Ferromagnetism and Lattice Distortions in the Perovskite YTiO$_3$

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The thermodynamic properties of the ferromagnetic perovskite YTiO$_3$ are investigated by thermal expansion, magnetostriction, specific heat, and magnetization measurements. The low-temperature spin-wave contribution to the specific heat, as well as an Arrott plot of the magnetization in the vicinity of the Curie temperature $T_C \simeq 27$ K, are consistent with a three-dimensional Heisenberg model of ferromagnetism. However, a magnetic contribution to the thermal expansion persists well above $T_C$, which contrasts with typical three-dimensional Heisenberg ferromagnets, as shown by a comparison with the corresponding model system EuS. The pressure dependences of $T_C$ and of the spontaneous moment $M_s$ are extracted using thermodynamic relationships. They indicate that ferromagnetism is strengthened by uniaxial pressures $p \parallel a$ and is weakened by uniaxial pressures $p \parallel b, c$ and hydrostatic pressure. Our results show that the distortion along the $a$- and $b$-axes is further increased by the magnetic transition, confirming that ferromagnetism is favored by a large GdFeO$_3$-type distortion. The $c$-axis results however do not fit into this simple picture, which may be explained by an additional magnetoelastic effect, possibly related to a Jahn-Teller distortion.

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1. INTRODUCTION

ABO$_3$ perovskites exhibit a large variety of electronic and magnetic properties. The titanate family ATiO$_3$ recently attracted particular interest, since YTiO$_3$ orders ferromagnetically below the Curie temperature $T_C \simeq 27$ K, whereas LaTiO$_3$ orders antiferromagnetically below the Néel temperature $T_N \simeq 150$ K. In these systems, the $S = 1/2$ spins localized on the Ti$^{3+}$ ions are responsible for the magnetic properties. A change from ferromagnetism to antiferromagnetism can be continuously tuned by varying the lanthanum concentration $x$ in the alloys Y$_{1-x}$La$_x$TiO$_3$, or by changing the lanthanide A (A = Yb→La) in the undoped ATiO$_3$. A GdFeO$_3$-type distortion is driven by ion-size mismatch and comprises rotations of the TiO$_6$ octahedra. It is responsible for the distorted structure of the ATiO$_3$ crystals, with the space group $Pbnm$. This distortion is more pronounced in YTiO$_3$ than in LaTiO$_3$, being favored by smaller A$^{3+}$ ions (A = Y,La). In YTiO$_3$, an additional elongation, by about 3%, of the TiO$_6$ octahedra is observed. This distortion has been ascribed to staggered ordering of the $t_{2g}$ orbitals (Ti$^{3+}$ ions). The switch from antiferromagnetism to ferromagnetism in the ATiO$_3$ perovskites is probably controlled by the extreme sensitivity of the magnetic superexchange interactions to the distortions of the lattice. However, the mechanism driving this transition is still a matter of considerable debate. For a proper description of the magnetic properties, it is thus crucial to carefully consider their dependence on the lattice distortion.

In this article, we present a study of the thermodynamic properties of YTiO$_3$. Experimental details will be given in Section 2. In Section 3 the specific heat, thermal expansion, magnetization, and magnetostriction data measured with magnetic fields applied along the easy $c$-axis will be presented. In Section 4 these results will be discussed and compared to the behavior expected within a three-dimensional (3D) Heisenberg ferromagnetic model. As a specific example, we will show data on the typical 3D Heisenberg system EuS. In Section 5 the relation between the distortion and the magnetic properties will be discussed in the light of our results. The dependence of the distortion on the A$^{3+}$ ionic sizes, on uniaxial pressures, and on the temperature will be considered.

2. EXPERIMENTAL DETAILS

Single crystals of YTiO$_3$ were prepared by the floating zone method using a four-mirror-type infrared image furnace from Crystal System Corporation. More details about the crystal growth are given in Ref. 17. Two samples have been investigated and the measurements presented here were obtained on the sample with the
sharpest transition at $T_C$. This sample was cut so that its faces are perpendicular to the $a$-, $b$-, and $c$-axes, its dimensions at room temperature being equal to $L_a^0 \approx 2$ mm, $L_b^0 \approx 4$ mm, and $L_c^0 \approx 3$ mm along $a$, $b$, and $c$, respectively, with a mass of 116 mg. Thermal expansion and magnetostriction were measured using a home-made high-resolution capacitive dilatometer, with temperature and field sweep rates of 20 mK/s and 0.5 T/min, respectively. Three sets of measurements were performed, where the length $L_i$ was measured along the $a$-, $b$-, and $c$-axes ($i = a$, $b$, and $c$, respectively). Specific heat and magnetization were measured using a Physical Properties Measurement System and a Magnetic Properties Measurement System, respectively (Quantum Design). For all measurements, the magnetic field $H$ was applied parallel to the easy axis $c$. The thermal expansion of EuS was measured using a 8 mm long single crystal grown from the melt by K. Fischer at the Forschungszentrum Jülich, as described elsewhere.

