Magnetism in nanoparticle LaCoO₃

A. M. Durand,¹ D. P. Belanger,¹ F. Ye,² S. Chi,² J. A. Fernandez-Baca,² C. H. Booth,³ and M. Bhat⁴

¹Department of Physics, University of California, Santa Cruz, CA 95064, USA
²Quantum Condensed Matter Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA
³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
⁴Castilleja School, Palo Alto, CA 94301, USA

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LaCoO₃ (LCO) nanoparticles were synthesized and their magnetic and structural properties were examined using SQUID magnetometry and neutron diffraction. The nanoparticles exhibit ferromagnetic long-range order beginning at \( T_C \approx 87 \) K that persists to low temperatures. This behavior is contrasted with the ferromagnetism of bulk LCO, which also starts at \( T_C \approx 87 \) K but is suppressed below a second transition at \( T_o \approx 37 \) K. The ferromagnetism in both systems is attributed to the tensile stress from particle surfaces and impurity phase interfaces. This stress locally increases the Co-O-Co bond angle \( \gamma \). It has recently been shown that LCO loses long-range ferromagnetic order when \( \gamma \) decreases below the critical value \( \gamma_c = 162.8^\circ \). Consistent with this model, we show that \( \gamma \) in nanoparticles remains larger than \( \gamma_c \) at low temperatures, likely a consequence of all spins being in close proximity to surfaces or interfaces.

The magnetism of LaCoO₃ (LCO) is well-known to be unusual. Both ferromagnetic and antiferromagnetic interactions have been proposed in the bulk material.¹ ² The dominant interaction above \( T = 100 \) K is antiferromagnetic; however, in our previous study, we did not find evidence of antiferromagnetic ordering upon decreasing \( T \).² We thus concluded that the antiferromagnetic interactions are strongly frustrated. We have also recently shown³ that weak ferromagnetic order occurs below \( T_C = 87 \) K in small applied fields, \( H \leq 100 \) Oe, yet is lost below \( T_o \approx 37 \) K. Studies of LCO nanoparticles⁴–⁷ and thin films⁸–¹⁷ also show the presence of a ferromagnetic phase transition near \( 87 \) K, though these materials do not exhibit the same loss of ferromagnetic long-range order seen in bulk LCO below \( 37 \) K.

The unusual low temperature magnetism in the bulk has been shown to correlate well with the behavior of the Co-O-Co bond angle, \( \gamma \). Experimental measurements³ indicate that ferromagnetism only exists when \( \gamma \) is greater than a critical value \( \gamma_c = 162.8^\circ \), which happens only for \( T > T_o \). Above \( T_o \), all of the lattice parameters, including \( \gamma \), show power-law behavior in \( T - T_o \). For \( T < T_o \), the lattice parameters show only a small, linear \( T \) dependence. The existence of ferromagnetism only for \( \gamma > 162.8^\circ \) is consistent with LCO thin film studies.¹⁰ Furthermore, recent band-structure calculations¹⁸ indicate that LCO is magnetic only for \( \delta y < 0.52 \), where \( \delta y \) is a measure of the rhombohedral distortion of the lattice. For the measured LCO lattice parameters, \( \gamma_c \) corresponds to \( \delta y = 0.53 \), which indicates excellent agreement between the calculations and experiments for bulk LCO. Thin film studies⁸¹⁶¹⁷¹⁹ have also found supporting evidence for a lattice distortion causing ferromagnetism. LCO material deposited on substrates that result in tensile strain show ferromagnetic order below \( T \approx 87 \) K, and the strength of the net ferromagnetic moment increases with the value of \( \gamma \). Based on the results of experiments on bulk LCO and LCO films grown on various substrates, a model has been proposed in which surface-induced lattice stress increases \( \gamma \) near the surfaces.³ This induces a transition to long-range ferromagnetic order at \( T_C \) throughout the LCO lattice. For moments far from the surfaces, \( \gamma \) becomes lower than \( \gamma_c \) below \( 37 \) K in bulk LCO. At these low temperatures the lattice loses ferromagnetic order, except near the surfaces where \( \gamma > \gamma_c \).

