Griffiths phase-like behaviour and spin-phonon coupling in double perovskite

\( \text{Tb}_2\text{NiMnO}_6 \)

Harikrishnan S. Nair,\(^1\) Diptikanta Swain,\(^2\) Hariharan N.,\(^3\) Shilpa Adiga,\(^1\) Chandrabhas Narayana,\(^2\) and Suja Elizabeth\(^3\)

\(^1\)Jülich Center for Neutron Sciences-2/Peter Grünberg Institute-4, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

\(^2\)Chemistry and Physics of Materials Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore 560064, India

\(^3\)Department of Physics, C.V. Raman Avenue, Indian Institute of Science, Bangalore 560012, India

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The Griffiths phase-like features and the spin-phonon coupling effects observed in \( \text{Tb}_2\text{NiMnO}_6 \) are reported. The double perovskite compound crystallizes in monoclinic \( P2_1/n \) space group and exhibits a magnetic phase transition at \( T_c \sim 111\ \text{K} \) as an abrupt change in magnetization. A negative deviation from ideal Curie-Weiss law exhibited by \( 1/\chi(T) \) curves and less-than-unity susceptibility exponents from the power-law analysis of inverse susceptibility are reminiscent of Griffiths phase-like features. Arrott plots derived from magnetization isotherms support the inhomogeneous nature of magnetism in this material. The observed effects originate from antiferromagnetic interactions which arise from inherent disorder in the system. Raman scattering experiments display no magnetic-order-induced phonon renormalization below \( T_c \) in \( \text{Tb}_2\text{NiMnO}_6 \) which is different from the results observed in other double perovskites and is correlated to the smaller size of the rare earth. The temperature evolution of full-width-at-half-maximum for the stretching mode at 645 cm\(^{-1}\) presents an anomaly which coincides with the magnetic transition temperature and signals a close connection between magnetism and lattice in this material.

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I. INTRODUCTION

Double perovskites $R_2BB'O_6$ ($R =$ rare earth; $B, B'$ = transition metal) are interesting systems owing to the variety of phenomena they display including large magnetocapacitance, magnetoresistance, cationic ordering, high temperature structural phase transitions and the predicted multiferroic properties. One of the most studied double perovskite, La$_2$NiMnO$_6$ displays large, magnetic-field-induced changes in resistivity and dielectric constant at 280 K – a temperature much higher than previously reported for such couplings. The combination of multiple functionalities with magnetic, dielectric and lattice degrees of freedom makes double perovskites a material of current interest with device application potential. $R_2BB'O_6$ compounds are reported to crystallize either in monoclinic $P2_1/n$ space group, in which case, layers of $B^{2+}$ and $B'^{4+}$ alternate periodically; or in orthorhombic $Pbnm$ structure where $B^{3+}$ and $B'^{3+}$ are randomly distributed in the lattice. Most of the ordered double perovskites exhibit ferromagnetism (FM) which originates from the superexchange interaction between ordered $B^{2+}$ and $B'^{4+}$ ions. In ordered La$_2$NiMnO$_6$, the Ni$^{2+}$ ($t_5^5e_g^4$)–O–Mn$^{4+}$ ($t_3^3e_g^0$) magnetic exchange leads to prominent ferromagnetic interactions. However, even in the ordered state, certain percentage of $B$ and $B'$ cations interchange their respective crystallographic positions leading to what is known as antisite disorder in these materials. Monte Carlo simulations as well as experimental investigations have revealed that this disorder markedly influences the magnetic properties and can lead to secondary magnetic phases at low temperature. Antisite disorder can introduce additional antiferromagnetic exchange interactions in the form of Ni$^{2+}$–O–Ni$^{2+}$ or Mn$^{4+}$–O–Mn$^{4+}$ which can result in reduction of ferromagnetic saturation magnetization, and such interactions, which get modulated by cationic size mismatch at the La site have been observed through magnetic measurements on La$_2$NiMnO$_6$. It must be noted that short range ferromagnetic correlations above $T_c$ have been observed in La$_2$NiMnO$_6$, confirmed by the anomalous softening of phonon modes due to spin-phonon coupling which extended up to high temperatures. X ray magnetic circular dichroism studies revealed clear signals above $T_c$ in La$_2$NiMnO$_6$ indicating the presence of short-range FM correlations. Majority of the existing literature on double perovskites addresses La-based systems whereas the effects of smaller, heavier magnetic rare earth at the $R$ site have received less attention. Recently investigations on a series of $R_2NiMnO_6$ compounds found that the Ni–O–Mn bond length and bond angle, which are directly in-
volved in superexchange interactions, are significantly modified with reduction in $R$-size.\textsuperscript{16}

