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Changzhao Chen, Qian Wang, Haiping Chen, Yiming Cao, and Zhe Li
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Changzhao Chen, Qian Wang, Haiping Chen, Yiming Cao, and Zhe Li

AFFILIATIONS
1 School of Mechanics and Optoelectronic Physics, Anhui University of Science and Technology, Huainan 232001, China
2 Center for Magnetic Materials and Devices, Qujing Normal University, Qujing 655011, China

ABSTRACT
It is an important task of single crystal Raman spectroscopy to identify the lattice vibration modes in terms of symmetry and further study the temperature-dependent behavior of various Raman modes. A$_4$B$_2$O$_9$ ($A = $ Co, Mn, Fe; $B = $ Nb, Ta) type magnetodielectric or magnetoelectric materials represented by Mn$_4$Nb$_2$O$_9$ not only have high structural anisotropy, but also have strong electron-phonon or spin-phonon coupling, which is very meaningful for the Raman scattering study. Here, we conduct the first investigation of the angle and temperature-dependent Raman scattering behaviors in highly crystalline Mn$_4$Nb$_2$O$_9$ crystals with perfect a-cut. Polarization experiments show that most of the Raman peaks can be clearly identified as $A_{1g}$ and $E_g$ vibration modes, showing a clear anisotropic structure. As the temperature increases from 83 K to 283 K, the Raman shifts of most Raman peaks of Mn$_4$Nb$_2$O$_9$ exhibit a linear softening behavior with the temperature coefficient in the range of $-0.010$ cm$^{-1}$ K$^{-1}$ to $-0.015$ cm$^{-1}$ K$^{-1}$. No remarkable change of Raman shifts occurs at antiferromagnetic (AFM) transition nearby, indicating that the change of the ion position in the AFM transition has little effect on its Raman scattering behavior.

I. INTRODUCTION
Recently, the huge magnetodielectric (MD) and magnetoelectric (ME) effects exhibited by the A$_4$B$_2$O$_9$ ($A = $ Co, Mn, Fe; $B = $ Nb, Ta) type compounds have attracted widespread attention, stemming from the interesting physical background (BG) behind the phenomenon and broad application prospects, such as multistate memories, sensors, spintronic devices, capacitive resonator, and so on.$^{1-9}$ Among them, Mn$_4$Nb$_2$O$_9$ was first prepared and studied by Bertaut et al.$^9$ Its crystal structure is derived from corundum $\alpha$-phase Al$_2$O$_3$, belonging to the trigonal system and space group $P3c1$ based on X-ray diffraction studies. The unit cell of Mn$_4$Nb$_2$O$_9$ contains two formula units, with the Mn and Nb ions distributed in the ratio of 2:1 at the Al site and the Mn ions occupying two nonequivalent crystal lattices, i.e., Mn1 (0.333, 0.6666, 0.019) and Mn2 (0.333, 0.6666, 0.3034) [see Fig. 1(a)]. Magnetic structure measurements show that Mn$_4$Nb$_2$O$_9$ is a collinear antiferromagnet with a Neel temperature of 110–130 K, and Mn magnetic moments are parallel to the c-axis, forming ferromagnetic chains along (1/3, 2z/3) (spin up) and (2/3, z/3) (spin down) lines with interchain antiferromagnetic (AFM) coupling.$^{9,10}$ The chemical unit cell and magnetic unit cell are identical, and a linear ME effect is expected, which was first confirmed by Fischer et al.$^9$ Furthermore, Fang et al.$^{11}$ demonstrated the MD effect and magnetic-induced electric polarization in polycrystalline Mn$_4$Nb$_2$O$_9$, whereas in our earlier work no signs of ME coupling was observed in Mn$_4$Nb$_2$O$_9$ single crystal under applied electric field except for a small amount of magnetostriction.$^1$ This discrepancy provides a strong interest in deepening the knowledge of their fundamental properties, including their structural and vibrational characteristics.

