Subtle Structural Changes in LaFeO₃ at High Pressure

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1. Introduction

Rare-earth (Ln) orthoferrites with the general formula LnFeO₃ are a class of perovskite materials which have great potential in technological applications such as in fuel cell cathodes, optoelectronic devices, chemical sensors, and catalysts. LaFeO₃ is the parent compound of many important perovskite series. The technological versatility of LaFeO₃ is due to it being a multiferroic, showing ferroelectric ordering above 475 K and antiferromagnetic ordering (with a small ferromagnetic canting) below ≈740 K. The ferromagnetic canting and dielectric properties are shown to be highly tunable with the substitution of Fe with Ni or Co. Pure LaFeO₃ theoretically shows favourable piezoelectric properties and has been demonstrated to improve the piezoelectric response when added as a dopant to K–Na–Nb ceramics.

The antiferromagnetic ordering in pure LaFeO₃ arises from the Fe³⁺ cations, in which the five 3d electrons arrange in a high-spin state t₂g⁵eg⁰ and are coupled across the structure by Fe³⁺–O²⁻–Fe³⁺ super-exchange interactions. This electronic configuration generates a local electric field, which induces a lattice distortion promoting ferroelectric ordering within the material.

At ambient conditions LaFeO₃ crystallises with orthorhombic symmetry (Pnma). Its crystal structure is shown in Figure 1, showing the alternating layers of corner-shared FeO₆ octahedra. The octahedra are irregular, consisting of two distinct oxygen positions. As such, the six Fe–O bonds of the octahedra consist of three independent bonds: Fe–O₁, a long Fe–O₂ and a short Fe–O₂'. The prime symbol (') is hereby used to denote the shorter of the two Fe–O₂ bonds. This structure can be described as a distortion of a high-symmetry cubic parent structure (Pm₃m, a ≈ 3.9 Å), accommodated by combined in-phase tilting (ϕ₀) of the octahedra about the orthorhombic a-axis (parent structure [110]) and out-of-phase tilting (ϕₐ₀) about the b- and c-axes of the orthorhombic cell (parent structure [001]).

In the cubic parent structure, the La atoms sit on interstitial sites coordinated by 12 oxygen atoms at the vertices of a regular cubeoctahedron. In certain orthoferrites, the tilting of the octahedra results in an effective decrease in the La coordination from 12 to 8. This depends on the ratio of A- and B-site cation radii. Here, we consider LaFeO₃ as eightfold coordinated, with two distinct La–O₁ and three distinct pairs of La–O₂ bonds.

Upon warming, LaFeO₃ exhibits a first-order phase transition to rhombohedral symmetry (R3c). This is reported from X-ray diffraction to occur above 1228 K, whereas high-resolution neutron diffraction shows the orthorhombic structure to be stable up to 1255 K. Linear extrapolation of the rhombohedral lattice parameters suggests a further transition to cubic symmetry at 2140 K. However, there is little structural information available on LaFeO₃ under high pressure. An X-ray diffraction study along the 300 K isotherm up to 48 GPa reports two structural transitions, neither of which have been seen with temperature. The first (21.2 GPa) is a second-order transition.
to a body-centred orthorhombic structure (Imma), and is associated with a shift in the La atom to $x = 0.5$ (see Figure 1a) (equivalent to $y = 0$ in the alternate Pbnm space group setting, with different origin). The second (38 GPa) is a first-order isostructural transition, evidenced by a deviation in unit-cell volume, and is associated with a high- to low-spin transition of the Fe$^{3+}$ ion.$^{[28]}$ The exact nature of the first transition is speculative, due to the limited information on the O positions relative to the La ion, whereas the second transition is almost certainly influenced by nonhydrostatic pressure conditions. In either case, the lack of correspondence between the high-temperature and high-pressure phases in this material is interesting, justifying further study.

The present work has used Raman spectroscopy and neutron diffraction to search for more subtle structural changes in LaFeO$_3$ up to 5.5 GPa at 300 K. Neutron diffraction data were also collected up to 6.4 GPa at 110 K to measure the effect of pressure on the magnetic structure of the sample.

