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2010 J. Phys.: Conf. Ser. 215 012030

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## Modifications of $\text{MnO}_6$ Octahedra in $\text{DyMnO}_3$ under High Pressure

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**Abstract.** Local geometry and electronic states of octahedrally coordinated Mn ions in orthorhombic  $\text{DyMnO}_3$  have been studied by partial-fluorescence-yield spin-selective x-ray absorption spectroscopy and *in-situ* Raman scattering. As evidenced in absorption near-edge structure and Raman spectra, the external pressure alleviates the  $\text{MnO}_6$  octahedral distortion and Jahn-Teller effect with enhanced octahedral tilt.

### 1. Introduction

Recently, dependence of external pressure on perovskite manganites  $\text{RMnO}_3$  with larger rare-earth ions ( $\text{R}=\text{La}$ ,  $\text{Pr}$  and  $\text{Nd}$ ) and their derivatives has been investigated in detail by using diffraction, a diverse array of spectroscopic methods, and electrical resistivity measurements. Loa *et al.* observed an insulator-metal (IM) transition in  $\text{LaMnO}_3$  at 32GPa and room temperature [1], ushering in contention and theoretical studies on the transition mechanism [2]. Additionally, Martín-Carrón *et al.* unveiled a significantly different pressure dependence of orthorhombic  $\text{PrMnO}_3$  and  $\text{TbMnO}_3$  by using Raman scattering up to 10GPa [3]. In contrast to the conventionally popular  $\text{LaMnO}_3$ , however, study on highly-distorted systems was still limited. Here we report the effect of pressure on the vibration modes and electronic structures of  $\text{DyMnO}_3$ , an end-member of orthorhombic  $\text{RMnO}_3$ , up to ~30GPa at room temperature by two local-sensitive probes -- Raman scattering and lifetime-broadening-suppressed spin-selective x-ray absorption near-edge structure (SSXANES) [4]. As a member of recently discovered “multiferroic” magnetoelectric (ME) materials,  $\text{DyMnO}_3$  shows a lattice modulation at  $T_N\sim 39\text{K}$  and strong and direct coupling between electric and magnetic polarizations [5]. In analogy to the internal chemical-induced distortion, we investigated the external pressure effect on modifications of local structure. Our data indicate that the  $\text{MnO}_6$  distortion and Jahn-Teller distortion (JTD) in  $\text{DyMnO}_3$  are continuously reduced as an external pressure being applied.

## 2. Experimental

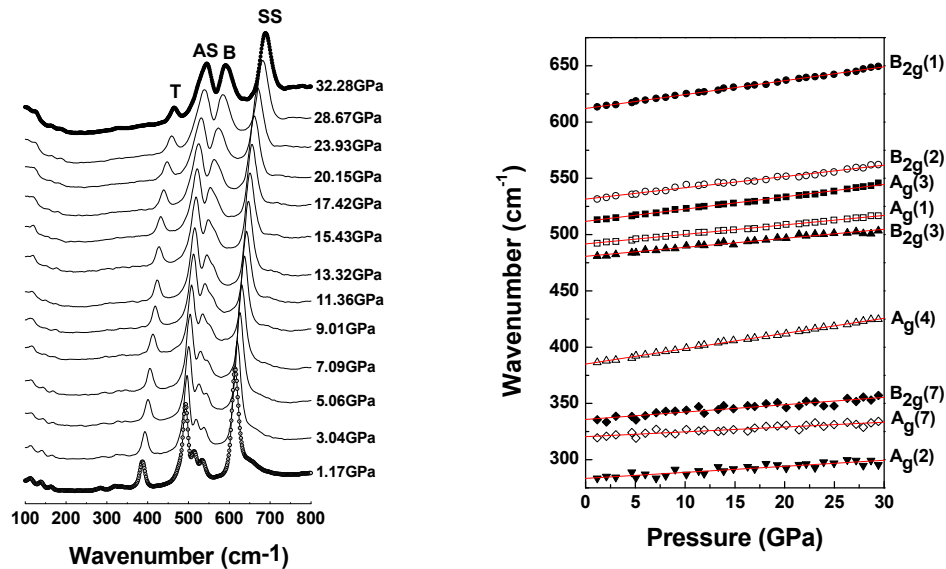
Polycrystalline  $\text{DyMnO}_3$  was synthesized by using conventional citrate-gel process and finely examined by synchrotron x-ray powder diffraction and structural refinement before subsequent high pressure experiments. The high pressure Raman analysis was carried out by using a Bassett-type diamond anvil cell (DAC) with a  $550\mu\text{m}$  culet size. The as-grown  $\text{DyMnO}_3$  powder, ruby spheres (pressure indicator), and 4:1 methanol/ethanol solution (pressure transmitting medium) were sealed into the  $235\mu\text{m}$ -diameter sample chamber of a 301 stainless steel gasket. Samples were exposed to the 514.5nm line of the *Coherent Innova 90 Ar-ion* laser, and all the Raman spectra were recorded in a back-scattering geometry using a *TRIAX 550* micro-Raman system. An *OLYMPUS 20X* microscope was used to focus the incident and back-scattered beams, and a *JOBIN-YVON SPEX SPECTRUM One* liquid-nitrogen-cooled charge-coupled device (CCD) detector was used to accumulate signals. Furthermore, a notch filter was used to suppress the elastic scattered light. We use an appropriate excitation power to avoid local heating and photo-induced degradation of our sample. The frequency and profile of each Raman peak were obtained using Gaussian curve fitting after best background subtraction and amplitude normalization. The Mn-K spin-selective x-ray absorption measurements were performed at the BL 12XU Taiwan inelastic x-ray scattering (IXS) beamline in SPring-8, Japan [6]. The procedures and details were described elsewhere [7].