In fact, the magnetic, electrical, and elastic properties of materials are closely related to their structures; therefore, clarifying the relationships between crystal structures and lattice vibrations is of great significance. Unfortunately, the available information on
FIG. 1. (a) Crystal structure of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) with side view and (b) a view. (c) XRD \( \theta-2\theta \) diffraction pattern of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single crystal and the (100) rocking curve shown in the inset with a Gaussian fit for the evaluation of FWHM.

structural properties in such a system is limited to experimental XRD investigations, and solid knowledge of the relations between structural distortions and phonon modes, and on a proper band assignment of vibrational modes in terms of symmetry and atomic displacement patterns has not been reported yet. However, to better understand the basic properties of the phonon spectrum and perform an assignment of the observed lines to specific lattice eigenmodes, it is important to perform a set of polarization measurements with varied incident and scattered light polarizations on the high quality crystal faces. Obtaining high-quality \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single crystals and performing precisely directional cutting is a prerequisite for conducting polarization Raman measurements, as any small deviation in the direction of the cut may result in errors in the phonon mode assignment.

In addition to its importance in the normal modes assignment of nonmetallic compounds, the Raman-scattering technique can also be used to detect any phonon-assisted phenomena such as structural transitions involving phonon softening or spin-phonon coupling, spin density wave orders, charge density wave orders, etc.\(^{13-15}\) In general, local changes in the bond length and bond angles across magnetic/structural/ferroelectric transitions manifest themselves as changes in phonon wavenumbers. Khanh et al.\(^ {16} \) have recently observed an anisotropic magnetic-dielectric coupling phenomenon in \( \text{Co}_2\text{Nb}_2\text{O}_9 \) single crystals, which was interpreted as the change of the force constant caused by lattice distortion. It was suggested to perform temperature-dependent Raman scattering to measure possible frequency shifts of optical phonon modes near the Neel temperature. We note that the Neel temperature of the present \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single crystal is about 110 K, which provides a suitable temperature window (77 K–room temperature) for conducting variable temperature Raman measurements under experimental conditions. Whether the antiferromagnetic phase transition is accompanied by structural phase transition is very worthwhile to carry out the study of the variable temperature Raman measurement.

In this paper, the angle and temperature dependent Raman measurements are carried out on the \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single crystals with precise \( a \)-cut. The changes in intensities of various Raman vibration modes with the rotation angle \( \theta \) are systematically studied under both parallel and vertical polarizations to determine the properties of each vibration mode combined with the group theory analysis of crystal symmetry. The variable temperature Raman measurements are used to observe the variation of the parameters of important Raman peaks with temperature, focusing on the intrinsic correlation between temperature-dependent lattice vibration and ion position changes, and detecting possible structural phase transitions driven by magnetic phase transitions. The current research not only fills in the blank of Raman spectroscopy of the \( A_4B_2O_9 \) type compounds, but also has important value for revealing the structural properties associated with mode symmetry and softening in such materials.

II. EXPERIMENTAL

\( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single-crystal samples were prepared by the optical floating-zone method based on a one-step method.\(^ {7} \) The orientation of the crystal was determined using a back-reflection Laue X-ray camera, and the crystal was \( a \)-cut using a low-speed diamond cutting machine.

The phase purity and crystallinity of the \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) single-crystal were checked by conventional X-ray \( \theta-2\theta \) scans, and the crystalline quality was further tested by (100) rocking curves using \( \text{Cu-K}_\alpha \) radiation (\( \lambda = 0.15406 \) nm). X-ray photoelectron spectroscopy (XPS) was used to determine the valence and composition of the...
elements on an ESCALAB 250 Xi spectrometer with the micro-focused Al Kα radiation (1486.6 eV) of 150 W power. The combined energy scale was referenced to the C1s peak at 284.8 eV to correct the charging effect. In polarized Raman measurements, a 532 nm excitation laser was focused on a single crystal surface with a 50× objective lens, and backscattered light was collected using a laser power of less than 3 mW and a spot size of about 2.5 μm. The backscattered light was dispersed by 1200 grooves/mm diffraction gratings on a Horiba Xplora Raman spectrometer. To show the effect of temperature on lattice vibration, a small variation in the Raman shift was captured using a Horiba high-resolution (HR) Evolution Raman spectrometer (2400 grooves/mm grating).

