Pressure-induced intermediate-to-low spin state transition in LaCoO₃

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Synchrotron x-ray powder-diffraction experiments reveal that the transition from a magnetic intermediate spin (IS) state $t_{2g}^5 e_g^1$ to a nonmagnetic low-spin ground state t_{2g}^6 in LaCoO₃ normally observed when cooling manifests itself under pressure by an anomalously low bulk modulus of 150(2) GPa and an initially very large Co-O bond compressibility of 4.8×10^{-3} GPa^{-1} which levels off near 4 GPa. The continuous depopulation of the IS state is driven by an increased crystal-field splitting resulting in an effective reduction of the size of the Co^{3+} cation.

The magnetic and electronic properties of the paradigmatic charge-transfer insulator LaCoO₃, which crystallizes in a rhombohedral distortion of the cubic perovskite structure with the $a^- a^- a^-$ tilt system,[1] continue to be topical. Magnetic susceptibility measurements reveal transitions at 100 and 500 K. The 100-K transition was first interpreted by Goodenough[2] as a spin-state transition of 50% of the Co^{3+} ions from a nonmagnetic low-spin (LS, t_{2g}^6, $S=0$) ground state to a high-spin state (HS, $t_{2g}^4 e_g^2$, $S=2$). The 500-K transition was assigned to an order-disorder transition, where the e_g electrons become itinerant and destroy the spin-state ordered superstructure. The latter, however, was never observed experimentally[3,4] and a dynamic disorder of HS and LS Co^{3+} was subsequently proposed.[5] An alternative interpretation based on photoelectron emission[6] and x-ray-absorption spectroscopy[7,8] led to the postulation of an intermediate spin (IS, $t_{2g}^5 e_g^1$, $S=1$) state and the two transitions were assigned to thermally activated LS-to-IS and IS-to-HS state transitions.[9] According to classical ligand field theory the IS state should always be energetically above the LS or HS state. However, local-density approximation and U calculations by Korotin *et al.*[10] established that the IS state could be energetically stabilized with respect to the HS state. Recent neutron powder-diffraction experiments by Radaelli and Cheong[11] show that the thermal lattice expansion is best fitted by such a LS-to-IS-to-HS state sequence without orbital degeneracy of the IS state. However, correction terms to a simple activated behavior and a significantly reduced HS effective moment are required, indicating that this model is, at present, incomplete.

Pressure can alter the magnetism of transition-metal oxides by inducing Mott[12] or spin state transitions.[13] The first is a consequence of the closure of the Mott-Hubbard or charge-transfer gap, whereas the latter results from a breakdown of strong Hund's rule coupling and occurs when the crystal-field splitting dominates over the exchange energy. A second order HS-to-LS transition under pressure leads to the collapse of the magnetic state in wuestite (Fe$_{0.94}$O) as shown by Mössbauer spectroscopy.[13] In RFeO₃ (R=La,Pr), a pressure-induced collapse of the Mott-Hubbard state and a subsequent continuous HS-to-LS transition was observed.[14] Takano *et al.* observed a first-order pressure-driven HS-to-LS transition in CaFeO₃ by *in situ* Mössbauer spectroscopy and x-ray diffraction.[15] In the following we present experimental evidence for a continuous IS-to-LS state transition occurring in LaCoO₃ under hydrostatic pressure at room temperature.

The experimental setup and detailed procedure for the high-pressure synchrotron x-ray powder-diffraction experiments performed at beam line X7A at the National Synchrotron Light Source at Brookhaven National Laboratory are described elsewhere.[16] Rietveld refinements were performed using the program GSAS.[17] The results of the fits are summarized in Table I. The lattice parameters and the volume of the unit cell reveal no discontinuity as a function of pressure (Fig. 1). Intriguingly, however, the value of the bulk modulus B_0 of 150(2) GPa obtained by fitting[18] a second-order Birch-Murnaghan equation of state[19] with $V_0 = 335.834(5)$ Å^3 and $B' = 4$ (by definition) to the pressure dependence of the unit-cell volume is significantly smaller than those observed for comparable perovskites with the $a^- a^- a^-$ tilt system such as LaAlO₃ [$B_0 = 190(5)$ GPa, Ref. 20] and PrAlO₃ [$B_0 = 205(8)$ GPa].[21] The Cornelius-Schilling model[22] predicts values of 180, 189, and 191 GPa for B_0 of LaCoO₃, LaAlO₃, and PrAlO₃ respectively. Our experimental value is therefore highly indicative of an unusually large volume compressibility in LaCoO₃.