3. RESULTS

3.1. Specific heat and thermal expansion

In Fig. 1 the specific heat $C_p$ of YTiO$_3$ is shown in a $C_p$ versus $T$ plot. Ferromagnetic ordering is characterized by an anomaly at $T_C = 26.8 \pm 0.3$ K, defined at the minimum of slope of $C_p(T)$. In Fig. 2 (a), the variation with $T$ of the relative lengths $\Delta L_i/L_i$ is shown for $i = a$, $b$, and $c$, $\Delta L_i/L_i$ being fixed to zero at room temperature. The linear thermal expansion coefficients $\alpha_i = (1/L_i)\partial L_i/\partial T$, with $i = a$, $b$, and $c$, are extracted from these data and are plotted in Fig. 2 (b). The volume change $\Delta V/V = \sum_{i=a,b,c} \Delta L_i/L_i$ and the related volume thermal expansion coefficient $\alpha_V = (1/V)\partial V/\partial T$ are also shown in Fig. 2 (a) and (b), respectively. As seen in Fig. 2 changes of slope in $L_a$, $L_b$, $L_c$, and $V$ are induced at $T_C$, leading to a positive anomaly in $\alpha_a$ and to negative anomalies in $\alpha_b$, $\alpha_c$, and $\alpha_V$. The volume decrease below $T_C$, which is similar to the invar effect, will be further related to the negative hydrostatic pressure dependence of $T_C$. From the thermal expansion data, we extract a Curie temperature $T_C = 26.8 \pm 0.05$ K at the extremum of slope of $\alpha_i(T)$. This is in good agreement with prior observation. At temperatures sufficiently higher than $T_C$, $L_a$, $L_c$, and $V$ increase with $T$, while $L_b$ decreases with $T$ (Fig. 2 (a)). This leads to the positive values of $\alpha_a$, $\alpha_c$, and $\alpha_V$ and to the negative values of $\alpha_b$ observed at high temperatures in Fig. 2 (b). The anisotropy of $\alpha_i$ at high temperatures is a consequence of the lattice distortions, which will be discussed in Section 5.

3.2. Magnetization and magnetostriction

In Fig. 3 the magnetization versus field $M(H)$ is shown for $H \parallel c$ in a log-log plot, at $T = 1.8$ K and $T = 26.5$ K $\approx T_C$. At $T = 1.8$ K, a linear increase of $M(H)$ is obtained for $\mu_0 H < \mu_0 H_0 \approx 0.06$ T and is related to the alignment of ferromagnetic domains. For $H > H_0^*$, the spins are aligned parallel to $H$ and the magnetization $M$ reaches $M_s \approx 0.8$ $\mu_B$. In this regime, a slight increase of $M(H)$ is observed. Indeed, $M_s$ is not yet fully saturated and is somewhat smaller than the full moment of 1 $\mu_B$ expected for the $S = 1/2$ Ti$^{3+}$ ions. At $T \simeq T_C$, $M$ increases first almost linearly with $H$, for $\mu_0 H < \mu_0 H^* \approx 0.02$ T, and then varies as $M \propto H^{1/2}$, with $\delta = 4.47 \pm 0.2$, for $\mu_0 H^* < \mu_0 H < 1$ T. This power

![FIG. 1: Variation with $T$ of the specific heat $C_p$ of YTiO$_3$.](image1)

![FIG. 2: Variation with $T$ (a) of the relative lengths $\Delta L_i/L_i$ for $i = a$, $b$, and $c$, and of the relative volume $\Delta V/V$ (b) of the thermal expansion coefficients $\alpha_i$ for $i = a$, $b$, $c$ and $V$.](image2)
law, observed above 1 T, is characteristic of the critical ferromagnetic regime. Deviations are observed when $M$ becomes close to $M_s$.

In Ref. 17, low temperature magnetization measurements were reported on the same sample as in the present work and moments of 0.84 and 0.82 $\mu_B$ were found for a magnetic field of 7 T applied along $b$ and $c$, respectively. These data agree well with the saturated magnetic moment of 0.84 $\mu_B$ reported in Ref. 21 and 22, and with the moments of 0.83 ± 0.05 and 0.84 ± 0.05 $\mu_B$, for the $a$- and $c$-axis, respectively, determined by recent Magnetic Compton Profile experiments.

In Fig. 3 the magnetostriiction coefficients $\lambda_i = (1/L_i)\partial L_i/\partial(\mu_0 H)$ are plotted as a function of $H$ on a log-log scale, at $T = 2.5$ K and $T_C = 26.7$ K, with $i = a$, $b$, and $c$, and $H \parallel c$. For all temperatures and magnetic fields, $\lambda_b$ and $\lambda_c$ are positive while $\lambda_a$ is negative. For the three configurations at $T = 2.5$ K, $|\lambda_i(H)|$ increases for $\mu_0 H < \mu_0 H^* \approx 0.05$ T and is almost constant for $H > H^*$, when the domains are aligned. At $T_C$, $|\lambda_i(H)|$ increases before reaching a maximum at $\mu_0 H^* \approx 0.02$ T. For $\mu_0 H > \mu_0 H^{**}$, a critical regime is observed, where $|\lambda_i(H)| \propto H^{-1/\delta_i}$, with $\delta_i = 2.64, 3.06,$ and $2.59 \pm 0.1$ for $i = a$, $b$, and $c$, respectively. While the power law is followed up to almost 10 T in $\lambda_b$, deviations are found for $\mu_0 H > 1$ T in $\lambda_a$ and $\lambda_c$.