III. RESULTS AND DISCUSSION

Figure 1(c) shows the XRD θ-2θ patterns recorded on a-cut slices, which have been identified by using back-reflection Laue photography. Within the range of 10°–80° of 2θ, three sharp reflection peaks can be easily identified as reflections from the (100) (l = 1, 2, 3) diffraction planes. No impurity phase is detected, and no reflections from other diffractive planes indicate that the current single crystal sample not only has a very high phase purity and good crystallinity, but also has a perfect cut with the cutting surface being exactly perpendicular to the a-axis of the crystal [see Fig. 1(b)]. As an important index for evaluating the crystal quality of single crystals, the full width at half maximum (FWHM) of the X-ray rocking curve has been widely adopted. As shown from the inset of Fig. 1(c), the high resolution X-ray rocking curve measurement of the crystal shows a strong peak corresponding to the (100) diffraction peak in the 2θ scan mode. The FWHM of the peak is only 0.068°, further indicating that the grown Mn$_2$Nb$_2$O$_9$ is a single crystal having a high crystal quality.

Figures 2(a) and 2(b) show the typical high resolution Mn 2p and Nb 3d core level XPS spectra of the Mn$_2$Nb$_2$O$_9$ sample, respectively. The C 1s peak with a binding energy of 284.8 eV from adventitious hydrocarbon contamination on the sample surface is calibrated as the reference. The Mn 2p$_{3/2}$ and 2p$_{1/2}$ spectra of the sample contain a single peak centered at a binding energy of 641.2 eV and 653.2 eV with spin-orbit separation of 12 eV. The peak position and difference indicate the +2 valence state of Mn ions. The observation of satellite peaks for the Mn 2p$_{3/2}$ and 2p$_{1/2}$ above the main peak at about 5 eV further indicates the existence of Mn$^{2+}$ states in the present sample. In Fig. 2(b), the binding energy of Nb 3d$_{5/2}$ and 3d$_{3/2}$ peaks with spin-orbit separation of 2.7 eV is located at 206.5 eV and 209.2 eV, respectively, meaning Nb ions are in the +5 oxidation state in the sample. The relative ratio of atomic concentrations of Mn and Nb is about 1.78:1, which is determined from the appropriate core level integrated peak areas and sensitivity factors after subtracting the Shirley background. It is worth mentioning that the stoichiometric ratio of Mn:Nb on the surface of the Mn$_2$Nb$_2$O$_9$ sample deviates from the nominal value of 2:1, which may have an important influence on the magnetic phase transition and the magnetic ground state of the compound. We note that the current antiferromagnetic transition temperature of Mn$_2$Nb$_2$O$_9$ single crystal is about 110 K, which is significantly smaller than the values reported in the previous literature (about 125 K). This decrease in the antiferromagnetic transition temperature is likely to be related to the deviation of the Mn and Nb elements from the stoichiometric ratio.

Figure 3(a) shows a typical Raman spectrum obtained from the Mn$_2$Nb$_2$O$_9$ single crystal at room temperature in a nonpolarized scattering configuration, which exhibits very rich Raman peaks. There are a total of 17 considerable Raman peaks in the frequency range of 40–1800 cm$^{-1}$, and the two points marked “+” are superimposed peaks consisting of two peaks actually, which can be clearly identified in the polarized angle-dependent Raman measurement, as shown in Figs. 3(b) and 3(c). The specific configurations of polarized Raman measurements are shown in the inset of Fig. 3. To understand the change in Raman scattering intensity relative to the fixed polarization of the incident laser with the adjustment of orientation of the sample, we use a laboratory coordinate system in which the X-axis coincides with the a-axis of the crystal. The incident laser propagates along the X axis with polarization directing the Y axis and unchanged during the experiment. The starting direction of the sample is adjusted to regulate the polarization vector of the incident laser perpendicular to the c-axis of the sample, indicating that the initial angle $\theta$ (defined as the angle between the Z-axis and the...
on group theory. Mns, all possible phonon modes in the crystal are discussed based on group theory. Mns crystallizes in the trigonal structure with space group P3c1(3m1, No. 165), with two formula units and 30 atoms in the primitive cell, leading to three acoustic phonon and 57 optical phonon branches in the Brillouin zone center. According to the point group notation, all vibrational modes in the zone center can be described as: 6A1g, 9A2g, 9A2u, 12E1g, 18E2g, and 18E2u, in which only A1g and E2g modes are Raman active. Therefore, the total Raman peaks of the Mns crystal should be 18, very close to the number of Raman peaks observed experimentally.

