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Tuning the Neel Temperature of Hexagonal Ferrites by Structural Distortion

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To tune the magnetic properties of hexagonal ferrites, a family of magnetoelectric multiferroic materials, by atomic-scale structural engineering, we studied the effect of structural distortion on the magnetic ordering temperature (T_N) in these materials. Using the symmetry analysis, we show that unlike most antiferromagnetic rare-earth transition-metal perovskites, a larger structural distortion leads to a higher T_N in hexagonal ferrites and manganites, because the K_3 structural distortion induces the three-dimensional magnetic ordering, which is forbidden in the undistorted structure by symmetry. We also revealed a near-linear relation between T_N and the tolerance factor and a power-law relation between T_N and the K_3 distortion amplitude. Following the analysis, a record-high T_N (185 K) among hexagonal ferrites was predicted in hexagonal $ScFeO_3$ and experimentally verified in epitaxially stabilized films. These results add to the paradigm of spin-lattice coupling in antiferromagnetic oxides and suggests further tunability of hexagonal ferrites if more lattice distortion can be achieved.

Spin-lattice couplings have a significant impact on magnetic properties. In antiferromagnetic (AFM) orthorhombic $RTMO_3$ (o-$RTMO_3$) for example, where R stands for rare earth, Y, or Sc, and TM stands for transition metal, a larger orthorhombic distortion from the cubic perovskite structure correlates with a lower Neel temperature (T_N) , which may be understood as the reduction of the AFM super-exchange interactions caused by the smaller TM-O-TM bond angles due to the orthorhombic distortions[1, 2].

The effect of spin-lattice couplings may be employed to tune the magnetic properties. Here we focus on increasing the T_N of hexagonal RFeO$_3$, a family of multiferroics materials that are promising candidates for applications because of their spontaneous electric and magnetic polarizations, and potential magnetoelectric effects due to the coupling between the ferroelectric and the magnetic orders [3, 4]. For widespread applications, it is important to increase the T_N of h-RFeO$_3$ [5], by, e.g. atomic-scale structural engineering based on the spin-lattice couplings.

On the other hand, in h-RFeO$_3$, T_N increases with the lattice distortion, which is a puzzling trend opposite to that in the AFM o-$RTMO_3$[see Fig. S1][6]. Previously, Disseler et al. discovered a correlation between T_N and lattice constants in h-RMnO$_3$ and h-RFeO$_3$ [7]. The higher T_N for smaller R has been attributed to closer Fe-Fe (or Mn-Mn) distances [7, 8]. This understanding is worth revisiting, since it cannot explain that in AFM o-$RTMO_3$, the smaller lattice constants do bring the TM atoms closer, but the reduced TM-O-TM bond angles actually decreases the AFM exchange interactions and T_N. Hence, there should be a distinct mechanism of magnetic ordering and spin-lattice coupling in h-RMnO$_3$ and h-RFeO$_3$. Elucidating this mechanism will not only provide guidance in increasing T_N of h-RFeO$_3$, but also add to the paradigms of spin-lattice coupling in AFM oxides.

In this work, we examine the role of the structural distortion in the magnetic ordering in h-RMnO$_3$ and h-RFeO$_3$. A symmetry analysis shows that the three-dimensional magnetic ordering is forbidden in the undistorted structure by symmetry, but can be induced by the K_3 distortion with a power-law relation between T_N and K_3 magnitude. Based on these revelations, we have predicted a record-high T_N in h-RFeO$_3$ when R=Sc and experimentally confirmed it in epitaxially stabilized films.