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4. FERROMAGNETIC PROPERTIES

4.1. Low temperature spin waves

In Fig. 3(a), the specific heat of $\text{YTiO}_3$ is plotted in a log-log plot of $C_p/T$ versus $T$. Well below $T_C$, the phonon contribution can be neglected and the signal, which varies as $C_p(T) \propto T^{1.4}$ up to 10 K, is believed to be only magnetic. This power law is compatible with isotropic 3D Heisenberg ferromagnetic spin waves, for which a $T^{1.5}$ law would be expected, and is thus in good agreement with the spin-wave dispersion observed by neutron scattering. The slight deviation from the $T^{1.5}$ law might result from a small spatial anisotropy of the exchange, the spin-wave contribution to the specific heat of a ferromagnet varying as $C_p(T) \propto T^{d/2}$, where $d$ is the dimensionality of the exchange. It may also be related to possible additional antiferromagnetic spin fluctuations and/or to spin anisotropies originating from spin-orbit coupling (see below).

In Fig. 3(b), the thermal expansion is plotted in a log-log plot of $|\alpha_i|$ versus $T$, for $i = a$, $b$, and $c$. Power laws $\alpha_i \propto T^{1.9}$ are found up to almost 20 K for $i = a$ and $c$, while no clear power law is observed for $i = b$. As simple 3D Heisenberg ferromagnetic spin waves should lead to $\alpha_i \propto C_p \propto T^{1.5}$, the different $T$-dependences of $C_p$ and $\alpha_i$ reported here may result from anisotropic exchange interactions, which lead to weak additional magnetic Bragg reflections due to canting of the ferromagnetic moments. Weak low-energy spin fluctuations around these wave vectors may contribute to the deviation of the
temperature dependence of the low-temperature specific heat and thermal expansion from the predictions of a simple ferromagnetic Heisenberg model. Further studies of the spin wave spectra (e.g., by neutron scattering) and detailed calculations are needed for a quantitative explanation of the results obtained here. Systematic studies by specific heat and thermal expansion of the ATiO$_3$ family, such as the work initiated in Ref. 6, may be of importance to understand the evolution of the low temperature magnetic properties.

4.2. Arrott plot and critical fluctuations

To analyze the critical ferromagnetic regime, the magnetization was measured as $M$ versus $H$ at several temperatures close to $T_C$. In Fig. 4 an Arrott plot of these data is shown as $M^{1/\beta}$ versus $(H/M)^{1/\gamma}$, for $25.9 \leq T \leq 27.1$ K. The critical exponents $\beta = 0.392 \pm 0.05$ and $\gamma = 1.475 \pm 0.1$ used in this plot were determined from a fit of $M(H,T)$ using Arrott's equation of state:

$$M^{1/\beta} = c_1 \left( \frac{H}{M} \right)^{1/\gamma} - c_2 (T - T_C),$$

(1)

for $0.02 < \mu_0 H < 1.3$ T and $25.9 \leq T \leq 27.1$ K. The value of $T_C = 26.44 \pm 0.05$ K obtained from this fit agrees well with that obtained from the specific heat and thermal expansion (Section 3.1). From Equation (1):

$$M(H,T_C) \propto H^{1/\delta},$$

(2)

with

$$\delta = (\beta + \gamma)/\beta.$$  

(3)

Using the exponents $\alpha$ and $\beta$ obtained with Arrott’s method, we calculate the critical exponent $\delta = 4.76 \pm 0.2$, which agrees favorably with $\delta = 4.47 \pm 0.2$ directly obtained from the fit by a power law of $M(H)$ at 26.5 K (Section 3.2).

In Table 1 the exponents $\beta, \gamma$, and $\delta$ expected for different classes of universality are listed for comparison. The exponents extracted from the Arrott plot of the magnetization of YTiO$_3$ are rather close to those of the 3D Heisenberg universality class. A similar plot was made in Ref. 28 using 3D Heisenberg exponents, but without a preliminary fit of the $M(H,T)$ data as done here. As already inferred from the behavior of the low temperature spin waves, the critical behavior of the magnetization, too, is thus consistent with a 3D Heisenberg picture of ferromagnetism (cf. Section 4.1 and Ref. 14).

In the following, the power laws reported for the magnetostricion at $T_C$ (Fig. 4) are related to the critical power law of the magnetization (Fig. 3) and to the critical exponents $\alpha$ and $\beta$. Using the Maxwell relation:

$$\lambda_i = \frac{1}{L_i} \frac{\partial L_i}{\partial (\mu_0 H)} = -\frac{\partial M}{\partial p_i},$$

(4)

the magnetostricion coefficients can be expressed as functions of the uniaxial pressure dependences of the magnetization. Assuming that $\partial c_1/\partial p_i = 0$, the derivative of Equation (1) leads to, at $T = T_C$:

$$\lambda_i(H,T_C) = -A \frac{\partial T_C}{\partial p_i} H^{-1/\delta'},$$

(5)

with $A = c_1^{-\gamma/\delta'} c_2 \gamma/\delta$ and $\delta' = (\beta + \gamma)/(1 - \beta)$. (6)

From the exponents $\alpha$ and $\beta$ obtained by the Arrott fit of the magnetization, a critical exponent $\delta' = 3.07 \pm 0.5$.
is expected to characterize the magnetostriction at $T_C$. This value is in good agreement with the values $2.59 \leq \delta_i \leq 3.06$ determined from the fits of $\lambda(H)$ at $T_C$ (see Section 3.2). For each set of $(\beta, \gamma)$, the corresponding $\delta'$ values are also given in Table I. These values are compatible with a 3D Heisenberg scenario of ferromagnetism for YTiO$_3$ associated with $\delta' = 2.77$. The slight variations of $\delta'_i$ with $i$ are not understood and may result from various secondary effects (anisotropic energy scales, defects etc.).