2. Results and Discussion

2.1. Phase Characterisation

The neutron diffraction pattern from the sample at ambient conditions, collected on the $2\theta = 52.21^\circ$ Polaris detector bank, is shown in Figure 2a. The nuclear structure was refined against the orthorhombic Pnma model discussed earlier in the article, and the magnetic structure was fitted using a $\Gamma_5$: Pnma' model with the magnetic moment constrained along the $c$-axis, forming a pure G-type antiferromagnet as previously reported for LaFeO$_3$.$^{[10,23,26,27]}$ The refined atomic structural parameters are consistent with those previously reported from neutron data.$^{[27]}$ and are shown in Table 1.

The refined structure suggests that the La may be considered as coordinated to eight first-nearest neighbour O atoms, forming two distinct La–O1 bonds and three distinct pairs of La–O2

Figure 1. a) Orthorhombic (Pnma) structure of LaFeO$_3$ at ambient conditions as viewed down [010]. The La atoms (green spheres) sit on Wyckoff 4c ($x, 1/4, z$); the Fe atoms (yellow spheres) sit on Wyckoff 4a (0, 0, 0); the O atoms (red spheres) sit on two distinct sites, O1 on Wyckoff 4c ($x, 1/4, z$) and O2 on Wyckoff 8d ($x, y, z$). One layer of FeO$_6$ octahedra, and the La–O bonds are omitted for clarity. b) The orientation of the orthorhombic cell relative to the undistorted cubic parent structure, viewed along the [010]/[001]c. The dashed spheres and dashed lines represent the atomic positions and unit cell of the cubic parent, respectively. The La atoms are partially omitted for clarity; the out-of-phase tilt angle of the Fe–O$_6$ octahedra away from the undistorted orientation, $\phi_{M}$, is shown. c) The orthorhombic cell shown relative to the cubic parent along the [100]/[110]c; the in-phase tilt angle, $\phi_{R}$, is shown.
bonds. The refined oxygen positions are used to decompose the structure against the cubic parent structure, according to symmetry-adapted basis vectors. At ambient pressure, the octahedral tilt angles are 7.06(2)/C14 and 12.16(3)/C14, in agreement with those published previously.

The antiferromagnetic order in LaFeO3 contributes strongly to the pattern with additional peak intensity arising from the magnetic scattering, most noticeably overlapping a weak nuclear peak close to 4.5 Å in Figure 2.

The Rietveld fit to the pattern is consistent with the G-type antiferromagnetic model previously reported for LaFeO3 and the refined total magnetic moment, $\mu = 3.72(1) \mu_B$, has its largest contribution along the c-direction. While the other components were non-zero, they were negligible, and the refinements were unable to converge without these constrained to zero. This suggests that there is indeed a ferromagnetic canting in the material, consistent with previous reports.

High-temperature X-ray diffraction measurements confirmed the crossover of the a- and c-axis lengths with increasing temperature at 694 K and also an increase in orthorhombic distortion with increasing temperature as previously reported.

DC magnetic susceptibility measurements were also performed and are consistent with those previously reported.

### 2.2. High-Pressure Neutron Diffraction

#### 2.2.1. Lattice Strain and a–c Crossover

LaFeO3 shows no change in symmetry with increasing pressure at both 290 and 110 K. A representative diffraction pattern collected at 290 K and 5.5 GPa and Rietveld fit is shown in Figure 2. The equation-of-state of LaFeO3 was determined at each temperature.

