I. INTRODUCTION

Perovskite manganites $\text{RMnO}_3$ and hole-doped manganites of composition $\text{R}_1-x\text{A}_x\text{MnO}_3$ (rare-earth ions $\text{R}$ and alkaline-earth ions $\text{A}$) exhibit fascinating physical properties, such as charge and orbital ordering, 1-3 metal-insulator transitions, 4 colossal magnetoresistance, 5-9 half-metallic behavior, 10,11 percolative phase separation, 12-16 and multiferroicity. 17-24 In many such phenomena, the electronic properties are related intimately to the crystal lattice, through a complicated interplay between the crystal lattice, spin, charge, and orbital degrees of freedom. 25-29 In particular, magnetoelastics, in which magnetism and ferroelectricity coexist and are mutually coupled have attracted renewed attention because of both their intrinsic scientific interest and prospective applications in novel magnetoelastic and magneto-optical devices. The magnetoelastic effect signifies an electric polarization generated with a magnetic field or a magnetization generated with an electric field in a material. Multiferroicity has been observed in such manganites as $\text{ TbMnO}_3$, $\text{ DyMnO}_3$, and $\text{ TbMn}_2\text{O}_5$. 17-19

Figure 1 shows the crystal structure of orthorhombic $\text{ DyMnO}_3$. The perovskite $\text{ DyMnO}_3$ structure contains the corner-sharing $\text{ MnO}_6$ octahedra with the $\text{ Mn}$ ion at their centers and $\text{ Dy}$ occupying holes between the octahedra. The small radius of the $\text{ Dy}$ ion in $\text{ RMnO}_3$ produces a cooperative buckling and tilting of the corner-shared $\text{ MnO}_6$ octahedra known as $\text{ GdFeO}_3$ distortions. At an ambient pressure and temperature, the perovskite $\text{ DyMnO}_3$ structure distorts to orthorhombic $\text{ Pbnm}$ symmetry. The $\text{ MnO}_6$ octahedron in $\text{ DyMnO}_3$ is highly distorted, and tilted with an average $\text{ Mn}–\text{ O}–\text{ Mn}$ bond angle of $\sim 145^\circ$ in the plane to be compared with a value of $\sim 155^\circ$ in $\text{ LaMnO}_3$. The $\text{ Jahn–Teller}$ ($\text{ JT}$) distortion of the $\text{ Mn}^{3+}\text{O}_6$ octahedra in $\text{ DyMnO}_3$ produces $\text{ Mn}$–$\text{ O}$ bonds in three pairs: one $\text{ Mn}–\text{ O}1$ for apical bonds along the $c$ axis, and two $\text{ Mn}–\text{ O}2$ for equatorial bonds in the $ab$ plane. In the basal $ab$ plane, long $\text{ Mn}–\text{ O}2$($l$) (2.22 Å) and short $\text{ Mn}–\text{ O}2$($s$) bonds (1.89 Å) alternate.

$\text{ DyMnO}_3$ shows an incommensurate crystallographic superstructure below the $\text{ Néel}$ temperature ($T_N = 39$ K) corresponding to a sinusoidal antiferromagnetic ordering of the...
Mn moments along the $b$ axis. The transition ($T \sim 18$ K) to a noncollinear spiral magnetic ordering in which inversion symmetry is broken is accompanied with a large spontaneous electric polarization along the $c$ axis ($\sim 2 \times 10^{-3}$ C m$^{-2}$). The appearance of ferroelectricity at the transition into the spiral structure of RMnO$_3$ with $R=\text{Tb}, \text{Dy},$ and $\text{Gd}$ was explained microscopically in terms of a spin supercurrent according to $P_{ij} = \eta e_{ij} \times (S_i \times S_j)$, in which appear electric polarization $P_{ij}$, magnetic moments $S_i$ and $S_j$, the unit vector $e_{ij}$ connecting sites $i$ and $j$, and factor $\eta$, which is proportional to the transfer integral. The magnetoelectric effect is thus correlated closely with the noncollinear spin configurations induced by a significant cooperative Jahn–Teller distortion of MnO$_6$ octahedra and a large octahedral tilt angle. The JT distortion and tilt angle of MnO$_6$ octahedra in DyMnO$_3$ can become modified when smaller ions or divalent cations are incorporated into the rare-earth sites or when hydrostatic pressure is applied. In addition to the induced structural disorders, doping with divalent cations or monovalent cations into rare-earth sites in RMnO$_3$ generally complicates the electronic structure, producing mixed valence states or oxygen-deficient states. External pressure is therefore an ideal tool to tune the extent of the JT distortion in rare-earth manganites.