The La^{3+} cation in LaCoO₃ is at the center of a distorted dodecahedron and coordinated by 12 oxygen atoms with three long, six intermediate, and three short distances (Fig. 2).[23] The three closest oxygen atoms to La are coplanar and the La p_x and p_y orbitals point at this plane. The p_z and d_{z^2} orbitals are orthogonal to this plane and have no overlap with the first coordination sphere of oxygen. The majority of the La-O bonding stems from the three short La-O bonds. As pointed out by Radaelli and Cheong[11] and others, the long and short La-O bonds are useful gauges for nonthermal lattice distortions. An increase in the long La-O distance accompanied by a decrease of the short one, leading to a more distorted environment for La, is indicative of an increase in the magnitude of the octahedral distortion. The Co^{3+} cation

TABLE I. LaCoO$_3$ high-pressure refinements.

P(GPa)	Ambient	0.63	2.64	3.98	5.99	7.23	8.08
a	5.44263(3)	5.43906(6)	5.4101(1)	5.3950(2)	5.3776(2)	5.3664(2)	5.3591(4)
c	13.09108(8)	13.0821(2)	13.0114(3)	12.9713(4)	12.9216(6)	12.8922(5)	12.868(1)
V	335.834(5)	335.162(9)	329.81(2)	326.97(2)	323.61(4)	321.53(3)	320.07(6)
La($U_{iso}\times100$)	0.76(2)	2.40(7)	2.2(1)	3.1(1)	2.5(1)	2.6(1)	1.8(1)
Co($U_{iso}\times100$)	0.26(3)	2.3(1)	3.0(2)	3.5(2)	3.4(2)	4.8(1)	4.7(2)
$\emptyset$($U_{iso}\times100$)	0.8(1)	0.8	0.8	0.8	0.8	0.8	0.8
O(x)	0.4488(7)	0.455(2)	0.471(3)	0.490(9)	0.485(6)	0.479(3)	0.474(4)
χ^2	2.765	2.807	2.272	1.983	2.832	3.875	1.193
La-O1$\times3$	3.000(4)	2.961(9)	2.86(2)	2.75(5)	2.77(3)	2.79(2)	2.82(2)
La-O2$\times3$	2.443(4)	2478(9)	2.55(2)	2.64(5)	2.61(3)	2.58(2)	2.54(2)
La-O3$\times6$	2.7031(4)	2.6977(8)	2.677(1)	2.665(1)	2.656(1)	2.651(1)	2.648(1)
La-O mean	2.712	2.709	2.691	2.680	2.673	2.668	2.664
Norm La-O	1.000	0.9989	0.9922	0.9882	0.9856	0.9838	0.9823
Co-O$\times6$	1.9329(5)	1.928(1)	1.908(1)	1.896(1)	1.891(1)	1.888(1)	1.888(2)
Norm Co-O	1.000	0.9969	0.9871	0.9809	0.9783	0.9768	0.9768
Average tilt $\langle\omega\rangle$	8.29	7.3	4.73	1.63	2.45	3.42	4.24

is at the center of a distorted octahedron surrounded by six equivalent oxygen atoms.

The effect of pressure on the individual metal-oxygen bond distances clearly reveals that there are two distinct regions with a change in slope near 4 GPa [Figs. 3(a) and 3(b)]. Initially the short La-O bonds increase, the long ones decrease, and the six intermediate ones also decrease, but by a much smaller amount. Under pressure, the Co-O bonds contract, as expected. When analyzing the individual linear bond compressibilities [$\beta_L = (-1/L)(\delta L/\delta P)_T$] up to 4 GPa, one observes that the contraction of the intermediate La-O bond ($\beta_{\text{La-O}_3}=3.6\times10^{-3}$ GPa^{-1}) matches the Co-O bond compressibility ($\beta_{\text{Co-O}}=4.8\times10^{-3}$ GPa^{-1}). In contrast, the three long La-O bonds contract very strongly ($\beta_{\text{La-O1}}=1.8\times10^{-2}$ GPa^{-1}), while the short ones expand ($\beta_{\text{La-O2}}=-1.76\times10^{-2}$ GPa^{-1}) at a comparable rate. This is a clear indication of significant changes in the magnitude of the octahedral tilting as discussed in the following paragraph.