Figure 3 shows the unit-cell volume ($V$) of LaFeO3 as a function of pressure at both temperatures. The volume decreases smoothly, and no discontinuous behaviour is observed. Experimental data at 290 K were fitted to a third-order Birch–Murnaghan equation of state and fitted values are shown in Table 2. The volume $V_0 = 243.18(3) \AA^3$, and the bulk modulus

| Present | Literature[27] |
|---------|----------------|
| $a$ [Å] | 5.56208(5)     | 5.56543(4) |
| $b$ [Å] | 7.85530(6)     | 7.85424(6) |
| $c$ [Å] | 5.55629(5)     | 5.55630(4) |
| $V$ [Å³] | 242.765(3)     | 242.878(3) |
| La$_x$ | 0.4706(1)      | 0.47130(11) |
| La$_z$ | 0.0063(2)      | 0.0069(3)  |
| O1$_x$ | 0.5134(2)      | 0.5140(2)  |
| O1$_z$ | 0.5768(3)      | 0.5742(3)  |
| O2$_x$ | 0.2190(1)      | 0.21720(16) |
| O2$_z$ | 0.0381(1)      | 0.03931(13) |
| O2$_y$ | 0.2812(1)      | 0.28158(16) |
| $\mu/\mu_B$ | 3.72(1)       | 3.686 |
| $wR_p$ [%] | 3.23           | – |
| $R_p$ [%] | 5.25           | – |
| $\chi^2$ | 3.49           | – |
| Fe–O1 [Å] | 2.0111(4)     | 2.0078(4) |
| Fe–O2 [Å] | 2.002(1)      | 2.0113(9) |
| Fe–O2' [Å] | 2.003(1)     | 2.0011(9) |
| La–O1 [Å] | 2.585(2)      | 2.5846(14) |
| La–O1 [Å] | 2.377(4)      | 2.416(3)  |
| 2 × La–O2 [Å] | 2.467(2)     | 2.4480(13) |
| 2 × La–O2 [Å] | 2.667(2)     | 2.6585(14) |
| 2 × La–O2 [Å] | 2.793(2)     | 2.7983(13) |

High-temperature X-ray diffraction measurements confirmed the crossover of the a- and c-axis lengths with increasing temperature at 694 K and also an increase in orthorhombic distortion with increasing temperature as previously reported.

DC magnetic susceptibility measurements were also performed and are consistent with those previously reported.

### Table 1. Rietveld refined structural and magnetic model, and determined bond lengths of LaFeO3 at ambient pressure and temperature from data collected on the Polaris diffractometer. La and O1 sit on Wyckoff 4c (x, 1/4, z), O2 sits on Wyckoff 8d (x, y, z), and Fe sits on the origin. These are compared with those measured on high-resolution neutron data (HRPD) from the literature, adopting the same standard setting.
of 175(1) GPa is in agreement with the value recently reported by X-ray diffraction of 172(2) GPa[21,28] with a third-order Murnaghan equation of state. The bulk modulus at 110 K was calculated by fitting a second-order Birch–Murnaghan equation of state ($B' = 4$); the number of data points at 110 K is insufficient to allow $B'$ to refine stably.

Analysis of the lattice parameters of LaFeO₃, and their variation as a function of pressure, is reported in the pseudocubic setting in Figure 3. The compressibility rates were determined for each temperature by a linear fit to the experimental data, and values are shown in Table 2. The divergence of the lattice parameters indicates an increase in orthorhombic distortion. A crossover of the $a$ and $c$ parameters is observed at approximately 2 GPa (Figure 3) at 300 K, in agreement with the previous X-ray study.[28] This crossover shifts to a lower pressure of 1.7 GPa at 110 K. Such behaviour has been previously reported in temperature-dependent X-ray and neutron diffraction characterisation around 700 K.[26,27] However, it is not directly associated with any phase transition, as the parameters then diverge with increased pressure, and orthorhombic symmetry is maintained throughout. The relationship $a > c$ for the $Pnma$ space group should be maintained for regular octahedra (O₂─Fe─O₂', 90°), though Woodward et al.[32] demonstrated that in the absence of tilts, a small (1°) distortion can result in a crossover of the $a$ and $c$ lattice parameters, an effect which is discussed further elsewhere in the literature.[33] In LaFeO₃, the octahedra are distorted with an O₂─O₂' angle of 91.24(1)°, in agreement with previously reported values.[27] However, the octahedral tilt provides a competing effect, such that $a > c$. With applied pressure the O₂─O₂' angle is almost invariant at each temperature considered, whereas the tilts decrease in magnitude, allowing $c$ to increase relative to $a$.