The insulator-metal transition (IMT) of rare-earth manganites mediated with an external hydrostatic pressure is reported. The variation of electron bandwidth under hydrostatic pressure is proposed to serve as a driving force to induce the IMT of rare-earth manganites, but the spectral evidence for a pressure-induced bandwidth variation of manganites is still sparse. X-ray absorption spectra (XAS) with chemical selectivity provide insight complementary to diffraction measurements into the local environment around an absorber atom of a material under pressure. The $K$-edge absorption spectra of transition-metal oxides reveal a strong dependence on the charge distribution and symmetry distortions of the probed site in a material, but 1$s$ core-hole lifetime broadening ($>1.15$ eV) in absorption precludes obtaining the spectra at high resolution, particularly the pre-edge features in the $K$-edge absorption spectra of transition-metal compounds.

In this work, we applied techniques derived from a resonant inelastic x-ray scattering called the lifetime broadening suppressed x-ray absorption spectroscopy in the partial fluorescence yield. The $K$-edge XAS spectra at high resolution, particularly in the pre-edge region, provide an accurate spectral information about the electronic structure and local structure of a material under pressure. The dependence of the orthorhombic $Pbnm$ perovskite structure of RMnO$_3$ ($R=\text{Dy}, \text{Gd},$ and $\text{Tb}$) on temperature and magnetic field is known, but the effect of hydrostatic pressure on highly distorted multiferroic DyMnO$_3$ is less investigated. In this work, we probed the variations of electronic structure and structural distortion in orthorhombic DyMnO$_3$ under external hydrostatic pressure using combined XAS and x-ray diffraction (XRD) techniques. The pressure-dependent Mn $K$-edge XAS spectra were compared with the results of the $ab\ initio$ electronic structure calculations and full multiple-scattering calculations using the code FDMNES.

II. EXPERIMENTS

Polycrystalline DyMnO$_3$ was synthesized with a conventional citrate-gel process. Dy$_2$O$_3$ and MnO in stoichiometric proportions were dissolved in aqueous solutions of citric and nitric acids. The solution was heated at 95 °C until a spongy gel was formed, and then heated at a higher temperature to produce dark-colored ashes. These ground ashes were first calcinated at 600 °C in air to remove organic residues, and then further calcinated 950 °C in air for 12 h to obtain adequate crystallinity. Orthorhombic DyMnO$_3$ of satisfactory quality was used for the subsequent high pressure experiments.

The dependence of an Mn $K$-edge x-ray absorption on pressure was measured at the Taiwan inelastic x-ray scattering beamline BL12XU in SPring-8. The synchrotron radiation from an undulator was made monochromatic with a Si(111) double-crystal monochromator and focused to a spot $\sim 16 \times 20$ μm$^2$ full width at half maximum (FWHM) in a diamond-anvil pressure cell using two mirrors in a Kilpatrick–Baez (KB) geometry. The emitted x-ray fluorescence was analyzed with a spectrometer comprising a synchronously moving, spherically bent Si (440) analyzer and a photon-counting detector on the 1-m-armed Rowland circle. The overall resolution, which is evaluated from the quasi-elastic scattering from the sample, had a FWHM of 0.9 eV. The incident energy was calibrated with the known Mn $K$-edge absorption inflection point at 6539 eV of an Mn foil. A sample DyMnO$_3$ as a finely grained powder was loaded into a hole (diameter 100 μm) of a Be gasket mounted on a Mao-Bell type diamond anvil cell (culet size 550 μm). Silicon oil served as a medium to transmit pressure. All measurements were performed at room temperature. The applied
hydrostatic pressure was averaged at multiple points through the line shift of the ruby luminescence before and after each spectral collection.

The pressure-dependent x-ray diffraction was measured at the beamline BL01C2 of National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The incident x rays (wavelength 0.4959 Å, 25 keV) were generated from the superconducting wavelength-shifter beamline with a Si(111) double-crystal monochromator. The DyMnO$_3$ powder as grown was filled into the pinhole diameter of 235 μm of a stainless-steel gasket with an Au powder as a pressure indicator and a mixture of methanol-ethanol-water 16:3:1 as a pressure-transmitting medium in a diamond anvil cell Mao-Bell type, culet size 550 μm. An Au powder standard was used to determine precisely the wavelength and the distance from the sample to the detector. The XRD pattern was recorded with a MAR345 imaging plate (exposure duration typically of ~20 min). The one-dimensional XRD pattern was converted with program FIT2D. The x-ray diffraction data was structurally refined with the Rietveld method as implemented in the general structure analysis system software package.

