | DyMnO\(_3\) |
|------------------|----------------------|-------------|-------------|-------------|-------------|
| \( A_1 \)        | \( Ag \)             | 147         | 146         | 146         | 143         |
| \( \delta \)     | R, O2 displacements  | 228         | 245         | 283         | 288         |
| \( \alpha \)     | in-plane MnO\(_3\) y rotation | 282         | 289         | 317         | 325         |
| \( \gamma \)     | out of phase MnO\(_3\) x rotations | 325         | 334         | 385         | 392         |
| \( \Omega \)     | O2 antistretching    | 463         | 467         | 495         | 494         |
| \( \beta \)      | MnO\(_3\) bending    | 490         | 494         | 513         | 516         |
| \( \eta \)       | R, O2 and O1 displacements | 160         | 161         | 164         | 169         |
| \( \mu \)        | R and O2 displacements | 208         | 210         | 310         | 312         |
| \( \nu \)        | O1(z)                | 309         | 313         | 338         | 338         |
| \( \lambda \)    | out-of-phase MnO\(_3\) bending | 448         | 450         | 480         | 481         |
| \( \kappa \)     | in-plane O2 scissorslike | 496         | 502         | 534         | 536         |
| \( \zeta \)      | in plane O2 stretching | 600         | 602         | 615         | 612         |
The common form of these last equations is a linear function

\[ Y = SX + B \]

where \( S \) is the slope and \( X \) is the square of the sublattice magnetization. The intercept \( B \), which is related to the effective force constant of orbital-spin-phonon coupling \( k_{OSP} \), is nonzero only if the interaction exists. This model is successfully used to

Figure 2. Temperature dependence of the \( A_2 \) phonon frequencies of PrMnO\(_3\), NdMnO\(_3\), TbMnO\(_3\) and DyMnO\(_3\). Dotted lines correspond to the anharmonic behaviour.

Figure 3. Temperature dependence of the \( B_{1g} \) phonon frequencies of PrMnO\(_3\), NdMnO\(_3\), TbMnO\(_3\) and DyMnO\(_3\). Dotted lines correspond to the anharmonic behaviour.
explain the frequency softening of LaMnO$_3$ phonons$^{27}$. However, detailed studies and more concrete experimental evidences are needed to confirm that the OSP coupling clearly exists, below $T_N$ in the $A$-type RMnO$_3$ compounds. To assess the validity of the OSP coupling in the case of PrMnO$_3$ (and NdMnO$_3$), we have examined the frequency softening behavior, not only of the high frequency modes at 490 cm$^{-1}$ (494 cm$^{-1}$) and 600 cm$^{-1}$ (602 cm$^{-1}$), but also of the low frequency mode at 228 cm$^{-1}$ (245 cm$^{-1}$) since it corresponds to a rotational Raman-active mode sensitive to the orbital ordering fluctuations as observed in KCuF$_3$.$^{30}$ The $\Delta \omega(T)$ of this in-phase MnO$_6$ rotation mode can be written as:

$$\Delta \omega(N)^{(2)}(T) = \omega_0 \left( \frac{m}{2} \right) \approx \frac{\partial^2 \mathcal{J}_{\text{zz}}}{\partial \mu_{\text{Rot}}^2} \left( \frac{\langle \tau^z \rangle_{xz} + \delta S_{xz}}{4\mu_B} \right)$$

where $\mu_{\text{Rot}}$ is the displacement vector of the $k$th O$^{2-}$ ion relative to the rotational mode. According to Granado model (eq. 1), the variation of $\log(\omega(T_N) - \omega(T))$ versus $\log(M_{\text{sub}}(T_{3.8\mu_B}))$ should yield a linear line with a slope of +2 if the spin-phonon coupling is solely responsible for the frequency softening below $T_N$. Figure 4(a) (Fig. 4(c)) shows a logarithmic plot of the frequency softening $\Delta \omega(T)$ of the 228 cm$^{-1}$, 490 cm$^{-1}$ and 600 cm$^{-1}$ modes in PrMnO$_3$. (c) and (d) represent their corresponding variations in NdMnO$_3$. The $\Delta \omega(T)$ is taken from Refs$^{15,22,31}$.