To our knowledge, YTiO$_3$ is the second ferromagnetic system known, after the itinerant ferromagnet UIr$^{29}$, where a critical power law is reported in the magnetostriction at $T_C$. We believe that such an effect is quite general and should be present in most ferromagnets, once the field and temperature ranges are properly chosen. We note that, more than 60 years ago, Belov has theoretically predicted a similar law$^{30}$, but only within a mean-field approach, which corresponds to $\beta = 0.5$, $\gamma = 1$, and $\delta = \delta' = 3$ (cf. Table I). Our approach is more general and permits to obtain the critical exponent $\delta'$ for each combination of $(\beta, \gamma)$ and thus, for each universality class.

### 4.3. High-temperature magnetic signal: deviation from a pure 3D Heisenberg ferromagnet

The distortion of the lattice induces the strong anisotropy observed in the high-temperature thermal expansion of YTiO$_3$ (see Fig. 2). This anisotropic lattice signal must be properly taken into account to extract the magnetic contribution to the thermal expansion. Since $\alpha_a$ and $\alpha_c$ are rather close above 100 K, we assume that the lattice contributions to $\alpha_a$ and $\alpha_c$ are similar, so that $\Delta \alpha = \alpha_a - \alpha_c$, which is plotted in Fig. 2(a), can be considered as a signal representative of the magnetic thermal expansion. In this plot, the thin red line is a guide to the eye indicating the “remaining” non-magnetic background and the yellow area corresponds to the estimated magnetic contribution. In Fig. 2(b), the thermal expansion $\alpha$ of cubic EuS$^{31}$, which is known as a prototype of 3D Heisenberg ferromagnetism$^{32,33,34}$, is shown for comparison. The thin blue line is a guide to the eye indicating the non-magnetic background and the magnetic contribution is estimated by the blue area. The estimates of the magnetic contribution to the thermal expansion of YTiO$_3$ and EuS are plotted in Fig. 2(c). In this plot, the magnetic thermal expansion coefficient $\alpha_{mag}^{*}$ is normalized by its maximal value $\alpha_{mag}^{max}$ and the temperature $T$ is normalized by $T_C$. Fig. 2(c) indicates that, in YTiO$_3$, the magnetic signal has a significant weight above $T_C$ and extends up to about $5 \times T_C$ while, in EuS, it has most of its intensity below $T_C$ and vanishes completely above about $2 \times T_C$. Thus, the magnetic fluctuations of YTiO$_3$ cannot be described as those of a simple 3D Heisenberg

| Critical exponents | $\beta$ | $\gamma$ | $\delta$ | $\delta'$ |
|--------------------|--------|--------|--------|--------|
| YTiO$_3$ (best fit) | 0.392 (50) | 1.475 (100) | 4.76 (20) | 3.07 (50) |
| 3D Heisenberg       | 0.367  | 1.388  | 4.78   | 2.77   |
| 3D XY              | 0.345  | 1.316  | 4.81   | 2.54   |
| 3D Ising           | 0.326  | 1.238  | 4.80   | 2.32   |
| 2D Ising           | 0.125  | 1.75   | 15     | 2.14   |
| Mean Field         | 0.5    | 1      | 3      | 3      |
ferromagnet.

As shown in the inset of Fig. 8, the specific heat \( C_p(T) \) and the volume thermal expansion \( \alpha_V(T) \) can be scaled at high temperatures by using an empirical parameter \( y = 3.96 \times 10^{-6} \text{ mJ/mol} \) defined by \( C_p = y \times \alpha_V \). Assuming that the magnetic contribution to \( C_p \) and \( \alpha_V \) is negligible above 200 K, and that there is a single Gruneisen parameter associated with the phonons for the [0,300 K] range, we can estimate the phonon contribution to the specific heat by \( C_p^{ph} = C_p - z \times (C_p - y \times \alpha_V) \), \( z = 0.2 \) being adjusted so that no anomaly remains at \( T_C \). The main frame of Fig. 8 shows that the magnetic contribution \( C_p^{mag}(T) \) to the specific heat. This plot confirms the conclusions in Fig. 7, i.e. that a magnetic contribution is present up to more than 100 K. Integration of the estimated magnetic heat capacity leads to the magnetic entropy \( \Delta S^{mag} \approx 4.5 \text{ J/mol}K \). This entropy is roughly equal to the full spin entropy \( \Delta S^{full} \approx 5.8 \text{ J/mol}K \) for \( S = 1/2 \) spin system; the fact that \( \Delta S^{mag} \approx 20 \% \) smaller than \( \Delta S^{full} \) may be imputed to the experimental error.

