Correlated-electron materials such as the 3d transition-metal (TM) oxides exhibit an exceptionally rich variety of physical properties. These include, for example, metal-insulator transitions (MIT), colossal magnetoresistance, superconductivity, and multiferroicity. It is well recognized now that the anisotropy in the TM 3d orbital occupation is a key factor for the extraordinary magnetic and electronic properties since it is intricately coupled to the charge, spin, and lattice dynamics.\textsuperscript{1-7} The MIT in VO\textsubscript{2}, V\textsubscript{2}O\textsubscript{3}, and Ca\textsubscript{2}RuO\textsubscript{4} was found to be associated with a redistribution of the orbital occupation.\textsuperscript{8-10} The occupation of the d\textsubscript{z}\textsuperscript{2} and d\textsubscript{xz} d\textsubscript{yz} orbitals with minority spin gives rise to a giant orbital moment about 2\mu\textsubscript{B} for Ca\textsubscript{3}CoO\textsubscript{2}O\textsubscript{4} and Ca\textsubscript{3}CoRhO\textsubscript{4}, respectively, elucidating the highly Ising-type magnetism.\textsuperscript{11,12} It was found that in CoO thin films the magnetic moments are oriented out of plane if the t\textsubscript{2g} hole is situated in an orbital characterized by a linear combination of the d\textsubscript{xy} and d\textsubscript{x2-y2} states and in plane if it is in the d\textsubscript{xy} orbital.\textsuperscript{13} In LiV\textsubscript{O}\textsubscript{2}, it was found that orbital ordering removes the spin frustration in the triangular lattice and drives the system into a spin-singlet state without any long-range magnetic order.\textsuperscript{14} In the manganese oxides, the orbital and charge ordering plays an important role for the colossal magnetoresistance and the metal-insulator transition.\textsuperscript{1,15} On top of this, orbital order could also lead to ferroelectricity.\textsuperscript{1,5,7}

In the R\textsubscript{2}MnO\textsubscript{3} (R=rare earth) system, the high-spin Mn ion has the t\textsubscript{2g}e\textsubscript{g}\textsuperscript{3} configuration. A strong Jahn-Teller (JT) distortion occurs to lift the degeneracy in the e\textsubscript{g} orbital and leads to a pattern of orbital ordering through the crystal lattice. The spin ordering is coupled to the ordered orbital pattern according to the Goodenough-Kanamori rules.\textsuperscript{1,6,17} The different displacements of the oxygen ions around the Mn ions in R\textsubscript{2}MnO\textsubscript{3} (R=Tb, Dy, and Gd) causes strong distortions and tilting of the MnO\textsubscript{6} octahedra as well as a reduction in Mn-O-Mn bond angles, thereby yielding a complicated pattern of orbital and spin ordering, which in turn is thought of as the origin of the observed ferroelectricity.\textsuperscript{1,18-20} Thus, orbital polarization and ordering in orthorhombic R\textsubscript{2}MnO\textsubscript{3} (R=Tb, Dy, and Gd) is an indispensable ingredient for the formation of complicated incommensurate spin structures at low temperatures.

Indeed, it was found recently that the Mn L\textsubscript{2,3}-edge x-ray absorption spectra of hexagonal Y\textsubscript{2}MnO\textsubscript{3} and Dy\textsubscript{2}MnO\textsubscript{3} exhibit a strong polarization dependence, indicative for the presence of distinct orbital occupations in the e\textsubscript{g} subshell. Yet, it is quite puzzling that such polarization dependence was not observed in the study on orthorhombic Dy\textsubscript{2}MnO\textsubscript{3}.\textsuperscript{21,22} We note that thin films were used in that study. Our objective is now to resolve this issue and to reinvestigated the orbital occupations of the Mn 3d states in orthorhombic Dy\textsubscript{2}MnO\textsubscript{3} using bulk single crystals.

Polarization-dependent x-ray absorption spectroscopy (XAS) at the 3d TM L\textsubscript{2,3} edge, complemented with multiplet cluster calculations, is a powerful method to determine the 3d orbital occupation in transition-metal oxides\textsuperscript{8,9,13,23} and have provided information of orbital ordering pattern in La\textsubscript{1-x}Sr\textsubscript{x}MnO\textsubscript{3} and La\textsubscript{2-x}Sr\textsubscript{x}MnO\textsubscript{4}.\textsuperscript{24-29}