Hexagonal $ScFeO_3$ (001) and $YbFeO_3$ (001) films (5×5 mm^2 and 10×10 mm^2 surface area, 70-200 nm thick) have been grown on Al_2O_3 (001) and yttrium stabilized zirconia (YSZ) (111) respectively using pulsed laser (248 nm) deposition in a 5 mTorr oxygen environment, at 750 °C with a laser fluence of about 1.5 J/cm^2 and a repetition rate of 2 Hz [9]. The film growth was monitored using the reflection high-energy electron diffraction (RHEED). The structural and magnetic properties have been studied using x-ray diffraction and spectroscopy, magnetometry

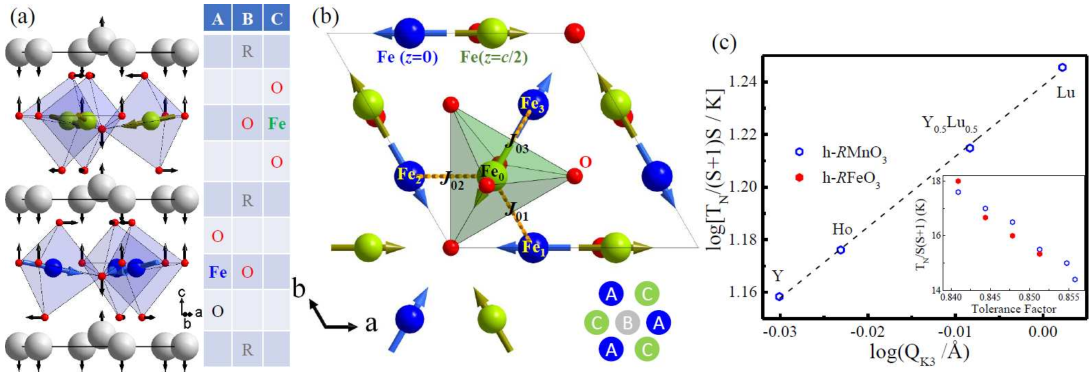

FIG. 1. (Color online) (a) Atomic structure of h-RFeO$_3$ depicted by a hexagonal unit cell. The arrows through the Fe atoms indicate the spins. The arrows from the atoms indicate the atomic displacements of the K$_3$ lattice distortion. The table indicates the hexagonal stacking. (b) The geometric arrangement of Fe atoms in the z=0 and z=c/2 layers. The arrows through the Fe atoms indicate the spins. The atom Fe$_0$ is highlighted by its FeO$_5$ trigonal bipyramid to depict the local symmetry. (c) logT_N/[S(S+1)] as a function of log(Q_{K_3}). Inset: T_N/[S(S+1)] as a function of the tolerance factor. The dashed line is a linear fit to the data. The data are from the literature (see text).

and neutron diffraction. X-ray diffraction experiments, including $\theta/2\theta$ scan, ϕ scan, and reciprocal space mapping were carried out using a Rigaku D/Max-B diffractometer with Co-Kα radiation (1.793 Åwave length) and a Rigaku SmartLab diffractometer with Cu-K radiation (1.5406 Å). X-ray absorption spectroscopy (including x-ray linear dichroism) with a 20° incident angle was studied at beamline 4-ID-C at the Advanced Photon Source at Argonne National Laboratory. Neutron diffraction experiments were carried out at beamline CORELLI at the Spallation Neutron Source (SNS) and HB3A four-circle diffractometer (FCD) at the High Flux Reactor (HFIR) with a thermal neutron wavelength of 1.546 Å, in the Oak Ridge National Laboratory. Temperature and magnetic-field dependence of the magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer with the field along the film normal direction.

The crystal structure of isomorphic hexagonal RMnO$_3$ and RFeO$_3$ (h-RMnO$_3$ and h-RFeO$_3$) has a P6$_3$cm symmetry, consisting of alternating FeO (or MnO) and RO$_2$ layers [Fig. 1(a)]. AFM orders occur in h-RMnO$_3$ and h-RFeO$_3$ below about 70-140 K with spins in the FeO (or MnO) layers forming 120-degree structures [7, 10–13]. Below about 1000 K, ferroelectricity in h-RMnO$_3$ and h-RFeO$_3$ is induced by a lattice distortion (K$_3$) [Fig. 1(a)] which tilts the FeO$_5$ (or MnO$_5$) local environment, shifts the R atoms along the c axis, and trimerizes the unit cell, with a sizable electric polarization ($P \approx 10\mu$C/cm^2) [14–17]. In addition, hexagonal RFeO$_3$ exhibits a weak ferromagnetism [7, 11, 15, 16, 18, 19] [Fig. 1(a)] due to the canting Fe spins.

