

Characteristic Size Effects on the Crystallographic Structure and Magnetic Properties of RMnO₃ (R = Eu, Gd, Tb, Dy) Nanoparticles

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journal or publication title	Journal of Physical Chemistry C
volume	125
number	26
page range	14474-14485
year	2021-06-24
URL	http://hdl.handle.net/10228/00008925

doi: <https://doi.org/10.1021/acs.jpcc.1c03497>

Characteristic size effects on crystallographic structure and magnetic properties of RMnO_3 ($\text{R} = \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}$) nanoparticles

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Abstract

We synthesized lanthanoid manganese oxide RMnO_3 ($\text{R} = \text{Eu}, \text{Gd}, \text{Tb}, \text{and Dy}$) nanoparticles with particle sizes ranging from approximately 6.5 to 23 nm and investigated both their crystal structure and magnetic properties. The RMnO_3 nanoparticles showed a strong correlation between crystal structure and magnetic properties, and particle size effects on these properties vary owing to the different atomic radii of the lanthanoid ions. The magnetic properties of all the nanoparticles exhibited significant changes as the lattice constants changed at characteristic sizes that depend on the lanthanoid ionic radius; however, the characteristic size for magnetic properties corresponded to the magnitude of the orthorhombic distortion $b/a = 1.10$, regardless of the lanthanoid ionic radius. With decreasing particle size, EuMnO_3 , GdMnO_3 , and TbMnO_3 nanoparticles induced tensile strain of MnO_6 octahedra whereas compressive strain occurred in DyMnO_3 nanoparticles. The deformation of MnO_6 octahedra changed the magnetic interactions, resulting in changes in the magnetic properties. As

the particle size decreased, for R = Eu, Gd, and Tb, the magnetic properties, such as transition temperature, coercive field, and blocking temperature, decreased; conversely, these values increased in DyMnO₃. The distortion of the unit cell induced changes in the magnetic ordering state due to decreasing particle size.

Introduction

Orthorhombically distorted perovskite manganite RMnO₃ (R: lanthanoid) is well known as a strongly correlated electron material. RMnO₃ exhibits colossal magnetoresistance effect, multiferroic behavior, and distinctive magnetoelectric characteristics. The magnetic and electronic phases of RMnO₃ vary depending of the ionic radius of the lanthanoid. The magnitude of the Jahn–Teller distortion can be controlled by the substitution of the lanthanoid, while the orbital and magnetic structures of RMnO₃ depend strongly on the ionic radius of the lanthanoid.^{1–11} As the ionic radius decreases, the magnetic ordering state at low temperatures changes from the A-type antiferromagnetic (A-AFM), to an incommensurate spin-cycloid, and then to the E-type antiferromagnetic (E-AFM) ordering state. In addition, the partial substitution of the lanthanoid induces changes in the magnetic state and transition temperature due to hole doping and the change in effective lanthanoid ion radius.^{12–21} For R = La, Nd, and Sm, the lowest magnetic ordering state is A-AFM, and the Néel temperature $T_N(\text{Mn}) \sim 60\text{--}130$ K decreases with decreasing ionic radius. EuMnO₃^{8,13,14,17,22} and GdMnO₃^{12,18,22,23} exhibit a phase transition from a paramagnetic to an A-AFM state below ~ 45 and 25 K, respectively, via an incommensurate state with $T_N(\text{Mn}) \sim 50$ and 43 K, respectively. The magnetic states of TbMnO₃^{11,12,23,24} and DyMnO₃^{19,20,23} change from paramagnetic to cycloidal spin order below ~ 25 K via the incommensurate state below $T_N(\text{Mn}) \sim 40$ K. For R = Ho, Er, Tm, Yb and Lu, the magnetic states change from paramagnetic to E-AFM via an incommensurate state below $T_N(\text{Mn}) \sim 40$ K.^{25,26} The magnetic phases and their transition temperatures depend on the Mn–O–Mn bond angles and Mn–O bond lengths in octahedral MnO₆, which vary according to the ionic radius of the lanthanoid. The decreas-

ing radius of the lanthanoid ion enhances the cooperative rotation of the MnO_6 octahedra (GdFeO_3 -type distortion) causing a reduction in the Mn–O–Mn bond angles. In addition, the combination of orbital order and next-nearest-neighbor superexchange interactions has a nontrivial effect on the magnetic ground state in systems with orbital degeneracy and a large GdFeO_3 -type distortion.^{1,5,27–30} The distortion of the unit cell of RMnO_3 thin films due to epitaxial strain induces changes in the magnetic state and transition temperature.^{31–37}

Because of the high proportion of surface atoms and finite size effects, nanoparticles possess unusual magnetic properties and crystal structures that differ from those of the bulk crystal. Nanoparticles of strongly correlated electron materials such as manganese oxide exhibit characteristic size effects on the crystal structure and magnetic properties owing to strong electron correlation and strong spin-orbit and spin-lattice coupling. Nanoparticles of strongly correlated materials, such as LaMnO_3 ,^{38,39} DyMnO_3 ,⁴⁰ GdMnO_3 ,⁴¹ DyMn_2O_5 ,⁴² and NiO ,⁴³ exhibit novel size effects on the magnetic properties and crystallographic structures, as already shown in our previous studies. These nanoparticles exhibit remarkable changes in crystal structure (i.e., on structural symmetry and lattice constants) and unique size effects on the magnetic properties. This study investigates on the size effects on the correlation between the magnetic properties and crystallographic structure of RMnO_3 ($\text{R} = \text{Eu, Gd, Tb, and Dy}$) nanoparticles, whose magnetic phase diagrams depend on the ionic radius of R . Emphasis was placed on the influence of atomic radius on the magnetic properties and crystal structures because of the variations in the magnetic state of the bulk crystals. The fact that RMnO_3 materials have the same crystal structure and their magnetic phase diagrams can be controlled by modulating the effective R ion radius by partial substitution of lanthanoids, RMnO_3 nanoparticles are an excellent testbed to study the effect of R ion size on magnetic properties. Previous studies have reported that nanoparticles of DyMnO_3 with particle size of 8.6–106 nm,^{44,45} GdMnO_3 with particle size of 52–270 nm,^{46–49} TbMnO_3 with particle size of 25 nm–3 μm ^{50–52} exhibited different behaviors from bulk crystals owing to changes in the particle size. In the case of RMnO_3 bulk crystals, the magnetic properties

and crystal structure have been investigated as a function of lanthanoid ionic radius, however, to the best of our knowledge, there have been no reports comparing size dependence of magnetic properties and crystal structure of RMnO_3 nanoparticles with similar particle size (approximately 10 nm) and different R ions. To clarify the size effects on the correlation between crystal structure and the magnetic properties of RMnO_3 (R = Eu, Gd, Tb, and Dy) nanoparticles, we conducted a systematic experimental study using the nanoparticle with same particle size region. We synthesized nanoparticles ranging in size from 6.5 to 23 nm. We herein report the size dependence of strong correlation between the crystal structure and the magnetic properties of RMnO_3 (R = Eu, Gd, Tb, and Dy) nanoparticles as well the effect of the magnetic ordering state of the bulk crystals on these size effects. In addition, these results provided a magnetic phase diagram of the nanoparticles as a function of lanthanoid ionic radius.

Experimental method

The RMnO_3 nanoparticles were synthesized in one-dimensional pores of mesoporous silica SBA-15 with a diameter of approximately 8 nm. SBA-15 has a well-ordered two-dimensional hexagonal mesoporous structure with one-dimensional pores separated by amorphous silica walls.⁵³ SBA-15 was used as a template to ensure equal particle size and prevent clumping of the synthesized nanoparticles. The RMnO_3 nanoparticles were synthesized by soaking SBA-15 in a stoichiometric aqueous solution of $\text{R}(\text{CH}_3\text{COO})_3 \cdot n\text{H}_2\text{O}$ and $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$. The soaked SBA-15 samples were then dried and calcinated in an oxygen atmosphere.^{40,41} The synthesis of DyMnO_3 nanoparticles in the pores of SBA-15 was confirmed via X-ray diffraction (XRD) and transmission electron microscopy (TEM). The mean particle size estimated from the TEM images was consistent with that obtained via XRD.⁴⁰ Previous studies have shown that the particle size of LaMnO_3 ,³⁸ DyMn_2O_5 ,⁴² and NiO ⁴³ nanoparticles synthesized in the pores of SBA-15 and obtained via XRD were consistent with the TEM

results. Therefore, it is reasonable to assume that, for the TbMnO₃, GdMnO₃, and EuMnO₃ nanoparticles also synthesized in the pores of SBA-15, the particle sizes estimated via XRD are valid. Therefore, XRD was used to estimate the particle sizes.