As a consequence, multiple magnetic interactions can develop in the system and lead to in-homogeneous magnetic states similar to the clustered or phase separated states observed in perovskite manganites. To strike a comparison with the case of manganites, quenched disorder arising from the random distribution of cations of different sizes and charges introduces phase inhomogeneity through size mismatch of cations and bond disorder of the Mn-O-Mn network, there by, paving the way for Griffiths phase.\textsuperscript{17,18}

Many manganites exhibit Griffiths phase-like feature, for example, (La$_{1-y}$Pr$_y$)$_0$Ca$_{0.3}$Mn$_{16/18}$O$_{3+10}$ Sm$_{0.5}$Sr$_{0.5}$MnO$_3$ nano-manganites.\textsuperscript{20} and Pr$_{0.5}$Sr$_{0.5}$Mn$_{1-y}$Ga$_y$O$_3$.\textsuperscript{21} The cationic disorder arising from the mixed occupancy at the $B$ site and the smaller size of the rare earth could lead to similar effects in double perovskites.

The phonon spectra of double perovskites have been actively investigated using Raman spectroscopy methods for example, in La$_2$NiMnO$_6$ and La$_2$CoMnO$_6$ bulk and thin films.\textsuperscript{7,22–24} Strong spin-phonon coupling has been reported in single crystals and epitaxial thin films of La$_2$NiMnO$_6$\textsuperscript{13,25} The effect of cationic size of the rare earth on the phonon properties has not been investigated yet. In a recent Raman study on Pr$_2$NiMnO$_6$, Truong et al. observed that with a smaller rare earth than La at the $R$ site, the spin-phonon coupling is weakened and the physical properties of rare earth double perovskite were a function of the type of $R$.\textsuperscript{20} Recent theoretical prediction\textsuperscript{5} about the multiferroicity in Y$_2$NiMnO$_6$ also points towards the importance of the type of $R$ in double perovskites. It was found theoretically that changing $R$ from La to Y drives the ground state from ferromagnetic to antiferromagnetic $E^*$ type which breaks inversion symmetry generating electric polarization. It is, therefore, rewarding to investigate the magnetic and phonon properties of double perovskites upon change in ionic size of $R$. In this report we present the results of detailed magnetization and Raman scattering experiments on Tb$_2$NiMnO$_6$ to explore the effect of substituting a magnetic rare earth at the $R$ site on the magnetism and spin-phonon coupling.

II. EXPERIMENTAL SECTION

Polycrystalline Tb$_2$NiMnO$_6$ used in the present study was prepared by conventional solid state synthesis. The precursors Tb$_2$O$_3$, NiO and MnO$_2$ (3N purity or higher) weighed in stoichiometric amounts were mixed and ground together in a mortar and was heat treated
initially at 1000°C for 24 h and further at 1300°C for 36 h, after re-grinding. Powder X-ray diffractogram (PXD) was obtained by a Philips X’Pert diffractometer (Cu Kα) and was analyzed by Rietveld method using FULLPROF suite of programs. Temperature dependent dc magnetization measurements were performed in a commercial SQUID magnetometer (Quantum Design) in zero field-cooled (ZFC) and field-cooled (FC) cycles with applied fields of 20, 100, 500, 20 kOe and 40 kOe. In addition, at 20 Oe, field-cooled warming/cooling (FCW/FCC) curves were also recorded. Raman scattering experiments were performed in a custom-built Raman spectrometer using a 532 nm frequency-doubled solid state Nd-YAG laser with 8 mW power. The measurements were carried out in back scattering geometry in the temperature range 77 to 300 K.

