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Low-Temperature Structural Behaviour of LaCoO_3 – A High-Resolution Neutron Study

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Abstract

We present the temperature evolution of the crystallographic structure of LaCoO_3 in the range 4-300 K. We observe no anomalies in the rhombohedral unit cell parameters at temperatures where electronic transitions are expected to occur. We also find no evidence of the monoclinic distortion of the unit cell proposed others. We parameterise the octahedral tilt and distortion as a function of temperature which show a linear evolution towards a more symmetric form.

Introduction

There continues to be significant research activity in the RECoO_3 perovskites (where RE rare earth cation). This is motivated in part as a result of their interesting electronic properties, but also for the potential for application in catalysis [1,2]. One of the most studied materials is LaCoO_3 in which the majority of the studies have focused on the electronic transitions of the cobalt cation. At low temperature the 3d electrons in the Co^{3+} cation are found to be in

a low spin (LS) state with the electronic configuration $t_{2g}^6 e_g^0$ ($S = 0$) [3]. At ~ 100 K a sharp anomaly in the magnetic susceptibility is observed, and with increasing temperature, the higher spin (HS) $t_{2g}^4 e_g^2$ configuration ($S = 2$) was originally believed to be progressively populated [3,4]. At higher temperatures still (above 650 K), long range ordering of the spin state and charge disproportionation is found to occur (forming Co^{2+} and Co^{4+} cations)[5]. At even higher temperatures ($T > 1210\text{K}$) there is a further electronic transition where the 3d electrons become delocalised [4]. However, the low temperature LS-HS interpretation has been found not to be supported by other techniques including temperature dependence of x-ray absorption [6,7] and photoemission spectra [8]. As a result, an intermediate spin state (IS) with the electronic configuration $t_{2g}^5 e_g^1$ ($S = 1$) has been proposed to exist between the LS and HS states with the transition from LS to IS being observed around 100 K [9,10]. This alternative sequence of electronic transitions, LS-IS-HS, provides a model which could explain the two anomalies in the magnetic and thermal expansion with increasing temperature [11, 12]. The intermediate spin state configuration has partially filled e_g orbitals would be expected to give rise to a strong Jahn-Teller distortion which would allow for the possibility of long range orbital ordering [13].

The aristotype perovskite structure is cubic with the space group $Pm-3m$ with a large cation (La, in this case) dodecahedrally coordinated in a cavity site and a smaller cation (Co, in this study) in octahedral coordination [14, 15]. This crystal structure imposes the strict constraint that the ratio of the two cation-anion bond lengths is $\sqrt{2}$, however, the majority of perovskite-structured materials do not crystallise in the cubic structure, but the octahedra are found to rotate around one or more of the tetrad axes thus permitting the smaller cation to retain 6-fold coordination and allowing a smaller cation into the cavity site. As a result, the octahedra in these hettotype phases are frequently distorted and are elongated or compressed along the rotation axis with a concomitant reduction in crystallographic point group symmetry. Often a series of structural phase transitions are observed with increasing temperature or pressure which show a progressive increase in crystal symmetry.

Neutron diffraction experiments have shown that the crystal structure of LaCoO_3 is rhombohedral with space group $R-3c$ [16,17]. This space group does not permit distortion of

the octahedra of the Jahn-Teller type for a perovskite-structured phase. However, more recently, a high-resolution single crystal and powder x-ray diffraction experiment has provided evidence for a monoclinic distortion (space group $I2/a$) which would permit Jahn-Teller distortion of the octahedra associated with long range e_g orbital ordering [13]. Both of the structural studies detailed above investigated the structure as a function of temperature and observe no deviation from the rhombohedral or monoclinic symmetry at low or high temperature. Thornton *et al* [16] suggested the possibility of the symmetry being reduced from $R-3c$ to $R-3$ at 668 K (which would support ordering of divalent and tetravalent Co cations), however no significant evidence for this was found beyond an improvement in goodness of fit parameters (i.e., no violations of the systematic absence conditions implied by the c-glide plane were observed) but this was not shown for any other data set either side of this temperature in the measured data series ($R-3$ $R_{\text{profile}}= 8.7\%$ & $R_{\text{expected}}=17.5\%$ and for $R-3c$ $R_{\text{profile}}= 9.4\%$ & $R_{\text{expected}}=17.6\%$). Given that the marginal improvement in the agreement parameters resulted from more refinable parameters, the existence of the $R-3$ phase is difficult to justify and that no data sets either side of that measured at 668 K show the same possibility of being in $R-3$ [16]. The more recent work of Kobayashi *et al* [18] shows that at 1700 K the material becomes metrically, and presumably structurally cubic as the rhombohedral unit cell angle becomes 60° via a second order phase transition [4]. We note that in order for the monoclinic cell to transform to the cubic metric at high temperature it either transforms via a first order phase transition. Alternatively, the structure first needs to undergo a first order transition from $I2/a$ to $R-3c$ prior to a discontinuous transition to $Pm-3m$.