An exceedingly useful measure of the distortion of a perovskite-type structure from the cubic aristotype ABO_3 is the tilt angle ϕ that gives the degree of rotation around the threefold axis of the BO_6 octahedra. O'Keefe et $al.$[24] have shown that the variation of ϕ with pressure in orthorhombic perovskites depends on the strength of the two bond compressibilities $\beta_{A\text{-O}}$ and $\beta_{B\text{-O}}$. If the A site is more compressible, $\beta_{A\text{-O}}>\beta_{B\text{-O}}$, ϕ should increase with pressure and the structure will distort away from cubic symmetry. If the bond compressibilities are reversed in magnitude, the tilt angle should decrease with pressure. These trends are indeed observed in the three isostructural orthorhombic systems ($Pbnm$, $b^-b^-a^+$) where ϕ increases in MgSiO$_3$ (Ref. 25) ($\beta_{\text{Mg-O}}=1.1\times10^{-3}$ GPa$^{-1}>\beta_{\text{Si-}O}=8.9\times10^{-4}$ GPa^{-1}) and decreases in LaMnO$_3$ (Refs. 26 and 27) ($\beta_{\text{La-O}}=2.8\times10^{-3}$ GPa$^{-1}<\beta_{\text{Mn-O}}=3.2\times10^{-3}$ GPa^{-1}) and YAlO$_3$ (Ref. 28) ($\beta_{\text{Y-O}}=2.0\times10^{-3}$ GPa$^{-1}<\beta_{\text{l-O}}=2.5\times10^{-3}$ GPa^{-1}). In the related system ScAlO$_3$, the com-
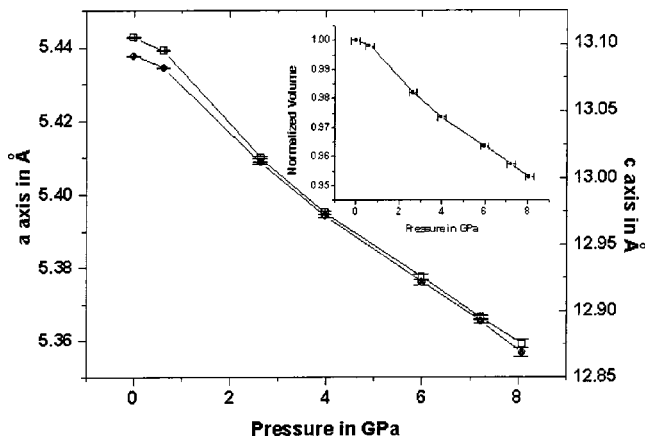

FIG. 1. Pressure dependence of a and c unit-cell axes in angstrom. Inset shows that the unit-cell volume reveals no discontinuity over entire pressure range.
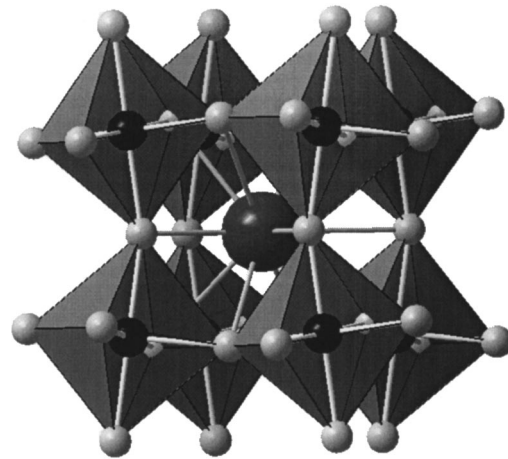

