Localized or itinerant TiO$_3$ electrons in RTiO$_3$ perovskites

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Abstract

A reinvestigation of nearly stoichiometric RTiO$_3$ samples shows that (1) the transition from ferromagnetic to antiferromagnetic Ti–O–Ti interactions with increasing R$^{3+}$-ion radius $r_{3+}$ occurs at $r_{3+} \approx 1.11$ Å where orthorhombic ($Pbnm$) RMO$_3$ perovskites universally change structure from a cooperative rotation of undistorted to distorted MO$_6^{1/2}$ octahedra about the orthorhombic $b$-axis, (2) the size of polaronic holes decreases progressively with $r_{3+}$ from about ten Ti sites in LaTiO$_3$ to small polarons in GdTiO$_3$, (3) the strength of the R–O–Ti interactions increases with the spin of the R$^{3+}$ ion in the ferromagnetic compounds, (4) the saturation magnetization of the ferromagnetic TiO$_3$ array at 5 K and the Curie temperature $T_C$ both increase with decreasing $r_{3+}$ where the R$^{3+}$ ions have no spin, and (5) there is no evidence of ‘cluster-glass’ behaviour where there is no variance of the R$^{3+}$-ion radii. The cooperative Jahn–Teller orbital ordering and small-polaron behaviour of the ferrimagnetic and ferromagnetic compounds would favour localized Ti-3d electrons. However, the lack of saturation to 1 $\mu_B$/Ti of the ferromagnetic TiO$_3$ array in the absence of a spin on the R$^{3+}$ ion suggests a separation of an orbitally ordered ferromagnetic phase and an orbitally disordered paramagnetic phase.

1. Introduction

All members of the RTiO$_3$ perovskite family (R = rare-earth or Y) have the Ti(IV)/Ti(III) and Ti(III)/Ti(II) redox couples separated by an energy gap that increases from 0.2 eV in antiferromagnetic LaTiO$_3$ to near 1.2 eV in ferromagnetic YTiO$_3$ [1–3]. The heavier rare-earth ions Gd–Yb all exhibit a ferromagnetic TiO$_3$ array that couples antiparallel to a ferromagnetic component on the rare-earth array to give a net ferrimagnetism below a Curie temperature $T_C$; the antiferromagnetic R–O–Ti interactions are reported to be weaker than the ferromagnetic Ti–O–Ti interactions [4, 5]. The lighter rare-earth ions Ce–Sm all have an antiferromagnetic

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Titanium oxide (TiO$_3$) array like LaTiO$_3$ below a $T_{N1}$ [6, 7]; the rare-earth moments order independently and antiferromagnetically below a $T_{N2} < T_{N1}$. The Curie temperature $T_C$ decreases with decreasing atomic weight of the R$^{3+}$ ion from Dy to Gd, and $T_{N1}$ increases from Sm to La [2, 8]. The long-range magnetic-ordering temperatures $T_{N1}$ and $T_C$ decrease to below 10 K at the crossover composition Sm$_{0.5}$Gd$_{0.5}$TiO$_3$ where there is no long-range orbital ordering [9].

The ferromagnetism of YTiO$_3$ below $T_C \approx 30$ K is the result of G-type orbital ordering below a $T_{OO} > T_C$ of the $\pi$-bonding $t$ electron into a $yz$ or $zx$ orbital on alternate Ti(III) ions of the TiO$_3$ array [10]; the orbital ordering couples half-filled and empty $\pi$-bonding $t$ orbitals on neighbouring Ti(III) ions to give ferromagnetic superexchange interactions in accordance with the Goodenough–Kanamori rules. However, at antiphase boundaries, $yz$–$yz$ or $zx$–$zx$ interactions between half-filled orbitals introduce an antiferromagnetic coupling across the boundary between ferromagnetic regions, which results in a low remanence [11].