The Raman scattering intensity is expressed as $I_s \propto \omega^4 |\mathbf{e}_i \cdot \mathbf{R} \cdot \mathbf{e}_s|^2$, where $\omega$ represents angular frequency of the scattered light. The three terms in the modulo reflect the relationship between incident polarization, reflection polarization, and crystal symmetry subject to the unit vectors of the incident ($\mathbf{e}_i$) and scattered light ($\mathbf{e}_s$) as well as the second-rank Raman tensor ($\mathbf{R}$). The zero elements in the $\mathbf{R}$ matrix are derived from group theory analysis, whereas the nonzero elements are determined experimentally. For the 3m1 point group,

$A_{1g} = \begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}$, $E_{1g} = \begin{pmatrix} c & 0 & 0 \\ 0 & -c & d \\ 0 & d & 0 \end{pmatrix}$, and $E_{2g} = \begin{pmatrix} 0 & -c & -d \\ -c & 0 & 0 \\ -d & 0 & 0 \end{pmatrix}$.

According to our laboratory frame, $\mathbf{R} \cdot \mathbf{e}_i$ can be expressed as follows:

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix}^{-1} \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos \theta & -\sin \theta \\ 0 & \sin \theta & \cos \theta \end{pmatrix},$$

where the intermediate $3 \times 3$ matrix corresponds to Raman tensors for $A_{1g}$ or $E_{2g}$ vibrational modes in the crystal coordinate system, and $\theta$ is the rotating angle. The Raman tensor elements in the laboratory frame can be given by

$$\alpha_{YY} = \alpha_{yy} \cos^2 \theta + \alpha_{yy} \sin 2\theta + \alpha_{ZZ} \sin^2 \theta,$$

$$\alpha_{YZ} = -\alpha_{yy} \sin \theta \cos \theta + \alpha_{zz} \sin \theta \cos \theta + \alpha_{yz} \cos 2\theta.$$

The intensity of the collected Raman peaks varies according to $I_s \propto |\alpha_{YY}|^2$ under parallel polarization geometry, whereas in the vertical scattering geometry, the intensity changes according to $I_s \propto |\alpha_{YY}|^2$. Table I lists the relationship between the intensity of the Raman peak and the rotating angle $\theta$ for $A_{1g}$, $E_{1g}$, and $E_{2g}$ Raman active patterns under parallel and vertical polarizations. The general characteristic of intensity variation with angle is that the $E_{2g}$ mode has zero intensity under both polarization states. As for $A_{1g}$ mode and $E_{1g}$ modes, angle-dependent oscillation with equal amplitude is exhibited under vertical polarization, and the period is $\pi/2$. Under parallel polarization, the oscillation is not necessarily equal to amplitude, and the period is either $\pi/2$ or $\pi$, depending

![FIG. 3. (a) Nonpolarization Raman spectrum of the Mns crystal in a semilog plot; the top left corner is the experimental setup for obtaining polarized Raman scattering signals. (b) and (c) are used to identify superimposed peaks near 170 cm$^{-1}$ and 600 cm$^{-1}$, respectively, and black solid lines indicate independent Raman scattering signals.](image-url)
TABLE I. Intensity variation rules from group theory and first-order temperature coefficient extracted from linear fitting for Mn$_4$Nb$_2$O$_9$ crystal.

| Raman mode | a cut | Experiment value (cm$^{-1}$) | $\chi$ (cm$^{-1}$ K$^{-1}$) |
|------------|-------|-----------------------------|---------------------------|
|            | V polarization |                                    |                           |
| $A_{1g}$   | $|a \cos^2 \theta + b \sin^2 \theta|^2$ | 168                         | -0.0142                   |
|            | $|(b-a) \sin \theta \cos \theta|^2$ | 403                         |                           |
| $E_{g1}$   | $|c \cos^2 \theta + d \sin 2\theta|^2$ | 540                         | -0.0113                   |
|            | $|c \cos \theta \sin \theta + d \cos 2\theta|^2$ | 607                         | -0.0072                   |
|            |                                                | 770                         |                           |
| $E_{g2}$   | 0                                              | 118                         | -0.0113                   |
| Unknown    | 66                                             | 127                         | -0.0072                   |
|            |                                               | 178                         |                           |
|            |                                               | 202                         |                           |
|            |                                               | 236                         | -0.0131                   |
|            |                                               | 256                         | -0.0111                   |
|            |                                               | 307                         | -0.0145                   |
|            |                                               | 323                         | -0.0144                   |
|            |                                               | 352                         | -0.0102                   |
|            |                                               | 593                         |                           |