In this work we have used high-resolution neutron powder diffraction to investigate the crystal structure of LaCoO_3 in the temperature range 4-300 K. We observe no evidence for the monoclinic distortion proposed by Maris *et al* [13] finding the structure remains rhombohedral over the entire temperature range studied. Despite the high resolution of the data, we see no evidence in the lattice parameters of the rhombohedral cell for any anomalies at 100 K relating to the LS-IS transition. However, we do observe an anomaly in one La-O bond distance in this temperature regime as previously suggested. We parameterise the octahedral tilt and strain as a function of temperature.

Experimental

The bulk powder sample of LaCoO_3 was prepared by mixing stoichiometric amounts of lanthanum and cobalt nitrates and dissolving in the minimum quantity of water. The water was then driven off at 350 K to produce a solid gel which was decomposed at 580 K in a furnace. The decomposed material was then annealed at 1270 K for 12 hours and subsequently cooled to room temperature, ground, and annealed further at 1370 K for 24 hours. Finally the sample was cooled to room temperature at a rate of 5 K min^{-1} . The phase purity was determined by X-ray diffraction and was shown to be phase pure with the rhombohedral symmetry, as reported previously by Thornton *et al* [16].

Time-of-flight (TOF) neutron diffraction experiments were performed on the HRPD instrument located at the ISIS Neutron Spallation Source, Rutherford Appleton. X grams of LaCoO_3 was loaded into a 5 mm thick aluminium slab can equipped with vanadium windows and gadolinium mask which was mounted on a centre stick and placed in a standard “Orange” Abingdon Scientific helium cryostat. The sample was initially cooled to 4.2 K and data collected for 2 hours, after which the sample was then warmed to 10 K and data collected for 15 minutes at each 5 K step following a period of equilibration up to a maximum temperature of 300 K (yielding a total of 40 data sets). The diffraction pattern was collected using the backscattering detectors over a TOF range of 30–130 ms, corresponding to a d -spacing of 0.6–2.6 Å. The data was reduced using in-house software and Rietveld refinement was performed using the GSAS package [19].

Results & Discussion

The high resolution neutron diffraction pattern of LaCoO_3 measured at 4.2 K is shown in Figure 1. Also shown in the figure are the results of the Rietveld structure refinement. The starting structure used for the refinement is that as previously reported by Thornton *et al* [16] in space group $R\bar{3}c$. In this structure the only refinable structural coordinate relate to the oxygen atom as the lanthanum and cobalt atoms are sited on the Wyckoff special positions $2a$ and $2b$ respectively at co-ordinates of $1/4, 1/4, 1/4$ and $0,0,0$. The results from the structural refinement are detailed in Table 1 along with details of the

refinement itself. The small number of weak unindexed peaks in the diffraction pattern can be accounted for by vanadium (from the cryostat tails), and low levels of La_2O_3 and CoO undetected in our X-ray diffraction measurements. We have performed the same analysis at 300 K and the results of the refinement are also tabulated in Table 1. Furthermore, we have attempted to refined a monoclinic model set using the proposed monoclinic cell (space group $I2/a$) and structural data of Maris *et al* [13] against our 300 K data. However, even with the high resolution of the HRPD instrument we are unable to resolve the 20-2 and 022 reflections which would be found at 2.2182 and 2.2184 Å respectively (when the data is refined with a monoclinic model) and hence we can provide no evidence of the monoclinic distortion despite an instrument resolution $\delta d/d$ of $\sim 4 \times 10^{-4}$. The quality of Rietveld fit for the monoclinic cell to our high resolution powder data at 300 K are also tabulated in Table 1 and we see a small decrease in fit quality using the monoclinic structure despite the increase in number of fitting parameters. The monoclinic unit cell values at 300 K are $a=5.38089(9)$, $b=5.44590(9)$, $c=7.65237(11)$ $\beta=90.972(1)$ $V=224.212(1)$. We note that the errors in the unit cell parameters are higher than those for the rhombohedral structure (Table 1) and are determined to a much higher precision than previously reported for the proposed monoclinic structure [13]. We have also studied the lineshape of the 400 reflection as per the work of Maris *et al* and find no evidence that the reflection is better fitted with a monoclinic distortion. Previously, the materials were measured using x-ray diffraction on a synchrotron source with an angular resolution of 0.001° per step [13]. The determined bond distances for the monoclinic structure when fitted to our 300 K data are 1.9302(7), 1.920(4) and 1.920(4) Å which when compared to 1.93251(4) Å for the rhombohedral setting (providing one Co-O distance) are shown to be only slightly distorted in favour of a Jahn Teller like distortion in the monoclinic structure. The comparable previously reported x-ray single-crystal structure give the Co-O bond distances as 1.874(7), 1.925(8) and 1.993(8) Å for which the errors are significantly larger [13] .