### III. RESULTS AND DISCUSSION

In Fig. 2, the representative x-ray diffraction patterns of orthorhombic DyMnO$_3$ over the hydrostatic pressure range ambient to ~30 GPa at room temperature were reproduced. Because of the decreased size of particles and the pressure gradients in the sample upon applying an external pressure, the x-ray diffraction peaks exhibit a gradual broadening with an increasing pressure, as shown in Fig. 2. In the entire range of pressure up to 30 GPa, the crystal structure of DyMnO$_3$ retains its initial $Pbnm$ symmetry.

To deduce the complete crystal structure including lattice parameters and atomic positions, we refined the x-ray powder diffraction data with the Rietveld method up to ~8 GPa. Figure 3 shows typical XRD patterns recorded at $P=1.2$ and 7.8 GPa with their corresponding Rietveld refinement. The experimental XRD data and their Rietveld refinement agreed satisfactorily according to the small magnitudes of the residuals. The structural parameters of DyMnO$_3$ calculated from the diffraction data for selected pressures are given in Table I. Experimental XRD data and their Rietveld refinement agreed satisfactorily according to the small values of reliability parameters $R_{wp}$, $R_p$, and $\chi^2$ shown in Table I. The values of structural parameters obtained at ambient pressure agree satisfactorily with those in the literature.

To illuminate the detailed pressure-induced structural distortion, we demonstrate in Fig. 4 the pressure dependence of Mn–O distances including the apical distance Mn–O$_1$ and equatorial distances Mn–O$_2$, and the in-plane Mn–O$_2$–Mn bond angle. These values are deduced from the structural parameters in Table I. As noted from Fig. 4(a), the short equatorial bond Mn–O$_2(s)$ and the apical distance Mn–O$_1$ remain virtually constant for a hydrostatic pressure less than 8 GPa, which is the largest effect being a shortening of the long equatorial bond Mn–O$_2(l)$.

This condition indicates that the Jahn–Teller distortion of...
TABLE I. Room-temperature structural parameters for DyMnO₃ (Pbnm) at four selected pressures calculated from the x-ray diffraction data.

<table>
<thead>
<tr>
<th>Pressure (GPa)</th>
<th>A(Å)</th>
<th>B(Å)</th>
<th>C(Å)</th>
<th>Volume (Å³)</th>
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Lattice parameters

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<th>O1(y)</th>
<th>O2(x)</th>
<th>O2(y)</th>
<th>O2(z)</th>
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<tbody>
<tr>
<td>0.982 42(30)</td>
<td>0.082 66(17)</td>
<td>0.1169(16)</td>
<td>0.4637(17)</td>
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<tr>
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</tr>
<tr>
<td>0.981 90(40)</td>
<td>0.080 86(19)</td>
<td>0.1165(20)</td>
<td>0.4640(21)</td>
<td>0.1824(17)</td>
<td>0.5550(11)</td>
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</tbody>
</table>

Reliability factors

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FIG. 4. Pressure dependence of (a) Mn–O distances including apical distance Mn–O1 and equatorial distance Mn–O2, and (b) Mn–O2–Mn bond angle of distorted MnO₆ octahedra in DyMnO₃.

The MnO₆ octahedra in DyMnO₃ becomes suppressed upon applying an external hydrostatic pressure. A similar observation is reported for LaMnO₃ under hydrostatic pressure. As noted from Fig. 4(b), the Mn–O2–Mn bond angle increases monotonically with an increasing hydrostatic pressure. Accordingly, the in-plane Mn–O2–Mn tilt angle of two adjacent MnO₆ octahedra [i.e., (180°–Mn–O2–Mn bond angle)/2] decreases monotonically with an increasing pressure. From the observation in Fig. 4, we infer a gradual symmetrization of the MnO₆ JT-distorted octahedra in DyMnO₃ with an increasing pressure.

In Fig. 5, the high-resolution Mn K-edge XAS spectra of polycrystalline DyMnO₃ collected at various pressures up to ~22 GPa were reproduced. The spectra were obtained as a partial fluorescence yield with the spectrometer energy fixed at the maximum of the Mn Kβ₁ line. The Mn K-edge XAS spectrum of DyMnO₃ at ambient pressure contains two well resolved prepeaks in the pre-edge region (labeled P1 and P2) and an asymmetric white line (labeled B) with a shoulder on the side of small energy, and a broad peak (labeled C) at a greater photon energy.

