FAST TRACK COMMUNICATION

Investigation of phonon behavior in Pr$_2$NiMnO$_6$ by micro-Raman spectroscopy

K D Truong, M P Singh, S Jandl and P Fournier

Regroupement québécois sur les matériaux de pointe, Département de Physique, Université de Sherbrooke, Sherbrooke, J1K 2R1, Canada

E-mail: mangala.singh@usherbrooke.ca

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Abstract

The temperature dependence of phonon excitations and the presence of spin–phonon coupling in polycrystalline Pr$_2$NiMnO$_6$ samples were studied using micro-Raman spectroscopy and magnetometry. Magnetic properties show a single ferromagnetic-to-paramagnetic transition at 228 K and a saturation magnetization close to 4.95 $\mu_B$/f.u. Three distinct Raman modes at 657, 642, and 511 cm$^{-1}$ are observed. The phonon excitations show a clear hardening due to anharmonicity from 300 down to 10 K. Further, the temperature dependence of the 657 cm$^{-1}$ mode shows only a small softening. This reflects the presence of a relatively weak spin–phonon coupling in Pr$_2$NiMnO$_6$, contrary to the case for other double perovskites previously studied.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Research interest in R$_2$NiMnO$_6$ (RNMO, R = rare earth cations) double perovskites arises owing to their various technologically important properties, such as ferromagnetic insulator, spin–phonon, and magnetoelectric coupling properties [1–8]. These complex physical properties are the result of competing interactions between magnetic (spins), structural (phonons), and polarization (charges) order parameters. The possibility of tuning the magnetoelectric [3–5] and spin–phonon coupling [9, 10] through meticulous modifications in their structural parameters is a step forward for their potential uses in spintronic devices. Additionally, these intricate modifications offer an opportunity to investigate the underlying mechanisms that govern the coupled properties.

Recent works, on this class of compounds, have been primarily focused on La$_2$NiMnO$_6$ (LNMO). They include the synthesis conditions that promote the Ni/Mn cation ordering and its impact on the physical properties [6]. In particular, magnetic properties are found to be sensitive to the Ni/Mn ordering. Hence, an ordered LNMO phase shows a single magnetic transition at about 280 K, while a partially ordered LNMO phase shows an additional transition at about 138 K [6]. Thus, these properties have been used as a tool for determining the structural quality of a given sample [9–12]. Despite the extensive work on LNMO [2–12], very little is known about the physical properties of other members of the RNMO family. In this context, Booth et al [13] have recently synthesized a series of RNMO samples in polycrystalline form and explored their structural and magnetic behaviors. This study shows that the size of the rare earth element significantly influences the structural and magnetic properties of RNMO subject to the intricate modifications of the Ni–O–Mn bond lengths and bond angle. These modifications are expected to significantly influence the electronic and magnetic ground states and subsequently modify the phonon dispersion, the magnetic interaction strength, and eventually the spin–phonon coupling.

Apart from for La$_2$NiMnO$_6$ [9, 10], no comprehensive information about the phonon behavior and spin–phonon coupling of other members of RNMO is available in the...
literature. This has prompted the present investigation of the temperature dependence of the phonon excitations and the spin–phonon coupling of Pr$_2$NiMnO$_6$ (PNMO) using polarized micro-Raman spectroscopy. We compare its physical properties with those of LNMO and find a relatively weak spin–phonon coupling in PNMO. We discuss the possible impact of the Pr ionic radius on the observed physical properties.

2. Experiments

Bulk Pr$_2$NiMnO$_6$ (PNMO) samples were synthesized using Pr$_6$O$_{11}$, NiO and MnO$_2$ as starting materials. First, the Pr$_6$O$_{11}$ were precalcined in air at 900°C. Stoichiometric quantities of these oxides were then mixed, ground and poured into an alumina crucible. The mix was subjected to several heating cycles between 1000 and 1300°C in air with various intermediate grinding steps to obtain a homogeneous mixture. In the final step, the resultant PNMO powder was pressed into pellets and annealed at 1450°C in air overnight. Although the sample was polycrystalline, the size of the constituting microcrystals was larger than that of the micro-Raman laser spot (see below).