III. RESULTS AND DISCUSSION

The crystal structure of Tb$_2$NiMnO$_6$ (TNMO) was refined in monoclinic space group P2$_1$/n (space group no.: 14) with an agreement factor, χ$^2$ = 3.74. The refined lattice parameters obtained from the analysis, $a = 5.2699(2)$ Å, $b = 5.5425(7)$ Å and $c = 7.5251(2)$ Å and the monoclinic angle β = 89.79° are in reasonable agreement with the previous report. The observed x ray diffraction pattern is analysed using Rietveld method in FULLPROF code. The results are presented in Fig. 1 along with a structural diagram depicting the schematic of the crystal structure. A minor impurity phase of Tb$_2$O$_3$ (4 wt%) was identified in the x ray pattern. The structural parameters and selected bond distances and angles from the analysis are presented in Table 1. The crystal structure adopted by $R_2BB'O_6$ compounds depends on cationic size, charge and the $R/B$ radius ratio which are empirically quantified in tolerance factor. A monoclinic unit cell is favoured if the tolerance factor,

$$t = \frac{r_R + r_B' + r_o}{\sqrt{2}(r_R^2 + r_B'^2 + r_o^2)}$$

(where $r_R$, $r_B$ and $r_o$ are ionic radii of rare earth, transition metal and oxygen, respectively), is less than unity. With a $t = 0.858$, a monoclinic unit cell is empirically expected for TNMO (the ionic radii values for calculating $t$ were taken from). The bond distances and angles obtained from the structural refinement compiled in Table 1 are comparable to the reported values of Ni$^{2+}$–O and Mn$^{4+}$–O distances there by indicating a nearly-ordered Ni$^{2+}$/Mn$^{4+}$ arrangement. A quantitative estimate of the valence states of the cations was obtained by calculating the bond valence sums (BVS). The calculated values, presented in Table 1 compare well with those reported for the Mn$^{4+}$–O and Ni$^{2+}$–O bonds.
FIG. 1. The experimental x-ray diffraction pattern of Tb$_2$NiMnO$_6$ along with the results of Rietveld analysis. A minor impurity phase of Tb$_2$O$_3$ was identified and quantified as 4 wt%. The inset presents a schematic of the crystal structure in monoclinic $P2_1/n$ space group. The blue spheres represent Ni/Mn; the green are oxygen and the pink are Tb. The network of corner-sharing octahedra is indicated.

thereby supporting a predominant Ni$^{2+}$/Mn$^{4+}$ cationic arrangement for TNMO.

The $M(ZFC)$ and $M(FC)$ magnetization curves of Tb$_2$NiMnO$_6$ at applied field of 100 Oe are presented in the main panel of Fig. 2 while the insets (a) and (b) show the same curves at higher applied fields of 500 and 20 kOe respectively. The $ZFC$ and $FC$ arms in Fig. 2 show a split at the magnetic transition temperature, $T_c \approx 111$ K where the system enters magnetically ordered state. On increasing the applied magnetic field, the $ZFC/FC$ arms begin to merge and at 20 kOe complete merging is attained. With the application of magnetic field the magnetization at low temperature is enhanced, typical of systems with a ferromagnetic component. At low applied fields, the $M(ZFC)$ shows a downturn below $\approx 15$ K which decreases as the applied field increases to 20 kOe. Other double perovskites like Nd$_2$CoMnO$_6$ display such a downturn which originates from the anti-parallel alignment of Tb moment with respect to the Ni/Mn moments.

The transition temperature observed in magnetization measurements was confirmed through specific heat, $C_p(T)$ as presented in Fig. 3 where a peak was observed at 111 K. Apart from the peak at $T_c$ and a low temperature hump that arises from the Schottky effect, the $C_p$ displays no anomalies or peaks from any impurities. The analysis of low temperature $C_p$
FIG. 2. Main panel: The ZFC and FC magnetization curves of Tb$_2$NiMnO$_6$ at 100 Oe. The magnetic transition is evident at $T_c \sim 111$ K. The insets (a) and (b) show the ZFC and FC curves at 500 and 20 kOe respectively.