The deviation of an orthorhombic perovskite from the cubic symmetry can be quantified through considering spontaneous strains ($e₁, e₂, ..., e₆$) away from the undistorted structure. These are calculated from the lattice parameters[34] and many of them reduce to zero through symmetry for $Pnma$, leaving three tensile ($e₁, e₂, e₃$) and one shear strain ($e₄$)

$$
e₁ = \frac{b/2 - a₀}{a₀}
$$

$$
e₂ + e₃ = \frac{a/√2 - a₀}{a₀} + \frac{c/√2 - a₀}{a₀}
$$

$$
e₄ = \frac{a/√2 - a₀}{a₀} - \frac{c/√2 - a₀}{a₀}
$$

These can be reduced through linear combination, to symmetry-adapted strains. For $Pnma$, we may define a volumetric strain $e_\text{v}$ and a tetragonal strain $e_\text{t}$ (with the tetragonal axis parallel to the x-axis)

$$
e_\text{v} = (e₁ + e₂ + e₃)
$$

$$
e_\text{t} = \frac{1}{√3}(2e₁ - e₂ - e₃)
$$

where $a₀$ is the pseudocubic lattice parameter at the same pressure/temperature condition. Full details are available in
the literature. As there is no known cubic structure at high pressure to relate these parameters to, $a_0$ is estimated from the pseudocubic lattice parameters of the orthorhombic phase (which makes $c/a = 0$ by definition)

$$a_0 \approx \sqrt[3]{\frac{a}{\sqrt{2}} \times \frac{b}{2} \times \frac{c}{\sqrt{2}}}$$ (6)

In LaFeO$_3$, $c/a$ is observed to be invariant, while $c/a$ decreases linearly with increased pressure, and becomes negative as the $a$ and $c$ parameters crossover (Figure 3). $c/a$ does not tend toward zero, but instead passes through it, suggesting no change in the overall symmetry. Similarly, any potential transition to tetragonal symmetry would be accompanied by an upturn in tetragonal shear. This does not preclude an isosymmetric phase transition, driven by A-site centering.[28] This phase diagram is in strong contrast with that previously reported at ambient pressure.[26,27]

2.2.2. Octahedral Tilts and Structure Variation

Through considering the total bond valence sum, and average bond lengths of the La- and Fe-sites at ambient conditions, it is possible to predict certain structural changes at high pressure. Following the work of Zhao et al. on GdFeO$_3$-type perovskites,[35] the value of the dimensionless site-parameter $M_A/M_B$ being $>1$ or $<1$ can give a reasonable indication of whether the structure is likely to become less or more distorted (in terms of octahedral tilt) at high pressure, respectively. For LaFeO$_3$, $M_A/M_B \approx 1.06$. This suggests that the Fe−O octahedra should be relatively more compressible than the La−O polyhedra, and that the structure may tend toward a less tilted structure at higher pressure.[35]

Figure 4 shows the variation in the Fe−O bonds with pressure at both temperatures. At 290 K all the bond lengths decrease linearly with increasing pressure. This is largely the same at 110 K, except that the Fe−O2' bond length becomes invariant (within error). The bonds are generally incompressible, and this octahedral rigidity is such that the volume reduction of the unit cell is mostly accommodated by tilting of the octahedra. The polyhedra decrease linearly in volume with increasing pressure at both temperatures (Figure 5). At 290 K the Fe octahedra are found to be more compressible than the La−O polyhedra, as expected from $M_A/M_B$, but at 110 K, they are found to be almost identical, suggesting a possible switch in behaviour at lower temperatures still.

Using the approach of symmetry-adapted basis vectors, the seven positional parameters of the Pnma structure can be recast as seven internal modes of distortion from the cubic parent structure.[29,36–40] $M_A^+$ and $R_4^+$ are irreducible representations related to octahedral tilts; $M_A^+$, $X_4^+$ (O), and $R_4^+$ (O) are related to octahedral distortions; and $X_3^+(A)$ and $R_3^+(A)$ are related to A-site cation displacements. The $M_A^+$ mode (in-phase) acts about the $b$-axis, whilst the $R_4^+$ mode (out-of-phase) is a tilt about the $a$-axis of the orthorhombic cell.

