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Influence of magnetic on ferroelectric ordering in LuMnO_3

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We have studied the influence of antiferromagnetic ordering on the local dielectric moments of the MnO_5 and LuO_7 polyhedra by measuring neutron powder-diffraction patterns of LuMnO_3 at temperatures near T_N . We show that the coupling is weak, because the magnetic exchange coupling is predominantly in the ab plane of the MnO_5 trigonal bipyramids, and the electric dipole moments, originating in the LuO_7 polyhedra, are oriented along the hexagonal c axis. Anomalies in the dielectric properties near T_N are thus caused by the geometric constraints between the MnO_5 and the LuO_7 polyhedra.

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Multiferroic magnetoelectrics are materials that combine ferroelectric and magnetic ordering. These materials are of fundamental and technological interest as coupling between different order parameters enables multiple ways to interact with these materials, such as pressure, electric, and magnetic fields. In most ionic materials the Coulomb repulsion between ions results in centered (i.e., nonpolar) crystal structures. Conventionally, only for ions with lone pairs and non-magnetic ions, sizable dipole moments can exist.¹ For few extraordinary materials magnetic and electric dipolar order can coexist. The coupling between the magnetic and electric order must originate either from magnetic ordering affecting the electric dipoles via striction, or the displacements at the dipolar ordering changing the magnetic order. These interactions depend intimately on the coupling between the magnetic and electric building blocks of the three-dimensional (3D) crystal structure.

Recently the distorted perovskites BiMnO_3 ,^{2,3} BiFeO_3 ,⁴ and also TbMnO_3 (Ref. 5) have been shown to combine magnetic and ferroelectric order. Another class of materials that combine magnetic and electric dipolar order are the hexagonal manganites with general formula AMnO_3 , which are antiferromagnetic and ferroelectric. Hexagonal AMnO_3 (h-AMnO_3), in particularly YMnO_3 , has attracted interest for applications, for instance in nonvolatile memory devices⁶ or as ferroelectric gate electrode.⁷ Progress has also been made in the understanding of the origin of the ferroelectric properties⁸ and the coupling between the ferroelectric and antiferromagnetic order.^{9,10} Fiebig *et al.* have shown that below the antiferromagnetic ordering temperature T_N , the ferroelectric domain walls, or twin boundaries, always act as antiferromagnetic (AFM) domain walls as well. Furthermore, AFM domain walls also exist in the bulk of the ferroelectric (FE) domains. This suggests not that the orientations of the FE order and the AFM order are linked, but that the transition from one FE orientation to the other forces or accommodates a transition in the AFM order.^{9,11} The coupling between electric and magnetic ordering requires detailed knowledge of the crystal structure. Unfortunately, there are conflicting results in the literature on the atomic positions when comparing neutron powder diffraction (NPD) and single-crystal x-ray diffraction (SXD). Neutron-diffraction results show anomalous variations in the bond lengths^{12,13} with temperature.

The crystal structure of h-AMnO_3 has two major differences compared with the perovskite structure. First, the Mn^{3+} ions (high spin $3d^4$) are located at the center of a trigonal bipyramid instead of an octahedron. The resulting crystal field splits the $3d$ levels in three energy levels, in order of increasing energy: xz and yz , xy and $x^2 - y^2$, and $3z^2 - r^2$. Consequently, $\text{Mn}^{3+} 3d^4$ has no partially filled degenerate levels and is therefore *not* Jahn-Teller active.¹⁴ Density of states calculations show some mixing between the Mn $3d$ and O $2p$ levels.⁸ Second, the MnO_5 polyhedra are corner linked in sheets, separated by a layer of A ions. This contrasts the MnO_6 3D network in perovskite manganites. As a result, h-AMnO_3 is pseudolayered, reflected for instance in the Mn spin being in the xy plane even above T_N .¹⁴⁻¹⁶

To explain how the AFM and FE orders are linked, we studied the temperature dependence of the crystal structure of LuMnO_3 around the antiferromagnetic ordering temperature $T_N = 88$ K which is much lower than the FE ordering temperature, $T > 573$ K.¹⁷ Furthermore, we discuss the relation between the ionic radius of the A ion r_A and the crystal structure.