The antiferromagnetic order of LaTiO$_3$ below a $T_{N1} = 140$ K is due to a TiO$_6$ site deformation from cubic to rhombohedral symmetry that stabilizes an $a_1$ orbital oriented along its [111] axis [12, 13]; moreover, the magnitude of the site deformation increases abruptly on cooling through $T_{N1}$. This orbital ordering has no preferred Ti–O–Ti axis and is, therefore, responsible for the G-type antiferromagnetic order found for the lighter R$^{3+}$ ions. Cwik et al [12] also observed that both the magnitude of the site deformation and $T_{N1}$ decrease with the size of the R$^{3+}$ ion in the RTiO$_3$ family; the site deformation, but not its cooperative rotation about the orthorhombic (Pbnm) $b$-axis, essentially disappears in the ferromagnetic compositions having a G-type ordering of the occupied $yz$ and $zx$ orbitals. However, left unresolved is whether orbital order drives the site deformation or the site deformation stabilizes the orbital order.

Here we report a reinvestigation of nearly stoichiometric samples of the RTiO$_3$ family to determine (1) the origin of the site deformations, (2) the evolution with R$^{3+}$-ion radius $r_{3+}$ of the activation energy of polaronic p-type transport in the TiO$_3$ array, (3) how the strength of the R$^{3+}$–O–Ti$^{3+}$ spin–spin interaction changes with the spin of the R$^{3+}$ ion in the ferromagnetic compositions, (4) how the saturation magnetization of the TiO$_3$ array approaches the spin-only value of $1 \mu_B$/Ti in the absence of a moment on the rare-earth ion, and (5) whether the report by Yoshii et al [14] of ‘cluster-glass’ behaviour in the R$_{1-x}$Nd$_x$TiO$_3$ perovskites with R = Ce or Pr is found where there is no variance of the R$^{3+}$-ion radius.

### 2. Experimental details

Polycrystalline samples of RTiO$_3$ (R = rare earth or Y) were prepared by solid-state reaction. Stoichiometric mixtures of R$_2$O$_3$ or Pr$_6$O$_{11}$ or Tb$_4$O$_7$ and Ti$_2$O$_3$ were ground together for each composition; the powders were cold-pressed into pellets, placed into a molybdenum crucible and put into a tube that was then evacuated to $\sim 10^{-6}$ Torr before firing at 1620 °C for 12 h.

A Perkin-Elmer TGA-7 thermogravimetric analyser was used to determine the oxygen content of the samples from the weight gain due to an oxidation of the Ti(III) ions to Ti(IV) on heating to 1000 °C in air. For all samples, the excess oxygen was smaller than 0.4%; they were oxygen-stoichiometric within experimental error.

Powder x-ray diffraction (XRD) patterns were recorded with a Philips PW 1729 powder x-ray diffractometer equipped with a pyrolytic graphite monochromator and Cu Kα radiation (1.540 59 Å); Si was the internal standard. Data were collected in steps of 0.020° over the range $20^\circ \leq \theta \leq 60^\circ$ with a count time of 20 s per step. Peak profiles for the XRD data were fitted with the program JADE. All samples were single-phase to XRD.

Magnetic susceptibility measurements were made with a Quantum Design dc SQUID magnetometer after cooling in zero field (ZFC) or after cooling in a measuring field (FC) of...
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1. Results

All samples of the orthorhombic $Pbnm$ perovskite family RTiO$_3$ were single-phase to XRD. Figure 1 displays the room-temperature variation of unit-cell volumes and lattice parameters with the R$^{3+}$-ion radius $r_{3+}$ as calculated for ninefold oxygen coordination. The lattice parameters also are listed in table 1. The lattice parameter $b$ increases with increasing $r_{3+}$ to GdTiO$_3$, where $r_{3+} = 1.11$ Å; it decreases with a further increase in $r_{3+}$ where $c/a < \sqrt{2}$ is found.

All the RTiO$_3$ samples were p-type semiconductors with a $\rho(T) \sim \exp(E_a/kT)$, where $E_a = \Delta H_m + (\Delta H_f/2)$ is the sum of the motional enthalpy and an enthalpy $\Delta H_f$ of trapping at the cation vacancy that created the mobile holes. Figure 2 shows that an $E_a \geq 0.23$ eV increases little with decreasing $r_{3+}$ on passing from GdTiO$_3$ to LuTiO$_3$ whereas $E_a$ increases sharply with decreasing $r_{3+}$ on passing from LaTiO$_3$ with $E_a = 0.035$ eV to GdTiO$_3$. From thermoelectric-power measurements $\alpha(T)$, we have shown that the mobile holes in LaTiO$_3$ occupy itinerant-electron clusters containing multiple Ti atoms [11], and the data of figure 2 are consistent with a cluster size that decreases progressively to that of a small polaron as $r_{3+}$ decreases. However, the high resistance of the samples with smaller $r_{3+}$ did not permit a good measure of $\alpha(T)$, so we were unable to determine reliably the separate contributions of $\Delta H_m$ and $\Delta H_f$ for samples other than LaTiO$_3$, and therefore their separate evolutions with $r_{3+}$.