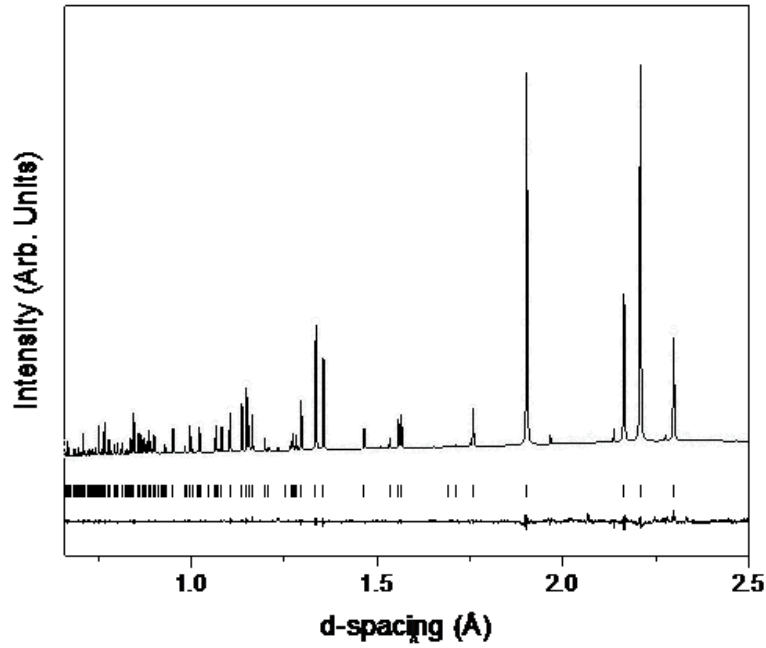


Figure 1. Neutron diffraction powder pattern and associated Rietveld fit from LaCoO_3 at 4.3 K (backscattering 168° bank). The raw data is shown by the open circles, the Rietveld fit to the data the solid line. The vertical lines show the reflections position expected from the rhombohedral structure. The bottom trace shows the residual to the fit.

	4.2 K	300 K
$a_{\text{rh}}(\text{\AA})$	5.34058(1)	5.38024(1)
$\alpha_{\text{rh}}(^{\circ})$	60.998(1)	60.797(1)
Volume (\AA^3)	110.129(1)	112.106(1)
La $U_{\text{iso}} (*100)$	0.319(22)	0.677(15)
Co $U_{\text{iso}} (*100)$	0.295(27)	0.482(32)
O x	0.19794(5)	0.20055(6)
O $U_{11}, U_{22}, U_{33},$ $U_{12}, U_{13}, U_{23} (*100)$	0.433(13), 0.433(13), 0.612(26) -0.205(16), -0.137(11), -0.137(11)	0.844(15), 0.844(15), 1.071(29) -0.450(19), -0.198(12), -0.198(12)
O $U_{\text{equiv}} (*100)$	0.49(4)	0.95(4)
wRp	2.87	2.76 (2.9)
Rp	2.91	2.60 (2.66)
χ^2	2.6	4.8 (5.3)

Table 1. Refined crystallographic parameters of LaCoO₃ at 4.3 and 300 K. The symmetry is given by the primitive rhombohedral space group R-3c for which the lattice parameters a , b and c are equal and the unit cell angles α , β and γ are also equal. The lanthanum atoms are sited on Wyckoff site 2a and the atomic co-ordinates $1/4, 1/4, 1/4$. Whilst the cobalt atoms are sited on the special position 2b with co-ordinates $0, 0, 0$. The oxygen atom is situated on the Wyckoff site 6e for which the x co-ordinate is $1/4 - 2e$, y is $1/4 + 2e$ and the z co-ordinate is 0.75 . The quality of refinement parameters are given for the overall fit of both the 90 and 168° bank of detectors combined. The numbers in brackets for the quality of fit in the 300 K dataset are when the more recent monoclinic cell ($I2/a$) is used to refine the data [13].