I. TEMPERATURE DEPENDENCE OF LuMnO_3

LuMnO_3 has been prepared with standard solid-state synthesis. Neutron powder diffraction has been performed at the Polaris time-of-flight instrument at ISIS. The data have been refined using the GSAS package,¹⁸ including isotropic temperature factors. Sample quality has been checked by measuring a neutron powder-diffraction pattern at ambient temperature. No reflections from impurity phases could be detected and the refined structure was in good agreement with single-crystal data.¹⁹ Temperature-dependent measurements, between 40 and 120 K, were performed at the same beam line, using a standard Orange cryostat. Typically quality factors for the refinements are $\chi^2 = 2.963$, $R(F^2) = 4.79\%$, and $R_p = 1.74\%$ for 47 variables.

Figure 1(a) shows the crystal structure of hexagonal manganite. It consists of nonconnected layers of MnO_5 trigonal bipyramids that are corner linked by in-plane oxygen ions O3 and O4. The apical oxygen ions O1 and O2 form two close-packed layers separated by a distorted layer of A^{3+}

FIG. 1. (a) View perpendicular to the c axis of the crystal structure of AMnO_3 . The trigonal bipyramids represent the MnO_5 and the circles the A ions. This sketch highlights the stacking of the MnO_5 layers. (b) Sketch of the $z=0$ layer of LuMnO_3 , showing the two inequivalent Mn-O bonds. Mn, O3, and O4 are shown as gray diamonds, closed and open circles, respectively. Mn-O3 and Mn-O4 bonds are indicated by solid and dashed lines, respectively. The thin line outlines the unit cell.

ions. In Fig. 1(b) a cross section through the $z \sim 0$ plane is given. The oxygen positions O1 and O2 are similar to the Mn positions, albeit with $z \sim \pm \frac{1}{6}$. The A site ions A1 (A2) are located exactly above the positions O3 (O4). In the next Mn ions containing layer ($z \sim \frac{1}{2}$), the Mn, O1, and O2 positions are located at x [Fig. 1(b)].

The space group of hexagonal LuMnO_3 in the ferroelectric phase is $P6_3cm$. The hexagonal unit cell contains six formula units; there are seven inequivalent positions with ten refinable parameters. Since all symmetry elements are parallel to the c axis, all z coordinates are “free.” For practical reasons, we have chosen to fix $z_{\text{Mn}}=0$. The atomic positions are listed in Table I.

In Fig. 2 the lattice parameters have been plotted versus the temperature. The a axis decreases with decreasing temperature at a rate of $8 \times 10^{-6} \text{ K}^{-1}$. The lattice parameter c is nearly independent of T , although a small discontinuity in c ($\sim 0.001 \text{ \AA}$) can be seen near T_N . SXD data at 295 K,¹⁹ $a = 6.038(1) \text{ \AA}$, are in agreement with the extrapolation of Fig. 2. Thermal expansion data have been reported on powdered YMnO_3 samples at higher temperatures.²⁰ The expansion coefficient $\sim 7 \times 10^{-7} \text{ K}^{-1}$ obtained from these data is one order of magnitude smaller than the value we find.

Compared to the paraelectric centrosymmetric structure,

TABLE I. The atomic positions of hexagonal manganite AMnO_3 . m is the multiplicity of the site.

Atom	$x(-)$	$y(-)$	$z(-)$	m
A1	0	0	$z_{A1} \sim \frac{1}{4}$	2
A2	$\frac{1}{3}$	$\frac{2}{3}$	$z_{A2} \sim \frac{1}{4}$	4
Mn	$x_{\text{Mn}} \sim \frac{1}{3}$	0	$z_{\text{Mn}} = 0$	6
O1	$x_{O1} \sim \frac{1}{3}$	0	$z_{O1} \sim \frac{1}{6}$	6
O2	$x_{O2} \sim \frac{1}{3}$	0	$z_{O2} \sim -\frac{1}{6}$	6
O3	0	0	$z_{O3} \sim 0$	2
O4	$\frac{1}{3}$	$\frac{2}{3}$	$z_{O4} \sim 0$	4

FIG. 2. Temperature dependence of lattice parameters of LuMnO_3 .