The magnetic susceptibilities $1/\chi_m(T)$ and $\chi_m(T)$ for R = La, Pr, Nd, and Sm are shown in figures 3 and 4; data were taken on heating after cooling in zero field (ZFC) and in the measuring field (FC) of $H = 100$ Oe, 1 kOe, or 10 kOe. All samples show a $T_{NI}$ that...
Figure 2. Variation with $r_{3+}$ of the activation energy $E_a$ of the resistivity $\rho(T) \sim \exp(E_a/kT)$ for the p-type RTiO$_3$ perovskites. Inset: $\rho \sim 1/T$ curves for several RTiO$_3$ samples. The straight lines are guides for the eye.

Table 1. Variation with $R$ in RTiO$_3$ of room-temperature lattice parameters.

<table>
<thead>
<tr>
<th>RTiO$_3$</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$V$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>5.633(1)</td>
<td>5.613(2)</td>
<td>7.942(2)</td>
<td>251.1</td>
</tr>
<tr>
<td>Pr</td>
<td>5.555(2)</td>
<td>5.615(1)</td>
<td>7.821(2)</td>
<td>244.0</td>
</tr>
<tr>
<td>Nd</td>
<td>5.524(1)</td>
<td>5.657(1)</td>
<td>7.795(1)</td>
<td>243.6</td>
</tr>
<tr>
<td>Sm</td>
<td>5.467(1)</td>
<td>5.669(1)</td>
<td>7.742(1)</td>
<td>240.0</td>
</tr>
<tr>
<td>Gd</td>
<td>5.402(2)</td>
<td>5.697(2)</td>
<td>7.680(2)</td>
<td>236.4</td>
</tr>
<tr>
<td>Tb</td>
<td>5.384(1)</td>
<td>5.678(1)</td>
<td>7.660(1)</td>
<td>234.2</td>
</tr>
<tr>
<td>Dy</td>
<td>5.363(3)</td>
<td>5.689(2)</td>
<td>7.647(1)</td>
<td>233.3</td>
</tr>
<tr>
<td>Y</td>
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<td>5.688(2)</td>
<td>7.621(1)</td>
<td>231.4</td>
</tr>
<tr>
<td>Ho</td>
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<td>5.689(2)</td>
<td>7.622(1)</td>
<td>231.5</td>
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<tr>
<td>Er</td>
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<td>5.674(3)</td>
<td>7.609(2)</td>
<td>229.7</td>
</tr>
<tr>
<td>Tm</td>
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<td>5.658(1)</td>
<td>7.597(3)</td>
<td>228.0</td>
</tr>
<tr>
<td>Yb</td>
<td>5.291(1)</td>
<td>5.629(1)</td>
<td>7.595(1)</td>
<td>226.0</td>
</tr>
<tr>
<td>Lu</td>
<td>5.275(1)</td>
<td>5.644(1)</td>
<td>7.581(2)</td>
<td>225.7</td>
</tr>
</tbody>
</table>

decreases progressively from 140 K in LaTiO$_3$ to about 120 K in PrTiO$_3$, 110 K in NdTiO$_3$, and 70 K in SmTiO$_3$ as determined by a divergence of the FC and ZFC curves below $T_{N1}$ in $H = 100$ Oe. This divergence is caused by a weak ferromagnetic component due to an antisymmetric exchange contribution $D_{ij} \cdot S_i \times S_j$ with $D_{ij}$ parallel to the $b$ axis, which is associated with a canting of the antiferromagnetically coupled spins of the TiO$_3$ array.