The temperature dependence (from 4 to 300 K) of the unit cell lattice parameters and unit cell volume are shown in Figure 2 along with the previously reported values of Thornton *et al* [16]. It can be seen that the within experimental error saturation of the lattice parameters and unit cell volume is observed until 35 K. Above this temperature, the unit cell length and volume both increases with increasing temperature and the rhombohedral angle α_{rh} decreases (as would be expected as distortion of the material is decreased and it is driven towards the idealised pseudo cubic metric value of 60°). However, this second order phase transition to a cubic structure is not expected to occur until ~1700 K [18] and extrapolation of our low temperature data to gives this transition as occurring at 1305 K, however, we do note that this is performed on the low temperature region only and leads to the predicted anomalous low temperature value compared to other studies. We can empirically, but accurately parametrize the temperature dependence of the unit cell volume in terms of the sum of two Einstein/Debye internal energy functions, one of which is associated with a negative Gruneisen constant.

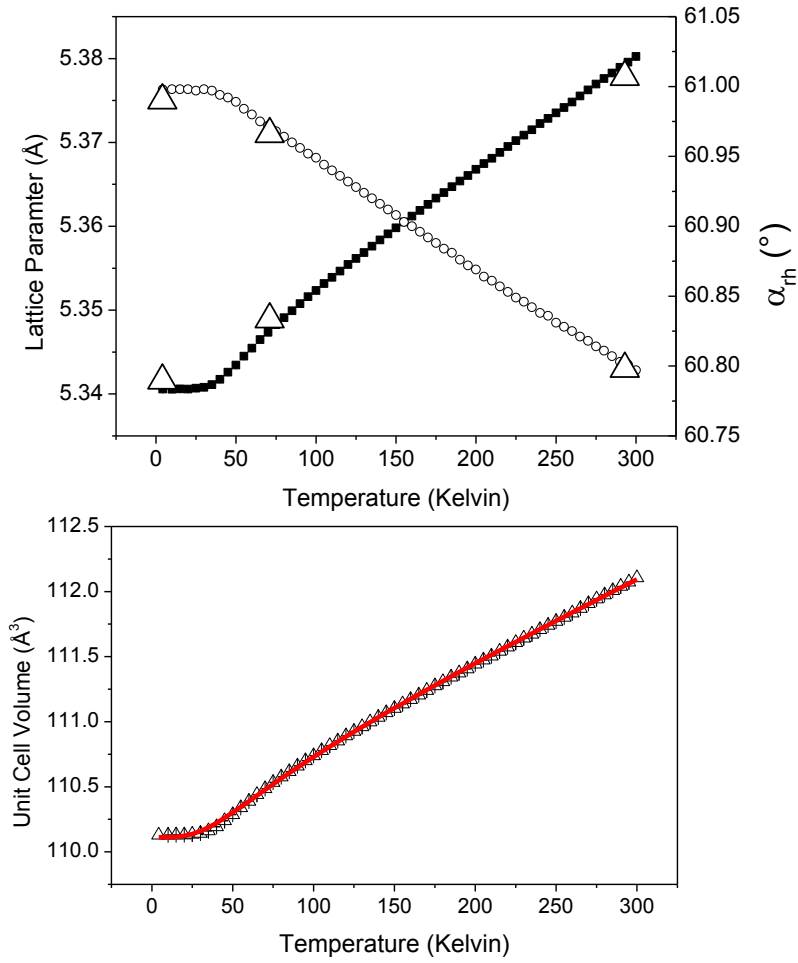


Figure 2. Determined unit cell parameters for LaCoO_3 as function of temperature. Top: Rhombohedral lattice parameter (solid squares) and rhombohedral unit cell angle (open circles). Bottom: Unit cell volume (Solid triangles) as a function of temperature. The fit to the volume data as described in the main text is shown as the solid red line. The errors are shown but significantly smaller than symbol plotted. Data from the work of Thornton are shown as open triangles [16].