In this Rapid Communication, we carried out our XAS study on orthorhombic Dy\textsubscript{2}MnO\textsubscript{3} single crystals using three independent polarizations, namely, E\textparallel a, E\textparallel b, and E\textparallel c, where E denotes the electric field vector and a, b, c the crystallographic directions of orthorhombic Dy\textsubscript{2}MnO\textsubscript{3}. In contrast with the results of previous experiments, we found that the Mn L\textsubscript{2,3} x-ray absorption spectra of orthorhombic Dy\textsubscript{2}MnO\textsubscript{3} single crystals do show a strong polarization dependence. We also performed ab initio band-structure calculations and obtained a strong zigzag e\textsubscript{g} orbital polarization in the ab plane with the d\textsubscript{yz-zx} (or d\textsubscript{yz-xz}) orbital occupation number close to 1. The corresponding orbital polarization is in excellent agreement with the analysis of the experimental spectra using the multiplet cluster calculations.
Untwined high-quality orthorhombic DyMnO$_3$ single crystals (space group: $Pbnm$) were grown by the high-temperature solution method with a PbF$_2$ flux in a Pt crucible. The rocking curve of the DyMnO$_3$ crystal has the full width at half maximum of $\sim$0.01$^\circ$ for the (0 0 2) Bragg reflection, indicating the excellent crystal quality. Two crystal surfaces with crystallographic directions of (100), (010) (i.e., $ab$ plane) and (100), (001) (i.e., $ac$ plane), respectively, were aligned using an x-ray diffractometer. Total electron yield Mn $L_{2,3}$-edge x-ray absorption spectra, with a photon energy resolution of $\sim$0.16 eV at 642 eV, were recorded at the Dragon beamline at National Synchrotron Radiation Research Center in Taiwan. The degree of linear polarization of the incident light was $\sim$99%. The crystals were mounted with the surface normal parallel to the Poynting vector of the light. Clean crystal surfaces were obtained by cleaving the crystals in situ in an ultrahigh-vacuum chamber with a base pressure $\sim$5 $\times$ 10$^{-10}$ Torr. A MnO single crystal was measured simultaneously in a separate chamber, which enabled us to achieve better than 0.02 eV accuracy in the relative energy alignment. Different DyMnO$_3$ crystals with the same gradient approximation plus on-site Coulomb interaction $U$ were aligned using the full-potential projected augmented wave method as implemented in the Vienna $ab$ initio simulation package (VASP). In the GGA$+U$ calculations, a Coulomb energy $U$=5.0 eV and an intra-atomic exchange parameter $J$=0.87 eV for the Mn 3$d$ electrons were used. The crystal-field potential due to the O$^{2-}$ ligands within the Mn$^{3+}$O$_6$ octahedra in DyMnO$_3$ splits the fivefold Mn 3$d$ orbitals into three lower-lying $t_{2g}$ ($d_{xy}$, $d_{xz}$, and $d_{yz}$) orbitals and two higher-lying $e_g$ orbitals. The $e_g$ doublet is split further into two subbands $e_g^{\uparrow}$ and $e_g^{\downarrow}$ resulting from a strong JT distortion. Three $d$ electrons are in the 1/2-filled $t_{2g}$ shell and one in the $e_g$. The key issue is the distribution of this $e_g$ electron between the in-plane $d_{3z^2-r^2}(d_{xy},d_{yz})$ and out-of-plane $d_{2z^2-r^2}(d_{xz},d_{yz})$ orbitals.

Figure 1(a) displays the orbital-projected partial density of states of fivefold Mn 3$d$ states for DyMnO$_3$ using a local coordination on the Mn(4) site based on the GGA$+U$ calculations. There is a small indirect gap between the JT-split Mn $e_g^{\uparrow}$ and $e_g^{\downarrow}$ bands. Based on the GGA$+U$ calculations, the occupied $e_g^{\uparrow}$ and unoccupied $e_g^{\downarrow}$ bands are dominated by $d_{3z^2-r^2}$ and $d_{2z^2-r^2}$ orbitals, respectively, in one coplanar Mn ion, whereas they exhibit predominantly $d_{3z^2-r^2}$ and $d_{2z^2-r^2}$ character, respectively, for the other coplanar Mn ion. Figure 1(b) shows the electronic valence charge-density contour on the basal plane of DyMnO$_3$. It clearly reveals the strong orbital polarization of the $e_g$ band with a staggered $d_{3z^2-r^2}$ ($d_{3z^2-r^2}$)-type orbital ordering pattern in the $ab$ plane.

Figure 2(a) shows our experimental polarization-dependent Mn $L_2,3$-edge absorption spectra of bulk DyMnO$_3$ single crystals for the three polarizations: $E$$\parallel$a (red line), $E$$\parallel$b (black line), and $E$$\parallel$c (blue line). The experimental linear dichroic (LD) spectra, namely, the difference between two polarizations, i.e., $(E\parallel c)-(E\parallel a)$, $(E\parallel b)-(E\parallel a)$, and $(E\parallel b)-(E\parallel c)$ are depicted in Figs. 2(c)–2(e). It is clear that our spectra exhibit a very strong polarization dependence along the three different crystallographic directions in sharp contrast to the results of previous experiments on DyMnO$_3$ thin films which showed practically only isotropiclike spectra (possibly due to strain effect on substrates). In our spectra, for example, the main peak for the $E$$\parallel$b polarization (i.e., the direction of spiral spin) lies at a lower energy than for polarizations $E$$\parallel$a and $E$$\parallel$c. Our spectra therefore, provide a clear indication for a large anisotropic orbital occupation of Mn $e_g$ states as expected for the strongly distorted MnO$_6$ octahedron.