Figure 4. (a) A logarithmic plot of the mode frequency softening $\{\omega(T_N) - \omega(T)\}$ with respect to the sublattice magnetization for temperatures between 5 K and 100 K in PrMnO$_3$. (b) $\Delta \omega$ as a function of $\left( M_{\text{sub}}(T_{3.8\mu_B}) \right)^2$ of the 228 cm$^{-1}$, 490 cm$^{-1}$ and 600 cm$^{-1}$ modes in PrMnO$_3$. (c) and (d) represent their corresponding variations in NdMnO$_3$. The variation of $\left( M_{\text{sub}}(T_{3.8\mu_B}) \right)^2$ is taken from Refs$^{15,22,31}$. 

This suggests that the spin-phonon coupling alone does not adequately explain the observed frequency softening below $T_N$ in PrMnO$_3$ and NdMnO$_3$. Figure 4(b) shows a good linear correlation between $\Delta \omega(T)$ and $X = \left( \frac{M_{\text{sub}}(T)}{3.8\mu_B} \right)^2$ which is in agreement with the linear function of equations 3, 4 and 5. The extrapolation of the linear function at $X = 0$ gives the intercept $B$: 

...
1.65, 0.94 and 0.71 for the 228 cm\(^{-1}\), 490 cm\(^{-1}\) and 600 cm\(^{-1}\) modes respectively. These behaviors are also observed in NdMnO\(_3\) with B values: 0.58, 0.73 and 0.29 for the 245 cm\(^{-1}\), 494 cm\(^{-1}\) and 602 cm\(^{-1}\) modes respectively (Fig. 4(d)). These finite positive values indicate that the spin and the orbital orders are also coupled in PrMnO\(_3\) and NdMnO\(_3\). In addition, the nonzero value of B at \(T_N\) implies that this coupling does not vanish completely above \(T_N\) but remains nonzero for a finite temperature range due to the magnetic correlations in the paramagnetic phase. The term B is interpreted as the effective force constant of the OSP coupling \(k_{OSP}\). The effective force constants \(k_{SP}\) (of spin-phonon coupling) and \(k_{OSP}\) (of orbital-spin-phonon coupling) are reported in Table 2.

### Table 2

| Compounds/modes | \(k_{SP}\) (dynes/cm) | \(k_{OSP}\) (dynes/cm) | \(k_{OSP}/k_{SP}\) (%) |
|-----------------|----------------------|------------------------|------------------------|
| Modes           | \(Ag(2)\) | \(Ag(3)\) | \(B1g(1)\) | \(Ag(2)\) | \(Ag(3)\) | \(B1g(1)\) | \(Ag(2)\) | \(Ag(3)\) | \(B1g(1)\) |
| LaMnO\(_3\)\(^{27}\) | — | — | 1000 | — | — | 70 | — | — | 70 |
| PrMnO\(_3\) | 651 | 865 | 2622 | 54 | 66 | 61 | 8.2 | 7.6 | 2.3 |
| NdMnO\(_3\) | 193 | 655 | 2413 | 20 | 51 | 25 | 10.3 | 7.7 | 1.0 |

Figure 5. (a) The filled red squares show the temperature dependence of the 615 cm\(^{-1}\) mode in TbMnO\(_3\). The filled black circles show the variation of \(-\gamma\omega_\alpha\Delta A/A_\alpha\) as a function of temperature where \(A = a \times b\). In (b) their corresponding variations in NdMnO\(_3\).