Powder XRD of the nanoparticles was conducted using a synchrotron radiation X-ray diffractometer with a Debye–Scherrer camera on the BL-8B beamline at the Photon Factory of the Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK). Incident X-rays with energy of 18 keV and a wavelength calibrated using the XRD pattern of CeO₂ powder were used. Figure 1(a) shows the powder XRD patterns for each nanoparticle. The mean particle sizes of the DyMnO₃, TbMnO₃, GdMnO₃, and EuMnO₃ nanoparticles were estimated to be 14.8, 15.6, 16.0, and 16.8 nm, respectively. The diffraction patterns of all RMnO₃ nanoparticles exhibited broad Bragg peaks, which were attributed to an orthorhombic symmetry with space group *Pbnm*, identical to that of the RMnO₃ bulk crystals^{7–9,54} shown in Fig. 1(b). The nanoparticles also contained the impurity R₂O₃ indicated by an asterisk in Fig. 1(a). The broad diffraction peaks were deconvoluted to those associated with RMnO₃ via multipeak fitting. The sizes of the RMnO₃ nanoparticles were estimated based on positions and full widths at half maximums of the Bragg peaks using the Scherrer equation. The XRD results confirmed the synthesis of RMnO₃ nanoparticles with sizes ranging from 6.5 to 23 nm. The lattice constants of the RMnO₃ nanoparticles were calculated from the relationship between the lattice constants and the plane indices determined from the Bragg peak angles of the deconvoluted peaks. The distortion of the MnO₆ octahedra was evaluated based on the assumption that the atomic positions of the nanoparticles were the same as in the bulk crystal. The Mn–O interatomic distances and the Mn–O–Mn bond angles were calculated using the lattice constants of the nanoparticles and the atomic position of the bulk crystal.^{7,9}

The magnetic properties of the nanoparticles were investigated via a superconducting quantum interference device magnetometer (Quantum Design, Inc.). The DC magnetic susceptibilities were measured in an external magnetic field of 100 Oe under both field-

cooling (FC) and zero-field-cooling (ZFC) conditions. The AC susceptibility was measured in an AC magnetic field with frequencies ranging from 0.1 to 1000 Hz and an amplitude of 3.8 Oe. Magnetization curves up to 5 T were obtained at 15 K to avoid the effects of antiferromagnetic magnetic ordering of the lanthanoid in RMnO_3 at $T_N(\text{R}) \sim 7$ K.

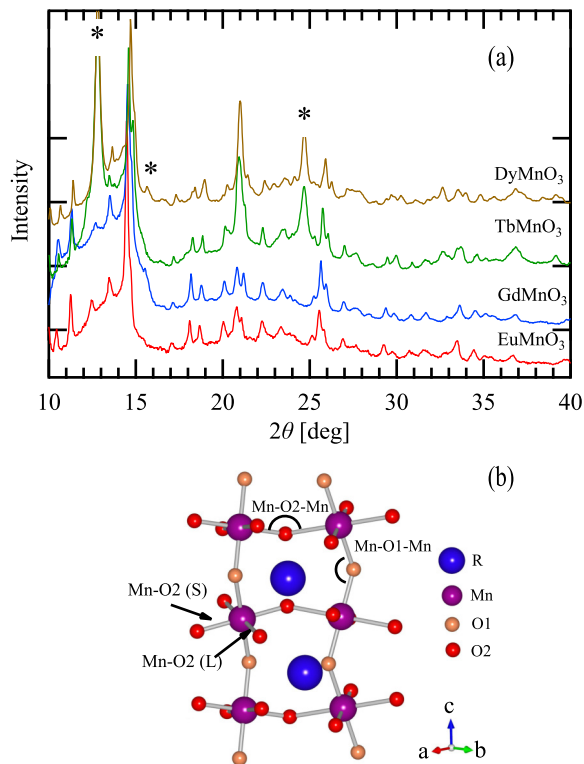


Figure 1: (a) Powder XRD patterns of DyMnO_3 , TbMnO_3 , GdMnO_3 , and EuMnO_3 nanoparticles with particle sizes of 14.8, 15.6, 16.0, and 16.8 nm, respectively. The wavelength of the incident X-rays was 0.688 \AA . The asterisks indicate the impurity phase R_2O_3 . (b) Schematic of crystal structure with orthorhombic symmetry of RMnO_3 .

Experimental results

DyMnO₃

Figure 2(a) shows the particle size dependence of the lattice constants a , b , and c , as well as the ratio of b to a for the DyMnO₃ nanoparticles. As the particle size decreased, the lattice constants a and c increased below the characteristic size of crystal structure $S_{c1}(\text{Dy}) = 12.5$ nm and remained constant for particle size between 8 and 11.5 nm. Thereafter, the two lattice constants increased monotonically below $S_{c2}(\text{Dy}) = 8.0$ nm. In contrast, the lattice constant b decreased with decreasing particle size, and showed two inflection points at $S_{c1}(\text{Dy})$ and $S_{c2}(\text{Dy})$ with decreasing particle size; however, the unit cell volume did not vary with particle size. The DyMnO₃ nanoparticles had a Jahn–Teller distorted orthorhombic structure (O' -type structure: $b > a > c / \sqrt{2}$). The orthorhombic distortion b/a of the nanoparticles with particle size less than 13 nm was smaller than that of the bulk crystal, $b/a = 1.105$.⁷ The modulation of the orthorhombic distortion suggested changes in the symmetry of the MnO₆ octahedra with decreasing particle size and a Jahn–Teller distortion from those of the bulk crystal. The orthorhombic distortion of the DyMnO₃ nanoparticles exhibited a pronounced reduction below $S_{c2}(\text{Dy})$. Above $S_{c2}(\text{Dy})$, b/a remained essentially constant, but increased slowly with increasing particle size above $S_{c1}(\text{Dy})$. These results suggest that the relaxation of orthorhombic distortion occurred once the particle size decreased below approximately $S_{c1}(\text{Dy})$ and was significant below $S_{c2}(\text{Dy})$. Figure 2(b) shows the size dependence of the Mn–O bond lengths of the MnO₆ octahedra in the DyMnO₃ nanoparticles. The MnO₆ octahedra have three distinct M–O bond lengths, Mn–O1, Mn–O2(S), and Mn–O2(L) (Fig. 1(b)). The size dependences of all Mn–O bond lengths exhibited pronounced changes at $S_{c1}(\text{Dy})$ and $S_{c2}(\text{Dy})$. As particle size decreased, the Mn–O1 bond length increased for particle sizes below approximately 11 nm, remained constant for sizes between 8 and 11 nm, and then increased for sizes below $S_{c2}(\text{Dy})$. In contrast, the Mn–O2(L) bond length decreased with decreasing particle size and exhibited two inflection points at approximately

8 and 11 nm. The Mn–O2(L) bond length remained essentially constant at particle sizes ranging from 8 to 10 nm and above 12 nm. Mn–O2(S) exhibited a similar behavior to that of Mn–O2(L), however, the bond length of Mn–O2(S) increased with decreasing particle size for particle sizes above $S_{c1}(\text{Dy})$. These results indicate that, as particle size decreased, the MnO_6 octahedra compressed along the ab -plane and expanded along the c -axis, that is, the DyMnO_3 nanoparticles displayed compressive strain, particularly in particle sizes below $S_{c2}(\text{Dy})$. Figure 2(c) shows the relationship between the Mn–O–Mn bond angles and particle size for DyMnO_3 nanoparticles. The two bond angles exhibited pronounced changes at approximately $S_{c1}(\text{Dy})$ and $S_{c2}(\text{Dy})$. As particle size decreased, the Mn–O1–Mn and Mn–O2–Mn bond angles increased and decreased, respectively.

Figure 2(d) shows the temperature dependence of the DC susceptibility of DyMnO_3 nanoparticles with a particle size of 11.3 nm. Both the FC and ZFC susceptibilities of the nanoparticles increased below approximately 45 K because of the antiferromagnetic ordering of Mn magnetic moments, which corresponds to $T_N(\text{Mn}) \sim 39$ K for DyMnO_3 bulk crystal.^{19,20,23} In this bulk crystal, Dy spins order antiferromagnetically below a $T_N(\text{Dy}) \sim 6$ K^{2,19,20,23} and the paramagnetic susceptibility of the Dy spins mask the antiferromagnetic transition of the Mn sublattice.²⁰ The rapid increase in both FC and ZFC susceptibilities below 10 K is attributed to the antiferromagnetic ordering of the Dy spins in the DyMnO_3 nanoparticles. In addition, the existence of paramagnet Dy_2O_3 may affect the increase in both FC and ZFC susceptibilities below 10 K. A pronounced magnetic irreversibility between the FC and ZFC susceptibilities was observed below $T_{\text{irr}} = 36$ K as indicated by the lower arrow in Fig. 2(d). The ZFC susceptibility exhibited a hump at approximately 20 K. The appearances of irreversibility and a peak of ZFC susceptibility are the characteristic behaviors of superparamagnetics. For superparamagnetic nanoparticles, typically, the FC susceptibility is constantly increasing like in paramagnetism, whereas the ZFC susceptibility exhibits a peak at the blocking temperature because of the existence of activation energy for the reversal of the magnetic moments. It then decreases toward zero with decreasing

