Spin-coupled phonons in multiferroic YbMnO$_3$ epitaxial films by Raman scattering

H Fukumura$^1$, N Hasuike$^1$, H Harima$^1$, K Kisoda$^2$, K Fukae$^3$, T Takahashi$^3$, T Yoshimura$^1$ and N Fujimura$^3$

$^1$ Department of Electronics, Kyoto Institute of Technology, Kyoto 606-8585, Japan
$^2$ Department of Physics, Wakayama University, Sakaedani, Wakayama 640-8510, Japan
$^3$ Department of Physics and Electronics, Osaka Prefecture University, Osaka 599-8531, Japan

E-mail: harima@kit.ac.jp

Abstract. YbMnO$_3$ epitaxial thin films were investigated by Raman scattering in the temperature range of 15-300K. We successfully observed some phonon modes ($5A_1+6E_2$) at 15K with mode assignment based on polarized Raman study. Furthermore, an $E_2$ mode at 253 cm$^{-1}$ which affected Mn-O-Mn bond angles showed anomalous temperature variation in frequency at temperature below ~80K. It suggested a spin-phonon coupling that occurred below $T_N$.

1. Introduction
Rare-earth and yttrium manganites, $R$MnO$_3$, crystallize in a hexagonal structure for small cations ($R=$Ho-Lu, or Y) with space group $P6_3cm$ [1, 2]. They show ferroelectricity and magnetic ordering simultaneously in the ordered phase, leading to a coupling effect called magnetoelectric effect: the onset of magnetic ordering can be controlled by electric field and vice versa. Such materials, called multiferroics, have high potential in opening a new field of innovative devices. The hexagonal YbMnO$_3$ also exhibits triangular antiferromagnetic ordering of Mn$^{3+}$ spins in the basal $ab$ plane and ferromagnetic ordering of Yb$^{3+}$ spins along the $c$ axis. These two spin systems are correlated and geometrically frustrated [3]. In investigating the mechanism, characterization of lattice properties coupled with magnetic ordering brings us rich information. Raman scattering is one of the powerful methods: lattice vibrations of Mn$^{3+}$ in the $ab$ plane coupled with magnetic ordering have been observed in HoMnO$_3$ and YMnO$_3$ [4, 5].

Phonon spectra of hexagonal YbMnO$_3$ have not been reported both on bulk and film samples. Here we observe Raman spectra of YbMnO$_3$ epitaxial thin films at 15-300K with phonon mode assignment. We found a clear evidence of spin-phonon coupling below $T_N$~80K.

2. Experiment
We prepared epitaxial thin YbMnO$_3$ films with thickness ~100 nm by pulsed laser deposition on a Pt (111)/sapphire (0001) substrate [6]. Figure 1 shows a typical x-ray diffraction pattern by $2\theta$ scan of the sample. It gives only sharp YbMnO$_3$ peaks in addition to Pt and Al$_2$O$_3$ substrate signals, showing that the sample includes no secondary phases and is highly oriented to the $c$ direction. Ferromagnetic and ferroelectric properties of this film are also confirmed by clear $M$-$H$ (below ~70K) and $P$-$E$ hysteresis loops, respectively [6, 7].
For the Raman scattering measurement at between 15 and 300 K, the sample was fixed to a cold finger of a closed-cycle He-gas cryostat. An Ar+ gas laser was used at 514.5 nm for excitation. It was focused by a lens at the sample surface, and the scattered light was observed in a quasi-back-scattering geometry by a double monochromator of focal length 85 cm (SPEX 1403). The Raman spectra were detected by a liquid-nitrogen-cooled charge-coupled-device (CCD) camera.

In the ferroelectric phase, a group theoretical analysis predicts 38 Raman active phonon modes at the Γ point in the Brillouin zone; \( \Gamma_{\text{Raman}} = 9A_1 + 14E_1 + 15E_2 \). When a polarized Raman spectrum is observed by back scattering from the \( c \) plane, we can detect the \( A_1 \) modes in parallel polarization and the \( E_2 \) modes by either parallel or crossed polarization, while the \( E_1 \) modes are not observed in this scattering geometry.