TABLE I. The structural parameters and selected bond distances and bond angles of Tb$_2$NiMnO$_6$ at room temperature. The atomic positions were Tb 4e(x,y,z), Ni 2c(0.5,0,0.5), Mn 2d(0.5,0,0) and O 4e(x,y,z). TM stands for the transition metal at the B site, Co or Mn. BVS indicates bond valence sum values.

| Space group       | $P2_1/n$          |
|-------------------|-------------------|
| Space group number| 14                |
| Lattice parameters| $a = 5.2699(2)$ Å, $b = 5.5425(7)$ Å, $c = 7.5251(2)$ Å, $\beta = 89.79^\circ$ |
| Bond distance     | TM-O $\approx 1.99$ Å |
| Bond angle        | TM-O$_1$-TM $\approx 140^\circ$ |
| BVS               | Tb = 3.6, Ni = 2.4, Mn = 4.1 |

was performed by assuming a polynomial expansion, $C_p = \gamma T + \beta_3 T^3 + \beta_5 T^5 + \beta_7 T^7$. Our fitting gave $\gamma = 0.42$ mJ/mol K$^2$ for the linear term and $\beta_3 = 6.2 \times 10^{-7}$ J/mol K$^4$ for the lattice term. The $\gamma$ value observed in Tb$_2$NiMnO$_6$ is smaller than the value observed in La$_{0.4}$Ca$_{0.6}$MnO$_3$ manganite showing Griffiths phase-like properties. The low value for $\gamma$ also suggests a low contribution from electronic conduction in this insulating double perovskite.
FIG. 3. Main panel: The specific heat of Tb$_2$NiMnO$_6$ confirming the phase transition of the Ni/Mn lattice at $T_c \sim 111$ K. A broad hump-like feature is observed at low temperature which is related to Schottky effect. The inset represents the fit to the low temperature $C_p$ assuming the model described in the text.

In the main panel of Fig. 4 the $1/\chi(T)$ plots at different applied magnetic fields of 20 Oe, 500 Oe, 20 kOe and 40 kOe derived from dc magnetization measurements are presented. The downturn observed in the $1/\chi(T)$ curves is reminiscent of systems described by Griffiths phase (GP)\textsuperscript{17,18} which was originally proposed for randomly diluted Ising ferromagnets.\textsuperscript{33} In the original formulation, Griffiths assumed randomly diluted Ising ferromagnets with nearest-neighbour exchange bonds of strength $J$ and 0 distributed with a probability $p$ and $1 - p$ respectively. Long range FM order is established only above a percolation threshold ($p > p_c$) in a reduced $T_C$ which is below the ordering temperature for an undiluted system, termed as Griffiths temperature $T_G$. In doped manganites, quenched disorder that arises from the $A$ site disorder is the reason for the random distribution of cations and the consequent random dilution. In a similar fashion, the site disorder in double perovskites can lead to random dilution of the $B$ lattice. The negative curvature of $1/\chi(T)$ in Fig. 4 is observed to diminish in magnitude as magnetic field increases from 20 Oe to 40 kOe. This trend of $1/\chi(T)$ conforms to the general features of a GP phase where inverse susceptibility deviates from Curie-Weiss (CW) description as $T \to T_c$ and is suppressed at higher magnetic field. In Fig. 4 (a), we identify $T_G; (\sim 164$ K) as the characteristic Griffiths temperature where $1/\chi(T)$ commences to deviate from CW description. The low-field magnetic susceptibility
FIG. 4. Main panel: The inverse susceptibility $1/\chi(T)$ at different applied fields 20 Oe, 500 Oe, 20 kOe and 40 kOe. As the applied magnetic field increases, the downward deviation is suppressed. The inset (a) presents the CW analysis of $1/\chi(T)$ at 20 Oe holds only at $T \gg T_c$. Inset (b) displays log-log plot of the power law analysis of low-field magnetic susceptibility, $\chi^{-1}(T) \propto (T - T_{RC})^{1-\lambda}$. The black solid lines represent the fit to the experimental data following the power law.