temperature. AC susceptibility exhibits a peak at the blocking temperature.⁵⁵ The ZFC susceptibility of DyMnO₃ nanoparticles exhibited a hump owing to the blocking phenomena and increased due to the paramagnetic susceptibility of Dy spins in DyMnO₃ nanoparticles and Dy₂O₃ with decreasing temperature. The temperature at the appearance of the hump in ZFC susceptibility corresponded to the blocking temperature obtained by AC susceptibility as shown in Fig. 2(f). These behaviors are consistent with the blocking phenomena of superparamagnetism. The upper panel of Fig. 2(e) shows the size dependence of T_{irr} , which displayed a constant value above characteristic size of magnetic property $S_{\text{m1}}(\text{Dy}) = 11.4$ nm, rapidly decreased at $S_{\text{m1}}(\text{Dy})$, and increased linearly with decreasing particle size below $S_{\text{m2}}(\text{Dy}) = 8.2$ nm. The AC susceptibility of the DyMnO₃ nanoparticles was measured in the frequency range of 0.1–1000 Hz. Figure 2(f) shows the temperature dependence of the AC susceptibility of the DyMnO₃ nanoparticles with a particle size of 11.3 nm at 100 Hz. Both the in-phase (χ') and the out-of-phase susceptibilities (χ'') of the nanoparticles increased below approximately 40 K and peaked at the blocking temperature (T_{B}). The peaks of both $\chi'(T)$ and $\chi''(T)$ shifted toward higher temperatures with increasing frequency. This relaxation behavior is indicative of superparamagnetic behavior. T_{B} at 100 Hz remained nearly constant above $S_{\text{m1}}(\text{Dy})$. Below $S_{\text{m1}}(\text{Dy})$, T_{B} increased with decreasing particle size and remained almost constant between $S_{\text{m1}}(\text{Dy})$ and $S_{\text{m2}}(\text{Dy})$. T_{B} increased below $S_{\text{m2}}(\text{Dy})$ (middle panel, Fig. 2(e)). Figure 2(g) shows the magnetization curve of DyMnO₃ nanoparticles with a particle size of 11.3 nm at 15 K which was lower than the T_{B} . The superparamagnetic behaviors show a hysteresis loop in the magnetization curve below blocking temperature, whereas they show a paramagnetic-like behavior without a hysteresis loop above T_{B} . In addition, the magnetization is described by a Langevin function. In fact, the DyMnO₃ nanoparticles exhibited a hysteresis loop in the magnetization curves below the blocking temperature and their magnetization curves were reproduced by a Langevin function for isolated spin assembly.⁴⁰ H_{c} at 15 K was essentially constant above $S_{\text{m1}}(\text{Dy})$ and increased rapidly with decreasing particle size below $S_{\text{m1}}(\text{Dy})$ (bottom panel, Fig. 2(e)). The

magnetic measurements indicate that the magnetic properties of the DyMnO₃ nanoparticles changed significantly at $S_{m1}(\text{Dy})$ and their magnetic parameters increased with decreasing particle size below $S_{m1}(\text{Dy})$.

TbMnO₃

Figure 3(a) shows the particle size dependence of the lattice constants a , b , and c , as well as b/a of the TbMnO₃ nanoparticles. Above $S_c(\text{Tb}) = 15.8$ nm, these values were essentially constant. As the particle size decreased, a and b increased, while the c decreased. The size dependences of the lattice constants of the TbMnO₃ nanoparticles differed from those of the DyMnO₃ nanoparticles shown in Fig. 2(a). Similar to the DyMnO₃ nanoparticles, the unit cell volume of the TbMnO₃ nanoparticles did not change with particle size. The TbMnO₃ nanoparticles had a Jahn–Teller distorted orthorhombic structure, similar to the DyMnO₃ nanoparticles. The orthorhombic distortion b/a remained essentially constant above $S_c(\text{Tb})$ and increased monotonically with decreasing particle size below $S_c(\text{Tb})$. These results indicate that the size dependence of the orthorhombic distortion of the TbMnO₃ nanoparticles was the opposite of that of the DyMnO₃ nanoparticles. Figure 3(b) shows the size dependence of the bond lengths of the MnO₆ octahedra in the TbMnO₃ nanoparticles. The size dependence of the Mn–O bond lengths exhibited a pronounced change at $S_c(\text{Tb})$ and remained constant above $S_c(\text{Tb})$. As particle size decreased, the Mn–O1 bond length decreased, while the Mn–O2(L) and Mn–O2(S) bond lengths increased. These results indicate that the MnO₆ octahedra expanded along the ab -plane and contracted along the c -axis, that is, tensile strain occurred as particle size decreased below $S_c(\text{Tb})$, which is the opposite behavior to that of DyMnO₃ nanoparticles that display compressive strain. Figure 3(c) shows the size dependences of the Mn–O–Mn bond angles of the TbMnO₃ nanoparticles. The two bond angles, Mn–O1–Mn and Mn–O2–Mn, were identical at 145.2°, and displayed constant values above approximately $S_c(\text{Tb})$. The two values diverged with decreasing particle size below $S_c(\text{Tb})$. Below $S_c(\text{Tb})$, the Mn–O1–Mn and Mn–O2–Mn bond angles decreased and

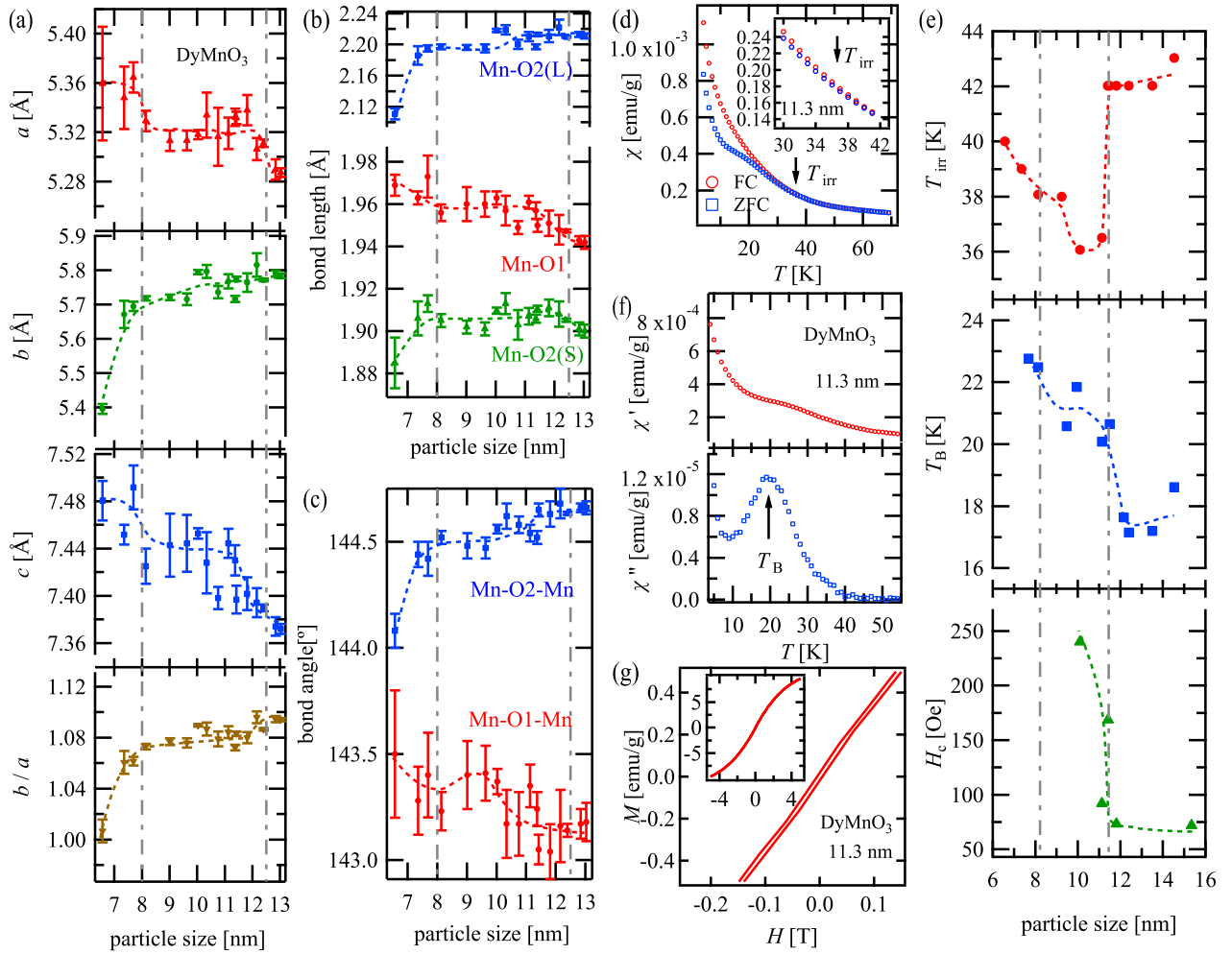


Figure 2: Particle size dependence of (a) lattice constants a , b , c , and b/a , (b) the Mn–O bond lengths, and (c) Mn–O–Mn bond angles of the DyMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{c1}(\text{Dy}) = 12.5$ nm and $S_{c2}(\text{Dy}) = 8.0$ nm. The bond lengths and bond angles were calculated using the lattice constants of the nanoparticles and the atomic position of the bulk crystal. Positional relationship of the three bond lengths and two bond angles are shown in Fig. 1(b). (d) Temperature dependence of DC magnetic susceptibilities of DyMnO₃ nanoparticles with a particle size of 11.3 nm in an external magnetic field of 100 Oe under FC (red circular symbols) and ZFC (blue square symbols) conditions. Inset shows magnified view around the T_{irr} as indicated by arrow. (e) Particle size dependences of T_{irr} , T_{B} , and H_{c} of the DyMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{m1}(\text{Dy}) = 11.4$ nm and $S_{m2}(\text{Dy}) = 8.2$ nm. (f) Temperature dependence of in-phase (upper panel) and out-of-phase (lower panel) susceptibilities of DyMnO₃ nanoparticles with a particle size of 11.3 nm at a frequency of 100 Hz in a zero DC field. Arrow indicates the T_{B} (g) Magnified low field region of the magnetization curve of DyMnO₃ nanoparticles with a particle size of 11.3 nm at 15 K. Inset shows overview of this magnetization curve ranging from -5 to 5 T.

increased monotonically, respectively, with decreasing particle size. The size dependences of the Mn–O–Mn bond angles of the TbMnO₃ nanoparticles differed from those of the DyMnO₃ nanoparticles shown in Fig. 2(c).