At 290 K, both the $M_A^+$ and $R_4^+$ tilting modes are much larger in magnitude and more strongly pressure dependent than the octahedral distortion modes, which remain close to zero. While there is no change in octahedral distortion, their volume decreases linearly with increasing pressure (bottom of Figure 5), and the degree of octahedral tilting (determined directly from the mode amplitudes $M_A^+$ and $R_4^+$, see ref. [29]) decreases toward the cubic parent structure (Figure 5), in agreement with the expected reduction in distortion from $M_A/M_B > 1$. In contrast, at 110 K only the $M_A^+$ mode (and therefore $\phi_M$ octahedral rotation angle) decreases with increasing pressure and the $R_4^+$ mode ($\phi_B$ tilt) is invariant (Figure 5). At 290 K, the variation in $X_3^+(La)$ and $R_4^+(La)$ is negligible, with values fluctuating close to zero. At 110 K, $R_4^+(La)$ decreases in amplitude and $X_3^+(La)$ increases negligibly.

2.2.3. Magnetic Structure

From the Rietveld fits of the neutron diffraction data, the modulus of the magnetic moment was refined and found to remain unchanged over the pressure range investigated, as shown in Figure 6. The magnetic moment has been proposed to be $\approx 4.6 \mu_B$ from a neutron diffraction study,[15] whereas recent calculations yielded a slightly lower value of $4.1 \mu_B$[41] at ambient temperature and pressure. Our data show that pressure does not affect the magnetic moment of LaFeO$_3$, which is found to
fluctuate around a value of $4 \mu_B$ at 290 K and $4.4 \mu_B$ at 110 K. This is consistent with the structural changes observed, primarily the lack of change in the O–Fe–O bond angles, which govern the superexchange interactions between neighbouring Fe moments.

2.3. High-Pressure Raman Spectroscopy

The Raman spectra of LaFeO$_3$ have been measured up to 7.6 GPa at 300 K; a representative spectrum at 5.4 GPa is shown in Figure 7 in the region 100–550 cm$^{-1}$ range. Vibrational mode symmetries are assigned according to previous polarisation-dependent Raman study of LaFeO$_3$.[42] Mode symmetries are assigned according to a previous ambient pressure study.[42] The vibration modes all appear to harden with increasing pressure, except the $B_{2g}$ mode at approximately 184 cm$^{-1}$ associated with the in-phase FeO$_6$ octahedra rotation about [110]c (Figure 7).

It has been previously shown that the tilt modes soften with decreasing tilt angle (at a rate of $\approx 22.5$ cm$^{-1}$ deg$^{-1}$ across the series AFeO$_3$, A = La…Dy).[42] Diffraction has shown the tilts to decrease with increasing pressure, though the Raman-active $A_g$ mode ($\approx 300$ cm$^{-1}$), associated with the in-phase FeO$_6$,
octahedra rotation about [110], hardens with increasing pressure. This is due to the mode also being associated with the displacement of La\(^{1-}\). Other modes such as \(B_{2g}\), associated with out-of-phase FeO\(_6\) octahedra rotation about [110], are weak and not observable due to the high background from the diamond anvil cell. Previous high-pressure Raman work showed the disappearance of one \(A_g\) mode and the appearance of a new mode at \(\approx 180\ \text{cm}^{-1}\) at around 4 GPa, and suggested that this is an indicator of the progression of a second-order \(Pnma\)–\(Ibmn\) phase transition occurring around 16 GPa.[48] We see no evidence of this mode appearing in our current study up to a pressure of 7.6 GPa. It should be noted that sample volume, and compression rate, can influence the observed structural changes. The Paris–Edinburgh press contains orders of magnitude greater sample volumes than a diamond anvil cell (DAC). Furthermore, X-ray diffraction from a DAC commonly uses a focused beam, measuring from a small part of the available sample volume, whereas neutron diffraction measures from the entire sample volume, giving much more representative data.