Where the $R^{3+}$ ions have a large moment, these moments dominate the $1/\chi_m(T)$ curves. Nevertheless, a deviation from Curie–Weiss behaviour below a $T_1$ is found for all the heavier $R^{3+}$ ions, figure 5; for these compounds, $T_1$ decreases systematically with decreasing $r_{3+}$ whereas $T_C$ varies irregularly with $r_{3+}$, figure 6. Magnetic parameters are listed in table 2.

Figure 8 shows the $M–H$ hysteresis loops taken at 5 K for the heavier $R^{3+}$ ions.

4. Discussion

In figure 1, the linear increase of $a$ and $c$ and the decrease in $c/a > \sqrt{2}$ with increasing $r_{3+} < 1.11$ Å are consistent with a cooperative rotation of the TiO$_6$ octahedra about
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Figure 3. Inverse molar magnetic susceptibility $1/\chi_m$ taken in $H = 100$ Oe for RTiO$_3$ with $R =$ La, Pr, Nd, and Sm.

Table 2. Variation with R in RTiO$_3$ of magnetic parameters.

<table>
<thead>
<tr>
<th>R</th>
<th>$T_{N1}$ (K)</th>
<th>$T_{N2}$ (K)</th>
<th>$T_C$ (K)</th>
<th>$T_1$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>140</td>
<td>120</td>
<td>82</td>
<td>70</td>
</tr>
<tr>
<td>Pr</td>
<td>120</td>
<td>82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd</td>
<td>110</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sm</td>
<td>70</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd</td>
<td>32</td>
<td>179</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tb</td>
<td>49</td>
<td>170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dy</td>
<td>60</td>
<td>150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>30</td>
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<tr>
<td>Ho</td>
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<td></td>
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</tr>
<tr>
<td>Er</td>
<td>42</td>
<td>120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tm</td>
<td>68</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yb</td>
<td>36</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

the orthorhombic $b$ axis that decreases in magnitude with increasing $r_{3+}$. The transition at $r_{3+} \approx 1.11$ Å is similar to that found by Marezio [17, 18] in the RFeO$_3$ family and has been interpreted [19] to be due to a distortion of the MO$_{6/2}$ octahedra that is superimposed on the cooperative site rotations as a result of R–O interactions that occur where an $r_{3+} > 1.11$ Å
Figure 4. Molar magnetic susceptibility $\chi_m$ for (a) LaTiO$_3$ with $H = 100$ Oe, PrTiO$_3$ with $H = 100$ Oe, 10 kOe; (b) NdTiO$_3$ and (c) SmTiO$_3$ with $H = 100$ Oe, 1 kOe, and 10 kOe. Inset of (a) and (b): derivative of $\chi_m(T)$ for PrTiO$_3$ and NdTiO$_3$. 
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Figure 5. Inverse molar magnetic susceptibility $1/\chi_m$ for RTiO$_3$ (R = Gd–Lu, Y), taken in $H = 100$ Oe. The dashed lines are guides to the eye.

is found. This interpretation is consistent with the observation of Cwik et al. [12] for the TiO$_3$ family. Accordingly, figure 1 shows that the unit-cell volume varies linearly with $r_{3+}$ in accordance with Végard’s law only in the region $r_{3+} < 1.13$ Å where $c/a > \sqrt{2}$ is found; for larger $r_{3+}$, a $c/a \leq \sqrt{2}$ signals that a TiO$_{6/2}$ octahedral-site deformation is superimposed on the rotation, and this deformation results in smaller volumes $V$ for R = Nd, Pr, and La than is predicted by extrapolation of $V$ versus $r_{3+}$ from compounds with a smaller $r_{3+}$.