in the Griffiths phase follows the power law behaviour, $\chi^{-1}(T) \propto (T - T_{RC})^{1-\lambda}$, where $\lambda$ is the magnetic susceptibility exponent whose value lies in the range $0 < \lambda < 1$. The magnetic susceptibility of $\text{Tb}_2\text{NiMnO}_6$ at $H = 20$ Oe was analyzed using the power law with great care to avoid an incorrect estimation of $T_{RC}$ which can lead to erroneous values of $\lambda$. Recent literature that offers a better protocol to perform the analysis was adopted to estimate $T_{RC}$ and $\lambda$ in the purely paramagnetic region. Following the procedure reported in literature, we first estimated the value of $T_{RC}$ in the purely paramagnetic region above $T_G$. A value of 56 K for $T_{RC}$ was estimated in this way which can be compared with that obtained by Zhou et al. Using this value of $T_{RC}$, fitting was performed in the GP regime to obtain a value of 0.88 for $\lambda$. The result of the analysis is presented in Fig. 4(b) plotted as $\log(1/\chi)$ versus $t_m = (T - T_{RC})/T_{RC}$. In the high temperature regime, we obtained $\lambda = 0.08$, signifying that the system has entered a completely paramagnetic phase. The Curie-Weiss analysis of the data above 200 K resulted in effective moment value of $\mu_{eff} = 14.1 \mu_B$. The spin-only moments of Ni and Mn assuming the combination of Mn$^{4+}$ ($3d^5$, $S = 3/2$) and Ni$^{2+}$ ($3d^8$, $S = 1$) yields $\mu_{eff} = 4.79 \mu_B$ and the combination of Mn$^{3+}$ ($3d^4$, $S = 2$) and Ni$^{3+}$ ($3d^7$, $S = 3/2$)
results in $\mu_{\text{eff}} = 6.24 \mu_B$. Assuming the rare earth paramagnetic moment to be $9.7 \mu_B^{16}$,

the calculated paramagnetic effective moment is $\approx 15.07 \mu_B$ for the Mn$^{3+}$/Ni$^{3+}$ combination and $14.53 \mu_B$ for the Mn$^{4+}$/Ni$^{2+}$ combination. A comparison with the experimentally observed value for effective moment suggests that the cationic combination in Tb$_2$NiMnO$_6$ is Mn$^{4+}$/Ni$^{2+}$. The $1/\chi(T)$ plot at an applied magnetic field of 20 Oe and the corresponding CW fit are presented in Fig. 4(a).

The isothermal magnetization plots of TNMO at 5, 10 and 50 K are illustrated in Fig. 5(a). The qualitative nature of the curves are different from the metamagnetic features observed at low temperatures by Troyanchuk et. al., in TbNi$_{0.5}$Mn$_{0.5}$O$_3$. The saturation magnetization $M_{\text{sat}} = 13.5 \mu_B$ at the highest applied field of 70 kOe is lower than the theoretical value of 23.2 $\mu_B$ which is calculated as $2gJ + 5.2\mu_B$ where, $g$ is the Landé g-factor, $J$ is the total angular momentum and 5.2 $\mu_B$ is the effective Ni-Mn spin-only moment value. In La$_2$NiMnO$_6$, the saturation magnetization at highest applied field is reported as 4.57 $\mu_B$ which is close to the theoretical value of 5 $\mu_B^{35}$ but the value of $M_{\text{sat}}$ has been observed to vary with the preparation method.\(^{10}\)

One of the basic characteristics of Griffiths phase is the existence of finite-size FM correlated spins but with no static long-range magnetization which can be verified through the Arrott plots. In Fig. 5(b) we present the Arrott plots – $M^2$ versus $H/M$ plots – derived from
FIG. 6. The FCC and FCW cycles at 20 Oe showing a prominent hysteresis of the first-order type resulting from the ferromagnetic clusters that form below $T_c$.

magnetization isotherms at 90, 110 and 120 K. The solid lines in Fig. 5 (b) are linear fits to the high-field region extrapolated to the axes so as to obtain the spontaneous magnetization. We observe no spontaneous magnetization in the temperature region close to $T_c$. The Arrott plots display positive slope, characteristic of second-order phase transitions as prescribed by the Banerjee criterion.\(^{36,37}\) Generally, the $M^2$ versus $H/M$ plots are linear for homogeneous ferromagnets\(^{38}\) and a deviation from linearity is suggestive of inhomogeneous behaviour. The presence of inhomogeneous magnetism in Tb$_2$NiMnO$_6$ is confirmed in Fig. 6, where FCW and FCC curves at an applied field of 20 Oe exhibit prominent hysteresis. Similar hysteresis behaviour of the FCC and FCW arms has been reported in magnetically phase-separated La$_{0.5}$Ca$_{0.5}$MnO$_3$.\(^{39}\)