Magnetic ordering relies on the underlying exchange interactions. In h-RFeO$_3$ and h-RMnO$_3$, although the exchange interactions within the FeO (or MnO) layers are strong, the inter-layer exchange interactions are weakened by the layered structure and hexagonal stacking. Using h-RFeO$_3$ as an example, Fig. 1(b) shows the arrangement of the Fe atoms and their spins in two neighboring FeO layers. The Fe atoms are on the hexagonal A and C sites in the two layers respectively. One Fe atom (Fe$_0$) in the $z = c/2$ layer is highlighted by its tilted FeO$_5$ trigonal bipyramid. The interlayer nearest-neighbor exchange energy for Fe$_0$ is $E_{inter} = \sum_{i=1}^{3} J_{0i}\vec{S}_0 \cdot \vec{S}_i$, where S_i is the spin on Fe$_i$, and J_{0i} is the exchange interaction coefficient between Fe$_0$ and Fe$_i$. When there is no lattice distortion, the local symmetry of Fe$_0$ is C$_{3v}$, leading to $J_{01} = J_{02} = J_{03}$ and $E_{inter} = 0$ because $\sum_{i=1}^{3} \vec{S}_i$=0. In other words, the interlayer exchange interactions are canceled; the spin alignment between the two layers is lost. Therefore, the three-dimensional magnetic ordering is forbidden in the undistorted P6$_3$/mmc structure by symmetry.

On the other hand, the K$_3$ lattice distortion [Fig. 1(a)] reduces the symmetry to C$_S$, making $J_{03} \neq J_{02} = J_{01}$. Consequently, nonzero lattice distortion leads to the three-dimensional magnetic ordering because $E_{inter} = (J_{01} - J_{03})S(S+1) \neq 0$ [20]. Since the inter-layer exchange interaction is the bottleneck of the three-dimensional magnetic ordering, one has $T_N \propto E_{inter} = (J_{01} - J_{03})S(S+1)$. The dependence of T_N on the K$_3$ distortion then hinges on the relation between $J_{01} - J_{03}$ and the magnitude of K$_3$ (Q_{K3}). Previously, Das et al. analyzed the relation between $J_{01} - J_{03}$ and Q_{K3} [3]. Expanding J_{01} and J_{03} with respect to Q_{K3} around $Q_{K3} = 0$, the odd terms are expected to be zero due to the symmetry at Q_{K3}=0, leaving $J_{01} - J_{03} \propto a_2 Q_{K3}^2 + a_4 Q_{K3}^4$, where a_2 and a_4 are coefficients. In Fig. 1(c), we plot the log{T_N/[S(S+1)]} as a function of log(Q_{K3}) of h-RMnO$_3$ measured using the neutron diffraction from the literature [21, 22] [see Fig. S2][6], where spin S is 2 for Mn. The data appear to fall on a straight line, in-