Figure 3(d) shows the temperature dependence of the DC susceptibility of TbMnO₃ nanoparticles with a particle size of 14.7 nm. Both the FC and ZFC susceptibilities of the nanoparticles increased below approximately 40 K, which was attributed to the antiferromagnetic ordering of Mn magnetic moments in the nanoparticles. The temperature corresponded to a $T_N(\text{Mn}) \sim 42$ K in TbMnO₃ bulk crystal.^{11,12,23,24} The rapid increase in both FC and ZFC susceptibilities below 10 K was attributed to the antiferromagnetic ordering of the Tb spins in TbMnO₃, which orders at $T_N(\text{Tb}) \sim 7$ K.^{2,23,24} The existence of paramagnet Tb₂O₃ affected the increase in both FC and ZFC susceptibilities below 10 K. A pronounced magnetic irreversibility between FC and ZFC susceptibilities was observed below $T_{\text{irr}} = 45$ K as indicated by an arrow in Fig. 3(d). The ZFC susceptibility exhibited a hump at approximately 20 K which corresponded to the T_B obtained by AC susceptibility (Fig. 3(f)). The temperature dependence of DC susceptibilities of TbMnO₃ nanoparticles were similar to those of the DyMnO₃ nanoparticles. T_{irr} of the TbMnO₃ nanoparticles varied with particle size as shown in Fig. 3(e). Above $S_m(\text{Tb}) = 15.6$ nm, T_{irr} was essentially constant at 64 K. Below $S_m(\text{Tb})$, T_{irr} decreased significantly and then remained at a constant value of 41 K below approximately 14 nm. The significant decrease in T_{irr} at around $S_c(\text{Tb})$ corresponded to that of the DyMnO₃ nanoparticles; however, the TbMnO₃ nanoparticles did not exhibit an increase in T_{irr} below $S_m(\text{Tb})$. The abrupt change in T_{irr} at $S_m(\text{Tb})$ is consistent with the change the TbMnO₃ nanoparticles at $S_c(\text{Tb})$. The AC susceptibility of the TbMnO₃ nanoparticles was measured in the frequency range of 1–1000 Hz. Both χ' and χ'' of the TbMnO₃ nanoparticles increased below approximately 40 K and peaked at T_B . The peaks of both $\chi'(T)$ and $\chi''(T)$ shifted toward higher temperatures with increasing frequency. The observed relaxation was attributed to superparamagnetic behavior. Figures 3(f) and (e) show the temperature dependence of the AC susceptibility and the size depen-

dence of T_B , respectively, at 100 Hz. T_B maintained nearly constant above approximately $S_m(\text{Tb})$. Below $S_m(\text{Tb})$, T_B decreased with decreasing particle size. Figure 3(g) shows the magnetization curve of TbMnO_3 nanoparticles with a particle size of 13.6 nm at 15 K. The magnetization exhibited a hysteresis loop owing to superparamagnetism, which was similar to that of the DyMnO_3 nanoparticles. H_c was essentially constant above $S_m(\text{Tb})$ and then decreased rapidly at $S_m(\text{Tb})$ as shown in Fig. 3(e). As particle size decreased, H_c decreased monotonically below $S_m(\text{Tb})$. The size dependence of H_c corresponded to that of T_{irr} and T_B . T_B and H_c of the TbMnO_3 nanoparticles exhibited opposite tendencies to those of the DyMnO_3 nanoparticles. The differences in size dependence of magnetic properties were attributed to the changes in crystal structure. The details of those behaviors are described later in the Discussion section.

GdMnO₃

The size dependence of the lattice constants and orthorhombic distortion of the GdMnO_3 nanoparticles are shown in Fig. 4(a). With decreasing particle size, the estimated lattice constants a and b increased whereas c decreased. The size dependence of the lattice constants of the GdMnO_3 nanoparticles were similar to those of TbMnO_3 , but differed from those of DyMnO_3 . The lattice constant a was almost constant above $S_{c1}(\text{Gd}) = 19.5$ nm and increased slightly with decreasing particle size below $S_{c1}(\text{Gd})$. The maximum value of b was observed at $S_{c1}(\text{Gd})$ and remained constant between 14 and 18 nm. Below $S_{c2}(\text{Gd}) = 13.9$ nm, b increased monotonically with decreasing particle size, while c decreased with particle size below $S_{c2}(\text{Gd})$. Similar to the DyMnO_3 and TbMnO_3 nanoparticles, the unit cell volume did not depend on the particle size. The relationship between the magnitudes of the lattice constants indicated that the GdMnO_3 nanoparticles had a Jahn–Teller distorted orthorhombic structure. The orthorhombic distortion b/a increased with decreasing particle size below $S_{c2}(\text{Gd})$ and exhibited a maximum value at $S_{c1}(\text{Gd})$. The size dependence of b/a of the GdMnO_3 nanoparticles was similar to that of the TbMnO_3 nanoparticles, except for

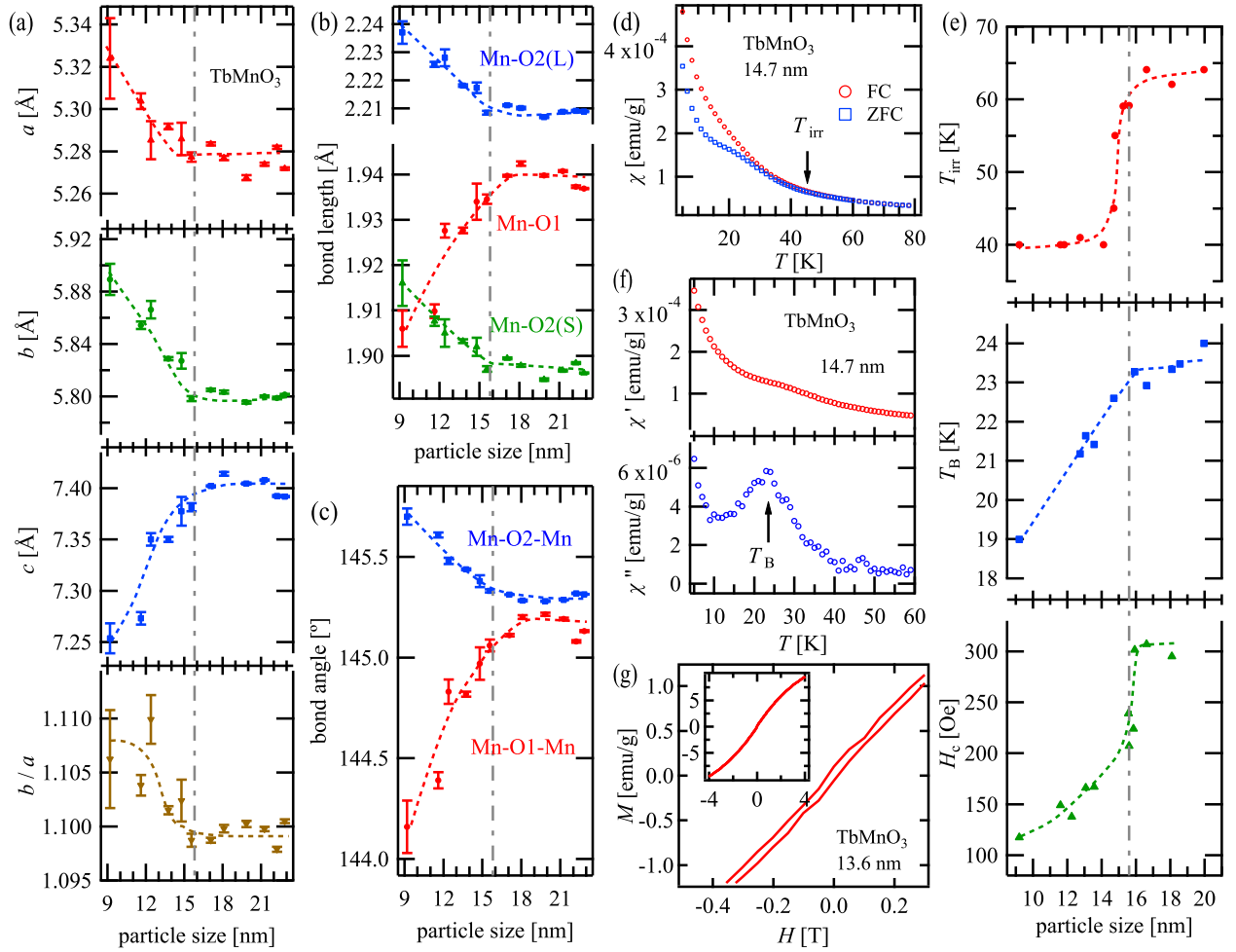


Figure 3: Particle size dependence of (a) lattice constants a , b , c , and b/a , (b) the Mn–O bond lengths, and (c) Mn–O–Mn bond angles of the TbMnO_3 nanoparticles. Vertical dashed lines indicate the characteristic size, $S_c(\text{Tb}) = 15.8$ nm. The bond lengths and bond angles were calculated using the lattice constants of the nanoparticles and the atomic position of the bulk crystal. (d) Temperature dependence of DC magnetic susceptibilities of TbMnO_3 nanoparticles with a particle size of 14.7 nm in an external magnetic field of 100 Oe under FC and ZFC conditions. Arrow indicates the T_{irr} . (e) Particle size dependences of T_{irr} , T_{B} , and H_c of the TbMnO_3 nanoparticles. Vertical dashed lines indicate the characteristic size, $S_m(\text{Tb}) = 15.6$ nm. (f) Temperature dependence of χ' and χ'' of TbMnO_3 nanoparticles with a particle size of 14.7 nm at a frequency of 100 Hz in a zero DC field. Arrow indicates the T_{B} . (g) Magnified low field region of the magnetization curve of TbMnO_3 nanoparticles with a particle size of 13.6 nm at 15 K. Inset shows overview of this magnetization curve ranging from -4 to 4 T.