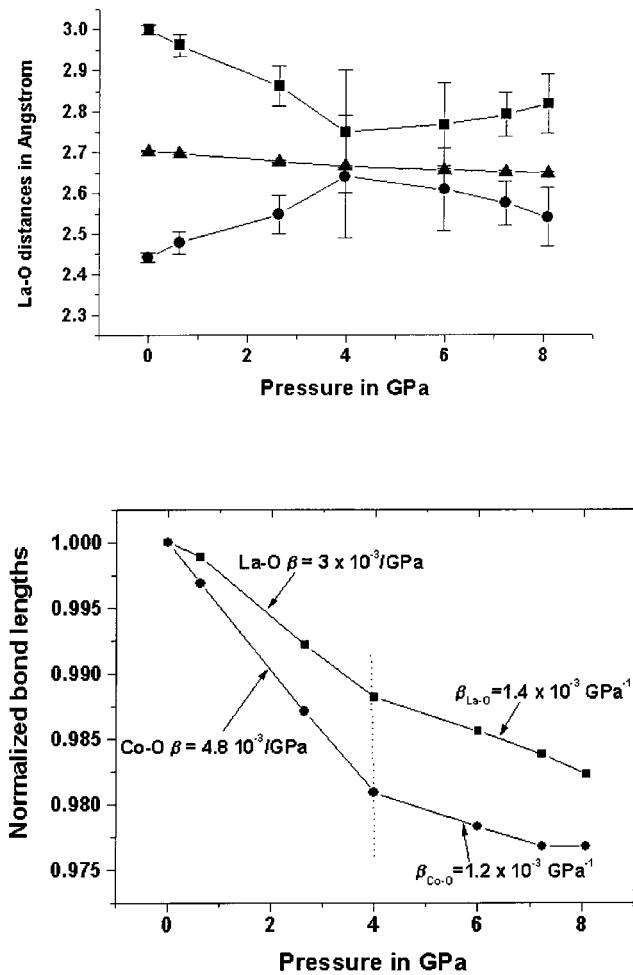FIG. 2. Perovskite structure showing octahedral and cubocta-hedral sites.

FIG. 3. (a) Pressure dependence of La-O bond lengths (a) and (b) normalized mean bond lengths in LaCoO$_3$. The individual bond compressibilities were determined below and above 4 Pa. Extrapolating data above 4 GPa back to zero pressure one obtains a Co-O bond distance of 1.905 Å very close to the expected value of 1.895 Å for a Co(LS)-O bond.

pressibilities of β_{Sc-O} and β_{Al-O} are essentially equal ($\simeq 1.5 \times 10^{-3}$ GPa^{-1}), and there is no significant change in ϕ with pressure.[29] To our knowledge, the only previously published detailed crystallographic data for a rhombohedral perovskite under pressure is the case of PrAlO$_3$,[21] which is isostructural with LaCoO$_3$ and also adopts the $a^-a^-a^-$ tilt system (space group $R\bar{3}c$) up to ca. 7 GPa. Above this pressure PrAlO$_3$ undergoes a phase transition into the $a^0b^-b^-$ tilt system (space group *Imma*). Similar to LaMnO$_3$ and YAlO$_3$, the A-O bond is less compressible ($\beta_{Pr-O}=2\times10^{-3}$ GPa^{-1} $<\beta_{Al-O}=2.6\times10^{-3}$ GPa^{-1}) and the tilt angle decreases with pressure. When considering the data to 4 GPa for LaCoO$_3$, once again the A site is less compressible ($\beta_{La-O}=3.0\times10^{-3}$ GPa^{-1}) than the B-site ($\beta_{Co-O}=4.8\times10^{-3}$ GPa^{-1}) and the tilt angle decreases. Therefore it appears that the argument forwarded by O'Keefe *et al.*[24] relating individual bond compressibilities to a distortion under pressure is also valid for perovskites that adopt other than orthorhombic crystal symmetry.
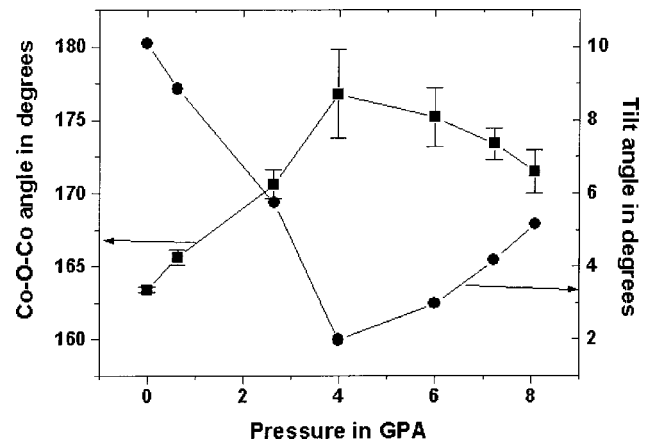
The variation of the tilt angle as well as the Co-O-Co