In Fig. 8, the estimated magnetic contributions to the thermal expansion \( \alpha^{mag}(T) \) and to the specific heat \( C_p^{mag}(T) \) are plotted together; above 50 K, the different shapes of the signals indicate the limit of the methods used here. Both plots indicate clearly the presence of a magnetic signal at temperatures well above ferromagnetic ordering. The origin of this behavior, which is not expected for usual 3D-Heisenberg ferromagnets (see Fig. 7), is yet not understood. In principle, a modified conventional spin-only fluctuation model, for example with competing (and possibly low-dimensional) antiferromagnetic and ferromagnetic interactions, could describe this anomalously high-temperature magnetic signal. However, this is in apparent contradiction with the magnon spectra reported by neutron scattering, which do not exhibit pronounced deviations from the predictions of a 3D Heisenberg model with nearest-neighbor interactions.

An alternative explanation of the extended magnetic fluctuation regime could be offered by spin-orbital fluctuations models, where an energy scale significantly exceeding the magnon bandwidth (in Ref. 41,42 orbital fluctuations were associated with an excitation at about 250 meV) could actuate ferromagnetic fluctuations at temperatures between \( T_C \) and room temperature. Further work is required to ascertain whether a quantitatively consistent picture of the spin\( ^{14} \) and orbital\( ^{14} \) excitation spectra and thermodynamics of YTiO\(_3\) can be obtained.

5. COUPLING BETWEEN THE LATTICE AND THE MAGNETIC PROPERTIES

5.1. Uniaxial pressure dependences - Comparison with LaTiO\(_3\)

Fig. 9 shows the anomalies at \( T_C \) in the specific heat and in the thermal expansion of YTiO\(_3\). These anomalies are typical of a second-order phase transition, whose jumps are estimated as \( \Delta C_p = 2.3 \pm 0.1 \text{ J/molK} \) in the specific heat and as \( \Delta \alpha = 6.6 \pm 0.3 \times 10^{-6} \text{ K}^{-1} \), \( \Delta \alpha_b = -3.4 \pm 4 \times 10^{-6} \text{ K}^{-1} \), and \( \Delta \alpha_c = -4.7 \pm 0.2 \times 10^{-6} \text{ K}^{-1} \) in the thermal expansion. Using the Ehrenfest relation:

\[
\frac{\partial T_C}{\partial p_i} = \frac{\Delta \alpha_i V_m T_C}{\Delta C_p},
\]

where \( V_m = 3.46 \times 10^{-5} \text{ m}^3/\text{mol} \) is the molar volume and \( p_i \) a uniaxial pressure applied along \( i \) (\( i = a, b, \) and \( c \)), we extract the uniaxial pressure dependences \( \partial T_C/\partial p_i \) reported in Table I. The sum of the three uniaxial pressure dependences of \( T_C \) gives the hydrostatic pressure dependence \( \partial T_C/\partial p = -6.0 \pm 0.6 \times 10^{-2} \text{ K/kbar} \). Assuming that, in YTiO\(_3\), \( \partial T_C/\partial p_b \) remains constant under hydrostatic pressure, ferromagnetism may be destroyed above \( p_b \approx 400 \text{ kbar} \).

For comparison, the uniaxial pressure dependences of \( T_N \), for the antiferromagnet LaTiO\(_3\), are also listed in Table II. To calculate them, \( T_C \) in Equation (7) was substituted by \( T_N \approx 146 \text{ K} \), \( \Delta C_p = 10 \text{ J/molK} \), \( \Delta \alpha_a = -5 \pm 0.5 \times 10^{-5} \text{ K}^{-1} \), \( \Delta \alpha_b = 5 \pm 0.5 \times 10^{-5} \text{ K}^{-1} \), and

### Table II: Uniaxial and hydrostatic pressure dependences of \( T_C \) and \( M_s \) for YTiO\(_3\) and of \( T_N \) for LaTiO\(_3\). The ratio \( \rho_i \) of the pressures dependences of \( T_C \) and \( M_s \) is given for YTiO\(_3\).  

| \( p_i \) (kbar) | \( \partial \ln T_C/\partial p_i \) (10\(^{-3}\text{kbar}^{-1}) \) | \( \partial \ln M_s/\partial p_i \) (10\(^{-3}\text{kbar}^{-1}) \) | \( \rho_i \)  |
|-----------------|----------------------|----------------------|---|
| \( p_a \)       | 9.9 \pm 1.0          | 2.7 \pm 0.4          | 3.7 \pm 1.0          | -1.9 \pm 0.4 |
| \( p_b \)       | -5.1 \pm 0.5         | -2.7 \pm 0.4         | 1.9 \pm 0.5          | 1.9 \pm 0.4 |
| \( p_c \)       | -7.1 \pm 0.7         | -0.77 \pm 0.15       | 9.1 \pm 2.5          | \approx 0   |
| \( p_d \)       | -2.3 \pm 0.3         | -0.77 \pm 0.15       | 2.9 \pm 1.0          | \approx 0   |
Although YTiO$_3$ is a localized ferromagnet, its saturated moment, at about 5 T, is only 80% of the fully saturated moment $M_{\text{sat}}^s = 1 \mu_B$. A small canting antiferromagnetic moment $M_{AF} \approx 0.1 \mu_B$ was reported by neutron scattering in YTiO$_3$, and explains partly why $M_s$ is reduced. In addition, the reduction of $M_s$ may indicate an enhanced phase space for quantum magnetic fluctuations. The question is whether this reduction comes from usual spin-only fluctuations, or if it results from more complicated fluctuations involving orbital degrees of freedom.$^{10,11}$ The high values of $\partial M_s/\partial p_b$ in YTiO$_3$ may result from the combination of two effects, which can be summarized as the uniaxial pressure-induced transfers of weight (i) between the ferromagnetic moment $M_s$ and the antiferromagnetic moment $M_{AF}$, and (ii) between $M_s$ and some quantum magnetic fluctuations $\delta M$. The second effect is similar to what happens in itinerant ferromagnets, where $M_s$ is reduced by quantum fluctuations $\delta M$ of the magnetic moment, and where the strong pressure dependences of $M_s$ are related to those of $\delta M$.