The temperature dependence of the magnetization ($M$–$T$) in 500 Oe applied magnetic field and its field dependence ($M$–$H$) at 10 K were measured using a superconducting quantum interference device (SQUID) magnetometer from Quantum Design. Phonon spectra with 0.5 cm$^{-1}$ resolution were recorded using a micro-Raman spectrometer in backscattering configurations with the 632.8 nm He–Ne laser line and a liquid-nitrogen-cooled CCD detector [9]. The laser spot size was kept at 3 μm. Such a diameter is perfectly adapted for studying polycrystalline samples with phonon symmetry selection rules [9, 10]. The size of the microcrystals studied (~10 μm) was relatively large enough to guarantee that phonons are not affected by boundary conditions. Further, the grain boundary and strain effects manifest usually in samples a few hundred Ångströms in size. Thus, such effects will be minimal in our experiments. Moreover, we would like to point out that a depolarization effect, which is likely to be found when studying this experimental configuration, could become important due to the shape of the microcrystals as compared to that of large single crystals. For the purpose of our experiments, the notch filter was set to a lower limit of about 200 cm$^{-1}$. Polarized spectra were measured in the HH (i.e., the incident and scattering radiation are parallel) and HV (i.e., the incident and scattering radiation are perpendicular) configurations. In order to avoid sample heating, a laser spot with 0.3 mW exciting power was used.

3. Results and discussion

The crystallinity and phase formation for our samples were studied using a Philips powder x-ray diffractometer operated in a $θ$–$2θ$ mode and equipped with Cu Kα radiation. A typical powder x-ray diffraction (XRD) pattern for a PNMO sample is presented in figure 1(a). It is characterized by a series of sharp peaks, revealing that the samples are polycrystalline in nature. These patterns are indexed on the basis of the monoclinic $P2_1/n$ symmetry [13]. The extracted lattice parameters are $a = 5.54$ Å, $b = 5.50$ Å, and $c = 7.70$ Å. These values are found to be close to the values reported in the literature [13]. Thus, XRD studies demonstrate that these samples are polycrystalline and possess a monoclinic symmetry.

A typical $M$–$H$ loop of a PNMO sample, measured at 10 K, is presented in figure 1(b). It shows that the PNMO sample is characterized by a well-defined hysteresis and a value of saturation magnetization as large as 4.95 $μ_B$/f.u. at 50 kOe field. This demonstrates that PNMO is ferromagnetic in nature. Although these samples show a coercivity of 450 Oe, the magnetic moments become fully saturated only for a large value of the applied magnetic field (5–10 kOe). This shows that parts of the magnetic domains are probably pinned due to the structural defects. In both ordered Ni$^{2+}$ ($d^8$; $t^2_2e_g^6$) and Mn$^{4+}$ ($d^3$; $t^2_2e_g^6$) and disordered low-spin Ni$^{3+}$ ($d^2$; $t^2_2e_g^6$) and high-spin Mn$^{3+}$ ($d^5$; $t^2_2e_g^6$) configurations, the theoretical value of the spin-only saturation magnetization is about 5 $μ_B$/f.u. [3, 6, 7]. This is very close to the observed value of the saturation magnetization for our PNMO samples. Thus relying on the measured value of the saturation magnetization, it remains difficult to determine the possible oxidation states of Ni/Mn in PNMO as was done for La$_3$CoMnO$_9$ (LCMO) [6, 7].
To get further insights, we measured the $M-T$ curve (see the inset of figure 1(b)). The $M-T$ data show that magnetization is independent of temperature at low temperature confirming that PNMO is ferromagnetic. They also show that the sample is characterized by a single ferromagnetic-to-paramagnetic magnetic transition around 228 K. Furthermore, no secondary magnetic transitions were observed in our samples at low temperature ($\sim 140$ K) as are often seen in the disordered LNMO and LCMO systems [6, 11, 12]. Thus, the absence of any additional magnetic transition at low temperature suggests that our PNMO samples are structurally ordered.

By drawing a parallel between LNMO and PNMO, the value of $FM-T_c$ at 228 K in PNMO can be assigned to the Ni$^{2+}$–O–Mn$^{4+}$ superexchange interaction modulated by relatively weak amplitude of the superexchange strength [3, 6, 7]. Within the 180$^\circ$ superexchange framework [7], the ferromagnetic transition temperature is determined by the magnitude of the spin-transfer integral that is governed by the overlap of the Ni/Mn–O wavefunctions. In other words, it is controlled by the Ni–O–Mn bond length and bond angle. Its amplitude decreases exponentially with increase in the bond length. In polycrystalline samples [13], the average Ni–O and Mn–O bond lengths in LNMO are 2.02 Å and 1.917 Å respectively, and the average Ni–O–Mn bond angle is 160.4°. In contrast, the average Ni–O and Mn–O bond lengths in PNMO are 2.029 Å and 1.928 Å respectively, and the average Ni–O–Mn bond angle is 158.6°. This relative enhancement in the total bond length of Ni–O–Mn and the decrease in the Ni–O–Mn average bond angle reduce the effective overlap of the Ni/Mn–O electronic wavefunctions leading to a net decrease in the amplitude of the spin-transfer integral. Consequently, compared to that for LNMO, a lower magnetic transition temperature is expected for PNMO, as observed.