FIG. 4. The evolution of Raman peak intensity by rotating the crystal from 0° to 360° in 20° steps, (a) and (b) vertical polarization, and (c) and (d) parallel polarization.
mainly on the relationship of nonzero elements in the Raman tensor element.

In order to validate our analysis, polarized Raman with \( X(YY)X \) and \( X(YZ)X \) configurations is performed on a single \( \text{Mn}_4\text{Nb}_2\text{O}_9 \). Figures 4(a)–4(d) show the Raman spectra corresponding to different rotation angles \( \theta \) under both the parallel and vertical polarizations with \( \theta \) varying from 0° to 360°, from which the intensity of each Raman peak as a function of angle under two polarizations can be obtained. Under the two polarizations, the angle dependences of the peak intensities are fitted by the formula shown in Table I. It is found that the Raman modes located at 168 cm\(^{-1}\), 403 cm\(^{-1}\), 540 cm\(^{-1}\), 607 cm\(^{-1}\), and 770 cm\(^{-1}\) are \( A_{1g} \) modes, whereas those positioned at 118 cm\(^{-1}\), 127 cm\(^{-1}\), 178 cm\(^{-1}\), 202 cm\(^{-1}\), 236 cm\(^{-1}\), 256 cm\(^{-1}\), 307 cm\(^{-1}\), 323 cm\(^{-1}\), 352 cm\(^{-1}\), and 593 cm\(^{-1}\) are attributed to the \( E_{g1} \) mode. The analysis process is stated as follows.

First, the angular oscillation of the \( E_{g1} \) mode takes two forms, as shown in Figures 5(a) and 5(b), respectively. In Fig. 5(a), the oscillations of peak intensities vs angle under both polarization directions are of equal amplitude with the oscillating periods of both \( \pi/2 \) and \( \pi \), and the two oscillations of the antiphase, meaning that the nonzero element \( c \) in the Raman tensor is much smaller than \( d \), so we get

\[
I_s(YY) \propto \sin^2 \theta \quad \text{and} \quad I_s(YZ) \propto \cos^2 \theta.
\]

The modes at positions 127 cm\(^{-1}\), 202 cm\(^{-1}\), 236 cm\(^{-1}\), and 256 cm\(^{-1}\) show the same oscillating behaviors as the mode at 307 cm\(^{-1}\), hence they have the same symmetry. In contrast, the angle-dependent evolution periods of scattering intensity of the remaining five \( E_{g1} \) modes at parallel and vertical polarization scattering configurations are \( \pi \) and \( \pi/2 \), respectively. As shown in Fig. 5(b), the peak intensity of angle-dependence of the 353 cm\(^{-1}\) Raman mode exhibits an “M” shape under parallel polarization with a period of \( \pi \), whereas the oscillation is equal-amplitude with a period of \( \pi/2 \) under vertical polarization. The data points in

![Reduced Raman peak intensity as a function of the rotating angle under parallel and vertical polarization scattering geometries for different Raman modes](image)
both cases can be fitted using the intensity formulas in Table I, and similar patterns are obtained at 118 cm$^{-1}$, 178 cm$^{-1}$, 323 cm$^{-1}$, and 593 cm$^{-1}$.