A similar analysis as the one presented here was reported for the itinerant weak ferromagnet Uf$_6$ (Ref. 29), in the framework of the Moriya’s spin fluctuation theory of itinerant magnetism.$^{38-39}$ By analogy, a spin fluctuation theory, adapted to the particular case of YTiO$_3$, may be appropriate.

### 5.2. Coupling between the GdFeO$_3$-type distortion and the magnetic ordering

In the ATiO$_3$ perovskites, the GdFeO$_3$-type distortion comprises a combination of tilts and rotations of the TiO$_6$ octaedra. This results in an orthorhombic structure, where $b > a \sqrt{2} > c / \sqrt{2} > a$, $a_0$ being the lattice parameter of an undistorted cubic structure.$^{38,40}$ In the alloys Y$_{1-x}$La$_x$TiO$_3$, La-substitution induces a decrease of the GdFeO$_3$-type distortion, which is believed to control the change from ferromagnetism to antiferromagnetism.$^{1,2,3,4,5}$ (Fig. 10). This picture, in which ferromagnetism is favored by a large GdFeO$_3$-type distortion, is qualitatively confirmed by the increase of the distortion of the $(a,b)$ plane induced below $T_C$ (see Fig. 24). In the following, we will further show that, for $p \parallel a$, the uniaxial pressure dependences of $T_C$ and $T_N$ are mainly controlled by those of the GdFeO$_3$-type distortion.

In YTiO$_3$ and LaTiO$_3$, the negative sign of $\partial T_C/\partial p_b$ and the positive sign of $\partial T_N/\partial p_b$ (see Table III), respectively, imply that a uniaxial pressure $p \parallel b$ can be seen equivalent to La-doping (cf. the corresponding arrow in Fig. 10). Conversely, the fact that $\partial T_C/\partial p_a$ is positive while $\partial T_N/\partial p_a$ is negative (Table III) implies that $p \parallel a$ is equivalent to Y-doping (see Fig. 11). As $p \parallel b$ induces a compression along $b$ and, because of elasticity, extensions along $a$ and $c$, its effects are very similar to those of reducing the GdFeO$_3$-type distortion. By analogy, $p \parallel b$ leads to a compression along $b$ and to small extensions along $a$. 

### FIG. 9: Ferromagnetic ordering anomaly (a) in the specific heat and (b-d) in the thermal expansivity coefficients along a, b, and c. In these curves, the jumps $\Delta C_p$, $\Delta \alpha_a$, $\Delta \alpha_b$, and $\Delta \alpha_c$ at the ferromagnetic ordering are indicated by arrows.
5.3. Distortion of the TiO$_6$ octahedra

5.3.1. Microscopic description

The lattice structure of YTiO$_3$ is represented schematically in Fig. 11 where the alternation of tilts and rotations of the TiO$_6$ octahedra (in blue) is due to the GdFeO$_3$-type distortion. An additional distortion consists of an elongation of each octahedron along a particular axis (orange arrows in Fig. 11), and of contractions perpendicular to this axis. In Ref. 4,5,7,8, the fact that the elongated axes vary from one site to another was ascribed to a staggered ordering of the $t_{2g}$ orbitals (Ti$^{3+}$ ions) via a collective Jahn-Teller effect. By geometrical considerations, we can qualitatively estimate the macroscopic distortion induced by the elongations of the octahedra. As seen in Fig. 11 the elongated axes are almost contained within the (a, b) plane, i.e. perpendicularly to the c-axis. This implies that the elongations of the octahedra induce a contraction of the c-axis. In the (a, b) plane, the elongated axes of two adjacent octahedra subtend an angle of about 60°, so that the elongations and contractions of the different octahedra almost cancel each other. Since the projections of the elongated axes are larger along b than along a (the elongated axes subtend an angle of about 30° with b and of about 60° with a), we finally conclude that the elongations of the octahedra are responsible for a small elongation of b and for

![Diagram of lattice structure of YTiO$_3$](image.png)

FIG. 11: Schematics of the lattice structure of YTiO$_3$. The Ti$^{3+}$ ions are represented by grey spheres, the Y$^{3+}$ ions by green spheres, and the O$^{2-}$ ions by red spheres. The TiO$_6$ octahedra are colored in blue, and orange arrows show their elongated direction, possibly due to the Jahn-Teller distortion.
a tiny compression of \( a \), in addition to the main effect, a compression along \( c \).