Since the site deformation has been found to be a general property of RMO$_3$ perovskites with $r_{3+} > 1.11$ Å where there is no orbital order, we may conclude that the site deformation is not driven by the orbital order; it is driven by the $R^{3+}$–O interactions caused by shortening of an R–O bond length in the VO rock-salt (001) planes by the octahedral-site rotation. The site deformations stabilize, in turn, an orbital ordering of the single d electron of a Ti atom into an $a_1$ orbital oriented along a site [111] axis, and the orbital order increases the magnitude of the site deformation. The strongly correlated electrons introduce a localized spin on the Ti$^{3+}$ ions; antiferromagnetic $a_1^{-}$–O–$a_1^+$ interactions between half-filled $a_1$ orbitals below $T_{N1}$ introduce an exchange striction that stabilizes further the orbital order, thereby enhancing the
Figure 6. Transition temperatures $T_1$, $T_C$, $T_{N1}$ and $T_{N2}$ versus $r_{3+}$ for RTiO$_3$. The dotted line is a guide to the eye of the Curie temperature for the RTiO$_3$ compounds without any moment on the R$^{3+}$ ion, i.e. R = Lu and Y. The curve is extrapolated to zero at Sm$_{0.5}$Gd$_{0.5}$TiO$_3$ where there is a crossover from ferromagnetic to antiferromagnetic coupling within the TiO$_3$ array.

site deformation. However, as the initial site deformation is reduced by introduction of a smaller R$^{3+}$ ion, stabilization of the $a_1^1$ configuration is more difficult, and $T_{N1}$ decreases. Where the initial site deformation becomes negligible, the orbital order in the TiO$_3$ array is stabilized by a cooperative Jahn–Teller distortion that minimizes the elastic energy and maximizes the ferromagnetic interactions. Cooperative Jahn–Teller distortions are a characteristic of localized electrons, and their orbital-ordering temperature increases (not shown in figure 6) as the bandwidth of the Ti$^{4+}$/Ti$^{3+}$ redox couple narrows.

The activation energies $E_a$ of figure 2 for the smaller R$^{3+}$ ions (R = Gd–Lu, Y) are typical for small-polaron conduction; those for the larger R$^{3+}$ ions become increasingly smaller from Sm to La. As the transitions from strong to weak electron correlations in a single-valent parent compound is approached from the strong-correlation side, holes introduced into the occupied redox couple (lower Hubbard band) may not be confined to a single cation site, i.e. be self-trapped as a small dielectric polaron. For example, holes introduced into antiferromagnetic La$_2$CuO$_4$ either by Sr substitution for La or by the introduction of interstitial oxide ions form polarons occupying five to six Cu centres in a CuO$_2$ plane [20, 21]. These larger polarons have a smaller motional enthalpy because the oxygen displacements that define the polaron are smaller where the hole population per cation centre within the polaron is reduced [22]. Similarly, stoichiometric LaTiO$_3$ is close to the transition from strong to weak electron correlations, i.e. to the Mott–Hubbard transition, and we have interpreted thermoelectric-power data for p-type LaTiO$_3$ to reflect polaronic conduction with a polaron size approaching ten Ti centres in a 3D matrix [11]. The activation energy $E_a$ for hole transport in LaTiO$_3$ is, therefore, small. In the RTiO$_3$ family, the bandwidth of the RTiO$_3$ couple decreases with decreasing $r_{3+}$, which should reduce the size of the polaron until, below a critical value of $r_{3+}$, it occupies only a single Ti site, i.e. is reduced to a small polaron. As the size of a polaron shrinks, the oxygen displacements that define it become larger, which increases the motional enthalpy $\Delta H_m$. Once the size of the charge carriers is reduced to that of a small polaron, no further reduction in size can occur. Nevertheless, as the bandwidth of the redox energy decreases further, the electron localization becomes greater and $E_a$ continues to increase, but less dramatically. From
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Figure 7. Variation of $T_1$ with the R$^{3+}$-ion spin.

these considerations, we interpret figure 2 to signal a reduction of the polaron size from that found in LaTiO$_3$ to that of a small polaron as $r_{3+}$ decreases between LaTiO$_3$ and GdTiO$_3$. The narrowing of the redox bands is also manifest in an increase in the $(U - W)$ energy gap between the Ti$^{4+}$/Ti$^{3+}$ and Ti$^{3+}$/Ti$^{2+}$ couples (the lower and upper Hubbard bands) from 0.2 eV in LaTiO$_3$ to 1.2 eV in YTiO$_3$ [1, 2].

The $1/\chi_m(T)$ curve for LaTiO$_3$, figure 3, shows a Weiss constant with an anomalously large magnitude ($\theta = -853$ K) as well as too large a $\mu_{\text{eff}} = 2.43 \mu_B$ for normal localized-electron behaviour; it has been accounted for by invoking orbital fluctuations [23], but it is also characteristic of itinerant-electron magnetism at the crossover to strongly correlated electrons. Below $T_{N1}$, the spins of the TiO$_3$ array order antiferromagnetically, but spin canting introduces a weak ferromagnetic component.