FIG. 4. Pressure dependence of tilt angle (circles) and Co-O-Co angle (squares) as a function of pressure.

angles for LaCoO$_3$ under pressure (Fig. 4) clearly emphasize what has already been noted from the pressure dependence of the bond distances, that in contrast to the unit-cell parameters there is an obvious change in the response of the bond distances and angles above ca. 4 GPa. Based on a comparison of the limited number of experimentally determined individual bond compressibilities in perovskites, it is clear that below 4 GPa, the Co-O bond is highly compressible ($\beta_{Co-O}=4.8\times10^{-3}$ GPa^{-1}). In fact it is *the most compressible B-O bond observed* to date (greater than Si^{4+}-O, Mn^{3+}-O, and Al^{3+}-O). Above 4 GPa, the compressibility is considerably lower ($\beta_{Co-O}=1.2\times10^{-3}$ GPa^{-1}), much more in line with the expected value for a *B-O* bond in a perovskite. To place these observations within our current framework of understanding, one needs to take into account the depopulation of the IS state under pressure. Asai *et al.*[30] have shown experimentally that the energy gap between LS and IS states increases under pressure. At pressures above 0.5 GPa this increase is found to be quadratic, indicating a very strong volume dependence of the IS state energy. Therefore the IS state will be depopulated under pressure and as a result a small but noticeable contraction of the Co-O bond is to be expected. This contraction occurs as a result of the depopulation of Co e_g orbitals, which are Co-O σ antibonding in character. This is the origin of the well-known fact that LS Co^{3+} has a smaller radius (0.685 Å) than HS Co^{3+} (0.75 Å).[31] If we estimate the radius of IS Co^{3+} as the arithmetic mean of LS and HS values (0.717 Å), it is gratifying to note that the expected IS Co^{3+}-O distance (1.927 Å) is close to the value of 1.933(1) Å observed at ambient pressure. The expected LS Co^{3+}-O distance (1.895 Å) is very close to 1.896(1) Å, the value observed at 3.98 GPa as well as the zero-pressure value of 1.905 Å extrapolated back from the region between 4 and 8 GPa.[32] Obviously, the fairly rapid and continuous contraction of the effective size of the cobalt centered octahedra leads to a decrease in the magnitude of the octahedral tilting distortion. Both the observed Co-O distances and the changes in the octahedral tilting strongly suggest that at 4 GPa, the IS is significantly depopulated. The dramatic change in Co-O bond compressibility, as well as the change from a decreasing to an increasing tilt angle that oc-

curs above 4 GPa, suggest that the spin-state transition from IS to LS is essentially complete at 4 GPa. The fact that at higher pressures the LS Co^{3+}-O bonds have a lower compressibility than the La-O bonds is responsible for the gradual increase in octahedral tilting between 4 and 8 GPa.

In summary, we have shown that $LaCoO_3$ has an anomalously low bulk modulus [$B_0 = 150(2)$ GPa]. Furthermore, individual bond compressibilities reveal a change in their pressure dependence near 4 GPa, indicating a change in the compression mechanism. This pressure behavior is caused by an ''unusually'' compressible Co-O bond. We argue that the reason for this is a pressure-induced continuous depopulation of the IS state over the 0–4 GPa pressure range. This depopulation is driven by the increased crystal-field splitting between the t_{2g} and e_g orbitals, which results in a reduction of the effective size of Co^{3+} as antibonding electrons are removed from the e_g orbitals. We encourage first-principles calculations of the electronic structure, taking into account this spin-state transition to compare with our experimental values. This is to our knowledge the first observation of a continuous pressure-induced IS-to-LS transition under pressure in a perovskite. Furthermore, we have demonstrated that high-pressure diffraction provides an excellent opportunity to probe the structural response of spin-state transitions.

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