We extend our previous study on bulk LCO to nanoparticles using the same neutron scattering and magnetometry techniques. The lattice parameters for both materials were determined over a range of temperatures \( 10 \leq T \leq 300 \) K, and the field-cooled and zero-field-cooled magnetization was tracked in fields of 20 Oe and 60 kOe. We show that nanoparticles of LCO exhibit a phase transition very close to the transition temperature found in bulk LCO. However, the magnetic order persists to low \( T \), sharply contrasting the bulk behavior where the ferromagnetism collapses below \( 37 \) K. The ferromagnetic moment is much larger than in the bulk particles and continues to increase as the temperature decreases. We will show that these behaviors can be understood with the same Co-O-Co bond angle and surface-induced distortion model developed for the bulk behavior.

LCO nanoparticles were synthesized using the amorphous heteronuclear complex DTPA as a precursor,²⁰ using a method similar to that described in Ref.²¹. A NaOH solution at 1.0 M concentration was added by drops to a mixture solution of La(NO₃)₃ and Co(NO₃)₃ to prepare fresh hydroxides. A stoichiometric amount of NaOH was used to ensure complete reaction of the metal cations. The excess Na ions were then removed via dialysis over approximately 24 hours. Equimolar amounts of DTPA were then added to the metal hydroxides to synthesize the complex precursor. The mixture was stirred as it was heated to 80°C. The resulting transparent so-
The diffraction patterns for both the bulk and nanoparticle LCO show small peaks corresponding to a Co$_3$O$_4$ phase. The CoO phase observed in the bulk was not evident in the nanoparticles. Refinements indicate a weight fraction of < 3.5% Co$_3$O$_4$ in the nanoparticles. The effect of these phases on the bulk has been previously discussed and it applies similarly to the nanoparticles. In addition to the Co$_3$O$_4$ phase, there are also some Bragg peaks that were not identified as expected oxides of La or Co. When comparing the bulk to the nanoparticle patterns, the lattice structures of these phases appear distinct from that of the LCO bulk. Unless there were a significant amount of impurity peaks directly overlapping the LCO peaks, we would not expect them to significantly affect the quality of the LCO parameter refinements. The magnetization data do not show any unusual behavior which can be readily attributed to these impurity phases, although calculations of the average effective Co moment may reflect the presence of non-LCO phases.

Fitted lattice parameters $a$ and $c$ for the hexagonal unit cell are shown for $0 < T < 300$ K in Fig. 2 and are compared to previous results obtained for bulk LCO. The Co-O-Co bond angle ($\gamma$), and the parameter $\delta y = \frac{d}{2} \cos(\gamma/2)$, where $d$ is the Co-O bond length, are also shown. The parameter $\delta y$ describes the deviation of the oxygen position from the straight line connecting neighboring Co ions and characterizes the amount of rhombohedral distortion of the lattice. Although $\delta y$ is a derived quantity from $a$ and $\gamma$, we include it in the fits so as to be consistent with other relevant papers which interpret their results in the context of $\delta y$. 

Contrasting the sharp changes observed near $T_n \approx 37$ K in bulk LCO, $\delta y$, $\gamma$, $a$ and $c$ show no abrupt change in slope in the nanoparticles. The value of $\gamma$ observed for the nanoparticles remains well above $\gamma_c$ throughout the entire range of temperatures studied.

The temperature dependence of the nanoparticle lattice parameters were fit using the Gruneisen expression with the Einstein model for thermal lattice expansion.
where the lattice parameter being fit is \( y(T) \), \( y(0) \) is its value at \( T = 0 \), \( T_E \) is the Einstein temperature, and \( \alpha \) is the thermal expansion coefficient for \( T >> T_E \). The lattice parameters are well fit by the thermal expansion model, but \( T_E \) is rather small and inconsistent among the various parameters. It is not surprising that data for lattice parameters that exhibit no sharp features can be fit by the simple temperature dependence of Eq. (1). No power-law behavior or phase transition is observed for nanoparticles, unlike the bulk LCO.

\[
y(T) = y(0)[1 + \alpha (\coth\left(\frac{T_E}{2T}\right) - 1)]
\]

over the range \( 32 < T < 84 \) K, the curvature is still not as large as normally expected for a FM phase transition. The non-critical contributions well below \( T_C \) preclude meaningful fits to the critical behavior.