existence of a hump at $S_{c1}(\text{Gd})$. Figure 4(b) shows the size dependence of the bond lengths of the MnO_6 octahedra of the GdMnO_3 nanoparticles. The size dependences of the Mn–O1 and Mn–O2(L) bond lengths exhibited pronounced changes at $S_{c2}(\text{Gd})$ and remained constant above $S_{c2}(\text{Gd})$. As particle size decreased, the Mn–O1 bond length decreased, while the Mn–O2(L) bond length increased below $S_{c2}(\text{Gd})$. The Mn–O2(S) bond length exhibited a gradual increase with decreasing particle size with two inflection points at $S_{c1}(\text{Gd})$ and $S_{c2}(\text{Gd})$. The MnO_6 octahedra expanded along the ab -plane and contracted along the c -axis with decreasing particle size, which indicated the presence of tensile strain, similar to the TbMnO_3 nanoparticles. The size dependence of the Mn–O–Mn bond angles of the GdMnO_3 nanoparticles is shown in Fig. 4(c). The two bond angles had identical values of 145.8° above approximately $S_{c1}(\text{Gd})$; however, the two bond angles diverged with decreasing particle size below $S_{c1}(\text{Gd})$. The Mn–O2–Mn bond angles remained constant above $S_{c1}(\text{Gd})$ and the Mn–O2–Mn bond angle increased monotonically with decreasing particle size below $S_{c1}(\text{Gd})$. In contrast, the Mn–O1–Mn bond angle remained constant above approximately $S_{c1}(\text{Gd})$ and began to decrease below approximately $S_{c1}(\text{Gd})$. Thereafter, the Mn–O1–Mn bond angle exhibited a significant decrease below 11 nm. The size dependence of the Mn–O–Mn bond angles of the GdMnO_3 nanoparticles were similar to those of the TbMnO_3 and differed from those of DyMnO_3 .

Figure 4(d) shows the temperature dependence of the DC susceptibility of GdMnO_3 nanoparticles with a size of 19.7 nm. Both the FC and ZFC susceptibilities of the GdMnO_3 nanoparticles increased below approximately 40 K, which was attributed to the antiferromagnetic ordering of Mn magnetic moments in the nanoparticles. The temperature corresponded to the $T_N(\text{Mn}) \sim 43$ K for GdMnO_3 bulk crystal.^{12,18,22,23} The rapid increase in both FC and ZFC susceptibilities below 10 K was attributed to the antiferromagnetic ordering of the Gd spins at $T_N(\text{Gd}) \sim 8$ K^{2,18,22,23} in the GdMnO_3 nanoparticles and was affected by the presence of the paramagnet Gd_2O_3 phase. The ZFC susceptibility exhibited a maximum at approximately 39 K which corresponded to the T_B obtained by AC susceptibility (Fig. 4(f)).

In contrast to the susceptibilities of the DyMnO₃ and TbMnO₃ nanoparticles, both the FC and ZFC susceptibilities increased rapidly at approximately 40 K. The rapid increase in the susceptibilities of the GdMnO₃ nanoparticles corresponded to ferromagnetic ordering similar to that displayed by LaMnO₃ nanoparticles,³⁸ where the LaMnO₃ bulk crystal exhibits an A-type antiferromagnetic ordering below T_N , similar to the GdMnO₃ bulk crystal. The pronounced increase in both the FC and ZFC susceptibilities at approximately 40 K because of the ferromagnetic-like behavior did not occur in particle with sizes below 14 nm. GdMnO₃ nanoparticles with a particle size less than $S_{m2}(\text{Gd}) = 14.0$ nm exhibited pronounced changes in their crystal lattice parameters. A pronounced magnetic irreversibility between FC and ZFC susceptibilities was observed below $T_{\text{irr}} = 61$ K. T_{irr} varied with particle size (upper panel, Fig. 4(e)). T_{irr} decreased rapidly at $S_{m1}(\text{Gd}) = 20.1$ nm and remained constant at $T_{\text{irr}} = 55$ K in the 14–18 nm range. Thereafter, T_{irr} decreased monotonically below $S_{m2}(\text{Gd})$. The abrupt changes in T_{irr} at $S_{m1}(\text{Gd})$ and $S_{m2}(\text{Gd})$ were consistent with the crystal lattice parameters of the GdMnO₃ nanoparticles at both $S_{c1}(\text{Gd}) = 19.5$ nm and $S_{c2}(\text{Gd}) = 13.9$ nm.

The AC susceptibility of the GdMnO₃ nanoparticles was measured in the frequency range of 1–1000 Hz. Both χ' and χ'' increased below approximately 40 K and peaked at the blocking temperature T_B . The GdMnO₃ nanoparticles exhibited relaxation phenomena owing to superparamagnetic behavior, similar to the DyMnO₃ and TbMnO₃ nanoparticles. Figure 4(f) shows the temperature dependence of the AC susceptibility at 100 Hz for a particle size of 19.7 nm. T_B at 100 Hz exhibited a size dependence similar to that of T_{irr} as shown in middle panel of Fig. 4(e). T_B was essentially constant above $S_{m1}(\text{Gd})$, decreased rapidly at $S_{m1}(\text{Gd})$, remained constant between 14 and 18 nm, and then decreased monotonically below $S_{m2}(\text{Gd})$. Figure 4(g) shows the magnetization curve of GdMnO₃ nanoparticles with a particle size of 17.3 nm at 15 K. A hysteresis loop owing to superparamagnetic behavior was observed. H_c at 15 K decreased rapidly at a particle size of approximately $S_{m1}(\text{Gd})$. As particle size decreased further, H_c remained constant between 14 and 18 nm, then decreased

below $S_{m2}(\text{Gd})$. As shown in bottom panel of Fig. 4(e), the size dependence of H_c was similar to that of T_{irr} and T_B . The size dependence of the magnetic properties of the GdMnO_3 nanoparticles exhibited a similar tendency to those of the TbMnO_3 nanoparticles.

EuMnO₃

The lattice constants and orthorhombic distortion of the EuMnO_3 nanoparticles depended on the particle size, as shown in Fig. 5(a). The lattice constant a did not exhibit a significant change below 21 nm. As the particle size decreased, the lattice constant b increased significantly above $S_{c1}(\text{Eu}) = 19.7$ nm, then exhibited a moderate increase between approximately 14 and 20 nm. Below $S_{c2}(\text{Eu}) = 14.8$ nm, b increased rapidly at $S_{c2}(\text{Eu})$ and exhibited a monotonical increase with decreasing particle size. In contrast, the lattice constant c remained constant above $S_{c2}(\text{Eu})$, decreased rapidly at $S_{c2}(\text{Eu})$, then decreased slightly with a further decrease in particle size. The unit cell volume did not vary with the particle size similar to other three nanoparticles, which suggests that the distortion of unit cell of all the nanoparticles was enhanced with decreasing particle size. The EuMnO_3 nanoparticles had a Jahn–Teller distorted orthorhombic structure. The orthorhombic distortion b/a increased with decreasing particle size below approximately $S_{c2}(\text{Eu})$; however, b/a remained constant above approximately $S_{c2}(\text{Eu})$. Figure 5(b) shows the size dependence of the bond lengths of the MnO_6 octahedra of the EuMnO_3 nanoparticles. The bond lengths Mn–O1, M–O2(S), and Mn–O2(L) exhibited pronounced changes at both $S_{c1}(\text{Eu})$ and $S_{c2}(\text{Eu})$. As the particle size decreased, the Mn–O1 bond length decreased, while the Mn–O2(S) and Mn–O(L) bond lengths increased. These results indicate that the MnO_6 octahedra expanded along the ab -plane and contracted along the c -axis with decreasing particle size, that is, tensile strain occurred, similar to the TbMnO_3 nanoparticles. Figure 5(c) shows the size dependence of the Mn–O–Mn bond angles for the EuMnO_3 nanoparticles. The two bond angles, Mn–O1–Mn and Mn–O2–Mn, were both 146.45° above $S_{c2}(\text{Eu})$, but exhibited a pronounced change at approximately $S_{c2}(\text{Eu})$. The Mn–O1–Mn bond angle began to decrease at $S_{c2}(\text{Eu})$ and