As mentioned above, the frequency softenings of phonons in TbMnO\(_3\) and DyMnO\(_3\) are much weaker than those in PrMnO\(_3\) and NdMnO\(_3\). The origin of their frequency softening remains unclear; it has been qualitatively assigned to a spin-phonon coupling\(^{22}\) or to an expansion in the Mn–O bond lengths\(^{22}\). However, there are no concrete experimental proofs to determine their true origin. The phonon frequency shifts induced by the change of the ionic binding energies due to the lattice expansion/contraction, is usually approximated by the Grüneisen law \(\Delta\omega_\alpha(T)/\omega_\alpha = -\gamma_\alpha(\Delta V/V_0)\) where \(\gamma_\alpha\) is the Grüneisen parameter for the normal mode \(\alpha\). This later approximation is applicable for isotopically expanded lattices. One should also consider the possibility of phonon frequency shifts due to lattice anomalies, even in the absence of a lattice unit cell volume change. Indeed, for some phonons the displacement of the involved atoms is either unidimensional or restricted in a plane. Blasco et al.\(^{16}\) have observed an expansion in TbMnO\(_3\) \(a\)-lattice parameter below 130 K and no significant changes are observed for the \(b\) and \(c\) parameters.

Figure 5 shows the temperature dependence of the frequency of \(B_{1g}(1)\) mode (red squares) in TbMnO\(_3\) (a) and NdMnO\(_3\) (b). The black dots indicate the variation of \(-\gamma\omega_\alpha\Delta A/A_\alpha\) as a function of temperature where \(A = a \times b\).
and $\gamma$ is the Grüneisen parameter. The frequency softenings of the $B_{1g}(1)$ mode are in agreement with the thermal expansion in the $ab$–plane with a Grüneisen parameter of $\sim 0.0416$ in the case of $\text{TbMnO}_3$ whereas it is clearly not the case of $\text{NdMnO}_3$ below $T \sim 80 \text{K}$. This confirms that in the case of $\text{TbMnO}_3$, the frequency shift of the $B_{1g}(1)$ mode is mainly due to an expansion in the $\text{Mn} - \text{O}$ distances related to discrete orbital rearrangements close to the magnetic order transition, a phenomenon not discussed before, in this much-distorted compounds $\text{RMnO}_3$ ($R = \text{Tb}$ and $\text{Dy}$). Indeed, the negative thermal expansion, recently observed in some magnetic materials ($\text{Ca}_2\text{Ru}_{1-x}\text{M}_x\text{O}_4$ where $M = \text{Mn}$ and Fe) at low temperatures, is attributed to a strong coupling between orbital and magnetic orders$^{33,34}$. In addition, the frustrated magnetic order in $\text{TbMnO}_3$ is usually attributed to its frustrated orbital ordering as compared to $\text{TbMnO}_3$.

Analysis of magnetic-field effects. In order to further investigate the spin-lattice coupling in a frustrated multiferroic system $\text{TbMnO}_3$ against a non-multiferroic compound $\text{PrMnO}_3$, we also study the evolutions of Raman active phonon frequencies of both compounds under an applied magnetic field at $4.2 \text{K}$, below $T_{N}^{\text{R} - \text{PrTb}}$.

Figure 6 shows the magnetic field dependence of the unpolarized macro-Raman spectra of $\text{PrMnO}_3$ (a) and $\text{TbMnO}_3$ (b) up to 7 Tesla. The applied magnetic field is quasi-parallel to the $c$–axis. While some of $\text{TbMnO}_3$ phonon frequencies are shifted as a function of magnetic field, those of $\text{PrMnO}_3$ remain unaffected. Similarly to $\text{TbMnO}_3$, these magnetic-field induced frequency shifts reflect the frustration of the spin configuration in $\text{TbMnO}_3$ and its sensitivity to the presence of a magnetic field. The most affected phonons in $\text{TbMnO}_3$, by the magnetic field, are the Jahn-Teller modes at $615 \text{ cm}^{-1}$ ($B_{1g}(1)$) and $513 \text{ cm}^{-1}$ ($A_{g}(3)$). Their frequencies soften by $\sim 1 \text{ cm}^{-1}$ and $\sim 2 \text{ cm}^{-1}$ at 7 Tesla respectively. These phonons involve mainly the $\text{O}_1$ oxygen vibrations in the $xz$–plane and the $\text{Mn} - \text{O}$ distances suggesting a magnetic-field modulation of the $\text{Mn} - \text{O} - \text{Mn}$ bond lengths. These findings are in agreement with previous results indicating that a magnetic field induces a magnetoelastic coupling in $\text{TbMnO}_3$.$^{36,37}$ Also, in our study of the $\text{Tb}^{3+}$ crystal-field excitations in $\text{TbMnO}_3$, single crystals, we have found that some excitations are significantly shifted under an applied magnetic field along the $c$–axis at $4.2 \text{ K}$. This observation is in favor of oxygen displacements under magnetic-field in agreement with a prominent role of the oxygen ions in the multiferroicity of $\text{TbMnO}_3$ and $\text{DyMnO}_3$, as recently reported by Huang et al.$^{39}$ Hence the ferroelectricity is related to local oxygen arrangements following the increase of the $\text{Mn} - \text{O}1$ bond length as induced by Dzyaloshinskii-Moriya interaction rather than a pure electronic mechanism as suggested by Kastura et al.$^{40,41}$