The shapes of the ZFC curves in the bulk and nanoparticles show a similar paramagnetic-like tail below \( T = 20 \) K, except that the nanoparticle moment appears to saturate at \( 0.054 \text{ emu} \cdot \text{mol}^{-1} \). Although the individual nanoparticles are fairly well ordered, there are likely moments at grain boundaries that contribute to the paramagnetic tail. The nanoparticle ZFC magnetization between \( T = 20 \) K and \( T_C \) is much larger than that of the bulk and probably represents randomly oriented net ferromagnetic moments of the nanoparticle grains which are not readily aligned by the applied field.

The \( M/H \) nanoparticle behavior for \( H = 60 \) kOe sharply contrasts that of the bulk particles. Whereas the bulk magnetization decreases with \( T \) below 90 K, with a minimum just below 40 K (Fig. 3 b), the nanoparticle moment increases monotonically as \( T \) decreases over the entire temperature range (Fig. 3 d). The transition is rounded for \( H = 60 \) kOe because the critical point is at \( H = 0 \). However, there is a slight inflection point near \( T_C \), which is more clear from \( H/M \) versus \( T \) data shown in Fig. 4. This indicates a strong influence of the ferromagnetic interactions in high field. The bulk
found that the magnetic susceptibility of their samples
strain, [4] and unit-cell expansion. [5, 7] Yan dering of the surface, [26, 27] surface-induced lattice
nanoparticles has been attributed to ferromagnetic or-
anoparticles, as well as a less negative
\( \mu \)
an even smaller value of
result in a less negative
A larger FM interaction in the nanoparticles could also
participating due to the less perfect crystallinity of the
impurities yield upper limits for transition temperatures) and
data indicate no such significant FM interaction at high
fields, consistent with the small net ferromagnetic moment
observed in the bulk and the disappearance of the
ferromagnetism below the transition at \( T_o \).

Figure 4 shows \( H/M \) versus \( T \) for the nanoparticles
at \( H = 60 \) kOe and 20 Oe. The steep drop in \( H/M \)
with decreasing temperature beginning at \( T = 100 \) K is indicative of ferromagnetism for 20 Oe. The slight
dip at the same temperature for 60 kOe demonstrates
that the ferromagnetic interactions are still significant.
Data at both fields show nearly the same paramagnetic behavior above 170 K. The straight line fit for
\( 170 \leq T \leq 300 \) K is interpreted as Curie-Weiss (CW) behavior using \( H/M = 1/\chi = (T - \theta_{CW})/C \). We obtain a
CW temperature \( \theta_{CW} = -121(3) \) K and Curie constant
\( C = 1.14(1) \) emu-K-mol\(^{-1}\) for the nanoparticles. This value of \( \theta_{CW} \) is consistent with \( T_C = 87 \) K (CW calculations yield upper limits for transition temperatures) and
suggests dominant antiferromagnetic interactions above 170 K. Both values are similar to those obtained for bulk
LCO, where \( \theta_{CW} = -138(4) \) and \( C = 1.31(2) \). Above
the magnetic transition at 87 K, the effective moment is
\( \mu_{eff} = 3.03(2) \) \( \mu_B \) per Co ion. This is smaller than
the bulk value of 3.23(2) \( \mu_B \). The less negative \( \theta_{CW} \) and
smaller \( \mu_{eff} \) perhaps indicate that fewer moments are
participating due to the less perfect crystallinity of the
nanoparticle powder compared to the bulk. The impurities present in the nanoparticles may also contribute to
an overestimation of the number of participating Co ions.
A larger FM interaction in the nanoparticles could also result in a less negative \( \theta_{CW} \). Notably, Fita et al. found
an even smaller value of \( \mu_{eff} = 2.44 \mu_B \) for their LCO nanoparticles, as well as a less negative \( \theta_{CW} \) of -48 K. [4]