As noted from Fig. 5, the Mn K-edge XAS spectra of DyMnO₃ at various pressures exhibit only a slight modification, implying that the local atomic environment about Mn in DyMnO₃ is not greatly altered under an external hydrostatic pressure up to ~22 GPa, which is consistent with the present XRD results. With an increasing external pressure, the intensity of the white line labeled B (6555–6565 eV) in the Mn K-edge spectra of DyMnO₃ increased progressively, whereas the shoulder of the white line became gradually suppressed, as shown in the insets of Fig. 5. At a greater pressure, the shape of the white line gradually became symmetric. With an increasing hydrostatic pressure, the absorption threshold labeled A and the broad peak labeled C in the Mn K-edge spectra of DyMnO₃ continuously shifted toward greater energy, whereas the pre-edge peak labeled P1 gradually shifted to smaller energy. Pre-edge peak P1 in Fig. 5 at P=22 GPa shifted to a smaller energy, ~0.3 eV, which is relative to that at P=0.3 GPa, as shown in the insets of Fig. 5.

To ensure an accurate assignment of the pre-edge features labeled P1 and P2 in Fig. 4, we performed band-structure calculations for orthorhombic DyMnO₃ in an A-type antiferromagnetic structure based on the experimental lattice parameters, as listed in Table I with 20 atoms in the...
configuration, with three electrons occupying the three minority spin states. The energy zero is at the Fermi energy.

For the spin-down channel, one eg↓ orbitals and two higher-lying eg↑ bands. Based on the GGA+U calculations, the occupied eg↑↑ and unoccupied eg↓↓ bands (~2 eV above E_F) are dominated by d_{3z^2-r^2} and d_{xy} orbitals, respectively, in one coplanar Mn ion, whereas they exhibit predominantly d_{3z^2-r^2} and d_{xy} character, respectively, for the other coplanar Mn ion. A strong orbital polarization in the eg band for DyMnO3 with a staggered d_{3z^2-r^2}/d_{xy}-type orbital ordering pattern in the ab plane is clearly revealed.

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The 1s → 3d transitions are generally considered to be weakly allowed either through a quadrupole interaction or via hybridization of the Mn 3d states with 4p states. Based on the band structure calculations, P1 in Fig. 5 is ascribed to transitions of Mn 1s core electrons into unoccupied, majority-spin Mn eg↑↓ states hybridized with neighboring Mn 4p states. P2 in Fig. 5 is assigned as a superposition of transitions into empty, minority-spin t_{2g} eg↓↓ and eg↑↑ states hybridized with neighboring 4p states. The white line, labeled B in Fig. 5, is attributed to transitions from Mn 1s to Mn 4p states. Feature C in Fig. 5 gains intensity from the multiple-scattering contribution of MnO6 surrounded by eight Dy.

As shown in Fig. 4, the pressure effect is most pronounced for the long equatorial distance Mn−O2(l) that relates to the larger compressibility along the b axis under pressure. The compressive anisotropy of MnO6 octahedra in DyMnO3 upon applying hydrostatic pressure leads to a modified density of states. The electronic bandwidth of eg↑↓ orbitals is a key parameter to drive the insulator-metal transition of manganites. The bandwidth of the eg↑↓ orbitals in manganites is closely related to the overlap between the JT-split Mn eg↑↑↑ and eg↓↓↓ bands. Based on the GGA+U calculations, the occupied eg↑↑↑↑ and unoccupied eg↓↓↓ bands (~2 eV above E_F) are dominated by d_{3z^2-r^2} and d_{xy} orbitals, respectively, in one coplanar Mn ion, whereas they exhibit predominantly d_{3z^2-r^2} and d_{xy} character, respectively, for the other coplanar Mn ion. A strong orbital polarization in the eg band for DyMnO3 with a staggered d_{3z^2-r^2}/d_{xy}-type orbital ordering pattern in the ab plane is clearly revealed.