## 3. Results and Discussion

Generally in an  $\text{ABO}_3$  perovskite structure, the low-wavenumber region below  $200\text{cm}^{-1}$  can be related to vibrations involving the A-site cations; in the higher-wavenumber region above  $350\text{cm}^{-1}$ , the vibration modes come primarily from vibrations of  $\text{O}^{2-}$  anions, involving the B-O bonds in breathing and bending of  $\text{BO}_6$  octahedra. Although B-site cation does not participate in any Raman active mode, we still can find indirect information about the variations of local geometry. Taking the mirror plane perpendicular to the c-axis, there are 24 ( $7A_g+5B_{1g}+7B_{2g}+5B_{3g}$ ) allowed modes in orthorhombic  $\text{RMnO}_3$  compounds (symmetry group *Pbnm*) [8][9]. Due to the compressed cell volume and the “hardening” atomic interactions, as shown in figure 1, all the Raman active modes monotonically shift to higher frequencies as the pressure increases. As, shown in table 1, the relative changes in the frequencies  $\beta$  of  $A_g(3)$  (bending) and  $A_g(4)$  (tilt) modes are both greater than those of the stretching (symmetrical and antisymmetrical) ones. Since the stretching modes are directly related to the force constants of Mn-O bonds, which are determined by the interatomic distances, yet the bending modes involve not only the Mn-O-Mn angle bending but also the R-O1 bonds stretching. This indicates that the compressibility of Dy-O bonds is greater than that of Mn-O bonds and therefore the Mn-O-Mn tilt angle is believed to be increased with pressure [3]. Furthermore, the relative changes of intensities of  $A_g(3)$  and  $A_g(1)$  modes infers that the external pressure would enhance the octahedral tilt but diminishes the cooperative JTD in such a highly distorted structure of  $\text{DyMnO}_3$ .

Figure 2 displays the Mn-K SXXANES spectra, which were collected in partial-fluorescence-yield with the spectrometer energy fixed at the maximum of Mn- $K_{\beta 1,3}$  emission line, of  $\text{DyMnO}_3$  under pressures. As noted, the spectral shapes of Mn-K SXXANES spectra of  $\text{DyMnO}_3$  under pressures are similar, consisting of a couple of pre-edge peaks and an intense main resonance at the edge. The pre-edge peaks “P” can be assigned to transitions from 1s to 3d empty states. These forbidden transitions become allowed since the Mn 3d orbitals indirectly hybridize with the 4p ones of neighboring Mn through intervening O 2p orbitals [10][11]. Next, the white-line peak “B” and the bulge region “C” between 6560~6580eV, which can be separately related to the 1s-4d transition and the result of multiple scattering between the ejected photoelectron and surrounding oxygen atoms, are both sensitive to the modifications of local geometry of the  $\text{MnO}_6$  octahedra, making them appropriate for elucidating the effects of temperature, chemical doping and external pressure on local lattice and electronic structures. When a hydrostatic pressure is applied, the absorption threshold “A” progressively shifts towards higher energy with enhancement of regions B and C. Given that the Mn valence remains unchanged, the edge shift can be ascribed to modifications in the Mn-O bond lengths of the nearest coordination shell [12]. On the other hand, as the gradually suppressed shoulder of

white line peak suggests, the splitting of main resonance from bonding anisotropy is getting reduced; the longer Mn-O2 bond, projected predominantly along the b-axis, greatly decreases its length, becoming closer to the shorter one projected predominantly along the a-axis [7]. Finally, the decrease of equatorial Mn-O2 distance and Mn-O2-Mn tilt angle (the “averaged” Mn-O-Mn tilt angle is increased) under pressure is expected to broaden the bandwidths of O-2p and Mn- $e_g \uparrow$  states [13], as indicated by shift of pre-edge peaks towards the Fermi level, and then enhance the metal (Mn)-ligand (O) hybridization.