### 5.3.1. Lattice parameters: comparison of the families \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \)

Here we propose a method, based on a comparison of the lattice parameters \( a \), \( b \) and \( c \) of the families \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \), to confirm the description made in Section 5.3.1 of the effects of the elongation of the octahedra on \( a \), \( b \) and \( c \). Assuming that these elongations are related to a Jahn-Teller distortion, the comparison of the lattice parameters of \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \) can be justified by the fact that, contrary to \( \text{Ti}^{3+} \), \( \text{Fe}^{3+} \) is not Jahn-Teller active so that \( \text{AFeO}_3 \) can be considered as a non-Jahn-Teller reference for \( \text{ATiO}_3 \).

In Fig. 12 (a) and (b), the unit cell volume \( V \) and the lattice parameters \( a \), \( b \), and \( c/\sqrt{2} \) are plotted versus the ionic radius of the \( \text{A}^{3+} \) ions, for several compounds of the families \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \) (A=Lu→La). The ionic radii of the \( \text{A}^{3+} \) ions are taken from Ref. 49 assuming a number of 8 nearest neighbors. While \( \text{LaTiO}_3 \) and \( \text{LaFeO}_3 \) are almost undistorted \((a \simeq b \simeq c/\sqrt{2})\), Fig. 12 (b) shows a strong distortion of the pseudo-cubic lattice in \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \), once \( \text{A}^{3+} \) is smaller than \( \text{La}^{3+} \).

In Fig. 12 (c), the unit cell volumes \( V^{\text{ATiO}_3} \) of the \( \text{ATiO}_3 \) compounds are scaled empirically with the unit cell volumes \( V^{\text{AFeO}_3} \) of the \( \text{AFeO}_3 \) compounds, using a scaling factor \( f = 1.01 \) defined by \( V^{\text{ATiO}_3} = V^{\text{AFeO}_3} \times f \). In Fig. 12 (d), the lattice parameters of \( \text{ATiO}_3 \) are scaled to those of \( \text{AFeO}_3 \) using the factor \( 1/f \). As the undistorted limit in the \( \text{ABO}_3 \) perovskites corresponds to a cubic lattice parameter \( a_0^{\text{ABO}_3} = 2(r_O + r_B) \), where \( r_O \) and \( r_B \) are the ionic radii of the \( \text{O}^{2-} \) and \( \text{B}^{3+} \) ions, respectively, we associate the empirical scaling factor \( f = 1.01 \) to the ratio \( a_0^{\text{ATiO}_3}/a_0^{\text{AFeO}_3} = 1.013 \), calculated with \( r_O = 1.35 \), \( r_{\text{Ti}} = 0.67 \), and \( r_{\text{Fe}} = 0.645 \) Å.

![Diagram](https://example.com/diagram.png)

**FIG. 12**: Variations, for the \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \) systems, of (a) the unit cell volume \( V \) and (b) the lattice parameters \( a \), \( b \), and \( c/\sqrt{2} \), as a function of the ionic radius of \( \text{A}^{3+} \). In (c) and (d), the volume and the lattice parameters of \( \text{ATiO}_3 \) and \( \text{AFeO}_3 \) are scaled together using the empiric factor \( f = 1.01 \).

Since the ionic radii of \( \text{Ti}^{3+} \) and \( \text{Fe}^{3+} \) are very close, we assume that, for the two families, the \( \text{GdFeO}_3 \)-type distortion induces similar variations of their lattice parameters in the scaled plot of Fig. 12 (d). Consequently, the elongations of the octahedra, which can be neglected in the non-Jahn-Teller compound \( \text{AFeO}_3 \), might be responsible for the slight differences, in Fig. 12 (d), between the scaled lattice parameters of the two families. This implies that the elongations of the \( \text{TiO}_6 \) octahedra in \( \text{YTiO}_3 \) induce a decrease of \( c/\sqrt{2} \) by
about 0.5 Å, accompanied by a smaller increase of $b$, by about 0.3 Å, and by no noticeable change of $a$. These conclusions, obtained using the scaled plot of Fig. 12 (d), confirm those deduced from geometrical arguments in Section 5.3.1.

5.3.3. Anomalous character of the c-axis?

When $T$ is reduced, the decrease of $c$ is slowing down as the ferromagnetic transition at $T_C$ is approached, which ends by an upturn below $T_C$, where $c$ increases with decreasing $T$ (see Fig. 2 (a)). The behavior of the $c$-axis contrasts with those of the $a$- and $b$-axes, whose variations are monotonic for $4 < T < 300$ K and are amplified below $T_C$ (see Fig. 2 (a)). The distortion of the $(a,b)$ plane results mainly from the GdFeO$_3$-type distortion, whose modifications also control the uniaxial pressure dependences of $T_C$ and $T_N$ for $p \parallel a, b$ (see Section 5.2). In Sections 5.3.1 and 5.3.2, $c$ was shown to be more sensitive than $a$ and $b$ to the elongations of the TiO$_6$ octahedra, possibly related to a Jahn-Teller effect. The sensitivity of $c$ to the distortions of the octahedra may be related to the anomalous uniaxial pressure-dependences of $T_C$ and $T_N$ for $p \parallel c$ (see Section 5.2), but also to the anomalous behavior of the $c$-axis in the spectral weight transfers of the optical conductivity$^{12}$. Our findings are in apparent contradiction to theories according to which the Jahn-Teller distortion is an essential prerequisite of ferromagnetism in YTiO$_3$ (Refs. 32, 33). Rather, the properties of YTiO$_3$ seem to be reminiscent of those of La$_{7/8}$Sr$_{1/8}$MnO$_3$, where a Jahn-Teller distortion is fully suppressed at the onset of ferromagnetism$^{30}$.