The large moments of the R$^{3+}$ ions dominate the $1/\chi_m(T)$ curves for R = Pr, Nd, and Sm. Below $T_{N1}$, only the weak ferromagnetic component of the TiO$_3$ array introduces an R–O–Ti interaction, and the R–O–R interactions are stronger. Therefore, the rare-earth ions order antiferromagnetically below a $T_{N2} < T_{N1}$ [4, 5] where they introduce an additional canted-spin ferromagnetic component that couples to that of the TiO$_3$ array [24]. From the peak in the $d\chi_m(T)/dT$ curve, see the inset of figure 4, we determine a $T_{N2} = 82, 80,$ and 45 K for R = Pr, Nd, and Sm, respectively. The larger divergence of the FC and ZFC $\chi_m(T)$ curves below $T_{N2}$ reflects the large crystalline anisotropy of the R$^{3+}$-ion ferromagnetic component and its coupling to the ferromagnetic component of the TiO$_3$ array.

The R–O–Ti interactions are stronger than the R–O–R interactions where the TiO$_3$ array orders ferromagnetically, and an antiferromagnetic R–O–Ti interaction gives ferromagnetic order below $T_C$ [5]. Nevertheless, the $1/\chi_m(T)$ curves for the heavier rare earths, figure 5, show a deviation from Curie–Weiss behaviour only below a $T_1 > T_C$ that decreases smoothly with $r_{3+}$, figure 6. Figure 7 shows that $T_1$ decreases linearly with the spin on the R$^{3+}$ ion. Therefore, we conclude that $T_1$ represents the onset of spin–spin coupling between the R$^{3+}$ and Ti$^{3+}$ ions in the paramagnetic phase. Figure 6 also shows that the coupling between the R$^{3+}$ and Ti$^{3+}$ spins tends to raise $T_C$ above the value it would have were there no rare-earth spin, as is the case for R = Lu and Y. In addition, the larger $T_C$ for LuTiO$_3$ than for YTiO$_3$ means that $T_C$ increases as the bandwidth narrows, which is characteristic of itinerant-electron magnetism rather than of spin–spin interactions between localized-electron spins that are well
described by perturbation theory. Therefore, we turn finally to the magnitudes of the saturation magnetization to see whether LuTiO₃ has a ferromagnetic magnetization at $T = 5$ K that is closer to the spin-only value of $1 \mu_B/Ti$.

The $M$–$H$ hysteresis loops of figure 8 show that at 5 K the saturation magnetization of LuTiO₃ reaches $0.9 \mu_B/Ti$ whereas that of YTiO₃ is only $0.8 \mu_B/Ti$. On the other hand, an $M_s(5K) = 6 \mu_B/Ti$ for GdTiO₃ corresponds to full spin-only ferrimagnetism; the Gd–O–Ti interaction both raises $T_C$ and fully magnetizes the TiO₃ array. There is no evidence of an orbital contribution that lowers the magnetization of the TiO₃ array. Moreover, the $M$–$H$ curves of the polycrystalline samples show no evidence of a large magnetocrystalline anisotropy. We are thus led to the conclusion that where there is no moment of the $R^{3+}$ ion, the Ti–O–Ti spin–spin interaction of the strongly correlated electrons of the insulating, ferromagnetic TiO₃ array is not strong enough to remove completely the spin degeneracy of the Ti-3d electrons.

Also noteworthy in figure 8 are the small remanences and coercivities of GdTiO₃, YTiO₃, and LuTiO₃. As pointed out elsewhere [11], the G-type $yz$, $zx$ orbital ordering of the ferromagnetic TiO₃ array is interrupted by antiphase boundaries across which the coupling is antiferromagnetic. Therefore, ferromagnetic blocks couple antiferromagnetically across these
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boundaries in zero applied magnetic field, but a modest applied field exerts a high enough torque to align the blocks ferromagnetically provided there is no large magnetocrystalline anisotropy; the magnetocrystalline anisotropy associated with the R$^{3+}$ ion and the R–O–Ti coupling inhibits rotation to give a large $M-H$ hysteresis loop.