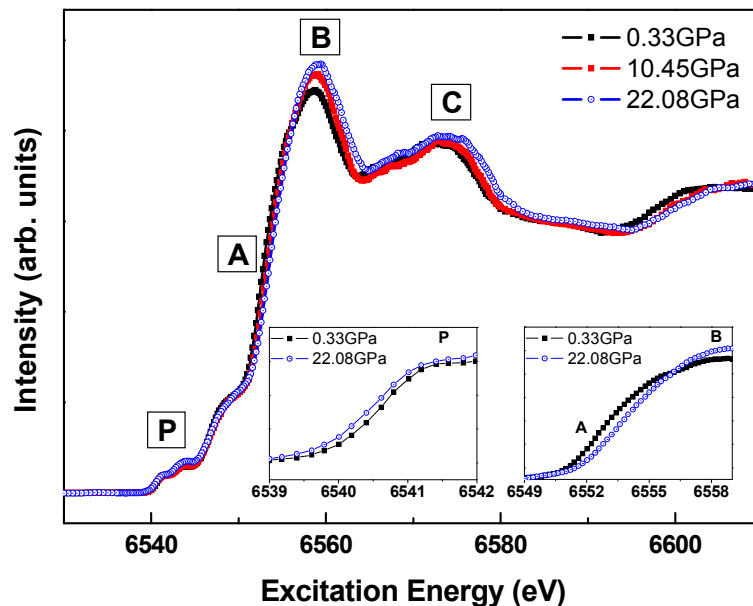
**Figure 1.** Raman spectra of DyMnO<sub>3</sub> as a function of pressure up to 30GPa (SS: symmetrical stretching; B: bending; AS: antisymmetrical stretching; T: tilt). The red linear-fitted lines are presented as a guide to the eye.

**Table 1.** Relative shifts  $\beta$  of selected Raman active modes for orthorhombic DyMnO<sub>3</sub>. The ambient-pressure frequencies  $\omega_{01}$  and  $\omega_{02}$  are from the results of linear-fitting in Fig. 1 and Ref. 8, respectively.

Mode	Main Atomic Motion	$\omega_{01}$	$\omega_{02}$	$\beta * 10^3$
B <sub>2g</sub> (1)	Symmetrical Stretching	611.7	613.5	2.08
A <sub>g</sub> (3)	MnO <sub>6</sub> Bending	510.4	513.4	2.35
A <sub>g</sub> (1)	Antisymmetrical Stretching	491.4	492.1	1.78
A <sub>g</sub> (4)	MnO <sub>6</sub> Rotation (Tilt)	384.9	386.0	3.57

#### 4. Conclusions

In summary, the variations of phonon modes and local structures of Mn in compressed orthorhombic DyMnO<sub>3</sub> were probed, respectively, by using *in-situ* Raman and Mn-K SXXANES spectroscopies at room temperature. The modifications in both kinds of spectral features suggest that the external pressure would alleviate the distortion of MnO<sub>6</sub> octahedra and concomitant Jahn-Teller effect. Further experimental and theoretical studies are under progress.



**Figure 2.** Selected Mn-K SSEXANES spectra of DyMnO<sub>3</sub> under pressures. The left and right insets are magnifications of pre-edge peaks and absorption threshold, respectively.

### Acknowledgements

We thank I. Jarriage (JAEA), Y. Cai (NSLS II) and C. C. Chen for their help during the experiments at the Taiwan beamline of SPring-8. This work is supported by the National Science Council of the Republic of China under grant No. 96-2113-M-213-007-MY3.

### References

- [1] Loa I, Adler P, Grzechnik A, Syassen K, Schwarz U, Hanfland M, Rozenberg G K, Gorodetsky P, and Pasternak M P 2001 *Phys. Rev. Lett.* **87** 125501
- [2] Fuhr J D, Avignon M, and Alascio B 2008 *Phys. Rev. Lett.* **100** 216402
- [3] Martin-Carron L, Sanchez-Benitez J, and Andres A 2003 *J. Solid State Chem.* **171** 313
- [4] de Groot F 2001 *Chem. Rev.* **101** 1779
- [5] Goto T, Kimura T, Lawes G, Ramirez A P, and Tokura Y 2004 *Phys. Rev. Lett.* **92** 257201
- [6] Cai Y Q, Chow P, Chen C C, Ishii H, Tsang K L, Kao C C, Liang K S, and Chen C T 2004 *AIP Conf. Proc.* **705** 340
- [7] Chen J M, Chou T L, Lee J M, Chen S A, Chan T S, Chen C K, Lu K T, Sheu H S, Lin C M, Hiraoka N, Ishii H, Yang T J 2009 *Phys. Rev. B* **79** 165110
- [8] Kreisel J and Bouvier P 2003 *J. Raman Spectroscopy* **34** 524
- [9] Iliev M N, Abrashev M V, Laverdiere J, Jandl S, Gospodinov M M, Wang Y Q, and Sun Y Y 2006 *Phys. Rev. B* **73** 064302
- [10] Elfimov I S, Anisimov V I, and Sawatzky G S 1999 *Phys. Rev. Lett.* **82**, 4264
- [11] Chen J M, Lee J M, Chen C K, Chou T L, Lu K T, Haw S C, Liang K S, Chen C T, Jeng H T, Huang S W, Yang T J, Shen C C, Liu R S, Lin J Y, and Hu Z 2009 *Appl. Phys. Lett.* **94** 044105
- [12] Ramos A Y, Tolentino H C N, Souza-Neto N M, Itié J-P, Morales L, and Caneiro A 2007 *Phys. Rev. B* **75** 052103
- [13] Cui C and Tyson T A 2004 *Appl. Phys. Lett.* **84**, 942