5.4. High-temperature extrapolation

![Diagram](https://via.placeholder.com/150)

**FIG. 13:** High temperature linear extrapolation of the lattice parameters $a$, $b$, and $c/\sqrt{2}$ of YTiO$_3$.

Equivalently to uniaxial pressures and variations of the A$^{3+}$ ion size, increasing the temperature leads to a reduction of the distortion in the ABO$_3$ perovskites. Indeed, the strong anisotropy of the thermal expansion coefficients $\alpha_i$, shown in Fig. 2 (b), is governed by the effects of temperature on the crystal distortion. Assuming constant thermal expansion coefficients above room temperature, Fig. 13 shows high-temperature extrapolations, up to 4000 K, of the lattice parameters $a$, $b$, and $c/\sqrt{2}$. This plot indicates that, in YTiO$_3$, a cubic structure with $a = b = c/\sqrt{2}$ might be recovered around 3000-4000 K. However, this temperature scale, characteristic of the lattice distortion, is inaccessible since it is far above the melting temperature of YTiO$_3$.

6. CONCLUSION

The thermodynamic study of the perovskite system YTiO$_3$ presented here allowed us to extract information about the ferromagnetic ordering and its coupling to the lattice distortions. While the low-temperature specific-heat data, as well as an Arrott plot of the magnetization close to $T_C$, are consistent with a 3D Heisenberg picture of ferromagnetism, deviations from this simple picture were observed in the thermal expansion data at low temperature, where an unexpected power law is found. Above $T_C$, a magnetic signal persists up to the remarkably high temperature of $5 \times T_C$. Further work is required to show whether models incorporating combined spin-orbital fluctuations, instead of spin-only fluctuations, could quantitatively describe this extended fluctuation regime.

Ehrenfest and Maxwell relations enabled us to extract the uniaxial pressure dependences of the Curie temperature $T_C$ and of the spontaneous moment $M_s$, which indicates that ferromagnetism is stabilized by uniaxial pressures $p \parallel a$ and is destabilized by uniaxial pressures $p \parallel b, c$ and by hydrostatic pressure. We interpreted the uniaxial pressure dependences of $T_C$ and $M_s$ obtained for $p \parallel a, b$ as resulting from uniaxial pressure-induced modifications of the GdFeO$_3$-type distortion. A high sensitivity of the $c$-axis to an additional distortion of the TiO$_6$ octahedra, possibly related to a Jahn-Teller effect, is believed to be responsible for the anomalous uniaxial pressure dependences of $T_C$ and $M_s$ observed for $p \parallel c$. This confirms that both kinds of distortion play an important role for the formation of ferromagnetism in YTiO$_3$, Jahn-Teller distortion being not a necessary condition for ferromagnetism in YTiO$_3$. While the $a$- and $b$-axes are more sensitive to the GdFeO$_3$-type distortion, the $c$-axis is more sensitive to the elongations of the octahedra. Finally, a high-temperature extrapolation of the lattice parameters led to the onset of the distortion at a virtual temperature of about 3000-4000 K. These results might be considered to further develop models for the electronic properties of the titanates.
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26. Well below the ordering temperature, ungauged ferromagnetic spin waves should lead to a $T^{d/2}$ contribution to the specific heat and thermal expansion, while ungauged antiferromagnetic spin waves should lead to a $T^{d}$ contribution ($d$ is the dimensionality of exchange). If there were the two kinds of branches in the low-energy excitations (strong ferromagnetic and weak antiferromagnetic-like spin waves), then two kinds of contributions should be present in both the specific heat and thermal expansion. In this case, the ferromagnetic contribution should dominate the specific heat because it has a higher intensity. Since the thermal expansion is related to the pressure dependence of the entropy, it is dominated by the most pressure-dependent energy scales. This means that weak antiferromagnetic-like spin waves could dominate the low-temperature thermal expansion if they were associated with a strongly pressure-dependent energy scale.
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In an undistorted perovskite structure, the lattice parameters $a$, $b$, and $c$ of the orthorhombic unit cell are related to the lattice parameter $a_0$ of the cubic unit cell by $a = b = c/\sqrt{2} = a_0\sqrt{2}$.

In YTiO$_3$, elongations by 3 % of the octahedra were explained by a Jahn-Teller effect in Ref. 4, 5, 7, 8. In the non-Jahn-Teller LaFeO$_3$ and YFeO$_3$, but also in LaTiO$_3$, elongations, by about 1 %, were reported in Ref. 6, 46, 47 and are presumably consequences from the GdFeO$_3$-type distortion.

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$i = r_0(1 + \Delta L_i/L_i)$, where $i = a, b, c$ (cf. Fig. 2 (a)), and where $a_0 = 5.331$, $b_0 = 5.672$, and $c_0 = 7.602$ Å were extracted from diffraction measurements at room temperature.