3. Conclusions

The high-pressure structural and magnetic behaviour of the perovskite structured LaFeO\(_3\) has been determined from isothermal compression at 110 and 290 K, using neutron diffraction. We have shown there is no significant change in bulk modulus at both temperatures (\(B_0 = 175(1)\) and 170(3) GPa at 290 and 110 K, respectively). Overall, both the FeO\(_6\) and LaO\(_8\) polyhedra decrease smoothly in volume with increasing pressure and show no measurable change in distortion at either isotherm. The decrease in unit-cell volume upon compression occurs as a result of a combination of both a decrease in the tilting of both the in- and out-of-phase tilted FeO\(_6\) octahedra and reduction in FeO\(_6\) and LaO\(_8\) polyhedral volume. We see no evidence of a drive toward a higher or lower symmetry phase. However, at 110 K we observe slight change in the in-phase tilt of the FeO\(_6\) octahedra with increasing pressure but a small increase in distortion. There is also an increase in orthorhombic distortion of the unit cell as shown in the change in shear (\(e_4\)) strain relative to that at 290 K. At the two temperatures measured, there is no change in magnetic moment with increasing pressure. The structural changes are consistent with the Raman spectra at room temperature.

4. Experimental Section

A phase-pure sample of polycrystalline LaFeO\(_3\) was prepared using a nitrate decomposition procedure. A stoichiometric mixture of La(NO\(_3\))\(_3\)·6H\(_2\)O and Fe(NO\(_3\))\(_3\)·9H\(_2\)O (99.999%; Sigma-Aldrich) was completely dissolved in distilled water. The water was removed by evaporation at 350 K, and the resulting gel was decomposed at 870 K over 24 h in air. The resulting gray powder was ground, pelletized, and further annealed in air at 1370 K for 12 h. Repeated grinding, pelletising, and annealing was performed until a single-phase material was obtained. The final powder was orange in colour. The phase purity was confirmed by neutron diffraction measurements carried out on the Polaris instrument at the ISIS facility.[49]

High-pressure neutron diffraction measurements were performed on the PEARL instrument[50] at temperatures of 110 and 290 K in the 0–6.4 and 0–5.5 GPa pressure range, respectively. A V3 Paris–Edinburgh press was used for the data collection. The sample was loaded into a Ti–Zr alloy gasket placed between single-toroidal ZrO\(_2\)–Al\(_2\)O\(_3\) (ZTA) anvils for measurements in the 0–6.4 GPa. Pb was included in the sample volume as pressure marker. Perdeuterated (hydrogenated) materials add a strong incoherent background to neutron diffraction patterns greater than the coherent scattering contribution and to remove such unwanted background deuterated samples are used in their place which do not have any significant level of incoherent scattering) methanol:ethanol (4:1 by volume) was used as a pressure transmitting medium. The experimental patterns were normalised, and corrected for attenuation effects using Mantid software,[31] and Rietveld refinement of the data was performed using the GSAS package.[52] The standard data collection frame of the PEARL instrument collects data in the q-spacing range 0.4–4.1 Å. By making use of the longer pulse of the fourth data frame, this range can be extended in principle to \(\approx 8.2\ \text{Å}\) with reduced data quality (for details, see ref. [50]) and in this study this long frame was used to measure the 011/101 reflection from LaFeO\(_3\) at high pressure and was included in the Rietveld refinement.

For the high-pressure Raman measurements, LaFeO\(_3\) was loaded into a stainless steel gasket within a Merrill–Bassett DAC.[31] The gasket was pre-induced from an initial thickness of 250 to 110 μm, and drilled with a sample hole of 300 μm diameter. A small ruby sphere was used as a pressure marker, determined by ruby fluorescence measurements.[31] Methanol–ethanol (4:1 by volume) was used as a pressure transmitting medium. Raman spectra were collected using an in-house Raman system equipped with a Princeton Instruments SP2500i spectrometer using a 1800 g holographic blaze grating. A diode laser (λ = 532.23 nm) was focused using a 20× Mitutoyo objective lens generating 5 mW power at the sample position to limit sample heating and fluorescence.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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