Conclusion

In this comparative Raman study of the $\text{PrMnO}_3$, $\text{NdMnO}_3$, $\text{TbMnO}_3$, and $\text{DyMnO}_3$, single crystals, the phonon frequency shifts in $\text{PrMnO}_3$ and $\text{NdMnO}_3$, observed below $T_{N}$, are explained by an orbital-spin-phonon coupling whereas those in $\text{TbMnO}_3$ and $\text{DyMnO}_3$, observed below 130 $\text{K}$, are attributed to an expansion of the $\text{Mn} - \text{O}$ distances. In our $\text{PrMnO}_3$ and $\text{TbMnO}_3$ magneto-Raman measurements, it is shown that some $\text{TbMnO}_3$ phonons are shifted as a function of magnetic field, while those of $\text{PrMnO}_3$ remain unaffected. The magnetic-field dependence...
of the $Tb Mn O_3$ phonon frequencies is associated to a magnetic modulation of the O1 oxygen displacements and suggests that $Mn – O1$ bond polarization may play a significant role in the magnetoelectric properties of $Tb Mn O_3$.

**Methods**

$R Mn O_3 (R = Pr, Nd, Dy and Tb)$ single-crystals were grown by the floating zone method as described in reference $6$. The Raman spectra were recorded at temperatures between 300 K and 5 K and were obtained in the backscattering configuration using a He – Ne laser (632.8 nm) and a Labram-800 micro-Raman spectrometer equipped with a $X = 50$ objective microscope (focus diameter around $\sim 3 \mu m$), an appropriate notch filter and a nitrogen-cooled CCD detector. The studied single crystals were mounted in a continuous flow temperature regulated liquid helium Janis cryostat. We have also measured the Raman active excitations under applied magnetic field up to 7 Tesla. The Raman measurements under magnetic field were obtained with an Ar$^+$ incident laser (514.5 nm) and with a magnetic field parallel to the c-axis.

**Data Availability.** Most data generated or analysed during this study are included in this published article. The Raman spectra of $R Mn O_3 (R = Pr, Nd, Dy and Tb)$ compounds at different temperatures are available from the corresponding author on reasonable request.

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Acknowledgements
The authors would like to thank M. Castonguay and S. Pelletier for their experimental help. S. Mansouri and S. Jandl acknowledge support from the Natural Science and Engineering Research Council of Canada and the Fonds Quebecois de la Recherche sur la Nature et les Technologies. A. Mukhin, V. Y. Ivanov and A. Balbashov acknowledge support from the Russian Scientific Foundation (Project No. 16-12-10531).

Author Contributions
S.M. and S.J. conceived the study. A.M., V.Y.I., and A.B. prepared the samples. S.M. performed the measurements. S.M. and S.J. analyzed the results. S.M. wrote the manuscript. All authors commented on the manuscript.

Additional Information
Competing Interests: The authors declare that they have no competing interests.

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