3. Results and Discussion

Figure 2 shows temperature variation of unpolarized Raman spectra for the YbMnO\(_3\) thin film sample at 15-300K. As the temperature is decreased from bottom to top, the phonon peaks become sharp and shift to higher frequency side. Absence of apparent or drastic spectral variation by structural phase transition indicates that the crystal structure of the sample remains in the hexagonal phase (\( \text{P}6_3\text{cm} \)) in this temperature range. Eleven phonon modes of YbMnO\(_3\) were clearly observed at 15K. These peaks were classified to \( A_1 \) and \( E_2 \) modes by polarization measurement as shown in the inset: the \( A_1 \) and \( E_2 \) modes were both observed by parallel polarization (upper), while only the \( E_2 \) modes were observed by crossed polarization (lower). Concerning the small number of phonons observed (=11) compared to that expected (24=9\( A_1 \)+15\( E_2 \)), we have to consider unresolved peaks as well as those lying in the lower frequency region if we refer to a calculation on isomorphic systems, HoMnO\(_3\) and YMnO\(_3\) [4, 8].

By careful observation, we find in Figure 2 peculiar temperature variation in some peak frequencies. The \( E_2 \) mode at 253 cm\(^{-1}\) (at 15K) is a representative case. Figure 3 (a) shows the variation in detail, where the peak positions determined by a curve fitting procedure are denoted by dots. As plotted in Fig.3 (b), the peak shows abrupt frequency variation at around 80K. Here, the dashed curves show theoretical fits to the data by a conventional formula for phonon frequency variation with temperature. The formula was derived by considering anharmonic phonon coupling terms up to four phonons [9],

\[
\omega(T) = \omega_0 + A \left[ 1 + \frac{2}{e^{x} - 1}\right] + B \left[ 1 + \frac{3}{e^{y} - 1} + \frac{3}{(e^{y} - 1)^2}\right]
\]

(1)
Here, \( x = \frac{\hbar \omega_0}{2kT} \), \( y = \frac{\hbar \omega_0}{3kT} \) with \( kT \) being the thermal energy, and \( A \), \( B \) and \( \omega_0 \) are fitting parameters. The observed anomalous variation at \(~80K\) cannot be fitted well by a single theoretical curve. Similar anomalies have been observed in isomorphic HoMnO\(_3\) and YMnO\(_3\) [4, 5]. The \( E_2 \) mode at 253 cm\(^{-1}\) corresponds to a displacement of Mn and O ions in the \( ab \) plane (see the inset of Figure 3) [4, 8]. This mode effectively affects Mn-O-Mn bond angles and, hence, the Mn-Mn exchange interaction. Therefore, this anomalous behavior at \(~80K\) suggests an onset of spin-phonon coupling in the magnetically ordered phase.

This is supported by the following experiments: Katsufuji \textit{et al.} measured magnetic susceptibility of a YbMnO\(_3\) bulk single crystal and found a pronounced anisotropy between \( \chi_c(T) \) sharply peaked at \( T_N=82K \) and \( \chi_{ab}(T) \) with no such clear anomalies [10]. Fiebig \textit{et al.} also revealed from optical second harmonic generation (SHG) experiment that Mn\(^{3+}\) moments ordered antiferromagnetically in the \( ab \) plane (\( B_2 \) type) at \( T_N \sim 80K [3] \). Although the magnetic structure of Mn\(^{3+}\) spin is not clarified by the present Raman experiment, we have seen clearly that the onset of its magnetic ordering can be sensitively probed from a lattice vibration of Mn\(^{3+}\) ions in the \( ab \) plane.
Figure 3. Temperature variation of E$_2$ phonon at ~253 cm$^{-1}$ in YbMnO$_3$ thin film. The dots in raw spectra (a) show peak positions determined by curve fitting. The fitting uncertainty is given almost by the dot diameters. Dashed curves in the peak-frequency plot (b) show theoretical fits to the data by considering anharmonic coupling effects up to four phonons. The inset shows ion displacements for the E$_2$ phonon mode [4].

4. Conclusion

We investigated hexagonal YbMnO$_3$ epitaxial films by Raman scattering in the temperature range of 15-300K. Many phonon peaks were successfully observed and classified to A$_1$ and E$_2$ modes by polarized measurement. As represented by an E$_2$ phonon mode, anomalous temperature variation of phonon frequency was observed at ~80K. It suggested a spin-phonon coupling that occurred below a critical temperature of $T_N$~80K.

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