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Polarization-dependent Mn K-edge x-ray absorption spectra of RMnO$_3$ (R=Tb, Dy) single crystals were previously observed to exhibit a notable anisotropy along three crystallographic directions, $E\parallel a$, $E\parallel b$, and $E\parallel c$, particularly for the white-line region. The white line in the polarized Mn K-edge spectrum of DyMnO$_3$ for the $E\parallel b$ polarization lies at an energy ~2.4 eV smaller than for polarizations $E\parallel a$ and $E\parallel c$, corresponding to a highly anisotropic Mn–O$_2$ bonding within the $ab$ plane and weak covalency along the $b$ axis in RMnO$_3$ (R=Tb, Dy). The origin of this energy difference is attributed to a Jahn–Teller distortion and orbital ordering of MnO$_6$ octahedra in RMnO$_3$ (R=Tb, Dy). A significant energy separation for the maximum of the white line of the polarized Mn K-edge spectrum along $E\parallel b$ relative to $E\parallel a$ and $E\parallel c$ produces an asymmetric profile of the white line, with a shoulder on the side of small energy of the Mn K-edge spectrum for polycrystalline DyMnO$_3$ at ambient pressure.

When the long equatorial bond Mn–O$_2$(l) projected predominantly along the $b$ axis is greatly shortened with an increasing hydrostatic pressure and approaches the length of the short equatorial bond Mn–O$_2$(s) projected predominantly along the $a$ axis, as evident in Fig. 4(a), the absorption edge of the Mn K-edge spectrum for $E\parallel b$ of DyMnO$_3$ gradually shifts to greater energy. The separation for the maximum of the white line of the Mn K-edge spectrum between $E\parallel b$ and $E\parallel a$ of DyMnO$_3$ decreases because of a diminished JT distortion of DyMnO$_3$ upon applying an external hydrostatic pressure. An increased overlap between the $E\parallel b$ spectrum and the $E\parallel a$ spectrum under hydrostatic pressure consequently generates an increased intensity of the white line in the Mn K-edge spectra of DyMnO$_3$, as supported by the gradually suppressed shoulder of white line with pressure in Fig. 5.

With the FDMNES code, we performed the Mn K-edge XAS calculations on DyMnO$_3$ based on the structural parameters at various pressures in Table I. In the present XAS simulation, a muffin-tin (MT) full-multiple-scattering (FMS) approach was applied with a cluster radius $R=5$ Å. We found that a spherical cluster of radius 5 Å satisfactorily reproduces all features of the absorption spectrum. The FMS calculations were performed using the MT potential constructed from 10% overlapped MT spheres of the specified radii. Figure 7 shows simulated Mn K-edge XAS spectra of DyMnO$_3$ with varied hydrostatic pressures. The intensity of the white line clearly increases with an increasing pressure. As shown in the insets of Fig. 7 with an increasing hydrostatic pressure, the absorption threshold of simulated Mn K-edge spectra of DyMnO$_3$ shifts toward greater energy, whereas the pre-edge peak shifts to smaller energy. The experimental and calculated Mn K-edge spectra agree satisfactorily.

IV. CONCLUSION

Pressure-induced variations of electronic structure and Jahn–Teller distortion in highly distorted multiferroic DyMnO$_3$ were probed on combining x-ray powder diffraction and lifetime-broadening-suppressed x-ray absorption spectroscopy recorded in the partial fluorescence yield. With an increasing external pressure, the short equatorial bond distance Mn–O$_2$(s) and the Mn–O$_1$ apical distance remained virtually constant for a pressure less than 8 GPa, the largest effect being a shortening of the long equatorial bond Mn–O$_2$(l). The in-plane Mn–O$_2$–Mn tilt angle of two adjacent MnO$_6$ octahedra decreased monotonically upon applying hydrostatic pressure. Based on these XRD results, a local JT distortion of Mn sites within MnO$_6$ octahedra in DyMnO$_3$ becomes suppressed with an increasing hydrostatic pressure. The intensity of the white line in Mn K-edge x-ray absorption spectra of DyMnO$_3$ increased progressively with an increasing pressure, whereas the shoulder of the white line was gradually suppressed. With an increasing hydrostatic pressure, the absorption threshold of Mn K-edge spectra of DyMnO$_3$ shifted toward greater energy, whereas the pre-edge line shifted slightly to smaller energy. The intensity enhancement of the white line of Mn K-edge spectra is attributed to a diminished Jahn–Teller distortion of MnO$_6$ octahedra in DyMnO$_3$ when a hydrostatic pressure is applied. We provide spectral evidence for the pressure-induced band broadening for manganites. The comparison of XAS data with ab initio electronic structure calculations and full multiple-scattering calculations using code FDMNES shows satisfactory agreement between experimental and calculated Mn K-edge spectra.

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154510-7 Pressure-dependent x-ray absorption of DyMnO$_3$


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