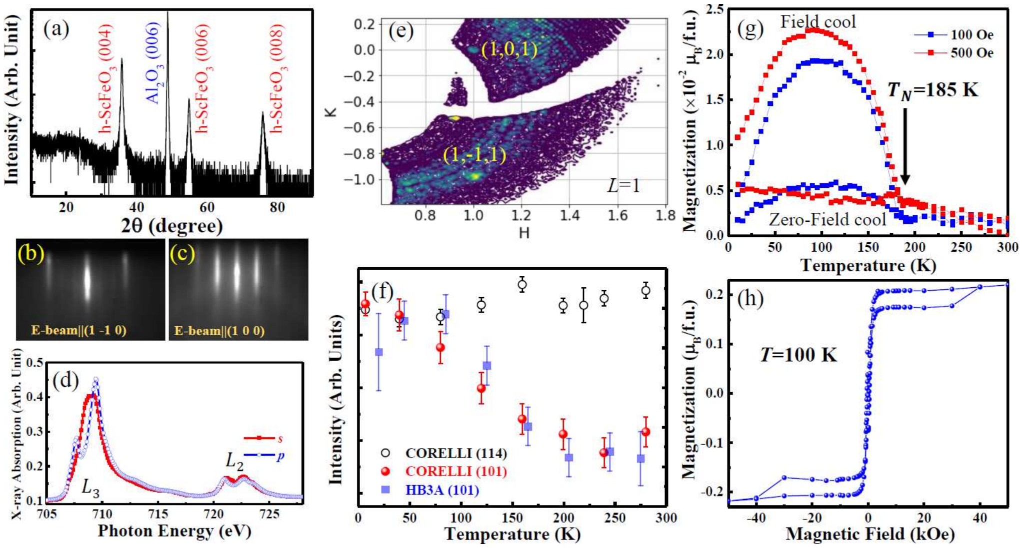

FIG. 2. (Color online) Structural and magnetic characterizations of h-ScFeO$_3$(001)/Al$_2$O$_3$ films. (a) $\theta/2\theta$ x-ray (1.789 Å) diffraction. (b) and (c) are the RHEED diffraction patterns measured when the electron beam are along the (1-10) and (100) directions respectively. (d) X-ray absorption spectra measured at the Fe L edges using s (in plane) and p (out of plane) linearly polarized x-ray beams. (e) A slice of the reciprocal space of h-ScFeO$_3$ at L=1 measured using neutron diffraction at CORELLI (see text). (f) Temperature dependence of the neutron diffraction intensities of the (101) and (114) peaks measured at CORELLI and HB3A. (g) Temperature dependence of the magnetization per formula unit (f.u.) measured during warming after field-cool (10 kOe) and zero-field-cool using 100 Oe and 500 Oe. (h) Magnetization-field hysteresis loop measured at 100 K. The magnetic field is along the film normal direction.

dicating a power-law relation $T_N/[S(S+1)] \propto Q_{K_3}^n$; a fit shows $n = 2.7\pm0.05$. Given that the tilt of FeO$_5$ and MnO$_5$ caused by the K$_3$ distortion is on the order of several degrees which is not so small [10, 21, 22], both the $a_2Q_{K3}^2$ and the $a_4Q_{K3}^4$ terms could play a role, resulting $2 < n < 4$.

It is challenging to predict the T_N using the direct dependence of T_N on the K$_3$ distortion however, because the K$_3$ distortion, which involves the displacement of oxygen atoms, is difficult to measure precisely. Tolerance factor $t = (r_R + r_O)/[(r_{TM} + r_O)\sqrt{2}]$ where r_R, r_{TM}, and r_O are atomic radius of R, TM and oxygen, is a good measure of lattice distortion from the cubic perovskite structure in o-RTMO$_3$. It could also be used to gauge the structural distortion in h-RFeO$_3$ and h-RMnO$_3$, because a smaller R atom is expected to reduce the in-plane lattice constant, which needs to be accommodated by a larger K$_3$ distortion to reduce the distances between Fe (or Mn) atoms within the FeO (or MnO) layers. In other words, smaller t is expected to lead to larger T_N, which is consistent with the data from the literature [Fig. 1(c) inset and Fig. S2] [6, 12, 21, 22], where a linear correlation between $T_N/[S(S+1)]$ and t in h-RFeO$_3$ and h-RMnO$_3$ is observed (S is 2 and 2.5 for Mn and Fe respectively).