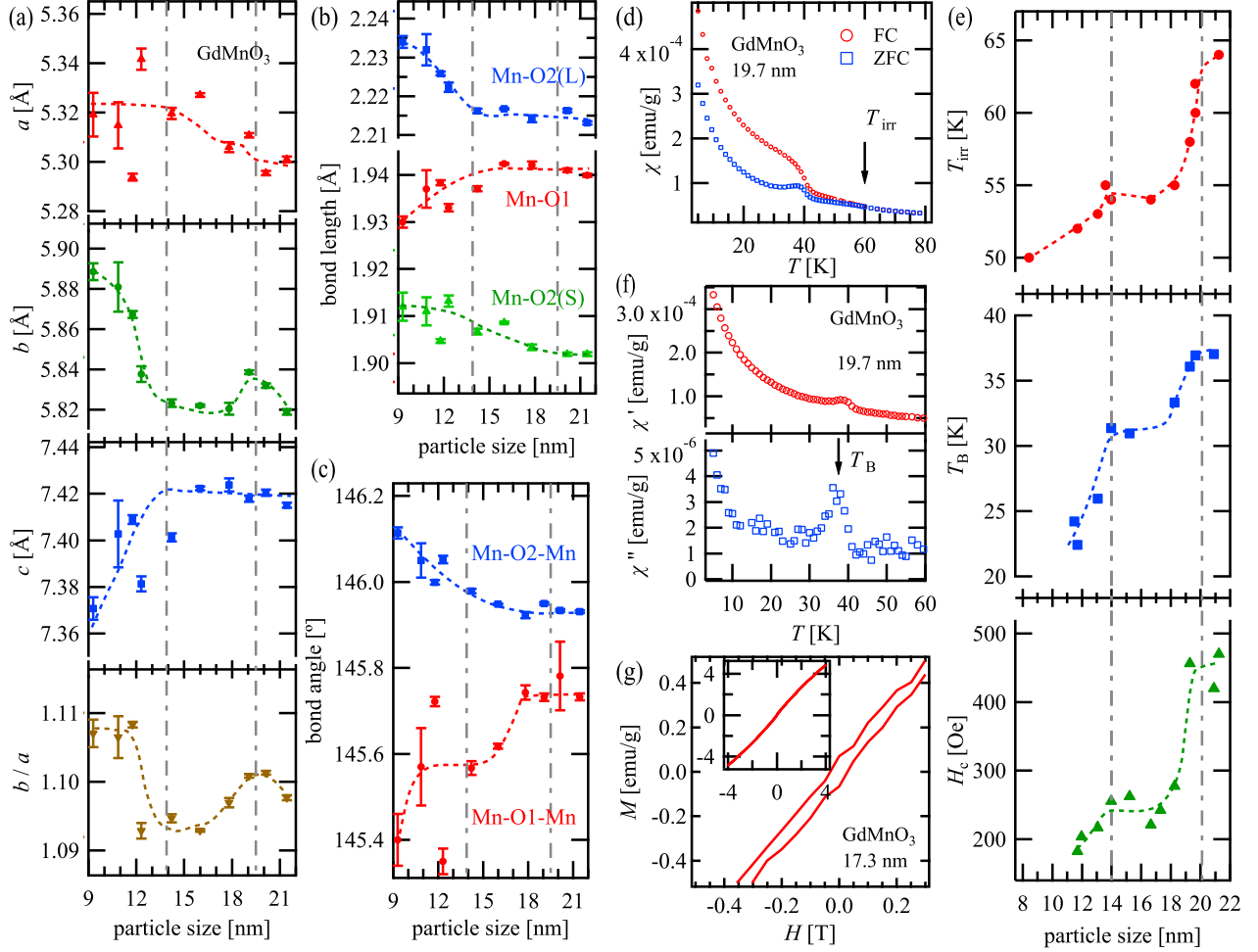


Figure 4: Particle size dependence of (a) lattice constants a , b , c , and b/a , (b) calculated Mn–O bond lengths, and (c) Mn–O–Mn bond angles of the GdMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{c1}(\text{Gd}) = 19.5$ nm and $S_{c2}(\text{Gd}) = 13.9$ nm. (d) Temperature dependence of DC magnetic susceptibilities of GdMnO₃ nanoparticles with a particle size of 19.7 nm in an external magnetic field of 100 Oe under FC and ZFC conditions. Arrow indicates the T_{irr} . (e) Particle size dependences of T_{irr} , T_B , and H_c of the GdMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{m1}(\text{Gd}) = 20.1$ nm and $S_{m2}(\text{Gd}) = 14.0$ nm. (f) Temperature dependence of χ' and χ'' of GdMnO₃ nanoparticles with a particle size of 19.7 nm at a frequency of 100 Hz in a zero DC field. Arrow indicates the T_B . (g) Magnetization curve up to 4 T of GdMnO₃ nanoparticles with a particle size of 17.3 nm at 15 K.

asymptotically approached 146.15° , while the Mn–O2–Mn bond angle increased rapidly at $S_{c2}(\text{Eu})$ and was essentially constant at 146.6° below 13 nm. The values of the two bond angles intersected at approximately 14 nm.

Figure 5(d) shows temperature dependence of the DC susceptibility of EuMnO_3 nanoparticles with a particle size of 15.4 nm. Both the FC and ZFC susceptibilities increased below approximately 40 K, which was attributed to the antiferromagnetic ordering of Mn magnetic moments in the nanoparticles. The temperature corresponded to $T_N(\text{Mn}) \sim 50$ K for EuMnO_3 bulk crystal.^{8,13,14,17,22} Both FC and ZFC susceptibilities increased monotonically owing to the paramagnetic susceptibility of Eu_2O_3 . A pronounced magnetic irreversibility between FC and ZFC susceptibilities was observed below $T_{\text{irr}} = 54$ K. The ZFC susceptibility exhibited a hump at approximately 30 K, which corresponded to the T_B obtained by AC susceptibility (Fig. 5(f)). For particle sizes larger than 15 nm, the EuMnO_3 nanoparticles exhibited ferromagnetic ordering behavior at approximately 40 K, similar to the GdMnO_3 nanoparticles. At particle size less than $S_m(\text{Eu}) = 15.3$ nm, the crystal lattice parameters of the EuMnO_3 nanoparticles exhibited pronounced changes and differed significantly from those above $S_{c2}(\text{Eu}) = 14.8$ nm. T_{irr} decrease rapidly below $S_m(\text{Eu})$, but remained almost constant above $S_m(\text{Eu})$ (upper panel, Fig. 5(e)). The size dependence of T_{irr} was similar to that of b/a . The AC susceptibility of the EuMnO_3 nanoparticles was determined in the frequency range of 1–1000 Hz. Both χ' and χ'' increased below approximately 40 K and peaked at the blocking temperature T_B . The EuMnO_3 nanoparticles exhibited relaxation phenomena consistent with superparamagnetic behavior. Figure 5(f) shows the temperature dependence of the AC susceptibility at 100 Hz for EuMnO_3 nanoparticles with a size of 15.4 nm. T_B decreased rapidly at approximately $S_m(\text{Eu})$ and remained essentially constant below approximately 14 nm (middle panel, Fig. 5(e)). This size dependence was similar to that of the T_{irr} of the EuMnO_3 nanoparticles. The magnetization curve of EuMnO_3 nanoparticles with a particle size of 15.5 nm exhibited a hysteresis loop owing to superparamagnetism at 15 K (Fig. 5(g)). The magnetization increased rapidly at around H_c , which is different

from the behavior of the DyMnO₃, TbMnO₃, and GdMnO₃ nanoparticles. In addition, the H_c of EuMnO₃ nanoparticles was more than double that of the other three nanoparticles. These results suggest that the difference in the magnetization curves is attributable to the magnetic phase of the bulk crystal at low temperatures, where the lowest magnetic ordering state of EuMnO₃ and GdMnO₃ bulk crystals is the A-type antiferromagnetic state. H_c at 15 K varied with particle size as shown in the bottom panel of Fig. 5(e). As the particle size decreased, H_c remained essentially constant above $S_m(\text{Eu})$, rapidly decreased at $S_m(\text{Eu})$, then remained constant below 14 nm. The size dependence of H_c was similar to that of T_{irr} and T_B . The size dependences of magnetic properties of EuMnO₃ nanoparticles displayed similar behavior to those of TbMnO₃ and GdMnO₃.

Discussion

The dependence of the lattice constants, bond angles, and bond lengths on the lanthanoid ionic radii for particles with a size of 10 nm was determined for each nanoparticle. Figure 6 shows the lattice constants, bond lengths, and bond angles as a function of ionic radius. The lattice constants a and b , and the ratio of b/a , decreased with decreasing ionic radius, while the lattice constant c exhibited a minimum at 1.10 Å for Tb. The trends in the lattice constants and the deformation of MnO₆ octahedra of the EuMnO₃ and TbMnO₃ nanoparticles were qualitatively the same as those of the bulk crystals. The lattice constants b , c , b/a , and bond lengths of the DyMnO₃ nanoparticles were significantly different from those of the other three compounds. The reduction in orthorhombic distortion with decreasing ionic radius was the opposite behavior to that of the bulk crystals. The difference in orthorhombic distortion between the nanoparticles and bulk crystals is significant. The changes in the crystal lattice parameters of nanoparticles with changing ionic radius were larger than those of the bulk crystals, indicating that the nanoparticles were more sensitive to changes in ionic radius than bulk crystals.