We found no evidence of ‘cluster-glass’ behaviour in any of our samples.

5. Conclusion

The orthorhombic (Pbnm) structure of the RMO$_3$ perovskites can be described by a cooperative rotation of the MO$_6^{1/2}$ octahedra about the $b$-axis if the R$^{3+}$ ion has an ionic radius $r_{3+} < 1.11$ Å; but an R–O interaction for $r_{3+} > 1.11$ Å creates, in addition, a deformation of the MO$_6^{1/2}$ site to rhombohedral symmetry. Therefore, the stabilization of electronic charge along a site [111] axis in the RTiO$_3$ perovskites with R = La to Sm is driven by the site deformation, not by a cooperative Jahn–Teller orbital ordering. Occupancy of the $a_1$ orbitals is responsible for antiferromagnetic order on the TiO$_3$ array, and $T_N$ decreases as the site deformation responsible for preferential occupancy of an $a_1$ orbital decreases. On the other hand, the heavier R$^{3+}$ ions and Y$^{3+}$ have an $r_{3+} < 1.11$ Å, and in these RTiO$_3$ perovskites the Ti$^{4+}$/Ti$^{3+}$ redox band is narrow enough to stabilize a cooperative Jahn–Teller orbital ordering; the G-type order of the occupied $yz$ and $zx$ orbitals introduces, as previously noted by others [10], ferromagnetic Ti–O–Ti interactions. Therefore, the change from antiferromagnetic to ferromagnetic order at an $r_{3+} \approx 1.11$ Å signals that the site deformations that determine the magnetic order are driven by cooperative Jahn–Teller orbital ordering for $r_{3+} < 1.11$ Å and by a structural site deformation for $r_{3+} > 1.11$ Å.

Holes introduced by a small cation (probably R$^{3+}$) deficiency are polaronic, but the size of the polarons progressively decrease with $r_{3+}$ from roughly ten Ti atoms per hole in LaTiO$_3$ to small polarons as the bandwidth narrows to that of GdTiO$_3$.

The R–O–Ti spin–spin coupling is stronger than the R–O–R coupling in the ferrimagnetic RTiO$_3$ compounds with $r_{3+} < 1.11$ Å, but the R–O–R coupling is the stronger in the antiferromagnetic compounds having an $r_{3+} > 1.11$ Å. In the ferrimagnetic compounds, the strength of the R–O–Ti interactions is proportional to the magnitude of the R$^{3+}$-ion spin.

Although the electrons of the TiO$_3$ array are strongly correlated in all members of the RTiO$_3$ family, LaTiO$_3$ is close to the threshold for a transition to metallic behaviour and, in the absence of a spin on the R$^{3+}$ ion, the saturation magnetization at 5 K of a ferromagnetic TiO$_3$ array increases with decreasing bandwidth of the Hubbard bands. Therefore, we conclude that the abnormal magnetic behaviour of LaTiO$_3$ reflects an itinerant-electron antiferromagnetism of the strongly correlated electrons. The Jahn–Teller cooperative orbital ordering and the apparent small-polaron behaviour found for compounds with $r_{3+} < 1.11$ Å would appear to signal localized-electron behaviour; the interatomic spin–spin interactions would then be described by a virtual charge transfer from a half-filled to an empty orbital in superexchange perturbation theory. However, in the absence of any evidence of a strong orbital magnetism or magnetocrystalline anisotropy of the TiO$_3$ array, the evidence for failure of the on-site electron–electron interactions to remove completely the spin degeneracy of the ferromagnetic Ti-3d electrons where there is no spin on the R$^{3+}$ ions either implies an incomplete orbital ordering as a result of a phase separation into an orbitally ordered phase and an orbitally disordered phase that decreases in volume fraction as the lower Hubbard band narrows or it poses a challenge to the theorist to develop a more adequate description of the evolution of magnetic properties from the onset of a strong-correlation energy gap to localized-electron ferromagnetism.

Finally, we found no evidence for ‘cluster-glass’ behaviour in our samples where there was no variance of the R$^{3+}$-ion radius.
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References