Following the trend in Fig. 1(c), a smaller R, corresponding to a smaller t, will lead to a higher T_N in h-RFeO$_3$ and h-RMnO$_3$. Since Sc has much smaller atomic radius than that of the rare earth and Y [23], T_N in h-ScFeO$_3$ is expected to be higher than that of other h-RFeO$_3$. To verify the prediction, we studied the magnetic ordering temperature in h-ScFeO$_3$. ScFeO$_3$ naturally crystallizes in bixbyite structure in bulk; high pressure growth of ScFeO$_3$ results in a corundum structure [24]. Previous studies show that partially substituting Lu with Sc in LuFeO$_3$ may stabilize the hexagonal structure[7, 8, 25]. However, the stabilization of pure ScFeO$_3$ in the P6$_3$cm structure has never been reported. In this study, we have successfully grown h-ScFeO$_3$ epitaxial films on Al$_2$O$_3$ (001) substrates. The crystal structure and epitaxial relations of the h-ScFeO$_3$ films were characterized using x-ray diffraction. As shown in Fig. 2(a), the $\theta/2\theta$ scan shows a typical pattern of the P6$_3$cm structure with the epitaxial relation: h-ScFeO$_3$ (001) ∥ Al2O3 (001). The ϕ scan [see Fig. S3][6] demonstrates the six-fold rotation symmetry and the in-plane epitaxial relation: h-ScFeO$_3$ (100) ∥ Al$_2$O$_3$ (100). The RHEED patterns [Fig. 2(b) and (c)], which are signatures of the h-RFeO$_3$ structure, indicate a flat surface. The FeO$_5$ trigonal bipyramid configuration is confirmed by the similarity between the x-ray linear dichroism spectroscopy of h-ScFeO$_3$ [Fig. 2(d)] and those of h-LuFeO$_3$ and h-YbFeO$_3$ observed previously [9, 26–28]. From the x-ray reciprocal space mapping [see Fig. S3][6], the lattice constants of h-ScFeO$_3$ were determined: $a = 5.742$ Åand $c = 11.690$ Å, smaller than the values of other h-RFeO$_3$[29–31], suggesting a larger lattice distortion[32].

T_N of h-ScFeO$_3$ was measured by the neutron diffraction experiments at CORELLI in addition to that of h-

$YbFeO_3$. Using a wide wavelength-band neutron beam and a two-dimensional detector at CORELLI, a three-dimensional portion of the reciprocal space [using the Miller indices (H, K, L) as the coordinates] can be measured without rotating the sample [see Fig. S4-S7][6]. The (101) and (114) diffraction peaks, were mapped out in the three-dimensional reciprocal space. As shown in Fig. 2(e), the two magnetic Bragg diffraction peaks (101) and (1-11), which are equivalent because of the six-fold rotational symmetry along the c axis, were observed. The (101) Bragg peak is forbidden for the nuclear diffraction due to the crystal structure symmetry of h-$R$$FeO_3$ (space group $P6_3cm$), but it is allowed for magnetic diffraction [10]. The observation of the (101) peak confirms the magnetic ordering in h-$R$$FeO_3$, as previously shown in h-$LuFeO_3$ and h-$R$$MnO_3$ [7, 10, 13]. The temperature dependence of the (101) peak intensity suggests a transition at about 200 K, which is corroborated by the measurements at HB3A [Fig. 2(f)]. In contrast, the intensity of the (114) peak, which mainly comes from the nuclear scattering, shows an insignificant temperature dependence. As shown in Fig. 2(g), a similar transition temperature is observed in the temperature dependence of the magnetization measured using a SQUID magnetometer on warming, after cooling the sample in a 10 kOe magnetic field (field cool or FC) and after cooling in a zero magnetic field (zero-field cool or ZFC). The FC and ZFC curves diverge at around 185 K, giving a more precise determination of T_N.

As predicted, h-$ScFeO_3$ shows a high T_N among all h-$R$$MnO_3$ and h-$R$$FeO_3$, as shown in Fig. 3(a), where our measurement on h-$YbFeO_3$ and data in the literature are also included [See Fig. S3 and S4] [6, 7, 10, 12–16, 18, 22]; the measured T_N of h-$ScFeO_3$ is slightly lower than the value predicted by extrapolating the linear relation between T_N and t, which is also true for h-$ScMnO_3$ [10]. The reduction of magnetization at low temperature in Fig. 2(g) hints a possible spin reorientation at about 100 K in h-$ScFeO_3$. However, the temperature dependence of the (101) peak intensity in Fig. 2(f) indicates that spin reorientation in h-$ScFeO_3$ may not be significant enough to change the spin structure from A_2 to A_1 [7].