Second, under vertical polarization sinusoidal oscillations with a period of $\pi/2$ are observed in the following Raman modes such as 168 cm$^{-1}$, 403 cm$^{-1}$, 540 cm$^{-1}$, 607 cm$^{-1}$, and 770 cm$^{-1}$, which is in accordance with the formula $I_s \propto |(b - a) \sin \theta \cos \theta|^{2}$. However, the dependence of peak intensity vs angle under parallel polarization appears in three forms, which is represented by 540 cm$^{-1}$, 607 cm$^{-1}$, and 770 cm$^{-1}$, which can be fitted using the intensity formulas in Table I, and can be seen from Figs. 5(c)–5(e), respectively. The oscillation periods of the five modes under parallel polarization are all $\pi$, and can be well fitted by the formulas $I_s \propto |a \cos^{2} \theta + b \sin^{2} \theta|^{2}$ in Table I. Hence, they all belong to the A$_{1g}$ mode. This diverse intensity evolution vs angle should relate to the vibrational behavior of each mode. Therefore, the combination of group theory analysis and parallel and vertical Raman scattering experiments can identify vibrational modes of different Raman shifts of the present Mn$_4$Nb$_2$O$_9$ crystals.

Finally, it should be mentioned that among the 17 modes that can be observed experimentally, the attribution of two modes is not solved, including 66 cm$^{-1}$ and 434 cm$^{-1}$. The two modes have no obvious angular dependence under both polarizations, probably because the peak is too weak to exceed the instrument’s ability, or it may be due to other causes.

We further perform temperature-dependent Raman scattering to explore the effect of electron-phonon coupling on the lattice vibrational modes and detect possible structural transitions near $T_N$, which has been suggested by Khanh et al.\textsuperscript{15} Figure 6(a) shows the temperature-dependence of Raman spectra for Mn$_4$Nb$_2$O$_9$ crystal recorded at different temperatures from 83 K to 283 K with a temperature interval of 5 K near $T_N$ and 10 K at other places. Clear shifts toward lower wavenumbers of the dominant Raman modes are observed as the temperature is increased, as shown in Fig. 6(b). Under the first-order approximation, the temperature relationship of the Raman peak can be explained by the Grüneisen model\textsuperscript{15}

$$\omega(T) = \omega_0 + \chi T,$$

where $\chi$ is the first-order temperature coefficient, which can be obtained from the slope of the curve between the Raman mode position and temperature, and $\omega_0$ is the Raman peak position at 0 K.

Figure 7 shows the relative change in frequency of different Raman modes as a function of temperature, which is defined as $\Delta \omega = \omega(T) - \omega(83K) = \chi(T - 83)$. In most Raman modes, the peak position does show a linear law with temperature changes, and the temperature coefficient is basically between $-0.010$ cm$^{-1}$ K$^{-1}$ and $-0.015$ cm$^{-1}$ K$^{-1}$, as shown in Table I. The softening phenomenon exhibited by these Raman peaks with increasing temperature is generally attributed to the contribution of the inharmonic and thermal effects in the Mn$_4$Nb$_2$O$_9$ crystal.\textsuperscript{22-27} It is worth noting that the current softening effect is continuous. When the temperature crosses the Neel temperature $T_N$, the antiferromagnetic phase transition does not cause a significant change in the Raman peak position of the Mn$_4$Nb$_2$O$_9$ crystal. Therefore, we believe that the change in the ion position across the antiferromagnetic transition has a small effect on
the Raman scattering behavior of the obtained Mn$_2$Nb$_2$O$_9$ crystal. In addition, the peak positions of two Raman modes at 403 cm$^{-1}$ and 770 cm$^{-1}$, both of which are A$_{1g}$ attributes, do not change substantially with temperature, which means that the two vibrational modes are very robust against temperature. In particular, the mode located at 770 cm$^{-1}$ is not only strong against temperature, but also has the strongest intensity of all the Raman peaks, which is of value in the calibration of the position of Raman peaks.

IV. CONCLUSIONS

In summary, we report the first experimental investigations of the angle and temperature dependences of Raman scattering in Mn$_2$Nb$_2$O$_9$ crystals. Mn$_2$Nb$_2$O$_9$ crystals are synthesized by the optical floating-zone method, which has very high crystallinity and perfect a-cut. Polarized Raman scattering spectroscopy and group theory analysis are used to clearly distinguish the vibrational modes in terms of symmetry and atomic displacement patterns. The effect of AFM transition on the lattice vibrational behavior is investigated by temperature-dependent Raman spectra above and below the $T_N$ ($110$ K). The linearly softening phenomena in the Raman shifts vs temperature of most modes are found, which can be ascribed to the inharmonicity of the lattice. The Grüneisen model fits the data well and no anomalies are observed at the Neel temperature, which is consistent with the thermal effects of the crystal.

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