The structural distortions resulting from the substitution of a smaller rare earth Tb at the $R$ site can couple with the spin system, the signature of which is discernible in Raman scattering experiments. Hence, we performed Raman scattering experiments on Tb$_2$NiMnO$_6$. The experimentally observed scattering intensity as a function of Raman shift is plotted in Fig. 7 (a) for different temperatures. In Fig. 7 (b), the intensity at 298 K is plotted as a function of Raman shift and along with deconvoluted peaks assuming Lorenzian peak shapes. Following earlier reports\(^{23,40}\) which established the similarity of Raman spectra of double perovskite La$_2$NiMnO$_6$ with orthorhombic LaMnO$_3$, we assign the respective peaks at 645 cm$^{-1}$ and 490
cm$^{-1}$ to \textit{stretching} and \textit{anti-stretching} vibrations of (Ni/Mn)O$_6$ octahedra.$^{23}$ Lattice dynamical calculations attribute mixed character to the 490 cm$^{-1}$ mode which involves both anti-stretching and bending vibrations whereas the 645 cm$^{-1}$ mode is purely a stretching mode.$^{24}$

The Raman spectra of Tb$_2$NiMnO$_6$ is similar to that of Pr$_2$NiMnO$_6$ which also crystallizes in monoclinic $P2_1/n$ symmetry.$^{26}$ The temperature dependence of phonon frequencies, $\omega(T)$, are shown in Fig. 8 (a) along with curve fits assuming a standard\textsuperscript{41} anharmonic dependence of phonon modes, $\omega_{\text{anh}}(T) = \omega_0 - C[1 + 2/(e^{\hbar\omega/k_B T} - 1)]$, where, $\omega_0$ is the temperature-independent part of linewidth, $C$ is a constant determined from curve-fit, $\hbar\omega$ is the phonon energy and $k_B$ is the Boltzmann constant. $RMnO_3$ perovskites which are $A$ type antiferromagnets and ferromagnetic double perovskites like La$_2$NiMnO$_6$ (LNMO) and La$_2$CoMnO$_6$ (LCMO) exhibit magnetic-order-induced phonon renormalization.$^{24,25,42–44}$ These systems display mode softening and a deviation from the $\omega_{\text{anh}}(T)$ dependence of phonon frequencies below $T_c$. However, in $RMnO_3$ systems with an incommensurate magnetic structure ($R$ = Eu, Tb or Y) no mode softening is observed.$^{42}$ However, the data on Tb$_2$NiMnO$_6$ yields a reasonably good fit to the standard expression for anharmonic dependence of phonons showing that the predominant effects in the phonon spectrum are anharmonic. The reduction in spin-phonon coupling is correlated to the size of the $R$ ion as strength of spin-phonon coupling shows a decreasing trend with reduction in rare earth size as reported in the case of Pr$_2$NiMnO$_6$.$^{26}$ In Fig. 8 (b), the temperature variation of full-width-at-half-maximum (FWHM) for pure \textit{stretching} mode at 645 cm$^{-1}$ is plotted. The linewidth of phonon is a measure of the phonon lifetime and is determined by temperature-dependent scattering from lattice defects or phonons. For Tb$_2$NiMnO$_6$, as clear from Fig. 8 (b), we observe three different regions in FWHM, with discontinuities at $T \sim 110$ K and at 180 K. Note that the discontinuities occur at the same value of temperature where the deviation from perfect CW description occurs in the $1/\chi(T)$ curves. This indicates a close correlation between magnetism and the lattice in Tb$_2$NiMnO$_6$.

To summarize the results, we have refined the crystal structure of Tb$_2$NiMnO$_6$ in monoclinic $P21/n$ space group that allows for a Ni$^{2+}$/Mn$^{4+}$ cationic arrangement. The estimated bond distances and the BVS values indicate a nearly-ordered $B$ site structure. The downturn of $1/\chi(T)$ curves from Curie-Weiss behaviour which decreases with the application of magnetic field is reminiscent of Griffiths phase in disordered systems. The presence of GP in Tb$_2$NiMnO$_6$ is further supported by the power-law analysis of $1/\chi(T)$ and the Arrott
FIG. 7. (a) Observed Raman scattering intensity curves of Tb$_2$NiMnO$_6$ at different temperatures. (b) The intensity at 298 K as a function of Raman shift, displaying peaks at $\sim$650 cm$^{-1}$, 510 cm$^{-1}$ and 490 cm$^{-1}$ (thick line). The shaded areas represent a curve-fit to the observed spectrum using Lorenzian line shape.