Figure 3 shows the variation in selected derived bond distances as a function of temperature including the previously reported values from Thornton *et al* [16]. The variation in the bonded Co-O and La-O distances shows increases with temperature beyond 35 K. In the rhombohedral space group $R\bar{3}c$, the point group symmetry of the Co site permits only one nearest neighbour Co-O bond distance. By contrast, 3 independent bond

lengths are observed for the La site with the long, non-bonded La-O distance showing significantly smaller variation in distance with increasing temperature than the bonded interactions. The guide to the eye for the non-bonded La-O distance, shown in the bottom right panel, exhibits a maximum at ~ 115 K, close to the transition from LS to IS, however, we do note the large relative visual scatter in this distance in the graph in the plotted scale. A similar behaviour can be implied from the limited data presented by Thornton *et al* [16] but beyond 300 K it increases but only by a small amount and has been studied well by Radaelli *et al* [11]. Mortimer *et al* have also observed an anomaly in one of the Co-O vibrational modes within this temperature region [20]. It has been shown that the the long La-O bond is sensitive to non-thermal lattice distortions [11]. The known transition at 100 K is associated with an increase of the La-O “long” bond length, indicating that the structure is expanding in an anomalous way [11].

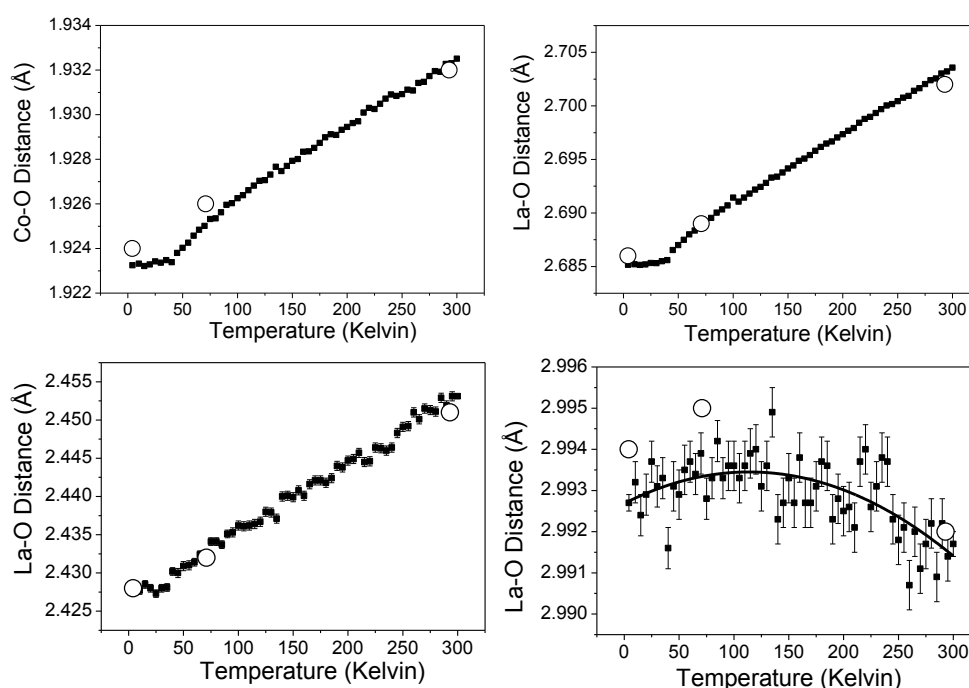


Figure 3. Variation of derived bond distances of LaCoO_3 with temperature. Top left octahedral Co-O distance. Top right La-O bond distance (6 x), Bottom left and right La-O distance (3 x each). Note where error bars are not visible they are plotted but smaller than symbol plotted and that for the “longer” La-O bond the variation in bond length is significantly smaller when compared to the other La-O distances for a given temperature increase. The line shown in the bottom right panel is a guide to eye. Data from the work of

Thornton et al are shown in all panels by the larger open circles (no errors were reported in the work) [11].