Finally, we discuss the effect of lattice distortion on the canting of Fe moments, which is responsible for the net magnetization M_{Fe} along the c axis. The M_{Fe} in h-$ScFeO_3$ can be inferred from the magnetometry data. As shown in Fig. 2(h), the $M-H$ curve shows a soft and a hard component, corresponding to two steps at $H \approx 0$ and $H \approx 30$ kOe respectively. This two-component feature has been observed in both h-$LuFeO_3$ and h-$YbFeO_3$ films [19, 26]. The jump of magnetization at the higher field corresponds to the intrinsic coercivity of the h-$R$$FeO_3$, while the jump at low field corresponds to the unavoidable structural boundaries in film samples of h-$R$$FeO_3$ that create uncompensated spins. From the 30-kOe jump, we found that $M_{Fe} = 0.015 \pm 0.002$ μ_B/Fe in h-$ScFeO_3$, which is smaller than that of h-$LuFeO_3$ and h-$YbFeO_3$ [19, 26], as shown in Fig. 3(b). This result is counter-intuitive, because a large K_3 distortion, corresponding to a larger tilt angle of the FeO_5 would seemingly generate a larger canting angle of the Fe moments (θ_{cant}). However, θ_{cant} results from a competition between the exchange interaction and the Dzyaloshinskii-Moriya (DM) interaction [33–35]. Relation between the canting angle (θ_{cant}) of the Fe moments, tilt angle of the FeO_5 (γ_{tilt}), lattice constant in the basal plane (a), and the intralayer exchange interaction coefficient J can be derived as $\theta_{cant} \propto a^2\gamma_{tilt}/J$ [See Fig. S8][6]. Although h-$ScFeO_3$ is expected to have a larger γ_{tilt} and smaller J, a is also smaller. Hence, the size of θ_{cant} cannot be simply linked to the amplitude of γ_{tilt}. If the effect of a dominates, M_{Fe} would decrease for smaller R, which is what we found in our previous first-principle calculations [32].

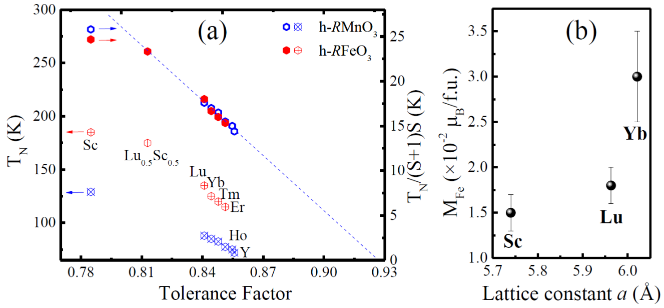

FIG. 3. (Color online) (a) The dependence of T_N and T_N/S(S+1) on the tolerance factor. The dashed line is a guide to the eye. (b) The magnetization from the canting of Fe spins (M_{Fe}) as a function of the in-plane lattice constant. Except for h-$YbFeO_3$ and h-$ScFeO_3$ in (a) and h-$ScFeO_3$ in (b), the data are from the literature (see text).

In conclusion, using symmetry analysis, we showed that the three-dimensional magnetic ordering in h-$R$$MnO_3$ and h-$R$$FeO_3$ are forbidden in undistorted structures by symmetry, but can be induced by the structural distortions. We also showed that dependence of T_N on structural distortions manifests as a near-linear relation with the tolerance factor and a possible power law with Q_{K3}, suggesting a higher T_N in h-$ScFeO_3$ with respect to other hexagonal ferrites studied so far, which was realized in this work in epitaxially stabilized films. In addition to indicating that the multiferroic ordering in h-$R$$FeO_3$ and h-$R$$MnO_3$ may be further enhanced with larger lattice distortions, these results also establish a paradigm of structural origin of magnetic ordering and spin-lattice coupling in AFM oxides.

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