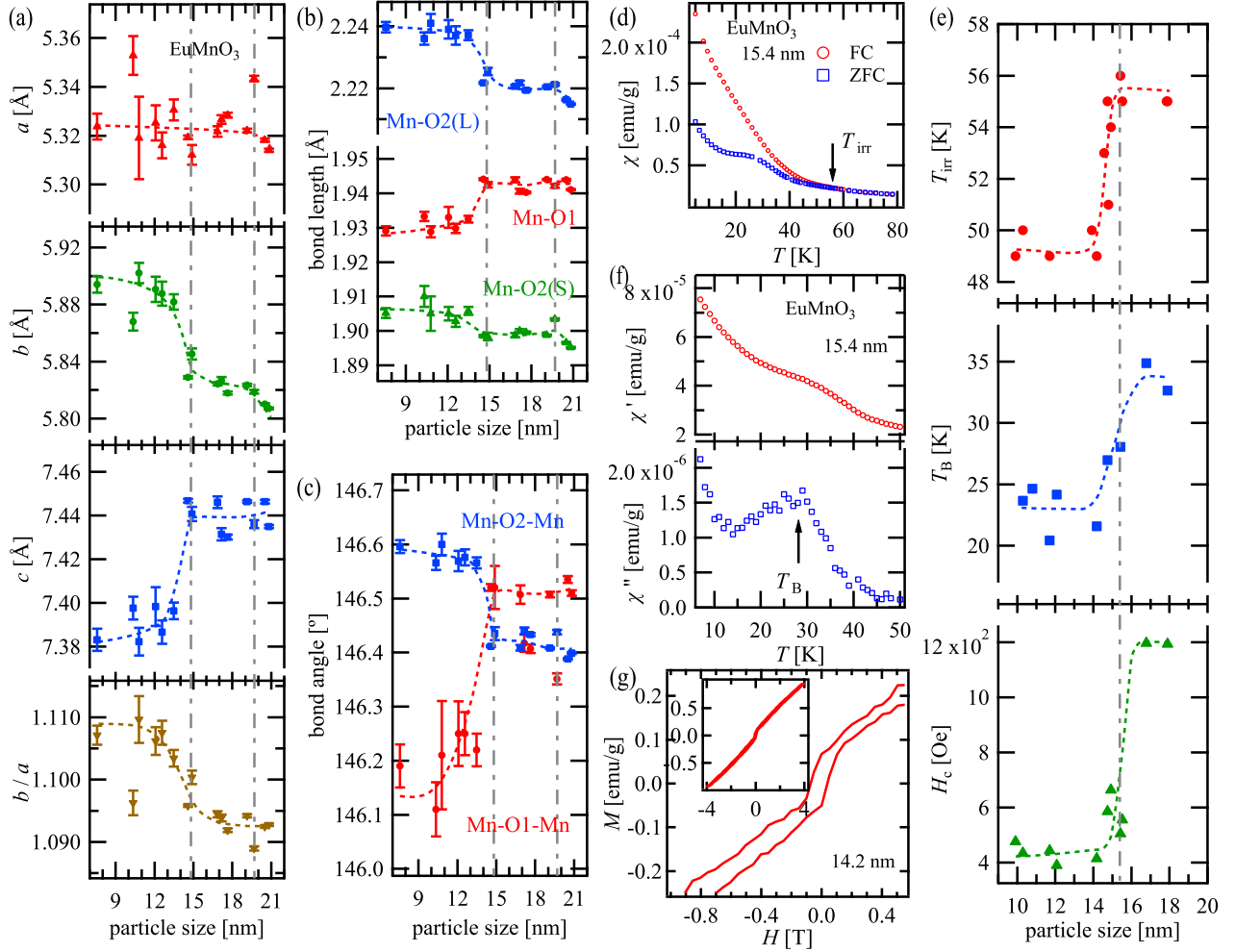


Figure 5: Particle size dependence of (a) lattice constants a , b , c , and b/a , (b) calculated Mn–O bond lengths, and (c) Mn–O–Mn bond angles (c) of the EuMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{c1}(\text{Eu}) = 19.7$ nm and $S_{c2}(\text{Eu}) = 14.8$ nm. (d) Temperature dependence of DC magnetic susceptibilities of EuMnO₃ nanoparticles with a particle size of 15.4 nm in an external magnetic field of 100 Oe under FC and ZFC conditions. Arrow indicates the T_{irr} . (e) Particle size dependences of T_{irr} , T_{B} , and H_{c} of the EuMnO₃ nanoparticles. Vertical dashed lines indicate the characteristic size, $S_{\text{m}}(\text{Eu}) = 15.3$ nm. (f) Temperature dependence of χ' and χ'' of EuMnO₃ nanoparticles with a particle size of 15.4 nm at a frequency of 100 Hz in a zero DC field. Arrow indicates the T_{B} . (g) Magnetization curve up to 4 T of EuMnO₃ nanoparticles with particle size of 14.2 nm at 15 K.

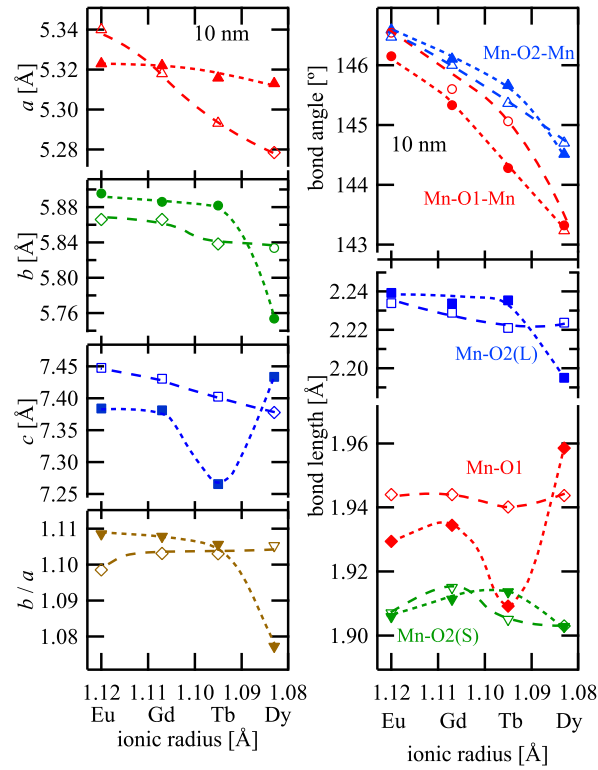


Figure 6: Lattice constants, Mn–O bond lengths, and Mn–O–Mn bond angles of nanoparticles with a particle size of 10 nm (solid symbols) and the bulk crystals (open symbols) as a function of the ionic radii of the lanthanoid ions. The values for the nanoparticles were extracted from their lattice parameters shown in Figs. 2–5.

The correlation between magnetic properties and crystal structures was discussed in detail. The crystal lattice parameters (lattice constants, bond angles, and bond lengths) and magnetic properties (T_{irr} , T_{B} , and H_c) exhibited pronounced changes below the equivalent characteristic particle sizes, S_c and S_m . The RMnO_3 bulk crystals displayed a pronounced magnetic irreversibility between FC and ZFC susceptibilities below the incommensurate antiferromagnetic transition temperature $T_{\text{N}}(\text{Mn})$.²² This suggests that the observed T_{irr} of the RMnO_3 nanoparticles corresponded to $T_{\text{N}}(\text{Mn})$. The change in T_{irr} corresponding to $T_{\text{N}}(\text{Mn})$ was qualitatively consistent with changes in the crystal lattice parameters. The size dependence of the orthorhombic distortion, Mn–O bond length, and Mn–O–Mn bond angles exhibited opposite tendencies for DyMnO_3 and the other three compounds. For TbMnO_3 , GdMnO_3 , and EuMnO_3 nanoparticles, the Mn–O1 decreased and the Mn–O2(L) and Mn–O2(S) increased with decreasing particle size below S_c , whereas those of DyMnO_3 nanoparticles exhibited opposite size dependence. That is, the MnO_6 octahedra of the EuMnO_3 , GdMnO_3 , and TbMnO_3 nanoparticles expanded along the ab -plane and contracted along the c -axis (tensile strain), whereas those of the DyMnO_3 nanoparticles compressed along the ab -plane and expanded along the c -axis (compressive strain), as shown by schematics in Fig. 8. As particle size decreased, the tensile and compress strain of the MnO_6 octahedra were enhanced below S_c . The results imply that the modulation of orthorhombic distortion, that is, Jahn–Teller distortion, of the nanoparticles was accompanied by changes in magnetic interactions as described later. Therefore, the sized dependence of T_{irr} , T_{B} , and H_c of DyMnO_3 nanoparticles exhibited opposite tendencies of those of the other three nanoparticles as well.