the MnO_5 bipyramids are rotated along an axis through the Mn ion and parallel to the O4-O4 bond. This buckling moves the O3 (O4) ions up (down) along the z axis and moves the O1 (O2) ions at $(\sim \frac{1}{3}, 0, \pm \frac{1}{6})$ along the x axis. Figure 3 shows the T dependence of the apical oxygen positions O1 and O2 of LuMnO_3 , plotted as the absolute difference with their paraelectric position at $x = \frac{1}{3}$. The x coordinate of these oxygen ions is a measure for the buckling of the MnO_5 trigonal bipyramid, but small changes in x_{O1} and x_{O2} do not have a significant effect on the Mn-O1 and Mn-O2 bond lengths. The linear fits suggest that the buckling might reduce with decreasing T , but the slope and its error are the same order of magnitude. The angle of the line through O1 and O2 with the xy plane changes from 84.7° at $T=120 \text{ K}$ to 84.8° at $T=40 \text{ K}$. We conclude that there is hardly any change in the buckling of the MnO_5 layers with temperature.

The out-of-plane A1-O3 and A2-O4 bond lengths are calculated using

$$A1-O3 = c(z_{A1} - z_{O3}) \quad (1)$$

and

FIG. 3. Temperature dependence of the x coordinate of the apical oxygen positions of LuMnO_3 . The absolute difference with the paraelectric position at $x = \frac{1}{3}$ is plotted. Triangles and squares depict O1 and O2, respectively. The dashed lines are least-squares linear fits.

FIG. 4. Sketch of the relation of the length of the two inequivalent in-plane Mn-O bonds, showing the effect of an in-plane Mn displacement. Symbols are the same as in Fig. 1(b). Thin dashed lines are lines parallel to the unit-cell axes at $\frac{1}{3}a$ intervals to guide the eye.

$$A2-O4 = c(z_{A2} - z_{O4}). \quad (2)$$

Since the temperature dependence of lattice parameter c is negligible, the T dependence of these bond lengths depend only on the T dependence of the z coordinates. We found in our refinements that the T dependencies of these z coordinates have strong positive correlations. Any changes in any of the z coordinates is mimicked closely by its companion. Therefore, the Lu1-O3 and Lu2-O4 bond lengths show no dependence on temperature.

Each Mn ion has two Mn-O4 bonds and one Mn-O3 bond as is shown in Fig. 1(b). The in-plane Mn-O3 bond length is given by

$$\text{Mn-O3} = \sqrt{a^2 x_{\text{Mn}}^2 + c^2 z_{\text{O3}}^2} \sim a x_{\text{Mn}}, \quad (3)$$

where in the approximation the effect of $z_{\text{O3}} \neq 0$ can be ignored, since the partial derivatives are proportional to the magnitude of x_{Mn} and z_{O3} . The other in-plane bond length is given by

$$\text{Mn-O4} = \sqrt{a^2 \{(x_{\text{Mn}} - 1/2)^2 + (\sqrt{3}/6)^2\} + c^2 z_{\text{O4}}^2}. \quad (4)$$

Mn-O3 and Mn-O4 depend both on lattice parameter a and on the x coordinate of the Mn ion. We can write $x_{\text{Mn}} = \frac{1}{3} - \delta$, where δ is the displacement of the Mn ion along the x axis from its paraelectric position at $(\frac{1}{3}, 0, 0)$, see Fig. 4.

Then, applying $x_{\text{Mn}} = \frac{1}{3} - \delta$, Mn-O3 equals $a(\frac{1}{3} - \delta)$ and Mn-O4 equals

$$\text{Mn-O4} = \sqrt{a^2 \{(1/6 + \delta)^2 + 1/12\} + c^2 z_{\text{O4}}^2} \sim a(1/3 + 1/2\delta), \quad (5)$$

where the effect of $z_{\text{O4}} \neq 0$ and δ^2 is negligible.

From these approximate formulas we can see that a change, of $-\delta a$, in the length of the Mn-O3 bond length,

FIG. 5. Temperature dependence of in-plane Mn-O bond lengths around $T_N = 88$ K.

due to a displacement δ of the Mn ion, is always accompanied with a change in the length of the Mn-O4 bond of opposite sign and half the magnitude ($+\frac{1}{2}\delta a$). These in-plane Mn-O bond lengths are plotted against temperature in Fig. 5. Local extrema near T_N are observed with the maximum value for Mn-O3 smaller than the minimum for Mn-O4. Below and above T_N the difference increases between the in-plane bond lengths. However the observed differences are not large, at most 0.041 Å.