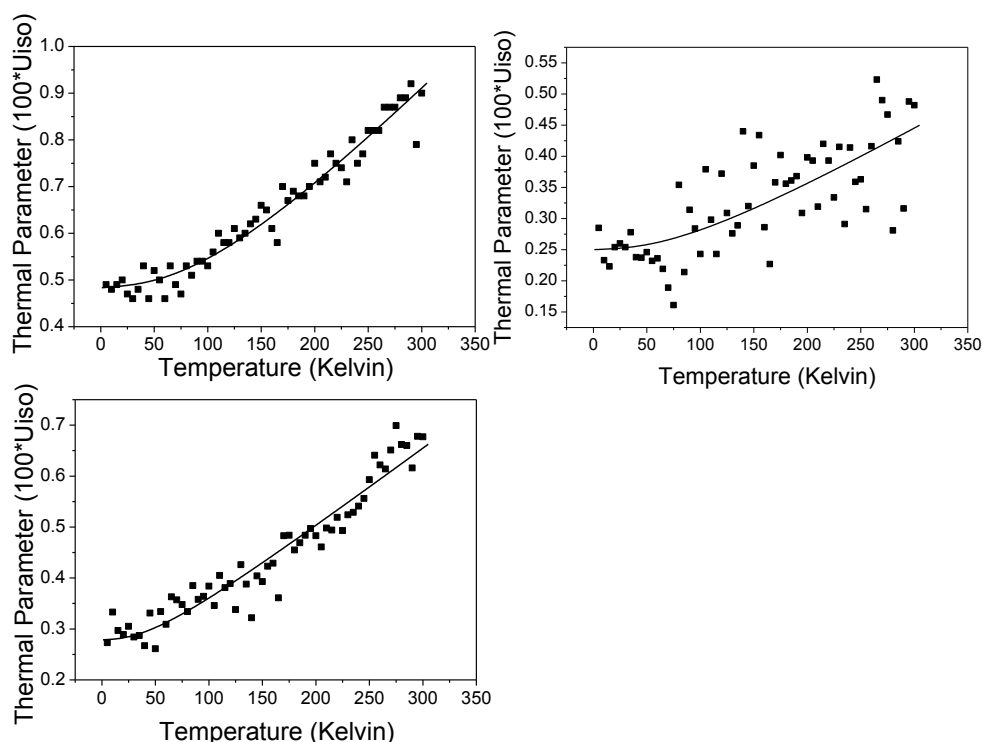


Figure 4. Variation of the atomic displacement parameters of atoms within LaCoO_3 with temperature. Top left: variation of Uiso of the lanthanum atom sited on the 2a Wyckoff site. Top right: variation of the cobalt atom sited on the 2b Wyckoff site. Bottom left: Uiso equivalent of the O atom sited on the 6e Wyckoff site. The thermal motion of the oxygen atom in the refinement was modelled anisotropically and the effective isotropic equivalent atomic displacement parameter is plotted. The solid line in each plot is the fit of the modified Debye model [21] as described in the text.

Figure 4 shows the variation in the atomic displacement parameters for each of the atoms in the LaCoO_3 structure. The thermal motion of the oxygen atom was modelled anisotropically in the Rietveld refinement and those for the cobalt and lanthanum atoms were refined isotropically. The isotropic equivalent thermal parameter for the oxygen atom is plotted in figure 4. The thermal motion for the oxygen and lanthanum atoms shows a reasonable increase in thermal motion with increasing temperature. However, we do note there is significant scatter and not such an obvious trend in the thermal parameters refined for the cobalt atom. The isotropic atomic displacement parameters for the cations, and the isotropic equivalent displacement parameter for the anions,

were fitted using the modified Debye model of Wood *et al.* [21] which permits the zero-point term to be an additional refinable variable in addition to the vibrational Debye temperature. Characteristic temperatures of 259(4) K for La, 499(25) K for Co and 617(7) K for O, the differences between the two cations reflecting the more open soft environment of the cavity site when compared to the octahedral site. Similar trends and values have been observed for other perovskites for example; BaCeO₃ the characteristic temperatures are found to be 200 K for La, 298 K for Ce and for oxygen 617 and 730 K [22] and for LaGaO₃ a determined value of 286 K for La, 496 K for Ga and 688/776 K for the oxygen atoms [23].