Raman spectroscopy is a sensitive technique for studying the spin–phonon coupling in strongly correlated oxides [14–20]. It has indeed been successfully used to study the phonon behaviors and spin–phonon coupling in a variety of perovskite oxide materials [14–20], including double perovskites (e.g., LNMO and LCMO) [9, 10]. The Raman spectra at room temperature of PNMO microcrystals in the HH and HV polarization configurations are shown in figure 2(a). For comparison, the Raman spectra of LNMO, measured in the same configurations, are also presented in figure 2(b). It is important to note that the two oxides exhibit similar Raman spectra. Two sharp phonon excitations in both polarization configurations are observed and the relative intensity of these phonon excitations depends on the polarization configurations. Despite these global similarities, the phonon features significantly differ from each other. For PNMO, these excitations are observed at 657 and 511 cm$^{-1}$ in the HH configuration, and at 642 and 511 cm$^{-1}$ in the HV configuration. For LNMO, these excitations appear at 671 and 530 cm$^{-1}$ for the HH configuration and at 668 and 530 cm$^{-1}$ for the HV configuration. Since LNMO, LCMO and PNMO have identical crystal structures, we use the LNMO and LCMO theoretical group analysis of Iliev et al [10] to interpret the observed phonon excitations in PNMO samples. The observed phonon modes at 657 and 511 cm$^{-1}$ can be associated with the stretching and antistretching vibrations of the (Ni/Mn)O$_6$ octahedra respectively.

In order to study the impact of temperature on the phonon behavior of PNMO, we measured the Raman spectra of our samples down to 10 K. The phonon spectra are presented in figure 3. For the sake of comparison with LNMO and LCMO, we focus our current study on strong intensity phonons of PNMO that are affected by the spin–phonon coupling. These data show that the intensity of the phonon excitations increases significantly while their linewidth decreases as we progressively cool the samples. This reflects the reduced phonon scattering at low temperature and enhanced Raman tensors possibly due to reinforced orbital polarization. Also, the frequency of these phonons shows clear temperature dependence. There are two important sources for the origin of this temperature dependence: (i) anharmonicity [14], and (ii) spin–phonon coupling [15]. Anharmonicity effects are reproduced by the following relation: $\omega(T) = \omega_0 - C[1 + 2/(\bar{\omega}^{\text{ph}}(0)/kT - 1)]$ [14]. Here $\omega_0$ and $C$ are adjustable parameters. Usually, as one cools the sample, the phonon frequencies harden and approach a plateau at low temperature. As one may note, both stretching and antistretching modes (figure 4) display a hardening down to 100 K. This illustrates that anharmonic effects are among the dominant contributions in the observed temperature dependence of PNMO’s phonon modes.

Within the mean-field approximation, the onset of long-range magnetic order induces a renormalization of the phonon frequency $\delta\omega_{\text{sp}}(T)$ [15] proportional to $(M(T)/M_0)^2$, where $M(T)$ is the magnetization at temperature $T$ and $M_0$ is
Figure 3. Raman spectra of PNMO at various temperatures measured in (a) the HH and (b) the HV configurations. The dotted line in (a) is a guide to the eye. Spectra are shifted vertically for clarity.

Figure 4. Temperature dependence shift in the Raman modes at (a) 657 cm\(^{-1}\) and (b) 511 cm\(^{-1}\). The solid red lines are fits to the anharmonic phonon effects (see the text).

the magnetization at 0 K. The relative shift in the temperature dependence of the symmetric excitation mode at 657 cm\(^{-1}\) in the HH configuration is shown in figure 3(a). In contrast to the case for LNMO and LCMO, the onset of its softening is roughly at 100 K, which is far below PNMO's ferromagnetic-to-paramagnetic transition point at 228 K. Moreover it is small, \(\sim 1.5\) cm\(^{-1}\), in comparison to the values for the corresponding modes in LNMO and LCMO, which can be as large as 7 cm\(^{-1}\) from the ferromagnetic transition down to low temperatures (\(\sim 10\) K) [9, 10]. Our experimental study reveals that the strength of the spin–phonon coupling in PNMO is weaker than those in LNMO and LCMO. This suggests that in PNMO the force constants are less influenced by the modulation of the exchange interaction between Ni/Mn and O ions [20]. Nevertheless, our study shows a significant impact of the size of the rare earth cation on the spin–phonon coupling and phonon behavior of RNMO, likely via a change in the Ni–O–Mn bond length and angle [20]. Studying the temperature dependence of the structural properties is warranted, to understand the origin of this relatively weak spin–phonon coupling in PNMO.

4. Summary

In summary, we have studied the temperature dependence of the phonon behaviors and the spin–phonon coupling of ferromagnetic PNMO. By comparing our results with related literature ones for LNMO, we found that it possesses a weak spin–phonon coupling and that the properties of RNMO double perovskites are strongly influenced by the type of the rare earth cations inserted in the crystal structure.

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