The out-of-plane Mn-O bond lengths are given by

$$\text{Mn-O}i = \sqrt{a^2 (x_{\text{Mn}} - x_{\text{O}i})^2 + c^2 z_{\text{O}i}^2} \sim c z_{\text{O}i} \quad (i=1,2), \quad (6)$$

where the x components are neglected in the approximation, since $x_{\text{Mn}} - x_{\text{O}i} \ll z_{\text{O}i}$ ($i=1,2$). The out-of-plane bond lengths also show local extrema near T_N , but the changes are less pronounced than for the in-plane bond lengths. The difference between the inequivalent out-of-plane Mn-O bond lengths is smaller than 0.02 Å for all T .

The out-of-plane bond lengths are much shorter than the in-plane bond lengths, respectively, ~ 1.87 Å and ~ 2.02 Å. This is related to the crystal-field splitting of the Mn 3d orbitals, with the unoccupied $3z^2 - r^2$ orbital in the out-of-plane direction. The antibonding character of the Mn 3d-O 2p interaction elongates the in-plane bond lengths.¹⁴

We note that with SXD,^{19,21-23} it is found that the Mn-O4 bond length is smaller than the Mn-O3 bond length, whereas here we find that Mn-O4 is larger than Mn-O3. However, the difference between the inequivalent in-plane bond lengths is small (< 0.05 Å). The out-of-plane Mn-O bond lengths are in line with the SXD data, and the difference between the inequivalent out-of-plane bond lengths is small (< 0.02 Å) in agreement with the SXD data. Other NPD experiments on the crystal structure of hexagonal manganites in the literature report larger differences between the in-plane or the out-of-plane Mn-O bond lengths. For instance, Katsufuji *et al.* report on LuMnO_3 at 300 K and find out-of-plane bond lengths of 1.98 Å and 1.78 Å.¹³ Muñoz *et al.* find for YMnO_3 at room temperature a difference between in-plane bond lengths $\Delta_{\text{in-plane}}$ of 0.1 Å.¹² Also older structure reports using SXD show large differences between in-plane Mn-O bond lengths or out-of-plane Mn-O bond lengths. Yakel reports $\Delta_{\text{in-plane}} = 0.08$ Å and $\Delta_{\text{out-of-plane}} = 0.09$ Å for LuMnO_3 .²⁴

FIG. 6. Temperature dependence of LuMnO₃ of the local dipole moments from the Lu1 and the Lu2 polyhedra near $T_N = 88$ K. Note that the right axis is reversed.

Isobe reports $\Delta_{\text{in-plane}} = 0.048$ Å and $\Delta_{\text{out-of-plane}} = 0.058$ Å for YbMnO₃ at $T = 295$ K.²⁵ These SXD experiments, however, did not include reflections from all regions of hkl space, which is necessary for SXD on non-centrosymmetric crystals.

In the preceding section, we have discussed the temperature dependence of the bond lengths. Now, we will investigate whether the observed changes have any effect on the local dipole moments and the macroscopic ferroelectric moment. In the remainder of this paper, we will define the local dipole moment associated with a cation site as the distance between the center of gravity of the nearest-neighbor O ions and the cation site.

In Fig. 5 we have shown that the in-plane Mn-O bond lengths show local extrema near T_N , with the difference between them smallest at T_N . This means that also their contribution to the local dipole moments on the Mn site is smallest at T_N . The space-group symmetry relates the local dipole moment created by the small in-plane displacement of the Mn ion to the local dipole moments originating from the other two Mn ions on the same plane in the unit cell. Due to the sixfold screw axis, the local dipole moments are rotated over an angle of 120° with respect to each other. As a result, there cannot be any contribution to the macroscopic ferroelectric moment by the in-plane displacements.

The difference between the out-of-plane Mn-O1 and Mn-O2 bond lengths creates a small local dipole moment < 0.02 Å from the Mn coordination. These local dipole moments are parallel to the c axis and they are not canceled by the crystal symmetry. However larger local dipole moments originate from the Lu1 and Lu2 coordination.⁸ The local dipole moments from the Lu coordination are at least an order of magnitude larger than the ones from the Mn coordination.

The local dipole moments associated with the LuO₈ polyhedra are shown in Fig. 6. The calculation of the center of gravity of the oxygen polyhedra includes the seven ions at ~ 2.4 Å and the one ion at ~ 3.2 Å. Note that the local dipole moments from the Lu2 coordination are antiparallel with the ones from the Lu1 coordination.