In the *R*-3c structure no distortion of the Co-O bonds in the CoO₆ octahedra (in a perovskite structure) can be determined and hence by symmetry non-distorted octahedra are observed. The oxygen fractional coordinate can be related to that of the psuedo cubic one by 1/4-2e, 1/4+2e, 3/4 [24], where e is displacement from the ideal cubic position. The effect of the displacement e is a rotation (tilt) of the octahedron about the rhombohedral [111] axis. In figure 5 the temperature-variation of the oxygen 2e parameter as determined from the expression above is shown. It can be see that the value of 2e tends towards the idealised cubic value of 0 with atomic position of 0.25 (e=0). The magnitude of the tilt angle of the octahedron, (ω), has been shown to related to the parameter e by the expression [24].

$$\tan\omega = 4\sqrt{3}e \quad (1)$$

In their analysis the pseudo cubic lattice parameter (a_{pc}) can (according to Megaw and Darlington) be approximated as $\sim 8 \text{ \AA}$ (4*TM-O) and the pseudo cubic subcell can be calculated directly from the rhombohedral cell length as $\sqrt{2}a_{rh}$. And according to Megaw and Darlington to a good approximation it is possible to compare the interaxial angles rhombohedral cell (α_{rh}) and pseudo cubic cell (α_{pc}) using the relationship [24].

$$90 - \alpha_{pc} = (3/2)^{0.5}(60 - \alpha_{rh}) \quad (2)$$

At 4.2 K this gives a psuedo cubic lattice parameters a_{pc} and α_{pc} of 7.55276 \AA and 91.22° respectively. The idealised values with perfect cubic symmetry would be 8 \AA (4*TM-

O) and 90° (and in LaCoO₃ only at a temperature of ~1700 K [18]) and the deviation from this value indicating the distortion away from the cubic symmetry. Another distortion shown to be present in perovskites with the rhombohedral symmetry of space group *R-3c* is a flattening or elongation of the octahedra and is described by a factor 1+ζ, referred to as the octahedron strain, and is derived from the lattice parameters after adjustment is made for the tilt [24]. If regular octahedra are assumed (ζ=0) it has been shown that the calculated value of the pseudo cubic interaxial angle (α_{pc}) is given by

$$\cos \alpha_{pc} = \frac{\sin^2 \omega}{3 - 2 \sin^2 \omega} \quad (3)$$

The work of Megaw and Darlington shows that the octahedron strain (ζ) can be deduced by comparison of the calculated and observed interaxial angles by

$$\cos(\alpha_{pc})_{obs} - \cos(\alpha_{pc})_{calc} = \left(\frac{2}{3}\right) \zeta \left[1 - \left(\frac{2}{3}\right) \sin^2 \omega\right]^{-1} \quad (4)$$

The evolution of calculated α_{pc} and octahedron strain with temperature is shown in figure 5. It can be seen that with increasing temperature, the angles, octahedral strain and tilt all tend towards the idealised pseudo cubic values. In figure 6 we show the variation of the determined octahedral strain and tilt angle which shows a strong trend – we note as did others that there is no geometric connection between these two derived values and hence that the evolution of the tilt angle and octahedron strain are coupled by the structural evolution with temperature [24].