On a microscopic level, parameters like the magnetic correlation length ($\xi$) derived from small-angle neutron scattering experiments can further illuminate about the Griffiths phase. For a conventional FM phase transition, $\xi(T)$ displays a gradual increase from zero at high $T$, then diverges as $T \rightarrow T_c$ whereas in the presence of spin correlations, it shows a sharp increase at the temperature where the clusters emerge. Electron spin resonance (ESR) studies also have been successfully employed to study the GP phase in disordered manganites. At this point, it is instructive to compare the case of La$_2$NiMnO$_6$, in which the
FIG. 8. (a) The temperature variation of phonon frequencies in Tb$_2$NiMnO$_6$. The red line is the fit according to the anharmonic phonon-phonon scattering. A vertical black dotted line marks the position of $T_c \approx 111$ K. (b) The FWHM for the peak at 645 cm$^{-1}$ calculated from the experimental Raman intensity as a function of temperature. Note the three different slopes in three different temperature ranges. The red dotted lines show typical behaviour of FWHM while the black solid line represents the anomalous region. The inset displays curves that correspond to peaks at 490 and 509 cm$^{-1}$ which do not show a slope change.

Short range ferromagnetic correlations above $T_c$ have been studied through x-ray magnetic circular dichroism$^{14}$ critical behaviour$^{47}$ and ESR$^{15}$ Contrary to the case of Tb$_2$NiMnO$_6$, a positive deviation of $1/\chi(T)$ from CW description was observed. However, it has been demonstrated that the degree of antisite disorder is a function of the kind of cation at the $R$ site and can be influenced through doping$^{48}$ Analysis of the Raman scattering data
showed that, in contrast to the behaviour seen in other DP like La$_2$NiMnO$_6$, magnetic-order-induced mode softening is not observed in Tb$_2$NiMnO$_6$. Normally, FWHM of Raman linewidth decreases with temperature as indicated by the red dashed line in Fig. S(b). However, we observe a marked deviation from linear behaviour below about 180 K, extending till $T_c$. In this region, FWHM shows a plateau-like region (black solid line in Fig. S(b)). The anomalous plateau-like behaviour of TNMO is suggestive of increase in phonon lifetime which originates from the disorder in the system that strongly couples the magnetic and lattice degrees of freedom. The antisite disorder leads to additional antiferromagnetic exchange interactions between Ni – Ni and Mn – Mn. It is significant to note that the range of temperature where deviation from linearity in FWHM occurs (Fig. S(b)) coincides with the range over which $1/\chi(T)$ deviates from CW description (Fig. 5). Our study projects that Raman scattering can be used as a tool for the characterization of materials exhibiting magneto-lattice coupling effects. The temperature variation of FWHM for other frequencies (presented in Fig. S(b)) do not show slope changes which points towards strong spin-phonon coupling present in the case of symmetric modes like the stretching mode. The role of Tb-magnetism in Tb$_2$NiMnO$_6$ is not significant since ESR studies have shown that the Ni–Mn sublattice interacts weakly with the rare earth. However, the small cationic radius of Tb has a marked impact on structural distortions and contribute to the spin-lattice coupling leading to stronger magnetocapacitive effects. This motivates us to investigate further the magneto-dielectric properties of this compound, in detail with emphasis on multiferroism in double perovskites.

IV. CONCLUSIONS

We observe Griffiths phase-like features in the magnetic properties of double perovskite Tb$_2$NiMnO$_6$ where the smaller rare earth size of Tb influences the spin-phonon coupling. The value estimated for the inverse susceptibility exponent $\lambda$ along with the absence of spontaneous magnetization observed through Arrott plots testify the inhomogeneous nature of magnetism in this material and confirm the Griffiths phase-like features. The observed features arise from the site disorder at the $B$ site supplemented by the lattice distortions brought about by the smaller radius of Tb. No mode softening of phonon frequencies is observed in Tb$_2$NiMnO$_6$ which is qualitatively different from the observation in other double
perovskites with a non-magnetic rare earth. Thus, we conclude that the magnetic and lattice properties of $R_2BB'O_6$ where $R$ is a magnetic rare earth are different from those of the non-magnetic counterparts.

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