EuMnO_3 , GdMnO_3 , and TbMnO_3 nanoparticles with the tensile strain exhibited a higher $T_{\text{N}}(\text{Mn})$ than the corresponding bulk crystals above S_{c2} . Figure 7 shows the relationship between the orthorhombic distortion b/a , particle size, and lanthanoid ionic radius. The S_m occurred along the boundary of $b/a = 1.10$, except for $S_{m2}(\text{Dy}) = 8.2$ nm of the DyMnO_3 nanoparticles, regardless of the type of strain. This behavior suggests that changes in the

orthorhombic distortion determine the characteristic sizes of magnetic properties. The study of the LaMnO_3 film with epitaxial strain revealed a strong correlation between lattice strain and magnetic interactions.^{28,31,33,36,56,57} Under high tensile strain, the $x^2 - y^2$ orbital strengthened the double exchange interaction to stabilize the ferromagnetic ordering in the MnO_2 plane, while the double exchange interaction between the MnO_2 planes reduced because of the negligible occupation of the $3z^2 - 1$ orbital, which stabilized the A-AFM ordering. In contrast, under high compressive strain, the higher occupancy of the $3z^2 - 1$ orbital led to a ferromagnetic coupling between the MnO_2 planes, while the reduced $x^2 - y^2$ occupancy induced antiferromagnetic ordering in the MnO_2 plane, stabilizing the C-type magnetic configuration. In addition, the theoretical study of magnetic exchange interactions in RMnO_3 revealed changes in the next-neighbor and next-nearest-neighbor interactions and magnetic phase diagram as a function of distortion of MnO_6 octahedra.^{5,27,29,30,58} These results show that the changes in the magnetic interactions of the EuMnO_3 , GdMnO_3 , and TbMnO_3 nanoparticles are due to tensile strain, which led to a strengthening of the double exchange interaction, resulting in the stabilization of the A-type antiferromagnetic state and an increase in $T_N(\text{Mn})$ compared to that of the bulk crystal above S_{c2} . Below S_{c2} , the magnetic properties of the EuMnO_3 and GdMnO_3 nanoparticles did not exhibit significant contribution of ferromagnetic coupling, while the crystal lattice parameters were similar to those of the bulk crystals with smaller ionic radii. Therefore, below $S_m(\text{Eu})$ and $S_{m2}(\text{Gd})$, the magnetic state of the EuMnO_3 and GdMnO_3 nanoparticles change from an A-AFM ordered state to a cycloidal spin ordered state. In contrast, it is believed that the C-type or E-type antiferromagnetic state is stabilized in the DyMnO_3 nanoparticles, which displayed compressive strain. In addition, the Mn–O–Mn bond angles and Mn–O bond lengths of the DyMnO_3 nanoparticles with a particle size of 10 nm were similar to those of ErMnO_3 bulk crystals⁷ with an E-type antiferromagnetic state. O. L. Makarova *et al.*⁵⁹ demonstrated that, in a neutron diffraction study of TbMnO_3 bulk crystal under high pressure, the modified structure induces commensurate order and changing the original incommensurate order with

microscopic changes in the exchange interactions. Under high pressure, the E-type commensurate spin structure is stabilized for Mn magnetic moments and change in the phase of the modulation between neighboring Mn chains and a reorientation of the Mn moments along a -axis. The E-type antiferromagnetic state is thought to be stabilized by lattice distortion in DyMnO₃ nanoparticles with particle size of smaller than $S_{m2}(\text{Dy}) = 8.2$ nm.

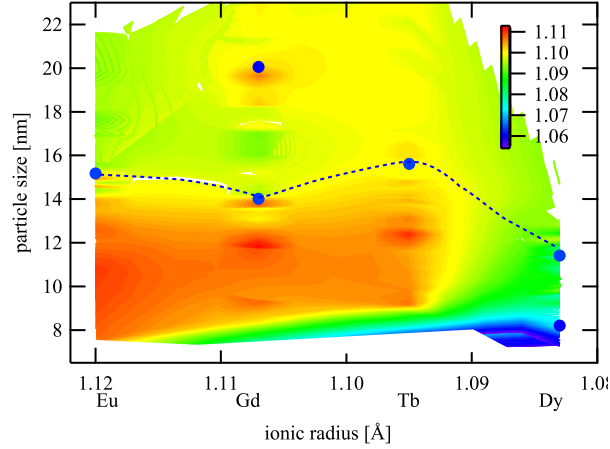


Figure 7: Contour plot of orthorhombic distortion b/a as a function of particle size and ionic radii of lanthanoid ion. The color change from red to blue indicates values of b/a ranging from 1.11 to 1.05. Circle indicate the magnetic characteristic size S_m determined by inflection points in the size dependences of the magnetic properties.

The magnetic phase diagram of the nanoparticles as a function of lanthanoid ionic radius and particle size was obtained from these results (Fig. 8). The value of T_{irr} was represented by a contour plot with change in color from red to blue. The $T_N(\text{Mn})$ of the nanoparticles exhibited a significant reduction below S_{c1} . Both the S_c and S_m changed with lanthanoid ionic radius, while the S_c and S_m of the DyMnO₃ nanoparticles were significantly smaller than those of other three nanoparticles. EuMnO₃ and GdMnO₃ with an A-AFM phase have a phase boundary around S_{m2} (S_{c2}), where their magnetic phase changes to a cycloidal spin ordered state below the S_{c2} and S_{m2} . In contrast, for DyMnO₃, a phase boundary between the cycloid spin and the E-AFM state was observed at approximately S_{m2} (S_{c2}). The two phase transitions were attributed to the distortion of crystal structure owing to the decreasing particle size. The magnetic properties of the nanoparticles essentially followed

the magnetic phase diagram of the bulk crystals; however, the modulation of the structure by Jahn–Teller distortion caused changes in the magnetic interactions, which consequently affected the magnetic properties of the nanoparticles.

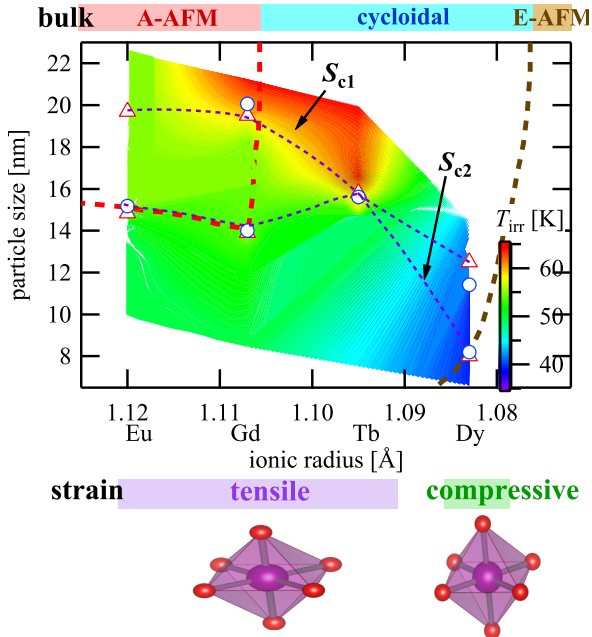


Figure 8: Magnetic phase diagram of the nanoparticles as a function of lanthanoid ionic radius and particle size at the lowest temperature. The magnetic phases of the bulk crystal at the lowest temperature is listed at the top of figure. The value of T_{irr} (i.e. $T_N(Mn)$) of the nanoparticles is represented by the color of the contour plot. Circles and triangles show the characteristic sizes of the magnetic properties (S_m) and that of the crystal structure (S_c), respectively, which indicate inflection points in the size dependence of magnetic properties and crystal lattice parameters, as shown in Figs. 2–5. The dashed line shows the phase boundaries between the A-AFM and the cycloid spin states, and between the cycloid spin and the E-AFM states. The nanoparticles with an A-AFM state exhibited a ferromagnetic-like behavior in DC susceptibilities. The type of strain experienced by the MnO_6 octahedra in the nanoparticles is listed and schematics of the MnO_6 octahedra with tensile and compressive strain were drawn at the bottom of the phase diagram.

Conclusion

We synthesized $RMnO_3$ ($R = Eu, Gd, Tb, \text{ and } Dy$) nanoparticles with particle sizes ranging from 6.5 to 23 nm. Subsequently, we investigated their crystal structures and magnetic

properties. The nanoparticles exhibited a strong correlation between crystal structure and magnetic properties, which depended on the particle size. Significant changes in the crystal lattice parameters at the characteristic sizes resulted in pronounced changes in the magnetic properties of the nanoparticles. The characteristic sizes depended on the lanthanoid ionic radius. The magnetic properties of all the nanoparticles correlated with the orthorhombic distortion (*i.e.*, Jahn–Teller distortion). The characteristic sizes of magnetic properties corresponded to the magnitude of the orthorhombic distortion $b/a = 1.10$, regardless of ionic radius. In addition, the size effects on the crystal structure and magnetic properties of the nanoparticles differed depending on the ionic radius of the lanthanoid. EuMnO_3 , GdMnO_3 , and TbMnO_3 nanoparticles exhibited tensile strain, whereas DyMnO_3 nanoparticles exhibited compressive strain. The magnetic properties of the DyMnO_3 exhibited different size dependences to those of the other nanoparticles. As particle size decreased, the values of the crystal lattice parameters of the nanoparticles were equivalent to those of bulk crystals with smaller ionic radii, resulting in a shift of the magnetic phase diagram to that of bulk crystals with smaller ionic radii, particularly in particles smaller than the characteristic size. The magnetic properties of the nanoparticles essentially followed the magnetic phase diagram of the bulk crystals, except for changes caused by modification of the crystal structure. Future work will focus on calculating the magnetic interactions based on the nanoparticle crystal structure to understand the relationship between magnetic properties, particle size, and lanthanoid ionic radii.

Acknowledgement

This work was supported by a Grant-in-Aid for Young Scientists (B) (No. 25870999) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan and funding from Fukuoka University (Grant No.205003). The synchrotron radiation experiments were performed using the BL-8B beamline located at the Photon Factory (Proposal No. 2013G523,

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TOC Graphic