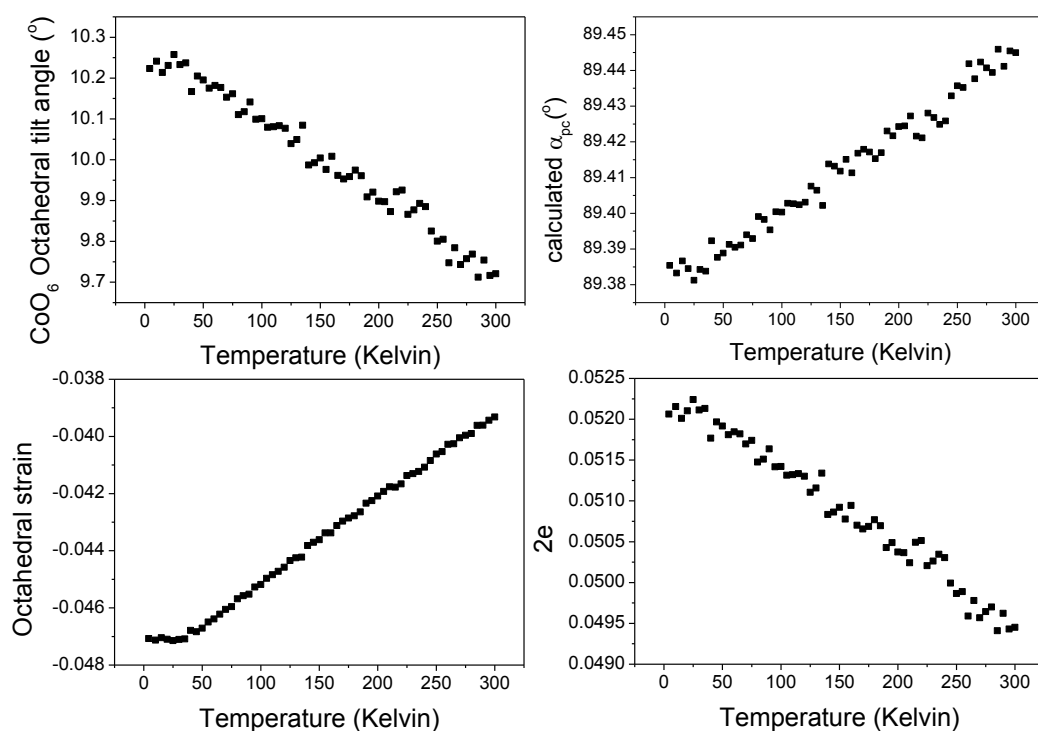


Figure 5. Top left: shows the derived octahedral tilt angle with increasing temperature. The tilt of the octahedra is decreasing in temperature showing a tendency to move towards a more idealised cubic structure. Top right panel shows the calculated pseudo cubic interaxial angle and shows a trend towards the idealised value of 90°. The bottom left panel shows the calculated pseudo cubic interaxial angle and shows a trend towards the idealised value of 90°. The bottom left panel shows the octahedra strain (or flattening or elongation of the octahedra in shape) variation with temperature again trending towards a value of zero. The bottom right panel shows the variation in the displacement away from the idealised cubic position (1/4) of the oxygen atom 2e with temperature.

In all of the structural parameters that have been refined and determined in this study, with increasing temperature we have observed no discontinuities, and only linear variations have been observed despite the electronic and magnetic transitions which are known to occur in LaCoO_3 in this temperature range. We suggest therefore that these may be manifest on a more local structural length scale beyond that shown by standard crystallographic methods. It has been suggested by others with a correlation length scale of 3.6 \AA close to that of the Co-O distance and occur randomly in every direction [25].

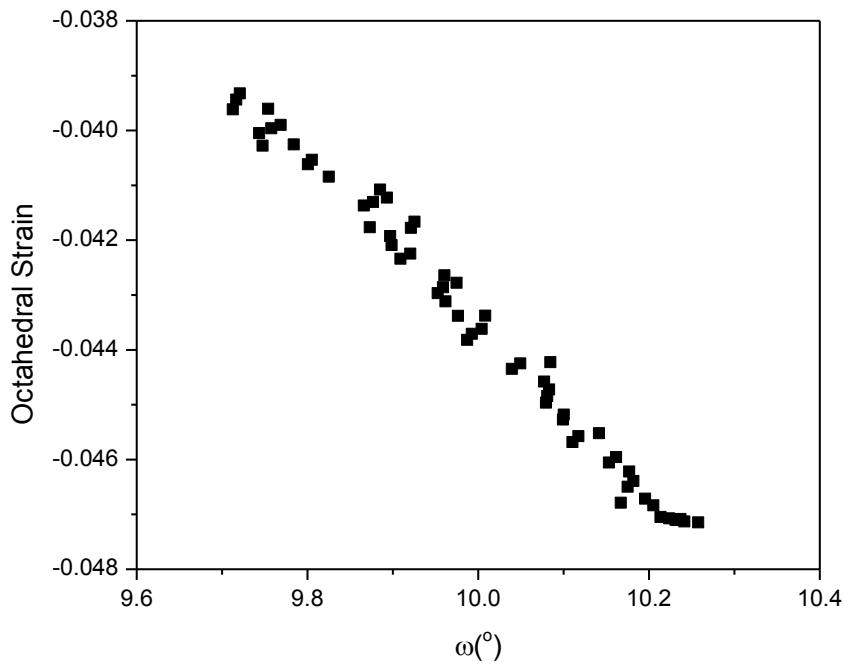


Figure 6. Temperature dependent octahedron strain ζ versus octahedron tilt angle ω for LaCoO_3 .

Conclusions

By making use of high-resolution neutron diffraction we have investigated the low temperature evolution of the crystallographic structure of LaCoO_3 . We find no evidence for a monoclinic structure at 300 K proposed by Maris et al [14] despite the high-resolution instrument used in this study. We observe no discontinuities in the crystal structure in the temperature range 4-300 K (the temperature range during which the LS-IS-HS transition in the cobalt 3+ transition metal ion occurs). We have shown how the octahedral tilt evolve

with increasing temperature and by use of octahedral strain how the deformation of the CoO_6 octahedra decreases with increasing temperature.

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