From Fig. 6 it is clear that cooling through the Néel transition has no significant influence on the local dipole mo-

FIG. 7. Lattice parameters for hexagonal AMnO₃ as a function of r_A ($A = \text{Lu, Er, Yb, and Y}$) at $T = 295$ K.

ments of LuMnO₃. However, we have shown in Fig. 5 that the local environment around the Mn ions does change. Since the Mn spins are in plane,¹⁴ even above T_N , the magnetic ordering transition at T_N is expected to have the largest effect on the in-plane Mn-O bond lengths. The ferroelectricity on the other hand depends mostly on the out-of-plane Lu-O bond lengths.⁸ Although the oxygen ions involved are the same, O3 and O4, the Mn-O bond lengths change mostly by a displacement δ of the Mn ion along the x axis, whereas the out-of-plane Lu-O bond lengths change because of an opposite movement of the Lu1 (Lu2) and O3 (O4) ions along the c axis. We conclude that there is no significant coupling between the ferroelectric moment of LuMnO₃ and the antiferromagnetic ordering temperature. This is in agreement with the conclusions from Ref. 9.

II. RARE-EARTH IONIC RADIUS

In the second part of this paper we will discuss the influence of the rare-earth ions, by their ionic radius r_A , on the local dipole moments. The data used in this analysis have been taken from Refs. 21 (YMnO₃), 22 (ErMnO₃), 23, (YbMnO₃), and 19 (LuMnO₃).

In Fig. 7, the lattice parameters a and c at $T = 295$ K are plotted against r_A . The values of r_A have been taken from Shannon and Prewitt.²⁶ We observe that with increasing r_A the lattice parameters increase. From LuMnO₃ to YMnO₃ lattice parameter a increases linearly, with a total increase of $\sim 1.7\%$. Lattice parameter c has a smaller increase of about 0.5% . We can clearly see from these data that the influence of r_A is larger on the in-plane lattice parameter than on the out-of-plane lattice parameter.

The crystal structure can be regarded as a stacking of hexagonally packed oxygen layers and A ion layers. One expects that O-O bond lengths are ~ 2.8 Å, ($r_O = 1.4$ Å) and A-O bond lengths are ~ 2.4 Å, ($r_A \sim 1.05$ Å). For instance, in LaMnO₃ the average O-O and La-O bond length (in the fcc-like close-packed OO and AO layers) is ~ 2.7 Å ($r_{\text{La}} = 1.2$ Å). The observed values for the interplane A-O1 and A-O2 bond lengths in hexagonal AMnO₃ (not shown here) are consistent with the expected values. Likewise the observed increase with increasing r_A of the A-O1 and A-O2

FIG. 8. Out-of-plane A-O bond lengths as a function of r_A .

bond lengths (on average 1.6%) is in excellent agreement with the increase of a with r_A .

We note that in hexagonal AMnO_3 both the hexagonally packed O layers at $z \approx \pm \frac{1}{6}$ and the MnO layers at $z \approx 0$ have intraplane O-O distances of ~ 3.6 Å. Similarly, the in-plane A-A distances are also ~ 3.6 Å. This is in contrast with the intraplane bond lengths in pseudocubic perovskites. These anomalously large “bond lengths” can be understood by considering the way the layers are stacked. Starting at the MnO layer at $z=0$, the stacking order is MnO-O-A-O-MnO with layer spacings of about $\frac{2}{12}c$, $\frac{1}{12}c$, $\frac{1}{12}c$, and $\frac{2}{12}c$. One can visualize that the A ion layer (at $z \approx \frac{1}{4}$) is clamped between the close-packed O layer (at $z \approx \frac{1}{6}$ and $z \approx \frac{1}{3}$). This will enlarge the spacing of the O and A ions in those layers. The larger the radius of the A ions, the more the O ions are pushed apart. However, the O-O bond length between the two neighboring O layers at $z \approx \frac{1}{6}$ and $z \approx \frac{1}{3}$ is reduced to ~ 2.8 Å, which corresponds to the value one expects ($2r_{\text{O}}$). In this simple model, changes in r_A can be accommodated completely by a change in the in-plane bond lengths and lattice parameter a .