In several previous studies, the ferromagnetism in LCO nanoparticles has been attributed to ferromagnetic or-
dering of the surface, [26, 27] surface-induced lattice strain, [4] and unit-cell expansion. [5, 7] Yan et al. [20]
found that the magnetic susceptibility of their samples
increased as the surface-to-volume ratio increased and
attributed this to localized spins on the surface of the material. Although they ruled out double exchange be-
tween Co(III) and Co(IV) atoms as the mechanism for the surface ferromagnetism, their study was inconclusive
as to the origin of the ferromagnetic interaction. Harada et al. [27] found similar results; the magnetization
increased with decreasing particle size and they sug-
gested the source to be chemisorption of oxygen atoms at
the surface. Again, the mechanism leading to ferromag-
etism was not made explicit. Fita et al. [4] examined the lattice parameters of LCO nanoparticles and found
that they increase with decreasing particle size but did not identify surfaces as the source of ferromagnetism. In-
stead, they pointed to the surface-induced lattice expan-
sion which persists throughout the material as the cause.
In the above studies, LCO crystals and powders were syn-
thesized using several different methods: floating-zone
single-crystal synthesis, solid-state reaction, crushing the
single-crystal into a powder, and a citric acid solution
method. It is interesting to note that in all but one case, the magnetic susceptibility increased monotonically with
surface area and the transition temperature remained fairly constant at \( T_C \approx 85 \) K. Wei et al. [7] found that
their nanoparticles showed a decrease in magnetization and \( T_C \) with particle size, despite also noting a similar increase in lattice parameters with the smaller sizes. It is possible that the citric acid sol-gel method employed in this case differed slightly from the one used by Harada et al., [27] but it is unclear how that would produce results that differ qualitatively from the others.

Tensile stress from substrates allows LCO thin films to order ferromagnetically. The resulting FM order is found throughout the material for films of order 100 nm [12] and the net moment increases with film thickness. [8] In nanoparticles, all of the LCO material is well within 100 nm of a surface. Hence, tensile stress from these surfaces should result in a larger average \( \gamma \) for the particles, although the exact process by which the strain changes \( \gamma \) requires further investigation. Our experiments show that \( \gamma \) does remain well above \( \gamma_c \) for all \( T \) (Fig. 2), which is consistent with the net FM moment being much larger than in bulk LCO and not collapsing below \( T = 37 \) K. Note that the lowest value of \( \gamma \) in the nanoparticles is comparable to the bulk value for \( T \approx 200 \) K, so we would expect the system to remain ferromagnetic for \( T < 87 \) K in small \( H \). This model, which correlates the stability of ferromagnetism with the stress-induced increase in \( \gamma \), is consistent with the observations made by most of studies noted above. The ferromagnetic transition at \( T = 87 \) K is a result of the stress at surfaces, but long-range ferro-

magnetic order takes place throughout the LCO lattice.

Only for bulk LCO is the long-range order observed to disappear below \( T = 40 \) K because only in this system is
\( \gamma \) observed to decrease below \( \gamma_c \).

Although \( \gamma \) is a useful parameter by which to gauge
the degree of magnetism in a sample, the mechanism by which it controls the ferromagnetism remains unclear. Calculations by Lee and Harmon indicate $\delta \gamma$ (closely related to $\gamma$) to be the controlling parameter in LCO and note that the amount of rhombohedral lattice distortion determines whether the ground state is magnetic.\cite{10}

According to this model, the degree of orbital overlap between the Co and O ions affects the balance between the repulsive Coulomb interaction and the exchange interaction: more distortion (and less overlap) leads to a non-magnetic ground state. Goodenough proposes that the local configurations of low-spin and high-spin Co$^{3+}$ and Co$^{4+}$ ions result in areas of ferromagnetism, antiferromagnetism, and paramagnetism.\cite{11} It is also conceivable in this interpretation that the Co-O-Co bond angle affects the spin state of the Co ions or groups of ions by allowing for increased or decreased overlap of the cobalt and oxygen orbitals.

In summary, we have shown that, for $T > 87 \text{K}$, the interaction strengths and paramagnetic behavior are comparable in bulk and nanoparticle LCO. On the other hand, the observed magnetic behaviors observed for $T < 87 \text{K}$ in LCO bulk and nanoparticles are very different. Nevertheless, the magnetic behaviors of bulk and nanoparticles can be modeled within the same framework: the interactions between spins in LCO are strongly dependent on the Co-O-Co bond angle $\gamma$. Magnetic order can only be sustained when $\gamma$ is larger than a critical value $\gamma_c \approx 162.8^\circ$. In bulk LCO, this occurs only for $T > T_c$, where $T_c \approx 37 \text{K}$. For $T < T_c$, magnetism in bulk LCO is associated only with regions of tensile stress near surfaces and interfaces with impurity phases. In LCO thin films and nanoparticles, all moments are near to surfaces so $\gamma$ is always larger than $\gamma_c$ and long-range ferromagnetic order is present for all $T < 87 \text{K}$.

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