To extract information on the orbital occupation from the polarization-dependent Mn $L_{2,3}$-edge XAS spectra of
negative integrals in the LD spectra \((E||b)-(E||a)\) and \((E||b)-(E||c)\) are indicative for a relatively large projection of the occupied \(d_{3z^2-r^2}\) and \(d_{3y^2-r^2}\) orbitals along the \(b\) direction. This is in good agreement with the orbital ordering pattern shown in Fig. 1(b), in which the angle between the \(d_{3z^2-r^2}\) (or \(d_{3y^2-r^2}\)) and the \(b\) axis is \(29^\circ\) (40° in LaMnO₃), reflecting the significant GdFeO₃-type distortion and the decrease in the Mn-O-Mn bond angle.\(^{38}\)

For the orbital polarization of the \(e_g\)-orbital wave function is generally described as

\[
\phi(\theta) = \cos(\theta/2)[3z^2-r^2] \pm \sin(\theta/2)[x^2-y^2].
\]

(1)

Here \(\theta\) defines the respective orbital component.\(^{3,39}\) The simplest case of an alternative \(d_{3z^2-r^2}\) and \(d_{3y^2-r^2}\) ordering corresponds to \(\theta=0^\circ\) and \(180^\circ\), respectively. The angle \(\theta\) can be estimated from the actual magnitude of the JT distortion and is given by the expression

\[
\tan(\theta) = \frac{\sqrt{3}(l-s)}{2m-l-s},
\]

(2)

here \(l, m\), and \(s\) denote the three Mn-O unit distances.\(^{3}\) We obtain a \(\theta\) angle of \(-113^\circ\) for Mn-O distances of 2.24, 1.94, and 1.89 Å in orthorhombic DyMnO₃. This is close to the 120° scenario corresponding to a staggered \(d_{3z^2-r^2}/d_{3y^2-r^2}\) type of orbital ordering, consistent with the present experimental results and GGA+U calculations. The larger differences between the three Mn-O distances in DyMnO₃ lead to the formation of a staggered \(d_{3z^2-r^2}/d_{3y^2-r^2}\) type of orbital ordering as compared with the smaller differences in the Mn-O distances of 2.00, 1.98, and 1.84 Å in La₀.5Sr₁.5MnO₄ exhibiting a cross-type orbital ordering of \(d_{3z^2-r^2}/d_{3y^2-r^2}\).\(^{26}\)

As shown in Fig. 1(b), the distortion leads to a shorter distance between \(O_3\) and \(O_4\), which in turn slightly changes the next-nearest-neighbor (NNN) AFM superexchange interaction through the Mn(1)-OₓMn(3) paths (\(J_2\) on the order of a few millielectron volts), since the occupied \(e_g\) orbitals in the Mn(1) and Mn(3) are parallel. At the same time, this distortion strongly suppresses the predominant NN ferromagnetic (FM) superexchange interaction \((J_1=\pm 13\) meV for LaMnO₃ and \(-\sim 2\) meV for DyMnO₃).\(^{18,40}\) Under the staggered \(d_{3z^2-r^2}/d_{3y^2-r^2}\) type of orbital ordering as shown in Fig. 1(b), the AFM NNN superexchange interaction between Mn(1) and Mn(3) (along the \(b\) axis) is stronger than that between Mn(2) and Mn(4) (along the \(a\) axis). Thus, a subtle balance of the competition between the NN FM and the NNN AFM superexchange interactions along the \(b\) axis leads to a frustrated spin system and gives rise to a noncollinear spin arrangement in the spiral phase at low temperatures.\(^{18,19}\)
In conclusion, we have observed a strong polarization dependence in the soft-x-ray absorption spectra at the Mn $L_{2,3}$ edge in orthorhombic DyMnO$_3$ single crystals. $Ab$ initio electronic-structure calculations clearly reveal a strong orbital polarization in the $e_g$ band with a staggered $d_{3z^2-r^2}/d_{3y^2-r^2}$ type of ordering pattern in the $ab$ plane. Configuration-interaction cluster calculations revealed that the $e_g$ electron is indeed constrained to the $d_{3z^2-r^2}$ or $d_{3y^2-r^2}$ orbital. The negative integral intensity of linear dichroic spectra $\langle E\parallel b \rangle - \langle E\parallel a \rangle$ and $\langle E\parallel b \rangle - \langle E\parallel c \rangle$ points toward a relatively large projection of the occupied $d_{3z^2-r^2}$ and $d_{3y^2-r^2}$ orbitals along the $b$ direction. The coexistence and competition between NN FM and NNN AFM interactions along the $b$ axis lead to a frustrated spin system giving rise to the complex magnetic structure.

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