The decreasing distances in the ab plane with decreasing r_A should also be reflected in the in-plane Mn-O bond lengths. The change of $\sim 1.6\%$ is in good agreement with the observed change of a with decreasing r_A . Possible changes in the out-of-plane Mn-O bonds are too small to be resolved within the scatter and error bars of the experiments. However, we observe a distinct relation between the A1-O3 and A2-O4 bond lengths and r_A , as shown in Fig. 8.

The short A1-O3 and A2-O4 bonds increase by 3.6% and 2.3% with increasing r_A . Therefore, the “extra long” out-of-plane A-O bond lengths should decrease with increasing r_A , since c is almost constant. Consequently, the dipoles of the A polyhedra decrease with increasing r_A . The increase in dipole moment from Y ($r_A = 1.075$ Å) to Lu ($r_A = 1.032$ Å) is about 10% as shown in Fig. 9.

The transition from the paraelectric centrosymmetric to the ferroelectric noncentrosymmetric structure consists of two atomic displacements. The first is the buckling of the MnO_5 network, displacing O1 and O2 in the xy plane and O3 and O4 along the z axis. The second is the alternate displacement of the A1 and A2 ions along the z axis away from the $z = \frac{1}{4}$ mirror plane.⁸ Formally, it has been shown

FIG. 9. Dipole moments of the A1 and A2 polyhedra of h-AMnO_3 . Note that the A2 dipole is plotted on a reverse scale. Both dipoles tend to increase with decreasing r_A .

that these atomic displacements consist of two modes. First, there is a K_3 mode, which changes the symmetry but can inherently not create a macroscopic ferroelectric moment. Second, there is a Γ mode, which does not change the space-group symmetry, but introduces the macroscopic ferroelectricity.^{27,28} To see which of these two modes is influenced more by chemical substitution, we have plotted in Fig. 10 the z coordinates of the A1 and the O3 sites. Both z coordinates of A1 and O3 are about $0.02c$ away from their centrosymmetric equilibrium position. Clearly, the changes in the z coordinate of O3 site are much larger than the changes in the z coordinate of the A1 site. The data in Fig. 10 therefore show that upon chemical substitution of the A site the buckling increases with decreasing r_A , which results in an increase of the deviation from the centrosymmetric positions. The displacement of the A ions from the mirror plane is more or less constant. This is supported by the changes in the x coordinates of the O1 and O2 sites. Both are about $0.025a$ off their symmetric position at $x = \frac{1}{3}$ and this deviation becomes larger by $\sim 10\%$ from $R = \text{Y}$ to $R = \text{Lu}$. We conclude that the change in the local dipole moment is caused by atomic rearrangement and not by expansion of the unit cell.

FIG. 10. Fractional z coordinates of the A1 and O3 position ($0, 0, z$) vs r_A . Clearly the z coordinates deviate more from their equilibrium positions, respectively $z = \frac{1}{4}$ and $z = 0$, with decreasing r_A .

The ferroelectric transition temperatures for these materials have been reported, but different authors report completely different values or only “higher than” values. Furthermore, there are indications that the ferroelectric ordering temperature and the non-centrosymmetric to centrosymmetric phase transition temperature are different by several hundred degrees.^{27,29} It is therefore not possible to relate the magnitude of the local dipole moments or the total dipole moment to the ferroelectric ordering temperature.

The effect of changing r_A can be summarized as follows. A decrease in r_A will reduce the “normal” A-O bond lengths. This will change the in-plane Mn-O bond lengths too. These changes are accompanied by an increased buckling of the MnO₅ bipyramids, parametrized by x_{O1} , x_{O2} , z_{O3} , and z_{O4} . The changes in the oxygen z coordinates induce an increase in the difference between the short and long A1-O3 and A2-O4 bond lengths. This increases the dipole moments from the A1 and A2 coordinations with decreasing r_A . However, the antiparallel coupling between the local di-

pole moments at the A1 and the A2 site prevents a clear effect on the total dipole moment.

In conclusion, the hexagonal AMnO₃ compounds exhibit both antiferromagnetic order and ferroelectric order. The magnetic exchange and spins are confined in the basal plane, whereas the dielectric moments originate predominantly from displacements parallel to the c axis. Consequently, the distortions due to magnetostrictive effects and dipolar ordering are only weakly coupled.

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